VOLUME I

INTERIM REPORT

PRACTICAL APPLICATION OF SPECIAL WASTE CO-DISPOSAL WITH MUNICIPAL REFUSE AT THE COASTAL PARK LANDFILL BIOREACTOR

Report to the

WATER RESEARCH COMMISSION

by

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FOREWORD

The term *special waste* refers to both liquid and solid industrial wastes which are potentially hazardous to living organisms. A vast array of special wastes possessing undesirable characteristics are being produced by industry and the uncontrolled disposal of such wastes has the potential to become a national environmental problem. In developing countries, these concerns are not any less than in the developed countries; they are possibly magnified, because of their sometimes limited resources.

The controlled co-disposal of special wastes with general wastes in suitably constructed landfills is a strategy which can play an important role in the overall management of these two waste streams. However, in South Africa, the co-disposal of special wastes with general wastes in sanitary landfills has not been widely implemented to date, due to various reasons. As a result of the foregoing, this research project was carried out with the objective of developing practical operational criteria for the landfill co-disposal of selected special wastes (such as metallic wastes) with general waste. The research was motivated by the desire to explore the potential of domestic landfill sites to act as final depositories for hazardous chemicals at minimal environmental risk, as South Africa does not have sufficient hazardous waste landfill sites.

Additional significance is given to this research as the issue of co-disposal of special wastes with non-hazardous wastes is also under close scrutiny in other parts of the world.

It is hoped that experimental studies of this nature will allow the development of Southern African guidelines which will enable landfill operators to delist certain special wastes, thereby enabling the disposal of special wastes of a low to medium hazard rating with the minimum of disturbance to the environment.

P E Odendaal
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EXECUTIVE SUMMARY

1: INTRODUCTION

South Africa's rapid population growth accompanied by urbanisation and industrialisation has resulted in a dramatic increase in the mass of both general and hazardous wastes being generated. Sanitary landfilling, whereby the solid waste is compacted and covered each day with a soil layer, offers the most versatile method for the disposal of wastes in an economical and environmentally sound manner. Landfill co-disposal (or joint disposal) in its widest sense, is understood to be the calculated and monitored interaction of municipal refuse with other selected difficult industrial and commercial wastes in a properly controlled landfill site (Department of the Environment - UK, 1993).

The results of previous research carried out by the Cape Town City Council provided practical operational criteria for the landfill co-disposal of domestic refuse and anaerobically digested waste-water sludge liquor (Novella *et al.*, 1996). It was concluded that the co-disposal of waste-water sludge liquor with refuse was a landfill strategy which could play an important beneficial role in the overall management of these two waste streams. The impact of pending sludge legislation policies in South Africa may prohibit the agricultural utilisation of sludges that contain high concentrations of pollutants such as heavy metals and pathogenic bacteria. In such instances, and also where there is no agricultural demand for the sludge, it is likely that much greater use will be made of landfill co-disposal as an alternative sludge disposal option. Furthermore, landfill co-disposal technology needs to be recognised by the policy and regulation community and managed by the waste management industry within the framework of the Minimum Requirements of the Department of Water Affairs and Forestry (DWAF, 1994) as well as of Section 20 of the Environment Conservation Act, No. 73 of 1989.

A vast array of special wastes possessing undesirable characteristics are produced by industry. The term special wastes refers to both liquid and solid industrial wastes which are potentially hazardous and necessitate further processing and transformation into end-products or special disposal to render them acceptable in terms of both environmental impact and public health legislation. Such special wastes are not permitted for discharge into the sewerage system as they would deleteriously affect the conventional biological purification processes. Wastes of this nature have to be treated separately for inactivation prior to disposal in a containment landfill site. However, many areas do not have such special waste treatment and disposal facilities and the problem is often circumvented by illegal dumping into the sewer, the stormwater system or onto vacant ground with subsequent pollution of ground and surface water resources.

The co-disposal of special wastes with general wastes in sanitary landfills is being practised in many overseas countries, especially in drier areas which have a perennial water deficit. However, different approaches to co-disposal have led to quite different experiences and

attitudes, with the result that different perceptions of the values and dangers of the co-disposal practice have developed. The major perceived problems with the disposal of special wastes on a landfill is the possible generation of a more polluted leachate (Department of the Environment - UK, 1993).

In comparison, the co-disposal of special wastes with general wastes in sanitary landfills in South Africa has not been widely implemented to date, due to various reasons. As a result of the foregoing, a three-year research project was negotiated between the Cape Metropolitan Council and the Water Research Commission with the objective of developing practical operational criteria for the landfill co-disposal of selected special wastes with general wastes. This could assist smaller landfill operators where only general waste landfills occur and where small volumes of special wastes must be disposed of.

2: AIMS AND MODUS OPERANDI OF THE PROJECT

2.1: AIMS OF THE PROJECT

- To determine practical norms for the landfill co-disposal of various selected special wastes (such as CCA - copper, chromium, arsenic), with general wastes under Western Cape conditions.

- To determine whether the attenuation mechanisms (physical, chemical and biological) inherent in a methanogenically mature landfill can prevent, or reduce, the potential hazard of the deposited special wastes.

- Quantify the rates of application of specific special wastes during a co-disposal operation.

- Establish if the co-disposal of special wastes with general wastes is an economic and environment-friendly concept, alternative to the expensive disposal of special wastes in containment sites.

- Monitor the quality of the leachate produced and estimate the possible effect on ground water quality.

2.2: MODUS OPERANDI OF THE PROJECT

The research was organised along the following lines so as to achieve the aims of the project:

- Laboratory-scale adsorption/desorption studies (Refer Chapters 5, 7 and 8).

- Pilot-scale landfill column studies (Refer Chapters 6, 7 and 8).

- Full-scale landfill cell studies at Coastal Park (Refer Chapter 9).

- Associated studies at Coastal Park (Refer Chapter 10).

Mr R H Ballard, an employee of the Cape Metropolitan Council, utilised the laboratory-scale adsorption/desorption studies and the pilot-scale landfill column studies for the purpose of obtaining a MSc (Engineering) degree through the Department of Chemical Engineering at the University of Cape Town (Ballard, 1997).

2.3: CONTRACT AGREEMENT

Although the contract agreement between the Water Research Commission and the Cape Metropolitan Council did not call for the appointment of a Steering Committee, one was established which met yearly. A Special Waste Co-disposal Co-ordinating Committee was also formed in order to control the project on a day to day basis.

The duration of the practical aspects and monitoring phases of the project was initially two years (1994 and 1995) but this was subsequently extended by a further year (1996) by mutual agreement.

2.4: EXTENDED CONTRACT AGREEMENT

On completion of this project (Volume 1) a proposal was submitted by the Cape Metropolitan Council for a further extension to research the phenomenon of how the landfill water balance at Coastal Park would be influenced by increasing the height of the landfill by a further 5 m (refer Item 7.1 for further details).

The Water Research Commission has subsequently approved an extension of 2 years to the contract term of the project (1998 - 1999). The extended project will be printed as Volume 2 of the final report.

3: MATERIALS AND METHODS

3.1: LABORATORY-SCALE ADSORPTION/DESORPTION STUDIES

The laboratory-scale batch reactor investigations comprised the following:

- **Kinetics of adsorption/desorption:** Evaluation of kinetic rate constants of metallic ion adsorption/desorption in solid-liquid reactions at pH values of 5,5, 6,4 and 7,0 (completed in triplicate).

- **Adsorption equilibrium studies:** Evaluation of equilibrium adsorption isotherms which describe the quantity of metals adsorbed.

  The adsorbent was shredded, fully-stabilised general wastes excavated from the Coastal Park sanitary landfill site while the adsorbate was copper, chromium and arsenic in combination and in solution in the form of CCA, which is used extensively for wood preservation. The specification of CCA as supplied on the product is as

follows: Copper (71 g per kg); Chromium (119 g per kg); Arsenic (128 g per kg). Both adsorption/desorption and the equilibrium studies utilised a modification of the US EPA Method 1311 Toxicity Characteristic Leaching Procedure (TCLP).

3.2: PILOT-SCALE LANDFILL COLUMN STUDIES

Three pilot-scale columns were constructed at Athlone, near Cape Town. The columns were 4 m in height, 0,8 m in diameter and contained approximately 700 kg of general landfill waste. The column design of other researchers was thoroughly reviewed to establish the design and construction of the Athlone columns. The pilot-scale research comprised the following:

- **Residence time studies:** Determination of the residence time distribution/deviation from ideal behaviour using $LiSO_4$ as a non-reactive tracer with pulse input. Such tracer response analysis is a technique used to characterise the type of flow and mixing that takes place in a continuous process vessel.

- **Co-disposal studies:** The final phase of the pilot-scale investigation was the placement of copper, chromium and arsenic in two of the columns previously recirculated. Analysis of the collected leachate (in terms of composition and flow over a period of 200 days was quantified in terms of the laboratory-scale adsorption kinetics and the measured residence time distribution data. In this manner it was possible to predict absolute values of the metals which can be retained by a full-scale landfill operation together with the composition of leachate exiting the landfill.

3.3: FULL-SCALE LANDFILL CELL STUDIES AT COASTAL PARK

The Coastal Park landfill, constructed in 1985 without a containment liner, is situated on the False Bay coastline above the Cape Flats aquifer, with an average separation of 2 m between the base of the waste pile and the water table, forming a "buffer" zone. It was envisaged that the calcareous sand in this buffer zone and encroaching sea water would attenuate leachate discharged from the site.

- **Location and Construction of the 5 Landfill Cells**

  Five infiltration cells were constructed from which leachate could be collected for monitoring. Cell 1 was constructed during March 1986 (control). Cells 2, 3, 4 and 5 were constructed in a line during August 1987 each with a 14 x 14 m HDPE sheet at the base draining via a pipe to a collection sump. The sheets were overlain with 2 m of sand and 2 x 2,5 m layers of refuse was placed above the sand. The final surface was covered with a 500 mm layer of sand. Every effort was made to simulate the usual sanitary landfill procedures when placing the refuse.

- **Special Wastes Applied to the Landfill Cells**

  The following types of special waste were applied to the surface of the cells during the period August 1988 to July 1995.

  a) Cell 2: Metallic waste: Copper, Chromium, Arsenic in the form of CCA.
  b) Cell 3: Tracer substance: LiBr and NaCℓ (Control cell)
  c) Cell 4: Phenolic wastes: such as effluent from the Cape Gas Works.
  d) Cell 5: Nitrogenous wastes: such as digested waste-water sludges and urea.

- **Monitoring Procedures of the Landfill Cells**

  a) Meteorological measurements such as rainfall and evaporation;
  b) Leachate volume measurements;
  c) Leachate chemical analyses;
  d) Supplemental wetting of the cells.

3.4: ASSOCIATED STUDIES AT COASTAL PARK LANDFILL

Various other landfill studies were carried out at Coastal Park dealing with the water balance, lateral movement of salts, importance of the vadose zone, mobility of leachate through the sand and determination of the proportion of leachate in the groundwater.

The associated studies were carried out by various research organisations and provided supplemental information relating to a co-disposal operation and considerably broadened the scope of the project. For this reason, these associated studies are included in this report.

4: RESULTS OF INVESTIGATIONS

4.1: RESULTS OF LABORATORY-SCALE STUDIES

4.1.1: Adsorption/Desorption Kinetic Studies

- The modification of the US EPA Method 1311 Total Characteristic Leaching Procedure (TCLP) to determine the kinetics of adsorption and desorption of metallic ions onto general landfill wastes proved appropriate. The modification has the potential to be extremely useful in determining the adsorption characteristics of a number of differing industrial wastes.

- The kinetic studies were described by the modified Freundlich equation developed by Kuo and Latse in 1974. This two-constant equation was developed by inserting a time-dependent expression into the Freundlich equation. This successfully described the rate of metallic ion adsorption in solid-fluid reactions. In all cases, sorption of the metallic ions was characterised by a rapid initial adsorption rate followed by a decreasing rate with increased time.

- Adherence to these modified Freundlich equations is indicative of heterogeneous adsorption. Additionally it was shown that diffusional constraints at the solid phase were evident.

- The desorption of chromium was insignificant. The desorption of copper was less than 4% of that adsorbed. Arsenic desorption was more significant, and averaged less than 10% of the arsenic adsorbed. Because of this the kinetics of desorption were not investigated further.

- The kinetic rate constants (Ka) for copper were the highest, arsenic intermediate with chromium being the lowest. Copper is very strongly absorbed as evidenced by the extremely short times calculated for the half reaction time which is indicative of the speed of the chemical reaction. The half reaction times are larger for chromium and arsenic but still average only 1 hour.

4.1.2: Adsorption Equilibrium Studies

- The equilibrium studies conformed to the Freundlich adsorption isotherms which were successfully constructed for copper at pH values 5,5 and 7,0; for chromium and arsenic at all three pH values, 5,5, 6,4 and 7,0. The values obtained for KF (equilibrium distribution coefficient) may be considered as a measure of affinity between the metals (solute) and general landfill wastes (adsorbent).

- Detailed analysis of the equilibrium data revealed a very strong relationship between initial solute concentration in solution and final solute concentration in solution, irrespective of pH in the range 5,5 to 7,0. The value obtained for the gradient of the linearised data (shown in brackets below) allows direct calculation of the equilibrium solute concentration in solution and hence, computation of the mass adsorbed by the adsorbent over the experimental range of initial solute concentrations.

  The degree of affinity of metals with general landfill wastes was:

$$Cu\ (0,140) >> As\ (0,758) > Cr\ (0,862)$$

4.2: RESULTS OF PILOT-SCALE STUDIES

4.2.1: Residence Time Tracer Studies

$LiSO_4$ was shown to be a suitable tracer in the landfill environment. In excess of 92% of the tracer was recovered. Of the 1027 mg of lithium added, 954 mg was recovered. The mean residence time of the tracer was 112 days while the total time of displacement of the tracer was approximately 300 days. Results from the tracer studies revealed the pilot-scale column conformed to a plug flow reactor, albeit with a great deal of non-ideality.

4.2.2: Co-Disposal Trials

The heavy metals co-disposed at pilot-scale enabled the accuracy of both the tracer studies and the chemical kinetics to be evaluated. Agreement between the co-disposal trials and that predicted from the trials was excellent.

4.2.3: Application of the laboratory and pilot-scale results to predict results at full-scale

- A model was developed from the laboratory and pilot-scale results to compute the mass of copper - chromium - arsenic solution that could be added to municipal solid waste. The computational method employed a conventional chemical engineering mathematical approach. The computation assumed that the only attenuation mechanisms was adsorption and a worst-case study was examined. Overall, the fit of the model to the experimental data was good and representative of heterogeneous adsorption.

- Computation showed it is possible to co-dispose 195 g of chromium together with 195 g arsenic and 67 g of copper per tonne of general landfill wastes with the minimum of environmental damage to any receiving water body. These masses are dictated by the composition of CCA used in the experiments.

- In general, the metal loading rates proposed from the experimental work and predicted by the modelling undertaken in this study, concurred with metal loading rates employed in the United Kingdom as recommended by the Department of the Environment (DOE) for a landfill depth of 3 m.

4.3: RESULTS OF FULL-SCALE STUDIES AT COASTAL PARK

4.3.1: The most striking finding of these studies is the small amount of leachate that found it's way to the base of the cells, on average 2,5% of the annual rainfall. It would appear that rain water was absorbed and mostly held by the landfilled general wastes, subsequently being drawn near the surface by capillary action, where it evaporated during the course of the year. Given a void space of 40% and an annual rainfall of 600 mm, the thickness of the layer affected by rainwater would be about 1500 mm.

4.3.2: The average rate of accumulation of leachate, 14 mm year, was far lower than that found in the associated pilot-scale column studies, where saturated conditions and low evaporation prevailed. At this rate, soluble salts added at the surface might be expected to take over three hundred years to pass through 5 m of general wastes. Most of the liquid collected over the nine years of the project must therefore have been present in the material when laid down.

4.3.3: Seasonal variations in leachate flow rate were evident to varying degrees in all cells, becoming somewhat more marked as the material aged. There was an average lag of two months between early winter rainfall peaks and leachate peaks, but late in the rainy season the response to rainfall was both more

immediate and more marked. As noted above, this does not necessarily mean that the some of the rain passed through the entire bed in one season. It is more likely that the presence of stored rain water in the upper layer of the bed increased the pressure and therefore the flow rate lower down.

4.3.4: It was possible to account for some of the features of the seasonal variations by assuming leachate production rate to be directly proportional to the amount of stored water. This model even gave a reasonable prediction of the much increased flow rate that resulted from the supplemental wetting program carried out on Cell 4 during the first seven months of 1996.

4.3.5: Evaporation plays such an important role in minimising the amount of leachate that it might be worthy of further study. For all except two or three months of the year, the evaporation rate in surface pans much exceeds rainfall, but leachate flow suggest that considerable volumes of stored water persist until late summer. The rate determining step is therefore probably the transport of stored water to the evaporation zone near the surface.

4.3.6: There is no evidence of breakthrough of any of the applied special waste chemicals or soluble tracer salts, into the leaches, over a period of 7 years. Not only were the total masses of chemicals found in the leachates a very small percentage of the applied amounts, but the amounts and concentrations found in the treated landfill cells were no more than those in the untreated comparison landfill cells. This finding is consistent with the expectation of long residence times resulting from low leachate production rates.

4.4: RESULTS OF ASSOCIATED STUDIES AT COASTAL PARK

4.4.1: Water balance, Evaporation, Leachate flow and Dilution at Coastal Park Landfill

- Measurements of rainfall and leachate outflow have enabled a complete water balance to be constructed for Coastal Park. This allows the actual evapotranspiration losses from the landfill surface to be evaluated. This amounts to 0,43 x A Pan Evaporation.

- The surface radiation balance at Coastal Park has been used to make independent calculations of the rate of evapotranspiration from the landfill. These appear to confirm the conclusions drawn from the water balance.

- A method has been suggested for evaluating the dilution of the leachate, leaving the landfill, by mixing with the groundwater flow. The results of this approach appear to be realistic provided there are no extraneous effects such as salt water intrusion from the sea.

4.4.2: Lateral Movement of Soluble Salts at Coastal Park Landfill

- Soluble substances migrating downward through landfilled general wastes have been observed to spread laterally to a considerable extent. Measurements in situ have shown that the macro-permeability of the general wastes is reasonably isotropic, and the lateral spreading cannot be ascribed to lateral flow on a macro-scale. An investigation of the lateral spreading via laboratory models has shown that with saturated flow conditions, lateral dispersion can be induced by the damming effect of plastic sheets with a small gap between them. It is suggested that this is a possible partial cause of the observed lateral spreading. However, the observed lateral migration has not been adequately explained, and a full explanation must still be sought.

4.4.3: Computer Model to Predict Movement of Leachate within a Landfill

- The purpose of this study was to develop a mathematical model, termed FLOW, which could be used to analyse waterflow in a domestic waste disposal site in terms of the rate at which water accumulates in the landfill or leachate is released from the landfill. The elements considered by the model are: precipitation, runoff, evaporation, evapotranspiration, percolation, horizontal flow and capillary movement. The way in which the model handles each of the elements of the overall water balance is described.

- The model FLOW was applied to the Coastal Park landfill. The results show that the model is capable of producing realistic values for the effect of surface vegetation, the moisture distribution in the landfill at the end of the wet and dry seasons, and the amount of leakage the landfill can be expected to generate. It was also shown that the model is quite sensitive for the initial moisture content of the landfill material, which means that this data should be obtained as accurately as possible when the landfill is started, or that accurate estimates should be made from similar case studies.

- The two parameters which had to be found experimentally (the fraction of excess water released into the lower layers,and the fraction of water which should move upwards under capillary action to equalize pore suctions) emphasize the need for further research in these areas.

4.4.4: Hydrological, Geochemical and Biological Significance of the Vadose Zone and its Role as a Buffer in Contaminated Soil Systems

The vadose zone can be defined as the variably-saturated zone between the land surface and the phreatic surface, and includes the soil water, the intermediate vadose zone and the capillary fringe. During unsaturated conditions, both chemical and hydrological factors control the subsurface transport of contaminants.

Attenuation processes may be broadly categorised into hydrodynamic processes, abiotic (nonbiological) processes and biotic processes. The geochemical attenuation capacity of this zone would be a function of clay content, organic matter and metal oxides (mainly iron and manganese). Other typical physical and chemical factors contributing to enhanced attenuation are redox, precipitation, dissolution, ion-exchange, filtration and dilution processes.

Biological attenuation occurs through microbial degradation or contaminants. The degradation of these xenobiotics can be influenced by adsorption phenomena, redox conditions, pH, nutrient amendments, and the type of substrate available to the microbes as an energy and carbon source.

The vadose zone might be capable of attenuating some of the chemical constituents in a leachate plume emanating from a landfill. However, it is unlikely that natural attenuation processes are sufficiently intense or sustainable to justify the exclusion of containment liners for prevention of groundwater contamination. The design and construction of co-disposal landfills which are totally reliant on the attenuation capacity of the vadose zone might be exposing groundwater to too great a risk of contamination, especially during wet seasonal periods.

4.4.5: Chemical Characterisation of Landfill Leachate and its Potential Mobility through the Cape Flats Sand

A critical threshold hydraulic conductivity (K) of 1 x 10^{-7} $cm.s^{-1}$ must be attainable if a material is to be used as a containment liner at a leachate generating landfill. Air dried samples of the Coastal Park soil were treated with 8% bentonite (swelling smectitic clay), 8% kaolinite (non-swelling clay) and 8% kaolinite plus a 4% gypsum (flocculant) treated middle layer, packed into rigid-wall perspex leaching columns and leached with landfill leachate after pretreatment with a 0,02 M $NaCO_3$, dispersant. The soil treatments were tested for their possible suitability as liner materials. The 8% kaolinite with 4% gypsum treated middle layer was the most effective sand amendment, maintaining a minimum K of $10^{-4.5}$ $cm.s^{-1}$, which, is still higher than the requirements of 1 x 10^{-7} $cm.s^{-1}$.

The LEACHM model was used to predict the quantity of leachate which could be generated over the wettest and average rainfall conditions. The model predicted that under average rainfall conditions and a 2 m soil cover depth, no leachate would be generated even with a 0% vegetation cover. However, under the wettest rainfall conditions, not even a 90% vegetation cover and 2 m soil depth is sufficient to prevent leachate generation over the period simulated. Under such conditions a more effective leachate management strategy, such as an efficient leachate drainage and collection system, should be implemented. The modelling exercise has demonstrated the use of LEACHM as an alternative approach to leachate generation predictions at landfills.

4.4.6: Evaluation of Chemical Composition of Leachate and Groundwater from the Coastal Park Landfill Site

Groundwater and leachate quality have been monitored at the Coastal Park landfill site since 1986. There are 5 infiltration cells to allow collection of leachate and 17 boreholes for sampling of groundwater. The objective of this study was to identify the most suitable chemical parameters as leachate indicators to enable the proportion of leachate in groundwater to be estimated. The following conclusions were drawn:

- Leachate COD concentrations were high during the early acid fermentation phases of landfill stabilisation, but thereafter declined to lower values.

- In contrast, potassium, ammonium and alkalinity increased as the COD declined and quite soon reached a steady state. There is a strong correlation evident between these ions. Potassium and ammonium are derived from vegetable and animal material while alkalinity mainly results from combination of ammonia and carbon dioxide.

- It was concluded that potassium, ammonium and alkalinity would be the best indicators of leachate in the middle years of life of the landfill site because of their greater contrast with the background levels in the uncontaminated groundwater.

- There are clear indications of increases in potassium, ammonium and alkalinity in 8 of the 17 boreholes. These levels can be used to estimate the proportion of leachate in the groundwater.

5: GENERAL CONCLUSIONS

The research achieved the main objectives of the project in exploring the potential of landfill sites in South Africa to act as final depositories for metallic wastes at minimal environmental risk. The main conclusions to be derived from this research are summarised as follows:

5.1: The material of concern in this investigation is a wood preservative commonly called CCA. This preservative consists of a mixture of copper, chromium and arsenic. The disposal of these substances, both as a waste solution or in combination with wood at the end of its lifecycle has the potential to become a global problem.

The Industry and Environmental Programme Activity Centre (IEPAC) operating under the umbrella of the United Nations is concerned about the current disposal options of treated timber such as the uncontrolled burning or disposal to landfill. If industrial wastes are disposed to a landfill then the wastes must be securely bound within that landfill, without the potential to provide environmental damage in future decades.

5.2: The results of this research have proved that metallic ions in materials such as CCA can be effectively immobilised by the process of adsorption onto the general wastes in a landfill. The amount of copper - chromium - arsenic in combination that could be co-disposed with general waste without adversely affecting leachate quality was:

copper at 67 g $Cu.tonne^{-1}$; chromium at 195 g $Cr.tonne^{-1}$ and arsenic at 195 g $As.tonne^{-1}$. The disposal ratio of these metals was dictated by the formulation of the CCA wood preservative. In general, the metal loading rates proposed from the experimental work and predicted by the modelling undertaken in this study, concurred with the metal loading rates employed in the United Kingdom as recommended by the Department of the Environment.

5.3: A significant aspect of this research was the emphasis placed upon adsorption as the only attenuation mechanism considered. The emphasis upon adsorption is a worst-case examination of co-disposal. Many previous researchers have concentrated upon strictly chemical affects such as reduction, precipitation and co-precipitation. Under anaerobic conditions other attenuation mechanisms are evident and are probably superior to adsorption in immobilising inherently non-biodegradable substances such as heavy metals. However, if none of the other attenuation mechanisms were present, this research has shown that adsorption has the capacity to immobilise the heavy metals under consideration.

5.4: If optimum attenuation is sought then co-disposal should be practised with stabilised (that has been deposited between 1 and 5 years) general wastes as compared to the acetogenic and methanogenic stages of a landfill life. The reason for this is the possible inhibiting effect of toxic industrial wastes on the biological degradation of the general wastes.

5.5: The application of chemical engineering techniques of reactor design and transport phenomena to determine behaviour of heavy metals in the landfill environment proved a welcome development from studies carried out elsewhere. Furthermore, the design, materials and mode of construction of the pilot-scale columns may be considered an improvement upon previous designs.

5.6: Additional moisture is added to a landfill during the co-disposal of liquid wastes. As a result, proper water balance management must be practised so as not to exceed the field capacity of the landfill, especially during wet seasonal periods. The vadose zone might be capable of attenuating some of the chemical constituents in a leachate plume emanating from a landfill. However, it is unlikely that natural attenuation processes are sufficiently intense or sustainable for prevention of groundwater contamination. Consideration should thus be given to the provision of containment liners so as to facilitate the collection, treatment and disposal of the leachate as an essential part of the overall landfill management.

5.7: The controlled co-disposal of hazardous wastes with general wastes is a landfill strategy which can play an important beneficial role in the overall management of these two waste streams. Landfill co-disposal technology needs to be recognised by the policy and regulation community in Southern Africa and managed by the waste management industry to the prescribed Minimum Requirements of the Department of Water Affairs and Forestry. Additional significance is given to this research as the

issue of co-disposal of hazardous waste with non-hazardous waste is under close scrutiny in Europe. In the United Kingdom, the practice of co-disposal on suitable existing landfill sites is strongly supported by the Department of the Environment. In comparison, the current European Community Landfill Directive prohibits the establishment of new co-disposal landfill sites.

5.8: The results of the research have economic implications for local authorities especially in the rural areas of Southern Africa which do not have sufficient hazardous waste landfill sites. The controlled co-disposal of metallic wastes with general wastes would enable a low-cost option to be utilised in the management of such chemical compounds.

5.9: The Coastal Park landfill is possibly one of the most researched sites in the world. Measurements of rainfall and leachate outflow have enabled a water balance to be constructed together with developed models to predict water flow and leachate generation. It is recommended that should the details of this report be utilised elsewhere, cognisance be taken of the local conditions in the Western Cape to assist in the adoption of the technology.

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7: SIGNIFICANCE OF THIS RESEARCH

Different perceptions of the values and dangers of the landfill co-disposal practice have developed. It is hoped that experimental studies of this nature will allow the development of Southern African guidelines which will enable landfill operators to dispose of wastes of a hazardous nature with the minimum of disturbance to the environment. Additional significance is given to this research as the issue of co-disposal of hazardous wastes with non-hazardous wastes is also under close scrutiny in other parts of the world.

8: RECOMMENDATIONS FOR FUTURE RESEARCH

8.1: Very little information is available on how the landfill water balance would be influenced by increasing the height of the landfill. On theoretical grounds it is postulated that higher landfills leach less, because compaction by the overburden load reduces the permeability of the waste.

A proposal was submitted by the Cape Metropolitan Council for an extension of the current project at the Coastal Park landfill to research the abovementioned phenomenon.

The Water Research Commission has subsequently approved an extension of 2 years to the contract term of the project (1998 - 1999). The extended project will be printed as Volume 2 of the final report.

The extended project will entail raising the surface of that section of the Coastal Park landfill, where the underlined cells 2 to 5 are located, by an additional two lifts of waste of 2.5 m each. The objectives of the extended project will be:

a) to study the resultant outflow of leachate, as the 5 m of refuse already in place are squeezed by the additional overburden load;
b) to study the amounts and rates of settlement, both of the existing 5 m of refuse and of the two 2.5 m layers placed over it, and;
c) to study if and by how much the ultimate rate of leaching of this section of the landfill is affected by the increased height.

8.2: The use of the large pilot-scale columns employed in this study would not be warranted for further research. It would however be advantageous to maintain the laboratory-scale experimental methodology and determine the adsorption characteristics of other industrial wastes. Various other heavy metals should be examined in combination and individually. Even the use of smaller columns would accelerate the experimental programme to more acceptable time-frames.

8.3: An important matter requiring further research when considering the co-disposal of heavy metals with general wastes is the possible remobilisation of heavy metals.

8.4: Soluble substances migrating downward through landfilled general wastes have been observed to spread laterally to a considerable extent and are not confined to vertical flow. The observed lateral migration has not been adequately explained and a full explanation must still be sought.

9: PAPERS EMANATING FROM THIS PROJECT

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Ballard, RH and Petrie, JG (1995) Use of lysimeters to determine the effects of special waste co-disposal on refuse stabilisation. *City of Cape Town & Institute of Waste Management Coastal Park Seminar*. Muizenberg Pavilion, Cape Town. 23 October.

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Stow, JG and Morrison, IR (1997) Evaluation of the chemical composition of leachate and ground water from the Coastal Park solid waste disposal site. *Institute of Waste Management, Landfill Specialist Interest Group Seminar*. Cape Town. 11 September.

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Dr S A Mitchell	Water Research Commission
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GLOSSARY OF TERMS/ACRONYMS

GLOSSARY

Anaerobic digestion	-	a microbial fermentation of organic matter to methane and carbon dioxide that occurs in the near absence of air.
Attenuation	-	the process of reducing leachate concentrations by means of natural physical (adsorption, filtration, extraction, ion exchange, etc.), chemical (precipitation, oxidation, reduction, acid-base reactions, etc.) and biological (hydrolysis, catabolism, fermentation, sulphate reduction, etc.) processes.
Biodegradable	-	a substance that can be broken down into smaller molecules by micro-organisms or their enzymes.
Bioreactor	-	the concept of designing and operating the landfill in order to promote controlled microbiological decomposition, reduce leachate strength, promote gas formation and to promote stabilisation of landfill surfaces.
Cell	-	the basic landfill unit of compacted solid waste which, when completed at the end of each day, is entirely contained by cover material.
Co-disposal	-	the mixing and joint disposal of special (hazardous) and general waste in the same landfill.
Containment	-	the separation of the waste body and any associated leachate from the underlying soil, rock and water regime, by means of a liner and a leachate collection system.
General waste	-	waste that does not pose an immediate threat to man or environment i.e. household waste, builder's rubble, garden waste, dry industrial and commercial waste. These waste are collected and disposed of by, or for, local authorities. Organic waste accounts for the largest part of general waste.

Landfill gas	-	a mixture of gases (mainly methane and carbon dioxide) produced by microbiological activity on biodegradable material deposited in a landfill site.
Leachate	-	an aqueous solution with a high pollution potential arising when water is permitted to percolate through decomposing waste.
Sanitary landfilling	-	uses the principles of engineering to confine the refuse to the smallest practical area, to reduce it to the smallest practical volume and to cover it with a layer of earth at the conclusion of each day's operation.
Special waste	-	refers to both liquid and solid industrial and commercial substances which represent a threat to human health and are potentially hazardous or toxic to the environment. Special wastes necessitate further processing and transformation into end-products or special disposal to render them acceptable in terms of both environmen-tal impact and public health legislation.
Stabilisation	-	refuse stabilisation in a landfill is a series of processes producing an end-product of such characteristics that its ultimate use will be acceptable in terms of both environmental impact and public health.
Unsaturated zone	-	the portion of the soil or rock profile situated above the principal water bearing formation i.e. water table. In this zone the soil pores are filled with gas and water as opposed to those in the saturated (phreatic) zone where pores are filled with water.
Vadose zone	-	extends from the ground surface to the water table. Water in the vadose zone exists primarily in the unsaturated state.

ACRONYMS

ASTM	-	American Society for Testing Materials
AWPI	-	American Wood Preserves Institute
CCA	-	a mixture of Copper, Chromium and Arsenic commonly termed Tanalith. These metals are in common use in combination as a water based wood preservative.
DEA	-	Department of Environment Affairs
DWAF	-	Department of Water Affairs and Forestry
FIFRA	-	Federal Insecticide, Fungicide and Rodenticide Act
GDP	-	Gross Domestic Product
IEPAC	-	Industry and Environmental Programme Activity Centre
ISWA	-	International Solid Waste Association
OECD	-	Organisation of Economic Cooperation and Development
RCRA	-	Resource Conservation and Recovery Act
TCLP	-	Total Characteristic Leaching Procedure
UNEP	-	United Nations Environment Programme

CHAPTER 1

INTRODUCTION

South Africa's rapid population growth accompanied by urbanisation and industrialisation has resulted in a dramatic increase in the mass of both general and hazardous wastes being generated. Sanitary landfilling, whereby the solid waste is compacted and covered each day with a soil layer, offers the most versatile method for the disposal of wastes in an economical and environmentally sound manner. Landfill co-disposal (or joint disposal) in its widest sense, is understood to be the calculated and monitored interaction of municipal refuse with other selected difficult industrial and commercial wastes in a properly controlled landfill site (Department of the Environment -UK, 1993).

The results of previous research carried out by the Cape Town City Council provided practical operational criteria for the landfill co-disposal of domestic refuse and anaerobically digested waste-water sludge liquor (Novella *et al.*, 1996). It was concluded that the co-disposal of waste-water sludge liquor with refuse was a landfill strategy which could play an important beneficial role in the overall management of these two waste streams. The impact of pending sludge legislation policies in South Africa may prohibit the agricultural utilisation of sludges that contain high concentrations of pollutants such as heavy metals and pathogenic bacteria. In such instances, and also where there is no agricultural demand for the sludge, it is likely that much greater use will be made of landfill co-disposal as an alternative sludge disposal option. Furthermore, landfill co-disposal technology needs to be recognised by the policy and regulation community and managed by the waste management industry within the framework of the Minimum Requirements of the Department of Water Affairs and Forestry (DWAF, 1994) as well as of Section 20 of the Environment Conservation Act, No. 73 of 1989.

A vast array of special wastes possessing undesirable characteristics are produced by industry. The term special wastes refers to both liquid and solid industrial wastes which are potentially hazardous and necessitate further processing and transformation into end-products or special disposal to render them acceptable in terms of both environmental impact and public health legislation. Such special wastes are not permitted for discharge into the sewerage system as they would deleteriously affect the conventional biological purification processes. Wastes of this nature have to be treated separately for inactivation prior to disposal in a containment landfill site. However, many areas do not have such special waste treatment and disposal facilities and the problem is often circumvented by illegal dumping into the sewer, the stormwater system or onto vacant ground with subsequent pollution of ground and surface water resources.

The co-disposal of special wastes with general wastes in sanitary landfills is being practised in many overseas countries, especially in drier areas which have a perennial water deficit. However, different approaches to co-disposal have led to quite different experiences and attitudes, with the result that different perceptions of the values and dangers of the co-disposal practice have developed. The major perceived problems with the disposal of special wastes on a landfill is the possible generation of a more polluted leachate (Department of the Environment - UK, 1993).

In comparison, the co-disposal of special wastes with general wastes in sanitary landfills in South Africa has not been widely implemented to date, due to various reasons. As a result of the foregoing, a three-year research project was negotiated between the Cape Metropolitan Council and the Water Research Commission with the objective of developing practical operational criteria for the landfill co-disposal of selected special wastes with general wastes. This could assist smaller landfill operators where only general waste landfills occur and where small volumes of special wastes must be disposed of.

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CHAPTER 2

AIMS AND MODUS OPERANDI OF THE PROJECT

2.1 AIMS OF THE PROJECT

- To determine practical norms for the landfill co-disposal of various selected special wastes (such as CCA - copper, chromium, arsenic), with general wastes under Western Cape conditions.
- To determine whether the attenuation mechanisms (physical, chemical and biological) inherent in a methanogenically mature landfill can prevent, or reduce, the potential hazard of the deposited special wastes.
- Quantify the rates of application of specific special wastes during a co-disposal operation.
- Establish if the co-disposal of special wastes with general wastes is an economic and environment-friendly concept, alternative to the expensive disposal of special wastes in containment sites.
- Monitor the quality of the leachate produced and estimate the possible effect on ground water quality.

2.2 MODUS OPERANDI OF THE PROJECT

The research was organised along the following lines so as to achieve the aims of the project:

- Laboratory-scale adsorption/desorption studies (Refer Chapters 5, 7 and 8).
- Pilot-scale landfill column studies (Refer Chapters 6, 7 and 8).
- Full-scale landfill cell studies at Coastal Park (Refer Chapter 9).
- Associated studies at Coastal Park (Refer Chapter 10).

Mr R H Ballard, an employee of the Cape Metropolitan Council, utilised the laboratory-scale adsorption/desorption studies and the pilot-scale landfill column studies for the purpose of obtaining a MSc (Engineering) degree through the Department of Chemical Engineering at the University of Cape Town.

2.3 CONTRACT AGREEMENT

Although the contract agreement between the Water Research Commission and the Cape Metropolitan Council did not call for the appointment of a Steering Committee, one was established which met yearly. A Special Waste Co-disposal Co-ordinating Committee was also formed in order to control the project on a day to day basis.

The duration of the practical aspects and monitoring phases of the project was initially two years (1994 and 1995) but this was subsequently extended by a further year (1996) by mutual agreement.

2.4 EXTENDED CONTRACT AGREEMENT

On completion of this project (Volume 1) a proposal was submitted by the Cape Metropolitan Council for a further extension to research the phenomenon of how the landfill water balance at Coastal Park would be influenced by increasing the height of the landfill by a further 5 m (refer Chapter 12 for further details).

The Water Research Commission has subsequently approved an extension of 2 years to the contract term of the project (1998 - 1999). The extended project will be printed as Volume 2 of the final report.

SECTION A

LABORATORY

AND

PILOT-SCALE

STUDIES

CHAPTER 3
LITERATURE REVIEW

3.1 INTRODUCTION

It is characteristic of all life that it takes suitable raw materials, and converts them into products of value to itself or its species. Unfortunately in doing so it inevitably produces waste material. In the case of modern human life the intake is of a much wider character and includes fuel, clothes and general commodities (Ministry of Housing and Local Government, 1970). Our waste is correspondingly large and varied, it includes air pollutants, water pollutants and solid wastes. A higher standard of living for the individual, means increased consumption of both materials and energy. This increase in living standards has always been accompanied by a larger volume of more complex residual waste. Industry is not an exception to the above. It uses raw materials, processes them to yield useful products, and is left with waste is possibly a large percentage of the mass of the raw materials used. It would seem probable, in the foreseeable future, as industry increases in extent and diversity so will the waste increase in amount and complexity.

A consideration of the Second Law of thermodynamics reinforces previous statements. The Second Law states "No apparatus can operate in such a way its only affect (in system and surroundings) is to convert heat adsorbed by a system into work" (Smith *et al*, 1975). A direct analogy may be drawn with human beings in virtually any form of their activities. There is not a process that can be operated without the production of waste in some manner or form. An important aspect of the Second Law is the concept of entropy. Entropy may be considered the degree of randomness or disorder in a system. Economists use this facet of the Second Law to illustrate that the recycling of materials cannot eliminate the production of waste (Cairncross, 1993). By implication, the concept of entropy indicates that recycling is inherently inefficient as there is an increasing tendency for entropy, and hence disorder, to increase to a state were nothing of value may be extracted. The logical conclusion is economic growth cannot be sustained by recycling. Economic growth can only be sustained by the consumption of larger amounts of energy and materials, creating larger amounts of waste.

For more than 5000 years land disposal of solid residues has been a key element in waste management (Ho *et al*, 1974). Thus, as the population has grown and become progressively more urbanised, a concomitant increase in the number, and size of landfill sites has been necessary. However, pressure to reduce the dependence on landfill as the major option for the disposal of wastes has been gathering momentum in recent years. The most potent driving force for change is the growing opposition from both the public and politicians to direct landfill as an environmentally acceptable disposable option (Campbell, 1993). In many of the industrialised countries, environmental legislation was introduced in the latter part of the

1980's and early part of the 1990's. This legislation focused primarily upon the pollution of water and air. This interest is now directed onto the management of solid waste. As greater attention (and legislation) is devoted to aqueous and atmospheric discharges, so industrialists and other producers will dispose of more waste to the land (Cairncross, 1993). Unfortunately, the present lack of reliable statistics describing the generation, treatment and disposal of waste arisings continues to impair the formulation of appropriate waste management strategies and the assessment of their effectiveness.

3.2 MUNICIPAL WASTES

Municipal wastes typically include household waste, certain white goods and bulky consumer wastes, as well as similar wastes from small commercial and industrial firms, institutions and markets, which are collected and disposed of by, or for, local authorities. There are, however, considerable variations in the exact definition of municipal waste between countries. Due to statistic gathering limitations, especially in developing world regions, the only accurate statement that can be made is that the volume of wastes is rising around the globe. The Organisation of Economic Cooperation and Development (OECD) estimated that, in 1990 alone, its member countries produced 420 Megatonnes of municipal wastes. Levels of municipal waste also continue to grow on a per capita basis (UNEP, 1993). In the mid-1970's a figure of 1.1kgday^{-1} (407kga^{-1}) was quoted for the OECD; by the end of the 1980's this had risen to 1.4kgday^{-1} (513kga^{-1}). Within the OECD it should be noted that over 90 percent of the population (100 percent of the urban population) has access to municipal collection services. Harris and co-workers (1988) notes that each American produces an average of 2.4kgday^{-1} (892 kga^{-1}).

More than 30 Megatonnes (2.15kg capita per day) of solid waste was generated in the Republic of Korea in 1990 (Lee *et al*, 1993), whilst in 1988, more than 200 Megatonnes of municipal solid waste was generated in the United States (Artiola, 1996). In 1991, the CSIR undertook a study to evaluate the composition and volume of wastes produced in South Africa (cited by Bredenhann *et al*, 1996). It was estimated that 15 million tonnes of municipal solid waste were being produced per annum. However, this figure excludes the former homeland states, now reinstated within the Republic of South Africa. It is believed the rate of increase in waste production was in excess of the average annual Gross Domestic Product (GDP) of 0.63 percent.

3.2.1 COMPOSITION OF MUNICIPAL SOLID WASTES

The composition of municipal wastes varies widely from country to country. Some general trends in the composition of municipal waste can however be recognised. Organic waste accounts for the largest part of municipal wastes. In industrialised countries there appears to be a decline in the percentage of paper and board, with an increase in the plastics content. The proportion of glass and metals have remained stable (UNEP, 1993).

TABLE 3.1 COMPOSITION OF MUNICIPAL SOLID WASTE IN DEVELOPING COUNTRIES

Component#	Percent Mass						
	Johannesburg South Africa 1991[a]	Soweto South Africa 1991[a]	Haifa Israel 1979[b]	Agra India 1993[c]	Sao Paulo Brazil 1986[d]	Melbourne Australia 1981[e]	Nairobi Kenya 1994[f]
Paper	34	4	30.3	3.7	28.4	22.9	37.6
Yard	-	-	3.1	10.4	2.3	5.1	1.3
Metal	6	1	3.1	-	4.9	8.3	0.7
Plastics	7	1	4.4	1.4	5.6	3.8	11.4
Food	30	15	54.7	4.3	3.0	41.8	-
Glass	10	2	3.0	0.6	3.1	15.1	-
Other	13	77*	-	79.6	52.7	3.0	49.0

* ash composed 45% of the total analysis

a Chapman & Ekama, 1991 b Raveh & Avnimelech, 1979 c Dayal *et al*, 1993
d Schmidell *et al*, 1986 e Musa & Ho, 1981 f Otieno, 1994

South Africa's past political development is indicated by the composition of it's municipal solid waste. The statistics for Johannesburg are similar to that quoted for those in the industrialised countries. Johannesburg was (as defined prior to 1994) predominantly racially categorised as white, its occupants middle class by global standards, their life style being similar to any of the countries being classified as industrialised or first world. Soweto, is largest "black" township in Africa. The population is almost exclusively African and working class. At the time of this survey (1991) large areas of Soweto were not electrified; this is evident by the low percentage of paper, absence of any yard (or garden) wastes, and high percentage of ash. It is probable that these constituents were being utilised as additional fuel for coal burning stoves. The absence of metal and plastic wastes indicates a high degree of scavenging and informal recycling. When considering the composition of municipal waste from Johannesburg the absence of yard wastes is also explainable. Many municipalities in South Africa's wealthier areas collect garden wastes separately.

TABLE 3.2 COMPOSITION OF MUNICIPAL SOLID WASTE IN INDUSTRIALISED COUNTRIES

Component#	Percent Mass				
	Paris France 1992[g]	Berlin FRG 1975[h]	Cincinnati Ohio USA 1982[i]	Typical European household waste 1989[j]	London United Kingdom 1979[k]
Paper	33.0	21.3	50.0	32	37.3
Yard	6.8	-	10.5	-	-
Metal	5.8	6.7	7.8	4	7.2
Plastics	11.7	5.3	8.1	7	3.8
Food	9.7	28.0	1.6	24	23.0
Glass	10.7	13.3	2.8	10	12.0
Other	22.3	25.4	19.2	23	16.7

g Attal *et al*, 1992 h Ehring, 1983 i Rickabaugh *et al*, 1993.
j Rosseaux *et al*, 1989

#The above tables conform to the categories reported by the United States Environmental Protection Agency in 1990 (USEPA, 1990).

3.2.2 DISPOSAL RATES OF MUNICIPAL SOLID WASTES

Burial in controlled landfills continues to be the most common means of disposing of municipal waste within the boundaries of the OECD. Approximately 70 percent is disposed of in this manner (UNEP, 1993). If one considers the major industrial countries, France disposes of 45 percent of its annual production of municipal solid waste by landfilling (Marticorena *et al*, 1993). The percentage of municipal solid waste landfilled exceeds 75 percent in the United Kingdom, Spain, Canada and the United States. Less than 40 percent of municipal solid waste is landfilled in Switzerland and Sweden due to the increased importance of incineration in these countries (Little *et al*, 1993). Large landfills in the former Soviet Union cover more than 140 thousand hectares (Nozhevnikova *et al*, 1993), of the 30 Megatonnes of solid waste generated in the Republic of Korea in 1990, 93 percent was landfilled (Lee *et al*, 1993), 200 Megatonnes of municipal solid waste was generated in the United States (Artiola, 1996) in 1988, 73 percent of this material was placed in over 6000 landfills (Reinhart, 1993). In South Africa, 95 percent of municipal solid waste generated is disposed to landfill, only 2.5 percent is recycled, the balance being littered or illegally disposed. It is estimated there are approximately 1200 municipal waste disposal landfill sites in South Africa (Bredenhann *et al*, 1996).

3.3 INDUSTRIAL AND HAZARDOUS WASTES

Industrial wastes encompass a wide range of substances of varying environmental toxicity. They usually include, general rubbish, packaging, food wastes, acids and alkalis, oils, solvents, resins, paints, and both organic and inorganic sludges. In the OECD area there has been a fifty percent increase in the generation of industrial wastes from 1980 to 1990. In 1990 the mass of industrial wastes generated was estimated at 1.5 Gigatonne per annum (OECD, 1991). A breakdown of disposal operations of hazardous wastes in the European countries of the OECD is shown below (Yakowitz, 1993).

A proportion of the wastes generated by industry are considered to be hazardous wastes as they contain substances that can be toxic to humans, plants or animals, are flammable, corrosive or explosive, or have high chemical reactivity. The OECD has compiled rough estimates of the volumes of industrial and hazardous wastes generated throughout the world. These are summarised below (data refer to the late 1980's) (OECD, 1991). Included in Table 3.4 is data gathered by the CSIR on behalf of the Department of Environment Affairs (DEA) in South Africa. The volumes of waste generated are small by global standards but are still considerable, especially in an African context.

TABLE 3.3 ULTIMATE DISPOSAL OF HAZARDOUS WASTES WITHIN THE OECD
(Yakowitz, 1993)

Disposal route	Quantity (Mta^{-1})	As a percentage of the total (%)
Landfill	14-18	70-75
Ocean disposal	0.7	2-5
Incineration	1.5	5-8
Physio-chemical treatment	1.0	4
Recovery	1.5-3.0	5-12

TABLE 3.4 GLOBAL INDUSTRIAL AND HAZARDOUS WASTE GENERATION

(OECD, 1991 & DEA*, 1992)

Region	Industrial wastes (Mta^{-1})	Hazardous and special wastes (Mta^{-1})
WORLD	2 100	338
OECD	1 430	303
North America	821	278
Europe	272	24
Pacific	333	
Eastern Europe	520	19
South Africa *	22	2
Rest of the World	158	14

UNEP as reported by the South African Department of Water Affairs and Forestry (DWAF, 1994b) defines hazardous waste as follows "Waste other than radioactive waste, which is legally defined as hazardous in the state in which it is generated, transported or disposed". The definition is based on chemical reactivity or toxic, explosive or other characteristics which cause or are likely to cause, danger to health or the environment, whether alone or in contact with other waste."

In the United Kingdom the term "hazardous waste" does not have any official meaning. The terms utilised are "notifiable waste" and "special waste" (Cook, 1984). Special waste is defined by the Control of Pollution Act (Special Waste) Regulations. The waste is regarded as special waste if the waste:

* can cause death or serious damage if $5cm^3$ were ingested by a 20kg child
* can cause serious damage to tissue on exposure for less than 15 minutes
* has a flash point of less than 21°C
* prescribed medicinal product

The United States Environmental Protection Agency employs the following criteria to determine whether a waste is hazardous (cited by Cope *et al*, 1983). A waste is hazardous if it is not excluded from other exhaustive listings, and exhibits any of the characteristics of hazardous waste in terms of ignitability, corrosivity, reactivity, or extractive procedure toxicity.

In South Africa, hazardous waste is defined as any waste that directly or indirectly represents a threat to human health or to the environment by introducing one or more of the following risks:

explosion or fire;
infections, pathogens, parasites or their vectors;
chemical instability, reactions or corrosion;
acute or chronic toxicity;
cancer, mutation or birth defects;
toxicity, or damage to the ecosystems, or natural resources;
accumulation in biological foodchains, persistence in the environment, or multiple effects.

The South African definition of hazardous waste is based on the UNEP definition stated above (DWAF, 1994b).

The options available for the disposal of hazardous waste in South Africa are; landfill; land treatment; incineration and marine disposal. Incineration is not widely practised in South Africa, there is a lack of facilities, and the high cost of incineration inhibits disposal by that method. Bredenhann *et al* (1996) states there are only approximately 8 incinerators operating in South Africa, all of which are devoted solely to medical waste. Marine disposal in South Africa is declining, in line with international trends, even though it is an inexpensive option. Land treatment is regarded as a pro-active choice of treatment but doubts are expressed in The minimum requirements for the handling and disposal of hazardous waste (1994) whether this method of treatment will attain the necessary environmental criteria. Hazardous waste may only be disposed at a landfill specifically designed for that purpose. Certain wastes may not be disposed to landfill, while other wastes may only be disposed by landfilling if they are pre-treated before disposal. Wastes that may not be disposed by landfilling are, explosive wastes; waste compressed gasses and radioactive wastes.

3.3.1 COMPOSITION OF INDUSTRIAL AND HAZARDOUS WASTES

The United Kingdom defines categories of hazardous waste, with further groups and subgroups (Department of the Environment, 1976). It should be noted the data is not comprehensive. Industrial producers add new chemical products at a rate which exceeds one per day, it would be impossible to produce an inclusive definitive list of hazardous wastes (Cope *et al*, 1983).

TABLE 3.5 CATEGORIES OF HAZARDOUS WASTES: I
(adapted from DOE, 1976)

Type of waste	Principle groups
Inorganic acids	All common inorganic acids
Organic acids and related compounds	All acids, acid anhydrides, acid chlorides, etc.
Alkalis	Alkali metal oxides and hydroxides, and proprietary alkaline cleaners
Toxic metal compounds	Cadmium, mercury, lead, arsenic and others.
Non-toxic metal compounds	Iron, etc.
Metals (Elemental)	Alkali, alkaline earth and other hazardous materials.
Metal oxides	Hazardous oxides.
Inorganic compounds	Cyanides, others that liberate toxic gases on acidification, oxidising compounds, toxic compounds, and others.
Other inorganic materials	Asbestos, slag, mineral processing wastes, etc.
Organic compounds	Hydrocarbons including, phenols, peroxides, halogenated compounds, organo-metalics, etc.
Polymeric materials and precursors	Polymeric materials and their associated precursors at all stages of manufacture, rubber, latex, etc.
Fuels, oils and greases	
Fine chemicals and biocides	Pharmaceutical, cosmetics, and biocides.
Miscellaneous chemical waste	Mixed inorganic and organic compounds.
Filter materials, treatment sludge and contaminated rubbish	
Interceptor wastes, tars, paint, dyes and pigments	
Miscellaneous wastes	Tannery and fellmongers wastes, celluloses, etc.
Animal and food wastes	All animal processing wastes.

A similar generalised list of hazardous waste is included in the South African legislation for the handling and disposal of hazardous waste (DWAF, 1994b). A table adapted from the Minimum requirements for the handling and disposal of hazardous waste (1994) is shown below.

TABLE 3.6 CATEGORIES OF HAZARDOUS WASTES: II
(adapted from DWAF, 1994b)

INORGANIC WASTES	OILY WASTES	ORGANIC WASTES
Acids and alkalis Cyanide wastes Heavy metal sludges and solutions Other solid residues	Primarily from the processing, storage and use of mineral oils	Halogenated solvents Non-halogenated solvent residues PCB wastes Paint and resin wastes Biocide wastes
PUTRESCIBLE ORGANIC WASTES	**HIGH VOLUME/LOW HAZARD WASTES**	**MISCELLANEOUS WASTES**
Wastes from the production of edible oils, slaughter house, tanneries and other animal based products	Wastes which based on their intrinsic properties present a relatively low hazard, but may pose problems because of their high volumes	Infectious waste from diseased human/animal tissue Redundant chemicals Laboratory wastes Explosive wastes from manufacturing or redundant munitions

The similarity of the wastes considered hazardous in the South African legislation to that considered hazardous in the United Kingdom is not surprising. South Africa, once a former member of the British Commonwealth, now again a current member, historically based legislation on that current within the United Kingdom.

3.3.2 DISPOSAL ROUTES FOR INDUSTRIAL AND HAZARDOUS WASTES

It can be seen from the table in section 3.3, the volumes of wastes are significant. Consider the data below for the disposal of hazardous waste in the United Kingdom (cited by Watson-Craik *et al*, 1992).

TABLE 3.7 DISPOSAL ROUTES OF HAZARDOUS WASTES IN THE UNITED KINGDOM

Method of disposal	Mass (ta^{-1})	Percentage of the total
Landfilling	1.3×10^6	70
Incineration	9.5×10^4	5
Sea dumping	1.9×10^5	10
Physical or chemical treatment (prior to landfilling)	2.9×10^6	15
Total	1.9×10^6	100

In the United States approximately 80 percent of hazardous waste is currently disposed by landfilling, surface impoundments, waste piles, lagoons, and underground injection wells (Reinhart *et al*, 1991). Referring to the Council for Scientific and Industrial Research (CSIR) study undertaken in 1991 (cited by Bredenhann *et al*, 1996), it was estimated that 1.6 million tons of hazardous waste was being generated per annum. Again, this figure excludes the former homeland states within the Republic of South Africa. Of this 1.6 million tons per annum it is estimated that approximately 1 million tons are inorganic wastes of which the largest part is cyanide wastes from gold mining. It is suspected that up 50 percent of the non-mining hazardous wastes are illegally disposed of onto municipal solid waste landfill sites, into sewers, or by illegal dumping (Bredenhann *et al*, 1996).

3.4 THE LANDFILL

landfill may be represented by a simple line diagram, its inclusion at this point will allow a general description and the introduction of terminology used in the following discussions.

The principal input and output streams to a landfill are shown below in Figure 3.1.

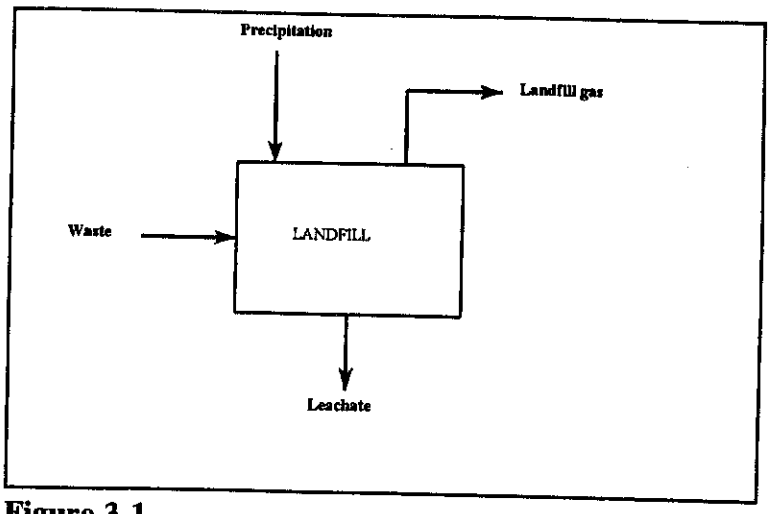

Figure 3.1
Landfills: principal input and output streams

3.4.1 WASTE

The majority of wastes disposed of to landfills are solid in nature, although the presence of municipal and industrial sludges is also common. Five major source categories can be identified. These are (Poland *et al* , 1986):

Residential;
Agricultural;
Commercial;
Municipal;
Industrial.

Landfills may be dedicated one specific type of waste (monofill); accept several types of waste (multifill); or may accept a mixture of municipal and industrial wastes (co-disposal) (DOE, 1986). Wastes originating from different source categories will contain different constituents which will also impart different associated characteristics to both the leachate and gas produced. The output streams are briefly discussed below.

3.4.2 LEACHATE

Precipitation or rainfall may fall onto the landfill. Initially, the solid wastes absorb this additional moisture until such time that field capacity is reached. The field capacity of solid waste is defined as the volume of liquid which can be absorbed by a given weight of solid waste without the release of excess water under the forces of gravity (Harris *et al*, 1988). The infiltration of rainfall into the landfill provides the transport phase for the leaching and migration of contaminants from the landfill. Mechanisms of contaminant removal include the leaching of inherently soluble materials, leaching of soluble biodegradation products of complex organic molecules, leaching of soluble products from chemical reaction, and washout of fines and colloids (Crawford, 1985).

Leachate is highly contaminated water that can emanate from the base of the landfill. It is one of the principal environmental concerns of landfill operation, the escape of leachate into either surface or ground water can significantly degrade their quality. It should be noted that some moisture may be derived from the input wastes, however, the major precursor of leachate formation is infiltration from rainfall.

3.4.3 LANDFILL GAS

Rainfall infiltrating into the landfill is a requirement for biological activity leading to methane production. Upon placement of the municipal solid waste aerobic decomposition will take place. Oxygen, either trapped on placement, or present in moisture, is consumed to produce principally carbon dioxide. After the oxygen is exhausted, anaerobic decomposition is initiated. Initially, carbon dioxide is mainly produced, however as anaerobic decomposition proceeds, methane production is established. The methane concentration of the gas generated from the landfill will eventually reach 50 to 60 percent. A landfill may generate methane at these concentrations for up to 20 years, possibly longer. After the cessation of gas production, anaerobic activity has then ceased, the landfill is said to be stabilised.

3.4.4 LANDFILL CLASSIFICATION

For convenience, from hydrogeological considerations, three categories of landfills may be recognised, although combined characteristics may be often apparent. These are containment sites; attenuation sites and rapid migration sites.

(a) Containment sites
Containment sites are isolated from the environment by the provision of a protracted integrity impermeable or semipermeable barrier of natural or synthetic materials. In Europe, this type of landfill site is often termed "Class I". This type of site is extensively utilised in the former Federal Republic of Germany (Senior, 1990). All hazardous wastes disposed to landfill in South Africa, must be disposed of in a containment site.

(b) Dilute and Disperse or attenuation sites
Protection from groundwater is affected by physicochemical and microbial intervention commonly termed attenuation. The key requirement is for slow leachate migration through sands and gravel, allowing, hopefully, a significant reduction in the pollutional characteristics of any leachate produced. In Europe, this type of landfill site is often termed "Class II". The majority of landfill sites operating in the United States and the United Kingdom fall within this category (Senior, 1990). Under current South African legislation, with the exception of the very small landfill sites, a dilute and disperse site would be unacceptable.

(c) Rapid migration sites
Rapid migration sites allow little or no environmental protection as leachates can migrate rapidly from the landfill.

3.4.5. LANDFILL OPERATION

When considering landfill operation one term must be defined at the outset, that of sanitary landfilling. The vast majority of landfills throughout the world are operated in this manner. It was not until the 1930's that the term "sanitary landfill" was introduced. Fresno, California, in a pioneering operation, started compacting solid waste and subsequently covering the compacted waste with soil (American Public Works Association, 1970). The term "sanitary landfill" is appropriate, since the solid waste is disposed in a sanitary manner. The American Society of Civil Engineers (American Society for Civil Engineers, 1976) define sanitary landfilling as "an engineered method of disposing solid waste onto land in a manner that protects the environment, by spreading the waste in thin layers, compacting it to the smallest volume and covering it with compacted soil by the end of each working day, or if necessary, more frequently". In the United Kingdom the term "controlled tipping" is more commonly used than sanitary landfill (Cope *et al*, 1983). In South Africa, landfills are required to be operated in accordance with the principles of sanitary landfilling (DWAF, 1994a).

Landfill operation may be generally classified by the type of waste it receives. As mentioned in Section 3.5.1, landfills may be dedicated to one specific type of waste (monofill). Examples of monofill landfills, are landfills dedicated to accepting power station ash, the disposal of tailings from mining and waste from the bulk production of inorganic chemicals. Multifill landfills accept a limited range of wastes; an example being certain industrial wastes of a similar nature, or mixtures of commercial and industrial wastes. A co-disposal landfill accepts both industrial wastes and municipal solid waste. This study investigates the immobilisation of copper, chromium and arsenic in municipal solid waste. If these materials were disposed of to landfill, usually, this material would be co-disposed. The co-disposal landfill is therefore discussed below in greater detail, than the other landfill operating modes.

(a) Co-disposal landfill and operation

The objectives of co-disposal are to absorb/adsorb, dilute and neutralise any liquids, and to provide a source of biodegradable materials (i.e. municipal solid waste) in order to encourage microbial activity that will assist in the degradation of hazardous compounds (DWAF, 1994b). However, industrial wastes may be present as either a liquid, sludge, solid or dust. For each of these forms of waste the correct method of co-disposal must be decided upon (DOE, 1986). Liquid wastes may be introduced into the landfill by trenching or lagooning; injection or irrigation.

To implement the trenching method, a trench is excavated in the municipal solid waste and liquid waste is then deposited within the trench. The aim of trenching is to provide sufficient interfacial surface area to allow seepage into the waste already deposited. Lagooning is similar to trenching; the difference being a shallow pit is usually excavated. Injection of liquid wastes is advantageous for wastes with a disagreeable odour. A common method of injection is to build up columns of tyres as the municipal solid waste is placed on the landfill. The liquid waste is then passed down to column and allowed to disperse. Irrigation is practised in the United Kingdom (DOE, 1986), but is not mentioned in the South African requirements possibly due to the danger of spray drift and the health of the landfill staff. Sludges may be

disposed of in trenches, or collected at the working face of the landfill, the covered immediately with municipal solid waste. Solids and dusts may be disposed in a similar manner. South African regulations (DWAF, 1994b) recommend a minimum ratio of one volume of hazardous waste to nine volumes of non-hazardous wastes in order for complete absorption, and to obtain an appropriate dilution of the hazardous waste.

3.5 WASTE DISPOSAL IN SOUTH AFRICA

Waste disposal in South Africa has been thoroughly overhauled in the 1990's. With the publication of Minimum requirements for waste disposal by landfill (DWAF 1994a), waste disposal methods are now comparable with those used in Europe and are stricter and more environmentally acceptable than regulations in countries such as the United Kingdom, where the principles of "dilute and disperse" are still embraced. The particular objectives of the Minimum requirements were the avoidance of degradation of the environment; of the landfill site itself; of the surrounding area; and the implementation of an environmentally acceptable landfilling process (Blight *et al*, 1992).

Historically, waste management in South Africa operated with a minimum of governmental control. Local municipalities such as the City of Cape Town operated landfill sites utilising guidelines initiated in Europe, such as the United Kingdom's Department of the Environment's Waste Management series. Until the promulgation of the Environment Conservation Act, No 73, 1989, there was an absence of any effective national control over waste management within South Africa. The promulgation of the aforementioned act did not fully rectify matters. It was not until August 1990 (Sterrenberg, 1996) that the relevant section on waste management was fully implemented. The major effect of the implementation of that section of the Environmental Conservation Act was, in future, landfill sites could only be operated with a permit from central government. The regulations cover the:

registration and licensing of landfill sites;
various impact surveys necessary;
monitoring boreholes, sample frequency and chemical analyses required;
fences, notice boards, etc.;
maintenance of records regarding waste type and volumes;
treatment and/or containment of any leachate produced;
procedure for landfill site closure, etc.

The major requirement from the landfill operator to central government is compliance with the regulations relating to the Minimum requirements for waste disposal by landfill (DWAF 1994a). First published for comment in the Government Gazette in 1985, there have been at least eight updates (Ball *et al*, 1992). The final draft was published in 1994 in three volumes. On publication, it was stated by the relevant minister, the Minister of Water Affairs and Forestry, that the document was open to comment from interested parties for a period of 3 years. The regulations are intended to facilitate conformity with international standards.

3.5.1 LANDFILL CLASSIFICATION

Under the South African system landfills are classified by three means, the; type of waste; size of the waste stream; potential for significant leachate generation.

(a) Waste type

Waste is sorted into two categories; general and hazardous. General waste comprises of what is usually termed municipal solid waste. Waste is considered hazardous if the waste even in low concentrations could have a significant effect on public health and/or the environment. The co-disposal of significant quantities of hazardous waste with general waste may only be practised on a hazardous waste landfill.

(b) Size of the waste stream

General waste landfills are classified into four groups: communal; small; medium, and large. This system was adopted to meet the variations that exist in South Africa, and indeed many developing countries. A small village could not be expected to meet the same requirements or have the same waste disposal needs as a large city. However, hazardous waste landfills are not classified by size, they are classified solely by the hazardous rating of the waste disposed of at that landfill. Any landfill which receives "significant quantities" of hazardous waste must be classified as a hazardous waste landfill.

(c) Leachate generation

The potential for leachate generation is assessed by means of a simplified climatic water balance. It is defined by:

$$B = R - E$$

Where,

B = Climatic water balance in mm of water
R = Rainfall in mm of water
E = Evaporation from the soil surface in mm of water

If the value of B is positive (a worst case scenario is employed) the landfill would be classified as having the potential for leachate generation. This unique system was introduced to compensate for the extreme variations of both climatic and socio-economic conditions existing in South Africa. Climatically, South Africa varies from arid desert, to humid rainforest. Socio-economically, conditions vary from those of a typical highly developed industrialised western economy, to those typical of a developing country with corresponding burgeoning population development and its associated poverty and rapid urbanisation (Ball *et al*, 1996).

With the exception of the small communal sites, all landfill sites classified as B+, require leachate management systems. Leachate management may be defined as (DWAF, 1994a) the collection and drainage of leachate to a point where it can be extracted for treatment. This requires a system of drains and a landfill liner. In certain instances, leachate management is synonymous with leachate containment.

Regardless of the climatic water balance, a hazardous waste landfill must be containment or Class I landfill sites. Therefore, all landfills accepting hazardous waste must be separated from the environment by a landfill liner and a leachate collection system.

3.5.2 GENERAL WASTE LANDFILLS

General waste is defined in the Minimum requirements as "waste that does not pose an immediate threat to man or the environment, i.e., household waste, builders' rubble, garden waste, dry industrial and commercial waste". As discussed in Section 3.5.1; general waste landfills are classified by the: size of the waste stream; potential for significant leachate generation. The legislative requirements are summarised below. It can be seen that far stricter measures are required at the larger landfill sites than the smaller.

TABLE 3.8 REQUIREMENTS OF GENERAL WASTE LANDFILL SITES IN SOUTH AFRICA
(adapted from DWAF, 1994a)

Waste classification	General waste		General waste		General waste		General waste	
Size of waste stream (tonnes day^{-1})	<1		>1 <25		>25 <500		>500	
Landfill classification	Communal		Small		Medium		Large	
Liner requisite	B-	B+	B-	B+	B-	B+	B-	B+
Compacted base layer	None	None	None	Reqd.	Reqd.	Reqd.	Reqd.	Reqd.
Leachate collection layer	None	None	None	Reqd.	None	Reqd.	None	Reqd.
First clay liner	None	None	None	Reqd.	None	None	None	Reqd.
Protecting geofabric	None	None	None	None	None	None	None	Reqd.
Leakage detection layer and underliner	None	None	None	None	None	None	None	Reqd.

3.5.3 HAZARDOUS WASTE LANDFILLS

Hazardous waste is defined in the Minimum requirements as "waste, other than radioactive waste, which is legally defined as hazardous in the state which it is generated, transported, or disposed of." The following types of hazardous waste are specifically mentioned in the Minimum requirements. Inorganic waste; oily waste; organic wastes; putrescible organic waste; high volume/low hazard waste, which contain small quantities of dispersed hazardous substances.

Hazardous waste landfills are categorised by nature of the hazardous waste received at that landfill. There are two categories of hazardous waste landfill sites in South Africa, they are designated "H:h" and "H:H". Landfills that are engineered to accept all types of hazardous wastes are designated "H:H", while landfills designated "H:h" accept waste that has been evaluated less hazardous. The engineering criteria of the two different classes of hazardous waste sites is shown below. Subsequently, the determination of the hazardous rating of the waste is addressed as this determines the class of landfill the waste may be disposed at.

TABLE 3.9 ENGINEERING REQUIREMENTS OF HAZARDOUS WASTE LANDFILL SITES IN SOUTH AFRICA
(adapted from DWAF, 1994a)

Waste Classification	Hazardous waste (H:h)	Hazardous waste (H:H)
Classification of hazardous waste	Moderate & low hazard waste only Hazard ratings 3 & 4	Extreme, high, moderate and low hazard waste Hazard ratings 1 - 4
Liner requisites		
Compacted base layer	Required	Required
Leachate collection layer	Required	Required
First clay liner	Required	Required
Protecting geofabric	Required	Required
Leakage detection layer and underliner	Required	Required
Second clay liner	Required	Required
Sand cushion layer	None	Required
Flexible membrane liner	None	Required

(a) Determination of the hazardous rating of a waste

Hazardous waste in South Africa is classified in terms of Hazard ratings. The following four sub-categories are employed:

Hazard rating 1:	Extreme hazard
Hazard rating 2:	High hazard
Hazard rating 3:	Moderate hazard
Hazard rating 4:	Low hazard

The following criteria must be assessed:

acute mammalian toxicity of compounds in the waste, expressed as LD_{50} ($mgkg^{-1}$);
acute ecotoxicity of compounds in waste, expressed as LC_{50} ($mgkg^{-1}$) of aquatic organisms;
biodegradability (COD or BOD) expressed as a percentage;
accumulation potential, expressed as the octanol/water coefficient, Pow:
persistence potential, expressed as soil adsorption, Koc:
Estimated Environmental Concentration (EEC)

The EEC is the controlling factor. The EEC is calculated from the supposition that the waste is disposed of directly into a body of water and the risk this action would generate. This is compared with the value of the acute ecotoxicity of compounds in waste, expressed as LC_{50} ($mgkg^{-1}$) multiplied by a safety factor of 10 percent, in order to determine the Hazard rating. The method of calculation is fully addressed in the Minimum requirements for the handling and disposal of hazardous waste (DWAF 1994b).

3.5.4 WASTE DISPOSAL IN SOUTH AFRICA - THE CURRENT STATUS

The Minimum requirements for waste disposal by landfill has already been adapted for use in Botswana, while other possible applications include Ghana, Tanzania and Uganda. Additionally, the International Solid Waste Association (ISWA) Working Group on Sanitary landfills, has utilised it as a basis for their document on landfilling in developing countries (Ball *et al*, 1996). This is indicative of the quality of the document and the competence of the researchers and personnel involved in the production of the Minimum requirements .

As stated previously the documents were introduced in 1994, and are open for comment until 1997. South African response to the document was generally mixed and tended to vary in accordance with the viewpoints of the persons involvement with landfilling. The two main criticisms were either the standards were too high, or the standards were not stringent enough. All comment received was considered, of relevant comment received, two main categories existed. There was firstly, a misunderstanding of the basic philosophy of the document. Secondly, there were valid ideas which identified areas which required further attention.

The basic philosophy of the document was to utilise a system which was relatively flexible and would be able to be utilised across the broad spectrum of South Africa society and in context with the varying climatic conditions in South Africa. This philosophy is still considered to satisfactory. Difficulties were not encountered with the waste classification system, some difficulties were encountered with the size of the operation classification, as the problem of the ultimate size of the landfill was not addressed within the classification system. This was addressed however, during the relevant section on environmental impact. The system to assess leachate generation caused some confusion, it was however still felt to be satisfactory, with some very small minor amendments.

The more important valid ideas to be incorporated into further updated editions of the Minimum requirements included:

prohibition of the landfilling of medical wastes;
public participation, greater emphasis was required;
liner design, to be amended with progress in technology;
scavenging, a problem in developing communities, could not be endorsed but required attention, and appropriate safety measures should be included as an appendix to the Minimum requirements.

Of special interest within this study is the issue of co-disposal. A co-disposal minimum ratio of one volume of hazardous waste to nine volumes of non-hazardous waste was initially recommended. Landfill operators were in accord that this ratio was conservative, especially in the drier areas of South Africa. It will now be recommended the site must be trafficable and free of liquid surfaces. The landfill site operator must manage the site in accordance with the climatic water balance. Simply stated, in a wetter climate possibly less liquid may be co-disposed, in a drier climate, more liquid may be co-disposed.

Ball *et al* (1996) concludes that the Minimum requirements for waste disposal by landfill have been successfully implemented and the are not any fatal flaws within the documentation. There is not any requirement for fundamental changes within the document, but the inclusion of worthwhile comment will further improve and augment it. Problems that could possibly arise in the South African context and in other African countries is the implementation of the Minimum requirements. There is a shortage of suitably trained personnel in South Africa and in other African countries. Formulating standards is advantageous only if implementation of those standards is satisfactory.

3.6 THE LANDFILL BIOREACTOR

From a chemical engineering viewpoint, a sanitary landfill is a chemical and biological reactor utilising a heterogeneous feedstock, being partially isolated from the atmosphere and the soil by diffusion gradients which are predetermined by the permeability of the fill material and the adjoining strata (Ellis, 1980). As with any reactor one must consider the reactions occurring, (in this case, the landfill stabilisation processes in general, and anaerobic digestion in particular) within the reactor, together with the various streams, leachate and landfill gas,

exiting from that reactor. Usually the different modes of reactor operation should also be examined. The following sections examine, initially, the disposal of municipal solid waste, the conventional mode of reactor operation, and subsequently, the effect of co-disposing industrial wastes with municipal solid waste. The co-disposal of copper, chromium and arsenic with municipal solid waste is the principal area of concern in this current work.

3.6.1 LANDFILL STABILISATION PROCESSES

After the placement of municipal solid waste within a landfill a complex sequence of physically, chemically, and biologically-mediated events occur. As a consequence of these events, municipal solid waste is degraded or transformed. A number of workers have investigated these processes of decomposition, the number of phases of landfill degradation being dependent on the objectives of their investigations. There are two main approaches, the four phase microbially based model developed by Barlaz *et al* (1989), and the five phase landfill stabilisation model developed primarily by Pohland (Poland *et al*, 1986a). Pohland's model correlates events occurring within the landfill with physical changes occurring in the leachate and gas produced by the landfill.

(a) Microbial based four phase model
(adapted from Barlaz *et al*, 1989)

Phase I Aerobic phase
Oxygen is present within the void space when the municipal solid waste is landfilled. Both oxygen and nitrate are present in the moisture associated with this solid waste. Both are consumed, with soluble sugars are the main source of carbon for microbial activity. All the trophic groups required for methanogenesis are present in fresh municipal solid waste (cellulolytics, acetogens, and methanogens), there is however, little change in their populations during this phase.

Phase II Anaerobic acid phase
Carboxylic acids accumulate, there is a corresponding decrease in the pH of the eco-system, with some cellulose and hemicellulose decomposition. The population of the methanonogenic bacteria begins to increase; methane is detected in the landfill gas.

Phase III Accelerated methane production phase
There is a rapid increase in the methane concentration of the landfill gas to values approaching 60 percent. A decrease in carboxylic acid concentrations is evident, together with an increase in system pH. There is little solids hydrolysis, but there are increases in the populations of cellulolytic, acetogenic and methanogenic bacteria.

Phase IV Decelerated methane production phase
Two microbial events occur during this phase. The production of methane, pH, bacterial populations of both cellulolytic and methanogenic bacteria remain constant. Within the same time frame, the production of methane decreases, the population of the acetogenic bacteria increases, and carboxylic acids are depleted. There is also an increase in the rate of cellulose and hemicellulose decomposition.

(b) Five phase landfill stabilisation model
(adapted from Poland *et al*, 1986a)

Phase I Initial adjustment

Initial waste placement and preliminary moisture accumulates.
Initial subsidence and closure of each landfill area.
Changes in environmental parameters are first detected to reflect the onset of stabilisation processes which are trending in a logical fashion.

Phase II Transition

Liquid is present in excess of field capacity and leachate is formed.
A transition from initial aerobic to anaerobic microbial stabilisation occurs.
The primary electron acceptor shifts from oxygen to nitrates and sulphates with the displacement of oxygen by carbon dioxide in the gas.
A trend toward reducing conditions is established. Measurable intermediates such as volatile organic fatty acids first appear in the leachate.

Phase III Acid formation

Intermediary volatile organic fatty acids become predominant with the continuing hydrolysis and fermentation of waste and leachate constituents.
A precipitous decrease in pH occurs with a concomitant mobilisation and possible complexation of metal species.
Nutrients such as nitrogen and phosphorous are released and utilised in support of the growth of biomass commensurate with the prevailing substrate conversion rates.
Hydrogen may be detected and this will affect the nature and type of intermediary products formed.

Phase IV Methane fermentation

Intermediary products appearing during the acid formation phases are converted to methane and excess carbon dioxide.
The pH returns from that controlled by the volatile organic fatty acids to one characteristic of the bicarbonate buffering system.
Oxidation-reduction potentials are at their lowest levels.
Nutrients continue to be consumed.
Complexation and precipitation of metals species proceed.
Leachate organic strength is dramatically decreased in correspondence with increases in gas production.

Phase V Final maturation

Relative dormancy following active biological stabilisation of the readily available organic constituents in the waste and leachate.
Nutrients may become limiting.
Measurable gas production all but ceases.
Natural environmental conditions become reinstated.
Oxygen and oxidised species may slowly reappear with a corresponding increase in oxidation reduction potential.

More microbially resistant organic materials may be slowly converted with the possible production of humic-like substances capable of complexing with, and re-mobilising heavy metals.

3.6.2 ANAEROBIC BIOLOGICAL PROCESSES
(adapted from Speece, 1983)

The bioconversion of organic material to methane is accomplished by a consortium of bacteria comprised of chemoheterotrophic, nonmethanogenic bacteria and methanogenic bacteria. Complex organics are first hydrolysed by the chemohetrotrophic nonmethanogens to free sugars, alcohols, volatile acids, hydrogen and carbon dioxide. Subsequently, the alcohols and volatile acids longer than two carbons are oxidised to acetate and hydrogen by obligate proton reducing organisms called acetogens, which must exist in symbiotic relation with hydrogen utilising methanogens.

In the final step, acetate and hydrogen are converted to methane by methanogenic bacteria. Acetate is the most important substrate for methanogens. Jeris *et al,* (1965) conducted a series of experiments with batch operated laboratory sewage sludge digester, in which they showed that acetic acid is the most prevalent volatile acid intermediate formed in the fermentation of fats, carbohydrates and proteins, and approximately 70 percent of the methane produced results from its degradation.

An obligate, syntropic relationship exists between the acetogens, which convert the higher volatile acids to acetate and hydrogen, and the hydrogen-utilising methanogens. Hydrogen partial pressure must be maintained at an extremely low level to enable favourable thermodynamic conditions for the conversion of volatile acids and alcohols to acetate. Under standard conditions of one atmosphere of hydrogen, the free energy change is positive for this conversion and thus precludes this reaction. An example of this is the conversion of propionate to acetate and hydrogen. The free energy does not become negative until the hydrogen partial pressure decreases below $10^{-9}Nm^{-2}$. It is therefore obligatory that the hydrogen utilising methanogens maintain these extremely low hydrogen partial pressures in the system; otherwise, the higher volatile acids, such as propionic and butyric will accumulate in the system. Fortunately, the hydrogen utilising methanogens in this physiological partnership are adept at this and normally perform this service with ease, to permit the reaction to proceed efficiently to full methane production.

The major groupings of bacteria and the reactions they mediate are as follows:

1: fermentative bacteria,
2: hydrogen-producing acetogenic bacteria,
3: hydrogen-consuming acetogenic bacteria,
4: carbon dioxide-reducing methanogens,
5: aceticlastic methanogens.

The metabolic steps and microbial groups involved in anaerobic digestion are shown below.

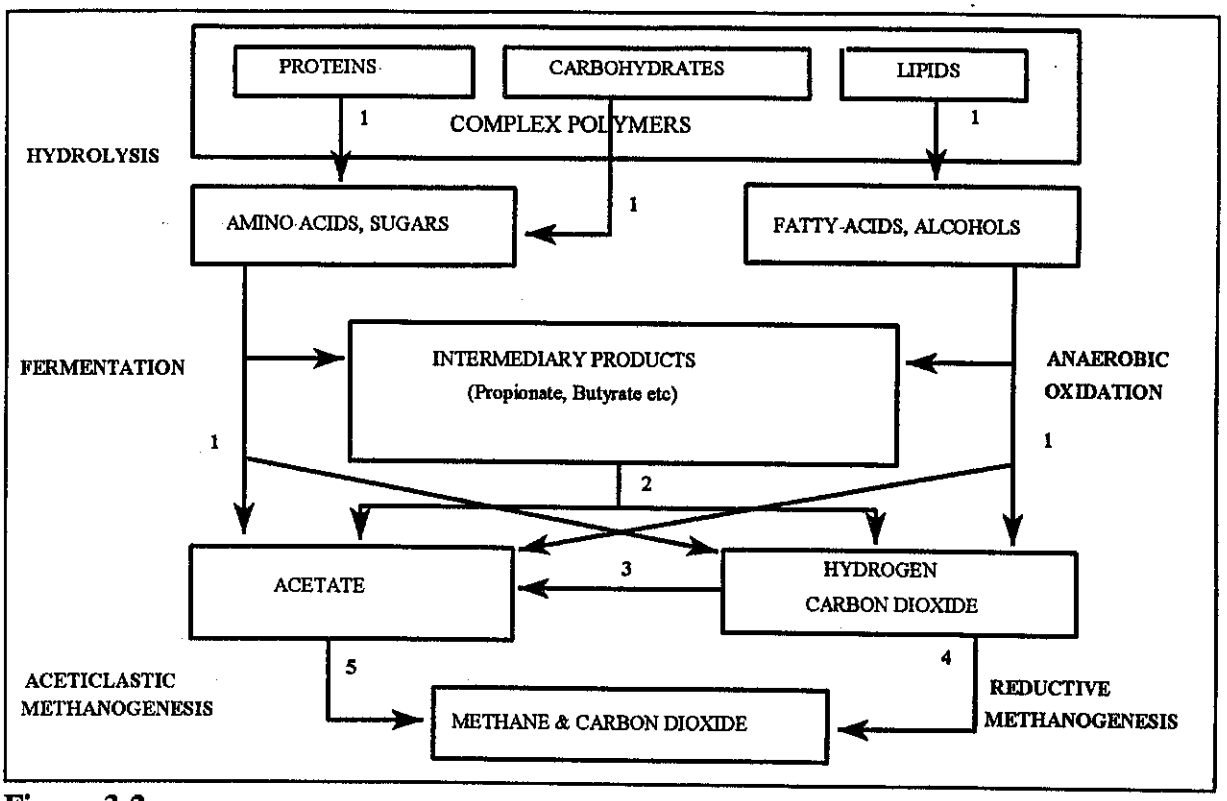

Figure 3.2
Reaction Scheme for the anaerobic digestion of polymeric materials
(cited by Pavlostathis *et al*, 1991)

The nature and chemical composition of the materials used in anaerobic digestion dictate those degradation sub-processes which are operative, and the microbial groups involved in these processes. The table below (Table 3.10) shows the composition of primary and activated sludge, common substrates for anaerobic digestion, with the inclusion of the composition of municipal solid waste for comparison. It can be seen from the table the substrates are similar in nature with only the cellulose content and protein content being significantly different. The major component of activated sludge is crude protein. Primary sludge has a relatively high lipids content. The principle substrates which decompose in landfills to form methane are cellulose and hemicellulose (Barlaz *et al*, 1989). The bioconversion of biopolymers (principally cellulose, hemicellulose, and protein) is accomplished by three trophic groups of anaerobic bacteria. These are:

hydrolytic and fermentative bacteria,
acetogenic bacteria,
methanogenic bacteria.

Barlaz *et al* (1989) found all these trophic groups present in fresh municipal solid waste.

TABLE 3.10 COMPOSITION OF PRIMARY SLUDGE, ACTIVATED SLUDGE AND MUNICIPAL SOLID WASTE

Component	Primary Municipal Sludge (Higgins *et al*, 1982)	Activated Sludge (US EPA, 1979)	Municipal Solid Waste (Barlaz, 1988)
Volatile solids	75.0	59-75	78.6
Lipids	10.3	5-12	-
Cellulose	32.2	7	51.2
Hemicellulose	2.5	-	14.9
Lignin	13.6	-	15.2
Crude protein	19.0	32-41	4.2
Volatile acids	6.4	-	-
Ash	25.0	25-41	21.4

3.7 THE LANDFILL BIOREACTOR - THE ASSOCIATED ENVIRONMENTAL HAZARDS HAZARDS

There is a need for the sound environmental management of every aspect of landfill activities in order to minimise, and whenever possible, eliminate, any adverse effects. These effects range from visual intrusion to more easily measurable impacts such as leachate and gas migration. Campbell (1993) was concerned with the following:

Leachate;
Gas;
Site Restoration;
General matters, including vermin, flies, birds, litter, dust, smell, mud on roads, visual intrusion, noise and traffic.

3.7.1 LEACHATE

Before 1965 very few people were aware of the fact that water passing through municipal solid waste in a landfill would become highly contaminated (Boyle *et al*, 1974). This water, termed leachate, was generally not a matter for concern because only a few causes had been noted were leachate was detrimental to the environment. Leachate from a landfill site containing biodegradable matter, such as municipal solid waste, may be defined (Harris *et al*, 1988) as

a complex organic liquid formed primarily by the percolation of precipitation water through the open landfill or through the cap of the completed fill. The resulting leachate is a complex and highly variable mixture of soluble organic, inorganic and bacteriological constituents and suspended solids in an aqueous medium. The exact composition is variable and site specific. Many workers have analysed leachates and details of their analyses abound in the literature (Robinson, 1980; Iza *et al*, 1992; Kennedy *et al*, 1988; Mott *et al*, 1987). Robinson *et al* (1982) cites the results of a survey undertaken by himself in 1979. He and his co-workers sampled 15 landfill sites in the United Kingdom. The results are summarised below in Table 3.11 and show the composition of leachates and emphasize the wide range of concentrations of the constituents.

TABLE 3.11 COMPOSITION OF LEACHATES FROM MUNICIPAL SOLID WASTE LANDFILLS, RANGES OF CONCENTRATION IN SAMPLES

(adapted from data cited by Robinson *et al* , 1982)

Determinand	Range	Determinand	Range
pH value	6.2-7.4	Mg	12-480
COD	66-11600	K	20-650
BOD	<2-8000	Ca	165-1 150
TOC	21-4400	Cr	<0.05-0.14
Amm.-N	5-730	Mn	0.32-26.5
Org.-N	ND-155	Fe	0.09-380
Nitrate-N	<0.5-4.9	Ni	<0.05-0.16
Nitrite-N	<0.2-1.8	Cu	<0.01-0.15
Ortho-P	<0.02-3.4	Zn	<0.05-0.95
Chloride	70-2777	Cd	<0.005-0.01
Sulphate	55-456	Pb	<0.05-0.22
Na	43-2500		

(All results, except pH, are expressed in $mg\ell^{-1}$)

As far back as 1982, groundwater contamination had become one of the United States most pressing environmental problems (Evans *et al*, 1982). The earliest documented case of groundwater pollution from impounded garbage was reported by Calvert in 1932 (Calvert, 1932). Calvert reported increased levels of calcium, magnesium, chlorides, total organic nitrogen, total solids and carbon dioxide in a well more than 150m from the impounding pit. Since this historic reference there have been many reported incidences where leachate has contaminated the surrounding soil and polluted an underlying groundwater aquifer or nearby surface water (Chain *et al*, 1976; Reinhard *et al*, 1984; Albaiges *et al*, 1986; Assmuth *et al*, 1993).

3.7.2 LANDFILL GAS

Landfill gas is a mixture of gases produced by microbiological activity on putrescible/biodegradable or other similar material deposited in a landfill site. When large amounts of solid waste accumulate, the landfill site acts as a bioreactor in which micro-organisms produce a biogas typically composed of approximately 35-40 percent carbon dioxide and 60-65 per cent methane (Freestone *et al*, 1994). In addition to the major components, landfill gas contains an extremely wide variety of components in trace amounts (DOE, 1986; Poland *et al*, 1986b). These components are too numerous to tabulate. A summary of these trace components contained in landfill gas is shown below;

TABLE 3.12 LANDFILL GAS COMPOSITION
(adapted from DOE, 1986)

Component	Typical value (mature refuse) [%volume]	Component	Typical value (mature refuse) [%volume]
Methane	63.8	Unsaturated hydrocarbons	0.009
Carbon dioxide	33.6	Halogenated compounds	0.00002
Oxygen	0.16	Hydrogen sulphide	0.00002
Nitrogen	2.4	Organosulphur compounds	<0.00001
Hydrogen	<0.05	Alcohols	<0.00001
Carbon monoxide	<0.001	Others (not included above)	0.00005
Saturated hydrocarbons	0.005		

There have been many cases reported where methane produced in domestic landfills has migrated into adjacent properties. Where explosive concentrations have accumulated and caused an explosion, the consequences have been property damage, personal injury and even loss of life. Such problems received little attention until the early 1970's (DOE, 1990). Even then, early efforts to evaluate gaseous emissions from landfills were primarily concerned with methane and the associated dangers of explosions, fires, and potential asphyxiation of surrounding residents in their homes. As studies in landfills increased in numbers and the level of technology improved, many incidents of toxic organic compounds were reported. The State of California has enacted a law to compel landfill owners to monitor for 26 volatile organic compounds (Rickabaugh *et al*, 1993).

Gas production in landfills is affected by many variables, Pohland reviewed a number of sources and considered the major variables on gas production (Poland *et al*, 1986) to be, the:

nature of the solid waste;
moisture content;
particle size and degree of compaction;
buffer capacity;
nutrients;
temperature;
method of gas extraction.

3.8 CO-DISPOSAL OF INDUSTRIAL WASTES WITH MUNICIPAL SOLID WASTES

The co-disposal of industrial wastes with municipal solid waste is regarded by some researchers, such as Rushbrook (1990), as a logical extension of the operation of municipal waste landfilling. Rushbrook considers that co-disposal is probably the easiest and quickest method to bring about an improvement in industrial waste management, especially in developing countries.

Since the early 1970's scientific research has examined the environmental aspects of co-disposal (DOE, 1975). A limited programme of research was started in March 1972 by the then Water Pollution Research Laboratory. They examined 19 landfill sites situated in various geological formations and accepting a wide range of hazardous wastes. Full scale studies were supported by further work at pilot and laboratory scale (Bromley *et al*, 1981). Co-disposal is widespread in the United Kingdom (Little *et al*, 1993) and is institutionally supported by the Department of Environment and the Harwell Laboratory, a prestigious institution that has principally been involved with nuclear development (Arnott, 1985).

In the United States, before the passage of the Resource Conservation and Recovery Act (RCRA) in 1976, there was very little control in many areas over the landfilling of industrial wastes (Lee *et al*, 1984). The co-disposal of industrial wastes with municipal solid wastes did not violate any regulatory laws, Graham (1985) estimates thousands of municipalities in the

United States accepted industrial wastes in their landfills as a service to local industries. Currently, in the United States (Little *et al*, 1993) there is not any federal legislation which expressly forbids the co-disposal of municipal and other waste provide that the appropriate treatment and landfill engineering standards are met. If the waste disposed with municipal solid waste, is classified as hazardous waste, then disposal standards for hazardous waste have to be met. There is thus an economic incentive not to dispose hazardous waste with municipal waste, and therefore co-disposal of such waste is not widely practised. In Denmark, municipal solid waste and industrial waste is separated into two distinct streams (Arnott, 1985). Co-disposal is practised in South Africa and is encouraged within the Minimum requirements documentation. A minimum ratio of one volume of hazardous waste to nine volumes of non-hazardous waste is recommended. This should allow sufficient dilution of the hazardous waste and allow the provision of sufficient absorptive capacity.

Co-disposal may be defined as the conscious deposition of hazardous wastes with household or similar wastes to obtain specified objectives, a key element of which is to take advantage of attenuation processes inherent within the landfill site (DOE, 1986). Co-disposal utilises those properties available in the municipal solid waste to attenuate the constituents present in the hazardous waste that could be detrimental to the environment. These attenuation mechanisms have been conveniently summarised (DOE, 1986).

Attenuation processes

Physical	Absorption, adsorption. filtration, dilution, dispersion.
Chemical	Acid-base interactions, oxidation, reduction, precipitation, co-precipitation, ion-exchange, ion formation.
Biological	Aerobic and anaerobic microbial degradation.

The effective co-disposal of substances which are inherently non-biodegradable (such as heavy metals), is dependent upon dilution to reach environmentally acceptable standards or immobilisation within the landfill (Watson-Craik, 1987). The concept of dilution is addressed in Section 3.9.1.1.

When one considers the above attenuating mechanisms it is also valuable to consider factors which could enhance the mobility of metal ions within the landfill environment. One example being the lowering of the pH, an example being a landfill within the acetogenic phase of activity. Other factors worthy of consideration are, redox changes, inorganic and organic complexation and microbially mediated species transformations such as biomethylation (Forstner *et al*, 1995).

3.8.1 PHYSICAL ATTENUATION MECHANISMS

3.8.1.1 ABSORPTION

When considering the mechanism of absorption within the landfill environment it is critical there is a thorough understanding of the landfill site water balance. The water balance or water budget technique is an application of the conservation of mass and continuity of flow of liquid to and from the landfill (Blight *et al*, 1992). Unfortunately, the task of determining the water balance for a particular site is not a simple matter. The interrelationships between climate, vegetation, soil characteristics, and their effect on run-off, evapotranspiration and vertical drainage are complex (Peyton *et al*, 1988). To obtain maximum absorption of co-disposed industrial wastes it is necessary to avoid any additional inputs of moisture such as groundwater infiltration. Additional factors to consider could include:

the rate of placement of the municipal solid wastes;
the rate and placement of any liquid waste;
moisture generated by metabolic activity;
moisture content of fresh solid waste;
composition of the emplaced municipal solid waste.

The infiltration of moisture into the landfill and its absorption by the solid waste can delay the formation of leachate. The are two predominant mechanisms for the retention of moisture in solid waste (DOE, 1986). Liquid may be absorbed into the waste and retained by capillary attraction within the microparticles of the solid waste, liquid may also fill and be subsequently retained by voidage volume formed upon the placement of the solid waste at the landfill site. The degree of compaction of the solid waste has a significant effect on the magnitude of water retention displayed by the solid waste, at higher compaction densities absorptive capacity falls sharply. At compaction densities of 700-800kgm^{-3} it is estimated the solid waste could absorb 0.1-0.2m^3 of added moisture per cubic metre of solid waste. When compaction densities are achieved, absorptive capacities may be reduced to as little as 0.02-0.03m^3 of moisture per cubic metre of solid waste (DOE, 1986).

3.8.1.2 DILUTION AND DISPERSION

The United Kingdom's Department of the Environment are strong proponents of the principle of the "dilute and disperse" approach to waste disposal. At low concentrations, wastes which at greater concentrations could be extremely hazardous can be safely disposed at landfill sites. Dilution and dispersion can occur naturally where these materials are randomly distributed in the waste, in other cases dilution can be achieved by spreading a consignment of the waste in question along the landfill working face, as more waste is then received, the compaction of that waste with waste previously received, the material would be "diluted and dispersed" within the landfill.

There is another aspect of the policy of dilution and dispersion to be considered. There is not only the dilution and dispersion of hazardous materials within the landfill but dilution and dispersion into the surrounding environment. To illustrate the principle of dilution and

dispersion consider the disposal of solid cyanide waste (DOE, 1976). Levels of cyanide that can be deposited are, $1000gm^{-3}$, at a Class I (Section 3.5.4 (a)), or containment site, $10gm^{-3}$ at a Class II (Section 3.5.4 (b)), or attenuation site and $1gm^{-3}$ at a Class III (Section 3.5.4 (c)) or rapid dispersion site. A further limitation is that for a Class I site the landfill must be limited to a cyanide content of $10gm^{-3}$ averaged over $1000m^3$, for a Class II site the cyanide content would be limited to $1gm^{-3}$ again averaged over $1000m^3$. This figure is justified by the British Authorities as surveys of municipal solid waste in the United Kingdom have found trace levels of $1gm^{-3}$. Further justification is outlined by the example included in the document by considering a landfill site receiving a volume of municipal solid waste approximating 100m x 100m x 2m per annum, the average cyanide concentration being $1gm^{-3}$. Assuming all the cyanide deposited within the landfill is leached at the same rate it is deposited, and passes directly into a large water body flowing at 45 $000m^3day^{-1}$. Then,

Mass of cyanide deposited per annum

$= \quad 100 \times 100 \times 2 \times 1 \quad = \quad 20\,000g$

Volume of water passing under landfill per annum

$= \quad 4\,500 \times 365 \quad = \quad 1.6425 \times 10^6\ m^3$

Concentration of cyanide would be elevated

$= \quad 20000/1.6425 \times 10^6 \quad = \quad 0.01mg\ell^{-1}$

The approach outlined above appears reasonable and uncomplicated to control. However, the variety and toxicity of wastes being co-disposed should not be underestimated. Cheyney (1984) tabulates wastes deposited in one section of the Stewartby landfill site in Bedford, United Kingdom, during the period 1978-1980. The wastes are to numerous to catalogue here; to indicate the extent of the wastes mentioned some examples are 579 tonnes of phosphoric acid, 2121 tonnes of biocide, 220 tonnes of toxic metals, 8300 tonnes of adhesive wastes, 1707 tonnes of mixed organic compounds, and 2908 tonnes of tannery wastes.

3.8.1.3 ADSORPTION

Adsorption is a process where, usually, molecules within a fluid phase become attached to a solid phase. However, the adsorbent surface may be an interface between gas and liquid, liquid and liquid, or liquid and solid. The process is usually selective in all practical applications, where one component within a multi-component mixture is preferentially adsorbed to a greater extent. Two types of adsorption may occur (Smith, 1981):

(a) Physical adsorption

Physical adsorption is non specific, and the forces holding the fluid molecules to the solid phase are relatively weak. The bond between the phase consists of van der Vaals' energy, dipole-dipole interactions or electrostatic energy as in the case of hydrogen bonding. The heat of physical adsorption is usually in the range, 2-15kcal $gmol^{-1}$, the larger values occurring in hydrogen bonding or in the cases of multiple point contact (Graham, 1959). Equilibrium between the solid surface and the solute molecules is usually rapidly achieved and readily reversible.

(b) Chemical adsorption (chemisorption)

Chemisorption is specific and involves forces greater than physical adsorption. The form of molecular bonding in chemisorption may be considered as a chemical bond, which is often irreversible. The heat of adsorption is usually in the range of 30-100kcal $gmol^{-1}$. Chemisorption differs from an ordinary chemical reaction in the fact the reacting atoms of the solid surface retain their identity with the original lattice (Graham, 1959). Chemisorption is usually preceded by physical adsorption, the chemical bond being formed only after the necessary activation has been provided. The major criteria for effective adsorption is intimate contact of the solution with the solid adsorbent thereby permitting the mass transfer of the solute ions to the adsorbent (Malina Jnr., 1967). An important characteristic of chemisorption is that the magnitude of adsorption will not exceed that corresponding to a monomolecular layer (Smith, 1981). This limitation occurs because the valence forces causing the molecule to adhere to the surface decrease rapidly with distance.

(c) Adsorption of heavy metals onto municipal solid waste

The extent and reversibility of adsorption of any material onto municipal solid waste is dependent on a number of factors. These include:

the chemical form of the metallic waste;
the available surface area for adsorption;
the pH of the municipal solid waste;
the character of the available surface area;

Watson-Craik (1990) examined factors influencing the adsorption of inorganic wastes, (such as heavy metals) onto municipal wastes. She admits there is a paucity of available data, and reviews two studies. Both studies examine the adsorption of arsenic onto municipal solid waste. The research methods employed by the two researchers are different, and Watson-Craik felt their conclusions, when compared, to be conflicting. The results of the two studies are shown overleaf in Table 3.13.

One of the studies Watson-Craik evaluated was presented by Blakey (1984) of the United Kingdom's Water Research Centre, Landfills Section. It is likely this work played a significant part in the development of the current practices in co-disposal in the United Kingdom and is therefore worthy of closer consideration. Blakey evaluated the adsorption of arsenic(III) onto municipal solid waste in the concentration range 1.25$mg\ell^{-1}$ - 100$mg\ell^{-1}$, and arsenic(V) in the range 2.5$mg\ell^{-1}$ - 200$mg\ell^{-1}$. The municipal solid waste was only categorised *fresh* and *aged*; the waste was not categorised further. The pH range of the investigation was 5 to 9; the investigation was executed at laboratory scale.

Adsorption tests were executed using distilled water as the aqueous carrier, desorption tests were executed with landfill leachate as the aqueous carrier. Adsorption equilibrium was generally reached in all cases in less than 24 hours, the results conformed to a conventional Freundlich isotherm. In general, an increase in pH increased the adsorption of arsenic(III), which was greatest in aged solid waste. The amount of arsenic(V) adsorbed reaches a maximum at pH 7, with little difference of the adsorption characteristics of the new and aged solid waste.

The principal differences between the studies conducted by Jones and co-workers (1978) and that conducted by Blakey (1984) were:

(i) Blakey employed authentic solid waste while Jones's solid waste was artificially assembled.
(ii) Blakey utilised anaerobic conditions, while Jones utilised aerobic conditions.
(iii) Blakey used distilled water as the liquid medium, Jones used a 82mM solution of acetic acid.

TABLE 3.13 ADSORPTION OF ARSENIC ONTO MUNICIPAL SOLID WASTE

(adapted from Watson-Craik, 1990)

	Study	
	(Blakey, 1984)	(Jones *et al*, 1978)
Substrate	1kg of pulverised municipal solid waste	10g of artificially assembled solid waste
Test conditions	Anaerobic, at a temperature of 25°C	Aerobic, at a temperature of 30°C
Arsenic concentration range ($mg\ell^{-1}$)	1.25 - 100 [arsenic(III)] 2.5 - 200 [arsenic(V)]	18 - 190 [arsenic(V)]
Isotherm derived	Freundlich	Langmuir
Dependency of adsorption on pH (pH5 to pH9)	Arsenic(III): Adsorption increased with pH Arsenic(V): Adsorption maxima at pH7	Arsenic(V): adsorption decreased with pH
Desorption	Arsenic(V): Desorption was less than 5 percent of that adsorbed from aged refuse, the pH range being 5 to 7.	Arsenic(V): Partial or complete desorption, the pH range being 7 to 9.

There would not appear to be any point of agreement in the results presented by the two researchers. This illustrates the difficulty of interpreting and subsequently implementing, research results by a practitioner of co-disposal of industrial wastes with municipal solid waste. The absence of standardised procedures for examining the adsorption characteristics coupled with the heterogeneous nature of solid waste received at landfill sites will possibly contribute conflicting information.

(d) Adsorption of heavy metals onto soils

The adsorption of the various heavy metals onto soils is well documented, and it is of great interest to examine factors which could be applicable to the landfill environment. Soil is a heterogeneous porous medium, normally consisting of about 95 percent inorganic material, and 5 percent organic material. The inorganic material is primarily composed of sand, silt and clay. Organic matter present is primarily composed of plant residues, the principal constituents being cellulose (15-60 percent dry weight), hemicellulose (10-30 percent dry weight) and lignin (2-30 percent dry weight). The pH of soil can vary from less than 5.5 to greater than 8.5. Areas of high rainfall, usually have higher levels of organic matter and hence tend to be acidic in nature. The oxygen content of soils is dependent on soil moisture content. In soils saturated with water, the soil oxygen content is very low (Pepper, 1996).

The similarities with municipal solid waste in the landfill environment are evident. Both are heterogeneous porous materials, existing in a similar pH range. Both anaerobic and aerobic conditions can exist in both soils and solid waste. The organic matter present, and its composition, in soil is similar to that present in solid waste (see Table 3.21). Additionally, soil is employed on the landfill as cover material and is compacted into the solid waste as successive layers of solid waste are deposited. The above, together with the paucity of data concerning the adsorption characteristics of solid waste, make examination of the behaviour of heavy metals in the soils medium relevant to this study.

Many researchers have examined various aspects of the behaviour of arsenic(III) and arsenic(V) in soils. The ranges of Eh and pH in soils can lead to either As(V) or As(III), microbial activity can cause methylation, demethylation and/or a change in oxidation state (O'Neill, 1990). Under strongly reduced environments, elemental arsenic and arsenic hydride (AsH_3) can exist. Under moderately reduced conditions, arsenic(III) dominates; arsenic(V) is the stable form in an oxygenated system (Deuel *et al*, 1972; Hess *et al*, 1976). This is obviously of great importance in the landfill environment where anaerobic conditions and hence reducing conditions exist (Gould *et al*, 1989). A survey conducted in the Tamar Valley, South West England, showed; in aerobic soils, 90 percent of the arsenic present was in the form of As(V) (arsenate); in anaerobic waterlogged soils As(V) was present 15 to 40 percent (O'Neill, 1990). Ferguson and Gavis (1972) in their review of the arsenic cycle in natural waters, state that at the high Eh values encountered in oxygenated waters, arsenic acid (As(V)) species (H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-}) are stable. At Eh values characteristic of mildly reducing conditions, arsenous acid (As(III)) species (H_3AsO_3; H_2AsO_3- and $HAsO_3^{2-}$) become stable. This indicates that arsenic added to an anaerobic landfill in the form of arsenic(V) would be fully reduced in time to form arsenic(III). Therefore, in the following discussion both arsenic(III) and arsenic(V) will be discussed.

Korte and co-workers (1976) investigated the relative mobilities of eleven trace elements in laboratory scale soil columns. The researchers objective was to determine which soil properties (physical and chemical) control the movement of the trace elements. Amongst the metals examined were copper(II), chromium(III) and arsenic(III), which are of specific interest to this current study. Copper was in the chloride form, while both chromium and arsenic were in the form of their oxides. An additional factor arising interesting this particular study; the aqueous carrier selected for the experimental procedure was municipal solid waste leachate. The initial concentration of metals in solution varied from 70 to 120mgℓ^{-1}. Unfortunately, the initial pH of the leachate was adjusted to 3 to prevent the precipitation of lead, one of the metals under examination. The pH of landfill leachate is usually in the range 6.2 to 7.4, for a methanogenic landfill. The researchers reported that copper was immobile in all the soils except one, a sandy Wagram soil. It's mobility was however, also low in that soil. The researchers reported the behaviour of copper could not be correlated with soil properties. Arsenic and chromium exhibited similar behaviour to one another; they were on average more mobile than other metals evaluated. The other metals included lead(II), and nickel(II) both relatively common constituents in landfill leachate. The researchers were unable to correlate soil chemical and physical properties with cation mobility even thought detailed statistical analysis of the results was practised.

Elfving and co-researchers (1994) scrutinised the mobility of arsenic and lead in old orchard soils in Ontario. Lead arsenate had been used for insect control for many years in the locality. The researchers confirmed the work of others, showing that arsenic(V) has a low mobility in soils; arsenic concentration in soil decreasing relatively sharply with depth. The researchers did not comment further on arsenic mobility. Sadler and others (1993) investigated soil and water contamination at a former tannery in Brisbane, Australia. The former tannery land is now the site of a school, the Craigslea State School. The researchers were surprised at the degree of arsenic contamination with depth, and mention previous studies that indicated a fairly limited arsenic mobility in soils. However, arsenic was used extensively in the form of sodium arsenite (arsenic(III)) at the former tannery, and cite a study where sodium arsenite was shown to be fairly mobile in sandy soils. During the same investigation laboratory leach tests were carried out with distilled water. Arsenic leached from the contaminated soils in all cases. Some soils leached arsenic in significant quantities; a soil concentration of 190mgkg^{-1} resulted in a leachate concentration of 47$\mu g\ell^{-1}$. Sadler concluded that arsenic mobility in soils was affected by the species of arsenic present together with the nature of the soil; arsenic(III) was more mobile than arsenic(V); the transformation from one to the other being influenced by the redox potential and the prevailing pH value. This information would appear to corroborate that stated by O'Neill (1990) in the previous paragraph were sorption of arsenic(III) by humics was less than that of arsenic(V).

The adsorption of arsenic onto the organic component of soils was examined by Thanabalasingam and Pickering in 1986 (cited by O'Neill, 1990) . The maximum sorption of arsenic(V) by humics occurred at pH5.5 with the arsenic(III) maxima occurring at higher pH values. In general, the humics sorbed 20 percent less arsenic(III) than arsenic(V) and the sorption behaviour could be described by a Langmuir-type isotherm, with some deviation at higher concentrations. It appeared the humics were acting as anion exchangers as the pH values became more alkaline the humics became more soluble, and their ability to remove

arsenic from solution was reduced (O'Neill, 1990). Unfortunately, the term "more alkaline" was not defined further. However, pH5.5 is near that of landfill and one would expect some degree of adsorption of arsenical compounds, especially arsenic(V).

Elkhatib and co-researchers (1984) investigated the sorption and desorption of arsenite (arsenic(III)) onto five West Virginian soils. The liquid carrier employed in the investigation was de-ionised water. The Freundlich equation described sorption over an initial concentration of 5 to 1000mgℓ^{-1}. The rate of sorption was rapid initially, but decreased with time. From all starting concentrations initial sorption was rapid, 80 percent of the maximum sorption was achieved within the first 30 minutes; subsequent to that sorption rates levelled out. The initial rapid sorption suggested a high energy sorption associated with low surface saturation. The slow reaction was assumed to be a result of increased surface negative charge and decreased sorption energy (Kuo *et al*, 1974). Desorption experiments indicated that arsenic(III) was irreversibly sorbed by the soils examined, only a small fraction of the arsenic(III) being desorbed from the soils. A modified Freundlich equation described the rate of arsenic(III) adsorption and desorption. The pH of the deionised water/soil mixture varied from 4.20 to 7.00. The pH being dependent on the nature of the soil employed.

Frost and Griffin (1977) investigated the adsorption behaviour of arsenic(III), arsenic(V) and selenium(IV) on the clay minerals, kaolinite and montmorillonite. Again, the aqueous carrier selected was municipal solid waste leachate. The researchers used a range of pH values, from pH3 to pH10; they found pH severely influenced the degree of adsorption of all the elements investigated. Adsorption of arsenic(III) increased with pH, in the pH range quoted. Adsorption of arsenic(V) was maximised at pH5.5, with a subsequent decrease in adsorption at higher levels of pH. Adsorption of selenium(IV) decreased with increase of pH in the range pH3 to pH9. The researchers concluded the disposal of arsenic and selenium in municipal landfills, especially under alkaline conditions could promote groundwater contamination. As mentioned previously, the pH of methanogenic municipal landfills is usually within the range 6.2 to 7.4, one could therefore expect arsenic mobility in that environment.

Summarising the information above reveals that under aerobic conditions arsenic(V) predominates, in the form of H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-} (Ferguson *et al*, 1972). Under anaerobic, and hence mildly reducing conditions arsenic(III) predominates (Deuel *et al*, 1972; Hess and Blanchar, 1976). The species of arsenic(III) present under these conditions are H_3AsO_3; $H_2AsO_3^-$; and $HAsO_3^{2-}$ (Ferguson *et al*, 1972). It is evident that these species would predominate within the landfill environment of neutral pH and mildly reducing conditions. There is conflicting information regarding the mobility of arsenic(III) and arsenic(V). Sadler (1993) states that arsenic(III) has a high mobility in soils; while Elkhatib and co-researchers (1984) report arsenic(III) being irreversibly sorbed by the soils examined, only a small fraction of the arsenic(III) being desorbed from the soils. Korte and co-workers (1976) concludes that arsenic(III) (however at pH3) was more mobile than other metals examined. Frost and Griffin (1977) found arsenic(V) be mobile, especially at alkaline conditions, while arsenic(III) exhibited an increase in adsorption with rising pH. Shown overleaf in Table 3.14 are details of adsorption studies on municipal solid waste and various type of soils together with a common form of the organic fraction of soils; humic acid.

In the case of arsenic(III) there would appear to be agreement that adsorption increases with increase in pH when considering municipal solid waste, humic acids and the clay minerals. There is also agreement that the adsorption of arsenic(V) decreases in an alkaline environment. There is conflicting evidence regarding mobility. It would appear that arsenic(V) is more mobile than arsenic(III) especially above pH5.5.

In general, the adsorption of copper(II) onto soils has been shown to obey the Freundlich isotherm, though the relatively slow rate at which copper(II) is absorbed onto soils makes data from adsorption studies difficult to interpret (Baker, 1990). Aringhieri and co-workers investigated the adsorption kinetics of copper(II) and cadmium(II) on a soil composed of 14 percent organic matter (Aringhieri *et al*, 1985). The initial pH of the solution was 5.4. The initial concentration of the metal ranged from 63.5 to 191$\mu g\ell^{-1}$ for copper and from 56 to 291$\mu g\ell^{-1}$ for cadmium. The mass of soil employed varied from 1 to 3g.

Copper exhibited a greater affinity than cadmium to the investigated soil. There was a tendency for copper to form stable organic complexes with organic matter in the soil. Adsorption processes were relatively fast, for both metals. Adsorption was fast for the first 2 minutes, then became slower; after 10 minutes 80 percent of the total adsorption was achieved.

The time dependence curve showed remarkable similarity to those reported by Elkhatib and co-researchers (1984) when they investigated the sorption and desorption of arsenite (arsenic(III)) onto five West Virginian soils. Similar trends were found for copper(II) adsorption by peat soils by Sapek (cited by Aringhieri *et al*, 1985). Sapek suggested from a qualitative viewpoint the adsorption process consisted of two distinct steps: an initial fast adsorption, followed by a much slower adsorption. These modes of adsorption were attributed to an initial rapid diffusion of ions to external soil surfaces, with subsequent diffusion into the inner soil surfaces. The experimental method adopted by Aringhieri and co-workers involved finely divided soil and continuous stirring, an unlikely combination for diffusion to regulate the reaction speed. The researchers reasoned from examination of the time-concentration curves the rate of the adsorption process was dependent on the concentration of the reactive species, the concentration of the substrate in solution, and on internal diffusion, which produced a decrease of the specific rate as a function of time.

The adsorption of the two metals was successfully described by the Langmuir isotherm.In the instance were adsorption is successfully described by the Langmuir isotherm, it is possible to represent the rate of that sorption process as a reversible first (Gosset *et al*, 1986; Chen *et al*, 1990; Sharma *et al*, 1993) or second order reaction. This approach proved unsuccessful. The researchers were unable to produce the suitable linear relationship to prove adherence to the rate law. Finally, the researchers reported different rate constants for different concentrations of Cu(II) and Cd(II) possibly, in an effort to provide some form of result. The researchers concluded the rate of adsorption of copper(II) and cadmium(II) onto an organic soil to be dependent on diffusion of the metallic cations through internal surfaces.

TABLE 3.14 ADSORPTION OF ARSENIC ONTO MUNICIPAL SOLID WASTE SOILS AND HUMIC ACIDS

	Study				
	Blakey, 1984	Jones *et al*, 1978	Thanabalasingam *et al*, 1986	Elkhatib *et al*, 1984	Frost *et al*, 1977
Substrate	solid waste	solid waste	humic acids	West Virginia soils	Clay minerals
Test conditions	Anaerobic	Aerobic	_	Aerobic	Aerobic
Liquid	Distilled water	82mM acetic acid	-	Deionised water	Landfill leachate
Arsenic speciation	As(III) and As(V)	As(V)	As(III) and As(V)	As(III)	As(III) and As(V)
Concentration range ($mg\ell^{-1}$)	1.25 - 200	18 - 190	-	5 - 1000	10 - 180 [As(III)] 50 - 650 [As(V)]
Isotherm derived	Freundlich	Langmuir	Langmuir	Freundlich	Non-linear
Dependency of adsorption on pH					
Arsenic(III)	Adsorption increased with pH		Adsorption increased with pH	-	Adsorption increased with pH
Arsenic(V)	Adsorption maxima at pH7	Adsorption decreased with pH	Adsorption maxima at pH5.5	-	Adsorption maxima at pH5.5
Desorption	Arsenic(V): Desorption was less than 5 percent of that adsorbed from aged refuse, the pH range being 5 to 7.	Arsenic(V): Partial or complete desorption, the pH range being 7 to 9.	-	Minimal desorption of arsenic(III)	-

Harter reported on the effect of competing ions on the absorption of copper and lead onto various soils from the Northeast of the United States (Harter, 1979). The solution pH was neutral at 7.0; adsorption data was described by the Langmuir adsorption isotherm. Harter observed that an increase in ionic strength of the solution apparently reduced the adsorption of the metallic elements onto the some of the soils, but increased adsorption in others. Unfortunately, conclusions could not be drawn from this. Harter was unsure if imprecise calculations contributed to these observations. The ionic strength of leachates commonly exceeds $500mSm^{-1}$. Information regarding this phenomenon would be useful to apply within the landfill environment. Details of the concentration of copper and lead in solution was not reported. Harter cited work by Irving and Williams (1948) were both copper and lead combined with ligands to form stable metal complexes and chelates. Subsequently, they should form stable complexes with soil organic matter. If one parallels this observation a similar fate should occur to copper within the landfill environment.

Msaky and Calvet (1990) examined the effect of pH within the range 4.5 to 5.5, on the adsorption of copper and zinc onto various soils. It was noted that as the pH value climbed, adsorption increased. This effect is well known and the authors cite a number of examples. Absorption isotherms could be described numerically by the van Bemelen-Freundlich formulation. This was in agreement with the results of other workers. Copper was strongly adsorbed at all pH values. The movement of copper in soil was reviewed by de Haan and Zwerman (1976). The researchers report the mobility of copper in soils to be low, and describe the adsorption of copper onto organic matter, clay minerals, and even pure quartz. Of great interest is a study completed by Lundblad and co-workers (1949). Over 250kg of copper (per hectare) was added to an acid peat soil. After 5 years had elapsed only 0.2 percent of the copper added was removed from the top 5cm of soil.

Chromium exists in a number of oxidation states, the most common being chromium(III) and chromium(VI). They have sharply contrasting chemical properties. Chromium(III) is much less mobile then chromium(VI) and adsorbs onto particulates more strongly (McGrath *et al*, 1990). Sheppard *et al* (1992) investigated the desorption of heavy metals from a sandy and a clay soil. They also investigated the efficacy of several extracting agents in removing several inorganic trace elements from these soils. One of the eight inorganic trace elements examined was chromium, in the form chromium(VI). The chromium was barely desorbed from a sandy soil. The fixation of chromium was so strong, the authors commented if soil remediation was required it would be less expensive to remove the soil, as chemical treatment would have to be extensive.

Evaluation of vertical chromium movement in soils has received a high level of attention, particularly sewage treated soils. Some evidence is contradictory, the overwhelming majority of reports have found a general lack of leaching below the zone of sludge incorporation. In one experiment chromium analysis of soils which had received metal contaminated sludge treatment from 1942 to 1961 showed no evidence of significant movement below the depth to which the soil was cultivated (McGrath *et al*, 1990).

3.8.2 CHEMICAL ATTENUATION MECHANISMS

Chemical attenuation processes include acid-base interactions, oxidation, reduction, precipitation, co-precipitation, ion-exchange, and ion formation.

(a) Precipitation and co-precipitation

When a salt is dissolved in water, there is a limiting amount which can dissolve per unit volume of water. This limiting concentration is called the solubility of the salt in the particular liquid. Additionally, if an excess of salt is added to a liquid, a state of dynamic equilibrium is achieved between the dissolution of the solid and precipitation of the ions to the solid state (Lowenthal *et al*, 1978). Consider the equilibrium between the solid substance (MX_2), and its aquated ions:

$$MX_2\ (s) \quad \rightleftharpoons \quad M^{2+}\ (aq) \quad + \quad 2X^-\ (aq)$$

The solubility product (K_{sp}), a type of equilibrium constant may be calculated,

$$K_{sp} \text{ for } MX_2 \quad = \quad [M^{2+}]\ [X^-]^2$$

If the solubility product of a particular substance is exceeded, precipitation of the compound occurs until the product of the ionic concentration is less than or equal to value of the solubility product. Co-precipitation may be defined as the simultaneous precipitation of a chemical agent in conjunction with other metals by any mechanism and at any rate (Alloway, 1990).

The solubility of chromium(III) decreases above pH4, and above pH5.5 complete precipitation occurs (McGrath *et al*, 1990). Therefore, chromium(III) would tend to be essentially immobile because of its low solubility. If one considers sewage treated soils, very stable organic complexes account for the very low availability of the element. However, complexing chromium(III) with soluble organic acids, and soil extracts of water-soluble organic matter, maintain chromium(III) in solution at higher pH levels than chromium(III) normally precipitates and hence enhances mobility (McGrath *et al*, 1990). James and Bartlett (1983) complexed chromium(III) with soluble organic acids, and soil extracts of water-soluble organic matter, and maintained chromium(III) in solution at higher pH levels higher than 5.5. (above pH5.5 complete precipitation would normally occur). Approximately 25 percent of the chromium(III) added remained in solution at pH6.7. In the complex environment of the landfill these conflicting vectors must be given consideration to evaluate the behaviour of chromium(III).

There are no significant solubility restraints on the concentration of chromium(VI) experienced in pH range normally encountered in the landfill eco-system. However, laboratory studies have shown that chromium(VI) can be readily reduced to chromium(III) in the presence of organic matter, especially at low pH (Calder, 1988). In soils, the presence of soil organic matter can produce the spontaneous reduction of chromium(VI) without regard to pH. In soils incubated with chromium(VI) for four weeks at field capacity moisture, this phenomena was apparent (Bartlett *et al*, 1976). The soil used in the experiment was dried prior to the experiment. This procedure reduces the effects of the soil organic matter (Bartlett *et al*, 1988).

The landfill environment abundance of organic matter would have a dramatic effect on the mobility of chromium(VI). The chromium(VI) would be reduced to chromium(III) which then should precipitate from solution. This information is of great value when examining the mobility of chromium(VI) in the landfill environment, it would appear that chromium(VI) would be immobile, but not for similar reasons as copper which were commented on previously.

The mobility of arsenic in soils is increased under reducing conditions, such as flooding soils, because of the increase in the proportion of arsenite (As(III)). Arsenite salts are estimated to be 5 to 10 times more soluble than the corresponding arsenates (As(V)) (Ferguson, 1990). Unfortunately, low molecular weight organic ligands, not necessarily humic in origin, can form soluble complexes with metals, thus preventing them being adsorbed or precipitated. Of particular concern in the landfill environment is that humic compounds with suitable reactive groups such as carboxyl groups form coordination complexes with metal ions. Carboxyl groups play a predominant role in metal binding in both humic and fulvic acids. The stability constants of chelates with metals tend to be in the following decreasing order:

$$Cu > Fe = Al > Mn = Co > Zn \text{ (Alloway, 1990).}$$

Another factor to consider is the activity of sulphate reducing bacteria in the landfill environment. Hydrogen sulphide is produced by sulphate reducing bacteria, it is a strong reducing agent, and can react and cause the precipitation of metals such as copper, and arsenic. The metals are precipitated as their insoluble sulphides. Arsenic may be co-precipitated with iron sulphide (the iron content of leachates is usually high) or may be directly reduced to arsenic sulphide (cited by Watson-Craik, 1990). In the United Kingdom regulations allow arsenic in the sulphide form to be co-disposed with municipal solid waste in the ratio of 10kg per tonne of solid waste. In general, arsenical waste may not be co-disposed with municipal solid waste in excess of 10g per tonne (Cossu *et al*, 1989). Ferguson and Gavis (1972) also comment on the strong affinity that arsenic(III) has for sulphur. Kugelman and Chin (1971) state that the most important complexing reaction for controlling toxicity in anaerobic waste treatment is the precipitation of heavy metals as sulphides. Copper is one of the most insoluble of the heavy metal sulphides (Lawrence *et al*, 1965). The table below shows the solubility of copper, and for comparison iron, one of the most soluble.

TABLE 3.15 SOLUBILITY OF COPPER AND IRON SULPHIDES
(adapted from Lawrence *et al*, 1965)

Metal	Sulphide salt	Solubility Product	Solubility ($mg\ell^{-1}$)
Copper	Cu_2S CuS	2.0×10^{-47} 8.5×10^{-45}	3×10^{-11} 9×10^{-18}
Iron	FeS	3.7×10^{-19}	5×10^{-5}

3.8.3 ENVIRONMENTAL ASPECTS OF CO-DISPOSAL

The main problems associated with the co-disposal of industrial wastes with municipal solid wastes may be summarised as follows (Cossu *et al*, 1989):

> The inhibiting effect on biological degradation of the municipal solid waste as a consequence of the toxicity of the industrial wastes.
>
> The emission of toxic substances into liquid and gaseous effluent from the landfill, in a higher degree than that from the disposal of municipal solid waste, solely.

The two concerns expressed above are inextricably linked; sterilising the landfill by exceeding the toxicity limit of the various microbial population groups and therefore inhibiting the degradation of the municipal solid waste. The latter aspect can be addressed by noting that a key element of co-disposal is to take advantage of attenuation processes available within the landfill. It must be ensured that the wastes to be co-disposed do not overwhelm the landfill eco-system as the emissions from the landfill are not only influenced by the solubility of the various substances but the interaction of the chemio-physical and biological phenomena. These phenomena can immobilise, degrade, and attenuate the mobility of each substance.

An aspect of co-disposal of major importance when considering landfill sterilisation and increase in pollutional aspects is of "loading rates". Loading rate was defined by the United Kingdom's Waste Management Practices, Landfill Practices Subgroup 2 in 1982 as the maximum quantity of an industrial waste that can be co-disposed with one kilogramme of domestic refuse without adversely affecting leachate quality (cited by Watson-Craik, 1987). As with many statements emanating from the waste disposal establishment in the United Kingdom there is a degree of oversimplification. Values tabulated are not extensive, and those which do exist appear to be extrapolated from past practices. An obvious difficulty is the extreme heterogenous mix of waste arriving at landfill sites, together with the possibility that problems arising from past operations are not yet become apparent.

Rushbrook (1990) tabulated various maximum loading rates quoted in the United Kingdom by the various United Kingdom Government publications (Table 3.16) .

(a) Effect of co-disposal on landfill stabilisation processes

Researchers have investigated the effect of the disposal of industrial wastes with municipal solid wastes. Watson-Craik (1987) investigated the co-disposal of phenolic wastewaters with municipal solid waste, while Reinhart (1989) investigated the fate of twelve selected organic compounds, such as dibromomethane, lindane, dieldrin and trichloroethane. It is however inorganic metallic compounds which are of greatest interest in this study. Newton (1977) investigated, at pilot-scale, the co-disposal of a cyanide sludge, an oil water emulsion, and a metal hydroxide sludge containing mainly nickel, chromium and iron. Unfortunately, Newton did not undertake landfill gas measurement, a good indicator of any disruption in the anaerobic degradation process. The leachate composition was examined and the researchers concluded that leachate composition, and hence anaerobic activity, were not obviously affected by the presence of the industrial waste.

TABLE 3.16 CO-DISPOSAL LOADING RATES

(adapted from Rushbrook,1990)

Constituent	Loading rate	Constituent	Loading rate
Chromium	$100gt^{-1}$	Sulphuric acid	$20kgt^{-1}$
Copper	$100gt^{-1}$	Hydrochloric acid	$5kgt^{-1}$
Lead	$100gt^{-1}$	Phenols	$2kgt^{-1}$
Arsenic	$10gt^{-1}$ $10kgt^{-1}$ (for As in sulphide form)	Oils	$2.5kgt^{-1}$
Mercury	$4gt^{-1}$	Pesticides	20g a.i.* t^{-1}
Cadmium	1kg batteries t^{-1}	PCB	$<50gt^{-1}$
Zinc	$100gt^{-1}$	Cyanide	1g of free CN t^{-1}
Tannery sludge	$66.6kgt^{-1}$		

* a.i. active ingredient

Pohland and other workers (Pohland *et al*, 1985; Poland *et al*, 1986a; Gould *et al*, 1989) at the Georgia Institute of Technology investigated the co-disposal of various metals with municipal solid waste at pilot-scale. A metal plating sludge containing zinc, chromium, nickel, cadmium, copper and iron was co-disposed with municipal solid waste (Pohland *et al*, 1985 & Pohland *et al*, 1986a) in pilot-scale landfill columns. Four columns were employed. Each column contained 400kg of municipal solid waste. One column was designated a control column (column 1) to which the researchers did not add any metal plating sludge, to the other columns differing amounts of the sludge were added; 33.6kg in column 2; 65.8kg in column 3, and 135.2kg in column 4. The researchers wished to determine the effects of the heavy metals on overall landfill stabilisation and assimilative capacity. Leachate was recycled to enhance stabilisation processes.

The addition of the metal hydroxide sludge slightly elevated the pH of the leachates, but not outside the near neutral range of pH necessary for anaerobic activity. The organic content (COD) of the leachate from control column reduced steadily as methanogenic conditions were established. This process was slower to be established in column 2, suggesting some microbial inhibition, with eventual acclimation of the anaerobic bacteria to the heavy metal sludge. In contrast, the organic loading of leachate from columns 3 and 4 remained high throughout the experimental period. This was considered to be direct evidence of interference to the landfill stabilisation processes. The researchers concluded additional research is required to better define limits of heavy metals to be co-disposed with municipal waste.

The co-disposal of mercury, lead, cadmium, chromium, nickel, and zinc with municipal solid waste was investigated also by largely the same research team (Gould *et al*, 1989) the principal metals of interest being mercury and lead. The foremost aspect of this study was evaluation of the chemical attenuation mechanisms available, the researchers did not appear to evaluate any disruption to the anaerobic degradation of the municipal solid waste.

An investigation on the impact of grazed pasture by copper, chromium and arsenic timber preservative on soil biological activity (Yeates *et al*, 1994), warrants scrutiny, as there is a paucity of data concerning those particular elements especially in combination. Initially, the researchers visually graded areas of the pasture in terms of heavy metal contamination. Normal healthy pasture, in a nearby uncontaminated area, was used as the control; bare ground was assessed as being highly contaminated; an area displaying stunted, yellowed plant cover was assessed as intermediate or medium contamination. Four levels of contamination were graded; uncontaminated, low contamination, medium contamination and highly contaminated. The researchers then sampled the site extensively in terms of degree of contamination and depth. The samples were then analysed for metal content, and various biological parameters were measured to determine the whether there was evidence of repression of biological activities.

There was a close correlation between heavy metal contamination and the initial visual assessment. All the biological parameters measured in the contaminated area showed correlation with levels of copper, chromium and arsenic. Microbial processes and populations declined with the degree of contamination of the heavy metals. Basal respiration declined significantly at each level of contamination, as did nematode diversity and grouping. Soil decomposition processes were also assessed, and were found to decline with increased levels of contamination. Enzyme activities were investigated. Dehydrogenase, urease, phosphatase and sulphatase activity declined with increased contamination. The researchers conclude that contamination by $100mgkg^{-1}$ of copper, chromium and arsenic caused little depression of soil biological activity, there was some suppression at $400mgkg^{-1}$, but at $800mgkg^{-1}$ normal biological processes were inhibited and herbage production was negligible. These results were comparable with other workers cited by Yeates and co-researchers.

Wong and Trevors (1988) cite a study completed by Drucker and co-workers. They examined the toxicity of chromium(III) in soil. Chromium(III) was added to soil at concentrations of 10 and $100mgkg^{-1}$; aerobic and anaerobic bacteria were reduced in number. The inhibition of bacterial activity would be detrimental to the establishment of methanogenic conditions in the landfill and hence increase the mobility of the metallic cations within the landfill environment.

The toxicity of heavy metals in the process of anaerobic digestion is well established and has been extensively investigated by various researchers principally investigating toxicity effects in waste water anaerobic digesters. An examination of these investigations is advantageous as it is directly applicable to the landfill environment. Studies undertaken at the Robert A. Taft Sanitary Engineering Centre (Barth *et al*, 1965) are often quoted when considering the effects of heavy metals on biological treatment processes. The researchers considered the effects of copper, hexavalent chromium, nickel and zinc on biological treatment processes. The work was carried out at pilot-plant scale, where the effects of heavy metals on the aerobic

and anaerobic process, over a ten year period. The researchers found that system response was dramatic, digestion either proceeded normally or ceased entirely. All the metals previously mentioned had a detrimental effect on anaerobic digestion as measured by an increase in liquid phase chemical oxygen demand when compared to a control digester.

The role of sulphide in the prevention of heavy metal toxicity was thoroughly investigated by Lawrence and co-workers (1965). They investigated the effects of copper, nickel, zinc and iron. They determined that the toxicity of heavy metals was dependent on the concentration in the soluble form, and not on the total concentration in the reaction environment. To determine the toxicity effects, the laboratory scale digesters were first operated with the daily addition of the relevant metals in the sulphate form. That allowed the metals to be precipitated as metal sulphides, the digesters continued to operate successfully. Addition of the metals in form of sulphates was then discontinued. The digesters were then operated with the addition of the relevant metals in the form of chlorides, thereby eliminating the sulphide precursor. The toxic effects of the metal addition was then observed. The researchers concluded copper, nickel and zinc were toxic to anaerobic digestion, the heavy metals affecting the acid forming bacteria at least as much as the methanogenic bacteria. Ferrous iron was found to be non-toxic even in the absence of sulphides.

Reid and fellow researchers (1968) evaluated the effects of metallic ions on a number of biological waste treatment processes, amongst them, anaerobic digestion at laboratory scale. They found that chromium (in the form Cr(VI)) concentrations as high as 85mgℓ^{-1} reduced biogas production by 18 percent, and copper when added in concentrations up to 2mgℓ^{-1}, reduced gas production by 8 percent. Kugelman *et al* (1971) extensively reviewed literature concerning toxicity in anaerobic waste treatment, the emphasis of the work being the toxicity of heavy metals. He concluded:

> much of the published data was erroneous and misleading, because of inadequate experimental techniques;
> toxicity effects of heavy metals could be eliminated by sulphide precipitation;
> volatile organic acids are not toxic to methanogens at concentrations less than 6000mgℓ^{-1};
> a substantial amount of additional research was required.

Mosey and co-researchers (1971, 1975) investigated various factors affecting the availability of heavy metals to inhibit anaerobic digestion at laboratory scale. One of the conclusions reached was that high chloride ion concentrations could reduce inhibition caused by lead. Both lead and chloride ion concentrations are traditionally high within the landfill environment. Metals shown to be toxic were zinc, cadmium, copper, and chromium. It was shown that the toxicity of chromium was similar whether in the trivalent or hexavalent form.

Hayes *et al* (1978) principally examined the distribution of heavy metals among the soluble, precipitated extracellular, and intercellular components using laboratory scale anaerobic digesters (Table 3.17). The effects of metal addition on anaerobic digestion were also collated. The metals examined included were cadmium, chromium(VI), chromium(III), copper, lead, nickel, and zinc. The digesters were dosed with the metals in a step- and pulse-like fashion.

TABLE 3.17 HEAVY METAL TOXICITY LIMITS FOR ANAEROBIC DIGESTION

(adapted from Hayes *et al*, 1978)

Heavy metal	Step-fed		Pulse-fed
	Inhibiting concentration ($mg\ell^{-1}$)	Toxic limit ($mg\ell^{-1}$)	Toxic limit ($mg\ell^{-1}$)
Chromium(III)	130	260	<200
Chromium(VI)	110	420	<180
Copper	40	70	<50
Nickel	10	30	>30
Cadmium	-	>20	>10
Lead	340	>340	>250
Zinc	400	600	<1 700

nickel, and zinc. The digesters were dosed with the metals in a step- and pulse-like fashion. Metal addition in a pulse-like fashion is akin to shock loading, while metal addition in a step-like function allows microbial acclimation to the addition of the metal. The inhibitory level of a heavy metal was defined as that time when any decrease in gas production became evident, toxic levels were taken to be that concentration at which gas production was reduced by 70 percent. The authors quote the following results.

The general ranking of heavy metal toxicity for those metals investigated was;
Ni > Cu >> Cr(VI) ≈ Cr(III) > Pb > Zn. Cadmium did not have any noticeable effect at concentrations used in the experimental study.

(b) Effect of co-disposal on leachate composition

The effect of co-disposal on leachate composition at pilot-scale and full scale operations is well documented by various researchers. The work undertaken by Pohland and his fellow workers has already been referred to in Section 3.8.3 (a). The researchers co-disposed a heavy metal hydroxide sludge containing zinc, chromium, nickel, cadmium, copper and iron with municipal solid waste at pilot-scale. They found when metal addition exceeded a certain level, anaerobic activity was inhibited, and the organic content of the leachate was not reduced with time. Levels of zinc, cadmium and nickel, in leachate from the columns were also affected detrimentally. Levels of zinc, cadmium and nickel in leachate from the column were co-disposal was not practised (column 1) and the column were the lowest amount of metal sludge was added (column 2) were described as "inconsequential". Leachate from the heavier loaded columns (columns 3 & 4) contained nickel, cadmium and zinc at levels higher than columns 1 and 2. Zinc was present at levels generally considered to be inhibitory to anaerobic digestion in the leachate from columns 3 and 4.

Levine *et al* (1989) evaluated leachate monitoring data from co-disposal, hazardous and sanitary waste disposal sites located in the United States. The researchers examined data from a total of 1 560 samples from 58 facilities over the period 1984 through 1987. The data was supplied from 88 co-disposal sites, 90 hazardous waste sites, and 49 sanitary landfills. The table shown overleaf (Table 3.18) is adapted from their results.

Analyses of leachate from the hazardous waste landfill sites shows metal levels in the leachate far above the co-disposal sites and the municipal sites. Co-disposal leachate is however, on average, higher in metallic contamination than that from the municipal sites. For comparative purposes data reported from the United Kingdom is shown overleaf in Table 3.19.

It can be seen (in Table 3.19), with the exception of cadmium, all of the metals shown overleaf occur in higher concentrations in leachate from landfill where only municipal solid waste is disposed. Two factors should be considered when comparing this data from the United States and the United Kingdom. The Authorities in the United Kingdom are very strong supporter of co-disposal; figures concerning leachate composition are extremely variable.

TABLE 3.18 METALS DETECTED IN LEACHATES FROM CO-DISPOSAL, HAZARDOUS AND MUNICIPAL LANDFILLS

(adapted from Levine *et al,* 1989)

Landfill	**Co-disposal**	**Hazardous**	**Municipal**
Metal	Mean value ($\mu g \ell^{-1}$)	Mean value ($\mu g \ell^{-1}$)	Mean value ($\mu g \ell^{-1}$)
Arsenic	33	507	14
Total chromium	138	215	57
Hexavalent chromium	104	303	149
Copper	46	268	35
Lead	76	79	48
Mercury	1	3	1
Nickel	272	1264	137
Zinc	1202	1085	791

TABLE 3.19 COMPOSITION OF LEACHATES FROM DIFFERENT CLASSES OF LANDFILLS

(adapted from DOE, 1986)

Metal	Household ($mg\ell^{-1}$)	43 percent Industrial ($mg\ell^{-1}$)
Chromium	0.05 - 1.0	0.05
Iron	0.1 - 2050	10
Nickel	0.05 - 1.7	0.04
Cobalt	0.01 - 0.15	0.09
Zinc	0.05 - 130	0.16
Cadmium	0.005 - 0.01	0.02
Lead	0.05 - 0.6	0.10

Assmuth (1992) conducted a 5 year study (1985-1990) examining 43 sites in southern and central Finland. The landfills examined may be defined as co-disposal. Wastes now defined as hazardous in Finland were disposed in an uncontrolled manner in local municipal landfill sites. Assmuth examined leachate composition, solid waste composition, interstitial water composition, and landfill gas composition. Assmuth reported considerable variance of attenuation mechanisms, but felt that the environmental toxicological risks from municipal co-disposal leachates to be small when compared with the impacts and risks from other sources. Assmuth considered the transport of both metals and organic contaminants such as dichloromethane, total xylenes, etc., and states the attenuation of heavy metals was greatest, and was logical considering their chemical behaviour, e.g. precipitation tendency. This statement is only partially correct, as some metals (obvious examples being arsenic(V), arsenic(III) or chromium(VI)) would not precipitate directly at common pH range operating within a landfill. From the examination of the behaviour of these metals in soils (Section 3.8.1.3) adsorption would surely provide a significant reduction in the concentration of these metals from solution.

As stated previously Assmuth examined the concentration of different fractions in solid waste samples, extracting metals with both strong and weak acids. The most easily extracted metals were lead and zinc; chromium, copper, arsenic, and nickel (in order of increasing mobility); being more strongly bound in the waste matrix. This work was confirmed by laboratory analyses of the leachate from the landfill sites. Zinc was found in the highest concentration in leachate from the landfills examined. Lead is probably precipitated as lead chloride, confirming work reported by Mosey and co-workers (Mosey et al, 1971) when investigating the ability of heavy metals to inhibit anaerobic digestion at laboratory scale (3.8.3 (a)). Although zinc is strongly adsorbed by clays and organic matter, the presence of soluble organic mater such as fulvic acids which are soluble over a wide range of pH can greatly

increase the solubility and mobility of zinc (Kiekens, 1990). Researchers investigating leachate from soil have found 60-75 percent of the total soluble zinc present was in the form of soluble organic complexes (Kiekens, 1990).

In a companion study (Assmuth *et al*, 1993) sampled groundwater at 16 co-disposal landfill sites. It was found that some impairment of groundwater quality was notable at almost all of the sites examined. However, in some of the cases that impairment could have been caused by other factors other than those related to landfills. Frequently, heavy metals were in abundance in the groundwater, the median value for zinc being 80ppb. Black *et al*, (1989) evaluated the environmental hazard presented by two large metropolitan landfills located near New York, in the United States. These landfills received both municipal and commercial waste in an uncontrolled manner. Data is presented on airborne contaminants, sediments and water bodies surrounding the two landfills. The researchers concentrated mainly on pollution from certain classes of organic chemicals. However copper was present in seepage samples at levels of 38-46$\mu g\ell^{-1}$, and 6-16$\mu g\ell^{-1}$ copper, was found in Jamaica Bay an adjoining body of water. Copper in seawater usually approximates 0.04-0.1$\mu g\ell^{-1}$ (Forstner *et al*, 1979).

Newton (Newton, 1977; DOE, 1975; Knox *et al*, 1990) conducted pilot-scale and laboratory scale investigations where he co-disposed three types of industrial wastes with municipal solid waste. The wastes studied were an aqueous oil emulsion, a cyanide heat treatment waste and a metal-hydroxide sludge. The metal hydroxide sludge was obtained from the effluent treatment plant of a plating works. The vessels were placed outdoors and subjected to natural rainfall. The sludge was composed principally of nickel and chromium, though small quantities of zinc, copper, lead and cadmium were present. Unfortunately, the researchers did not undertake landfill gas measurements. The experiment was terminated after three years. During this period concentrations of cadmium, copper and zinc in the leachate did not increase, however, the nickel concentration rose to 51mgℓ^{-1}, and the chromium concentration rose to 5.7mgℓ^{-1}. This was felt be acceptable by the researchers.

Knox and Gronow (1990) compiled and reviewed data gathered concerning anaerobic digesters, laboratory scale experiments, pilot-scale studies and activities at full-scale landfills. The data is conveniently segregated into four groups of compounds co-disposed with municipal solid waste. These are; phenols, cyanides, acids and heavy metals. The researchers consider the landfill to be a stationary fixed film reactor, and compare range and loading of waste inputs while concomitantly examining effluent (leachate) quality. The six most studied metals were zinc, copper, nickel, chromium, lead, and cadmium. The data examined was derived from twelve projects based in the United States, United Kingdom, and Hong Kong. Of the twelve experimental projects ten were laboratory or pilot-scale column studies, two of the experimental studies were equilibrium tests.

The researchers comment that the attainment of methanogenic conditions appeared to be of importance. In one study nickel was added to two reactors at approximately 157mg per kilogram of solid waste. The nickel content of the leachate of the acetogenic reactor rose to 86mgℓ^{-1} while in the methanogenic reactor the nickel content did not exceed 0.46mgℓ^{-1}. It is probably physio-chemical effects which predominate in this instance. The higher, near neutral pH commonly experienced with methanogenic activity, in comparison with the lower pH

associated with acetogenic activity. The metallic compounds mobility being enhanced at the lower pH.

Few of the studies reviewed by the researchers directly examined the effects of metal loadings on the biological processes; however, leachate composition was obviously noted. Where the metals had been added as metallic sludges the leachates showed little enhancement of leachate metal concentration, but in experiments were the metals were added in solution showed elevated metal concentration. It is probable the pH effect was being demonstrated here, the alkali content of the metal sludge reducing metal ion mobility. Of interest, two studies reported enhanced metal content with leachate organic content. Where methanogenic conditions were established there was insufficient evidence of inhibition caused by the presence of heavy metals. The researchers evaluated data from five full scale landfill sites being operated in the United Kingdom. Where methanogenic conditions were firmly established there was no inhibition of methanogenic activity. However, even with the additional loading of heavy metals by co-disposal with the municipal solid waste, the sum of the applied metals plus those metals associated intrinsically with the municipal solid waste did not exceed the values commonly reported to be inhibitory in anaerobic digesters.

(c) Effect of co-disposal on landfill gas composition

Early efforts to evaluate gaseous emissions from landfills were primarily concerned with methane and the associated dangers of explosions, fires, and potential asphyxiation of surrounding residents in their homes (Rickabaugh *et al*, 1993). Recent measurements at landfills in the United Kingdom indicate workers may be exposed to concentrations of toxic substances which exceed United Kingdom Occupational Health Legislation (cited by DOE, 1990). Researchers have concentrated on the emission of volatile organic compounds (Deipser *et al*, 1994; Rickabaugh *et al*, 1993), although when Blakey (1984) investigated the behaviour of arsenical wastes when co-disposed with municipal solid waste he noted that under anaerobic conditions, arsenic compounds are reduced and methylated to di- and tri-methylarsine by a number of species of anaerobic bacteria. However, the production of arsine in soils is the primary mechanism for gaseous loss of arsenicals in soils when compared to methylation. Blakey expressed concern on the migration of volatile arsenical species into the gaseous emissions from the landfill. Elfving and co-researchers (1994) cite an example where biomethylation of arsenic and the evolution of methylarsine occurred. The removal of arsenic by bioremediation from soils contaminated by lead arsenate has been accomplished by adding apple pomace as a carbon source, and flooding the surrounding area to establish anaerobic conditions.

An extreme example of the effect of co-disposal on the composition of the biogas has been reported from the United Kingdom (DOE, 1986) where the hydrogen sulphide concentration of the biogas exceeded 30 percent. Hydrogen sulphide concentrations do not normally exceed 10 ppm in landfill gas. In this case, gas emitted from the landfill presented a considerable hazard to workers at the site. The problem was traced to the presence within the landfill of material containing high concentrations of sulphate. Arsine generation has also been reported when cover material containing arsenic was utilised at another landfill site in the United Kingdom (DOE, 1986). Several toxic metals were co-disposed with municipal solid waste in pilot-scale landfills at the Georgia Institute of Technology (Pohland *et al*, 1986a; Gould *et al*,

1989). The metals examined were mercury, lead, zinc, chromium, nickel, cadmium, copper, and iron. The researchers concluded that mercury was reduced to the neutral metal and that would facilitate the volatilisation of the metal which would then be transported in the gas phase leaving the landfill.

3.9 THE HEAVY METALS UNDER EXAMINATION: COPPER, CHROMIUM AND ARSENIC

The metallic elements of concern to this investigation are copper, chromium and arsenic. These metals are in common use in combination, as a water based wood preservative, traditionally named CCA, or Tanalith. The preservative commonly consists of a mixture of copper in the form of its sulphate salt ($CuSO_4$); chromium, in the form of sodium dichromate ($Na_2Cr_2O_7$) and arsenic in the form of arsenic pentoxide (As_2O_5). Copper and arsenic are the principal pesticidal agents, whereas the purpose of the chromium salt is to affix the two former compounds within the wood (DOE, 1980). It is advantageous to consider each of the reagents of this formulation separately, then to consider the mixture in its entirety.

3.9.1 COPPER

Copper (Cu) is the first element of subgroup IB of the Periodic Table. Copper has an atomic number of 29 and an atomic weight of 63.546. The effects of copper pollution in rivers was examined by researchers in western Wales, in the United Kingdom (cited by Gaufin, 1974). The River Dove was examined and was found to be contaminated by organic matter, but appeared to be recovering a few miles downstream. A discharge of industrial effluent to the waterway then occurred. Industrial effluent from a copper processing plant was discharged into the river, the average copper content in the river was raised to 1ppm and above. This discharge had an extremely stressful result on the river ecosystem. All the animals, which above the copper processing plant consisted of Tubificidae, *Chironomus*, *Asellus*, leeches and mollusks, disappeared. None were found in the next 11 miles to the confluence with the Dove, where the copper content had fallen to 0.6ppm. The algae were also seriously effected.

Under normal conditions copper is benign agent for humans. The total body copper content of a human being is about 100-150mg, a normal diet provides 1-5mg of copper per day. It is difficult to formulate a diet with less than 1mg of copper per day (Baker, 1990).
There are however, examples in the literature of copper poisoning (Forstner *et al*, 1979). The example cited by Forstner concerns the poisoning of fish off the coast of Holland in 1965. Innumerable dead fish of widely diversified species were found between Scheveningen and Ijmuiden. It was established the seawater contained a concentration of copper as copper(II) of several hundred micrograms per litre. The normal concentration varies from 1-3 micrograms per litre. The source of the copper pollution was only found accidentally; several kilograms of copper sulphate crystals were found buried under sand near Noordwijk. Copper, in the form of copper sulphate, is used extensively for the prevention of algal growths, especially in and around swimming pools (Perkins, 1978). It is one of five metals on the EPA list of most commonly discharged priority pollutants (cited by Novotny, 1995). The other most commonly discharged priority pollutants are zinc, chromium, lead and nickel.

3.9.2 CHROMIUM

Chromium (Cr) is a *d*-block transition metal of Group VIB of the Periodic Table. Chromium has an atomic number of 24 and an atomic weight of 51.996. Chromium has been used in alloy steels since about 1877, chrome plating commenced in approximately 1926. It is resistant to oxidation, and its used industrially in alloys which are resistant to corrosion. It usually occurs in +3 and +6 oxidation states in the environment, though Chromium(III) is the most stable state (McGrath *et al*, 1990).

Chromium is one of the least toxic of the heavy metals. In general, the mammalian body can tolerate 100 to 200 times its normal total body content of chromium without harmful effects. Chromium(VI) compounds are, in general, approximately 100 times more toxic than chromium(III) salts. Stomach acidity reduces chromium(VI) to chromium(III), gastro-intestinal absorption of chromium(III) is less than 1 percent of that of chromium(VI) (Forstner *et al*, 1979). The link between occupational exposure to chromates and the increased risk of lung cancer is well established. Over a century has passed since Newman reported a case of nasal cancer in a chrome pigment worker in 1890 (cited by Yassi *et al*, 1988). Later in 1936, German health authorities accepted that lung cancer in chromate producing workers as an occupational disease. Authorities in the United States concurred 10 years later.

Forstner *et al* (1979) quotes an example of catastrophic heavy metal poisoning concerning chromium that occurred in the early 1970's around Tokyo, Japan. The Nippon Chemical Industry Company deposited approximately 530000 tonnes of unreduced slimes and wastes containing hexavelant chromium; the waste material gained extensive use in constructional projects. Additionally, complete housing blocks along Tokyo Bay have been erected upon spoil heaps containing toxic chromium(VI) compounds. The extent of the tragedy had not been completely evaluated at the time of writing (1979), official figures at that time revealed 30 dead, 200 people incurably ill. Investigations of groundwater near the deposits contained more than 2000 times the official limit. More alarming still, the effluent from the Nagoya municipal wastewater treatment plant turned yellow. Chromium is one of five metals in the EPA list of the most commonly discharged priority pollutants (cited by Novotny, 1995), the others being zinc, copper, lead and nickel.

3.9.3 ARSENIC

Arsenic(As) is a metalloid, located in Group VB of the Periodic Table. Arsenic has an atomic number of 33 and an atomic weight of 74.9216. Elemental arsenic exists as a metallic modification commonly called grey arsenic, as well as a non-metallic modification commonly called, yellow arsenic (Sienko *et al*, 1966). Over 200 arsenic containing minerals have been identified, approximately 60 percent being arsenates, 20 percent being sulphides and sulphosalts, the remaining 20 percent, arsenides, arsenites, oxides, and elemental arsenic. The most common of the various forms of arsenic is arsenopyrite, the chemical formula being FeAsS (O'Neill, 1990).

Arsenic occurs most frequently in nature in the pentavalent state as arsenate. It is in this form it has been applied as a insecticide, usually in the form of lead arsenate. Many orchards in Missouri, United States, have been treated with lead arsenate for 20 to 80 years causing the arsenic concentration in the soil be in excess of 100 ppm (Hess *et al*, 1976). Sadler and fellow workers (1993) quote examples of orchard sites with maximal soil arsenic concentrations of 124 238 and 2000mgkg^{-1} at three different sites. This gross contamination must be seen against naturally occurring or background levels of arsenic in the environment. For water the expected range is 0.01 to 1mgℓ^{-1}, for soil, 1 to 500mgkg^{-1}, 0.1 to 1.6mgkg^{-1} for grass, 0.01 to 0.05mgℓ^{-1} for milk and 0.06 to 1.1mgkg^{-1} for meat (Onken *et al*, 1995). Arsenic in aquatic systems has a complex chemistry, reactions involving oxidation-precipitation, ligand exchange, precipitation and adsorption all take place. It is stable in four oxidation states, namely, +5, +3, 0, -3, under conditions occurring in aquatic systems (Ferguson *et al*, 1972). The toxicity of arsenic varies with its oxidation states, trivalent arsenic is of substantially greater toxicity then pentavalent arsenic (Thomas, 1994). Ghosh *et al* (1987) specify the toxicity scale of arsenic as follows:

Arsine > arsenite > arsenate > alkyl arsenic.

Abernathy *et al* (1992) report a number of catastrophic episodes involving arsenical compounds. In the United Kingdom, during 1900, sugar contaminated by arsenic was used in the production of beer, this resulted in the deaths of more than 70 people, and illness occurred in a further 6000. This resulted in the formation of a Royal Commission of Inquiry. The Commission found that the malt had been contaminated to dangerous levels, from the arsenical content of the coal fuel used in the kiln (Brame *et al*, 1961). One death occurred in Virginia, United States, coupled with illness in eight other family members. The cause, of significance in this investigation, was contaminated groundwater. An average person of mass, 70kg, contains approximately 10mg of Arsenic. The human liver continually extracts arsenic, converting it to mainly dimethylarsinic acid, this then is excreted by the body in urine. This methylated version of arsenic has only 1 percent of the toxicity of inorganic arsenic in the form arsenic(III) (Emsley, 1985).

3.10 THE COPPER-CHROMIUM-ARSENIC WOOD PRESERVATIVE

Wood, a raw material of biological origin, is vulnerable to attack by bacteria, fungi, insects and marine borers, treatment by a suitable agent can considerably reduce the deterioration of the original product. Timber preservation is practised globally, and is an important component of the forest products industry. In 1990, there were approximately 3300 pressure-treatment plants operating in the world, their production is estimated at 30 000 000 m^3 of timber products per annum. The global nature of the industry is illustrated in Table 3.20 overleaf (cited by UNEP, 1994).

The total production of the various chemicals used for wood preservation is estimated to be excess of 550 000 tonnes per annum. There are three principal preservatives; a waterborne preservative; an organic solvent, and various tar oils, composed of mainly creosote. The distribution of their production is as follows:

Category	Production
Tar oil	350 000 tonnes per annum
Waterborne	9 0000 tonnes per annum
Organic solvent	110 000 000 litres per annum

Copper/chrome/arsenic (CCA) is grouped within the waterborne preservatives. The initial formulation was first patented by S. Kamesam in 1933 and is known as *Ascu*.This first formulation was composed of 55 percent potassium dichromate ($K_2Cr_2O_7$), 33 percent copper sulphate (as $CuSO_4.5H_20$) and 12 percent arsenic pentoxide (as $As_2O_5.2H_2O$). This formulation resembled the acid copper chromate commercially known as *Celcure* which had been in use since 1927. The primary difference being that a proportion of the copper sulphate was replaced by arsenic pentoxide.

A number of different parties used similar preparations. From 1936 to 1948 the Boliden Mining Company in Sweden produced wood preservation products called *Boliden BIS* and *Boliden S25*. The former was a zinc-chromium-arsenic formulation, the latter a zinc-copper-chromium-arsenic formulation. Unfortunately, these products were not as successful as the original *Ascu* product they were modelled on. The lower chromium content allowed easier leaching under adverse conditions. Boliden marketed a copper-chromium-arsenic product but the various elements in the form of their oxides, probably to avoid infringement of Kamesan's *Ascu* patent. In the United States, the Bell Telephone Company released results of a survey of telephone pole treatment, in 1942.The preservative developed was called *Greensalt*, a product similar to *Ascu*. During this period in the United Kingdom, the original *Ascu* was replaced by *Celcure "A"* and *Tanalith "C"*, both copper-chrome-arsenic products (Hickin, 1971).

TABLE 3.20 MAJOR PRODUCERS AND PRODUCT RATES OF PRESERVATIVE TREATED WOOD

(cited by UNEP, 1994)

Country or Area	Production of preservative treated wood (m^3annum^{-1})	Country or Area	Production of preservative treated wood (m^3annum^{-1})
France (1988)	219 000	South Africa (1988)	430 000
Germany/FRG (1988)	1 000 000	Japan (1988)	408 000
Scandinavia & Finland (1989)	1 369 000	Australia (1988)	942 000
United Kingdom (1989)	1 968 000	New Zealand (1986-87)	1 460 000
USA (1988)	16 009 000		

The chemicals under discussion, by their very nature, and their toxicity to living organisms, can be hazardous to personnel handling them, the general public should they inadvertently come into contact with them, and to the environment at large.

3.11 THE DISPOSAL OF COPPER-CHROMIUM-ARSENIC TREATED WOOD PRODUCTS

This subject is currently a controversial topic amongst researchers, regulatory organisations and interested pressure groups. In the United Kingdom, the Department of Environment is a protagonist of a liberal viewpoint, in line with the philosophy of "dilute and disperse". It would be apt to outline their policies as stated in Waste Management Paper No, 16: Wood-preserving wastes (DOE, 1980).

It was estimated in 1970-72 approximately 11 000 tonnes of inorganic salts were required for the annual production of the waterborne preservatives, the most common type being the CCA wood preservative. Of this, approximately 1370 tonnes were consumed in the United Kingdom, the remainder being exported. The primary use, over 50 percent is the treatment of building timbers, 20 percent is used to treat fencing, the remainder mainly miscellaneous industrial applications. Also, at that time, the amount of timber treated by all wood-preservation methods was estimated at $2Mm^3$. In 1988, analysts Jermer and Evans (cited by UNEP, 1994) quoted the figure of 1 968 $000m^3annum^{-1}$, it would appear from this that statistics quoted in 1970 could be relatively unchanged, and are good indicators of usage and disposal today in the United Kingdom.

Details are supplied by the Department of the Environment regarding the usual treatment specifications for the CCA treatment of new wood. The specifications vary with respect to the intended end use of the wood. The treatment of building and fencing timber typically relates to a minimum 1.4kg of arsenic (approximately 5kg total salt) per tonne of wood. For cooling tower internals or marine timbers this relates to 6kg of arsenic (approximately 10 kg total salt) per tonne of wood. Approximately half of the arsenic can be lost during service, however, a typical tower may contain between 200 and 350 tonnes of packing. From approximations such as these various indicators for future waste disposal are estimated. However, it is stated in the document the very reasonable conclusion that at a future date the annual arisings from demolitions etc., will equate to current treatment levels of 1370 tonnes of CCA salt, or 500 tonnes of arsenic per annum.

Open burning of wood from demolished buildings in the United Kingdom was, in 1980, a widely used disposal method for CCA-treated wood. The Department of the Environment recommended the continuation of this practice with the *proviso* that the wood should be burnt at least 100m from continuously occupied buildings; not more than half a tonne of wood be burnt at any one fire; not more than one tonne of wood per day be burnt any single site. The burning of cooling tower fill, in open fires, was also a widely used disposal method. The Department forbids the disposal of cooling tower fill and marine timber by burning in open fires as the CCA salt content is approximately triple that of building materials (see above) and suggested disposal in a suitably designed incinerator. If these disposal routes were not

available it was thought the CCA-treated wood could be placed in an appropriate landfill site. As the copper, chromium and arsenic are *securely* bound within the wood, there is no requirement for restriction. Wood regardless of species is composed of two principal materials: cellulose, which is approximately 70 percent of the volume, and lignin, nature's glue for holding the cells and fibres together (Clauser *et al*, 1963). The remainder is composed of minerals, waxes, tannins, oils, etc.

The American Public Works Assocation (1970) initiated two research projects into composting in 1953, one of the projects in Savannah, Georgia, determined chemical composition of municipal solid waste; researchers were interested in changes that occur during the composting process. Barlaz also addressed the chemical composition of municipal solid waste (Barlaz, 1988) when determining the contribution of the various fractions of municipal solid waste to methane production. Rees (cited by Watson-Craik, 1987) provided analyses of the chemical composition of municipal solid waste from two representative locations. Results from their studies are tabulated below.

It can be seen the combined cellulose and hemi-cellulose content of municipal solid waste range from approximately 40 to 60 percent. One could therefore expect excellent adsorption of CCA within the landfill environment. However, as often occurs, conflicting reports can be quoted. Sadler and co-workers (1993) refer to soil in contact with wood treated with CCA. Observed arsenic soil residues ranged from 70 to 220mgkg^{-1}. This would not seem to indicate secure adsorption within the wood.

The American Wood Preserves Institute (AWPI) has a home page on the Internet where it addresses the issue of the life cycle of pressure-treated wood (http://www.awpi.org, 1996). A document of several pages is available for electronic perusal. Treated wood products in the United States can be regulated at federal, state, or by local juristriction. The document refers mainly to Federal Law, though caution that users should conform to local and state requirements.

The treated wood product is covered by distinctly different regulations than the chemical utilised for wood treatment. The chemicals such as CCA are regulated by the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA). Additionally, treated wood waste has not been treated as a hazardous waste under the Federal Resource Conservation and Recovery Act (RCRA). In 1992, the EPA published in the Federal register that arsenical-treated wood products disposed of by the end user are exempt from classification as a hazardous waste regardless of results from the Total Characteristic Leaching Procedure (TCLP) for specified constituents from any individual sample. Nevertheless, if the wood product exceeded regulatory requirements for any other constituent it would forgo it's exemption. Therefore as a non-hazardous material pressure treated wood by CCA may generally be disposed at municipal landfills. The EPA publish consumer information sheets containing data on the disposal of pressure-treated wood. Consumers are warned never to dispose of treated wood by means of open fires.

TABLE 3.21 CHEMICAL COMPOSITION OF MUNICIPAL SOLID WASTE

Savannah, Georgia, 1958		Barlaz, 1988		Rees, 1985		
Component	% dry weight	Component	% dry weight	Component	% dry weight	% dry weight
Lipids (ether soluble)	10.1	Cellulose	51.2	Cellulose	35.1	37.1
Crude fibre	35.9	Hemi-cellulose	11.9	Hemi-cellulose	1.6	4.4
Total sugar	4.9	Protein	4.2	Protein	5.8	5.6
Starch	8.1	Lignin	15.2	Lignin	7.6	8.5
Protein (6.25N)	8.2	Starch	0.5	Starch	0.3	0.4
Volatile solids	92.2	Pectin	< 3.0	Lipids	< 0.1	< 0.1
		Soluble sugars	0.35	Soluble sugars	0.4	0.7
		Volatile solids	78.6	Volatile solids	50.9	56.8

The Industry and Environmental Programme Activity Centre (IEPAC) operating under the umbrella of the United Nations is concerned about the disposal of treated timber (UNEP, 1994). The amount of timber being treated globally continues to rise, at present over 30 million cubic metres of wood are being industrially treated, and after 30 years, disposal will then be required. It comments that current disposal options are not encouraging, uncontrolled burning is *out of the question*, incineration of such volumes *impractical*, and disposing to landfill is *not encouraging*.

3.12 SUMMARY

Globally, volumes of solid waste (both industrial and municipal) continue to increase. A developing country such as South Africa strives for a higher standard of living for its citizens. A higher standard of living has always been associated with greater consumption of energy and resources, resulting in a larger production of waste materials. Co-disposal of hazardous chemicals with municipal solid waste is practised in South Africa, in suitably constructed containment landfills. However, even with a contained landfill, leachate will be produced and will require treatment either prior to discharge to the municipal sewerage system, or to a suitable waterway. When co-disposal is practised, it is of importance that the emission of toxic substances from the landfill is not increased to levels that can be detrimental to the surrounding environment. There is a paucity of available data concerning co-disposal ratios and much of the information is conflicting and causes confusion.

The material of concern in this investigation is a wood preservative commonly called CCA, or Tanalith. The preservative is consists of a mixture of copper, chromium and arsenic. These chemicals, either individually, or in combination, can be hazardous to personnel handling them, to the general public, and to the environment. The disposal of these substances, both as waste solution, and in combination with wood at the end of its lifecycle, has become a matter of concern to such august organisations as IEPAC. The objective of this current study is the development of guidelines for the disposal of CCA within the landfill without any additional degradation of the surrounding environment.

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CHAPTER 4
THEORETICAL CONSIDERATIONS

4.1 INTRODUCTION

The concepts of adsorption isotherms, chemical kinetics and tracer response analysis, are employed throughout the investigation into the immobilisation of copper, chromium and arsenic in stabilised domestic refuse. These concepts are discussed below.

4.2 ADSORPTION ISOTHERMS

An adsorption isotherm represents the functional relationship between the adsorbed phase concentration, and the fluid phase concentration of the solute, at equilibrium. There are four main adsorption isotherms: the Freundlich isotherm, the Langmuir isotherm; the BET (Brunaer, Emmett, and Teller) and the Gibbs Isotherm (Tan, 1993). The two most commonly used adsorption isotherms are the Langmuir and Freundlich isotherms, which were first introduced approximately 70 years ago. The success of these isotherms reflects their ability to fit a wide variety of adsorption data quite well. It may also partly reflect the appealing simplicity of the isotherm equations and the ease with which their adjustable parameters can be estimated. Both isotherm equations can be transformed to a linear form and so their two adjustable parameters are easily estimated by graphical means, or by linear regression (Kinniburg, 1986). It is however, important to note, like empirical rate laws, adsorption isotherms equations cannot be interpreted to indicate any particular adsorption mechanism, or even if adsorption, *as opposed to precipitation, has actually occurred* (Sposito, 1989). Data presented in Chapter 5 is described by the Freundlich Isotherm, but as reference is made in the text to the Langmuir Isotherm, both are described below.

4.2.1 FREUNDLICH ISOTHERM

The Freundlich isotherm is not derived from theoretical concepts but is based on empirical relationships. It does however, have the ability to describe adsorption data obtained at constant temperature (Sposito, 1980). The equation has often been associated with adsorption by heterogeneous surfaces (Tan, 1993). It may be expressed as (Malina, Jr., 1967):

$$q = K_F C_e^{M} \qquad 4.1$$

Where,

q	=	solute adsorbed per unit weight of solid adsorbent
K_F	=	Freundlich equilibrium distribution coefficient
C_e	=	Concentration of solute remaining in fluid at equilibrium
M	=	Freundlich power coefficient

Data are usually fitted to the logarithmic form of the equation:

$$\ln(q) = M \ln(C_e) + \ln(K_F)$$

If the Freundlich adsorption isotherm is suitable, a logarithmic plot of solute adsorbed (q) versus equilibrium solute fluid concentration (C_e) results in a straight line with a slope equal to the Freundlich power coefficient (M) and an intercept equal to the value of the logarithmic form of the Freundlich equilibrium distribution coefficient (K_F). The Freundlich equilibrium distribution coefficient may be considered as a measure of affinity (Murali *et al*, 1983).

Numerous examples exist in the literature where the Freundlich isotherm has been used to describe the adsorption of solutes by a solid matrix. Smith (1981) cites as examples, the adsorption of; hydrogen gas on tungsten and aqueous sulphur dioxide on activated carbon. Examples involving the adsorption of solutes onto the soil matrix abound (Travis *et al*, 1981). In an excellent survey of sorption relationships in soil, Travis and Etnier (1981) cite more than 30 examples of the adsorption of various solutes onto the soil matrix where the Freundlich equation has described the adsorptive process. The solutes diverge from anions such as sulphate, metallic ions, to herbicides, pesticides and various hydrocarbons.

4.2.2 LANGMUIR ISOTHERM

The Langmuir equation for isothermal adsorption may be deduced from kinetic considerations or from the thermodynamics of adsorption. It is based on the following assumptions:

(1) Maximum adsorption corresponds to a saturated monolayer of solute molecules on the surface of the adsorbent;
(2) Energy of adsorption is constant at all adsorption sites;
(3) No transmigration of adsorbed molecules in the plane of the surface.

The Langmuir equation may be written as (Murali *et al*, 1983):

$$q = \frac{K_L C_e Q}{(1 + K_L C_e)} \qquad 4.2$$

Where,

q = solute adsorbed per unit weight of solid adsorbent
K_L = Langmuir equilibrium distribution coefficient
C_e = Concentration of solute remaining in fluid at equilibrium
Q = Adsorption capacity

A convenient linearised form of the Langmuir equation is,

$$\frac{1}{q} = \frac{1}{Q} + \frac{1}{K_L C_e Q} \qquad 4.2(a)$$

If the Langmuir isotherm is obeyed, a plot of 1/q versus $1/C_e$ the intercept at $1/C_e = 0$, allows the calculation of the reciprocal of the Adsorption capacity (Q). The Langmuir equilibrium distribution coefficient (K_L) is a measure of the adsorption energy, as is the steepness of the adsorption isotherm (Murali *et al*, 1983). The Langmuir adsorption isotherm was developed by Langmuir (1918) to describe the adsorption of gases by solids. Assumption(1) leads to the concept of an upper limit of adsorption. The Freundlich isotherm does not generae any information indicating the process of adsorption is completed (Tan, 1993). However, although the Langmuir isotherm provides a useful reference standard of ideality for theoretical study, equilibria in real systems are often better represented by the Freundlich isotherm (Graham, 1959).

4.3 CHEMICAL KINETICS

The word "kinetics" is a general term, referring to time dependent phenomena.The term chemical kinetics is used to describe the quantitative study of change in concentration or pressure with time, resultant from a chemical reaction (Latham *et al*, 1977). Chemical reactions may be divided into two broad categories: homogeneous and heterogeneous. Chemists, and textbooks of chemistry, often confine themselves to homogeneous reactions, especially in the examination of chemical kinetics. In this investigation which examines the adsorption of metallic ions onto municipal solid waste, it was necessary to investigate the work of other researchers working in the similar area. An area of science where kinetic theories are adapted to the adsorption of various ions onto heterogeneous surfaces is soil chemical processes.

Since the initial development of the science of soil chemistry, attention has been given to equilibrium processes. It was only in 1989, that the first comprehensive study of time dependent soil chemical processes was promulgated by Sparks; Kinetics of soil chemical processes (Sparks, 1989). Harter (1986), a major contributor to the field of soil science, reviewed key papers in adsorption phenomena of various researchers from the 1800's to the present day. Harter thought, at that time, the state of knowledge regarding chemical kinetic studies was incomplete. The selection of papers would possibly be incautious, and instead included a bibliography of papers together with a review of recent findings and thoughts. However, with the similarities between the two areas of research, it was likely that the work of researchers in the field of soil science would be relevant.

4.3.1 CHEMICAL INTERACTIONS IN SOIL REACTIONS

Chemical reactions at the solid phase may comprise of: the formation or rupture of a bond between sorbate and surface; further reaction between adsorbed species; rearrangement of the solid structure and formation and disappearance of solid species. It is often incorrect to apply simple kinetic models to such interactions because reacting solid surfaces are rarely homogeneous and also the effects of transport phenomena and chemical reactions are often inseparable (Sparks, 1989). Harter (1991) notes that commonly used kinetic techniques are based on the assumption that the reactions are either unidirectional or discrete, while soil sorption reactions are often both reversible and multiple, and it is seldom possible to be definitive in calculating rate coefficients attributed to a specific reaction.

The heterogeneity of soils can be further enhanced by the variation of constituents of the soils, the differing particle sizes; types of surface sites, etc. If one considers the organic solids within soils, it is not even possible to describe a developed molecular structure for the compounds present (Sposito, 1984). The analogy of adsorption of solutes onto soils with the adsorption of solutes onto municipal solid waste is evident. The heterogeneity of municipal solid waste regarding composition, size and size range cannot be disputed. The heterogeneity of the surface is also apparent. Therefore, conclusions regarding kinetic models for adsorption of solutes onto soils should be equally applicable for municipal solid wastes.

4.3.2 MECHANISMS OF SOIL REACTIONS

Soil adsorption reactions may be classified as slow or rapid. Slow reactions are those in which processes taking place at the solid phase are rate determining. These processes may include: surface diffusion; diffusion within the micropores; penetration into the bulk of the solid or chemical interactions. Rapid soil reactions are, in general, reactions which transport at the solid phase does not influence the reaction rate to any significant extent (Aharoni *et al*, 1991a).

4.3.3 APPLICATION OF CHEMICAL KINETICS TO THE ADSORPTION OF METALLIC IONS ONTO MUNICIPAL SOLID WASTE

The application of chemical kinetics to (even) homogeneous solutions is often arduous. When kinetic theories are applied to heterogenous soil constituents, the problems and difficulties are magnified (Sparks, 1989). A similar comment could be stated for municipal solid waste surfaces, especially when those surfaces are composed of differing materials. An array of kinetic equations including zero-, first-, and second order, fractional power, Elovich, and parabolic-diffusion equations have been employed over the years to describe the kinetics of soil chemical phenomena. Kuo and Lotse (1974) successfully described the kinetics of phosphate sorption and desorption on hematite and gibbsite by the use of the fractional power or modified Freundlich equation. This equation is often termed the two-constant rate equation, and is discussed below.

4.3.4 TWO-CONSTANT RATE EQUATION

Kuo and Lotse (1974) developed a two-constant rate equation, adapted from the Freundlich equation by inserting a time-dependent expression into the Freundlich equation. The Freundlich equation is usually presented as shown below.

$$q = K_F C_e^{M} \qquad 4.1$$

The insertion of a time dependent expression results in an expression of the form,

$$q = K_a C_o t^{1/m} \qquad 4.3$$

where

Co	=	initial solute concentration
K_a	=	constant
t	=	time
m	=	constant

The two-constant rate equation was also used to describe arsenite sorption and desorption in soils (Elkhatib *et al*, 1984), potassium-calcium exchange on soils (Sparks *et al*, 1980), and by Jopony and Young (1987) to study the kinetics of copper desorption from soil and clay minerals. The modified Freundlich equation is generally considered empirical (Aharoni *et al*, 1991b).

4.3.5 APPLICABILITY OF EMPIRICAL EQUATIONS TO SLOW SOIL REACTIONS

In many cases kinetic data experimentally obtained for activated reactions does not fit equations derived from theoretical models, but may be described by an empirical expression. These expressions, applicable to soil reactions, are also applicable to various other chemical processes involving solid-fluid reactions (Aharoni *et al*, 1991a). The three principal equations are the: modified Freundlich equation; Elovich equation; pseudo-first-order equation.

(a) Modified Freundlich or fractional power equation

Another representation of the modified Freundlich equation is;

$$q = kt^{v} \qquad 4.4$$

where

q	=	quantity adsorbed at time, t.
k	=	constant
v	=	constant

(b) Elovich equation

The Elovich equation is one of the most widely used equations to describe the kinetics of heterogeneous chemisorption of gases onto solid surfaces (Taylor *et al*, 1952; Low, 1960). It has subsequently been used extensively to describe the adsorption and desorption of various solutes with differing soils (Atkinson *et al*, 1970; Chien *et al*, 1980; Hodges *et al*, 1987).

The Elovich equation may be represented by;

$$q = A + (1/b)\ln(t + t_o) \qquad 4.5$$

where

A	=	constant
b	=	constant

The parameter t_o is often small at the range where t is applied and may often be disregarded.

The applicability of the relationship may be verified by plotting q/q_∞ versus $\log_e t$. Where;

q_∞ = amount sorbed at $t = \infty$

(c) Pseudo-first-order equation

The pseudo-first-order equation may be represented by;

$$q/q_\infty = 1 - \beta \exp(-\alpha t) \qquad 4.6$$

where

β = constant
α = constant

The applicability of the relationship can be verified by plotting $\log_e(1 - q/q_\infty)$ versus t.

4.3.6 RELATIONSHIP BETWEEN EMPIRICAL EQUATIONS AND DIFFUSION

A generalised equation may be derived by closely examining the applicability of equations (4.4), (4.5) and (4.6) to experimental data (Aharoni *et al*, 1991a). These generalised expressions are obtained by differentiating the empirically based formula and writing them as the reciprocal of the rate. Consider equation (4.4)

$$q = kt^v \qquad 4.4$$

Then,

$$Z = (dq/dt)^{-1} = (1/vK)t^{1-v} \qquad 4.7$$

A similar exercise may be performed for equations (4.5) and (4.6).

Plots of the reciprocal of the adsorption rate (Z) versus time (t) for various soil reactions, and other solid-fluid processes are usually S-shaped: convex at small values of time, concave at large values of time, and linear at some intermediate value of time. It is often more convenient to plot experimental data as q (amount sorbed) versus $\log_e t$. This representation will also produce S-shaped plots. These S-shaped plots do not contradict the empirical equations whenever they are valid. The equations may be applicable, over the entire experiment, if all the points measured are within its range of validity. It should be noted however that equations (4.4) and (4.5) cannot be valid at large values of time as they give infinite sorption at infinite time. These two equations must be superseded at some time by an equation that predicts a finite saturation value at infinite time, such as equation (4.6). The generalised expression, S-shaped Z(t) plots may be explained by models based on diffusion. Equations for diffusion in a homogeneous medium lead to S-shaped Z(t) plots in which the final and initial curved parts are dominant. Equations for diffusion in a heterogeneous medium lead to S-shaped Z(t) plots in which the intermediate linear part is dominant.

4.4 NON-IDEAL REACTORS AND TRACER RESPONSE ANALYSIS

A continuous reactor may behave very much like a plug flow reactor or a perfect mixer, but it can never completely achieve either of these ideal states. In an ideal plug flow reactor, all reactant and product molecules at a given axial position move at the same rate in the direction of the bulk fluid flow, while in real flow reactors, fluid velocity profiles, turbulent mixing and molecular diffusion cause molecules to move with a variety of speeds and directions. These inevitable deviations from ideal reactor conditions lead to fundamental problems in reactor design and analysis (Dudukovic *et al*, 1983).

4.4.1 RESIDENCE TIME DISTRIBUTION

(adapted from Levenspiel, 1962 and Denbigh *et al*, 1971)

Consider a fluid flowing at steady state, without reaction, or density change, then,

$$\bar{t} = V/v \qquad 4.8$$

Where,

$\bar{t}$ = mean residence time (h)
V = volume (m^3)
v = volumetric flowrate (m^3h^{-1})

A dimensionless variable may be defined which measures time in units of mean residence time. This dimensionless variable is termed reduced time and is defined below.

$$\theta = t / \bar{t} = vt/V \qquad 4.9$$

Where,

θ = reduced time (dimensionless)

(a) Exit age distribution (E and E(t))

Let **E** be a measure of the distribution of ages of all elements of the fluid stream leaving the vessel. Thus, **E** is a measure of the distribution of residence times of fluid within the vessel. Then,

$\mathbf{E}\, d\theta$ = fraction of material in the exit stream between the ages θ and $\theta + d\theta$

Consider Figure 4.1, shown below

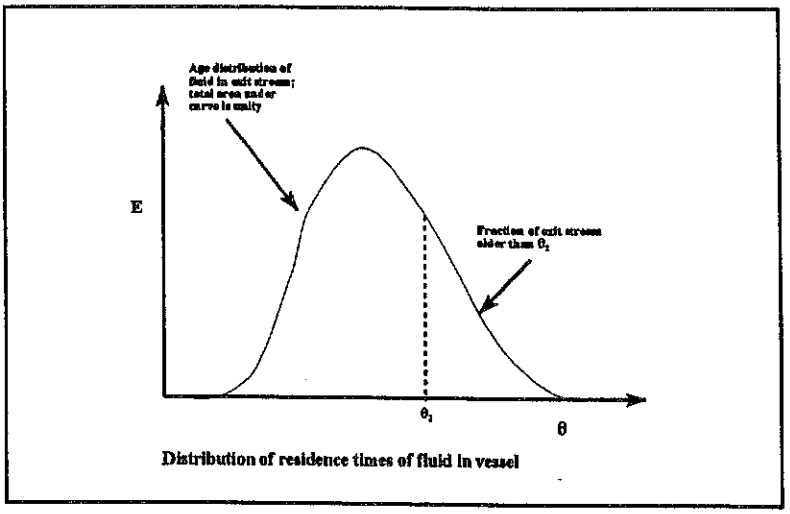

Figure 4.1
Exit age distribution or distribution of residence times of fluid in a vessel (adapted from Levenspiel, 1962)

The area under the E versus θ curve can be expressed

$$\int_0^\infty \mathbf{E}\, d\theta \quad = \quad 1 \qquad 4.10$$

The fraction of the material in the exit stream younger than age θ_2 is

$$\int_0^{\theta_2} \mathbf{E}\, d\theta$$

Then the fraction of material older than θ_2 , is defined,

$$\int_{\theta 2}^\infty \mathbf{E}\, d\theta \quad = \quad 1 \quad - \quad \int_0^{\theta_2} \mathbf{E}\, d\theta$$

Age distribution functions may be expressed in terms of real time units rather than in dimensionless time units. The exit age distribution is designated E(t). Now E(t) dt becomes the fraction of material in the exit stream of age between t and t + dt, then

$$\mathbf{E} \quad = \quad \bar{t}\, \mathbf{E(t)}$$

with,

$$\int_0^\infty \mathbf{E(t)}\, dt \quad = \quad 1 \qquad 4.11$$

also,

$$\bar{t}\theta \quad = \quad t$$

with

$$\bar{t} \quad = \quad V/v \quad = \quad \bar{t}_E \quad = \quad \int_0^\infty t\, \mathbf{E(t)}\, dt$$

4.4.2 EXPERIMENTAL METHODS - THEORETICAL CONSIDERATIONS

The measurement of the exit age distribution functions cannot be made directly. An experimental method within a group of techniques classed as stimulus-response techniques must be utilised. The experimental method employed in this research, used a pulse input signal. Therefore, the subsequent discussion is limited to this approach.

(a) The C(t) curve

The curve that describes the concentration-time function of a tracer in the exit stream of a vessel in response to a pulse injection is termed here, the C(t) curve. Concentration and real time co-ordinates are employed. The C(t) curve may be related to the E(t) curve in the following manner.

Consider a small quantity of a suitable tracer of quantity M is introduced into the fluid entering the vessel. Consider the tracer leaving the vessel between t and t+dt. From the definition of E(t);

Quantity of tracer leaving the vessel between t and t+dt = $ME(t)dt$

Let the concentration of tracer as a function of time = $C(t)$

Also the quantity of tracer leaving the vessel between t and t+dt = $C(t)v dt$

Therefore,

$$E(t) = \frac{vC(t)}{M} \qquad 4.12$$

Thus, excluding the scale factor v/M, the graphical construction of C(t) is identical to that of E(t).

(b) Mean and variance of a distribution

Associated with every age distribution $y = f(x)$ are two sets of parameters called moments of the distribution. Two moments are used throughout all areas of tracer evaluation. The first moment about the origin, commonly called the mean or centroid of the distribution is the location parameter of the distribution and may be defined;

$$\mu = \int_0^\infty x f(x)dx \; / \; \int_0^\infty f(x)dx \qquad 4.13$$

For a continuous function measured at a number of equidistant points then

$$\mu = \sum x_i f(x_i) \Delta x \; / \; \sum f(x_i) \Delta x = \sum x_i f(x_i) \; / \; \sum f(x_i) \qquad 4.14$$

The second moment about the mean, is commonly termed the variance. The variance measures the spread of the distribution about the mean and is equivalent to the square of the radius of gyration of the distribution. It is defined for a continuous distribution as

$$\sigma^2 = \int_0^\infty (x - \mu)^2 f(x)dx \; / \; \int_0^\infty f(x)dx \qquad 4.15$$

For a continuous function measured at a number of equidistant points then

$$\sigma^2 = \sum (x_i - \mu)^2 f(x_i)\Delta x \; / \; \sum f(x_i)\Delta x = \left(\sum x_i^2 f(x_i) \; / \; \sum f(x_i) \right) - \mu^2 \qquad 4.16$$

These properties may be evaluated for the **E** curve, as shown below.

The mean age of the exit stream may be defined in terms of reduced time,

$$\theta_m = \int_0^\infty \theta \, \mathbf{E} \, d\theta = \sum \theta \, \mathbf{E} \; / \; \sum \mathbf{E} = \sum \theta \mathbf{E} \Delta\theta \qquad 4.17$$

The variance of the **E** distribution may be defined,

$$\begin{aligned} \sigma^2 &= \int_0^\infty (\theta - 1)^2 \, \mathbf{E} \, d\theta \\ &= \int_0^\infty \theta^2 \, \mathbf{E} d\theta - 1 \\ \sigma^2 &= \left(\sum \theta^2 \, \mathbf{E} \; / \; \sum \mathbf{E} \right) - 1 \\ &= \sum \theta^2 \, \mathbf{E} \Delta\theta - 1 \end{aligned} \qquad 4.18$$

The mean age of the exit stream may be also be defined in terms of real time,

$$\bar{t} = \int_0^\infty t \, \mathbf{E} \, dt = \sum t \, \mathbf{E}(t) \; / \; \sum \mathbf{E}(t) = \sum t \mathbf{E}(t) \Delta t \qquad 4.19$$

The variance of the E(t) distribution may be defined,

$$\begin{aligned} \sigma_t^2 &= \bar{t}\sigma^2 = \int_0^\infty (t - \bar{t})^2 \, \mathbf{E} \, dt \\ &= \int_0^\infty t^2 \, \mathbf{E}(t) dt - \bar{t}^2 \\ &= \left(\sum t^2 \, \mathbf{E}(t) \; / \; \sum \mathbf{E}(t) \right) - \bar{t}^2 \\ &= \sum t^2 \, \mathbf{E}(t) \Delta t - \bar{t}^2 \end{aligned} \qquad 4.20$$

4.4.3 EXPERIMENTAL METHODS - PRACTICAL CONSIDERATIONS

(a) The pulse experiment

The simplest and most direct method of evaluating the residence time distribution employs a non-reactive tracer. The method of evaluation is described below (Levenspiel, 1993). M units (mass or moles) of non-reactive tracer is introduced simultaneously into the fluid entering the vessel. The volumetric flowrate and the concentration of the tracer within that fluid is then

recorded. A response curve of concentration (C) versus time (t) is then constructed (C(t) curve). The area under the curve, the mean of the curve, and the variance are then evaluated with the equations shown below.

$$\text{Area under the curve} = \int_0^\infty \mathbf{C}\, dt = \sum \mathbf{C}_i \, \Delta t_i$$

$$\text{Mean of the curve } (\bar{t}) = \int_0^\infty t\, \mathbf{C}\, dt \,/\, \int_0^\infty \mathbf{C}\, dt$$

$$= \sum \mathbf{C}_i \, t_i \, \Delta t_i \,/\, \sum \mathbf{C}_i \, \Delta t_i$$

$$\text{Variance } (\sigma_t^2) = \left(\int_0^\infty t^2\, \mathbf{C}\, dt \,/\, \int_0^\infty \mathbf{C}\, dt \right) - \bar{t}^2$$

$$= \left(\sum \mathbf{C}_i \, t_i \, \Delta t_i \,/\, \sum \mathbf{C}_i \, \Delta t_i \right) - \bar{t}^2$$

The calculated results are then evaluated for consistency, by use of material balance computations. The equations are shown below.

$$\text{Area under the curve} = M/v$$

$$\text{Mean of the curve} = \bar{t} = V/v$$

From the concentration-time data the construction of the **E**(t) or **E** curve is now possible, by use of the formula shown below.

$$\mathbf{E}(t) = \mathbf{C} \,/\, \sum \mathbf{C} \Delta t$$

and,

$$\mathbf{E} = \bar{t}\mathbf{E}(t)$$

$$\theta = t \,/\, \bar{t}$$

The **E**(t)curve may be utilised to find the behaviour of the reactor directly as shown below.

4.4.4 CONVERSION DIRECTLY FROM TRACER INFORMATION

Consider a liquid containing a solute A, that is successfully adsorbed by a suitable adsorbent. If the liquid is passed through a bed of adsorbent, initially free of the adsorbate, A, the uppermost layer of adsorbent, adsorbs the solute rapidly, subsequent layers of adsorbent remove further solute from solution until the fluid exiting the column (assuming the depth of adsorbent is sufficient) is free of solute (Treybal, 1968). These statements assume the fluid to be flowing in perfect plug flow, with the rate of adsorption of the solute to be more rapid than the vertical movement of the fluid down the column. The computation of the concentration of solute A in the exit stream in this case is relatively simple. To convert data obtained from tracer information, a sophisticated method of computation is required.

The computation to calculate the degree of adsorption of a solute employs a conventional chemical engineering mathematical approach used to solve, in the presence of unsteady state conditions. The E(t) curve allows the calculation of the volume of liquid leaving the column at any time increment during the total time, and hence, the velocity of that element of fluid. The calculation is then performed incrementally, in a manner similar to that of the art of screen printing (where different colours are applied at different times) for the differing residence time frames of the various elements of fluid flowing through the column. Each incremental residence time is overlaid upon the previous shorter residence times until the longest residence time is the last time frame to compute.

The increment depth of the adsorbent is firstly decided upon. In most cases, the thinner the increment of depth the greater the accuracy of the calculation. From the E(t) data the volume of liquid passing, over a particular time period can be computed. Therefore, the residence time of the fluid per increment of depth can be calculated. CAo is then calculated in terms of mass of solute per mass of adsorbent in the increment. It is assumed the initial solute concentration is in proportion to volume of liquid flowing in that time increment. From the kinetic expression the theoretical mass of solute to be adsorbed is calculated. This is then compared with the solute concentration within the increment. Solute may be adsorbed fully, adsorbed partially, or not at all, if the solute has already reached its equilibrium value in that increment. The concentration of solute in the fluid is reduced by the applicable amount, and this reduced fluid solute concentration then enters the next increment and the aforementioned process begins again. This process is then repeated to the final increment of the adsorbent layer. The next element of fluid from the E(t) data is then manipulated in the same manner until the total residence time of all fluid elements is reached. A graphical plot of concentration of solute in the exit stream versus time may then be constructed. The computational method is shown diagrammatically in Figure 4.2

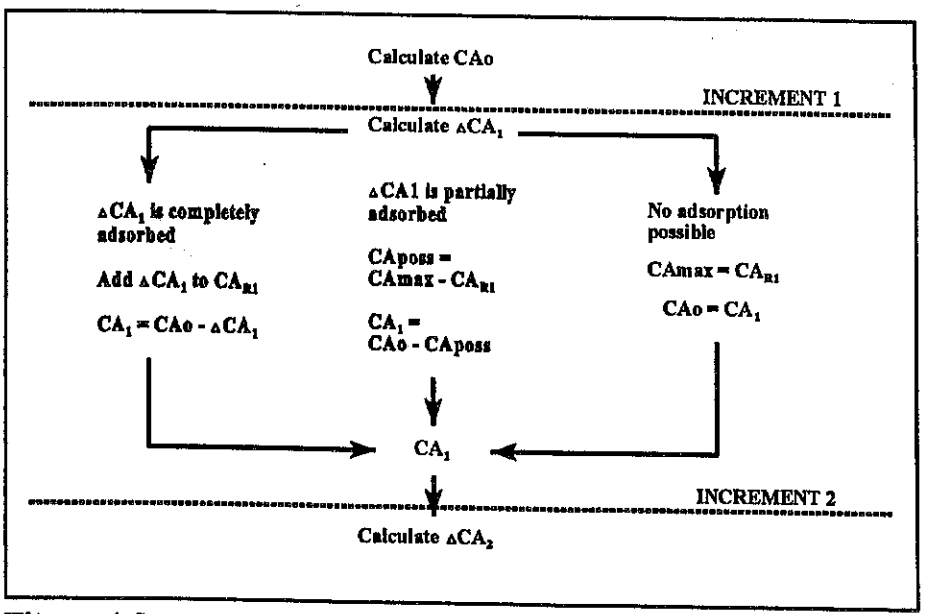

Figure 4.2
Illustration of computational method

Nomenclature

CAo	=	Solute concentration in fluid at t = 0 (gkg^{-1})
CA poss	=	Equilibrium solute concentration in adsorbent (gkg^{-1})
$\triangle CA_n$	=	Solute adsorbed in increment n (gkg^{-1})
CA_n	=	Solute concentration in fluid entering increment n (gkg^{-1})

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CHAPTER 5
MATERIALS AND METHODS: LABORATORY-SCALE ADSORPTION/DESORPTION STUDIES

5.1 INTRODUCTION

The kinetics of adsorption/desorption of copper, chromium and arsenic, were appraised at laboratory scale. Equilibrium adsorption studies were also effected. The metals examined were in the form of CCA (or Tanalith). This chemical is used extensively for wood preservation.

5.2. LABORATORY-SCALE INVESTIGATION

The laboratory scale investigation was also constituted of two integral sections:
Evaluation of kinetic rate constants, adsorption and desorption;
evaluation of adsorption isotherms.

5.3 MUNICIPAL SOLID WASTE

At the outset of the experimental study it was an objective to study the effect of the co-disposal of the heavy metals with methanogenic municipal solid waste. To achieve this purpose, 5000kg of municipal solid waste deposited at Coastal Park Sanitary Landfill Site for approximately 1 year was excavated. By excavating previously deposited waste, it was thought the stabilisation process could be accelerated allowing the experimental study to proceed more rapidly, possibly partially by-passing the acetogenic phase of landfill stabilisation. This objective was not achieved. The waste excavated was virtually stabilised i.e. at the end of the methanogenic stage of landfill stabilisation; the waste was probably deposited far in excess of the estimated time of 1 year. The interest of the study changed to examine the effect of the co-disposal of heavy metals with fully stabilised municipal solid waste.

After excavation the municipal solid waste was transported to the Swartklip Pulverising Plant were the waste underwent size reduction. The waste was shredded for three main reasons:

to avoid gross liquid bypassing in the pilot-scale landfill columns;
to achieve a similar degree of compaction to that achieved at the full-scale landfill;
to obtain a similar degree of dimensional similarity between the pilot-scale columns and the full-scale operation.

5.3.1 SAMPLING OF THE MUNICIPAL SOLID WASTE

Sampling of the municipal solid waste from Coastal Park Sanitary Landfill Site was given considerable thought. Municipal solid waste is complex in composition, and of a non-homogeneous nature. The United States Environmental Protection Agency have compiled information regarding the sampling of solid waste, but this information was not available. In order to proceed with the investigation other avenues were investigated. These are outlined below.

Initial sampling is discussed in Municipal refuse disposal (American Public Works Association, 1970). If collecting from an area in a city, it is suggested that one truckload should be adequate, the initial sample from that truck should be 225kg. The sample should then be reduced in size to less than 4cm. After size reduction, it is recommended the sample size be reduced by quartering to approximately 4 samples, each of 100g. Moisture analysis is then performed in quadruplicate, the four samples are then reconstituted for further analyses.

Ham and fellow researchers (Ham *et al*, 1993) characterised landfill refuse from Fresh Kills Landfill on Staten Island, New York. The Fresh Kills landfill was created in 1948, and is today, the largest solid waste disposal site in the world. It covers 12000 hectares, and receives 15500 tonnes of waste per day. Thirteen (13) boreholes were drilled, several hundred kilograms of solid waste was sampled in 100kg increments. These samples were then reduced in mass to 25kg. The method of size reduction was not discussed in detail. However, as the placing of the sample on a large sheet of plywood is mentioned, it would appear the samples were quartered. A total of 31 samples of municipal solid waste were collected in this manner. Each increment was individually reduced in size to approximately 1.9cm. Each increment of the now shredded municipal solid waste was then mixed thoroughly, and half of each individual increment discarded. Finally, the remaining 12.5kg of shredded solid waste was separated by riffling into 16 approximately 0.75kg increments. Five (5) of these sub-samples were used for replicate analysis. In some instances these 5 sub-samples were combined in equal amounts for analysis.

Klee and Carruth (Klee *et al*, 1970) investigated sample weights in solid waste composition studies. Both researchers were employed at that time by the United States Bureau of Solid Waste Management and had access to studies conducted by the Bureau. They examined samples taken at nine different incinerator sites. Samples taken at the sites were varied in three different mass ranges, the largest sample being approximately 750kg, the smallest being 90kg. The researchers found no significant differences with regard to precision for the studied sample mass groups of 75kg to those of greater mass. It should be noted there was no significant difference between the mass of waste divided nine subgroups such as food wastes, garden waste, etc. The researchers concluded it was not advantageous to take samples of mass greater than 75kg, to analyse any given waste stream.

Musa and Ho (Musa *et al*, 1981) also investigated the optimum sample size for solid waste analysis. Initially, they examined the work of other researchers and organisations. They cite the Institute of Public Cleansing in the United Kingdom who advised in 1964, a sample be taken of not less than 1 tonne in total mass, from not less than 100 premises. They examined

the results of four waste surveys undertaken in Australia. Unfortunately, the researchers are primarily interested in household waste surveys. However, one important result of their studies was their results indicated the number of increments taken was of greater importance, with regard to accuracy of results, than the total mass of the sample.

The American Society for Testing Materials (ASTM) practices for sampling various solid materials including solid waste, were also examined. Those standards examined included:

Standard Practice for Sampling Aggregates Designation: D75 - 87 (Reapproved 1992)

Standard Test Methods for Collection of a Gross Sample of Coal Designation: D2234 - 89

Standard Test Method for Determination of the Composition of Unprocessed Municipal Solid Waste Designation: D5231 - 92

When sampling aggregates, the larger the nominal size of the aggregate the larger the minimum sample size. For coarse aggregate of size 90mm, coupled with sampling from a stockpile (an unsatisfactory sampling situation), a minimum of 3 increments is recommended of minimum mass per increment, 55kg. The sampling of raw or uncleaned coal was also examined. It is recommended for uncleaned coals above 150mm in size, the minimum number of increments be 35, of minimum mass 7kg. This method would be statistically correct for a total mass of raw coal not exceeding 900 tonnes. The ASTM method for sampling unprocessed municipal base is based on sampling to allow examination of waste sampled into various categories such as paper, plastic, etc. It is recommended a sample size of 91 - 136kg would be representative of a vehicle load of municipal solid waste.

All of the above were considered to ensure representative sampling of the excavated municipal solid waste. Key points noted were: the correct sample size should approximate 75kg (Klee *et al*, 1970); the correct sample size should approximate 225kg (American Public Works Association, 1970); the greater the number of increments the greater the degree of accuracy that can be expected (Musa *et al*, 1981); when sampling uncleaned coal above 150mm in size, of total mass 900 tonnes, the minimum number of increments be 35, of minimum mass 7kg (ASTM, 1993).

The total mass of excavated municipal solid waste from Coastal Park Sanitary Landfill approximated 5000kg. The solid waste was sampled after size reduction, prior to transportation to pilot-scale landfill column. Reduction of size before sampling is advantageous as the homogeneity of the solid waste is improved. As the solid waste was loaded for transportation, incremental sampling was practised at equally spaced time and mass intervals. A total of 20 increments were taken, the average weight of each increment being approximately 11kg. Therefore the total mass of the sample of municipal solid waste was 230kg. This method of sampling should eliminate any sources of error and ensure samples taken for use in the laboratory were fully representative of that municipal solid waste loaded into the pilot-scale landfill columns.

After sampling, the incremental samples were placed in thick plastic bags, sealed with nylon cord. These plastic bags were then subsequently placed in another plastic bag, that outer plastic bag being sealed in an similar manner. This method was utilised to ensure that any moisture associated with the municipal solid waste was not lost, as the first step in the sample preparation was the analysis of moisture content.

5.3.2 SAMPLE PREPARATION: MUNICIPAL SOLID WASTE

On arrival at the laboratory each incremental sample was opened individually and the municipal solid waste placed onto a clean dry concrete area. Each increment was then mixed rapidly, cut into quarters, a shovel full taken from each quadrant until it was judged sufficient mass, in this case approximately 5kg, was available for the determination of moisture content. The remainder of the increment being labelled, re-bagged and stored. The municipal solid waste for moisture determination was then placed within the drying oven. The sample was then dried at 75°C for 48 hours (American Public Works Association, 1970). It was then removed from the oven and allowed to cool, and weighted, the weight being noted. The incremental sample was then replaced within the oven for a further 24 hours. The sample was then removed from the oven, allowed to cool and reweighed. If no further weight change was evident, the sample was made available for size reduction. The results of moisture determination are shown overleaf.

After moisture determination, the incremental samples were then individually reduced in size to approximately $5cm^2$ by use of hand scissors and tin snips. It is advised by the American Public Works Association's Tentative methods of analysis of refuse and compost (American Public Works Association, 1970) to discard inorganic materials such as glass, metals and ceramics. In South Africa, with the extremely efficient scavenging of waste (indicative of it's socio-economical problems) at landfills, and prior to disposal, there was a marked absence of commodities of this nature. After the first stage of size reduction, the incremental sample was then reduced in mass by the method previously described to approximately 2kg. The remainder of the increment being labelled, re-bagged and stored. The incremental sample of mass 2kg was then further reduced in size with a laboratory electrically driven hammer mill, to pass through a 1mm sieve.

This degree of size reduction conforms with the size range specified by the United States Environmental Protection Agency Method 1311 Toxicity Characteristic Leaching Procedure (US EPA Method 1311 TCLP) (US EPA, 1992). It is a requirement of the US EPA the solid waste must pass through a 9.5mm standard sieve. The Public Works Association's Tentative methods of analysis of refuse and compost (American Public Works Association, 1970), require the waste to be ground to pass through a 1mm sieve. There is not mention of a minimum size in the documentation supplied by the US EPA. After final size reduction, each sample increment was placed in a 2ℓ plastic bucket fitted with a snap-fit plastic lid. Prior to storage each increment was well mixed, and a small amount, approximately 200g, was removed from each increment and placed in an additional pail. This increment was labelled sample 21 and was deemed fully representative of the solid was previously placed in the pilot-scale landfill columns.

TABLE 5.1 MOISTURE CONTENT OF MUNICIPAL SOLID WASTE FROM COASTAL PARK SANITARY LANDFILL SITE

Sample No.	Initial increment mass (kg)	Mass of sample to be dried (g)	Mass of dried sample (g)	Percent moisture (dry)	Percent moisture (wet)
1	9.0	3720.1	2893.6	28.6	22.2
2	8.5	4156.3	3209.8	29.5	22.8
3	12.5	6235.5	4979.4	25.2	20.1
4	23.3	5425.6	4282.7	26.7	21.1
5	10.5	4506.4	3640.7	23.8	19.2
6	10.5	5012.1	3963.7	26.5	20.9
7	10.6	5516.6	4396.3	25.5	20.3
8	10.1	5397.0	4296.0	25.6	20.4
9	9.2	4452.7	3598.3	23.7	19.2
10	10.8	4381.7	3529	24.2	19.5
11	9.3	4634.7	3709.8	24.9	20.0
12	8.5	3993.5	3246.3	23.0	18.7
13	12.6	5417.5	4324.1	25.3	20.2
14	14.3	5688.2	4626.4	23.0	18.7
15	9.7	5271.8	4238.7	24.4	19.6
16	13.6	6047.8	4726.8	27.9	21.8
17	14.7	5667.8	4469.0	26.8	21.2
18	8.3	3896.3	3024.3	28.8	22.4
19	10.6	4805.3	3898.4	23.3	18.9
20	12.7	6910	5424.5	27.4	21.5
Average				25.7	20.4

5.3.3 CHARACTERISATION OF THE MUNICIPAL SOLID WASTE

(a) Metal content

TABLE 5.2 METAL CONTENT: MUNICIPAL SOLID WASTE SAMPLED AT COASTAL PARK SANITARY LANDFILL SITE

Sample No.	Copper	Chromium	Zinc	Cadmium	Nickel	Lead	Potassium	Phosphorous
3	28	37	345	1.3	6	142	1047	5.4
6	22	11	116	1.3	11	46	823	106
9	15	5	135	1.5	9	32	1249	5.7
12	18	8	127	0.8	35	48	621	2.4
15	34	16	212	1.7	15	143	1261	5.5
18	31	21	309	1.4	4	60	1195	193
Average	25	16	207	1.3	13	79	1033	53
21	29	12	265	0.8	17	45	1240	32

All results quoted above in ppm (w/w)

Sample No. 21 being the cumulative sample, of all the incremental samples taken.

ENCON Associates conducted a field scale landfill project at the Mountain View Landfill, in California (Pacey, 1989). The researchers examined the process of methane gas generation in municipal solid waste landfills, and evaluated the effectiveness of different methods used to enhance methane generation. Six large test cells were constructed each containing approximately 7500 tonnes of municipal solid waste. The cells were treated with differing stabilisation enhancement techniques, one cell remained untouched, and was used as a control. After five years, the cells were subjected to rigorous municipal solid waste sampling. Additionally, adjacent solid waste was sampled. They examined 28 samples, with 5 replicate analyses per sample. The only heavy metal identified for analysis was nickel. Nickel has been identified as possibly inhibitive in the landfill environment. It is of interest to examine the results from the control cell, and that of adjacent refuse, and compare these with the results of municipal solid waste excavated from Coastal Park Sanitary Landfill Site which was estimated to be of age 1 year.

It is difficult to compare results because of the variable composition of municipal solid wastes as received at landfill sites in different countries. However, the low percentage of volatile solids in the municipal solid waste excavated from Coastal Park Landfill Site is probably indicative that the solid waste was actually in excess of 1 year of age. The percentage volatile solids of the solid waste excavated from Coastal Park Sanitary Landfill site averaged 24 percent. The solid waste excavated from Mountain View Landfill was 43.5 percent in the control cell and 27 percent in the adjacent solid waste, after being deposited for 5 years.

(b) Additional analyses

TABLE 5.3 ADDITIONAL ANALYSES: MUNICIPAL SOLID WASTE SAMPLED AT COASTAL PARK SANITARY LANDFILL SITE

Sample No.	pH	Volatile solids (percent)	Total Kejldahl Nitrogen
3	7.7	32.6	20
6	8.0	19.2	10
9	7.8	23.5	40
12	7.7	16.4	20
15	8.2	24.9	10
18	8.4	27.6	10
Average	8.0	24.0	20
21	8.1	17.4	20

Except pH, results quoted above in ppm (w/w)

TABLE 5.4 CHARACTERISATION OF MUNICIPAL SOLID WASTE: MOUNTAIN VIEW AND COASTAL PARK

Component	Mountain View (control cell)	Mountain View (adjacent municipal solid waste)	Coastal Park (average values)
Moisture content (%)	40.0	22.0	20.4
pH	6.7	6.8	8.0
Volatile solids (%)	43.5	27.1	24.0
Kjeldahl Nitrogen (ppm [w/w])	0.4	0.3	20
Phosphorous (ppm [w/w])	279	185	53
Nickel (ppm [w/w])	6.3	3.7	13

5.4 COPPER-CHROMIUM-ARSENIC WOOD PRESERVATIVE

5.4.1 CHARACTERISATION OF THE COPPER-CHROMIUM-ARSENIC WOOD PRESERVATIVE

The copper-chromium-arsenic product employed in this investigation is marketed by Rentokil South Africa (Pty) Ltd., it is designated *Celcure A Paste*. The specification as supplied on the product is as shown overleaf:

Copper:	71g per kg
Chromium:	119g per kg
Arsenic:	128g per kg

The relative density of the solution is quoted as 1.85.

The method of data presentation employed by Rentokil South Africa (Pty) Ltd., tends to obscure the actual composition of the product. The composition as stated in the Material Safety Data Sheet is as shown below (Rentokil South Africa, 1994):

Component	Percent weight by weight
Arsenic pentoxide	24.63
Sodium dichromate	38.25
Copper sulphate	30.42

Analysis in the laboratory revealed the following mixture of the following composition:

Component	Grams per litre
Arsenic (as As)	270.2
Chromium (as Cr)	269.6
Copper (as Cu)	93.1

The solution was also analysed to determine speciation of the chromium and arsenic. Analysis revealed the chromium to be composed of 94.8 percent chromium(VI); the arsenic was composed of 97.1 percent arsenic(V). The European Economic Community Classification is Corrosive (Harmful); the Hazard Symbol employed is "Corrosive".

5.5 EVALUATION OF THE KINETICS OF ADSORPTION AND DESORPTION OF COPPER, CHROMIUM AND ARSENIC AT LABORATORY-SCALE

The kinetics of adsorption of the solution of copper, chromium and arsenic was examined by modifying the US EPA Method 1311 Toxicity Characteristic Leaching Procedure (TCLP). The procedure is described in detail in Appendix X of Ballard (1997).

5.5.1 MODIFICATION OF THE ENVIRONMENTAL PROTECTION AGENCY METHOD 1311 TOXICITY CHARACTERISTIC LEACHING PROCEDURE: KINETICS OF ADSORPTION

The TCLP was modified to enable the determination of the degree of adsorption, and the rate of that adsorption of industrial waste onto municipal solid waste. The extraction fluid used is composed of glacial acetic acid, sodium hydroxide and deionised water. The composition is shown below:

Component	Percent volume
Glacial acetic acid	0.57
Sodium hydroxide	4.00
Deionised water	95.43

This solution is termed Extraction fluid #1 in Appendix X of Method 1311. The solution's acetate buffered system would appear to provide a good approximation of leachate from a landfill in the acetogenic phase of stabilisation. The procedure for the preparation of the extraction fluid; addition of the copper-chromium-arsenic; pH adjustment, is described in depth below. Equivalent attention to detail in chemical procedures was practised

throughout. However, in the interest of brevity, the reader is referred to this section (Section 5.5.1) when similar chemical procedures are discussed. The modification of the EPA TCLP was effected in the following manner. The solution was formulated as shown above. Upon formulation, the pH was determined to ensure the fluid was correctly produced. If the procedure is followed correctly, the pH of the solution should be 4.93 +/- 0.05 pH units.

The copper-chromium-arsenic solution was available in a 25ℓ container. The contents of the container was firstly well mixed. From that container, an aliquot of volume 2.5ℓ was taken and placed in a glass winchester bottle. This bottle was subsequently used in all ensuing experiments. From this container, after ensuring the contents were well mixed, 10mℓ of the concentrated copper/chrome/arsenic solution was then transferred by pipette into a 100mℓ volumetric flask, deionised water was then added to the volumetric flask to the prescribed point. The reason for this exercise being, the copper-chromium-arsenic solution is viscous and dilution was necessary to maintain accuracy. Approximately 500mℓ of the extraction fluid was then transferred into a 2ℓ glass measuring cylinder, to this was added 10mℓ of the diluted copper-chromium-arsenic solution, the solution was then mixed with a glass rod. Further extraction fluid was then added to glass measuring cylinder until the solution was 1ℓ in volume. The solution was again stirred to assure uniformity. It had been previously calculated that this degree of dilution would provide a solution of composition:

copper, approximately 80mg;
chromium, approximately 300mg;
arsenic, approximately 260mg.

It is a requirement, when conducting adsorption studies, that sufficient heavy metals are available at the start of the study to ensure an excess of metal in solution at completion of the experiment.

A sample of volume 25mℓ was then taken. The pH of the solution was then measured. The pH of the solution was then adjusted with a 1N sodium hydroxide until the desired pH was achieved. Three pH values were chosen, pH5.5; pH6.4; and pH7.0. These pH values were selected as these values cover the usual range of pH encountered in full scale landfill operations. The measuring cylinder was then placed on the laboratory bench for approximately 30 minutes. This allowed any precipitation of the metals in solution to occur. After precipitation had occurred, the supernatant was then transferred into another measuring cylinder. A 25mℓ sample was then taken for analysis.

All 21 samples of the prepared municipal solid waste were available in the laboratory. To assure the results of the kinetic studies to be reproducible, and to eliminate any bias from the municipal solid waste it was decided to perform the experiments in triplicate at the three pH values. Another provision was made to assure reproducibility; at the three pH values one sample of the cumulative sample (sample 21) was used, the other two samples being differing sub-samples. This was done at every stage of the laboratory investigation.

A 50g portion of the prepared municipal solid waste was weighted and placed in the extractor vessel. The extractor vessel employed was a 2ℓ Schott bottle, fitted with a screw neck, with an internal teflon seal, within the plastic screw top. Exactly 1ℓ of the relevant pH-adjusted, dilute copper-chromium-arsenic solution was then added to the extractor vessel. The extractor vessel was then placed in the agitation device and agitation began. Samples of the dilute copper-chromium-arsenic solution, of volume 25mℓ, were then taken at designated time intervals throughout the duration of the experiment. These samples were taken at time zero, then subsequently after 0.5h, 1.0h, 2.0h, 4.0h, 8.0h, 16.0h, and 32.0h. From the examination of adsorption studies of conducted by soil scientists examining the adsorption of various metals onto soils it was thought an total experimental duration of 32 hours would be adequate. To confirm this, an initial trial was undertaken. After completion of the experiment the pH of the solution in the extractor vessel was determined.

The pH of the solutions was elevated during the experimental procedure. This elevation of pH is discussed in Chapter 8. The initial and final values of solution pH are shown below in Table 5.5.

5.5.2 MODIFICATION OF THE ENVIRONMENTAL PROTECTION AGENCY METHOD 1311 TOXICITY CHARACTERISTIC LEACHING PROCEDURE: KINETICS OF DESORPTION

On completion of the adsorption procedure, the contents of each extractor vessel were then filtered. Deionised water was added to the extractor vessel to ensure all solid particles were removed from the vessel, onto the filter paper. The filter paper plus solids was then removed from the Buchner funnel and placed in a stainless steel tray. The tray was then placed into a drying oven adjusted to a temperature of 50°C. The trays remained in the oven until all traces of moisture were removed.

TABLE 5.5 CHANGE IN pH DURING EXPERIMENTAL PROCEDURE

Coding	Initial pH	Final pH	Coding	Initial pH	Final pH
A	5.5	7.0	F	6.4	8.0
B	5.5	7.0	G	7.0	8.2
C	5.5	7.0	H	7.0	8.6
D	6.4	8.0	I	7.0	8.1
E	6.4	8.0			

The dried solids were then transferred into the extractor vessel. Approximately, 1ℓ of the relevant pH-adjusted extraction fluid was then prepared. A small aliquot was then taken for analysis, and exactly 1ℓ of the extraction fluid was added to the extractor vessel (a sample subjected to adsorption at a particular pH value was desorbed at the same pH value). The extractor vessel was then placed in the agitation device and agitation began. Samples of the extraction fluid of volume 25mℓ, were then taken at designated time intervals. Samples were taken at time zero, then subsequently after 0.5h, 1.0h, 2.0h, 4.0h, 8.0h, 16.0h, and 32.0h. On completion of the experiment the samples were preserved by the addition of the relevant quantity of 10M nitric acid (APHA Standard Methods, 1992).

5.6 LABORATORY-SCALE EVALUATION OF ADSORPTION ISOTHERMS

The kinetic studies commenced with initial concentrations of copper, chromium, and arsenic of approximately, 80; 300; and 260mgℓ^{-1}, respectively. To construct adsorption isotherms, additional data at lower concentrations is a requirement.

A similar procedure was then undertaken to that described previously in the evaluation of adsorption kinetic rate constants (Section 5.5.1). Again, three pH values were chosen, pH5.5; pH6.4; pH7.0. Differing amounts of the diluted copper-chromium-arsenic solution were then added to the pH adjusted extraction fluid. The concentration range was:

Copper (mgℓ^{-1})	80	50	40	15
Chromium (mgℓ^{-1})	300	200	150	60
Arsenic (mgℓ^{-1})	260	180	130	50

The samples taken during the evaluation of the kinetic rate constants for the adsorption of the various metals onto the municipal solid waste had already been analysed and the results partially evaluated. There did not appear to be any difference in the adsorption/desorption characteristics displayed by the various sub-samples of the municipal solid waste. However, it was decided to be prudent and to vary the sub-samples again. All 21 samples of the municipal solid waste were available in the laboratory. The cumulative sample (sample 21) was employed at each varying concentration of the copper-chromium-arsenic solution, the remaining two samples being differing subsamples from those employed in the kinetics investigation. Samples of the dilute copper-chromium-arsenic solution, of volume 25mℓ, were then taken prior to the commencement of agitation. A final 25mℓ sample of the solution was then taken for analysis after 32 hours had elapsed. On completion of the experiment, all samples were then preserved by the addition of the relevant quantity of 10M nitric acid (APHA Standard Methods, 1992).

5.7 ANALYTICAL PROCEDURES

Chemical analysis was performed at the Laboratory of the Department of Chemical Engineering of the University of Cape Town, and at the Laboratory of the Scientific Services Branch, City Engineer's Department, City of Cape Town. In some instances analysis was duplicated, being accomplished at both establishments to ensure accuracy. Analysis of the kinetics experiments was such an instance. The initial analysis of copper chromium, and arsenic was undertaken at the Department of Chemical Engineering. Copper and chromium analysis was then repeated at Scientific Services Branch on approximately 25 percent of the samples to ensure accuracy. In the case of copper agreement was excellent; some degree of instrument drift was noted in the analysis of chromium; the relevant samples were re-analysed were necessary.

TABLE 5.6 ANALYTICAL RESPONSIBILITIES

Component	Establishment
Characterisation of the municipal solid waste	Scientific Services Branch
Characterisation of the copper-chromium-arsenic wood preservative	Department of Chemical Engineering
Laboratory scale adsorption and kinetic trials	Department of Chemical Engineering, certain samples being repeated at the Scientific Services Branch

(a) Characterisation of the municipal solid waste

The municipal solid waste was analysed for the following:
Moisture content; copper; chromium; zinc; cadmium; nickel; lead; potassium; phosphorous; pH; percentage volatile solids; and total kejldahl nitrogen.

(b) Characterisation of the copper-chromium-arsenic wood preservative

The wood preservative was analysed for copper; chromium and arsenic.

(c) Laboratory-scale investigation into kinetics and adsorption properties of the CCA wood preservative

All samples taken were analysed for copper, chromium and arsenic

The analytical equipment employed is detailed below.

TABLE 5.7 ANALYTICAL EQUIPMENT

Analysis	Instrument
Conductivity	EDT Instruments BA 380
pH	Orion Research Model 601
Metal content	GBC Model 902 Atomic Adsorption Spectrophotometer

The analysis of metals was undertaken at the University of Cape Town, a Varian SpectrAA 30 Atomic Adsorption Spectrophotometer was employed.

5.8 SUMMARY

Municipal solid waste was excavated from Coastal Park Sanitary Landfill Site. The municipal solid waste was reduced in size and transported to the laboratory. The municipal solid waste was fully characterised in terms of moisture content, metal content, pH, volatile solids and Total Kejldahl nitrogen. The metals of concern in this investigation, copper, chromium and arsenic are in the form of CCA (or Tanalith), a chemical commonly employed for wood preservation. This chemical was also fully characterised.

The kinetics of adsorption and desorption of the solution of copper, chromium and arsenic onto municipal solid waste was examined. Equilibrium studies were also completed. Both adsorption/desorption and the equilibrium studies utilised a modification of the US EPA Method 1311 Toxicity Characteristic Leaching Procedure (TCLP).

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CHAPTER 6
MATERIALS AND METHODS: PILOT-SCALE LANDFILL COLUMN STUDIES

6.1 INTRODUCTION

Pilot-scale landfill columns were constructed at Athlone, Cape Town. Tracer studies were then undertaken at pilot-scale. Tracer studies enable the deviation from ideal flow to be determined. The combination of the results from the kinetic studies and the results from the tracer studies allow the computation of the exit stream composition. Heavy metals were then co-disposed at pilot-scale to evaluate the accuracy or otherwise of both the tracer studies and the chemical kinetics. The combination of the laboratory scale and pilot-scale studies should then allow the prediction of the amount of copper, chromium and arsenic which can be retained in a full-scale landfill operation.

6.2 PILOT-SCALE INVESTIGATION

This investigation advanced on two fronts:
Determination of the residence time distribution/deviation from ideal behaviour of the pilot-scale landfill columns.
Evaluation, at pilot-scale, of the kinetic rate constants determined at laboratory scale.

6.3 DESIGN OF PILOT-SCALE LANDFILL COLUMNS

Pilot-scale landfills have been utilised to observe and quantify phenomena occurring in landfills for over twenty five years. Many different types of experiments have been conducted, and their use is well documented. The column design of other researchers was thoroughly examined before construction of the Athlone pilot-scale columns commenced.

6.3.1 DESIGN AND CONSTRUCTION OF THE ATHLONE PILOT-SCALE LANDFILL COLUMNS

The initial step in the design of the pilot-scale landfill columns was to survey the literature and to review the constructional techniques employed by previous researchers. These are summarised in tabular form below. In evaluating the designs tabulated, one can observe a gradual simplification of the design of the pilot-scale columns, with the design Pohland pioneered (Pohland, 1975), becoming virtually a standard. The design of the University of

Cape Town pilot-scale columns was very similar to the column that originated in Atlanta, at the Georgia Institute of Technology, designed by Pohland.

TABLE 6.1 DESIGN ASPECTS OF PILOT-SCALE LANDFILL COLUMNS: I

Researchers	Number of columns	Height of columns (m)	Cross-sectional Area (m^2)	Configuration	Material of construction
Qasim & Burchinal (1970a, 1970b)	4	1.2, 2.4, 3.6, & 4.8	0.6362	Circular	Concrete
Fungaroli & Steiner (1971)	1	3.96	1.83	Square	Low carbon steel coated with fibreglass
Rovers & Farquhar (1973)	3	4.3	2.545	Circular	
Pohland (1975)	4	-	0.65	Circular	Steel
Newton (1977)	-		5.0	Rectangular	Concrete internally coated with epoxy
DeWalle *et al* (1978)	18	0.75	0.255	Circular	Steel walls with plastic liner
Raveh & Avnimelch (1979)	16	2.5		Circular	Poly Vinyl Chloride
Pohland (1980)	2	5.2	9.0	Square	Reinforced concrete coated with sealant
Tittlebaum (1982)	4	3.4	0.7854	Circular	Epoxy coated corrugated steel pipe

TABLE 6.1 DESIGN ASPECTS OF PILOT-SCALE LANDFILL COLUMNS: I (continued)

Researchers	Number of columns	Height of columns (m)	Cross-sectional Area (m^2)	Configuration	Material of construction
Ham & Bookter (1982)	8	1.5	165.62	Rectangular	One wooden wall, three concrete walls
Collins & Spillman (1982)	8	5.0 to 6.0	19.64	Circular	Poly ethylene flexible walls
Pohland *et al* (1985, 1986)	4	4.27	0.65	Circular	Corrugated steel pipe
Gould *et al* (1989)	10	4.27	0.65	Circular	Steel
Reinhart & Pohland (1991)	2	3.0	0.65	Circular	Steel
Pohland (1992)	5				
Pohland *et al* (1993)	3	3.25	0.65	Circular	Steel
Otieno (1994)	4	-	0.159	Circular	
Chapman & Ekama (1991); Novella *et al* (1996)	6	4.25	0.283	Circular	Galvanised steel coated with epoxy

TABLE 6.2 DESIGN ASPECTS OF PILOT-SCALE COLUMNS: II

Researchers	Underdrain	Distributor	Instrumentation	Environment	Insulation
Qasim & Burchinal (1970a, 1970b)	Size graded clinker,(8 - 13cm) 20mm steel outlet pipe	-	Thermocouples	Outdoor	None
Fungaroli & Steiner (1971)	Sand & glass beads	Perforated plastic pipe	Thermocouples	Indoor	Insul-ation plus heating tapes
Rovers & Farquhar (1973)		Perforated tubing	Thermocouples	Outdoor & Indoor	Indoor cell, Insulated
Pohland (1975)		Positioned in soil top cover			
Newton (1977)	-			Outdoor	
DeWalle *et al* (1978)	Gravel (15cm)	Sprinkler	Thermocouples	Indoor	None
Raveh & Avnimelch (1979)	Glass beads	0.3m sand		Indoor	None
Pohland (1980)		Positioned in gravel between MSW & top cover		Outdoor	Styro-foam
Tittlebaum (1982)	0.3m of sand	PVC pipe placed in sand layer		Indoor	None
Ham & Bookter (1982)		None	Thermocouples	Outdoor	None

TABLE 6.2 DESIGN ASPECTS OF PILOT-SCALE COLUMNS: II (continued)

Researchers	Underdrain	Distributor	Instrumentation	Environment	Insulation
Collins & Spillman (1982)			Thermocouples	Outdoor	
Pohland *et al* (1985, 1986)	Graded aggregate	Placed in aggregate layer between topsoil and MSW		Outdoor	None
Gould *et al* (1989)	Graded aggregate	Placed in aggregate layer between topsoil and MSW		Outdoor	None
Reinhart & Pohland (1991)				Indoor	
Pohland (1992)					
Pohland *et al* (1993)	Soil		Thermocouple		
Otieno (1994)	Gravel (100mm) placed on grate	Placed in 200mm gravel top layer		Indoor	None
Chapman & Ekama (1991): Novella *et al* (1996)	Graded pebbles, 20mm steel pipe	Perforated tubing	Thermocouple	Outdoor	40mm glass fibre

A diagram of the pilot-scale landfill columns constructed at Athlone is shown overleaf. Subsequently, the principal design considerations are discussed.

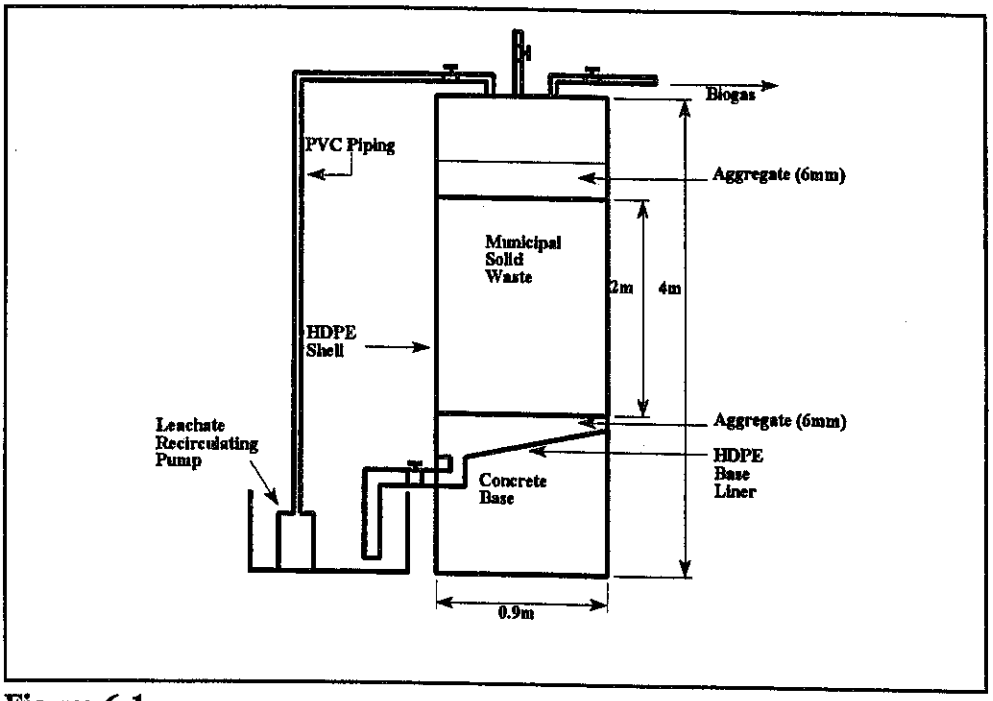

Figure 6.1
Diagrammatic representation of the Athlone pilot-scale landfill columns

(a) Column Shell

Problems had been experienced with the previous columns at the University of Cape Town. Attention had been paid to the durability of the columns, the 2mm gauge steel had been hot-dipped galvanised prior to an internal coating of epoxy paint. Corrosion problems occurred and Novella *et al* (1996) had difficulty in the latter stages of his experimental programme preserving the integrity of the columns.

The envisaged material should be inert to the products of decomposition of the municipal solid waste, such as the low pH leachate experienced; able to withstand the elements, as it was envisaged the pilot-scale columns would be outdoor; mechanically strong enough to hold the municipal solid waste. It was extremely important that chemical wall effects be avoided. A plastic type material was considered to be one of the better options available. Tittlebaum (1982) successfully constructed a pilot-scale landfill column shell from polyvinylchloride. Scrap High Density Poly Ethylene (HDPE) pipe became available from the City Engineers Department of the City of Cape Town. The dimensions of this pipe were internal diameter 0.70m, external diameter 0.90mm, the pipe was available in varying lengths. It was decided that five columns would be sufficient to meet the aims and objectives of the project. The pipes were firstly cut to a length of 4.1m.

(b) Underdrain

The next step in the design of the pilot-scale landfill columns was to determine the underdrain design. Again, the design of previous columns were surveyed. It was decided to cut the columns near to the base at an angle near to the base of the column, seal the base of the column with a HDPE plate, and to use a layer of 6mm aggregate as the underdrain.

(c) Column shell construction
The pipe was then cut 1m from the base at an angle approximating 30 degrees to the horizontal plane. The 0.9m base was then secured to a concrete plinth by means of steel tie-rods, the base being partially filled with concrete. A square notch was then cut into the HDPE base at the lowest point of the 30 degree cut. Shuttering was then placed around the notch and the remaining space within base filled with concrete.

The longer of the two lengths of HDPE pipe was then sealed with an elliptical plate of HDPE. Prior to sealing a 50mm hole was drilled in the sheeting at what was anticipated to be the lowest point of the column. A short stub of 50mm polyvinylchloride pipe was securely fixed into the hole, by means of a plastic securing lock-nut either side of the plate. An articulated crane lifted the 3.2m length of HDPE piping into the vertical position; the pipe was then lowered onto the base. The upper section was secured to the base by means of a steel collar, the column was further secured to the external wall of a single storey building located behind the column. On completion of the erection of the column shell, a 50mm polyvinyl chloride ball valve was affixed to the 50mm stub, leading to a U-bend, on the outside of the column. A plastic grid was then glued to the stub in the inside of the column. The columns were then filled completely with water to test their integrity.

(d) Distributor
Again the design of previous columns was examined, it was felt earlier designs could be simplified further. It was thought, if one placed a layer of aggregate of sufficient depth above the municipal solid waste within the column, adequate dispersion of any liquid added would occur before contact with the solid waste. A layer of 6mm aggregate of thickness 45cm would be sufficient.

(e) Associated pipework and tankage.
As mentioned, it was decided to use 50mm diameter polyvinylchloride pipe as the outlet pipe from the base of the column. This relatively large diameter pipe was used to discourage any blockages. To enhance landfill stabilisation, leachate recirculation is necessary. This was provided by placing a 80ℓ vessel at the base of the column. Within the vessel was placed a small submersible pump. All other associated pipework was 25mm diameter polyvinylchloride.

(f) Instrumentation
The design of previous columns was examined. Early columns were often fitted with a number of thermocouples, usually positioned with varying depth. Fugaroli and Steiner (1971) placed 4 thermocouples in a column containing solid waste of height 2.4m, while DeWalle and co-workers (1978) placed 3 thermocouples in a column containing solid waste of height 0.6m. Later columns were usually only constructed with one thermocouple in position (Chapman *et al*, 1991; Pohland *et al*, 1993). The Athlone pilot-scale columns employed one thermocouple per column, the thermocouple being positioned centrally in the solid waste.

g) Insulation
The wall thickness of the column shell is 50mm, the material of construction being HDPE, a material of low thermal conductivity. It was considered that in the Cape Town, with it's

Mediterranean climate, insulation was not required. The HDPE column shell was black in colour. When the columns were first erected it was mid-Summer, it was noticed that the outer skin temperature became relatively hot. Before the municipal solid waste was placed in the columns the outer column shell was painted white. This immediately alleviated the problem.

(h) Municipal Solid Waste

For the purposes of our investigation, the height of municipal solid waste in the column was to be 2m. This height was dictated by prevailing conditions used by the City of Cape Town in their full scale landfill operations. The landfill sites within the municipality are operated such that there is a 2m layer of waste, soil cover, another 2m layer of waste, soil cover, and so on. This also conformed to the configuration used by other researchers in the field. The solid waste was reduced in size to between 25-40mm before introduction into the column. Again, this conformed to methods pioneered by other researchers. The bulk density of the municipal solid waste at the full scale landfills in Cape Town approximates 1000kgm^{-3}. To model the full scale landfill at pilot-scale it is desirable to achieve densities of that order. Both Newton (1977) and Pohland (1975) were censured by Cope (1983) regarding the density of the municipal solid waste in their work. The average bulk density of the municipal solid waste in the pilot-scale landfill columns was 922kgm^{-3}.

After the 6mm aggregate drainer was placed in the column shell; the column was drained after hydraulic testing; the column was then measured internally and marked at a distance exactly 2m from the top of the underdrain. The shredded municipal solid waste was incrementally weighted prior to placing in the columns. The pulverised solid waste was then periodically compressed by hand to ensure the correct densities were achieved. The results are shown below.

TABLE 6.3 PILOT-SCALE LANDFILL COLUMNS: PHYSICAL CHARACTERISTICS OF THE MUNICIPAL SOLID WASTE

Column	Internal diameter (m)	Height of MSW (m)	Mass of MSW (kg)	Volume (m^3)	Density (kgm^{-3})
1	0.7	1.88	694	0.7235	959
2	0.7	1.94	669	0.7466	896
3	0.7	1.94	668	0.7466	895
4	0.7	1.94	676	0.7389	915
5	0.7	1.94	694	0.7351	944
Average					922

6.3.2 OPERATION OF THE PILOT-SCALE LANDFILL COLUMNS

In this section, the general operation will be discussed initially. Subsequently, detailed consideration will be given to the different aspects of the monitoring.

The operation and monitoring of the column temperatures commenced on Wednesday, February 8th, 1995; designated Day Zero (0). Soon thereafter, on Day 12, water was added to the pilot-scale columns, to bring the municipal solid waste to field capacity. Water was added at a rate of 30ℓ per day over a period of 5 days; Day 12, Day 13, Day 14, Day 15 and Day 16. A total of 150ℓ was added. There was no further addition of moisture for a period of one month. The temperature of the columns continued to be monitored daily, and every 7 days the outlet of the pilot-scale landfill was opened and examined for leachate. No excess moisture was found during this period. Addition of water again commenced on Day 44. Water was added at a rate of 30ℓ per day over a period of 5 days; Day 44; Day 45; Day 46; Day 47; Day 48; a total of 150ℓ was added, the total volume of water added to the pilot-scale columns now being 300ℓ.

After the addition of the additional water, monitoring the columns for biogas commenced. Monitoring of the pilot-scale landfills every 7 days continued. The next occasion the outlets were examined (after the second addition of water), no leachate was present. Leachate was present when the column drains were examined on Day 60. The columns were then drained until the flow of leachate ceased. The volume of leachate was measured, and a sample of leachate taken for analysis. The leachate was then pumped back to the top of the column and added to the municipal solid waste, to enhance the stabilisation process. The initial draining of the columns provided a relatively large quantity of leachate. With the second draining and subsequent recirculation the quantity of leachate was reduced substantially, this value is used in the table overleaf showing the field capacity of the municipal solid waste in the column. The volume of leachate drained is deducted from that added. Probably, the initial relatively large quantity of leachate drained from the columns was caused by a mixture of liquid by-passing and wall effects.

(a) Leachate recirculation

Leachate first became evident on Day 60. The following procedure was then followed. Leachate was drained until the flow diminished to a slow drip. While the leachate was flowing a sample was taken for analysis. On these samples the following analyses were performed:

pH;
Electrical conductivity;
Chemical Oxygen Demand (COD), unfiltered;
Chemical Oxygen Demand (COD), filtered;
Chloride content;
Total Alkalinity;
Bicarbonate Alkalinity;
Orthophosphate.

From the analyses of total alkalinity, bicarbonate alkalinity and orthophosphate, the volatile acid alkalinity was then calculated.

After the leachate flow diminished to a slow drip, the outlet valve from the pilot-scale column was then closed and the volume of leachate drained was measured. This was accomplished with a calibrated dip stick. The leachate was then pumped to the top of the column by means of the permanently located submersible pump. The recirculation procedure was performed every 7 days, until Day 118. Recirculation was ceased at this point as the temperature inside the columns had dropped to below 15°C, and there was no evidence of biogas production. The lower temperatures were due to the onset of the South African winter season.

Recirculation of leachate recommenced on Day 231, as ambient temperatures were beginning to rise, as the southern hemisphere summer season was beginning. The recirculation procedure then continued as before the procedure being repeated after a time interval of 7 days. The procedure ceased on Day 358, as there was no resumption of biogas production.

TABLE 6.4 PILOT-SCALE LANDFILL COLUMNS: FIELD CAPACITY OF THE MUNICIPAL SOLID WASTE

Column	Initial total mass (kg)	Initial mass of water present (kg)	Initial mass of bone dry MSW (kg)	Water added - Leachate drained (kg)	Total mass of water Day 67 (1995-03-16)	Percent moisture content (wet)
1	694	142	552	267	409	41.8
2	669	136	533	260	396	42.6
3	668	136	532	247	383	41.9
4	676	138	538	263	401	42.7
5	694	142	552	256	398	41.9
Average						42.2

(b) Volumetric biogas monitoring

Volumetric biogas monitoring commenced Day 54 prior to the addition of water, on Day 60. The instrument employed was a wet type gas flow meter manufacturer by Alexander Wright & Company (Westminster) Limited, model DM3A. One gas meter was used to monitor all 5 columns. The mode of operation was as outlined below.

The meter was placed within the building against which the pilot-scale landfill columns were secured. A hole was drilled through the building wall through which was placed a small bore plastic pipe. One end of the pipe was connected to the gas outlet positioned at the top of the columns, the other end being connected to the gas meter. The biogas from each column was measured every 5 days. The biogas vent from the columns being left open to atmosphere for the remaining 4 days. Leakage of biogas was noticed on Day 65.

The initial design of the columns featured a removable top cover, this was found to leak. Difficulties in effecting repair were experienced. It was then decided to treat the top covers in an identical manner to the base of the column and to heat weld the HDPE plates to the column shell. This was successful. The consequences of these problems was monitoring of the evolution of the biogas was severely curtailed. It should be noted the experimental study involved 5 columns and it was not known when biogas evolution would start, and the volume of biogas that would be evolved; this further complicated matters

The problems are shown chronologically below:

Day 65	Gas leakage first detected
Day 65 - Day 86	Repairs effected
Day 105	Repairs effected
Day 105 - Day 117	Only small amounts of biogas evolved, further leakage suspected
Day 117	HDPE heat welded onto the horizontal column shell
Day 118	Biogas monitoring resumed

Monitoring recommenced. but further problems were now experienced. Ambient temperatures began to fall with the onset of the southern hemisphere winter. Biogas production ceased completely from all of the pilot-scale columns on Day 128, the temperature of the columns had declined to below 10°C

When ambient temperatures began to rise at start of Spring, volumetric monitoring recommenced on Day 205. Monitoring continued until Day 348, biogas was not detected from any of the pilot-scale columns during this period. It was then decided to cease monitoring. It would appear the columns were now completely stabilised as no further evidence of biogas evolution was present. While biogas was present the maximum biogas volumetric flowrates were:

Pilot-scale landfill column No. 1	7.01 ℓday^{-1}
Pilot-scale landfill column No. 2	4.78 ℓday^{-1}
Pilot-scale landfill column No. 3	7.01 ℓday^{-1}
Pilot-scale landfill column No. 4	0.57 ℓday^{-1}
Pilot-scale landfill column No. 5	1.16 ℓday^{-1}

(c) Analysis of biogas composition

Samples were taken from the biogas outlets on three occasions. A small plastic inflatable container was employed for this purpose. The flexible vessel was secured to the gas outlet, the biogas allowed to fill the container by means of it's own pressure. The container was then evacuated prior to securing to the biogas outlet, then allowed to fill twice, on the third expansion, this sample was retained for analysis. The composition of the gas was then determined by means of a Varian 3300 Gas Chromatograph.

Samples were taken on Day 93, Day 124 and Day 127. The results are shown below. It should be noted, numerous attempts were made to sample biogas but as the biogas production from the columns was limited, only the results below can be shown.

TABLE 6.5 PILOT-SCALE LANDFILL COLUMNS: COMPOSITION OF GENERATED BIOGAS

Day	Sample	Percent methane	Percent carbon dioxide	Percent oxygen	Percent nitrogen
Day 93	Column 1	53.4	40.5	0.3	5.8
Day 124	Column 1	40.4	20.4	6.5	32.7
Day 127	Column 1	43.2	27.8	3.5	25.5
Day 93	Column 2	No gas production			
Day 124	Column 2	22.8	18.6	5.7	52.9
Day 127	Column 2	26.7	24.9	2.6	45.8
Day 93	Column 3	32.8	29.1	2.2	35.9
Day 124	Column 3	No gas production			
Day 127	Column 3	No gas production			
Day 93	Column 4	46.1	34.4	2.2	17.3
Day 124	Column 4	23.7	18.7	2.4	55.2
Day 127	Column 4	31.4	25.3	2.0	41.3
Day 93	Column 5	40.8	35.1	2.0	22.1
Day 124	Column 5	No gas production			
Day 127	Column 5	No gas production			

6.4 RESIDENCE TIME DISTRIBUTION: PILOT-SCALE LANDFILL COLUMNS

A continuous reactor may behave in a manner comparable to a plug flow reactor or as a perfect mixer, but it can never achieve these idealised states. In an ideal plug flow reactor, all reactant and product molecules move at the same rate in the direction of the bulk fluid flow, while in real flow reactors, fluid velocity profiles, turbulent mixing, and molecular diffusion cause molecules to move with a variety of speeds and directions. These inevitable deviations in ideal reactor conditions lead to several fundamental problems in reactor design and analysis (Dudukovic *et al*, 1983).

Tracer response analysis is a technique which is used to characterise the type of flow and mixing that takes place in a continuous process vessel. The technique is also applicable to biological systems, hydrological systems, and in general to any system through which a fluid flows continuously. In this case it is applied to the pilot-scale landfill columns.

The simplest method of determining the residence time distribution of a fluid within a reactor involves the use of a physical or non-reactive tracer. A number of different experimental techniques are available, the simplest to interpret are the pulse or the step experiment. For the purposes of this investigation it was decided to employ a non-reactive tracer with pulse input.

6.4.1 DETERMINATION OF NON-REACTIVE TRACER

It is of importance that the tracer utilised should behave in a manner identically to the fluid molecules within the reactor. No tracer should be lost within the system by reaction or adsorption with the reactor walls, or internal packing, if present. The internal packing within the pilot-scale landfill columns is municipal solid waste; it was relevant to investigate the adsorption characteristics of any tracer selected with that substance. A frequently used non-reactive tracer employed in aqueous systems are the various salts of lithium. Lithium chloride is commonly used as a non-reactive tracer. Lithium is readily detectable in aqueous solutions on an atomic adsorption spectrometer operating in the emission mode. The minimum lithium concentration detectable is approximately 0.2 $\mu g\ell^{-1}$ with a sensitivity of 0.04mgℓ , the optimum working range being 0.1 to 2mgℓ^{-1} (APHA Standard Methods, 1992).

As the chloride content of landfill leachate is often at elevated levels, it was consequently decided to investigate the adsorption characteristics of lithium sulphate. Potable water would be added to the columns to replace the leachate drained from the column. Potable water in the Cape Town municipal area has a chloride content of approximately 27mgℓ^{-1}. The decrease in chloride content in the leachate as the tracer response experiment progressed could well serve as an inverse tracer if problems were experienced with the lithium sulphate tracer.

The TCLP was modified to enable the determination of the degree of adsorption of lithium sulphate onto municipal solid waste. The extraction fluid, with it's acetate buffered system would appear to provide a good approximation of leachate from the pilot-scale landfill columns. The modification was effected in the following manner.

The solution was formulated, in the same manner as described previously (Section 5.5.1). The pH of this solution was then adjusted with 1N sodium hydroxide until the pH of the solution was 6.8. This pH was decided upon as it was the average of all pH measurements taken of the leachate from the pilot-scale landfill columns at that time.
Sufficient lithium sulphate was added to this solution for the lithium content to approximate $10mg\ell^{-1}$. To assure the results of the lithium sulphate adsorption studies to be reproducible, and to eliminate any bias from the municipal solid waste it was decided to perform the experiments in triplicate. Again, one sample of the cumulative sample (sample 21) was used, the other two samples being differing sub-samples.

A 50g portion of the prepared municipal solid waste was weighed and placed in the extractor vessel. A 25mℓ sample of the lithium sulphate solution was then taken from the measuring cylinder. Exactly 1ℓ of the relevant pH-adjusted, dilute lithium sulphate solution was then added to the extractor vessel. The extractor vessel was then placed in the agitation device and agitation began. Agitation continued for a period of 32 hours. After 32 hours had elapsed the agitator was stopped, another sample of volume 25mℓ was then taken for analysis. Details of the analysis, and degree of adsorption is shown below.

TABLE 6.6 ADSORPTION OF LITHIUM AT LABORATORY SCALE

Sample No.	Initial lithium concentration ($mg\ell^{-1}$)	Final lithium concentration ($mg\ell^{-1}$)	Percentage lithium adsorption
2	10.123	10.021	1.00
13	10.225	10.046	1.75
21	10.225	10.046	1.75

The percentage adsorption of lithium of less than 2 percent was considered acceptable and probably within experimental error for the analysis coupled with the degree of purity of the lithium sulphate employed.

6.4.2 MASS OF NON-REACTIVE TRACER UTILISED

A solution of approximately $1000mg\ell^{-1}$ of lithium, in the form of the sulphate salt was prepared. This solution was analysed in triplicate. The concentration of the solution was found to be $1027mg\ell^{-1}$. To determine the mass of lithium tracer to be added the following reasoning was applied. The total volume of water present in the pilot-scale columns approximated 400ℓ, the average weekly flowrates were approximately 35ℓ. There are two extreme *scenarios* to

consider: if perfect plug flow conditions existed; if perfect mixing conditions were prevalent. If 1000mg of lithium were added and the reactor functioned as a perfect mixer the outlet concentration would approximate $0.025mg\ell^{-1}$, if the reactor functioned as a perfect plug flow reactor the outlet concentration of lithium would approximate $29mg\ell^{-1}$. Both these concentrations are detectable by the analytical procedure employed.

6.4.3 METHOD OF INJECTION OF NON-REACTIVE TRACER

It was decided to use Column 4 for the residence time studies, this was an arbitrary decision. Leachate was withdrawn in the usual manner, the leachate being drained until the flow diminished to a slow drip. While the leachate was flowing a sample was taken for analysis. On these samples the following analyses were performed:

pH;
Electrical conductivity;
Chemical Oxygen Demand (COD), unfiltered;
Chemical Oxygen Demand (COD), filtered;
Chloride content;
Total Alkalinity;
Bicarbonate Alkalinity;
Orthophosphate;
Lithium content.

From the analyses of total alkalinity; bicarbonate alkalinity and orthophosphate, the volatile acid alkalinity was then calculated.

After the leachate flow diminished to a slow drip, the outlet valve from the pilot-scale column was then closed and the volume of leachate drained was measured. This was accomplished with a calibrated dip stick. The contents of the 80ℓ drainage tank were then pumped to waste. The same volume of potable water was then placed in the leachate drainage tank. At the top of the column exactly 1ℓ of the $1000mg\ell^{-1}$ lithium solution was poured onto the aggregate distributor. The pump was then started, the contents of the drainage tank pumped to the top of the column washing the tracer into the solid waste matrix.

6.4.4 MONITORING OF THE NON-REACTIVE TRACER

Every 7 days the leachate was drained; sampled; measured; and pumped to waste. The same volume of potable waste added to the drainage tank and pumped to the top of the pilot-scale landfill column. This exercise was repeated until chemical analysis revealed the lithium content of the sample of leachate diminished to a level similar to that of the first sample of leachate taken. The results were then examined to determine the residence time distribution of the landfill column, these are shown in Chapter 7.

6.5 PILOT-SCALE EVALUATION OF THE KINETIC AND TRACER STUDIES

After the completion of the laboratory-scale experiments and the pilot-scale tracer response study, the results were examined. A requirement was that sufficient copper-chromium-arsenic solution was co-disposed with the municipal solid waste in the column to obtain a response in the liquid effluent from the column. The following data were revealed from the laboratory-scale experiments:

the quantity of the metals adsorbed by the municipal solid waste;
the rate of that adsorption

The pilot-scale tracer study revealed the residence time distribution within the column. Results indicated adequate time for the adsorption reactions to reach completion. To estimate the mass of copper-chromium-arsenic solution the maximum adsorption was initially calculated. This was calculated in the following manner.

Mass of municipal solid waste in laboratory scale experiments = 50g
Mass of municipal solid waste in pilot-scale column ≈ 668kg

Example
Average mass of copper sorbed at pH7.0 = 23mg
Maximum mass of copper adsorbed at pilot-scale = (23/50)×668 = 308g

The calculation was completed for all relevant pH values, the results are shown in Table 6.7 overleaf.

Another factor that was considered before the addition of the solution was particle size. The municipal solid waste was reduced in size to below 1mm for the laboratory scale kinetic trials. The solid waste employed in the pilot-scale columns was reduced in size to between 25 and 40mm. The surface area presented for adsorption would consequently be vastly different.

The copper-chromium-arsenic solution is supplied by the manufacturer in the following composition (Section 5.4.1). Copper, is present at 93.1 $g\ell^{-1}$, chromium is present at 269.6$g\ell^{-1}$, and arsenic is present at 270.2$g\ell^{-1}$. It can be seen from Table 6.7, at pH7.0, the probable leachate pH, the expected masses of metal to be adsorbed were:

Copper = 307g
Chromium = 281g
Arsenic = 548g

TABLE 6.7 MAXIMUM ADSORPTION OF THE COPPER, CHROMIUM AND ARSENIC

Metal	pH	Average Mass sorbed (mg)	Average Mass sorbed (mg g^{-1})	Anticipated adsorption (g)
Copper	5.5	50.9	1.02	681
	6.4	14.1	0.28	187
	7.0	23.0	0.46	307
Chromium	5.5	53	1.06	708
	6.4	31	0.62	414
	7.0	21	0.42	281
Arsenic	5.5	70	1.40	935
	6.4	36	0.72	481
	7.0	41	0.82	548

It was anticipated that virtually all the copper would precipitate within the column, thus attention was focused upon the chromium and the arsenic. If the approximate minimum mass of arsenic was added (548g), then approximately the same mass of chromium would be added, from the calculations above this would greatly exceed the expected adsorption, and additionally no allowance had been made for particle size. It was then considered sufficient to add near the theoretical maximum of chromium (281g), the difference in particle size and hence surface area should allow both chromium and arsenic to be present in the leachate.

The volume of copper-chromium-arsenic added to the municipal solid waste was 950mℓ, the mass of metals added is shown below:

Mass of chromium added = 256.1g
Mass of copper associated = 88.4g
Mass of arsenic associated = 256.8g

6.5.1 EXPERIMENTAL PROCEDURE - CO-DISPOSAL OF COPPER-CHROMIUM-ARSENIC SOLUTION

It was decided to use Columns 3 and 5 for the co-disposal studies, these columns had exhibited the most consistent volumetric leachate flowrates. Leachate was withdrawn in the usual manner, the leachate being drained until the flow diminished to a slow drip. While the

leachate was flowing a sample was taken for analysis. On these samples the following analyses were performed:

pH;
Electrical conductivity;
Chemical Oxygen Demand (COD), unfiltered;
Chloride content;
Copper content;
Chromium content;
Arsenic content.

After the leachate flow diminished to a slow drip, the outlet valve from the pilot-scale column was then closed and the volume of leachate drained was measured. This was accomplished with a calibrated dip stick. The contents of the 80ℓ drainage tank were then pumped to waste. The same volume of potable water was then placed in the leachate drainage tank. At the top of the column exactly 950mℓ of the concentrated copper-chromium-arsenic solution was poured onto the aggregate distributor. The pump was then started, the contents of the drainage tank pumped to the top of the column washing the solution into the solid waste matrix.

6.5.2 MONITORING OF THE PILOT-SCALE CO-DISPOSAL EXPERIMENT

Every 7 days the leachate was drained; sampled; measured; and pumped to waste. The same volume of potable waste added to the drainage tank and pumped to the top of the pilot-scale landfill column. This exercise commenced on Day 567 and was repeated until Day 754. The results were then examined to determine the degree of agreement between the laboratory and pilot-scale studies. The results are shown in Chapter 7.

6.6 ANALYTICAL PROCEDURES

Chemical analysis was performed at the Laboratory of the Department of Chemical Engineering of the University of Cape Town, and at the Laboratory of the Scientific Services Branch, City Engineer's Department, City of Cape Town.

TABLE 6.8 ANALYTICAL RESPONSIBILITIES

Component	Establishment
Biogas analysis	Scientific Services Branch
Leachate analysis	Scientific Services Branch

(a) Biogas
Biogas was analysed for percentage: methane; carbon dioxide; oxygen and nitrogen.

(b) Leachate - tracer response study
Leachate was analysed for: pH; electrical conductivity; Chemical Oxygen Demand (COD), unfiltered; Chemical Oxygen Demand (COD), filtered; chloride content; total alkalinity; bicarbonate alkalinity; orthophosphate and lithium content.

(c) Leachate - pilot-scale co-disposal studies
Leachate was analysed for: pH; electrical conductivity; Chemical Oxygen Demand (COD), unfiltered; chloride content; copper content; chromium content; arsenic content.

The analytical equipment has been detailed in Table 5.14, the exception being the analysis of biogas. Biogas analysis was performed with a Varian 3300 Gas Chromatograph.

6.7 SUMMARY

The design of pilot-scale landfill columns constructed by previous researchers was reviewed to establish the design and construction for the Athlone pilot-scale landfill columns. Operation of the Athlone pilot-scale columns included leachate recirculation and biogas monitoring. Residence time distribution trials were undertaken at pilot-scale. A laboratory scale investigation established that lithium sulphate would be suitable for use as a tracer. A solution of copper, chromium and arsenic was then co-disposed at pilot-scale.

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CHAPTER 7
RESULTS AND CALCULATIONS: LABORATORY AND PILOT-SCALE STUDIES

7.1 INTRODUCTION

As reported in Chapters 5 and 6, the experimental programme comprised of two complimentary investigations:

(i) Laboratory scale investigation;
(ii) Pilot-scale investigation.

These two complimentary investigations were then further sub-divided into manageable, associated elements.

Laboratory scale investigation
The laboratory scale investigation was also constituted of two integral sections:
Evaluation of kinetic rate constants, adsorption and desorption;
evaluation of adsorption isotherms.

Pilot-scale investigation
This investigation advanced on two fronts:
Evaluation of the residence time distribution/deviation from ideal behaviour of the pilot-scale landfill columns.
Evaluation, at pilot-scale, of the kinetic rate constants determined at laboratory scale.

7.2 LABORATORY SCALE INVESTIGATIONS

7.2.1 RESULTS FROM THE ADSORPTION STUDIES

Adsorption studies were undertaken at three pH values; pH5.5, pH6.4, and pH7.0. Initial (0.0h) and final (32.0h) results from the kinetic studies were also utilised in the construction of the adsorption isotherms. The results are shown in Appendix B, Table B-1 (pH5.5); Table B-2 (pH6.4); Table B-3 (pH7.0) of Ballard (1997). Freundlich isotherms were successfully constructed for copper at pH values 5.5 and 7.0; for chromium and arsenic at all three pH values, 5.5, 6.4 and 7.0. The constructions are shown in section 7.4.2

7.2.2 RESULTS FROM THE KINETICS STUDIES

The kinetics experiments were undertaken in triplicate at three pH values, 5.5 (coded A, B and C) 6.4 (coded D, E and F) and 7.0 (coded G, H and I). As reported in section 4.5, the experimental method made available data for analysis of the kinetics of adsorption and desorption of the metallic ions. The adsorption results are reported as analysed in the laboratory and are shown in Appendix B, Table B-4 (pH5.5); B-5 (pH6.4) and B-6 (pH7.0) of Ballard (1997). The desorption results are reported Table B-7 (pH5.5); B-8 (pH6.4) and B-9 (pH7.0) of Ballard (1997). Graphical representations of the analytical results from the adsorption kinetic trials are shown overleaf (Figures 7.1 to 7.27). As with most experimental data, a degree of scatter can be observed in the experimental results, this is addressed in the interpretation of the data in section 7.4.3. The degree of scatter is however, most noticeable at the lower experimental time frames. Chemisorption is often preceded by physical adsorption, which is easily reversible (Section 3.8.1.3). This would explain the scattering of data points at short experimental times. The cationic ions being only loosely bound by physical adsorption to the solid waste matrix, at low experimental values of time.

In all cases, sorption of the metallic ions is characterised by a rapid initial sorption, the sorption rate decreasing with increased time. The analogy between the adsorption of solutes onto soils has been discussed (Sections 3.8.1.3(a) and 4.3.1). Rapid soil reactions are, in general, reactions which transport at the solid phase do not significantly influence the reaction rate. Conversely, slow reactions are often characterised by diffusional mass transfer limitations (Section 4.3.2). On initial inspection, these conditions would appear apparent. This phenomena, together with a proposed reaction mechanism is discussed fully in Chapter 8.

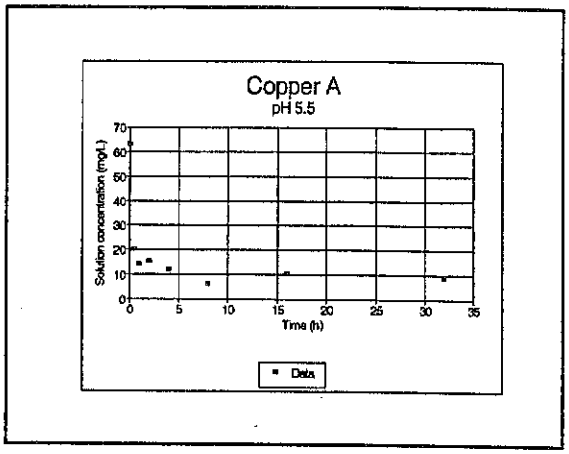

Figure 7.1
Adsorption of copper (A): pH 5.5

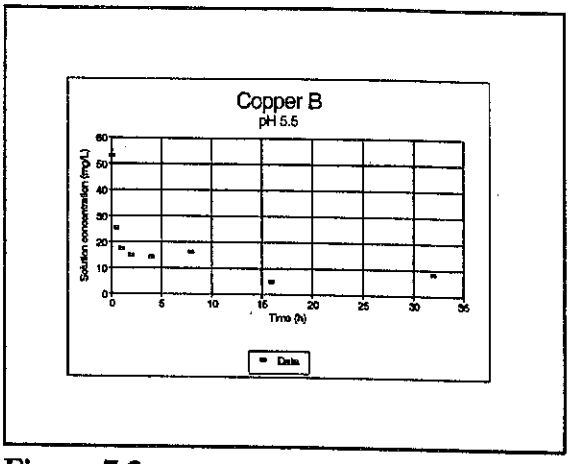

Figure 7.2
Adsorption of copper (B): pH 5.5

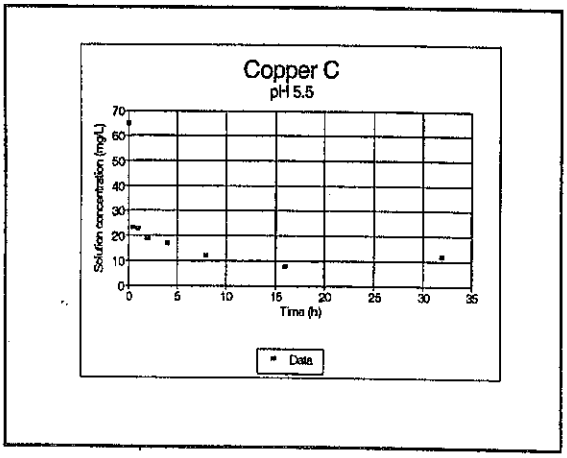

Figure 7.3
Adsorption of copper (C): pH 5.5

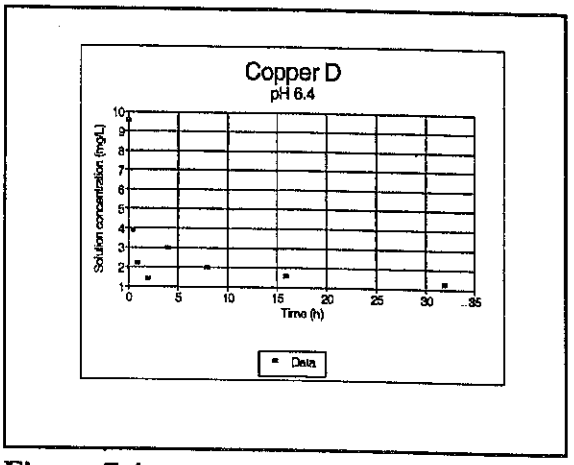

Figure 7.4
Adsorption of copper (D): pH 6.4

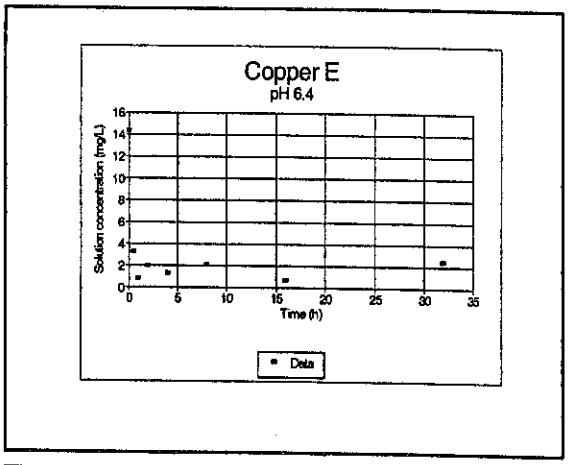

Figure 7.5
Adsorption of copper (E): pH 6.4

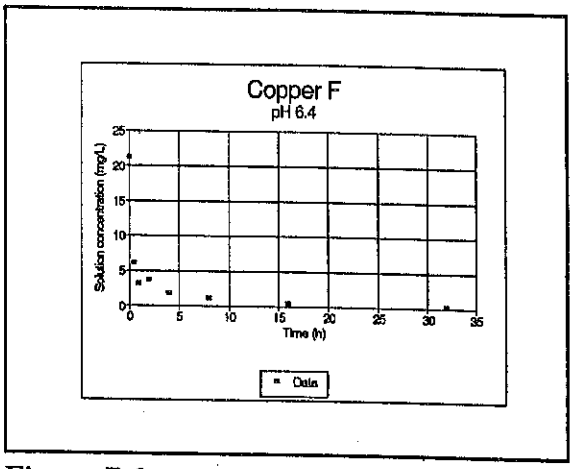

Figure 7.6
Adsorption of copper (F): pH 6.4

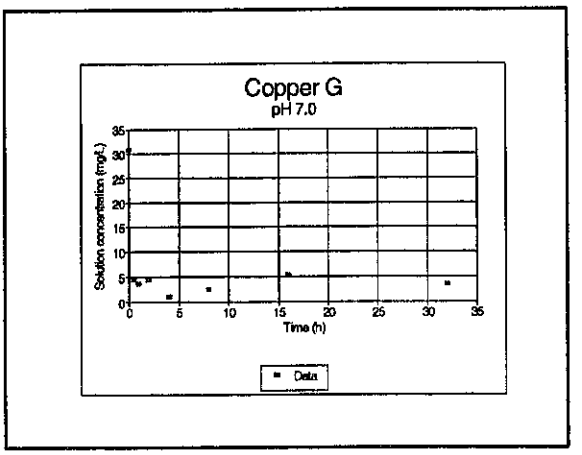

Figure 7.7
Adsorption of copper (G): pH 7.0

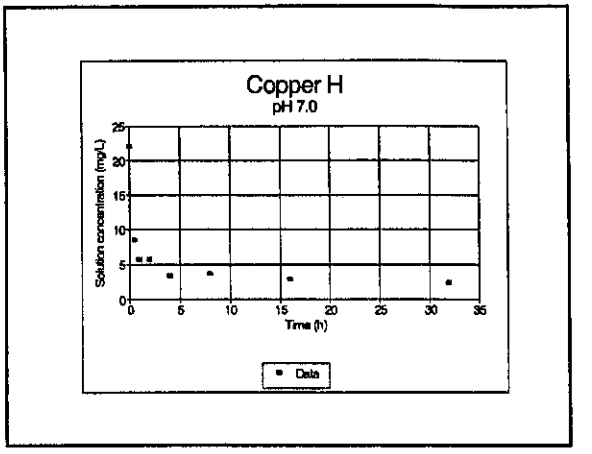

Figure 7.8
Adsorption of copper (H): pH 7.0

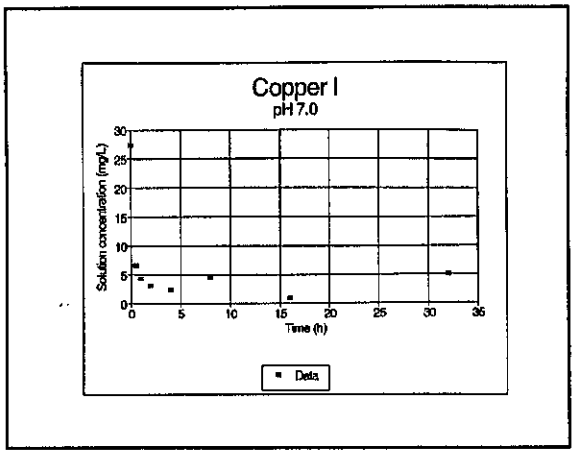

Figure 7.9
Adsorption of copper (I): pH 7.0

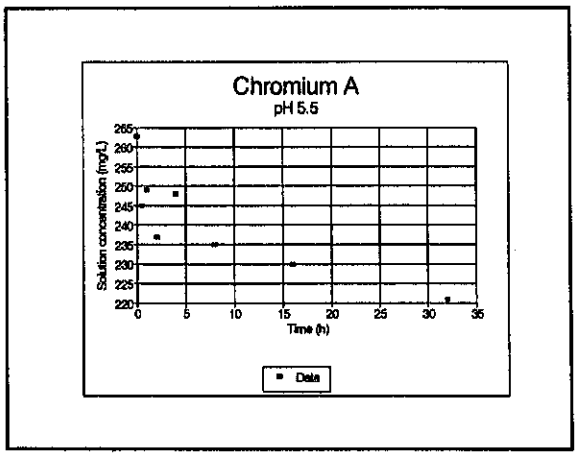

Figure 7.10
Adsorption of chromium (A): pH 5.5

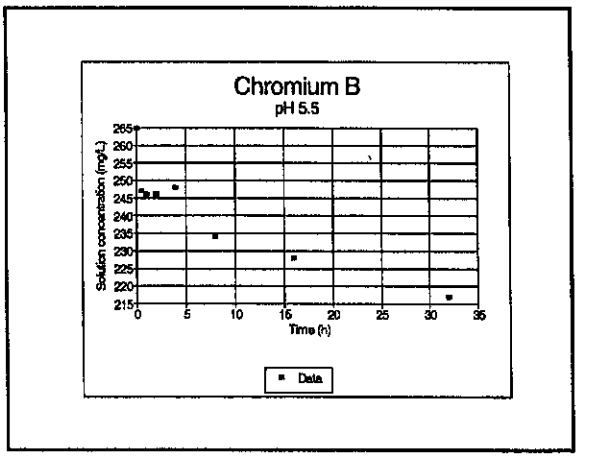

Figure 7.11
Adsorption of chromium (B): pH 5.5

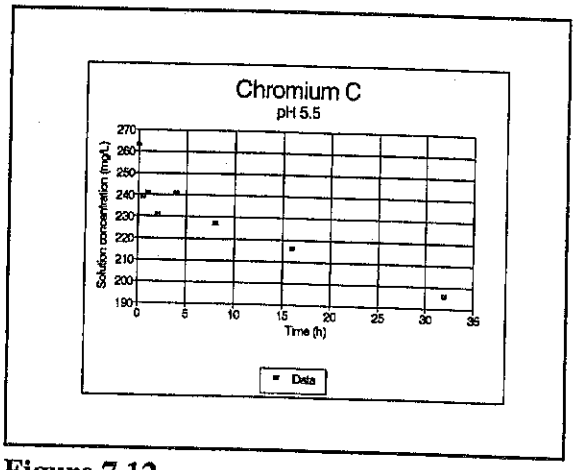

Figure 7.12
Adsorption of chromium (C): pH 5.5

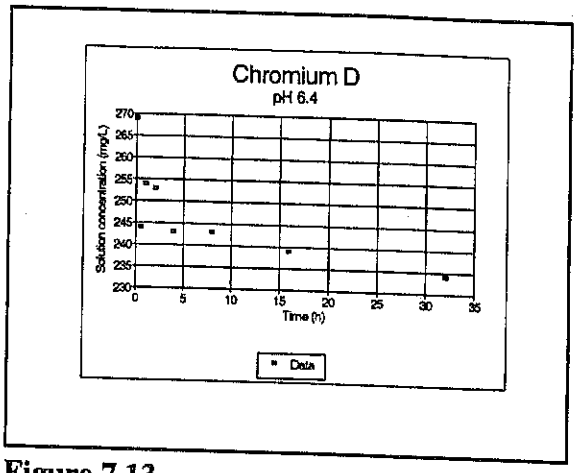

Figure 7.13
Adsorption of chromium (D): pH 6.4

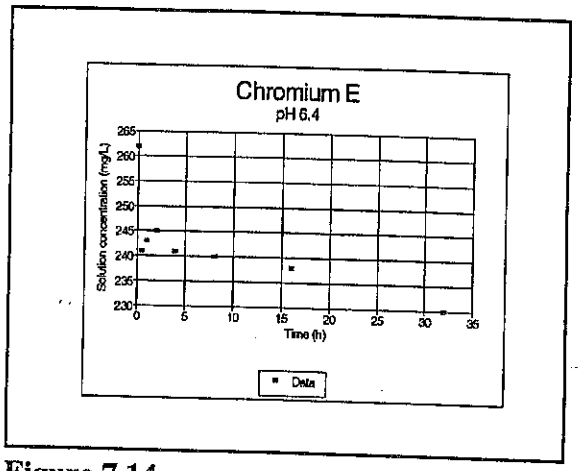

Figure 7.14
Adsorption of chromium (E): pH 6.4

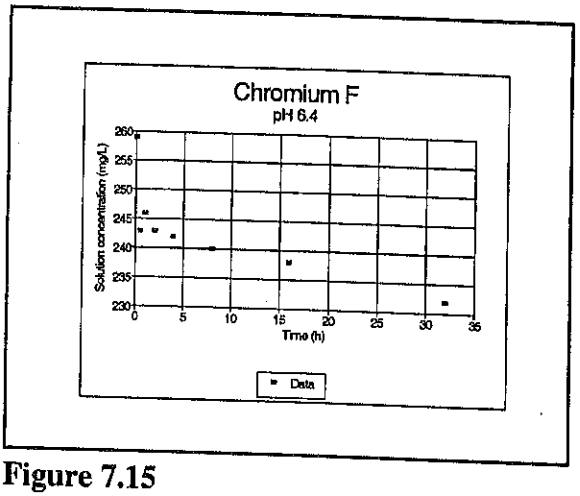

Figure 7.15
Adsorption of chromium (F): pH 6.4

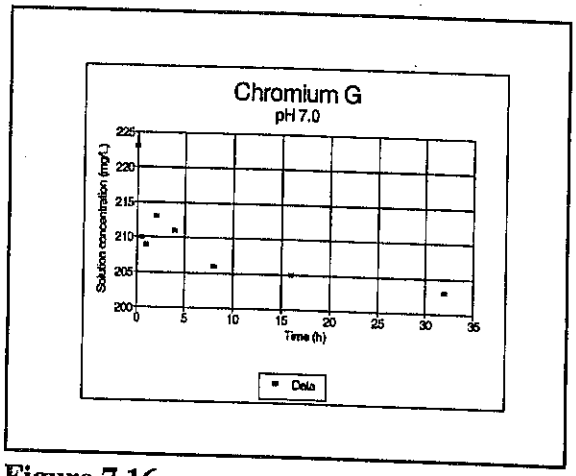

Figure 7.16
Adsorption of chromium (G): pH 7.0

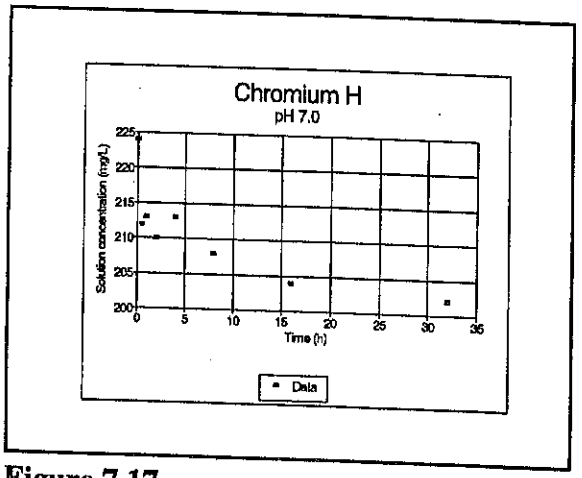

Figure 7.17
Adsorption of chromium (H): pH 7.0

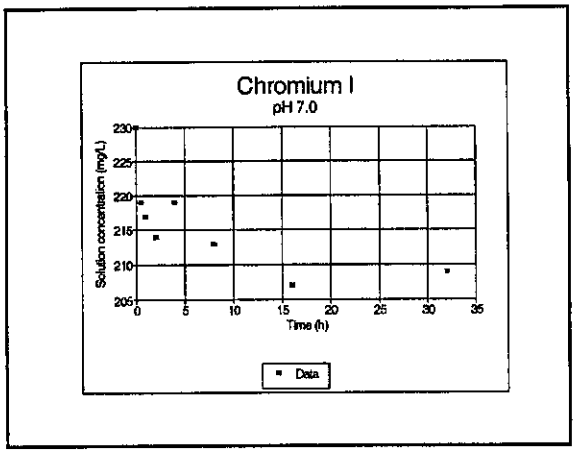

Figure 7.18
Adsorption of chromium (I): pH 7.0

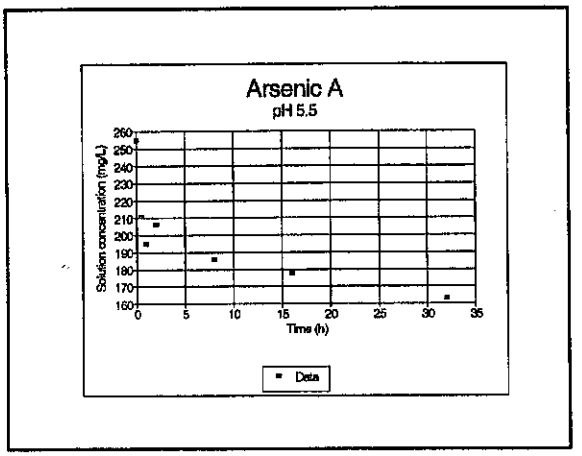

Figure 7.19
Adsorption of arsenic (A): pH 5.5

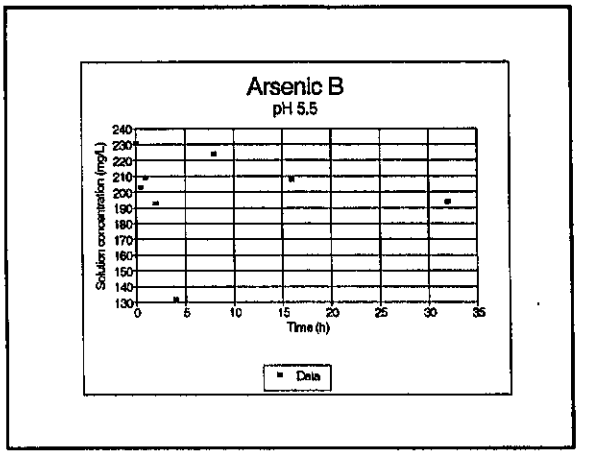

Figure 7.20
Adsorption of arsenic (B): pH 5.5

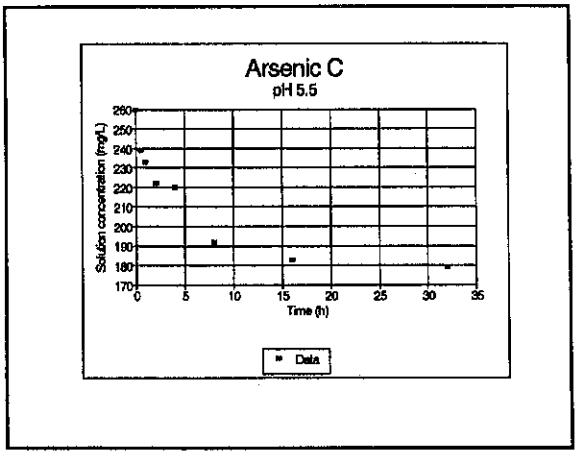

Figure 7.21
Adsorption of arsenic (C): pH 5.5

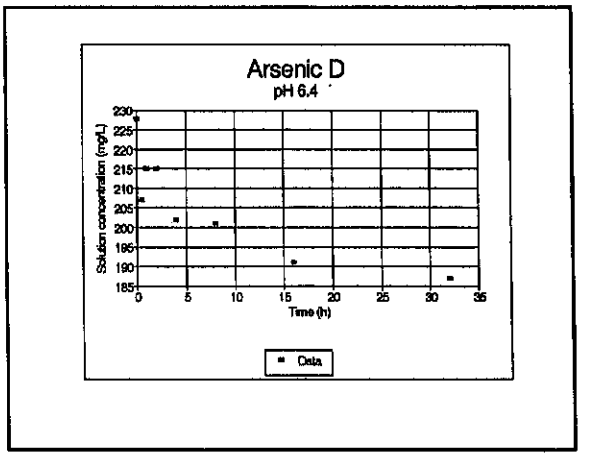

Figure 7.22
Adsorption of arsenic (D) : pH 6.4

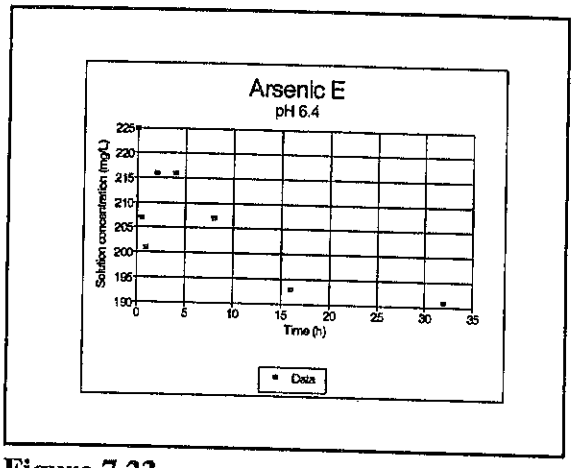

Figure 7.23
Adsorption of arsenic (E): pH 6.4

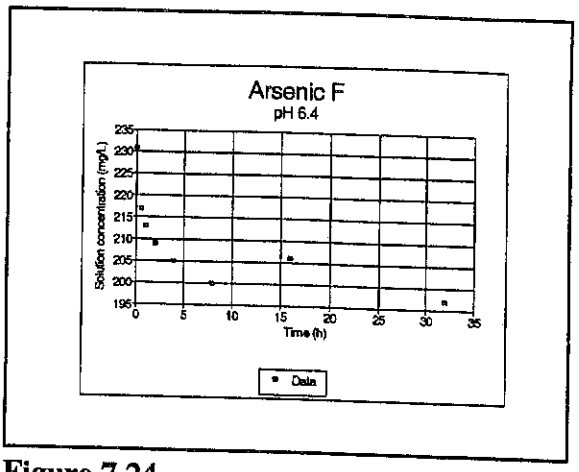

Figure 7.24
Adsorption of arsenic (F): pH 6.4

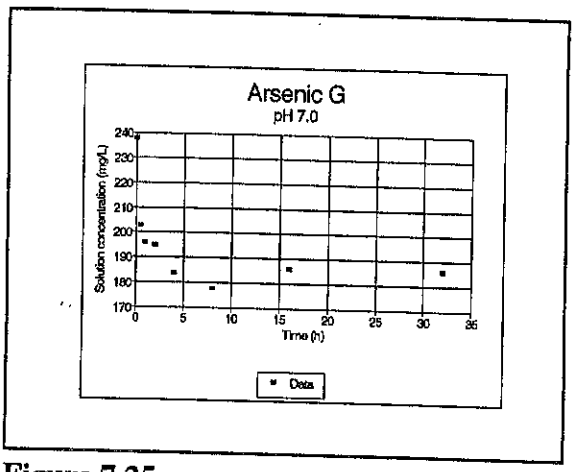

Figure 7.25
Adsorption of arsenic (G): pH 7.0

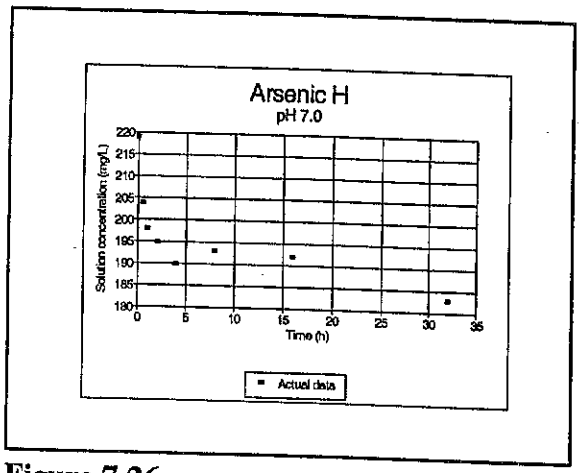

Figure 7.26
Adsorption of arsenic (H): pH 7.0

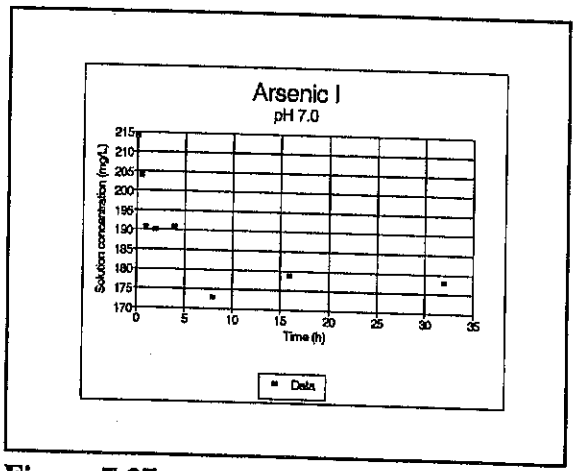

Figure 7.27
Adsorption of arsenic (I): pH 7.0

7.3 PILOT-SCALE INVESTIGATIONS

7.3.1 LEACHATE RECIRCULATION

As reported in Chapter 6, leachate first became evident on Day 60. Leachate was drained until the flow diminished to a slow drip. The volume of leachate obtained was measured on cessation of flow. While the leachate was flowing a sample was taken for analysis. On these samples the following analyses were performed:

pH;
Electrical conductivity;
Chemical Oxygen Demand (COD), unfiltered;
Chemical Oxygen Demand (COD), filtered;
Chloride content;
Total Alkalinity;
Bicarbonate Alkalinity;
Orthophosphate.

From the analyses of total alkalinity; bicarbonate alkalinity and orthophosphate, the volatile acid alkalinity was then calculated. Results of the chemical analysis, together with the volume of leachate drained are shown in Appendix C of Ballard (1997).

The recirculation procedure was performed every 7 days, until Day 118. Recirculation ceased at this point as the temperature inside the columns had dropped to below 15°C, and there was no evidence of biogas production. The lower temperatures were due to the onset of the South African winter season.

Recirculation of leachate recommenced on Day 231; ambient temperatures were beginning to rise, as the southern hemisphere summer season was beginning. The recirculation procedure then continued as before; the procedure being repeated after a time interval of 7 days. The procedure was discontinued on Day 358, as there was no resumption of biogas production. Column 4 was only recirculated until Day 118. From Day 231, column 4 was employed for tracer studies. The results obtained until Day 118 for column 4 are shown in Appendix C, Table C-5 of Ballard (1997). The results obtained from columns 1, 2, 3 and 5 are discussed briefly below.

The average pH of leachate from columns 1, 2, 3 and 5 averaged 7.0. The highest pH value recorded was 7.3, the lowest was 6.6. Initial measurements of electrical conductivity were performed on an undiluted sample. It was found the measurements varied and were inconsistent. This method of analysis continued until Day 110, thereafter leachate was diluted, and the value of electrical conductivity reported was adjusted to the degree of dilution. Electrical conductivity measurements (from Day 110) were relatively consistent from all the columns (apart from the occasional high or low value), and averaged 1068mSm^{-1} from column 1; 1050mSm^{-1} from column 2; 1042mSm^{-1} from column 3, and 1029mSm^{-1} from column 5.

Leachate was analysed for COD in the un-filtered and filtered, state. This was a precautionary

measure, as it was initially considered the presence of particulate matter would adversely affect data trend analysis. The COD content of the leachate showed an initial rapid reduction from approximately 6000mgℓ^{-1} to approximately 2000mgℓ^{-1} during the first 110 days. The COD continued to decrease until leachate recirculation ceased on Day 358. The COD then approximated 1200mgℓ^{-1} in the unfiltered samples. All of the columns exhibited similar behaviour.

Chloride levels remained consistent throughout the recirculation period; there was little difference in chloride measurements from individual columns. Chloride content averaged 1077mgℓ^{-1} from column 1; 1154mgℓ^{-1} from column 2; 1052mgℓ^{-1} from column 3; 998mgℓ^{-1} from column 5. Both Total Alkalinity and Bicarbonate Alkalinity gradually decreased throughout the duration of the recirculation, the Total alkalinity decreasing from approximately 4500mgℓ^{-1} to 3800mgℓ^{-1}. The bicarbonate alkalinity showed a similar trend the values being consistently lower by approximately 300mgℓ^{-1}. The volatile acid alkalinity of leachate from the columns showed an initial sharp decrease from approximately 550mgℓ^{-1} to 300mgℓ^{-1}, and stabilised at this value for the duration of the experiment. Levels of ortho-phosphate in the leachate showed a similar trend from all the columns. The results were extremely erratic over the duration of leachate recirculation, but decreased to very low levels (0.1mgℓ^{-1}) by Day 358.

Results from previous column studies conducted at the University of Cape Town employing "fresh" municipal solid waste are extremely well documented (Chapman *et al* 1991). After 50 weeks of recirculating leachate the researchers reported the following results: pH levels of 5.7; COD levels of 27000mgℓ^{-1} ; bicarbonate alkalinity of 120mgℓ^{-1} ; volatile acid alkalinity of 13000mgℓ^{-1} ; electrical conductivities approximating 1500mSm^{-1}; ortho-phosphate, 15mgℓ^{-1}. The columns did not generate biogas, acetogenic conditions were evident. The United Kingdom's Department of Environment (DOE, 1986) report values of leachate from "aged wastes". They report pH values of 7.5; COD levels of 1160mgℓ^{-1} and phosphate levels of approximately 1mgℓ^{-1}. This together with the low levels of biogas production from the columns (section 6.3.2) confirm the municipal solid waste was well stabilised prior to placement within the pilot-scale landfill columns.

7.3.2 LITHIUM SULPHATE PULSE EXPERIMENT

Results from the lithium sulphate pulse experiment are shown in Appendix D of Ballard (1997). Table D-1 details the volumetric displacement of leachate; the lithium concentration of the leachate; the mass of lithium obtained per sample, and the cumulative mass of lithium. Table D-2 characterises the leachate in terms of pH, COD, etc.. The mass of lithium sulphate introduced in the system was 1027.7mg, of this 954.3mg was successfully recovered, a recovery rate of 92.9 percent. The time duration of the experiment was 317 days, the average volumetric displacement of leachate was 36.5ℓweek^{-1} . Maximum lithium recovery occurred after 84 days, the lithium concentration of the leachate at that time was 2.003mgℓ^{-1}. Leachate was sampled and recirculated approximately every 7 days. The volumetric displacement of leachate from the column varied, and additionally, on occasion, sampling and recirculation could not be effected on the designated day. The conventional graphical representation reporting results of this nature is in terms of concentration-time, because of the variation in both volumetric displacement and on occasion time increments a far more satisfactory representation of the experimental data is mass (of lithium in leachate) versus time. This shown below in Figure 7.28

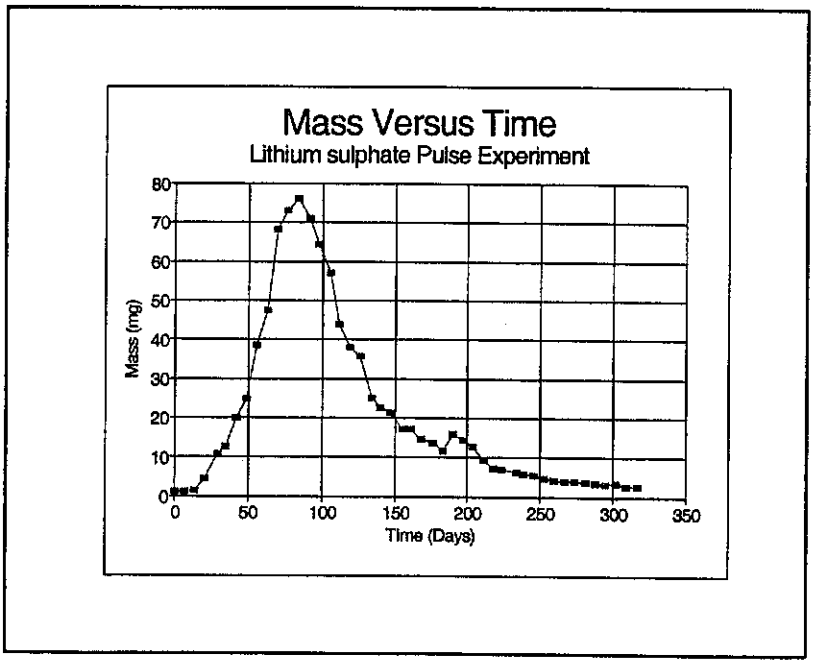

Figure 7.28
Results of lithium pulse experiment

The mass-time curve reveals a system that is non-ideal. In an industrial reactor of this nature i.e. a packed column, assuming ideal behaviour, one would anticipate plug flow, the graphical representation of the data should then resemble a thin spike located at maximum tracer concentration. The large base is indicative of axial dispersion of the fluid; the early initial commencement of the curve is a manifestation of channelling; the long tail is symptomatic of stagnant areas within the column. The curve is however consistent, except for a small secondary peak occurring around Day 200. This phenomena is indicative of stagnant flow areas within the column. The only deviation from ideality that one would not experience on a full scale landfill is the high degree of initial channelling. It is probable that wall effects from the column are a contributory factor. The curve is further examined in section 7.4.4.

*(a) **Chemical characteristics of leachate collected during the lithium pulse experiment***
As would be expected when draining leachate to waste, and replacing the leachate with an equal volume of fresh potable water, all the determined chemical parameters (except for pH) showed a steady decline. Initial COD levels approximated 2000mgℓ^{-1} reducing to just above 100mgℓ^{-1}, chloride levels diminished from 900mgℓ^{-1} to around 40mgℓ while electrical conductivity decreased from 1100mSm^{-1} to about 200mSm^{-1}.

7.3.3 CO-DISPOSAL OF COPPER, CHROMIUM AND ARSENIC AT PILOT-SCALE

As reported in section 6.5.1 a concentrated solution of copper, chromium and arsenic was co-disposed with the municipal solid wastes in columns 3 and 5. Analytical results are reported in Appendix E of Ballard (1997). Tables E-1 and E-3 tabulate leachate volumes and metal concentrations for columns 3 and 5 respectively; Tables E-2 and E-4 tabulate the associated chemical data (pH, COD, etc.,) for columns 3 and 5. The mass of metals introduced into both columns 3 and 5 was copper, 88.4g; chromium, 256.1g and arsenic, 256.7g. The time duration of the experiment with column 3 was 235 days, the average volumetric displacement of leachate was 19.2ℓweek^{-1}. The time duration of the experiment with column 5 was slightly shorter, 221 days. The average displacement of leachate was 18.5ℓweek^{-1} . The volumetric displacement of leachate, although similar to column 3, tended to vary slightly more.

(a) Copper content in leachate from columns 3 and 5

Results from the monitoring of copper concentration of leachate from columns 3 and 5 are shown graphically in Figure 7.29. The initial concentration of copper in the leachate from column 3 was 0.05mgℓ^{-1}, after 14 days the copper concentration in the leachate had risen to 0.11mgℓ^{-1}, the highest concentration recorded. This initial rise in copper concentration was probably caused by rapid liquid flow through the column symptomatic of a combination of preferential fluid channelling and wall effects. Subsequently, the copper concentration was lower at 0.04mgℓ^{-1}, slightly lower than the initial base-line reading of 0.05mgℓ^{-1}. From Day 170 to Day 202, the copper concentration stabilised at 0.06mgℓ^{-1}. At Day 235 the copper concentration was slightly elevated at 0.08mgℓ^{-1}. Over the entire period of monitoring (235days), the concentration of copper in the leachate from column 3 averaged 0.05mgℓ^{-1}, i.e. no higher than the initial reading at Day zero.

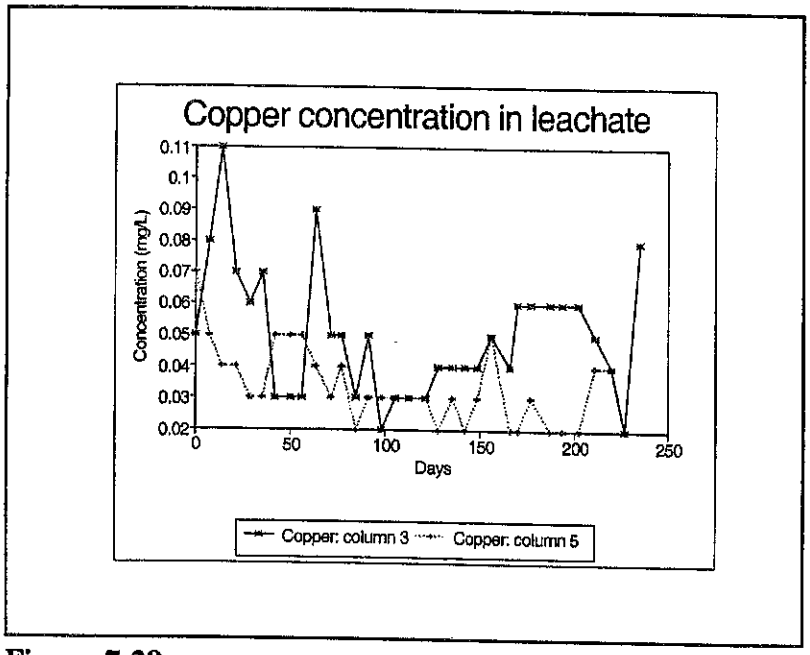

Figure 7.29
Copper concentration in leachate from columns 3 and 5

The initial concentration of copper in the leachate from column 5 was 0.07mgℓ^{-1} a value that was not exceeded for the entire duration of the experiment. The final copper concentration after 221 days was 0.04mgℓ^{-1}. Over the entire period of monitoring (221days), the concentration of copper in the leachate from column 3 averaged 0.03mgℓ^{-1}.

(b) Chromium content in leachate from columns 3 and 5

Results from the monitoring of chromium concentration of leachate from columns 3 and 5 are shown graphically in Figure 7.30. Initially, chromium in the leachate from column 3 was not detectable. The chromium content of the leachate rose steadily over the next 90 days to 0.04 mgℓ^{-1} , this value was not exceeded for the duration of the experiment, the final chromium concentration was 0.03mgℓ^{-1} on Day 235. The average chromium content in the leachate from column 3 over the entire duration of monitoring was 0.03mgℓ^{-1}

The initial chromium content of leachate from column 5 was 0.06mgℓ^{-1}, this dropped, and then steadily rose to 0.06mgℓ^{-1} by Day 90. The chromium concentration then stabilised at approximately this level until Day 180, whereafter metal content dropped very slightly. The final chromium concentration was 0.02 mgℓ^{-1} on Day 221. The average chromium content in the leachate from column 5 over the entire duration of monitoring was 0.04mgℓ^{-1}.

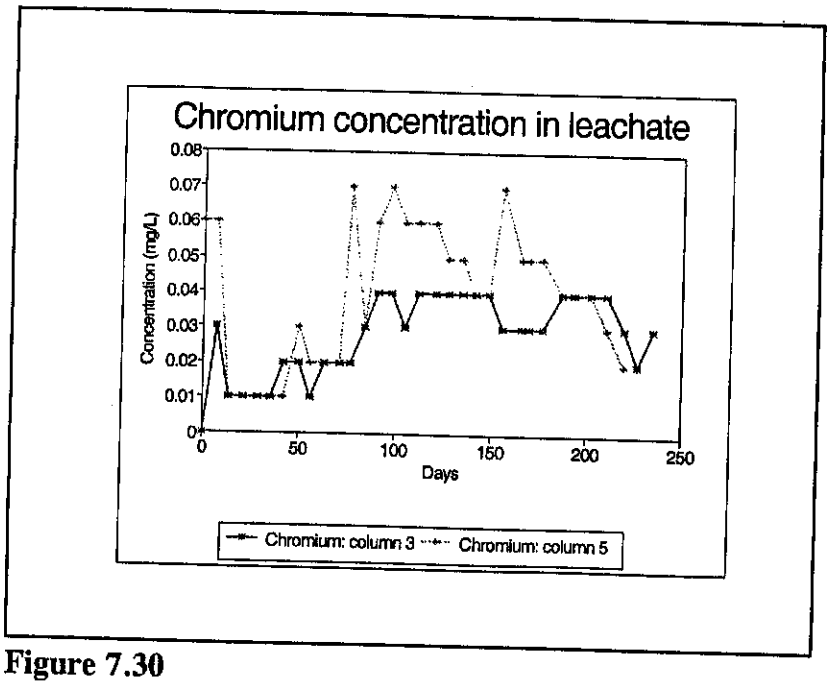

Figure 7.30
Chromium concentration in leachate from columns 3 and 5

(c) Arsenic content in leachate from columns 3 and 5

The behaviour of the co-disposed arsenic was by far the most interesting of the three metals. Results from the monitoring of arsenic concentration of leachate from columns 3 and 5 are shown graphically in Figure 7.31. The initial concentration of the arsenic in the leachate from column 3 was 17$\mu g\ell^{-1}$ rising in a near exponential manner to Day 135 where the arsenic concentration exceeded 1000$\mu g\ell^{-1}$. Subsequently, the concentration of arsenic in the leachate reduced to approximately 830$\mu g\ell^{-1}$ and stabilised at that level until Day 194 when the concentration exceeded 2000$\mu g\ell^{-1}$. Arsenic concentration in the leachate from column 3 remained at that level until the cessation

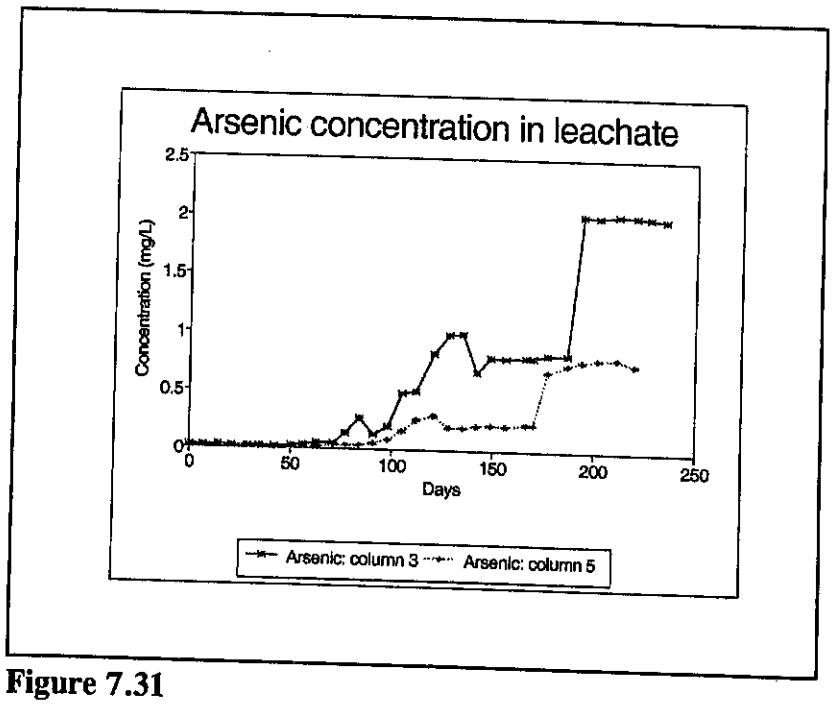

Figure 7.31
Arsenic concentration in leachate from columns 3 and 5

of monitoring on Day 235. Column 5 mirrored the behaviour of column 3 though at a reduced manner. The maximum arsenic concentration attained was 802$\mu g\ell^{-1}$ at Day 213; results were relatively constant from Day 188 at that level.

(d) Chemical characteristics of the leachate from columns 3 and 5

The chemical characteristics of the leachate from both columns 3 and 5 were very similar. Initial COD levels approximated 1200 reducing to 400$mg\ell^{-1}$, chloride levels diminished from 1000$mg\ell^{-1}$ to around 200$mg\ell^{-1}$ while electrical conductivity decreased from 500mSm^{-1} to about 300mSm^{-1}.

7.4 CALCULATIONS

7.4.1 ADSORPTION ISOTHERMS

(a) Freundlich Isotherm

The Freundlich or van Bemmelen equation may be expressed as:

$$q = K_F C_e^{\ M} \qquad 4.1$$

Where,

q	=	solute adsorbed per unit weight of solid adsorbent
K_F	=	Freundlich equilibrium distribution coefficient
C_e	=	Concentration of solute remaining in fluid at equilibrium
M	=	Freundlich power coefficient

Data are usually fitted to the logarithmic form of the equation:

$$\ln(q) = \ln(K_F) + M * \ln(C_e)$$

If the Freundlich adsorption isotherm is suitable, a logarithmic plot of solute adsorbed (q) versus equilibrium solute fluid concentration (C_e) results in a straight line with a slope equal to the Freundlich power coefficient (M) and an intercept equal to the value of the logarithmic form of the Freundlich equilibrium distribution coefficient (K_F)

(b) Method of examination of adsorption data

Initially, a logarithmic plot of solute adsorbed(mg) versus solute equilibrium concentration ($mg\ell^{-1}$) was constructed. This plot was then examined for any obvious outlying data points. As the numerical values obtained from the Freundlich Isotherm may only be considered as indicative, a more sophisticated form of statistical analysis (as undertaken for the kinetic studies) was not pursued. These outlying data points were then eliminated and the remaining results were examined by means of regression analysis.

7.4.2 FREUNDLICH ISOTHERM - COPPER, CHROMIUM AND ARSENIC

Freundlich Isotherms were successfully constructed for copper adsorption at two of the three pH values of 5.5, 6.4 and 7.0. The Freundlich isotherm was successful at the pH values of 5.5 and 7.0. Freundlich Isotherms were successfully constructed for chromium and arsenic adsorption at the three pH values of 5.5, 6.4 and 7.0. The graphical constructions are shown below, and subsequently tabulated are the total number of data points available, the number of data points utilised in the construction, the variance (R squared) between the actual results and the calculated isotherm, the value of the Freundlich equilibrium distribution coefficient (K_F) and the Freundlich power coefficient (M) for each metal at the various pH values.

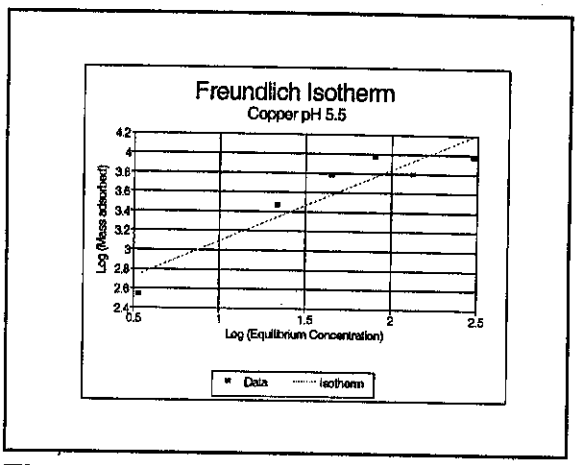

Figure 7.32
Freundlich Isotherm: copper @ pH 5.5

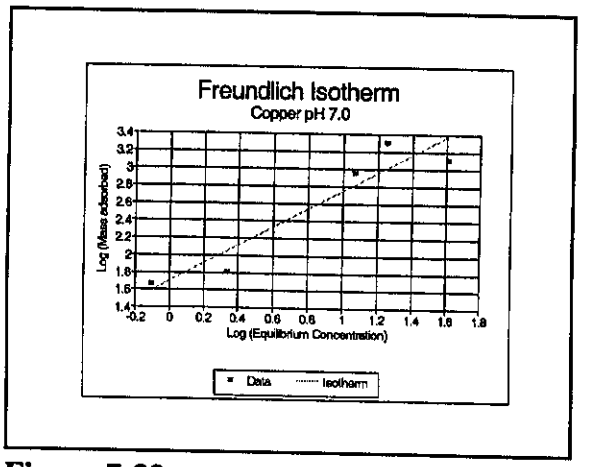

Figure 7.33
Freundlich Isotherm: copper @ pH 7.0

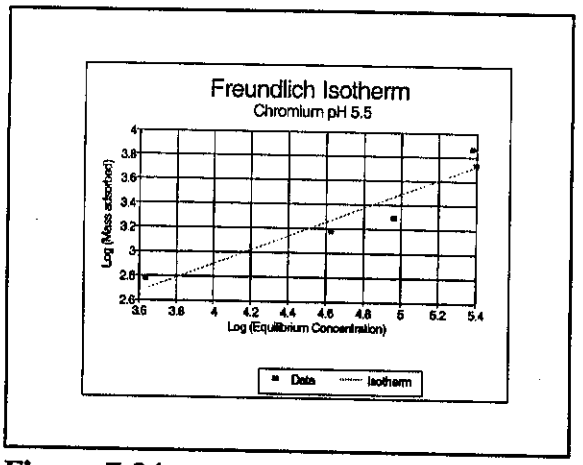

Figure 7.34
Freundlich Isotherm: chromium @ pH 5.5

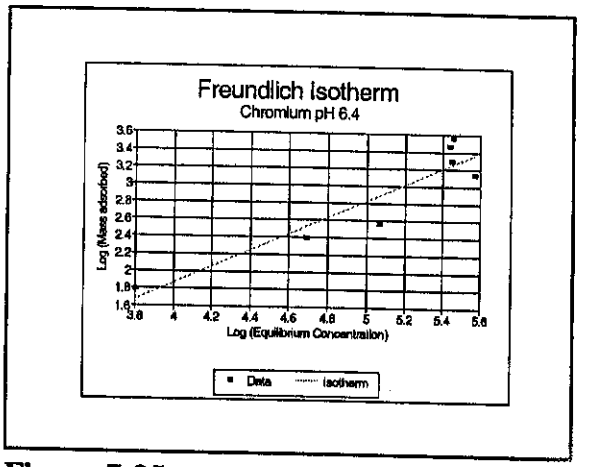

Figure 7.35
Freundlich Isotherm: chromium @ pH 6.4

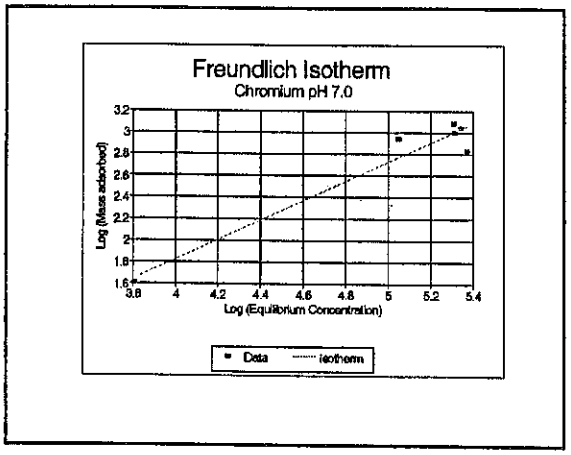

Figure 7.36
Freundlich Isotherm: chromium @ pH 7.0

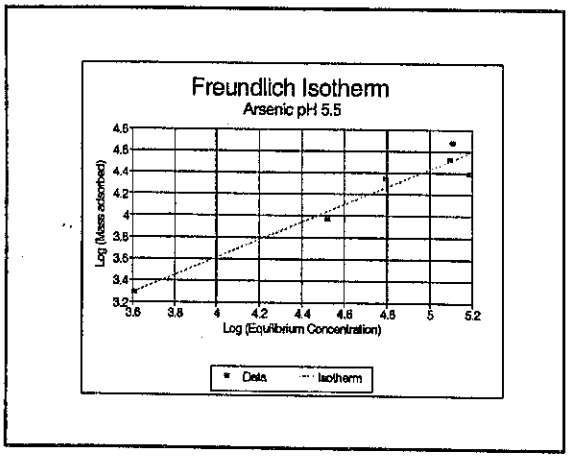

Figure 7.37
Freundlich Isotherm: arsenic @ pH 5.5

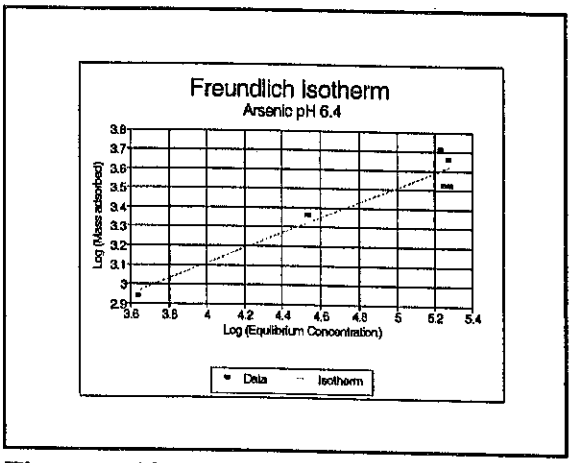

Figure 7.38
Freundlich Isotherm: arsenic @ pH 6.4

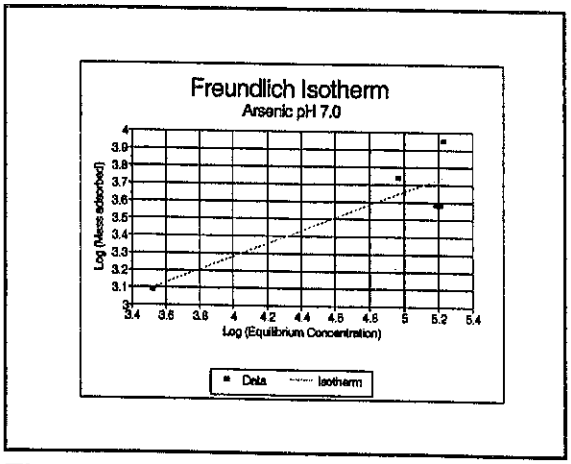

Figure 7.39
Freundlich Isotherm: arsenic @ pH 7.0

Consider Table 7.1 shown overleaf. The variance (R squared) ranged from 0.760 (arsenic at pH7.0) to 0.943 (chromium at pH7.0). As mentioned in section 5.7, copper and chromium analysis could be repeated in some instances. That facility was not available for arsenic. There appears to be no physical meaning of the exponent of the concentration term in the Freundlich equation (M) (Kuo *et al*, 1974). Researchers rarely comment these numerical values, usually reporting that analytical results conform to one type of adsorption isotherm and quoting the degree of agreement achieved. Therefore, there would not appear to be any great relevance in discussing at these numerical values at length.

However, if one considers soils, typically experimental data for power of the concentration term (M) approximates 1, an example being the adsorption of many pesticides at dilute concentrations (Tan, 1993). It can be seen that the power term for both copper and chromium conformed to this generalised rule. Arsenic adsorption only conformed at pH5.5. Elkhatib and fellow workers (1984) quote values of M obtained from arsenite (As(III)) adsorption on five West Virginian soils. The values range from 0.399 to 0.958. The calculated results shown in Table 7.1 range from 0.38 to 1.04.

Freundlich equilibrium distribution coefficient (K_F) may be considered as a measure of affinity between solute and adsorbent (Murali *et al*, 1983). The degree of affinity of the metals with municipal solid waste is copper > arsenic > chromium; a factor of 10 differentiating between the three metals, at pH5.5. At pH6.4, arsenic >> chromium. At pH7.0, copper ≈ arsenic >> chromium.

TABLE 7.1 CALCULATED RESULTS - FREUNDLICH ADSORPTION ISOTHERMS

Metal	pH	Maximum regression observations available	Utilised number of regression observations	R squared	Freundlich equilibrium distribution coefficient (K_F)	Freundlich power coefficient (M)
Copper	5.5	7	6	0.859	0.21	0.74
Copper	7.0	7	5	0.895	0.11	1.04
Chromium	5.5	7	5	0.911	$35E10^{-3}$	0.58
Chromium	6.4	7	7	0.871	$2.8E10^{-3}$	0.96
Chromium	7.0	7	6	0.943	$3.4E10^{-3}$	0.90
Arsenic	5.5	7	6	0.941	$2.8E10^{-2}$	0.82
Arsenic	6.4	7	6	0.915	$9.7E10^{-2}$	0.40
Arsenic	7.0	7	5	0.760	$12E10^{-2}$	0.40

7.4.3 INITIAL EVALUATION OF ADSORPTION AND DESORPTION OF COPPER, CHROMIUM AND ARSENIC ONTO MUNICIPAL SOLID WASTE

The results from the kinetic trials were first examined to appraise; the degree of variability of the results; the effect of pH, and the degree adsorption and desorption of the metallic ions. adsorption/desorption are shown (Figures 7.40, 7.41 and 7.42). The tabulated results are

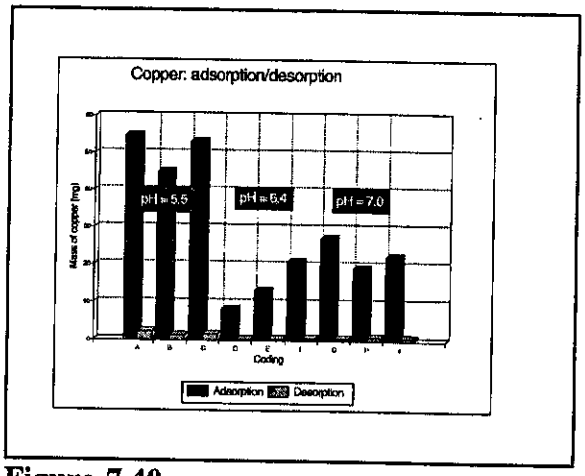

Figure 7.40
Mass of copper adsorped/desorped at pH 5.5, 6,4 and 7.0

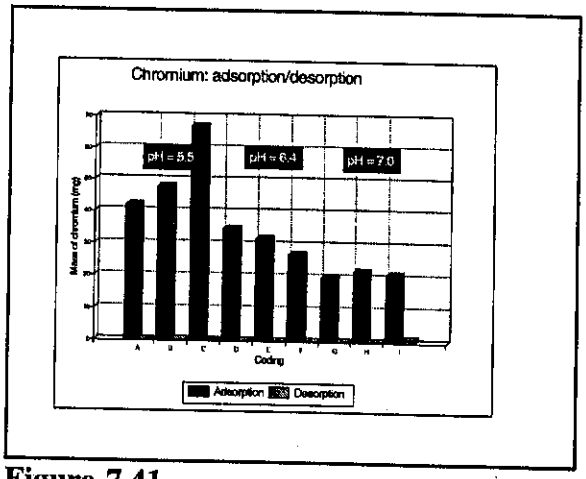

Figure 7.41
Mass of chromium adsorped/desorped at pH 5.5, 6.4 and 7.0

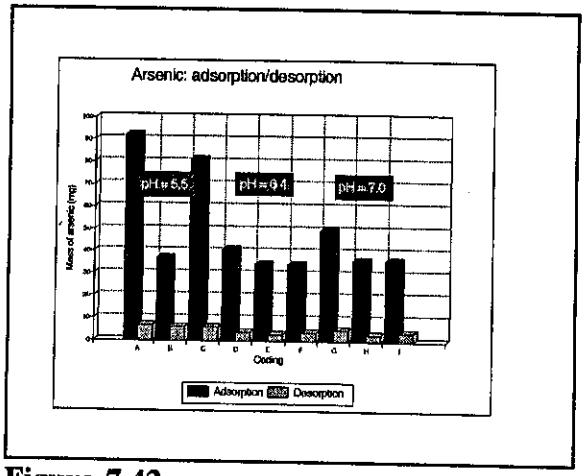

Figure 7.42
Mass of arsenic adsorped/desorped at pH 5.5, 6.4 and 7.0

assembled in Appendix F of Ballard (1997). It can be seen in Figures 7.40, 7.41 and 7.42 there is a degree of variability between samples especially when considering adsorption. This phenomena was not unexpected, municipal solid waste is an extremely heterogeneous solid. This was the primary reason that the kinetic experiments were completed in triplicate at the three pH values. In some cases there is however, a substantial anomaly in results. Considering Figure 7.41, the adsorption of chromium shows a large difference between the three samples designated A, B and C. The initial concentration of chromium in the sample was virtually identical at 263mg (A), 265mg (B) and 263mg (C). Nonetheless, sample C adsorped 70mg of chromium while sample A adsorped 42mg and sample B adsorped 48mg, the latter two exhibiting a similar degree of adsorption. This difference can only be explained by the differing composition of the adsorbent. A similar phenomena is present in Figure 7.42, the adsorption of arsenic at pH7.0 is extremely variable. There is a large difference between the initial arsenic concentrations but a reversal of the observations regarding chromium. Samples A and B with widely differing initial concentrations (225mg and 260mg, respectively) show a similar degree of adsorption (92mg. and 81mg, respectively). Sample B with an initial arsenic solution concentration of 231mg only adsorbs 37mg.

The effect of pH upon adsorption does not appear significant. Initial solute concentration is the primary variable. Figures 7.43, 7.44 and 7.45 show the effect of initial concentration on mass of solute adsorped. Initial concentration decreases with respect to the y-axis in all three figures. The pH value of that experiment is also shown together with the experimental coding.

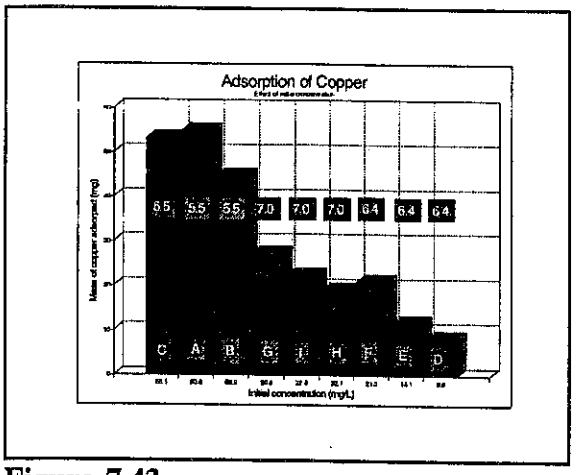

Figure 7.43
Copper adsorption with respect to initial solute concentration

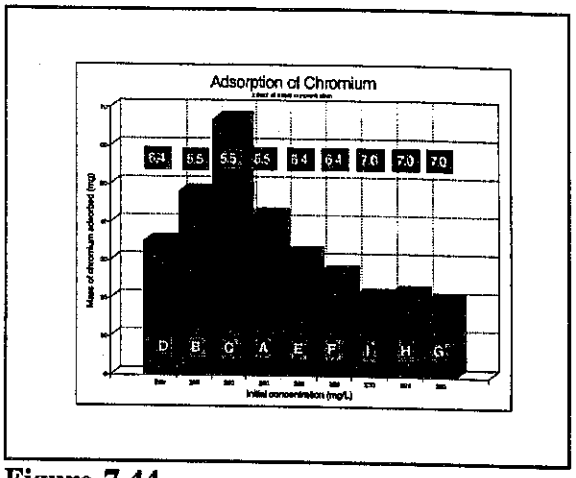

Figure 7.44
Chromium adsorption with respect to initial solute concentration

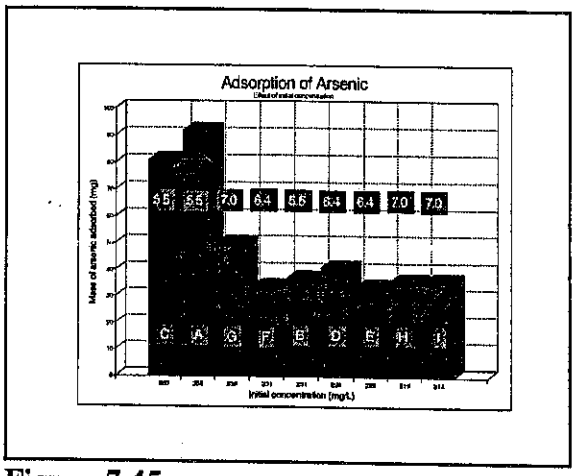

Figure 7.45
Adsorption of arsenic with respect to initial solute concentration

High rates of adsorption occur for copper at low pH levels (Figure 7.43) as a result of the experimental method (Section 7.4.3). Before commencement of the kinetic trials the pH of the solution was adjusted, after the addition of the metals to the solution. This allowed any precipitation to occur prior to evaluating adsorption. Therefore, at lower pH levels higher levels of copper were present due to solubility constraints. Lower adsorption rates for both chromium and arsenic appear to occur because the initial concentration of those metals was higher at the lower pH level. Again this may be attributed to the experimental method. When adjusting the pH precipitating copper entrained both chromium and arsenic resulting in lower concentrations of copper and arsenic at time zero of the kinetic trials. This may be seen in Appendix B, Table B-4 of Ballard, (1997). In all cases the original concentration (prior to pH adjustment) of chromium was approximately 270mgℓ^{-1} and between 270 and 280mgℓ^{-1} of arsenic. It may be clearly seen in the figures the initial concentration of both chromium and arsenic is substantially lower at the higher pH values. The effect of pH upon solute adsorption is further examined in Chapter 8.

The table below shows average values of adsorption and desorption at the various pH values for the three metals under consideration.

TABLE 7.2 COMPARISON OF MASS OF COPPER, CHROMIUM AND ARSENIC ADSORBED AND DESORBED AT PH 5.5, 6.4 AND 7.0

Metal	pH	Average Mass sorbed (mg)	Average Mass desorbed (mg)	Percentage of metal adsorbed that is desorbed
Copper	5.5	50.9	1.7	3.3
	6.4	14.1	0.5	3.5
	7.0	23.0	0.8	3.5
Chromium	5.5	53	0.2	0.4
	6.4	31	0.2	0.6
	7.0	21	0.5	2.4
Arsenic	5.5	70	6	8.6
	6.4	36	4	11.1
	7.0	41	4	9.8

The desorption of chromium was insignificant, the desorption of copper was less than 4 percent of that adsorped. Arsenic desorption was more significant, it did however, average less than 10 percent of the arsenic adsorped.

Analytical considerations of the method of analysis are of importance when appraising results at relatively low concentrations. The method of arsenic analysis employed to analysis of the leachate samples was hydride generation. Hydride generation is an extremely sensitive method allowing measurement in the parts per billion range. The limit of detection is $2\mu g\ell^{-1}$, accuracy is estimated at approximately 92 percent, within the optimum working range. This method was not available for analysis of the samples taken during the kinetic trials. The only analytical method available was flame atomic adsorption where the optimum working range was 50 - $200mg\ell^{-1}$, the sensitivity within the optimum range being $0.78mg\ell^{-1}$. This method was suitable for adsorption studies as the samples could be diluted to within the optimum range. However, at low concentrations (such as those experienced in the desorption trials) the degree of accuracy of the determination of arsenic can only allow the results to be utilised to examine trends. Calculation of kinetic constants from these results would be inaccurate. Levels of desorption were relatively low, especially in the case of copper and chromium, the kinetics of desorption were not investigated further, and attention was limited to the adsorption kinetics.

7.4.4 KINETICS CALCULATIONS

The rate of adsorption of all the metals onto the municipal solid waste was initially rapid and decreased with prolonged reaction time. The results from the kinetics experiments were examined extensively. An array of kinetic equations including zero-, first-, and second order and fractional power, were examined and found to be unsuccessful in describing the adsorption of the metallic ions on municipal solid waste. Attention was then directed to reversible orders of reaction. These were equally unsuccessful. A two-constant rate equation was found to be effective in describing the rate of metallic cation adsorption. Kuo and Lotse (1974) developed the two-constant equation to study the kinetics of phosphate sorption and desorption on hematite and gibbsite. The kinetic equation was developed by inserting a time-dependent expression into the Freundlich equation. The modified Freundlich equation used was in the form;

$$q = K_a C_o t^{1/m} \qquad 4.3$$

where,

q	=	metal adsorped per unit weight of solid (mg)
K_a	=	sorption rate coefficient (h^{-1})
C_o	=	initial metal concentration ($mg\ell^{-1}$)
t	=	reaction time (h)
1/m	=	constant

The results from the kinetic experiments were analysed in the manner shown below.

(a) Method of Kinetic data examination

Initially, a logarithmic plot of chromium adsorped (mg) versus time (h) was constructed. This logarithmic plot was then examined for any erroneous data points (see section (a) below). Erroneous data points were then eliminated and the remaining results were examined by means of regression analysis. Regression analysis principally supplied the following information:

Constant, or y-axis intercept of the regression;
R squared, or variance of the model;
X Coefficient (gradient of the linearised data).

Data generated by the regression analysis was then employed as shown.

$$q = K_a C_o t^{1/m}$$

Taking natural logarithms of both sides of the equation

$$\ln(q) = (1/m)\ln(t) + \ln(K_a C_o)$$

Plotting ln(q) versus ln(t):

(1/m)	=	X Coefficient
$\ln(K_a C_o)$	=	Constant, or y-axis intercept of the regression

The value of C_o, the initial concentration of the metal in solution is known, this allows the calculation of the sorption rate coefficient, K_a.

A plot was then prepared of the actual mass of metal sorbed (mg) and the calculated mass sorbed(mg) versus time (h), utilising all of the reported data (i.e. data points were not rejected). This plot allows the visual examination between the experimental data and that calculated from the regression analysis. To determine the degree of agreement between the measured data and the calculated data, the standard error of estimate (SE) was calculated (Steel and Torrie, 1960).

The standard error of estimate is defined as:

$$SE = [\sum (C_m - C_c)^2/(n-2)]^{1/2}.$$

Where,

C_m = measured metal sorbed by the soil at time, *t*
C_c = calculated metal sorbed by the soil at time, *t*
n = number of measurements

The lower the SE values the better the particular values calculated for the modified Freundlich equation describe the kinetics of the sorption of the metallic ions.

(b) Significance and rejection of experimental data

The method of data analysis described above, was repeated in an iterative manner. Where any doubt existed regarding the choice of any possible erroneous data points in the initial logarithmic plot, the logarithmic plot was then re-constructed releasing those of doubt and reinserting those initially disregarded. The SE was then recalculated again using all eight of the data points to ensure, ultimately, the minimum value of SE was obtained, and therefore the best representation of the experimental data.

To illustrate the method of kinetic data the analysis of chromium at pH7.0 is shown below (i.e. Chromium H).

TABLE 7.3 ADSORPTION OF CHROMIUM AT PH7.0 (CHROMIUM H)

Time (h)	Chromium concentration ($mg\ell^{-1}$)	Chromium sorbed (mg)	Ln (sorbed)	Ln (Time)
0.0	224	0		
0.5	212	12	2.485	-0.693
1.0	213	11	2.398	0.000
2.0	210	14	2.639	0.693
4.0	213	11	2.398	1.386
8.0	208	16	2.773	2.079
16.0	204	20	2.996	2.773
32.0	202	22	3.091	3.466

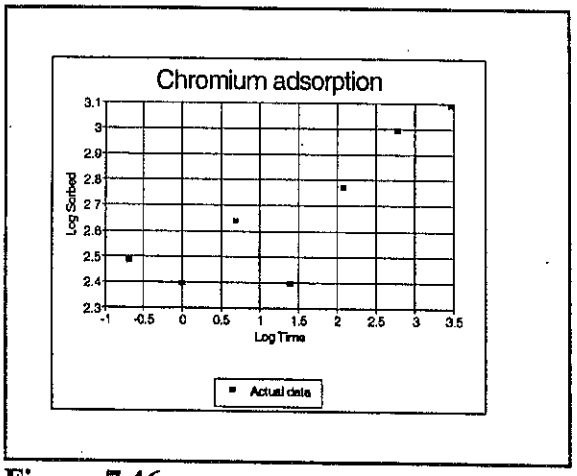

Figure 7.46
Logarithmic plot of measured data: Chromium H

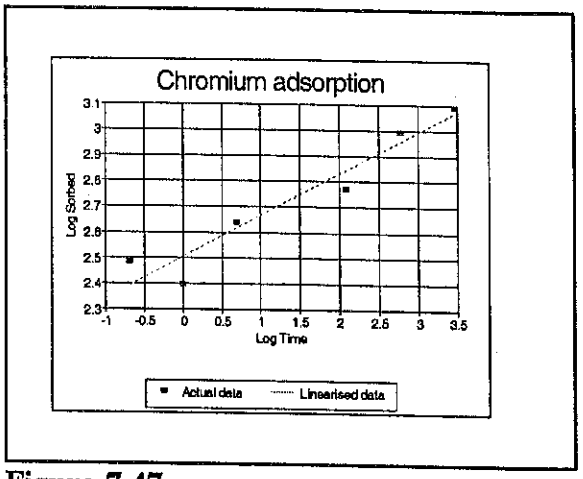

Figure 7.47
Linear regression: Chromium H

Examination of Figure 7.46 it would appear the chromium concentration at time = 4.0h (Log time = 1.386) is erroneous. Examining the remaining results by regression analysis.

Regression Analysis

Constant	=	2.5054
Standard error of Y estimate	=	0.0830
R squared	=	0.928
No. of observations	=	6
Degrees of freedom	=	4
X coefficient	=	0.1622
Standard error of coefficient	=	0.0226

The graphical presentation of these results is shown in Figure 7.44.

Now,				
(1/m)	=	X Coefficient	=	0.162
$\ln(K_a C_o)$	=	Constant, or y-axis intercept of the regression	=	2.5054
As,				
C_o	=	initial metal concentration ($mg\ell^{-1}$)	=	224
Then,				
K_a	=	sorption rate coefficient (h^{-1})	=	0.055

Substituting the measured values into the modified Freundlich equation gives the graphical presentation shown below (Figure 7.48).

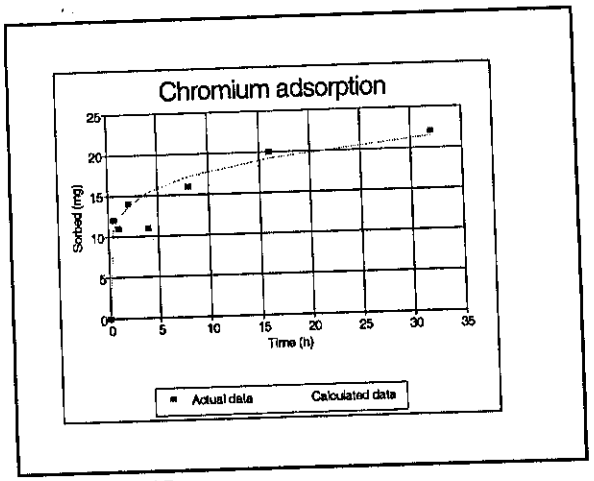

Figure 7.48
Calculated model & actual data: Chromium H

It can be seen by visual inspection the value obtained at time = 4h is probably erroneous. The final step of the analysis is the computation of the standard error, employing all eight data points. This is shown below in Table 7.4. It can be seen there is close agreement between the calculated results and the experimental values, except for the experimental data point at t= 4.0h, confirming that point to be erroneous. That point is the major contributor to the total standard error of 1.99. Graphical representation of all the kinetic trials are shown in Appendix G (Figures G-1 to G-25; of Ballard, 1997), together with details of the regression analysis (Tables G-1 to G-3).

Experimental data together with the modeled data for copper at all pH values is shown in Figures G-1 to G-8 of Ballard (1997). Visual examination, reveals in all cases, the adsorption rate of copper is extremely rapid, the rate of adsorption decreasing with time.

TABLE 7.4 STANDARD ERROR OF ESTIMATE (SE): CHROMIUM H

Time (h)	Measured chromium sorbed (mg)	Calculated chromium sorbed (mg)	SE
0	0	0	0.00
0.5	12	11	0.19
1.0	11	12	0.26
2.0	14	14	0.01
4.0	11	15	3.13
8.0	16	17	0.22
16.0	20	19	0.11
32.0	22	21	0.04
	SE =	square root of total =	1.99

Overall, the fit of the model to the experimental data is good, the experimental data points deviating from the model do not exhibit any trend in the manner of their deviation. The adsorption rate of chromium also has characteristic curve at all pH values (Figures G-9 to G-17; of Ballard, 1997). The initial rate of adsorption is slower than copper, absorption still continuing at extended time. For chromium adsorption at pH5.5 (Figures G-9 to G-11) the model under predicts, and for two (of the three) cases at pH6.4 (Figures G-13 and G-14). At pH7.0 (Figures G-15 to G-17) the model is well behaved. The adsorption rate of arsenic displays similar characteristics to that of chromium (Figures G-18 to G-25). There is again a slight tendency to over predict though this is in most cases near the degree of accuracy of the analytical method employed (see section 7.4.3). Again, as with copper, the experimental data points deviating from the model do not exhibit any trend in the manner of their deviation.

Table 7.5 tabulates the various calculated values obtained for the kinetic trials.

TABLE 7.5 CALCULATED RESULTS - KINETIC EXPERIMENTS

Coding	pH	Initial concentration [C_o] ($mg\ell^{-1}$)	Sorption rate coefficient [K_a] (h^{-1})	Constant [1/m]	Standard Error [SE]
Copper A	5.5	63.6	0.722	0.055	2.93
Copper B	5.5	53.2	0.677	0.063	3.95
Copper C	5.5	65.1	0.668	0.068	2.37
Copper D	6.4	9.6	0.629	0.096	0.92
Copper E	6.4	14.4	0.817	0.061	1.40
Copper F	6.4	21.3	0.766	0.081	1.00
Copper H	7.0	22.1	0.738	0.059	1.02
Copper I	7.0	27.4	0.825	0.064	2.74
Chromium A	5.5	263	0.080	0.182	5.93
Chromium B	5.5	265	0.076	0.237	4.98
Chromium C	5.5	263	0.096	0.243	7.18
Chromium D	6.4	269	0.057	0.252	5.55
Chromium E	6.4	262	0.065	0.152	3.07
Chromium F	6.4	259	0.051	0.189	2.03
Chromium G	7.0	223	0.062	0.099	2.59
Chromium H	7.0	224	0.055	0.162	1.99
Chromium I	7.0	230	0.057	0.162	2.58
Arsenic A	5.5	255	0.199	0.157	5.32
Arsenic C	5.5	260	0.107	0.347	8.84
Arsenic D	6.4	228	0.099	0.166	6.83
Arsenic E	6.4	225	0.096	0.138	10.33
Arsenic F	6.4	231	0.090	0.155	3.77
Arsenic G	7.0	238	0.167	0.089	6.48
Arsenic H	7.0	219	0.090	0.185	3.32
Arsenic I	7.0	214	0.101	0.149	6.38

7.4.5 LITHIUM SULPHATE PULSE EXPERIMENT

As mentioned in Section 6.3.2, leachate was sampled and recirculated approximately every 7 days. The time taken to displace the lithium from the column was 317 days. The experimental results are shown in Appendix D of Ballard (1997). The volumetric displacement of leachate from the column varied, and additionally, on occasion, sampling and recirculation could not be effected on the correct day. The conventional graphical representation and subsequent mathematical analysis of results of this nature is in terms of concentration-time, because of the variation in both volumetric displacement and on occasion, time increments, it was found to be more consistent to evaluate the data in discrete time increments, the mass of lithium discharged in the leachate being employed in the calculations. Utilising the concentration term would not make allowance for the variance in effluent volumetric displacement, and the differing time increment.

Firstly, the response curve of mass(m) versus time (t) was constructed (Figure 7.28). The area under the curve, the mean of the curve, and the variance are then evaluated with the formulae shown below. To maximise the accuracy of these calculations, the number of increments conformed to the number of measurements taken experimentally.
In terms of mass;

$$\text{Area under the curve} = \int_0^\infty m\,dt = \sum_0^\infty m_i \Delta t_i$$

$$\text{Mean of the curve } (\bar{t}) = \int_0^\infty t\,m\,dt \Big/ \int_0^\infty m\,dt$$

$$= \sum m_i t_i \Delta t_i \Big/ \sum m_i \Delta t_i$$

$$\text{Variance } (\sigma^2) = \left(\int_0^\infty t^2\,m\,dt \Big/ \int_0^\infty m\,dt\right) - \bar{t}^2$$

$$= \left(\sum m_i t_i^2 \Delta t_i \Big/ \sum m_i \Delta t_i\right) - \bar{t}^2$$

The calculated results should be then evaluated for consistency, by use of material balance computations. The equations are shown below.

$$\text{Area under the curve} = M/v \quad \text{(in terms concentration units)}$$

$$\text{Mean of the curve} = \bar{t} = V/v$$

Where,

M	=	mass of tracer added
v	=	volumetric flowrate (volume per unit time)
V	=	volume available for flow

Observation of the mass-time graph (Figure 7.28) reveal the graph to be consistent. The tabulated calculations for the evaluation of the area under the curve, the mean of the curve, and the variance are assembled in Appendix H of Ballard (1997).

(a) Graphical data

The calculations are shown in Appendix H, Table H-1 0f Ballard (1997).

Area under the curve = $\sum m_i \Delta t_i$ = 6709.1 mg day

Mean of the curve ($\bar{t}$) = $\sum m_i t_i \Delta t_i / \sum m_i \Delta t_i$ = 759738.6/6709.1
= 113.2 days

Variance (σ^2) = $(\sum m_i t_i^2 \Delta t_i / \sum m_i \Delta t_i) - \bar{t}^2$
= $(108428295/6709.1) - (113.2)^2$
= 3338

(b) Evaluation for consistency

Area under the curve = M/v (in terms of concentration units)

Mean of the curve = $\bar{t}$ = V/v

The concentration-time graphical representation was not employed in these calculations as discussed previously (Section 7.3.2); both time and volume increments were irregular. The area under the curve for concentration-time could not be calculated directly. Also the experimentally obtained mean of the curve could not be compared with the calculated value using the formula shown above. The actual volume available for flow within the packed bed of municipal solid waste cannot be determined as the solid waste is itself permeable. There is however a further means of evaluating consistency, the mass of tracer recovered may be compared with that initially added.

Mass of tracer added = 1026.7 mg
Mass of tracer recovered = 954.3 mg

Percent recovery = 92.95

The degree of recovery of the lithium sulphate tracer is satisfactory, showing the choice of tracer to be correct, and analytical methods to be adequate.

(c) Construction of the E(t) and E curve

The **E**(t) curve is constructed by use of the mass-time data. The area under the curve must equal unity. The mass of lithium in the liquid outlet is divided by the area under mass-time curve; the y-axis is still in units of real time. The **E** curve is then transposed from the **E**(t) curve. The **E** term (y-axis) is computed by multiplying **E**(t) by the mean of the mass-time curve($\bar{t}$). The dimensionless time function (x-axis) is computed by dividing the real time values(t) by the mean of the concentration-time curve($\bar{t}$). Again, the area under the curve must equal unity. The calculated data are assembled in Appendix H, Table H-2 of Ballard

(1997); the graphical representations are shown below (Figures 7.49 and 7.50).

The mean of the curve was calculated to be 113.2 days, this is conveniently represented on the E curve (Figure 6.50) as "1" on the reduced time x-axis. It can be seen the mean residence time in the column is displaced from the maximum value attained for "E". This phenomena is a sure indication of preferential areas of fluid flow (channelling) within the column.

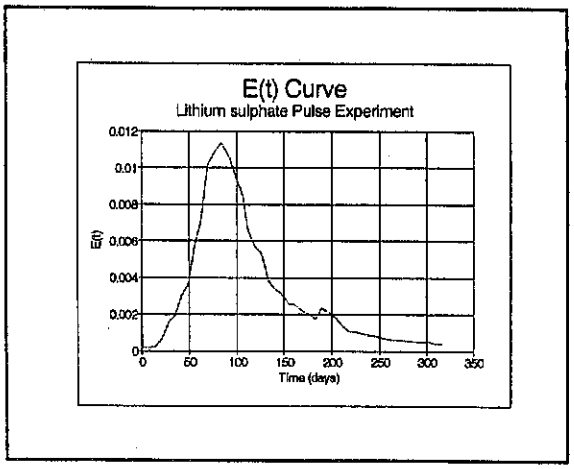

Figure 7.49
E(t) curve: Column 4

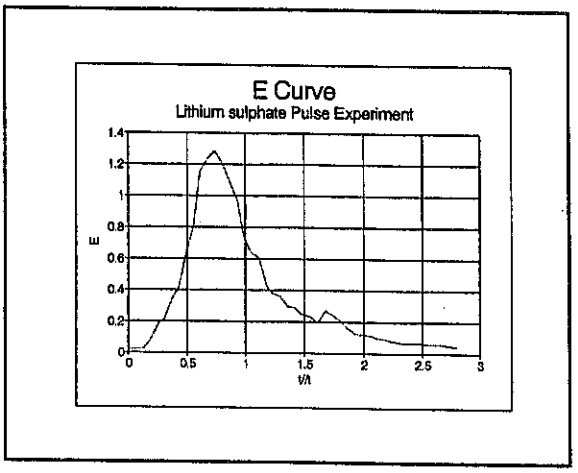

Figure 7.50
E curve: Column 4

The elongation of the base of the curve when compared with the usual thin spike expected for plug flow, is a visual representation of the high value of the variance obtained ($\sigma^2 = 3338$). This can be caused by many different flow phenomena, the consequences being either, longitudinal mixing and/or incomplete mixing in the radial direction. A small value of the variance indicates ideal plug flow, the larger the value the greater the deviation from ideality.

7.4.6 PILOT-SCALE CO-DISPOSAL EXPERIMENT

The calculated results from section 7.4.5, together with the kinetic constants calculated in section 7.4.4 are now employed to calculate the concentration of the three metallic ions in the outlet of the leachate from column 3. The analytical results from columns 3 and 5 are similar, but as the co-disposal experiment was marginally longer for column 3 attention is focused upon that column.

(a) Method of transforming residence time distribution data

The results from the lithium sulphate pulse experiment on column 4 are employed to supply residence time distribution data for column 3. This is a reasonable action as:

(i) the municipal solid waste employed in all the columns is from a common source;
(ii) the municipal solid waste was reduced to the same size range;
(iii) the degree of compaction obtained within the columns is similar for all;
(iv) the height of municipal waste is in the columns is virtually identical;
(v) the process of size reduction "homogenised" the municipal solid waste
(vi) the larger mass of municipal solid waste used in the pilot-scale studies (approximately 700kg) versus the 50g utilised in the laboratory scale experiments should minimise differences between individual columns.

However, the volumetric displacement of leachate employed during the tracer study averaged $5.21\ell day^{-1}$ whilst the volumetric displacement of leachate through column 3 averaged $2.75\ell day^{-1}$ therefore the residence time data from column 4 required mathematical manipulation to realise the conditions in column 3. Examining the data, a number of methods to achieve this objective were tried. The most successful was to adjust the number of days to correspond with the smaller volumetric displacement obtained from column 3. This was successful, the volume of liquid flowing in the initial increments i.e. 7 days remained the same but the time duration to obtain that volume was proportionally increased to 13.2 days ($7 \times 5.21/2.75$). This transformation was continued for all the data from the lithium pulse experiment. The characteristic curve is then maintained and no further calculation is required. A similar exercise was performed on the data obtained for the calculation of the mean for column 4, and the variance; new values may then be obtained for column 3. The tabulated calculations for the evaluation of the area under the curve, the mean of the curve, and the variance are assembled in Appendix I of Ballard (1997).

(b) Graphical data

The calculations are shown in Appendix I, Table I-2 (Ballard, 1997).

Area under the curve = $\sum m_i \Delta t_i$ = 12695.7 mg day

Mean of the curve ($\bar{t}$) = $\sum m_i t_i \Delta t_i / \sum m_i \Delta t_i$ = 2720477.6/12695.7

= 214.3 days

Variance (σ^2) = $(\sum m_i t_i^2 \Delta t_i / \sum m_i \Delta t_i) - \bar{t}^2$

= $(734706779/12695.7) - (214.3)^2$

= 11953

The time taken to displace lithium from the experimental system for the tracer study was 317 days. The total residence time is now calculated to be 600 days.

The transformed graphs are shown overleaf (Figures 7.51, 7.52 & 7.53), the calculations are shown in Appendix I, Table I-1 of Ballard (1997). It can be seen in Figures 7.51 to 7.53, that the method of transformation from the larger volumetric displacement in column 4 to the smaller volumetric displacement in column 3, retains the characteristic curve obtained in the

lithium sulphate pulse experiment (Figures 7.28, 7.49 and 7.50). The mathematical transformation extends the base of the curve to accommodate the longer residence time of the lower volumetric displacement.

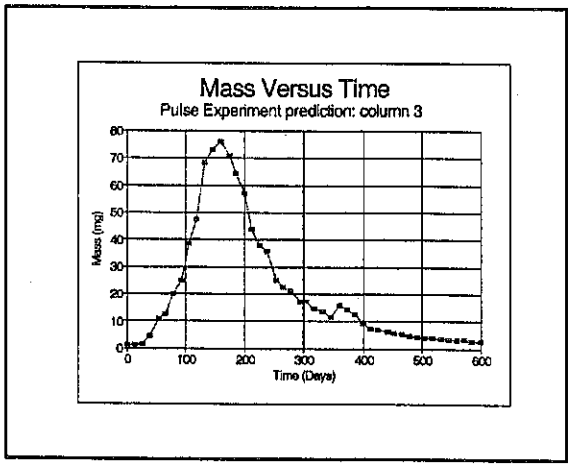

Figure 7.51
Predicted lithium mass versus time relationship for column 3

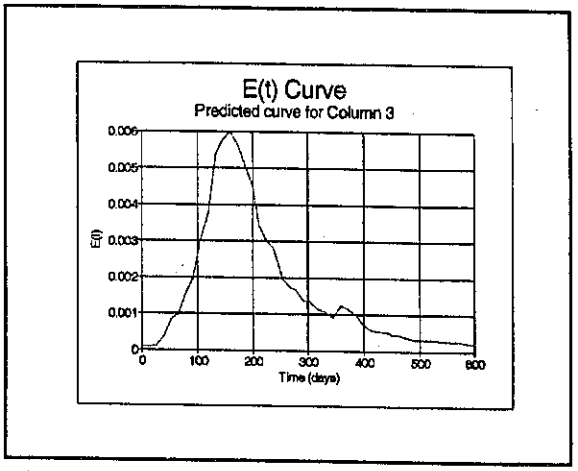

Figure 7.52
Predicted **E**(t) curve for column 3

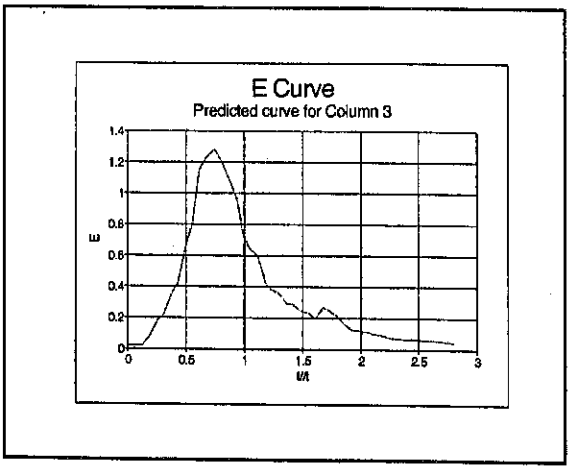

Figure 7.53
Predicted **E** curve for column 3

(c) Calculation of metallic ion concentration in leachate

Two mathematical methods were considered to calculate the concentration of the ions in the liquid effluent from the column. Both use the residence time data as a basis. The **E**(t) curve data allows one to calculate the volume of liquid leaving the column at any time increment during the total time. Both methods are dependent on the manner in which one envisages the liquid to behave in the column. One can view the column as a number of pipes of differing diameter through which the liquid of differing residence times flow, none of the elements of fluid hinder one another, and any metal adsorped does not affect any subsequent liquid of longer residence time.

Another method, is to consider that all the liquid passes through the column in the same path, leaving in its wake adsorped metal which then reduces the capacity of the adsorbate to adsorb metal contained in liquid elements of longer residence time. This adsorbed metal has to be allowed for in the calculation. It would appear probable that at short liquid residence times that the first *scenario* is correct whilst at longer residence times the latter scenario is the more accurate of the two proposed methods. Both methods of calculation were attempted. It was found that the latter method more accurately predicted the behaviour of the metal content in the leachate to the available data obtained from column 3, consequently this method is employed in the subsequent calculations.

The mathematical computation employs a conventional chemical engineering mathematical approach used to solve unsteady state conditions (Section 4.4.4) The calculation is performed incrementally allowing for the differing residence time frames of the various elements of fluid flowing through the column. Each incremental residence time is overlaid upon the previous shorter residence time until the longest residence time is the last time frame to compute.

As the rate of adsorption is initially rapid and decreases with time, the depth increment must be minimised to ensure the calculation accurately reflects the real situation within the column, where the low residence time elements of fluid flow rapidly and will not reach equilibrium with the solid waste. The depth increment was therefore minimised to 20mm. The time increment was also minimised (to ensure accuracy was maximised), to the minimum possible provided by the experimental procedure, approximately 13 days.

The method adopted for the formulation of the copper-chromium-arsenic solution at the various pH values made allowance for precipitation at the relevant pH (section 5.5.1). The solution employed during the kinetic trials was first formulated at a low pH, adjusted to the relevant pH by use of sodium hydroxide, and precipitation allowed to occur. The initial values of the kinetic trials where then the maximum concentration of the metal that would occur at that pH. When the combined copper/chromium/arsenic solution was prepared in the laboratory there was a substantial reduction of the copper in solution from approximately $80mg\ell^{-1}$ to $22mg\ell^{-1}$ due to precipitation. It would appear, that although 88.4g of copper are added, virtually all of this copper would precipitate upon introduction into the column.

With a full scale landfill water can only come from three sources; moisture provided by a precipitation event (rainwater); moisture from deposited solid waste, and moisture produced from anaerobic activity. The major source of moisture is rain water. Rainwater has a negligible alkalinity content and therefore would not raise the pH of the deposited copper solution. Additional rainwater would mobilise any soluble copper present. However, when water is in contact with stabilised municipal solid waste very high levels of alkalinity can be observed. This is evident in the results quoted in this chapter, where the alkalinity approximated $4000mg\ell^{-1}$ (section 7.3.1). It may be concluded that virtually all the copper deposited with municipal solid waste would precipitate as copper hydroxide at or near proximity to its place of deposition. Analytical results confirm these statements.

Extremely low levels of copper were detected in the leachate from columns 3 and 5. Copper concentration in the leachate from column 3 did not exceed $0.11mg\ell^{-1}$. Over the entire period

of monitoring (235 days), the concentration of copper in the leachate from column 3 averaged 0.05mgℓ^{-1}, i.e. no higher than the initial reading at Day zero. The initial concentration of copper in the leachate from column 5 was 0.07mgℓ^{-1} a value that was not exceeded for the entire duration of the experiment. The final copper concentration after 221 days was 0.04mgℓ^{-1}. Over the entire period of monitoring (221 days), the concentration of copper in the leachate from column 3 averaged 0.03mgℓ^{-1}. For these reasons the calculation of copper content was not computed.

The computation to predict chromium concentration employed the results obtained from the laboratory scale kinetic trail designated "chromium H". This outcome of this trial was the lowest standard error of the three trials at pH7.0 (1.99), the approximate pH of leachate exiting the pilot-scale columns. The values employed are:

K_a	=	sorption rate coefficient (day^{-1})	=	0.0916
1/m	=	constant	=	0.1622
Maximum sorption	=	21mg per 50g adsorbate	=	0.42gkg^{-1}

The calculation is shown in Appendix J of Ballard (1997). The predicted concentration of chromium over the total time period of 600 days (Figure 7.54) is extremely interesting, dispelling commonly held views.

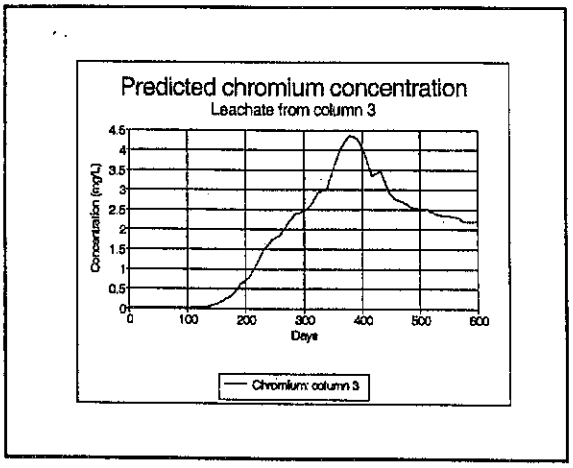

Figure 7.54
Predicted concentration of chromium in leachate from column 3

One would anticipate chromium concentration in the leachate to be initially high, as hydrodynamic factors such as fluid channelling and by-passing would convey chromium through the adsorbent. This does not occur, and the column behaves as a plug flow reactor, albeit a reactor with high degree of non-ideality. The maximum chromium concentration occurs on Day 390 at 4.4mgℓ^{-1} The secondary peak occurring at approximately Day 430 is a product of the smaller secondary peak which occurred in lithium pulse experiment.

For graphical scalar considerations, two figures are presented to illustrate the predictions of the computed model and that achieved in practice. Figure 7.55 shows predicted and actual results until Day 194; Figure 7.56 shows results until cessation of monitoring on Day 235. Considering Figure 7.55, until Day 142 the model realises actual measurements well, with very little deviation. From Day 142 the model begins to overpredict actual conditions. Results from monitoring continue in the region of 0.03mgℓ^{-1} whereas the model begins to predict chromium concentrations in excess of 2mgℓ^{-1} (Figure 7.56) in that time frame.

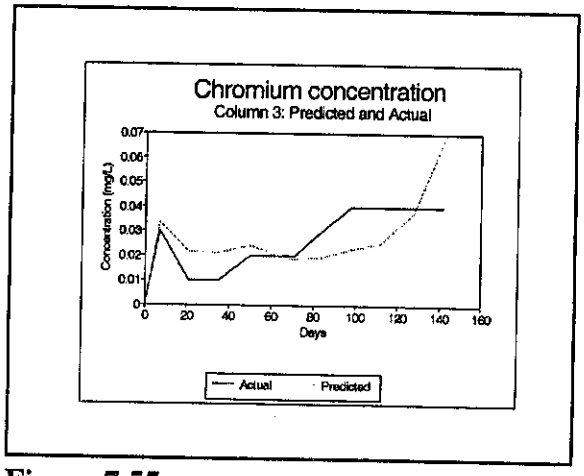

Figure 7.55
Predicted and actual concentration of chromium in leachate from column 3 until day 142

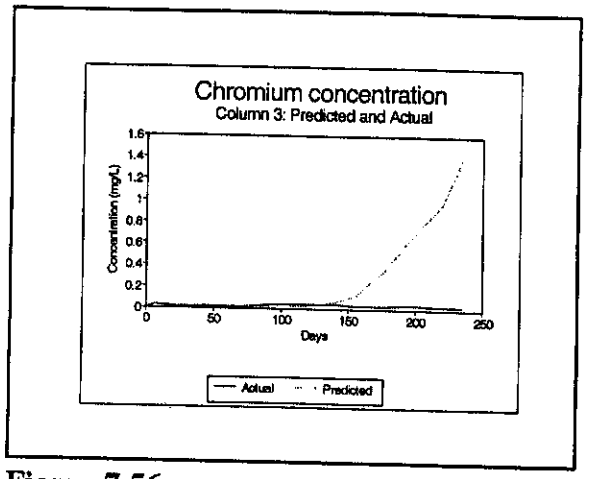

Figure 7.56
Predicted and actual concentration of chromium in leachate from column 3 until day 234

There are three obvious factors to consider:

(i) the affinity for chromium exhibited the solid waste in the pilot-scale landfill columns was not realised in the kinetic trials;

(ii) the method of computation does not model conditions in the pilot-scale columns with sufficient accuracy;

(iii) the transposing of the information obtained from the tracer studies undertaken on column 4 to column 3 could not be supported in practice.

The deviation of predicted values from that achieved in practice is only exhibited after a relatively long period of time has elapsed (160 days). It is therefore unlikely that comments (ii) and (iii) are the major contributory factor. It is probable that factor (i) is appropriate. Soil science researchers, Bartlett and James (1988) document similar occurrences. The drying and storage of soils can alter the surface characteristics of that soil. If this is applicable to soils, a similar analogy can be drawn from municipal solid waste. Another additional factor is the sample size utilised in the kinetic experiments. Only 50g was used, while the pilot-scale columns where packed with approximately 700kg of municipal solid waste. While sampling was exhaustive, solid waste is an extremely heterogeneous substance.

The predicted arsenic concentration employed the results obtained from the laboratory scale kinetic trial designated "arsenic H". This outcome of this trial was the lowest standard error of the three trials at pH7.0 (Section 7.4.4(a)), the approximate pH of leachate exiting the pilot-scale columns. The values employed are:

K_a	=	sorption rate coefficient (day^{-1})	=	0.1613
1/m	=	constant	=	0.1853
Maximum sorption	=	36mg per 50g adsorbate	=	$0.72gkg^{-1}$

The predicted outcome of the co-disposal of arsenic was calculated in the same manner as that of chromium. Calculations predicted there would be an absence of arsenic in the leachate from column 3 during the total time period of 600 days. The results quoted in section 7.3.3(c) showed a maximum arsenical content of the leachate of approximately $2mg\ell^{-1}$. The results from desorption kinetic trials (Section 7.4.3) showed that arsenic was the only metal of those under consideration that displayed any significant degree of desorption. This could not be allowed for in the calculation, and could account for the extremely low degree of error that is evident.

The method of computation allowed the graphical representation of the results in terms of metal saturation with depth and time. These are shown below in Figures 7.57 and 7.58.

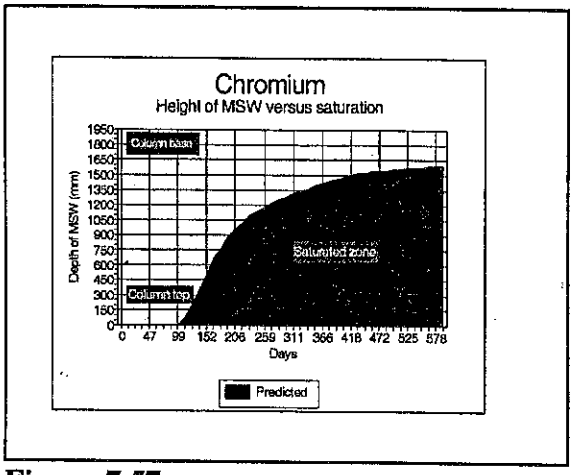

Figure 7.57
Chromium saturation versus column depth

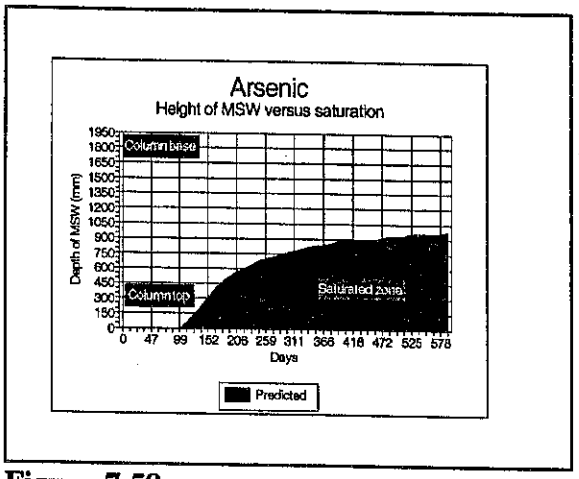

Figure 7.58
Arsenic saturation versus column depth

After 99 days both metals started to reach their equilibrium maximum value in the initial 20mm of municipal solid waste. The total height of municipal solid waste in column 3 was 1940mm. Chromium almost completely saturated the column and further addition of chromium would result in high levels of chromium in leachate. The mass of chromium added to the column was 256.1g. The degree of column saturation is due mainly to the low maximum chromium equilibrium value of 0.42g of chromium per kilogram of municipal solid waste. The final depth of saturation for chromium was 1600mm. The mass of arsenic added was 256.7g. The degree of arsenic saturation is far less than that of chromium reaching only 980mm, approximately half the column depth. The equilibrium saturation concentration is high in comparison with the other metals under consideration, at $0.72gkg^{-1}$. These graphical representations indicate the importance of the maximum saturation value. The rate of reaction is not dissimilar between chromium and arsenic however the high affinity of arsenic to the municipal solid waste results in far less mobility within the column. The mean residence time in the column was computed to be 214 days, at that time chromium 1020mm, and arsenic 600mm.

Analytical results are only available for comparison for the first 235 days of an anticipated 600 day residence time period. In this 235 day time frame the modelled results are an

excellent response to that experienced at pilot-scale. The results for copper cannot be compared as precipitation occurs. Both chromium and arsenic analytical results compare vary favourably with that predicted. There are additional factors to consider. These are discussed in Chapter 8.

7.4.7. APPLICATION OF THE PILOT-SCALE STUDIES TO THE FULL SCALE LANDFILL

In this sub-section the results obtained at pilot-scale are utilised to provide functional data that may be applied by the landfill practitioner. It was decided to employ a worst-case study. The assumptions of this worst-case study are detailed below.

(i) Precipitation occurring in the heaviest precipitation month proceeded to fall on a continual basis;
(ii) no loss of moisture from the landfill, such as evapotransportation or run-off;
(iii) the landfill was at field capacity prior to co-disposal;
(iv) metal content in leachate from the landfill should not exceed the most stringent requirements prescribed by current South African legislation.

The municipal solid waste utilised in this study was excavated from Coastal Park Sanitary Landfill Site (section 5.3). Therefore, to continue with a site-specific study, detailed precipitation data was available and was obtained for the Coastal Park Sanitary Landfill Site for the period 1991 to 1994 (City of Cape Town, 1994). During this period the greatest amount of precipitation occurred during June 1994. Rainfall approximated 290mm. In South Africa, the quality of water discharged into a catchment, where water in that catchment area will be subsequently purified to drinking water quality, is determined by The Water Act, 1956 (Act No. 54 of 1956) (DWA, 1956). The Water Act was originally promulgated in 1956, though there have been many subsequent amendments. The Special Standard (DEAF, 1984) defines the requirements of wastewater or effluent draining into a catchment area. The maximum allowable concentration of copper is $0.02mg\ell^{-1}$; the maximum allowable concentration of chromium is $0.05mg\ell^{-1}$; the maximum allowable concentration of arsenic is $0.1mg\ell^{-1}$.

As shown in section 7.4.6(c), predicted chromium concentration in the leachate from column 3 exceeded analytical measurements ($4.4mg\ell^{-1}$ *versus* $0.03mg\ell^{-1}$). Conversely, predicted arsenic concentration in the leachate from column 3 was exceeded by analytical measurements (zero *versus* $2mg\ell^{-1}$). It would appear reasonable to assume, if predicted chromium concentration is reduced to a maximum of $0.05mg\ell^{-1}$, actual concentration in arsenic in leachate would approximate zero. Attention is therefore focused on leachate chromium concentration.

Firstly, precipitation data were transposed into leachate volumetric displacement.

Maximum rainfall	=	290mm (June 1994)
Landfill column, cross-sectional area	=	$0.25 \times \pi \times 0.7^2$
	=	$0.3848m^2$

Volumetric flow = $0.29 \times 0.3848 \times 1000/30$
= $3.73\ell day^{-1}$

The residence time data obtained from the tracer studies (section 7.3.2) was then transformed in the same manner as reported in section 7.4.6(a). The same exercise was executed for the calculation of mean of the curve and the variance. The transformed graphs are shown below (Figures 7.59; 7.60 and 7.61) together with the calculated values for the mean and variance.

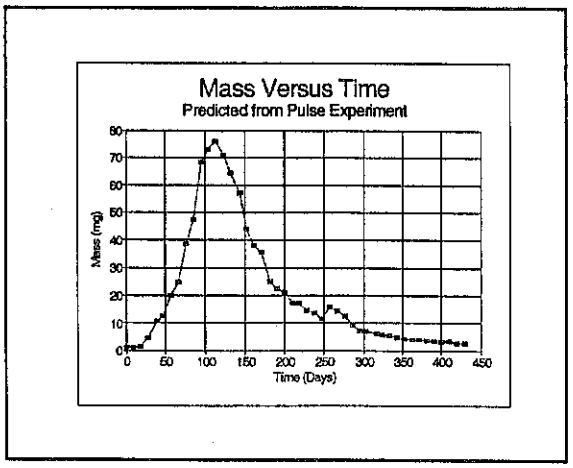

Figure 7.59
Predicted lithium mass versus time relationship: $3.73\ell day^{-1}$

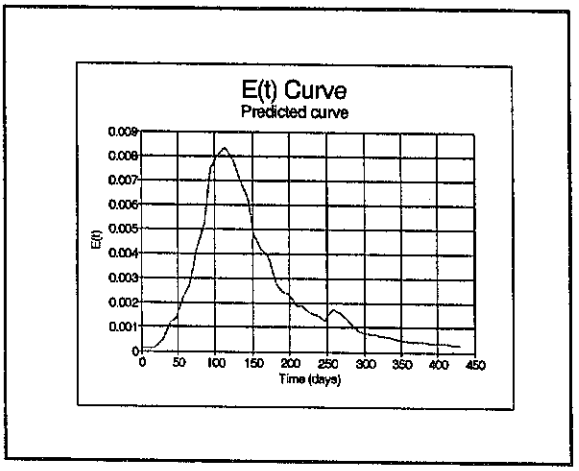

Figure 7.60
Predicted **E**(t) relationship: $3.73\ell day^{-1}$

Mean of the curve ($\bar{t}$) = 153.4days
Variance (σ^2) = 6123

The total residence time for the pilot-scale column at a displacement rate of leachate of $3.73\ell day^{-1}$ is 430 days.

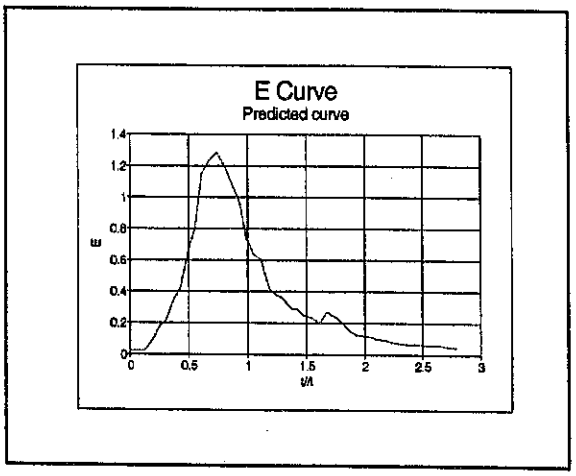

Figure 7.61
Predicted **E** relationship: $3.73\ell day^{-1}$

The computation to predict chromium concentration in leachate employed the same numerical values utilised in 7.4.6(c). The initial mass of chromium co-disposed at pilot-scale in column 3 was 256g. The

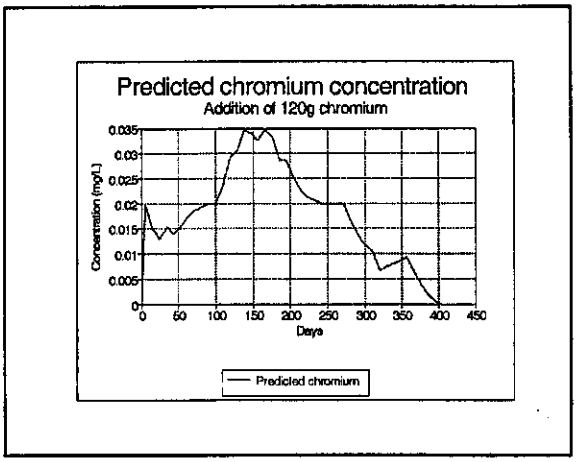

Figure 7.62
Predicted chromium concentration: Assumed addition of 120g of chromium

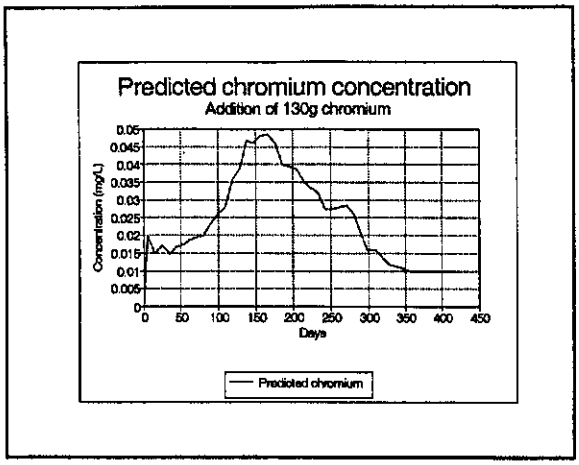

Figure 7.63
Predicted chromium concentration: Assumed addition of 130g of chromium

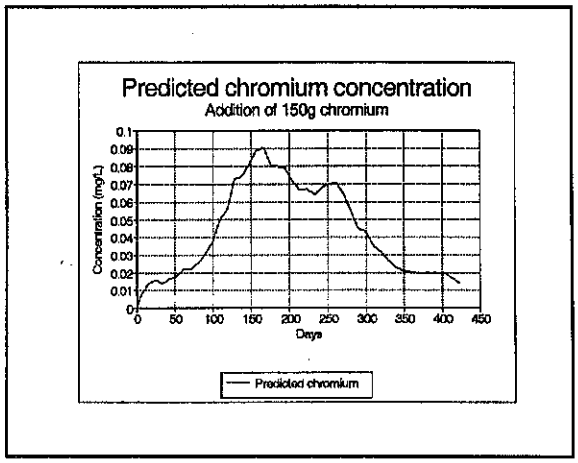

Figure 7.64
Predicted chromium concentration: Assumed addition of 150g of chromium

predicted maximum chromium concentration in leachate was then 4.4mgℓ^{-1}. Therefore, to have a predicted chromium concentration of 0.05mgℓ^{-1} in the leachate, the mass of chromium would have to be far less than 256g. Three modelled calculations were completed; 100g; 120g, and 150g of chromium, being assumed to be added to the column. The graphical representations are shown (Figures 7.62; 7.63 and 7.64). It can be seen that, with the assumed addition of 150g of chromium, predicted leachate chromium concentration reaches a maximum of 0.09mgℓ^{-1} (Figure 7.64) at Day 165. This exceeds the maximum allowable concentration of chromium of 0.05mgℓ^{-1}. With the assumed addition of 100g of chromium, predicted leachate chromium concentration reaches a maximum of 0.035mgℓ^{-1} (Figure 7.62) at Day 165. This concentration is within acceptable limits, but there is sufficient tolerance to add additional chromium. It can be seen from Figure 7.63 the assumed addition of 130g of chromium would result in a predicted chromium concentration of 0.048mgℓ^{-1}. Any further addition of chromium would result in the predicted concentration exceeding the maximum allowable chromium concentration of 0.05mgℓ^{-1}.

The mass of municipal solid waste contained in column 3 was 668kg. The maximum amount of chromium that could be co-disposed with acceptable risk of environmental damage is therefore 195gtonne^{-1}. This chromium would be co-disposed with the proportional amount of arsenic and copper, as dictated by the composition of the CCA solution. The laboratory scale equilibrium and kinetic studies and the pilot-scale co-disposal trials were conducted with the CCA solution. The CCA (Tanalith) solution has been characterised fully in section 5.4.1. The ratio of copper: chromium: arsenic is 1 : 2.9 : 2.9. Therefore, if 195g of chromium were co-disposed with municipal solid waste, there would be 195g of arsenic and 67g of copper associated with that amount of chromium.

7.5 SUMMARY

Adsorption equilibrium studies and kinetic studies were undertaken at laboratory scale, at three pH values; pH5.5, pH6.4, and pH7.0. The adsorbent being municipal solid waste, the adsorbate being copper, chromium and arsenic in aqueous solution. Data obtained at equilibrium was successfully described by the Freundlich Isotherm (section 7.4.2).

The kinetic studies revealed a reaction characterised by an initial rapid adsorption rate, the rate of adsorption subsequently decreasing at larger values of time. This reaction could be successfully described by a modification of the Freundlich equation (section 7.4.4) usually termed, the modified Freundlich equation, or the two-constant equation. The modified Freundlich equation was developed by Kuo and Lotse in 1974.

Tracer studies were undertaken at pilot-scale. The tracer employed was lithium sulphate. Tracer studies revealed (as expected) a system which conformed with a plug flow reactor, albeit with a great deal of non-ideality. Co-disposal experiments were then undertaken at pilot-scale. A solution of copper-chromium-arsenic was added to two of the pilot-scale columns. The effluent from the columns was closely monitored. Conventional chemical engineering reactor design allows the computation of reactor effluent composition from results from tracer studies in combination with kinetic results, together with details of the reactor feed.

The pen-ultimate phase of the investigation comprised of a comparison of the results obtained at pilot-scale with that predicted from the laboratory scale studies. Agreement was good between results obtained at pilot-scale with results predicted from the laboratory scale studies. Predicted chromium concentration in the leachate from column 3 exceeded analytical measurements ($4.4 mg\ell^{-1}$ *versus* $0.03 mg\ell^{-1}$). Actual arsenic concentration in the leachate from column 3 exceeded that predicted ($2 mg\ell^{-1}$ *versus* zero) (section 5.4.6(c)).

The final phase of the project employed the model developed from the laboratory scale results to compute the mass of copper-chromium-arsenic solution that could be added to municipal solid waste. A worst-case study was examined (section 7.4.7). Computation showed it is possible to co-dispose 195g of chromium together with 195g of arsenic and 67g of copper per tonne of municipal solid waste with the minimum of environmental damage to any receiving water body.

7.6 REFERENCES

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CHAPTER 8
DISCUSSION: LABORATORY AND PILOT-SCALE STUDIES

8.1 INTRODUCTION

The results and subsequent calculations generated by the experimental study are examined and discussed in this chapter. The speciation and physical characteristics of the metals are scrutinised. The laboratory scale equilibrium and kinetic studies are examined and a sorption mechanism is proposed. The pilot-scale tracer studies and co-disposal trials are assessed and discussed. The computational method developed to model the pilot-scale studies is appraised and any deficiencies uncovered. The results established at pilot-scale, are applied to the full scale landfill. The effect of the co-disposal of copper, chromium and arsenic in an acetogenic, methanogenic and stabilised landfill assessed.

8.2 SPECIATION OF THE METALS PRESENT IN THE EQUILIBRIUM AND KINETIC TRIALS

It is advantageous to discuss firstly the speciation and the copper, chromium and arsenic under prevailing conditions. Chromium from the CCA wood preservative is present in the form of Chromium(VI), arsenic is in the form of arsenic(V) and copper is in the form of copper(II). Ionic equilibria for copper, chromium and arsenic in an aqueous solution are detailed below, together with their ionic structure in an aqueous medium.

8.2.1 COPPER(II)

The Cu^{2+} ion, at ordinary concentrations, begins to hydrolyse above pH4, and precipitation as the oxide (Cu_2O) or the hydroxide ($Cu(OH)_2$) begins soon after. The hydrated ion has the formula $Cu(H_2O)_6^{2+}$ and has a distorted octahedral structure (Jahn-Teller effect). This is a consequence of its d^9 configuration (Nicholls, 1974). Two of the water molecules are in the trans position, these are further removed from the Cu^{2+} ion than the other four, which are coplanar (Cotton *et al*, 1972). The ionic radii of the copper ion in aqueous solution is 0.87Å. The bond lengths are 1.94Å for the coplanar bonds and 2.4Å for the trans bonding ions (Burgess, 1988). It is important to note that copper is present in aqueous solutions in the form of a cation.

Structural details of the hydrated copper ion are shown in Figure 8.1.

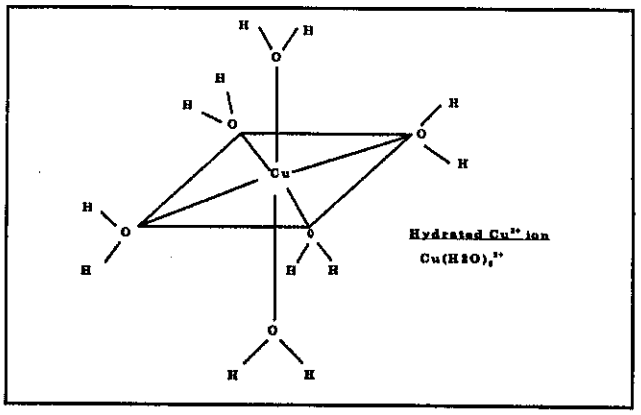

Figure 8.1
Structural details of the hydrated copper ion

8.2.2 CHROMIUM(VI)

Chromium(VI) hydrolyses extensively, so only neutral or anionic species occur in water. The speciation, well established by extensive data are $HCrO_4^-$, CrO_4^{2-}, and $Cr_2O_7^{2-}$. However $Cr_2O_7^{2-}$ is only dominant at chromium(VI) concentrations above 0.01M, in acidic media (Bates *et al*, 1976).

The equilibria for chromium(VI) in aqueous solutions is shown below,

$$H_2CrO_4 + H_2O \rightleftharpoons HCrO_4^- + H_3O^+ \quad pK_a = 0.74$$

$$HCrO_4^- + H_2O \rightleftharpoons CrO_4^{2-} + H_3O^+ \quad pK_a = 6.49$$

CrO_4^- (monohydrogen chromate ion) is the predominant species between pH0.75 and pH6.45, while CrO_4^{2-} (chromate ion) predominates at pH values greater than 6.45. The chromate ion has a tetrahedral structure, with four oxygen atoms bound to a central chromium atom. The mutual repulsion of the four electron clouds direct the oxygen atoms to the corners of an inscribed tetrahedron. Therefore, the monohydrogen chromate ion would have a distorted tetrahedron structure. The ionic radii of the chromium(VI) ion in aqueous solution is approximately 0.63Å. Structural details of the chromate ion are shown in Figure 8.2.

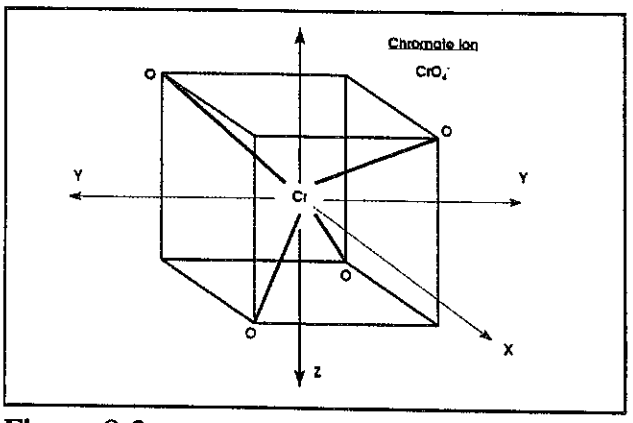

Figure 8.2
Structural details of the chromate ion

Metal to oxygen distances for metal ions in aqueous solutions parallel those obtained for crystal ionic radii and are very similar to those reported for analogous crystal hydrates (Burgess, 1988). This information is relevant. It is difficult to obtain bond lengths for every metal in combination with oxygen in aqueous solutions. The bond length quoted for Cr(III) in aqueous solution by Burgess (1988) is 1.94Å (X-ray diffraction), 1.98Å (EXAFS) and for a crystal hydrate 2.02Å. Wells (1975) quotes the following:

TABLE 8.1 BOND LENGTH: CHROMIUM(III) AND CHROMIUM(VI)

Cr(III) and Cr(VI)	Cr^{III}- 6O (Å)	Cr^{VI}- 4O (Å)
Cr_5O_{12}	1.97	1.65
KCr_3O_8	1.97	1.60
$LiCr_3O_8$	2.05	1.66
$CsCrO_8$	1.96	1.63

It would appear reasonable to estimate the chromium-oxygen bond length in aqueous solution to approximate 1.63Å.

8.2.3 ARSENIC(V)

Arsenic(V) in aqueous solution forms an oxyacid whose properties closely resemble dissolved phosphorous(V), which forms H_3PO_4. The dissociation constants and hence their dissociation

equilibria are extremely similar. The structure of both phosphoric and arsenic acid is better represented by formulas of the type $MO(OH)_2$.

The equilibria for arsenic acid (arsenic(V)) is aqueous solutions is shown below.

$$H_3AsO_4 + H_2O \rightleftharpoons H_2AsO_4^- + H_3O^+ \quad pK_a = 2.25$$

$$H_2AsO_4^- + H_2O \rightleftharpoons H_2AsO_4^{2-} + H_3O^+ \quad pK_a = 6.77$$

$$HAsO_4^{2-} + H_2O \rightleftharpoons AsO_4^{3-} + H_3O^+ \quad pK_a = 11.60$$

$H_2AsO_4^-$ (mono-ortho-arsenate ion) is the predominant species for pH values from 3.6 to 7.3, whereafter $HAsO_4^{2-}$ (di-ortho-arsenate ion) predominates. Arsenic achieves simple tetrahedral structures in the arsenate ion (Cartmell *et al*, 1961) by use of its sp^3 hybrid orbitals. The mutual repulsion of the four electron clouds direct the oxygen atoms to the corners of an inscribed tetrahedron (Toon *et al*, 1973). Therefore, the mono-ortho-arsenate ion and the di-ortho-arsenate ion would have a distorted tetrahedron structure. The ionic radii of the arsenic(V) ion, in aqueous solution, is approximately 0.70Å. Structural details of the arsenate ion are shown in Figure 8.3.

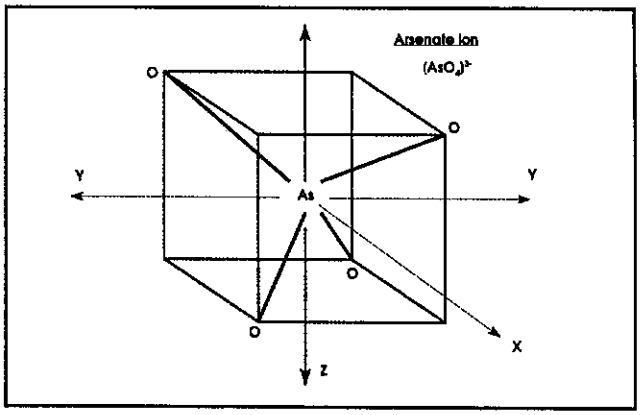

Figure 8.3
Structural details of the arsenate ion

For similar reasons to chromium(VI), the bond lengths relevant to the arsenate ion were not readily available. However, $HAsO_4^-$ has been studied in $(NH_4)HAsO_4$ and $Na_2HAsO_4.7H_2O$ and the bond lengths are As-O; 1.67Å and As-OH; 1.74Å (Wells, 1975).

8.3 ADSORPTION ISOTHERMS

The results obtained from the equilibrium studies were successfully described by the Freundlich isotherm. The Freundlich isotherm results from a consideration of the heterogeneity of the surface, when applied to the adsorption of vapours onto solid surfaces. If adsorption data fit the

equation, it is possible, but not proven, that the surface is heterogeneous (Adamson, 1982). If one considers the adsorbent being municipal solid waste there would appear to little doubt the surface is heterogeneous, and the suitability of the Freundlich isotherm, in this instance, is acceptable.

The numerical values of the constants, in addition to the degree of agreement or variance are shown in Table 8.2 below. The variance (R squared) ranged from 0.760 (arsenic at pH7.0) to 0.943 (chromium at pH7.0). As reported in section 5.7, copper and chromium analysis could be repeated in some instances. That facility was not available for arsenic. This could have affected the value obtained for the variance. As previously mentioned in section 7.4.2, numerical values obtained for the Freundlich constants do not appear to be of great value, and their significance was briefly discussed in that section. They do appear useful for the determination of trends, such as the degree of affinity for a solute for an adsorbent, this is discussed below.

TABLE 8.2 CALCULATED RESULTS - FREUNDLICH ADSORPTION ISOTHERMS

Metal	pH	R squared	Freundlich equilibrium distribution coefficient (K_F)	Freundlich power coefficient (M)
Copper	5.5	0.859	0.21	0.74
Copper	7.0	0.895	0.11	1.04
Chromium	5.5	0.911	$35E10^{-3}$	0.58
Chromium	6.4	0.871	$2.8E10^{-3}$	0.96
Chromium	7.0	0.943	$3.4E10^{-3}$	0.90
Arsenic	5.5	0.941	$2.8E10^{-2}$	0.82
Arsenic	6.4	0.915	$9.7E10^{-2}$	0.40
Arsenic	7.0	0.760	$12E10^{-2}$	0.40

Other forms of isotherms were examined and found unsuitable. However, detailed analysis of the equilibrium data revealed a very strong relationship between initial solute concentration in solution and final solute concentration in solution, irrespective of pH. This is displayed graphically below (Figures 8.4, 8.5 and 8.6).

The degree of agreement for this form of representation was surprising; regression analysis supplied the variance (R squared) and the X coefficient (gradient of the linearised data). These calculated values are shown below in Table 8.3. This form of relationship is not uncommon. The value obtained for the X coefficient allows direct calculation of the equilibrium solute concentration in solution and hence, computation of the mass adsorbed by the adsorbent, over the experimental range of initial solute concentrations (Equation 8.1).

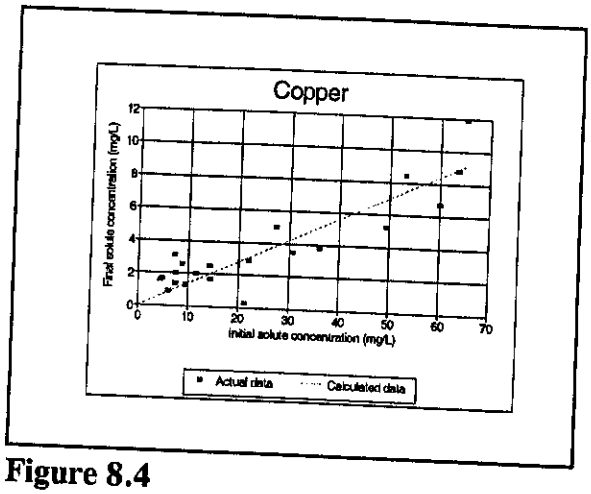

Figure 8.4
Copper: relationship between initial and final solute concentration

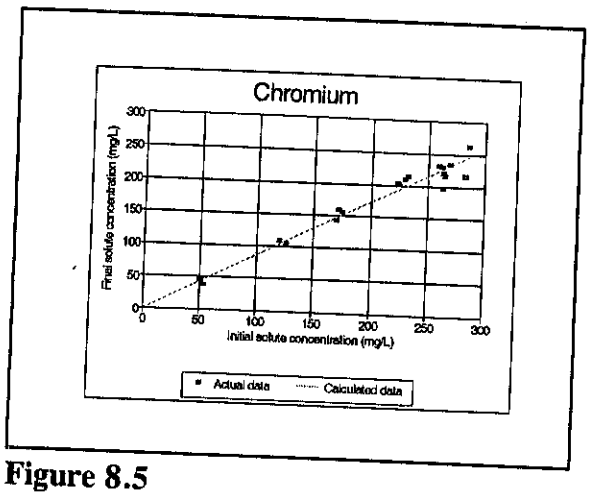

Figure 8.5
Chromium: relationship between initial and final solute concentration

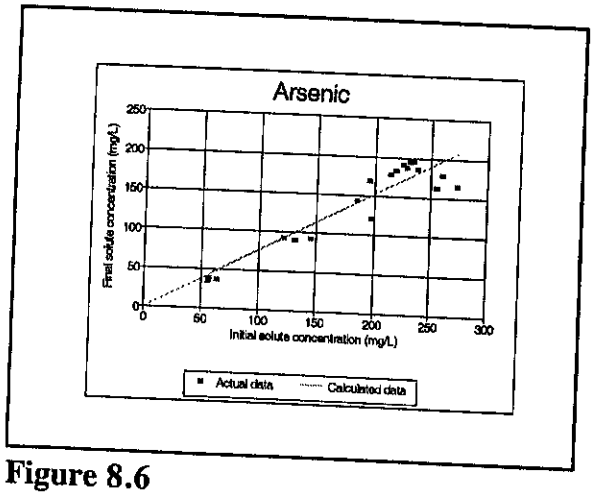

Figure 8.6
Arsenic: relationship between initial and final solute concentration

TABLE 8.3 DETAILS OF REGRESSION ANALYSIS: RELATIONSHIP BETWEEN INITIAL AND FINAL SOLUTE CONCENTRATIONS

Metal	R squared	X coefficient	No. of observations
Copper	0.807	0.140	21
Chromium	0.967	0.862	21
Arsenic	0.884	0.758	21

It is also of importance to examine the values of the X coefficient generated. The relationship can be expressed as shown below:

$$CAe = X.\,CAo \qquad 8.1$$

where,

CAe = Solute concentration at equilibrium
CAo = Initial solute concentration
X = X coefficient or gradient of the linearised data

In this case, the smaller the numerical value for the X coefficient, the greater the degree of affinity of the municipal solid waste to the metal in question. The degree of affinity is therefore; copper (0.140) > arsenic (0.758) > chromium (0.862).

By nature of a comparison, the Freundlich equilibrium distribution coefficient (K_F) may be considered as a measure of affinity between solute and adsorbent (Murali *et al*, 1983). The degree of affinity of the metals with municipal solid waste is copper > arsenic > chromium; a factor of 10 differentiating between the three metals, at pH5.5. At pH6.4, arsenic >> chromium. At pH7.0, copper ≈ arsenic >> chromium. There would appear to be good agreement between the degree of affinity reported by the Freundlich isotherm and the values quoted above. The discrepancy at pH7.0 is probably a result of the poor variance value (0.76) obtained for the Freundlich isotherm for arsenic.

Also evident from Table 8.3 is the *apparent* absence of the influence of pH on equilibrium solute concentrations, in the pH range measured. It is important to note the experimental pH range was narrow, being only 5.5 to 7.0, and the experimental technique adopted in this investigation was not entirely satisfactory to observe this phenomena. Often, the initial concentration of the adsorbing ions was not similar in each experiment trial, also three metals were simultaneously adsorbing from solution.

If a soil is reacted with a series of aqueous solutions with the same initial metal cation concentration but the aqueous solutions having an increasing value of pH, the degree of cationic adsorption will usually increase with increasing pH. A limitation can however be introduced, that of competing ligands in the soil solution. In the absence of competing ligands, a plot of metal cation adsorbed versus pH has a characteristic sigmoid shape known as an "adsorption edge" (Sposito, 1989). Anion adsorption onto soils is characterised by a plot termed an "adsorption envelope", and is a result of changes in the net proton charge on the soil particles, if the adsorptive anion does not protonate significantly. The decrease in hydrogen ion concentration with increasing pH produces a repulsion of the adsorptive anion from the soil particle. Therefore at low pH values, adsorption is high, rising to a maximum, then subsequently decreasing with increasing solution pH (Sposito, 1989).

To observe this adsorption phenomena directly from the analytical results was not possible (the results of the equilibrium studies are shown in Appendix B, Tables B-1, B-2 and B-3) of Ballard (1997). The analytical results are difficult to evaluate, as the initial concentrations differ

significantly for all of the metals, over the pH range. In the case of copper, solubility constraints were experienced. The initial concentration of copper in solution was the major influence on the mass of solute adsorped, and in the case of copper this value was determined by the pH. At pH5.5 copper in solution approximated 60mgℓ^{-1}, while at pH7.0, copper in solution approximated 27mgℓ^{-1}. In two instances in the kinetic trials, the maximum copper in solution at pH6.4 was lower than that at pH7.0. The probable cause of this oddity was the too rapid addition of sodium hydroxide whilst adjusting the pH, causing excess precipitation of copper, an effect of localised high pH. There is another form of representation of the effect of pH on adsorption, that is to evaluate the percentage adsorption with change in pH. This is a less sensitive method of data analysis, but can be used to examine trends. This is shown in Table 8.4. For all the metals under consideration, the highest percentage adsorption was achieved at pH5.5, while the percentage adsorption at pH6.4 and pH7.0 was very similar.

TABLE 8.4 VARIATION OF ADSORPTION WITH pH

Metal	pH	Percent adsorption	Metal	pH	Percent adsorption
Copper	5.5	86.9	Chromium	5.5	21.1
	6.4	78.9		6.4	10.3
	7.0	79.1		7.0	10.4
Arsenic	5.5	34.3			
	6.4	20.6			
	7.0	23.2			

8.4 KINETICS OF ADSORPTION

The kinetics of the adsorption of copper, chromium and arsenic onto municipal solid waste were successfully described by the modified Freundlich equation shown below.

$$q = K_a C_o t^{1/m}$$

where,

Co = initial solute concentration
t = time
K_a = constant
m = constant

The modified Freundlich equation is generally regarded as empirical (Aharoni *et al*, 1991b). However, the commonly used kinetic techniques are based on the assumption that the reactions are either unidirectional or discrete (Harter, 1991). The reaction under consideration involves three metals, themselves relatively complex in nature, reacting with a heterogeneous solid, municipal solid waste. It would seem probable that even if the reaction conformed to one of the simple kinetic orders of reaction it would only be fortuitous rather than an indication of the reaction mechanism. Chemical interactions between the solute and adsorbent may comprise of (Sparks, 1989):

(i) formation or rupture of a bond between sorbate and surface;
(ii) further reaction between adsorbed species; and,
(iii) rearrangements of the solid structure and formation or disappearance of solid species.

Sparks (1989) states that (with soils) it is often incorrect to apply simple kinetic models such as first- or second-order to activated adsorption, as reacting solid surfaces are rarely homogeneous, and because the effects of transport phenomena and chemical reaction are often experimentally inseparable. There would appear no reason why this statement should not equally apply to heterogeneous solids such as municipal solid waste.

The use of mechanistic rate laws to study adsorption phenomena assumes that only chemical kinetics are being studied, any physical aspects are ignored (Skopp, 1986). Most soil reactions of interest to soil scientists are heterogeneous solid-liquid reactions. These reactions usually take place by means of a multi-step mechanism that include mass transfer limitations, as well as chemical reactions (Aharoni *et al*, 1991a). The application of the simple kinetic relationships to complex systems is fraught with problems and caution should be exercised. Sposito discusses transport controlled adsorption kinetics in Chemical equilibria and kinetics in soils (1994) and states that *any surface reaction that involves chemical species in aqueous solution must involve a precursory step in which these species move toward a reactive site in the interfacial region.* He notes that *if the time scale for the transport step is comparable or much longer than that of the chemical reaction, the kinetics of adsorption will reflect transport control, not reaction control.*

Expressions such as the modified Freundlich equation are often successful when applied to various processes involving solid-fluid reactions, although initially developed by researchers investigating solute adsorption on soils. The characteristics of a reaction conforming to the modified Freundlich equation are rapid initial adsorption, the sorption rate decreasing with time. A generalised diagram is shown below.

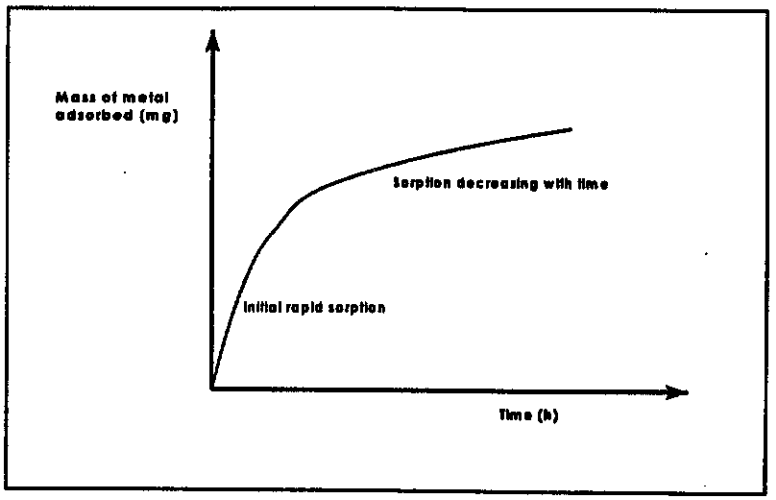

Figure 8.7
Characteristic curve of the modified Freundlich equation

8.4.1 KINETIC RATE CONSTANTS

The kinetic constants (K_a) for copper and chromium are consistent at the various pH values. The rate constants for arsenic show a greater variability. The results for copper and chromium were analysed in duplicate and any discrepancies in results were re-analysed. This ensured accurate reporting of these analytical results. This option was not available when analysing arsenic and probably accounts for the greater variability of the results. Rate constants for copper were the highest, arsenic intermediate, with chromium being the lowest. The relevant results are tabulated below in Table 8.5. Also tabulated is a parameter often reported by researchers; the half reaction time ($0.5t_{total}$). The half reaction time is indicative of the speed of the chemical reaction. It is defined as the time taken for 50 percent of the total reaction to occur. Copper is very strongly adsorbed, as can be seen by the extremely short times calculated for the half reaction time ($0.5t_{total}$). The half reaction times are longer for chromium and arsenic but still average only 1 hour. This method of data analysis is not sensitive. It does, however, provide an indication of the relative speeds of the adsorptive reaction.

A complete summary of the results from the kinetic trials is shown below in Table 8.5 as constant reference is made to these results during this chapter.

TABLE 8.5 SUMMARY OF RESULTS FROM KINETIC TRIALS

Coding	pH	Initial concn. [C_o] ($mg\ell^{-1}$)	Final concn. [Ce] ($mg\ell^{-1}$)	Mass sorbed (mg)	Sorption rate coefficient [K_a] (h^{-1})	Constant [1/m]	SE	Half reaction time [$0.5t_{total}$] (h)
Copper A	5.5	63.6	8.8	55.6	0.722	0.055	2.93	0.0001
Copper B	5.5	53.2	8.4	44.8	0.677	0.063	3.95	0.0000
Copper C	5.5	65.1	11.9	53.2	0.668	0.068	2.37	0.0000
Copper D	6.4	9.6	1.3	8.3	0.629	0.096	0.92	0.0223
Copper E	6.4	14.4	2.5	11.9	0.817	0.061	1.40	0.0000
Copper F	6.4	21.3	0.3	20.7	0.766	0.081	1.00	0.0039
Copper H	7.0	22.1	2.4	19.7	0.738	0.059	1.02	0.0002
Copper I	7.0	27.4	5.0	22.4	0.825	0.064	2.74	0.0000
Chromium A	5.5	263	221	42	0.080	0.182	5.93	0.8
Chromium B	5.5	265	217	48	0.076	0.237	4.98	1.8
Chromium C	5.5	263	196	67	0.096	0.243	7.18	1.8
Chromium D	6.4	269	234	35	0.057	0.252	5.55	1.9
Chromium E	6.4	262	230	32	0.065	0.152	3.07	0.5
Chromium F	6.4	259	232	27	0.051	0.189	2.03	0.9
Chromium G	7.0	223	203	20	0.062	0.099	2.59	0.04
Chromium H	7.0	224	202	22	0.050	0.174	1.99	0.9
Chromium I	7.0	230	209	21	0.057	0.162	2.58	0.4
Arsenic A	5.5	255	163	92	0.199	0.157	5.32	0.5
Arsenic C	5.5	260	179	76	0.107	0.347	8.84	4.3
Arsenic D	6.4	228	187	41	0.055	0.368	6.83	1.1
Arsenic E	6.4	225	191	34	0.024	0.567	10.3	0.4
Arsenic F	6.4	231	197	34	0.090	0.155	3.77	0.3
Arsenic G	7.0	238	186	52	0.167	0.089	6.48	0.01
Arsenic H	7.0	219	183	36	0.090	0.185	3.32	0.6
Arsenic I	7.0	214	178	36	0.070	0.286	6.38	0.6

8.5 RATE OF REACTION: ADDITIONAL CONSIDERATIONS

The modified Freundlich equation is often successful when applied to various processes involving solid-fluid reactions. In the case of soils, kinetic data obtained experimentally often do not conform to the rate laws, but often can be described by some simple semi-empirical equation, such as the modified Freundlich equation. At low values of time, the modified Freundlich equation is frequently germane, at intermediate values of time the Elovich equation is typically applicable, at high values of time the pseudo first-order equation being appropriate (Aharoni *et al*, 1991a).

Adsorption reactions on soils may be classed as slow or rapid. Slow reactions are those in which processes taking place at the solid phase are rate determining (section 4.3.2). These rate determining processes may include: surface diffusion; diffusion in micropores; penetration of the solute into micropores in the solid; diffusion into the bulk of the solid, etc. (Aharoni *et al*, 1991a).

Researchers in the soil science field have examined this phenomena (Aharoni *et al*, 1991b) and have found when processes taking place at the solid phase are rate determining, it is often observed that a plot of the reciprocal of the rate against time is S-shaped, and other semi-empirical equations may be applicable at different reaction times. The phenomena of the S-shaped curve is indicative that reactions at the solid phase are associated with activated diffusional processes, such as surface diffusion or bulk penetration, where chemical bonds are ruptured and formed along the diffusional path.

Analysis of the experimental results indicated the rate of the chemical reaction was determined by activated diffusion processes taking place on the solid phase. Further analysis of the data showed the data conformed to a generalised model indicative of heterogeneous adsorption. This is a process where a solute diffuses in solid media that has different properties.

Consider the modified Freundlich equation, where

$$q = kt^{v} \qquad 3.11$$

Then,

$$Z = (dq/dt)^{-1} = (1/vK)t^{1-v} \qquad 3.14$$

Plots of the reciprocal of the adsorption rate (Z) versus time(t) or q (amount sorbed) versus $\log_e t$, for various soil reactions and other solid-fluid processes are usually S-shaped: convex at small values of time, concave at large values of time, and linear at some intermediate range of time. The generalised expression, S-shaped Z(t) plots may be explained by models based on diffusion. Equations for diffusion in a heterogeneous medium lead to S-shaped Z(t) and q (amount sorbed) versus $\log_e t$ plots in which the intermediate linear part is dominant.

Consider the rate of adsorption of copper onto municipal solid waste at pH7.0, the coding being "copper H" (Figure 8.2). The adsorption of copper is initially extremely rapid. The rate of

reaction slows rapidly as the reaction progresses indicative in this case of diffusion control. Unfortunately measurements ceased after 32 hours therefore the latter part of the S-curve (convex at large values of time) is unavailable. Aharoni *et al* (1991b) reports the modified Freundlich is linear for times less than 50 hours when data is plotted as amount sorbed (q) versus the square root of time ($\sqrt{t}$), after the initial inflexion at low values of time. The linear relationship between the square root of time and mass of solute adsorped is a characteristic of intraparticle diffusion.

Consider the rate of adsorption of chromium onto municipal solid waste at pH6.4, the coding being "chromium D". The adsorption of chromium is rapid, diffusional control is evident by the beginning of the S-shaped curve. Again measurements ceased after 32 hours. Consider the rate of adsorption of arsenic onto municipal solid waste at pH7.0, the coding being "arsenic F". The adsorption of arsenic is rapid, diffusional control is evident by the beginning of the S-shaped curve. As mentioned, equations for diffusion in a heterogeneous medium lead to S-shaped Z(t) and q (amount sorbed) versus $\log_e t$ plots in which the intermediate linear part is dominant. It can be seen the linear part of the curve is dominant in all cases, though more pronounced with chromium and arsenic (Figures 8.11 and 8.13, respectively).

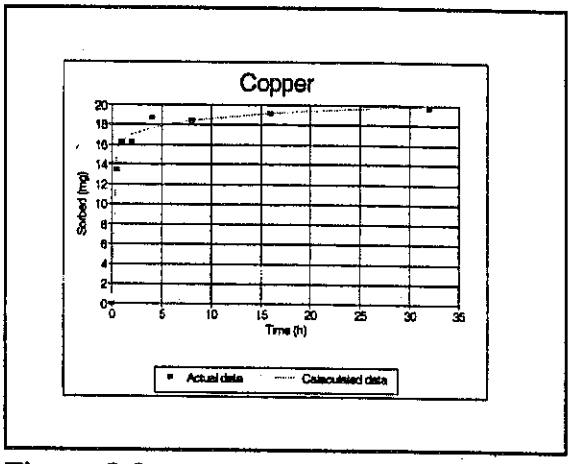

Figure 8.8
Adsorption of copper at pH 7.0 (copper "H")

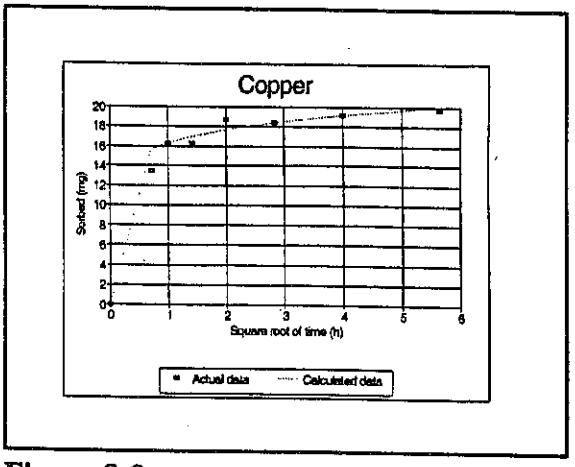

Figure 8.9
Mass of copper adsorbed (mg) versus square root of time (h)

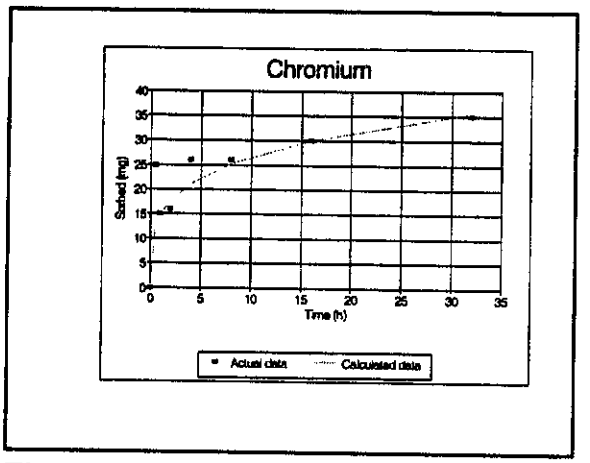

Figure 8.10
Adsorption of chromium at pH 6.4 (chromium "D")

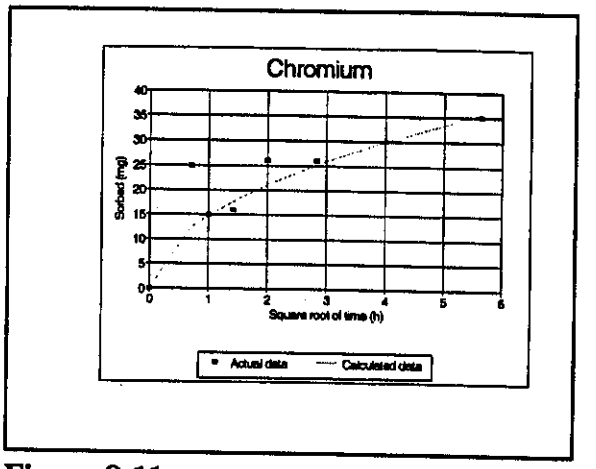

Figure 8.11
Mass of chromium adsorbed (mg) versus the square root of time (h)

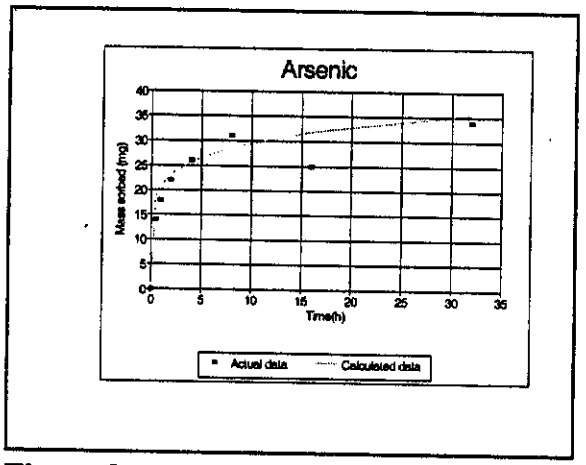

Figure 8.12
Adsorption of arsenic at pH 7.0 (arsenic "F")

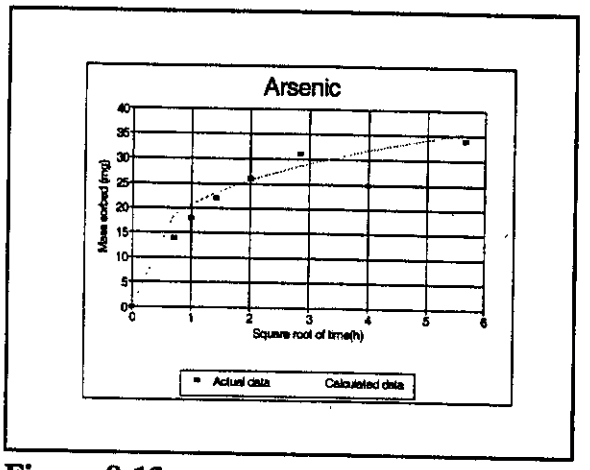

Figure 8.13
Mass of arsenic adsorbed (mg) versus the square root of time (h)

The results of this method of data analysis conformed to a generalised model indicative of heterogeneous adsorption. This confirms the results from the equilibrium studies, where the results obtained were successfully described by the Freundlich isotherm. Adherence to the Freundlich isotherm is generally considered to indicate adsorption onto a heterogeneous surface.

8.6 ADSORPTION RATE

The kinetic experiments were carried out at three pH levels; 5.5, 6.4 and 7.0. These pH values were adopted as they virtually cover the range which can occur in the full size landfill. It is important therefore, to examine the effect of pH on adsorption rate. The quantity of adsorption that occurs at these pH values has been examined in section 8.3. The three modelled fits are shown overleaf for each metal at the relevant pH values.

Adsorption of copper at all three pH values is characterised by a curve that rises sharply to a plateau (Figures 8.14, 8.15 and 8.16). The initial concentration of the solution plays a larger role than one would anticipate, accelerating adsorption rate. This can be immediately observed in Figure 8.14 where copper A and C are identical and copper B is displaced as the initial concentration was lower by $10mg\ell^{-1}$ (see Table 8.5). The characteristic curve is similar at all pH levels investigated. Also, the effect of initial concentration is consistent at the different pH levels. For copper, agreement is good between the different experiments at the same pH.

The characteristic curve depicting the adsorption rate of chromium is more rounded than that of copper, adsorption continuing at a faster rate than that of copper, at higher values of time (Figures 8.17, 8.18 and 8.19). At pH5.5 (Figure 8.17) there is close agreement between chromium A and chromium B, whereas chromium C differs substantially. The lack of agreement is caused by the unusually large degree of adsorption of chromium C when compared with the two other experiments conducted at the same pH. All three trials commenced with the virtually the same initial concentration. On completion of the trial, adsorbent A adsorped 42mg, adsorbent B adsorped 48mg, while adsorbent C adsorped 67mg. This discrepancy can only be attributed to the adsorbent. At pH6.4 (Figure 8.18), the higher the initial chromium concentration, the greater the mass of chromium adsorbed. Chromium initial concentrations were 269mg (D); 262mg (E) and 259mg (F). Chromium adsorbed was 35mg (D); 32mg (E) and 27mg (F). At pH7.0 (Figure 8.16) agreement between experiments is good, with only a slight dispersion at larger values of time. There is only a difference of 2mg between the final equilibrium values.

Arsenic adsorption at pH5.5 (Figure 8.20) gives widely differing characteristic curves. The characteristic curve for the adsorption of arsenic (in general) is similar to that of chromium. Arsenic A is similar to the characteristic curve at other pH values, has a lower standard error (5.32 *versus* 8.84) and is probably more representative than Arsenic C. At pH6.4 (Figure 8.21), agreement is excellent between arsenic E and F with arsenic D again varying at larger values of time. The effect of initial concentration is not evident with arsenic D. Arsenic D has the lowest initial concentration of the three trials (187mg) and shows the largest degree of adsorption (41mg). In comparison, Arsenic E and F initial concentrations were 225mg and 231mg respectively, the mass of arsenic absorbed being 34mg in both cases. At pH7.0 (Figure 8.22) agreement is also good for arsenic adsorption, with the larger initial concentration in experiment G displacing the rate curve.

Another factor to consider is the half reaction time ($0.5t_{total}$) (calculated values are shown in Table 8.5). The half reaction time is indicative of the speed of the chemical reaction. It is defined as the time taken for 50 percent of the total reaction to occur. The half reaction time, in this case, is not a particularly sensitive method of analysis, but it can be seen that the half reaction times did not differ substantially throughout the range of pH values employed. The effect of pH on reaction rate was not significant. The half reaction time for the adsorption of copper is almost instantaneous. For both chromium and arsenic the adsorption rate was slower. It is of interest to examine the experimental trials with the lowest standard error in each pH range. For arsenic the lowest standard error occurs for trials A, F and H. The average half reaction time for these three trials is 0.4h. For chromium the lowest standard error occurs for trials B, F and H; the average half reaction time for these trials is 1.2h.

In evaluating the information above, it is important not to underestimate the initial concentration

of solute in solution when considering the rate of adsorption and the mass of solute adsorbed. This has a radical effect on rate of adsorption. It is also evident that the rate of copper adsorption far outstrips both chromium and arsenic. The rate of adsorption may be categorised in the following order:

copper >> arsenic > chromium

With an heterogeneous adsorbent such as municipal solid waste there is a surprising degree of similarity in the results from the kinetic trials, especially when considering only 50g of solid waste was employed in each separate experiment. It is probable that, if larger sub-samples were employed in the experimental procedure, variances between individual experiments conducted at the same pH value could be minimised.

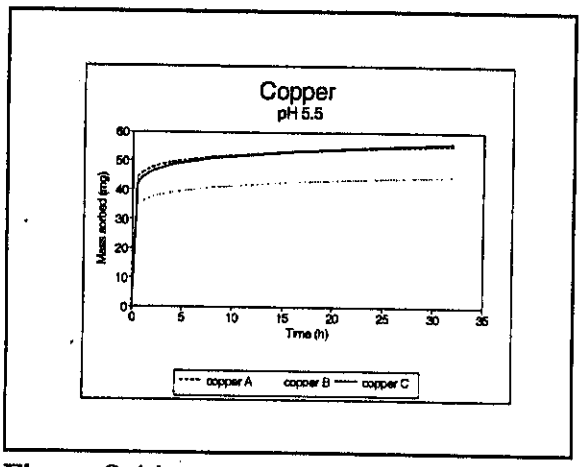

Figure 8.14
Copper: model fit at pH 5.5

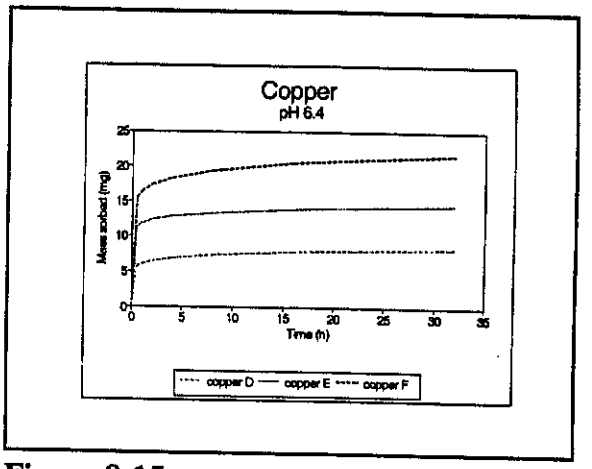

Figure 8.15
Copper: model fit at pH 6.4

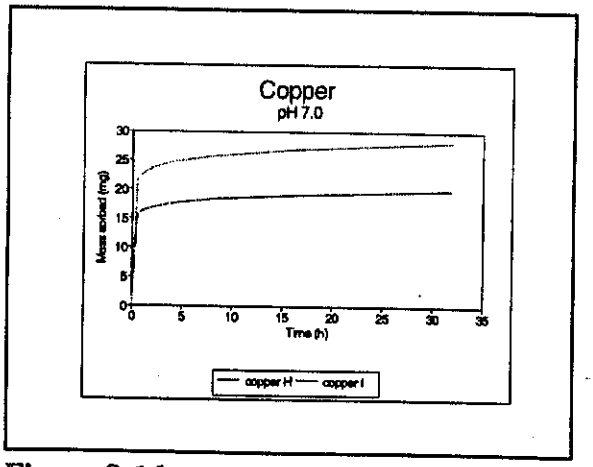

Figure 8.16
Copper: model fit at pH 7.0

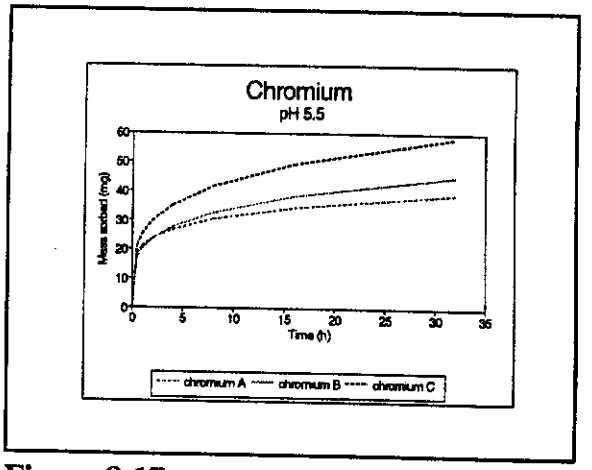

Figure 8.17
Chromium: model fit pH 5.5

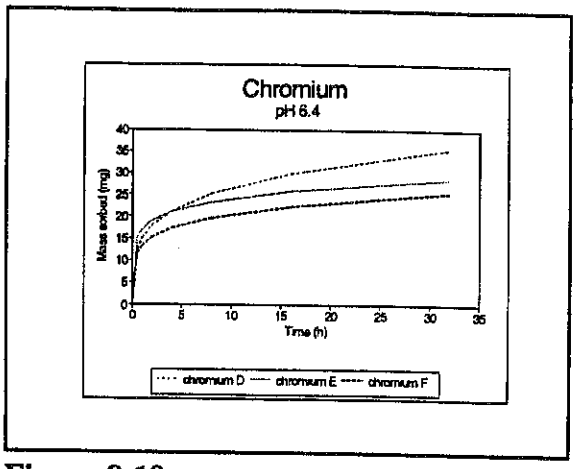

Figure 8.18
Chromium: model fit at pH 6.4

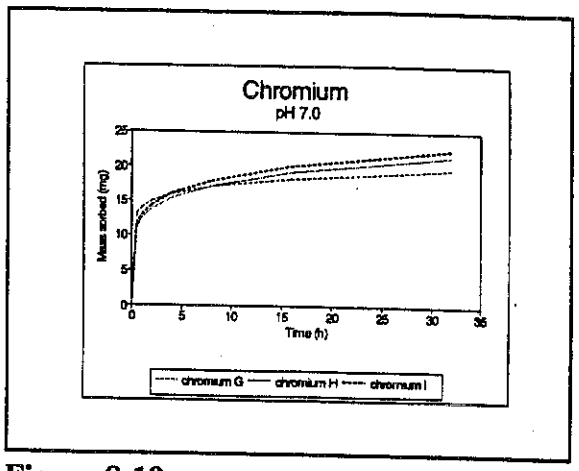

Figure 8.19
Chromium: model fit at pH 7.0

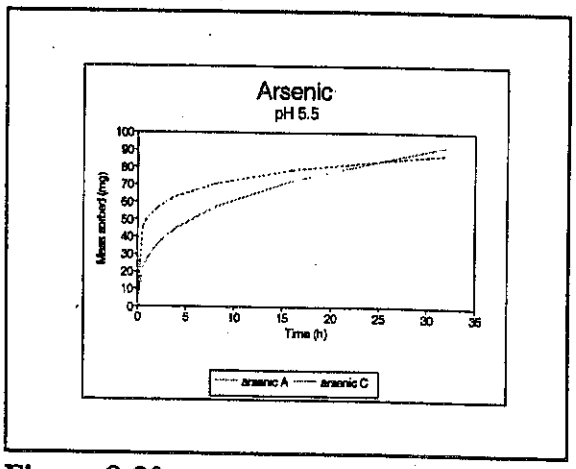

Figure 8.20
Arsenic: model fit at pH 5.5

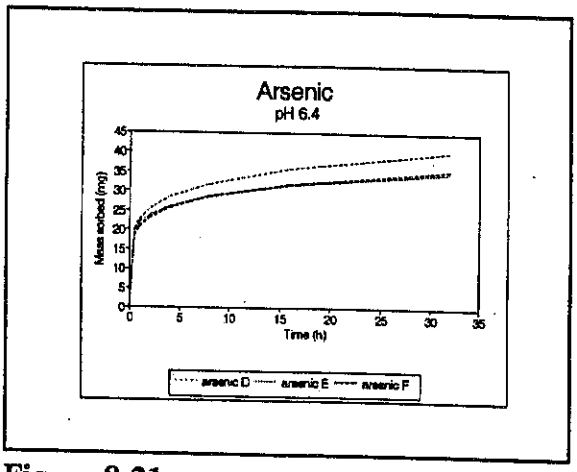

Figure 8.21
Arsenic: model fit at pH 6.4

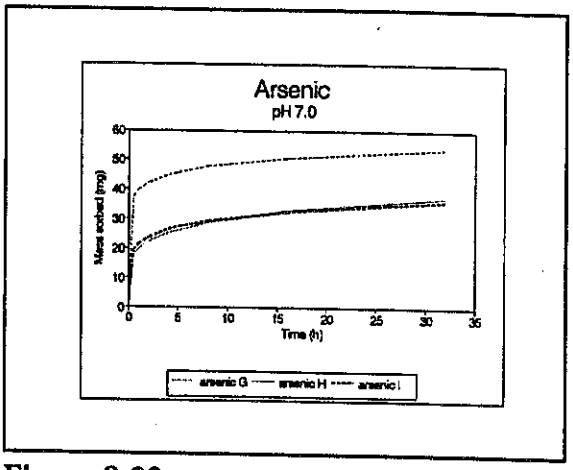

Figure 8.22
Arsenic: model fit at pH 7.0

8.7 ADSORPTION MECHANISM

The following items have been discussed; speciation of metals present, and their physical characteristics; the compliance of the metallic ions to the Freundlich isotherm, and the affinity of the various metallic ions to the adsorbent; the significance of the suitability of the modified Freundlich equation in describing the kinetics of adsorption and the rate of sorption of copper, chromium and arsenic. Information from the preceding sections will now be reviewed with the objective of characterising the solute adsorption mechanism. However, at the outset it should be noted that formulating reaction mechanisms for heterogeneous adsorbents can be tenuous (Harter, 1991). In principle, the requirements to investigate an adsorption mechanism include accurate adsorption data on well defined surfaces from well defined solutions at various temperatures, coupled with reliable thermodynamic data (Parfitt *et al*, 1983). All of the aforementioned are lacking.

In section 8.2 the speciation and size of the metallic ions was scrutinised. Copper is present in the form of a divalent cation. In aqueous solution, in the pH range under consideration, the hydrated ion is present as $Cu(H_2O)_6^{2+}$ and has a distorted octahedral structure. Chromium is present in the hexavalent form. The chromate ion (CrO_4^{2-}) predominates at pH values greater than 8.45. The chromate ion has a tetrahedral structure with four oxygen atoms bound to a central chromium atom. Arsenic is present in the pentavalent form. $H_2AsO_4^-$ (mono-ortho-arsenate ion) is the predominant species for pH values from 3.6 to 7.3. Mono-ortho-arsenate ion has a distorted tetrahedron structure.

In section 8.3 adsorption isotherms were discussed. Two important factors were revealed. Adherence to the Freundlich isotherm is generally considered to indicate adsorption onto a heterogeneous surface. Values obtained for the Freundlich equilibrium distribution coefficient (K_F) may be considered as a measure of affinity between solute and adsorbent. Over the pH range of the laboratory studies, the degree of affinity of the metals with municipal solid waste was copper > arsenic > chromium; this was confirmed by additional graphical analysis.

In section 8.5 the modified Freundlich equation was examined to determine reasons for its success in describing solid-fluid reactions. Researchers in the field of soil science have found the use of the modified Freundlich equation is indicative that reactions at the solid phase are associated with activated diffusional processes. Additional examination showed the data conformed to a generalised model indicative of heterogeneous adsorption. This examination confirmed observations from equilibrium studies, where adherence to the Freundlich isotherm is generally considered to indicate adsorption onto a heterogeneous surface.

In section 8.6 the rate of sorption was studied. It was found that the rate of copper adsorption was extremely rapid, the rate of adsorption of arsenic being intermediate, with chromium adsorption being the slowest of the three metals. The initial concentration of the metal in solution was of importance when examining both the mass of solute adsorbed and the rate of sorption.

The adsorption of small ions is strongly but not exclusively determined by electrical interactions (Lyklema, 1983). However, the relative size of the ions in solutions was investigated. As a first approximation, the presence of the hydrogen ions was neglected, if more stringent calculations

were required (i.e. if the relative size of the ions were close), they would be performed. Additionally, there are undoubtedly hydrogen ions clustered around both the chromate ion and the arsenate ion as in the case of copper ion, in an aqueous solvent. It can be seen below in Table 8.6, the copper ion is far larger than both the chromate and arsenate ions which are of a similar size. Copper is adsorbed far more rapidly than either chromium or arsenic, indicative that the adsorption in this case is determined by electrical interactions, and not the size of the relevant ions. Copper is present in the form of a cation while both chromium and arsenic are in the form of an anion.

TABLE 8.6 COMPARISON OF PHYSICAL DATA OF THE RELEVANT IONS

Ion	Formula	Ionic radii (Å)	Bond length (Å)	relative size to the chromate ion
Copper	$Cu(O)_6^{2+}$ (H ions neglected)	0.87	1.94 (x) 2.40 (y).	2.5
Chromium	CrO_4^{2-}	0.63	1.63.	1.0
Arsenic	AsO_4^{3-}	0.70	1.67	1.1

Unfortunately, a good fit of adsorption data to the less complex linear isotherms, such as the Langmuir or Freundlich isotherm does not in itself constitute any proof of any specific adsorption mechanism. Attempts were made to fit the equilibrium results to the system of isotherm classification, developed by Giles and co-workers (1974a; 1974b); the S, L, H and C isotherms. These isotherms can by used to assist in interpretation of adsorption mechanisms, and much useful information can be obtained. There were insufficient data points to for these isotherms to be properly constructed. However, the significance of the Freundlich isotherm to characterise adsorption onto a heterogeneous surface was reinforced by the applicability of the modified Freundlich equation in section 8.5, where equations for diffusion in a heterogeneous medium lead to S-shaped Z(t) and q (amount sorbed) versus $\log_e t$ plots in which the intermediate linear part is dominant. Also the applicability of the Freundlich power coefficient to determining the affinity of the various solutes to the adsorbent was confirmed by the additional graphical constructions in section 8.3.

In the determination of an adsorption mechanism there are a number of facts to consider, two of which are readily apparent. In aqueous solutions, adsorbents are usually charged as there is always ionic species present and typically there is preferential absorption/desorption of those species. At any solid/aqueous interface adsorption of these ions is the rule rather than the exception. Both the solution and the adsorbent must maintain electronic neutrality. If a cation is adsorped there is either the co-adsorption of an anion or the desorption of a corresponding cation (Lyklema, 1983). As shown in Table 5.5, there was a change in pH in the course of the

experimental procedure during the kinetic trials. The experiments conducted at initial solution pH5.5 furnished a final solution pH of 7.0; the experiments conducted at initial solution pH6.4 provided a final solution pH of 8.0 and the experiments conducted at pH7.0 showed a final pH varying from 8.1 to 8.6. There is an obvious increase in hydroxyl ions during the course of the experiment. This would appear to indicate an exchange of the anions, chromium and arsenic for hydroxyl groups. Lindsay suggested (cited by de Haan *et al*, 1976) that all copper reactions in soil could be summarised by the general equation,

$$Cu^{2+} + \text{soil} \rightleftharpoons \text{Cu-soil} + 2H^{+}.$$

This reaction with the municipal waste would maintain electroneutrality, the corresponding anion exchange between chromium and arsenic for hydroxyl ions would also maintain electroneutrality. Additionally, this postulated reaction mechanism is confirmed by the pH measurements, and the indications that the surface is heterogeneous, allowing hydrogen ions and hydroxyl ions to be present at the solid interface. There is far less copper in solution than either chromium or arsenic. Therefore the pH would rise during the course of the experiment as less hydrogen ions would be exchanged than hydroxyl ions. This analysis would be complimentary to the influence of diffusion. The diffusional influence is caused by the ions diffusing past each other in an effort to get to the surface of the adsorbent, not diffusion of ions into the inner recesses of the solid phase, as would be commonly encountered.

Adsorption of three metallic ions onto a heterogeneous substance such as municipal solid waste is a complex system. To definitively examine the adsorption mechanism is extremely difficult, especially considering the adsorptive medium in conjunction with the metallic ions. However, in the absence of further experimental data the above conclusions appear reasonable.

8.8 TRACER STUDIES

Initial laboratory work (section 6.4.1) indicated the suitability of lithium sulphate as a tracer in an environment where municipal solid waste is predominant. The percentage of lithium adsorbed was less than 2 percent (Table 6.6). This was confirmed in the pilot scale studies were the recovery of lithium bettered 92 percent. Of the 1027mg of lithium added, 954mg was recovered. The pilot-scale tracer studies ceased after 317 days, at that point lithium was still evident, albeit in a very low concentration. It is probable, that if monitoring had continued, the recovery of lithium would have been greater.

The characteristic curve of the tracer conformed to that expected. A high degree of non-ideality was exhibited, the variance was calculated at 3338, while the mean residence time was 113 days. Maximum lithium recovery occurred after 84 days, the lithium concentration of the leachate at that time was 2.003mgℓ^{-1}. The only departure from that expected on a full scale landfill is probably the initial rapid rise of lithium in the leachate, probably caused by a combination of preferential channelling and wall effects from the column. The characteristic curve, although not ideal, is not unlike commonly occurring E curves obtained from industrial equipment where the peak of the curve does not necessarily occur at the mean time and "tailing" does often occur (Denbigh *et al*, 1971). The rapid initial rise commented on earlier, is not a common phenomena.

8.9 CO-DISPOSAL AT PILOT-SCALE

As reported in section 6.5, a concentrated solution of copper, chromium and arsenic was co-disposed with the municipal solid wastes in columns 3 and 5. Analytical results are reported in Appendix E of Ballard (1997). Tables E-1 and E-3 tabulate leachate volumes and metal concentrations for columns 3 and 5 respectively; Tables E-2 and E-4 tabulate the associated chemical data (pH, COD, etc.,) for columns 3 and 5. The mass of metals introduced into both columns 3 and 5 was copper, 88.4g; chromium, 256.1g and arsenic, 256.7g. The time duration of the experiment with column 3 was 235 days, the average volumetric displacement of leachate was 19.2ℓweek^{-1}. The time duration of the experiment with column 5 was slightly shorter, 221 days. The average displacement of leachate was 18.5ℓweek^{-1}.

8.9.1 COPPER

Results from the monitoring of copper concentration of leachate from columns 3 and 5 are shown graphically in Figure 7.29. The initial concentration of copper in the leachate from column 3 was 0.05mgℓ^{-1}, the highest copper concentration was recorded was 0.11mgℓ^{1}. Over the entire period of monitoring (235 days), the concentration of copper in the leachate from column 3 averaged 0.05mgℓ^{-1}, The initial concentration of copper in the leachate from column 5 was 0.07mgℓ^{-1} this was not exceeded for the entire duration of the experiment. The final copper concentration after 221 days was 0.04mgℓ^{-1}.

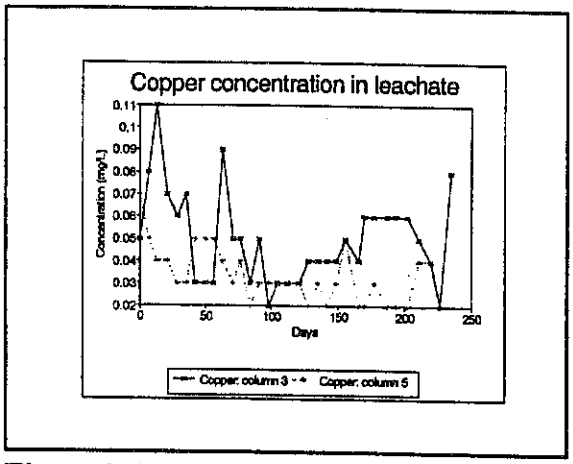

Figure 7.29
Copper concentration in leachate from columns 3 and 5

As stated in Section 7.4.6(c), although 88.4g of copper were added, virtually all of this copper would precipitate upon introduction into the column, a consequence of solubility effects. There was not any doubt concerning the lack of mobility of copper in the landfill environment, even an acetogenic landfill were pH levels approximate 5.5, at the outset of this investigation. The mobility of copper in various soils was reported in section 3.9.1.3(d) All the researchers reviewed (Korte *et al*, 1976; Aringhieri *et al*, 1985; Sapek cited by Aringhieri *et al*, 1985) commented on the low mobility of copper, even at low pH levels. Korte and co-workers (1976) examined the mobility of copper with an initial solution of landfill leachate at a pH of 3. Copper was immobile in all the soils except a sandy Wigram, even then, its mobility was low. The kinetic trials only served to confirm this, the rapid adsorption of copper has already been discussed in this chapter. Additionally, only 4 percent of the copper adsorbed was desorbed in the desorption trials. It is probable that desorbed copper would be re-adsorbed, as the liquid flows through the column contacting the remaining copper ions with adsorbent. The analytical results of the leachate from the pilot-scale columns confirms the work of previous researchers.

8.9.2 CHROMIUM

Results from the monitoring of chromium concentration of leachate from columns 3 and 5 are shown graphically in Figure 7.30. Initially, chromium in the leachate from column 3 was not detectable. The chromium content of the leachate rose steadily to a maximum of 0.04mgℓ^{-1}, this value was not exceeded for the duration of the experiment, the final chromium concentration was 0.03mgℓ^{-1} on Day 235. The average chromium content in the leachate from column 3 over the entire duration of monitoring was 0.03mgℓ^{-1}. The initial chromium content of leachate from column 5 was 0.06mgℓ^{-1}, The final chromium concentration was 0.02mgℓ^{-1} on Day 221. The average chromium content in the leachate from column 5 over the entire duration of monitoring was 0.04mgℓ^{-1}.

The predicted chromium concentration in the leachate from column 3 is shown in Figure 7.54. Until Day 160 the model realises actual measurements well, with very little deviation. From Day 160 the model begins to overpredict actual conditions. Results from monitoring continue in the region of 0.03mgℓ^{-1} whereas the model begins to predict chromium concentrations in excess of 2mgℓ^{-1} in that time frame, with predicted chromium concentration rising to a maximum of 4.4mgℓ^{-1} on Day 390.

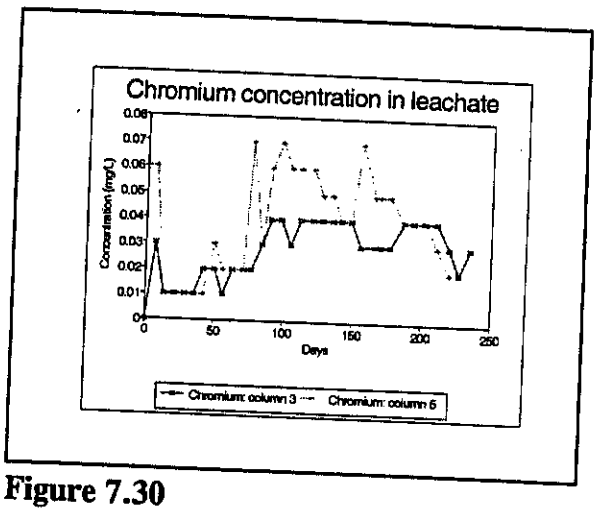

Figure 7.30
Chromium concentration in leachate from columns 3 and 5

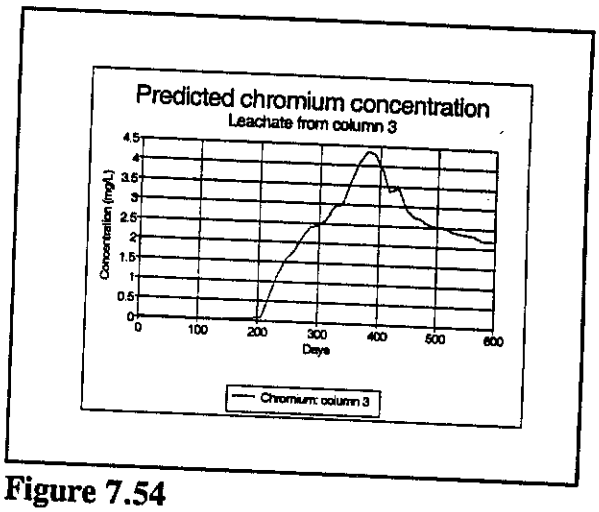

Figure 7.54
Predicted concentration of chromium in leachate from column 3

Some experimental considerations and the effect of the computational method were discussed briefly in section 7.4.6(c) and will not be repeated here. Although monitoring ceased on Day 235 and the calculations indicated a total residence time of 600 days this is not regarded as detrimental to a comparison of these results. It is extremely unlikely there would be any increase in actual chromium concentration in the column effluent. The computations assume the only attenuation mechanism to be adsorption. There are other possible attenuation mechanisms (such as precipitation) available to inhibit chromium mobility. Again, at the outset of the experimental work indications from the literature review indicated that chromium to be immobile in the landfill environment. A brief review of the work of other researchers confirms this.

Researchers in the field of soil science consistently reported a low mobility of chromium(VI) in soils (section 3.9.1.3(d)). Sheppard *et al* (1992) investigated the desorption of chromium from both a sandy and clay soil. The authors reported that if soil remediation was required, it would be less expensive to remove the soil that attempt any chemical treatment as the chromium was so firmly fixated. McGrath *et al* (1990) reported on a trial that had taken place over 19 years, where soils had received a sewage sludge containing chromium; there had been no significant movement of the chromium during that time period. Other researchers (Calder, 1988; Bartlett *et al*, 1976) reported the reduction of chromium(VI) to essentially immobile chromium(III) in the presence of organic matter, under anaerobic conditions, regardless of pH.

The composition of leachate from the columns (Appendix E of Ballard, 1997), the low percentage volatile solids of the municipal solid wastes (section 5.3.3(b)), plus the very low volume of biogas generated (section 6.3.2(b)) confirmed the municipal solid waste to be fully stabilised. The configuration of the columns, the length of time the columns have been at field capacity, the large volume of water present in the columns, are all factors that indicate that viable areas of anaerobic conditions would likely exist in the columns. The kinetic studies were completed in an aerobic environment. In that environment the behaviour of the metals under consideration can be regarded as ideal.

Conventional theory dictates the pilot-scale landfill column should be considered as a packed column. Traditional columns employed in industry are composed of adsorbents such as activated carbon, silica gel or activated alumina. Adsorbents are generally available as irregular granules, extruded pellets and formed spheres. The size of adsorbents rarely exceed 6mm, the size reflecting the need to pack as much surface area as possible into a given volume (Coulson *et al*, 1991). The municipal solid waste was reduced in size prior to placement in the column, increasing the surface area. This reduction in size did not approximate the reduction in size of the solid waste employed in the laboratory scale trials (section 5.3.2). A major difference between the solid waste and conventional columns is that liquid can flow through certain components of the waste such as paper, cardboard etc. It is probable the area available for adsorption is increased greatly by this mechanism, increasing adsorption. This analogy is given credibility by the nature of the characteristic curve obtained from the tracer studies. The liquid initially flows rapidly through existing channels, longer exit times are provided by fluid passing through the particles of solid waste. Here also an additional variable is introduced. A requirement of industrial adsorbents is structural integrity. In an aqueous environment components of the solid waste will lose structural rigidity and will start to collapse, delaying elements of the liquid.

As mentioned in section 7.4.6(c), an additional factor worthy of consideration is the sample size utilised in the kinetic experiments. Only 50g was used, while the pilot-scale columns were packed with approximately 700kg of municipal solid waste. While sampling was exhaustive, solid waste is an extremely heterogeneous substance.

8.9.3 ARSENIC

Results from the monitoring of arsenic concentration of leachate from columns 3 and 5 are shown graphically in Figure 7.31. The initial concentration of the arsenic in the leachate from column 3 was 17$\mu g\ell^{-1}$ rising in irregular steps to Day 194 when the concentration exceeded 2000 $\mu g\ell^{-1}$.

Arsenic concentration in the leachate from column 3 remained at that level until the cessation of monitoring on day 235. Column 5 mirrored the behaviour of column 3, though at a reduced manner. The maximum arsenic concentration attained was 802$\mu g\ell^{-1}$ at Day 213; results were relatively constant from Day 188 at that level.

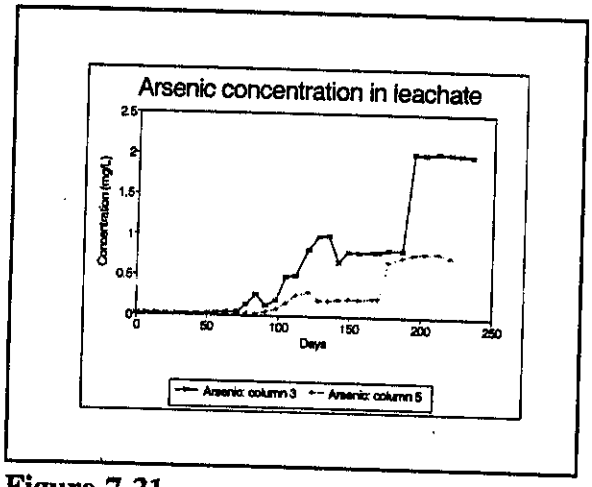

Figure 7.31
Arsenic concentration in leachate from columns 3 and 5

The predicted outcome of the co-disposal of arsenic was calculated in the same manner as that of chromium. Calculations predicted there would be an absence of arsenic in the leachate from column 3 during the total time period of 600 days. The results from desorption kinetic trials (section 7.4.3) showed that arsenic was the only metal of those under consideration that displayed any significant degree of desorption. This could not be allowed for in the calculation, and could account for the extremely low degree of error that is evident. There are not any significant solubility constraints with arsenic, whether it is in the form of arsenic(III) or arsenic(V), and if anaerobic conditions were experienced this would probably enhance the mobility of any arsenic present. In section 3.9.1.3(d) the behaviour of arsenic in soils under reducing conditions was reported. Reducing conditions convert arsenic(V) to arsenic(III). Arsenic(III) is 5 to 10 times more soluble than arsenic(V) increasing mobility.

In the case of arsenic it was unfortunate that the trials to did not proceed further, as reports of arsenic mobility are inconsistent (section 3.9.1.3(d)). However the degree of agreement between actual and predicted concentrations is excellent the maximum degree of error only being 2mgℓ^{-1} over the 235 day trial. Additionally, results appear to have stabilised at that level.

8.10 COMPUTATIONAL METHOD - GENERAL COMMENTS

The method employed to calculate the exit stream composition was reported in section 4.4.4 and section 7.4.6. The computation from the residence time data obtained from column 4 to provide suitable residence time data for column 3 and for the application of the pilot-scale studies to the full scale landfill proved to be successful. The calculated values for the mean, variance, total residence time and volumetric displacement of leachate are shown below in Table 8.7. The computational method retained the characteristic curve obtained in the lithium sulphate pulse experiment.

TABLE 8.7 SUMMARY OF ACTUAL AND COMPUTED RESULTS: RESIDENCE TIME DISTRIBUTION

	Volumetric displacement (ℓday^{-1})	Mean (t)	Variance (σ^2)	Total residence time (days)
Tracer studies (Column 4)	5.21	113.2	3338	317
Co-disposal trials (Column 3)	2.75	214.3	11953	600
Application of pilot-scale studies to the full-scale landfill	3.73	153.4	6123	430

The computational method employed to calculate the exit stream metal concentrations employs a conventional chemical engineering mathematical approach. The computational method is shown below in Figure 4.2

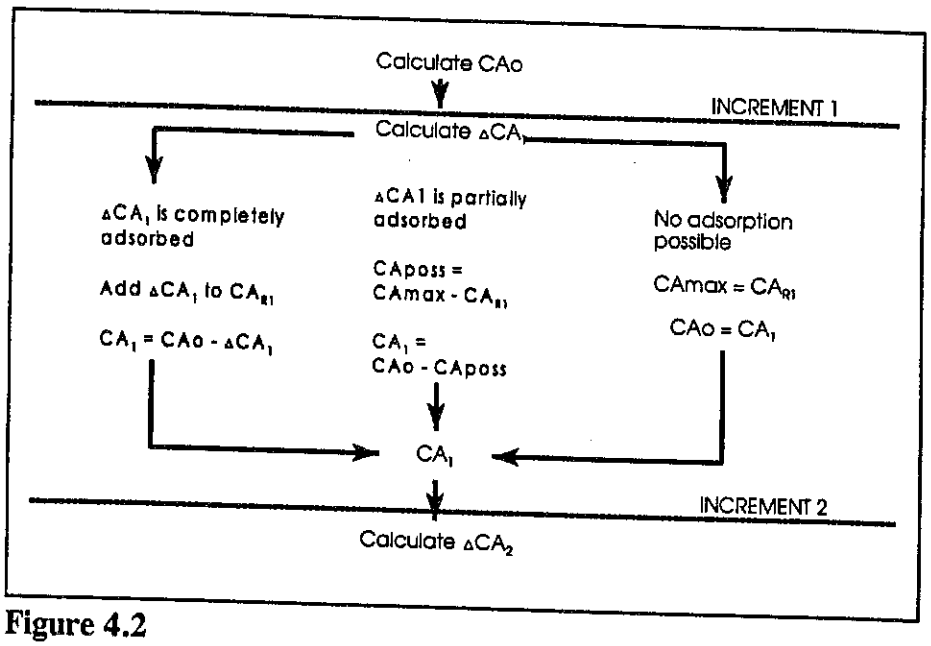

Figure 4.2
Illustration of computational method

Nomenclature

CAo	=	Solute concentration in fluid at t = 0 (gkg^{-1})
CA poss	=	Equilibrium solute concentration in adsorbent (gkg^{-1})
$\triangle CA_n$	=	Solute adsorbed in increment n (gkg^{-1})
CA_n	=	Solute concentration in fluid entering increment n (gkg^{-1})

The method is rigorous and accurate at low values of time. At larger time values the degree of accuracy is lowered. The incremental depth of the adsorbent is the problem area. The depth increment must be minimised for maximum accuracy, as the rate of adsorption is initially rapid and decreases with time. The depth increment must therefore be minimised to ensure the calculation accurately reflects the real situation within the column, where the residence time elements of fluid flow do not exceed the time required to reach equilibrium with the solid waste. The depth increment was minimised to 20mm. Using incremental depth of 20mm requires over 95 increments, as the column depth is 1940mm. This, together with the minimised time increment, requiring over 45 separate increments results in a spreadsheet in excess of 1.7Mb. At large values of time a smaller depth increment would ensure that each separate time increment of fluid would not spend excessive time in each increment of depth. Thus, at large values of time, it is possible the computed exit concentrations could be higher than that actually experienced.

8.11 APPLICATION OF THE PILOT-SCALE STUDIES TO THE FULL SCALE LANDFILL

As detailed in section 7.4.7 the application of the pilot-scale studies to the full scale landfill involved a worst-case study. The assumptions were:

(i) Precipitation occurring at Coastal Park Sanitary Landfill (from which the municipal solid waste was excavated) in the heaviest precipitation month falling on a continual basis;
(ii) no loss of moisture from the landfill, such as evapotransportation or run-off;
(iii) the landfill was at field capacity prior to co-disposal;
(iv) metal content in leachate from the landfill should not exceed the most stringent requirements prescribed by current South African legislation.

The assumptions are very stringent, and there is no doubt that the amounts of copper, chromium and arsenic determined to be suitable, would not cause any additional environmental damage to the area surrounding the landfill. The calculations revealed that when disposing of these metals in combination the mass of copper should not exceed $67gt^{-1}$; the mass of chromium in the form of chromium(VI) should not exceed $195gt^{-1}$; the mass of arsenic should not exceed $195gt^{-1}$. Rushbrook (1990) tabulated various maximum loading rates quoted in the United Kingdom by the various United Kingdom authorities. The values are shown in section 3.9.3, Table 3.16). The values for copper, chromium, and arsenic are shown below in Table 8.8, together with the proposed values obtained in this study. When considering the co-disposal of heavy metals, the United Kingdom's Department of the Environment state that *limited evidence suggests an initial loading of 100g of soluble chromium, copper, lead or zinc per tonne of mature household waste*

is unlikely to produce a significant change in leachate concentration 3 metres distance from the heavy metal waste (DOE, 1986). It should be noted that the DOE recommend, that if optimum attenuation is sought that co-disposal be practised with mature (that has been deposited between 1 and 5 years) municipal solid waste.

TABLE 8.8 CO-DISPOSAL LOADING RATES

Constituent	Loading rate	Proposed loading rate
Chromium	$100gt^{-1}$*	$195gt^{-1}$
Copper	$100gt^{-1}$*	$67gt^{-1}$
Arsenic	$10gt^{-1}$* $10kgt^{-1}$* (for As in sulphide form)	$195gt^{-1}$

* adapted from Rushbrook, 1990

The calculated loading rates compare favourably with that quoted by the DOE. It must be noted:

(i) the loading rates quoted by the DOE are for a total heavy metal loading of $100gt^{-1}$ whereas the proposed loading rate totals $262gt^{-1}$ for chromium and copper in combination;

(ii) the DOE quote a depth of 3m while the proposed loading rates were calculated with a depth of 2m of municipal solid waste.

Discussion of the loading rate quoted for arsenic is more complex. The value quoted by Rushbrook is not repeated in the DOE literature such as Waste Management Paper No 20, Arsenic-bearing wastes (1980) or Waste Management Paper No 26, Landfilling wastes (1986). Both publications express concern that the concentration of arsenic in leachate does not exceed $10mg\ell^{-1}$. Cossu *et al* (1989) reviewed the co-disposal of industrial wastes, including the disposal of arsenic wastes. The researchers affirm the value quoted by Rushbrook, that of $10gt^{-1}$, and refer to test work completed by Blakey (1984) (section 3.9.1.3(c)). It would appear that the leachate concentration is the controlling variable. If one does not exceed an arsenical concentration of $10gt^{-1}$ of municipal solid waste, the value of $10mg\ell^{-1}$ arsenic in leachate, will not be exceeded.

It is evident the loading rate values quoted by the DOE for arsenic are conservative. The DOE is concerned with additional factors such as the generation of arsine gas (section 3.9.3(c)). Arsine (AsH_3) is an extremely poisonous gas, with no effective antidote (DOE, 1980). Arsine is produced whenever a reaction generating nascent hydrogen occurs in the presence of arsenic.

Hydrogen generation can occur under anaerobic conditions, especially acetogenic conditions (section 3.7.2).

In general, loading rates proposed from experimental work undertaken in this study concur with loading rates employed in the United Kingdom, recommended by the United Kingdom's Department of the Environment.

8.11.1 FULL SCALE LANDFILL OPERATION - ADDITIONAL FACTORS

The life of a landfill may be classified into three primary time frames (section 3.7.1): the acetogenic or acid producing phase; the methanogenic or methane producing phase; the stabilised or final maturation phase. The pilot-scale studies together with the kinetic experiments explored the adsorption of the relevant heavy metals onto stabilised municipal solid waste. A stabilised landfill is characterised by a leachate comprising of a; neutral pH; high level of alkalinity; low level of carboxylic acids; low degree of organic contamination or Chemical Oxygen Demand (COD) and an extremely low production of biogas from the landfill. An acetogenic landfill is characterised by a leachate comprising of a; low pH; low level of alkalinity; high level of carboxylic acids; high degree of organic contamination with a virtual absence of biogas production from the landfill. A methanogenic landfill is categorised by leachate with a neutral pH; substantial generation of biogas with all other parameters being intermediate between the acetogenic and stabilised landfill.

Pohland *et al* (1986b) compiled data from a number of sources, indicative of the three primary stages of landfill life. This is shown in Table 8.9. Copper, chromium and arsenic are of primary interest. Other metals are also shown, for comparative purposes.

(a) Copper

It would be envisaged that copper would be relatively immobile in any age of landfill. The results collated by Pohland shown in Table 8.9 indicate copper to be mobile in an acetogenic landfill, less so in a methanogenic and a stabilised landfill. It is not unexpected that copper has a low degree of mobility in a methanogenic or a stabilised landfill. It is however surprising that it is mobile in an acetogenic landfill. Most researchers report the relative immobility of copper in organic soil, and report a tendency for copper to form stable organic complexes with organic matter in soil (section 3.9.1.3(d)). Also, soils having higher levels of organic matter are usually acidic in nature, as is the leachate from an acetogenic landfill. Other researchers report the mobility of copper in soils to be low, and describe the adsorption of copper onto organic matter, clay minerals, and even pure quartz. Soil scientists have conducted trials examining the movement of various metals in soils over extended periods. Lundblad and co-workers (1949) added over 250kg of copper (per hectare) to an acid peat soil. After 5 years had elapsed only 0.2 percent of the copper added was removed from the top 5cm of soil (section 3.9.1.3(d)).

Results from this current study are presented in Table 8.10. Copper is strongly adsorbed at all the pH levels shown, there is little evidence of significant desorption. (section 3.9.1.3(d)).

TABLE 8.9 **COMPOSITION OF LANDFILL LEACHATE AND BIOGAS FROM LANDFILLS OF DIFFERENT AGE**
(adapted from a review by Pohland *et al*, 1986b)

Constituent	Acetogenic landfill	Methanogenic landfill	Stabilised landfill
pH	4.7 - 7.7	6.3 - 8.8	7.1 - 8.8
Total Alkalinity ($mg\ell^{-1}$ as $CaCO_3$)	140 - 9650	760 - 5050	1460 - 4840
Total Volatile acids ($mg\ell^{-1}$ as CH_3COOH)	3000 - 18000	250 - 4000	Essentially absent
COD ($mg\ell^{-1}$ as O)	1500 - 71100	580 - 9760	31-900
Copper ($mg\ell^{-1}$)	0.005 - 2.2	0.03 - 0.18	0.02 - 0.56
Chromium ($mg\ell^{-1}$)	0.06 - 18	0.05	0.05
Lead ($mg\ell^{-1}$)	0.01 - 1.44	0.01 - 0.1	0.01 - 0.1
Nickel ($mg\ell^{-1}$)	0.03 - 79	0.01 - 1.0	0.07
Zinc ($mg\ell^{-1}$)	0.65 - 220	0.1 - 4.0	0.4
Cadmium ($mg\ell^{-1}$)	70 - 3900	76 - 490	76 - 254
Iron ($mg\ell^{-1}$)	90 - 2200	115 - 336	4 - 20
Methane (%)	< 1	30 - 60	0 - < 10
Carbon dioxide (%)	10 - 30	30 - 60	< 40
Nitrogen (%)	60 - 80	< 20	> 20
Oxygen (%)	0 - 5	0 - 5	> 5
Hydrogen (%)	0 - 2	< 0.1	Essentially absent

TABLE 8.10 MASS AND PERCENTAGE OF COPPER ADSORBED AND DESORBED AT PH 5.5, 6.4 AND 7.0

Metal and species	pH	Average mass sorbed (mg)	Percentage adsorption	Average mass desorbed (mg)	Percentage of metal adsorped that is desorbed
Copper(II)	5.5	50.9	86.9	1.7	3.3
	6.4	14.1	78.9	0.5	3.5
	7.0	23.0	79.1	0.8	3.5

The mobility of copper is severely restrained in both a methanogenic and a stabilised landfill. The solubility of copper is very limited in an aqueous solution, in an anaerobic reducing environment even more so. The subject of sulphate reducing bacteria was addressed in section 3.9.3(a). Hydrogen sulphide is produced by sulphate reducing bacteria. Hydrogen sulphide is a strong reducing agent, it can react with copper causing precipitation of the copper as insoluble copper sulphide.

Table 8.9 reveals copper to be one of the least mobile metals tabulated. The work of other researchers, together with results obtained in this study (Table 8.10), are in agreement.

(b) Chromium

It would be anticipated that the mobility of chromium(VI) would be limited in any landfill of any age. The kinetic trials showed that although mass of chromium adsorbed was proportionally less than copper or arsenic, chromium was strongly bound, and showed little evidence of desorption (Table 8.11).

Examination of Table 8.9 shows that the chromium content of a leachate from an acetogenic landfill to be relatively high when compared with a methanogenic or stabilised landfill. Leachate from an acetogenic landfill contains high levels of soluble organic acids enhancing the mobility of chromium. The pH of the leachate is low, adsorption of chromium(VI) was satisfactory in the kinetic trials at similar pH levels. The TCLP extraction fluid contains a carboxylic acid; acetic acid, which should approximate a leachate from an acetogenic landfill.
The degree of approximation was not adequate in this instance.

TABLE 8.11 MASS AND PERCENTAGE OF CHROMIUM ADSORBED AND DESORBED AT PH 5.5, 6.4 AND 7.0

Metal and species	pH	Average mass sorbed (mg)	Percentage sorbed	Average mass desorbed (mg)	Percentage of metal adsorped that is desorbed
Chromium (VI)	5.5	53	21.1	0.2	0.4
	6.4	31	10.3	0.2	0.6
	7.0	21	10.4	0.5	2.4

The low level of chromium in leachate from a methanogenic landfill is not surprising. By definition, a methanogenic landfill is anaerobic, and reducing conditions are prevalent. Chromium(VI) is readily reduced to chromium(III) in the presence of organic matter, especially at low pH. The solubility of chromium(III) decreases rapidly above pH4, with complete precipitation occurring above pH5.5. There are conflicting vectors however. The presence of soluble organic acids can maintain chromium(III) in solution at pH levels above 5.5.

It is envisaged that levels of chromium in leachate from a stabilised landfill would be low, possibly lower than that from a methanogenic landfill. The complete absence of carboxylic acids, the strong fixation of chromium to municipal solid waste shown in this study, indicate a low chromium mobility. Pohland *et al* (1983) expresses concern the more microbially recalcitrant materials could produce humic-like substances which could provide soluble organic material which could then remobilise any heavy metals present. There is the possibility of the occurrence of this phenomena, but this could only occur after a number of years, or even decades.

Soil scientists have evaluated vertical chromium movement in soils. In one experiment, chromium analysis of soils, which had received metal contaminated sludge treatment from 1942 to 1961, showed no evidence of significant movement below the depth to which the soil was cultivated (McGrath *et al*, 1990). Table 8.8 reveals chromium to be one of the least mobile metals tabulated. The work of other researchers together with results obtained in this study (Table 8.10) are in agreement.

(c) Arsenic

Unfortunately the review of leachate contaminants completed by Pohland *et al* (1986b) did not include arsenic. The behaviour of arsenic is the most complex of the three metals under consideration. The results from the kinetic trials are shown in Table 8.12. Arsenic is well adsorbed throughout the pH range under discussion. Arsenic is also the only metal which exhibits any significant desorption.

TABLE 8.12 MASS AND PERCENTAGE OF ARSENIC ADSORBED AND DESORBED AT pH 5.5, 6.4 AND 7.0

Metal and species	pH	Average mass sorbed (mg)	Percentage adsorption	Average mass desorbed (mg)	Percentage of metal adsorped that is desorbed
Arsenic(V)	5.5	70	34.3	6	8.6
	6.4	36	20.6	4	11.1
	7.0	41	23.2	4	9.8

The mobility of arsenic in soils is increased in anaerobic conditions. This increased mobility is a consequence of the reduction of arsenic(V) to arsenic(III). Arsenic(III) is estimated to be 5 to 10 timer more soluble, and hence more mobile then arsenic(V). The subject of sulphate reducing bacteria was addressed in section 3.9.3(a). Hydrogen sulphide is produced by sulphate reducing bacteria. Hydrowen sulphide is a strong reducing agent, it can react with arsenic (as with copper) causing precipitation of arsenic as insoluble arsenic sulphide. Another attenuation mechanism to consider is the co-precipitation of arsenic with iron sulphide. The iron content of leachates is generally high (see Table 8.9). Iron content is shown ac low in leachate from a methanogenic landfill as a consequence of attenuation mechanisms as just discussed.

The mobility of arsenic in the acetogenic landfill and the stabilised landfill are more difficult to envisage. Some of the attenuation mechanisms available in the methanogenic landfill would not be available. As reported in section 3.9.1.3(d) there is conflicting information regarding the mobility of arsenic(III) and arsenic(V). Sadler (1993) states that arsenic(III) has a high mobility in soils; while Elkhatib and co-researchers (1984) report arsenic(III) being irreversibly sorbed by the soils examined, only a small fraction of the arsenic(III) being desorbed from the soils. Korte and co-workers (1976) concludes that arsenic(III) (however at pH3) was more mobile than other metals examined. Frost and Griffin (1977) found arsenic(V) be mobile, especially at alkaline conditions, while arsenic(III) exhibited an increase in adsorption with rising pH.

It would appear there are substantial attenuation mechanisms available to reduce the mobility of arsenic in a methanogenic landfill. Adsorption would appear to be the principal mechanism in both the acetogenic and stabilised landfill. Arsenic adsorption was satisfactory throughout the pH range under scrutiny. There would not appear to be a great deal of difference in the behaviour of arsenic in an acetogenic landfill or that of a stabilised landfill, though adsorption of arsenic(V) is substantial at the lower pH values.

An additional problem that must be addressed when considering the co-disposal of arsenic on an acetogenic landfill is that of the generation of arsine gas (section 3.9.3(c)). Arsine (AsH_3) is an extremely poisonous gas, with no effective antidote (section 8.11). Arsine is produced whenever a reaction generating nascent hydrogen occurs in the presence of arsenic. Hydrogen can be generated in the acetogenic phase of landfill age. It is produced by hydrogen producing acetogenic bacteria (section 3.7.2). These hydrogen producing acetogenic bacteria convert the higher volatile acids to acetate and hydrogen. Pohand *et al* (1986b) reveals in Table 8.9 that hydrogen levels in gas from an acetogenic landfill have been recorded as high as 2 per cent by volume. For this reason it would appear that caution should be exercised in the co-disposal of arsenical waste in an acetogenic landfill.

(d) General

The calculations revealed that when disposing of these metals in combination the mass of copper should not exceed $67gt^{-1}$; the mass of chromium in the form of chromium(VI) should not exceed $195gt^{-1}$; the mass of arsenic should not exceed $195gt^{-1}$. A specific area which has not been addressed in the preceding section is that of the inhibiting effect of toxic industrial wastes on biological degradation of the municipal solid waste (section 3.9.3(a)). When practising co-disposal of industrial wastes with municipal solid wastes, avoidance of sterilising the landfill by exceeding the toxicity limit of the various microbial population groups and therefore inhibiting the degradation of the municipal solid waste is one of the two premier objectives. The other objective is that the emission of toxic substances in liquid and gaseous effluent from the landfill should not be greater than that from the disposal of only municipal solid waste. The latter objective was addressed in the initial assumptions of the calculation, were a worst case study was employed (section 7.4.7). The inhibition of anaerobic digestion was extensively examined in section 3.9.3(a), there is however, a number of interesting investigations deserving of further examination, for comparative purposes.

The work completed by Pohland and other workers (1985; 1986a; Gould *et al*, 1989) at the Georgia Institute of Technology, is one such study. A metal plating sludge containing zinc, chromium, nickel, cadmium, copper and iron, was co-disposed with municipal solid waste in pilot-scale landfill columns. In the control column (no addition of metal plating sludge) methanogenic conditions were established. In column 2 the onset of methanogenisis was delayed, addition of metal sludge was $84kgt^{-1}$. Where the sludge was added in a greater quantity, methanogenic conditions were not established.

Another investigation requiring further review is that undertaken by Yeates *et al* (1994). The researchers investigated the impact of copper, chromium and arsenic timber preservative on soil biological activity. Initially, the researchers visually graded areas of the pasture in terms of heavy metal contamination. Four levels of contamination were graded; uncontaminated, low contamination, medium contamination and highly contaminated. The researchers then sampled the site extensively in terms of degree of contamination and depth. The samples were then analysed for metal content and various biological parameters were measured to determine the whether there was evidence of repression of biological activities.

There was a close correlation between heavy metal contamination and the initial visual assessment. All the biological parameters measured in the contaminated area showed correlation with levels of copper, chromium and arsenic. The researchers concluded that contamination by

100mgkg^{-1} of copper, chromium and arsenic caused little depression of soil biological activity, there was some suppression at 400mgkg^{-1}, but at 800mgkg^{-1} normal biological processes were inhibited and herbage production was negligible. These results were comparable with other workers cited by Yeates and co-researchers.

The toxicity of heavy metals in the process of anaerobic digestion is well established and has been extensively investigated by various researchers principally investigating toxicity effects in waste water anaerobic digesters. Reid and fellow researchers (1968) evaluated the effects of metallic ions on a number of biological waste treatment processes, amongst them, anaerobic digestion at laboratory scale. They found that chromium (in the form, chromium(VI)) concentrations as high as 85mgℓ^{-1} reduced biogas production by 18 percent, and copper when added in concentrations up to 2mgℓ^{-1}, reduced gas production by 8 percent.

Hayes *et al* (1978) collated information concerned with the effect of metal addition on anaerobic digestion. The digesters were dosed with the metals in a step- and pulse-like fashion. Metal addition in a pulse-like mode is akin to shock loading, while metal addition in a step-like function allows microbial acclimation to the addition of the metal. The full results from the study are tabulated in Table 3.17. It was found that copper was more toxic than chromium. The shock loading toxic limit for; chromium(VI) was less than 200mgℓ^{-1}; copper was less than 50mgℓ^{-1}. The inhibiting concentration allowing microbial acclimation for; chromium(VI) was 110mgℓ^{-1}; copper was 40mgℓ^{-1}.

If one considers the work presented by Hayes and co-workers, it would appear there would not be any inhibition in anaerobic activity as the values quoted are high. Similarly, the value of 33.6kgt^{-1} (Pohland *et al*, 1985; Pohland *et al*, 1986a; Gould *et al*, 1989), would appear to be extremely high, a complete inhibition of anaerobic activity would have been expected, instead of only the delay of establishment of methanogenic conditions. The values presented by Reid and fellow researchers (1968) are of the same order as those presented by Hayes. Values for chromium are similar, but values presented for copper display variance. By far the most relevant of the work examined is that undertaken by Yeates and co-workers. There would appear to be some suppression at 400mgkg^{-1}.

To fully utilise the adsorptive capacity of the municipal solid waste, it would be required to co-dispose 457gkg^{-1} of copper-chromium-arsenic solution. It would appear possible that the co-disposal of the copper-chromium-arsenic solution at the proposed limits in a methanogenic landfill could inhibit methanogenic activity. The work of other workers does not absolutely confirm this, but the values quoted by Reid and fellow researchers (1968) where copper when added in concentrations up to 2mgℓ^{-1}, reduced gas production by 8 percent appear appropriate. It is conceivable that methanogenesis could be initially inhibited but it would be extremely unlikely that the anaerobic processes would not become acclimatised and proceed smoothly. This statement is confirmed by work carried out by Pohland and other researchers (1985; 1986a; Gould *et al*, 1989).

8.12 SUMMARY

The micro-physical characteristics of the metals under scrutiny, copper, chromium and arsenic were examined, and detailed. Results from the equilibrium studies were scrutinised. The Freundlich isotherm indicated the order of the degree of affinity of the metals to municipal solid waste was:

copper >> arsenic > chromium.

This was confirmed by additional graphical analysis. The effect of pH on adsorption was appraised. For all the metals under consideration the highest percentage adsorption was achieved at pH5.5 with percentage adsorption at pH6.4 and pH7.0 being similar.

Results from the kinetic trials were inspected, and reasons for the applicability of the modified Freundlich equation assessed. It was shown that diffusional effects at the solid phase were rate determining. The suitability of the Freundlich equilibrium isotherm in characterising adsorption is often taken to be indicative of adsorption onto a heterogeneous surface. Further analysis of the data showed agreement to a generalised model representative of heterogeneous adsorption. The rate of adsorption was also examined. Analysis showed the rate, and mass of adsorption increased as the initial solute concentration increased. Additionally, the rate of adsorption may be categorised in the following order:

copper >> arsenic > chromium.

Sorption mechanism was also investigated. It was evident that the relative size of the ions was not the controlling mechanism, but adsorption was probably determined by electrical interaction. Tracer studies were examined, together with the pilot-scale co-disposal trials. Results from the tracer studies showed the pilot-scale column to behave as a non-ideal plug flow reactor. Results from the co-disposal trial showed good agreement with that predicted from the modelled results from the laboratory investigation. Defects in the computational method were also discussed.

The application of the pilot-scale study to a full scale landfill were discussed, in conjunction with values promulgated by the United Kingdom's Department of the Environment. Loading rates predicted by computer model were of the same order as those utilised in the United Kingdom. The final sections of the Discussion centred around the behaviour of copper, chromium and arsenic in landfills of different age together with the effect of co-disposal of those metals at the proposed loading rates on anaerobic activity.

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Data are usually fitted to the logarithmic form of the equation:

$$\ln(q) = M \ln(C_e) + \ln(K_F)$$

If the Freundlich adsorption isotherm is suitable, a logarithmic plot of solute adsorbed (q) versus equilibrium solute fluid concentration (C_e) results in a straight line with a slope equal to the Freundlich power coefficient (M) and an intercept equal to the value of the logarithmic form of the Freundlich equilibrium distribution coefficient (K_F). The Freundlich equilibrium distribution coefficient may be considered as a measure of affinity (Murali *et al*, 1983).

Numerous examples exist in the literature where the Freundlich isotherm has been used to describe the adsorption of solutes by a solid matrix. Smith (1981) cites as examples, the adsorption of; hydrogen gas on tungsten and aqueous sulphur dioxide on activated carbon. Examples involving the adsorption of solutes onto the soil matrix abound (Travis *et al*, 1981). In an excellent survey of sorption relationships in soil, Travis and Etnier (1981) cite more than 30 examples of the adsorption of various solutes onto the soil matrix where the Freundlich equation has described the adsorptive process. The solutes diverge from anions such as sulphate, metallic ions, to herbicides, pesticides and various hydrocarbons.

4.2.2 LANGMUIR ISOTHERM

The Langmuir equation for isothermal adsorption may be deduced from kinetic considerations or from the thermodynamics of adsorption. It is based on the following assumptions:

(1) Maximum adsorption corresponds to a saturated monolayer of solute molecules on the surface of the adsorbent;
(2) Energy of adsorption is constant at all adsorption sites;
(3) No transmigration of adsorbed molecules in the plane of the surface.

The Langmuir equation may be written as (Murali *et al*, 1983):

$$q = \frac{K_L C_e Q}{(1 + K_L C_e)} \qquad 4.2$$

Where,

q = solute adsorbed per unit weight of solid adsorbent
K_L = Langmuir equilibrium distribution coefficient
C_e = Concentration of solute remaining in fluid at equilibrium
Q = Adsorption capacity

A convenient linearised form of the Langmuir equation is,

$$\frac{1}{q} = \frac{1}{Q} + \frac{1}{K_L C_e Q} \qquad 4.2(a)$$

If the Langmuir isotherm is obeyed, a plot of 1/q versus $1/C_e$ the intercept at $1/C_e = 0$, allows the calculation of the reciprocal of the Adsorption capacity (Q). The Langmuir equilibrium distribution coefficient (K_L) is a measure of the adsorption energy, as is the steepness of the adsorption isotherm (Murali *et al*, 1983). The Langmuir adsorption isotherm was developed by Langmuir (1918) to describe the adsorption of gases by solids. Assumption(1) leads to the concept of an upper limit of adsorption. The Freundlich isotherm does not generae any information indicating the process of adsorption is completed (Tan, 1993). However, although the Langmuir isotherm provides a useful reference standard of ideality for theoretical study, equilibria in real systems are often better represented by the Freundlich isotherm (Graham, 1959).

4.3 CHEMICAL KINETICS

The word "kinetics" is a general term, referring to time dependent phenomena.The term chemical kinetics is used to describe the quantitative study of change in concentration or pressure with time, resultant from a chemical reaction (Latham *et al*, 1977). Chemical reactions may be divided into two broad categories: homogeneous and heterogeneous. Chemists, and textbooks of chemistry, often confine themselves to homogeneous reactions, especially in the examination of chemical kinetics. In this investigation which examines the adsorption of metallic ions onto municipal solid waste, it was necessary to investigate the work of other researchers working in the similar area. An area of science where kinetic theories are adapted to the adsorption of various ions onto heterogeneous surfaces is soil chemical processes.

Since the initial development of the science of soil chemistry, attention has been given to equilibrium processes. It was only in 1989, that the first comprehensive study of time dependent soil chemical processes was promulgated by Sparks; Kinetics of soil chemical processes (Sparks, 1989). Harter (1986), a major contributor to the field of soil science, reviewed key papers in adsorption phenomena of various researchers from the 1800's to the present day. Harter thought, at that time, the state of knowledge regarding chemical kinetic studies was incomplete. The selection of papers would possibly be incautious, and instead included a bibliography of papers together with a review of recent findings and thoughts. However, with the similarities between the two areas of research, it was likely that the work of researchers in the field of soil science would be relevant.

4.3.1 CHEMICAL INTERACTIONS IN SOIL REACTIONS

Chemical reactions at the solid phase may comprise of: the formation or rupture of a bond between sorbate and surface; further reaction between adsorbed species; rearrangement of the solid structure and formation and disappearance of solid species. It is often incorrect to apply simple kinetic models to such interactions because reacting solid surfaces are rarely homogeneous and also the effects of transport phenomena and chemical reactions are often inseparable (Sparks, 1989). Harter (1991) notes that commonly used kinetic techniques are based on the assumption that the reactions are either unidirectional or discrete, while soil sorption reactions are often both reversible and multiple, and it is seldom possible to be definitive in calculating rate coefficients attributed to a specific reaction.

The heterogeneity of soils can be further enhanced by the variation of constituents of the soils, the differing particle sizes; types of surface sites, etc. If one considers the organic solids within soils, it is not even possible to describe a developed molecular structure for the compounds present (Sposito, 1984). The analogy of adsorption of solutes onto soils with the adsorption of solutes onto municipal solid waste is evident. The heterogeneity of municipal solid waste regarding composition, size and size range cannot be disputed. The heterogeneity of the surface is also apparent. Therefore, conclusions regarding kinetic models for adsorption of solutes onto soils should be equally applicable for municipal solid wastes.

4.3.2 MECHANISMS OF SOIL REACTIONS

Soil adsorption reactions may be classified as slow or rapid. Slow reactions are those in which processes taking place at the solid phase are rate determining. These processes may include: surface diffusion; diffusion within the micropores; penetration into the bulk of the solid or chemical interactions. Rapid soil reactions are, in general, reactions which transport at the solid phase does not influence the reaction rate to any significant extent (Aharoni *et al*, 1991a).

4.3.3 APPLICATION OF CHEMICAL KINETICS TO THE ADSORPTION OF METALLIC IONS ONTO MUNICIPAL SOLID WASTE

The application of chemical kinetics to (even) homogeneous solutions is often arduous. When kinetic theories are applied to heterogenous soil constituents, the problems and difficulties are magnified (Sparks, 1989). A similar comment could be stated for municipal solid waste surfaces, especially when those surfaces are composed of differing materials. An array of kinetic equations including zero-, first-, and second order, fractional power, Elovich, and parabolic-diffusion equations have been employed over the years to describe the kinetics of soil chemical phenomena. Kuo and Lotse (1974) successfully described the kinetics of phosphate sorption and desorption on hematite and gibbsite by the use of the fractional power or modified Freundlich equation. This equation is often termed the two-constant rate equation, and is discussed below.

4.3.4 TWO-CONSTANT RATE EQUATION

Kuo and Lotse (1974) developed a two-constant rate equation, adapted from the Freundlich equation by inserting a time-dependent expression into the Freundlich equation. The Freundlich equation is usually presented as shown below.

$$q = K_F C_e^{M} \qquad 4.1$$

The insertion of a time dependent expression results in an expression of the form,

$$q = K_a C_o t^{1/m} \qquad 4.3$$

where

Co	=	initial solute concentration
K_a	=	constant
t	=	time
m	=	constant

The two-constant rate equation was also used to describe arsenite sorption and desorption in soils (Elkhatib *et al*, 1984), potassium-calcium exchange on soils (Sparks *et al*, 1980), and by Jopony and Young (1987) to study the kinetics of copper desorption from soil and clay minerals. The modified Freundlich equation is generally considered empirical (Aharoni *et al*, 1991b).

4.3.5 APPLICABILITY OF EMPIRICAL EQUATIONS TO SLOW SOIL REACTIONS

In many cases kinetic data experimentally obtained for activated reactions does not fit equations derived from theoretical models, but may be described by an empirical expression. These expressions, applicable to soil reactions, are also applicable to various other chemical processes involving solid-fluid reactions (Aharoni *et al*, 1991a). The three principal equations are the: modified Freundlich equation; Elovich equation; pseudo-first-order equation.

(a) Modified Freundlich or fractional power equation

Another representation of the modified Freundlich equation is;

$$q = kt^{v} \qquad 4.4$$

where

q	=	quantity adsorbed at time, t.
k	=	constant
v	=	constant

(b) Elovich equation

The Elovich equation is one of the most widely used equations to describe the kinetics of heterogeneous chemisorption of gases onto solid surfaces (Taylor *et al*, 1952; Low, 1960). It has subsequently been used extensively to describe the adsorption and desorption of various solutes with differing soils (Atkinson *et al*, 1970; Chien *et al*, 1980; Hodges *et al*, 1987).

The Elovich equation may be represented by;

$$q = A + (1/b)\ln(t + t_o) \qquad 4.5$$

where

A	=	constant
b	=	constant

The parameter t_o is often small at the range where t is applied and may often be disregarded.

The applicability of the relationship may be verified by plotting q/q_∞ versus $\log_e t$. Where;

q_∞ = amount sorbed at $t = \infty$

(c) Pseudo-first-order equation

The pseudo-first-order equation may be represented by;

$$q/q_\infty = 1 - \beta \exp(-\alpha t) \qquad 4.6$$

where

β = constant
α = constant

The applicability of the relationship can be verified by plotting $\log_e(1 - q/q_\infty)$ versus t.

4.3.6 RELATIONSHIP BETWEEN EMPIRICAL EQUATIONS AND DIFFUSION

A generalised equation may be derived by closely examining the applicability of equations (4.4), (4.5) and (4.6) to experimental data (Aharoni *et al*, 1991a). These generalised expressions are obtained by differentiating the empirically based formula and writing them as the reciprocal of the rate. Consider equation (4.4)

$$q = kt^v \qquad 4.4$$

Then,

$$Z = (dq/dt)^{-1} = (1/vK)t^{1-v} \qquad 4.7$$

A similar exercise may be performed for equations (4.5) and (4.6).

Plots of the reciprocal of the adsorption rate (Z) versus time (t) for various soil reactions, and other solid-fluid processes are usually S-shaped: convex at small values of time, concave at large values of time, and linear at some intermediate value of time. It is often more convenient to plot experimental data as q (amount sorbed) versus $\log_e t$. This representation will also produce S-shaped plots. These S-shaped plots do not contradict the empirical equations whenever they are valid. The equations may be applicable, over the entire experiment, if all the points measured are within its range of validity. It should be noted however that equations (4.4) and (4.5) cannot be valid at large values of time as they give infinite sorption at infinite time. These two equations must be superseded at some time by an equation that predicts a finite saturation value at infinite time, such as equation (4.6). The generalised expression, S-shaped Z(t) plots may be explained by models based on diffusion. Equations for diffusion in a homogeneous medium lead to S-shaped Z(t) plots in which the final and initial curved parts are dominant. Equations for diffusion in a heterogeneous medium lead to S-shaped Z(t) plots in which the intermediate linear part is dominant.

4.4 NON-IDEAL REACTORS AND TRACER RESPONSE ANALYSIS

A continuous reactor may behave very much like a plug flow reactor or a perfect mixer, but it can never completely achieve either of these ideal states. In an ideal plug flow reactor, all reactant and product molecules at a given axial position move at the same rate in the direction of the bulk fluid flow, while in real flow reactors, fluid velocity profiles, turbulent mixing and molecular diffusion cause molecules to move with a variety of speeds and directions. These inevitable deviations from ideal reactor conditions lead to fundamental problems in reactor design and analysis (Dudukovic *et al*, 1983).

4.4.1 RESIDENCE TIME DISTRIBUTION

(adapted from Levenspiel, 1962 and Denbigh *et al*, 1971)

Consider a fluid flowing at steady state, without reaction, or density change, then,

$$\bar{t} = V/v \qquad 4.8$$

Where,

$\bar{t}$ = mean residence time (h)
V = volume (m^3)
v = volumetric flowrate (m^3h^{-1})

A dimensionless variable may be defined which measures time in units of mean residence time. This dimensionless variable is termed reduced time and is defined below.

$$\theta = t / \bar{t} = vt/V \qquad 4.9$$

Where,

θ = reduced time (dimensionless)

(a) Exit age distribution (E and E(t))

Let **E** be a measure of the distribution of ages of all elements of the fluid stream leaving the vessel. Thus, **E** is a measure of the distribution of residence times of fluid within the vessel. Then,

$\mathbf{E}\, d\theta$ = fraction of material in the exit stream between the ages θ and $\theta + d\theta$

Consider Figure 4.1, shown below

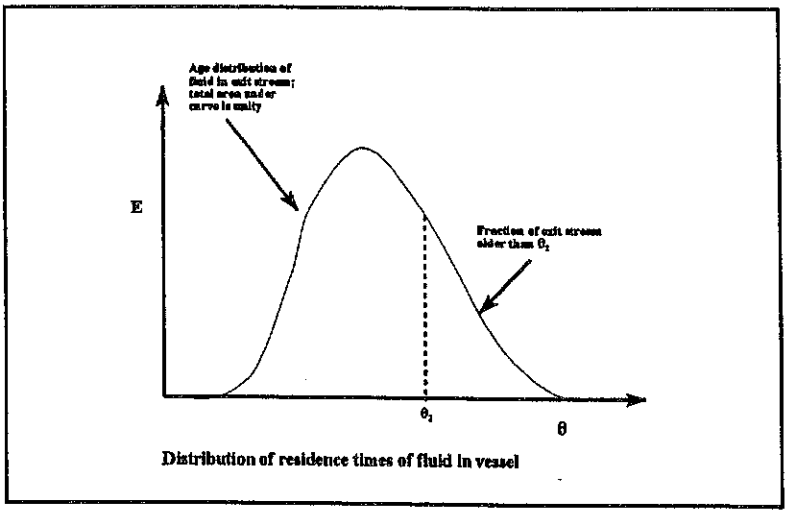

Figure 4.1
Exit age distribution or distribution of residence times of fluid in a vessel (adapted from Levenspiel, 1962)

The area under the E versus θ curve can be expressed

$$\int_0^\infty \mathbf{E}\, d\theta \quad = \quad 1 \qquad 4.10$$

The fraction of the material in the exit stream younger than age θ_2 is

$$\int_0^{\theta_2} \mathbf{E}\, d\theta$$

Then the fraction of material older than θ_2 , is defined,

$$\int_{\theta 2}^\infty \mathbf{E}\, d\theta \quad = \quad 1 \quad - \quad \int_0^{\theta_2} \mathbf{E}\, d\theta$$

Age distribution functions may be expressed in terms of real time units rather than in dimensionless time units. The exit age distribution is designated E(t). Now E(t) dt becomes the fraction of material in the exit stream of age between t and t + dt, then

$$\mathbf{E} \quad = \quad \bar{t}\, \mathbf{E(t)}$$

with,

$$\int_0^\infty \mathbf{E(t)}\, dt \quad = \quad 1 \qquad 4.11$$

also,

$$\bar{t}\theta \quad = \quad t$$

with

$$\bar{t} \quad = \quad V/v \quad = \quad \bar{t}_E \quad = \quad \int_0^\infty t\, \mathbf{E(t)}\, dt$$

4.4.2 EXPERIMENTAL METHODS - THEORETICAL CONSIDERATIONS

The measurement of the exit age distribution functions cannot be made directly. An experimental method within a group of techniques classed as stimulus-response techniques must be utilised. The experimental method employed in this research, used a pulse input signal. Therefore, the subsequent discussion is limited to this approach.

(a) The C(t) curve

The curve that describes the concentration-time function of a tracer in the exit stream of a vessel in response to a pulse injection is termed here, the C(t) curve. Concentration and real time co-ordinates are employed. The C(t) curve may be related to the E(t) curve in the following manner.

Consider a small quantity of a suitable tracer of quantity M is introduced into the fluid entering the vessel. Consider the tracer leaving the vessel between t and t+dt. From the definition of E(t);

Quantity of tracer leaving the vessel between t and t+dt = $ME(t)dt$

Let the concentration of tracer as a function of time = $C(t)$

Also the quantity of tracer leaving the vessel between t and t+dt = $C(t)v dt$

Therefore,

$$E(t) = \frac{vC(t)}{M} \qquad 4.12$$

Thus, excluding the scale factor v/M, the graphical construction of C(t) is identical to that of E(t).

(b) Mean and variance of a distribution

Associated with every age distribution $y = f(x)$ are two sets of parameters called moments of the distribution. Two moments are used throughout all areas of tracer evaluation. The first moment about the origin, commonly called the mean or centroid of the distribution is the location parameter of the distribution and may be defined;

$$\mu = \int_0^\infty x f(x)dx \; / \; \int_0^\infty f(x)dx \qquad 4.13$$

For a continuous function measured at a number of equidistant points then

$$\mu = \sum x_i f(x_i) \Delta x \; / \; \sum f(x_i) \Delta x = \sum x_i f(x_i) \; / \; \sum f(x_i) \qquad 4.14$$

The second moment about the mean, is commonly termed the variance. The variance measures the spread of the distribution about the mean and is equivalent to the square of the radius of gyration of the distribution. It is defined for a continuous distribution as

$$\sigma^2 = \int_0^\infty (x - \mu)^2 f(x)dx \; / \; \int_0^\infty f(x)dx \qquad 4.15$$

For a continuous function measured at a number of equidistant points then

$$\sigma^2 = \sum (x_i - \mu)^2 f(x_i)\Delta x \; / \; \sum f(x_i)\Delta x = \left(\sum x_i^2 f(x_i) \; / \; \sum f(x_i) \right) - \mu^2 \qquad 4.16$$

These properties may be evaluated for the **E** curve, as shown below.

The mean age of the exit stream may be defined in terms of reduced time,

$$\theta_m = \int_0^\infty \theta \, \mathbf{E} \, d\theta = \sum \theta \, \mathbf{E} \; / \; \sum \mathbf{E} = \sum \theta \mathbf{E} \Delta\theta \qquad 4.17$$

The variance of the **E** distribution may be defined,

$$\begin{aligned} \sigma^2 &= \int_0^\infty (\theta - 1)^2 \, \mathbf{E} \, d\theta \\ &= \int_0^\infty \theta^2 \, \mathbf{E} d\theta - 1 \\ \sigma^2 &= \left(\sum \theta^2 \, \mathbf{E} \; / \; \sum \mathbf{E} \right) - 1 \\ &= \sum \theta^2 \, \mathbf{E} \Delta\theta - 1 \end{aligned} \qquad 4.18$$

The mean age of the exit stream may be also be defined in terms of real time,

$$\bar{t} = \int_0^\infty t \, \mathbf{E} \, dt = \sum t \, \mathbf{E}(t) \; / \; \sum \mathbf{E}(t) = \sum t \mathbf{E}(t) \Delta t \qquad 4.19$$

The variance of the E(t) distribution may be defined,

$$\begin{aligned} \sigma_t^2 &= \bar{t}\sigma^2 = \int_0^\infty (t - \bar{t})^2 \, \mathbf{E} \, dt \\ &= \int_0^\infty t^2 \, \mathbf{E}(t) dt - \bar{t}^2 \\ &= \left(\sum t^2 \, \mathbf{E}(t) \; / \; \sum \mathbf{E}(t) \right) - \bar{t}^2 \\ &= \sum t^2 \, \mathbf{E}(t) \Delta t - \bar{t}^2 \end{aligned} \qquad 4.20$$

4.4.3 EXPERIMENTAL METHODS - PRACTICAL CONSIDERATIONS

(a) The pulse experiment

The simplest and most direct method of evaluating the residence time distribution employs a non-reactive tracer. The method of evaluation is described below (Levenspiel, 1993). M units (mass or moles) of non-reactive tracer is introduced simultaneously into the fluid entering the vessel. The volumetric flowrate and the concentration of the tracer within that fluid is then

recorded. A response curve of concentration (C) versus time (t) is then constructed (C(t) curve). The area under the curve, the mean of the curve, and the variance are then evaluated with the equations shown below.

$$\text{Area under the curve} = \int_0^\infty \mathbf{C}\, dt = \sum \mathbf{C}_i \, \Delta t_i$$

$$\text{Mean of the curve } (\bar{t}) = \int_0^\infty t\, \mathbf{C}\, dt \,/\, \int_0^\infty \mathbf{C}\, dt$$

$$= \sum \mathbf{C}_i \, t_i \, \Delta t_i \,/\, \sum \mathbf{C}_i \, \Delta t_i$$

$$\text{Variance } (\sigma_t^2) = \left(\int_0^\infty t^2\, \mathbf{C}\, dt \,/\, \int_0^\infty \mathbf{C}\, dt \right) - \bar{t}^2$$

$$= \left(\sum \mathbf{C}_i \, t_i \, \Delta t_i \,/\, \sum \mathbf{C}_i \, \Delta t_i \right) - \bar{t}^2$$

The calculated results are then evaluated for consistency, by use of material balance computations. The equations are shown below.

$$\text{Area under the curve} = M/v$$

$$\text{Mean of the curve} = \bar{t} = V/v$$

From the concentration-time data the construction of the **E**(t) or **E** curve is now possible, by use of the formula shown below.

$$\mathbf{E}(t) = \mathbf{C} \,/\, \sum \mathbf{C} \Delta t$$

and,

$$\mathbf{E} = \bar{t}\mathbf{E}(t)$$

$$\theta = t \,/\, \bar{t}$$

The **E**(t)curve may be utilised to find the behaviour of the reactor directly as shown below.

4.4.4 CONVERSION DIRECTLY FROM TRACER INFORMATION

Consider a liquid containing a solute A, that is successfully adsorbed by a suitable adsorbent. If the liquid is passed through a bed of adsorbent, initially free of the adsorbate, A, the uppermost layer of adsorbent, adsorbs the solute rapidly, subsequent layers of adsorbent remove further solute from solution until the fluid exiting the column (assuming the depth of adsorbent is sufficient) is free of solute (Treybal, 1968). These statements assume the fluid to be flowing in perfect plug flow, with the rate of adsorption of the solute to be more rapid than the vertical movement of the fluid down the column. The computation of the concentration of solute A in the exit stream in this case is relatively simple. To convert data obtained from tracer information, a sophisticated method of computation is required.

The computation to calculate the degree of adsorption of a solute employs a conventional chemical engineering mathematical approach used to solve, in the presence of unsteady state conditions. The E(t) curve allows the calculation of the volume of liquid leaving the column at any time increment during the total time, and hence, the velocity of that element of fluid. The calculation is then performed incrementally, in a manner similar to that of the art of screen printing (where different colours are applied at different times) for the differing residence time frames of the various elements of fluid flowing through the column. Each incremental residence time is overlaid upon the previous shorter residence times until the longest residence time is the last time frame to compute.

The increment depth of the adsorbent is firstly decided upon. In most cases, the thinner the increment of depth the greater the accuracy of the calculation. From the E(t) data the volume of liquid passing, over a particular time period can be computed. Therefore, the residence time of the fluid per increment of depth can be calculated. CAo is then calculated in terms of mass of solute per mass of adsorbent in the increment. It is assumed the initial solute concentration is in proportion to volume of liquid flowing in that time increment. From the kinetic expression the theoretical mass of solute to be adsorbed is calculated. This is then compared with the solute concentration within the increment. Solute may be adsorbed fully, adsorbed partially, or not at all, if the solute has already reached its equilibrium value in that increment. The concentration of solute in the fluid is reduced by the applicable amount, and this reduced fluid solute concentration then enters the next increment and the aforementioned process begins again. This process is then repeated to the final increment of the adsorbent layer. The next element of fluid from the E(t) data is then manipulated in the same manner until the total residence time of all fluid elements is reached. A graphical plot of concentration of solute in the exit stream versus time may then be constructed. The computational method is shown diagrammatically in Figure 4.2

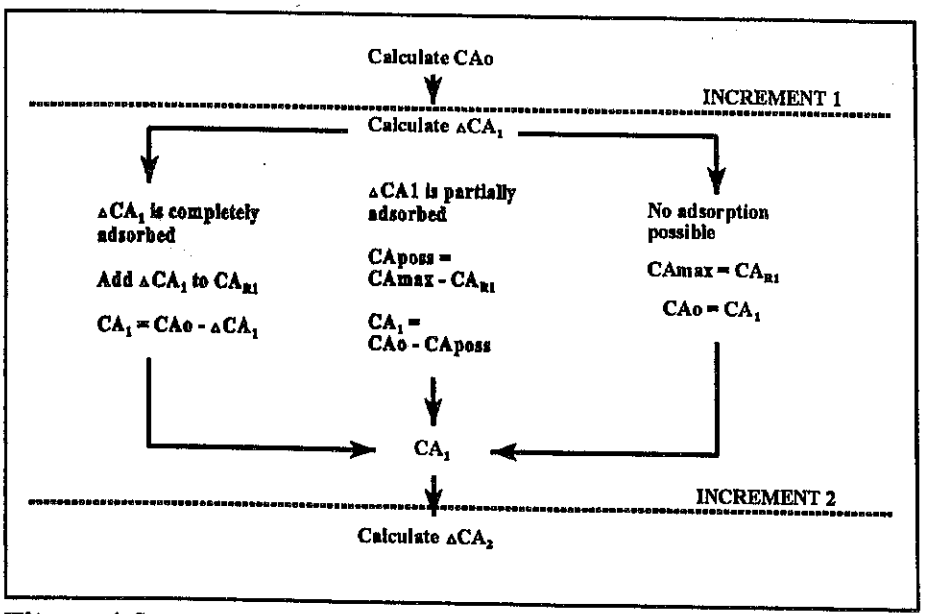

Figure 4.2
Illustration of computational method

Nomenclature

CAo	=	Solute concentration in fluid at t = 0 (gkg^{-1})
CA poss	=	Equilibrium solute concentration in adsorbent (gkg^{-1})
$\triangle CA_n$	=	Solute adsorbed in increment n (gkg^{-1})
CA_n	=	Solute concentration in fluid entering increment n (gkg^{-1})

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CHAPTER 5
MATERIALS AND METHODS: LABORATORY-SCALE ADSORPTION/DESORPTION STUDIES

5.1 INTRODUCTION

The kinetics of adsorption/desorption of copper, chromium and arsenic, were appraised at laboratory scale. Equilibrium adsorption studies were also effected. The metals examined were in the form of CCA (or Tanalith). This chemical is used extensively for wood preservation.

5.2. LABORATORY-SCALE INVESTIGATION

The laboratory scale investigation was also constituted of two integral sections:
Evaluation of kinetic rate constants, adsorption and desorption;
evaluation of adsorption isotherms.

5.3 MUNICIPAL SOLID WASTE

At the outset of the experimental study it was an objective to study the effect of the co-disposal of the heavy metals with methanogenic municipal solid waste. To achieve this purpose, 5000kg of municipal solid waste deposited at Coastal Park Sanitary Landfill Site for approximately 1 year was excavated. By excavating previously deposited waste, it was thought the stabilisation process could be accelerated allowing the experimental study to proceed more rapidly, possibly partially by-passing the acetogenic phase of landfill stabilisation. This objective was not achieved. The waste excavated was virtually stabilised i.e. at the end of the methanogenic stage of landfill stabilisation; the waste was probably deposited far in excess of the estimated time of 1 year. The interest of the study changed to examine the effect of the co-disposal of heavy metals with fully stabilised municipal solid waste.

After excavation the municipal solid waste was transported to the Swartklip Pulverising Plant were the waste underwent size reduction. The waste was shredded for three main reasons:

to avoid gross liquid bypassing in the pilot-scale landfill columns;
to achieve a similar degree of compaction to that achieved at the full-scale landfill;
to obtain a similar degree of dimensional similarity between the pilot-scale columns and the full-scale operation.

5.3.1 SAMPLING OF THE MUNICIPAL SOLID WASTE

Sampling of the municipal solid waste from Coastal Park Sanitary Landfill Site was given considerable thought. Municipal solid waste is complex in composition, and of a non-homogeneous nature. The United States Environmental Protection Agency have compiled information regarding the sampling of solid waste, but this information was not available. In order to proceed with the investigation other avenues were investigated. These are outlined below.

Initial sampling is discussed in Municipal refuse disposal (American Public Works Association, 1970). If collecting from an area in a city, it is suggested that one truckload should be adequate, the initial sample from that truck should be 225kg. The sample should then be reduced in size to less than 4cm. After size reduction, it is recommended the sample size be reduced by quartering to approximately 4 samples, each of 100g. Moisture analysis is then performed in quadruplicate, the four samples are then reconstituted for further analyses.

Ham and fellow researchers (Ham *et al*, 1993) characterised landfill refuse from Fresh Kills Landfill on Staten Island, New York. The Fresh Kills landfill was created in 1948, and is today, the largest solid waste disposal site in the world. It covers 12000 hectares, and receives 15500 tonnes of waste per day. Thirteen (13) boreholes were drilled, several hundred kilograms of solid waste was sampled in 100kg increments. These samples were then reduced in mass to 25kg. The method of size reduction was not discussed in detail. However, as the placing of the sample on a large sheet of plywood is mentioned, it would appear the samples were quartered. A total of 31 samples of municipal solid waste were collected in this manner. Each increment was individually reduced in size to approximately 1.9cm. Each increment of the now shredded municipal solid waste was then mixed thoroughly, and half of each individual increment discarded. Finally, the remaining 12.5kg of shredded solid waste was separated by riffling into 16 approximately 0.75kg increments. Five (5) of these sub-samples were used for replicate analysis. In some instances these 5 sub-samples were combined in equal amounts for analysis.

Klee and Carruth (Klee *et al*, 1970) investigated sample weights in solid waste composition studies. Both researchers were employed at that time by the United States Bureau of Solid Waste Management and had access to studies conducted by the Bureau. They examined samples taken at nine different incinerator sites. Samples taken at the sites were varied in three different mass ranges, the largest sample being approximately 750kg, the smallest being 90kg. The researchers found no significant differences with regard to precision for the studied sample mass groups of 75kg to those of greater mass. It should be noted there was no significant difference between the mass of waste divided nine subgroups such as food wastes, garden waste, etc. The researchers concluded it was not advantageous to take samples of mass greater than 75kg, to analyse any given waste stream.

Musa and Ho (Musa *et al*, 1981) also investigated the optimum sample size for solid waste analysis. Initially, they examined the work of other researchers and organisations. They cite the Institute of Public Cleansing in the United Kingdom who advised in 1964, a sample be taken of not less than 1 tonne in total mass, from not less than 100 premises. They examined

the results of four waste surveys undertaken in Australia. Unfortunately, the researchers are primarily interested in household waste surveys. However, one important result of their studies was their results indicated the number of increments taken was of greater importance, with regard to accuracy of results, than the total mass of the sample.

The American Society for Testing Materials (ASTM) practices for sampling various solid materials including solid waste, were also examined. Those standards examined included:

Standard Practice for Sampling Aggregates Designation: D75 - 87 (Reapproved 1992)

Standard Test Methods for Collection of a Gross Sample of Coal Designation: D2234 - 89

Standard Test Method for Determination of the Composition of Unprocessed Municipal Solid Waste Designation: D5231 - 92

When sampling aggregates, the larger the nominal size of the aggregate the larger the minimum sample size. For coarse aggregate of size 90mm, coupled with sampling from a stockpile (an unsatisfactory sampling situation), a minimum of 3 increments is recommended of minimum mass per increment, 55kg. The sampling of raw or uncleaned coal was also examined. It is recommended for uncleaned coals above 150mm in size, the minimum number of increments be 35, of minimum mass 7kg. This method would be statistically correct for a total mass of raw coal not exceeding 900 tonnes. The ASTM method for sampling unprocessed municipal base is based on sampling to allow examination of waste sampled into various categories such as paper, plastic, etc. It is recommended a sample size of 91 - 136kg would be representative of a vehicle load of municipal solid waste.

All of the above were considered to ensure representative sampling of the excavated municipal solid waste. Key points noted were: the correct sample size should approximate 75kg (Klee *et al*, 1970); the correct sample size should approximate 225kg (American Public Works Association, 1970); the greater the number of increments the greater the degree of accuracy that can be expected (Musa *et al*, 1981); when sampling uncleaned coal above 150mm in size, of total mass 900 tonnes, the minimum number of increments be 35, of minimum mass 7kg (ASTM, 1993).

The total mass of excavated municipal solid waste from Coastal Park Sanitary Landfill approximated 5000kg. The solid waste was sampled after size reduction, prior to transportation to pilot-scale landfill column. Reduction of size before sampling is advantageous as the homogeneity of the solid waste is improved. As the solid waste was loaded for transportation, incremental sampling was practised at equally spaced time and mass intervals. A total of 20 increments were taken, the average weight of each increment being approximately 11kg. Therefore the total mass of the sample of municipal solid waste was 230kg. This method of sampling should eliminate any sources of error and ensure samples taken for use in the laboratory were fully representative of that municipal solid waste loaded into the pilot-scale landfill columns.

After sampling, the incremental samples were placed in thick plastic bags, sealed with nylon cord. These plastic bags were then subsequently placed in another plastic bag, that outer plastic bag being sealed in an similar manner. This method was utilised to ensure that any moisture associated with the municipal solid waste was not lost, as the first step in the sample preparation was the analysis of moisture content.

5.3.2 SAMPLE PREPARATION: MUNICIPAL SOLID WASTE

On arrival at the laboratory each incremental sample was opened individually and the municipal solid waste placed onto a clean dry concrete area. Each increment was then mixed rapidly, cut into quarters, a shovel full taken from each quadrant until it was judged sufficient mass, in this case approximately 5kg, was available for the determination of moisture content. The remainder of the increment being labelled, re-bagged and stored. The municipal solid waste for moisture determination was then placed within the drying oven. The sample was then dried at 75°C for 48 hours (American Public Works Association, 1970). It was then removed from the oven and allowed to cool, and weighted, the weight being noted. The incremental sample was then replaced within the oven for a further 24 hours. The sample was then removed from the oven, allowed to cool and reweighed. If no further weight change was evident, the sample was made available for size reduction. The results of moisture determination are shown overleaf.

After moisture determination, the incremental samples were then individually reduced in size to approximately $5cm^2$ by use of hand scissors and tin snips. It is advised by the American Public Works Association's Tentative methods of analysis of refuse and compost (American Public Works Association, 1970) to discard inorganic materials such as glass, metals and ceramics. In South Africa, with the extremely efficient scavenging of waste (indicative of it's socio-economical problems) at landfills, and prior to disposal, there was a marked absence of commodities of this nature. After the first stage of size reduction, the incremental sample was then reduced in mass by the method previously described to approximately 2kg. The remainder of the increment being labelled, re-bagged and stored. The incremental sample of mass 2kg was then further reduced in size with a laboratory electrically driven hammer mill, to pass through a 1mm sieve.

This degree of size reduction conforms with the size range specified by the United States Environmental Protection Agency Method 1311 Toxicity Characteristic Leaching Procedure (US EPA Method 1311 TCLP) (US EPA, 1992). It is a requirement of the US EPA the solid waste must pass through a 9.5mm standard sieve. The Public Works Association's Tentative methods of analysis of refuse and compost (American Public Works Association, 1970), require the waste to be ground to pass through a 1mm sieve. There is not mention of a minimum size in the documentation supplied by the US EPA. After final size reduction, each sample increment was placed in a 2ℓ plastic bucket fitted with a snap-fit plastic lid. Prior to storage each increment was well mixed, and a small amount, approximately 200g, was removed from each increment and placed in an additional pail. This increment was labelled sample 21 and was deemed fully representative of the solid was previously placed in the pilot-scale landfill columns.

TABLE 5.1 MOISTURE CONTENT OF MUNICIPAL SOLID WASTE FROM COASTAL PARK SANITARY LANDFILL SITE

Sample No.	Initial increment mass (kg)	Mass of sample to be dried (g)	Mass of dried sample (g)	Percent moisture (dry)	Percent moisture (wet)
1	9.0	3720.1	2893.6	28.6	22.2
2	8.5	4156.3	3209.8	29.5	22.8
3	12.5	6235.5	4979.4	25.2	20.1
4	23.3	5425.6	4282.7	26.7	21.1
5	10.5	4506.4	3640.7	23.8	19.2
6	10.5	5012.1	3963.7	26.5	20.9
7	10.6	5516.6	4396.3	25.5	20.3
8	10.1	5397.0	4296.0	25.6	20.4
9	9.2	4452.7	3598.3	23.7	19.2
10	10.8	4381.7	3529	24.2	19.5
11	9.3	4634.7	3709.8	24.9	20.0
12	8.5	3993.5	3246.3	23.0	18.7
13	12.6	5417.5	4324.1	25.3	20.2
14	14.3	5688.2	4626.4	23.0	18.7
15	9.7	5271.8	4238.7	24.4	19.6
16	13.6	6047.8	4726.8	27.9	21.8
17	14.7	5667.8	4469.0	26.8	21.2
18	8.3	3896.3	3024.3	28.8	22.4
19	10.6	4805.3	3898.4	23.3	18.9
20	12.7	6910	5424.5	27.4	21.5
Average				25.7	20.4

5.3.3 CHARACTERISATION OF THE MUNICIPAL SOLID WASTE

(a) Metal content

TABLE 5.2 METAL CONTENT: MUNICIPAL SOLID WASTE SAMPLED AT COASTAL PARK SANITARY LANDFILL SITE

Sample No.	Copper	Chromium	Zinc	Cadmium	Nickel	Lead	Potassium	Phosphorous
3	28	37	345	1.3	6	142	1047	5.4
6	22	11	116	1.3	11	46	823	106
9	15	5	135	1.5	9	32	1249	5.7
12	18	8	127	0.8	35	48	621	2.4
15	34	16	212	1.7	15	143	1261	5.5
18	31	21	309	1.4	4	60	1195	193
Average	25	16	207	1.3	13	79	1033	53
21	29	12	265	0.8	17	45	1240	32

All results quoted above in ppm (w/w)

Sample No. 21 being the cumulative sample, of all the incremental samples taken.

ENCON Associates conducted a field scale landfill project at the Mountain View Landfill, in California (Pacey, 1989). The researchers examined the process of methane gas generation in municipal solid waste landfills, and evaluated the effectiveness of different methods used to enhance methane generation. Six large test cells were constructed each containing approximately 7500 tonnes of municipal solid waste. The cells were treated with differing stabilisation enhancement techniques, one cell remained untouched, and was used as a control. After five years, the cells were subjected to rigorous municipal solid waste sampling. Additionally, adjacent solid waste was sampled. They examined 28 samples, with 5 replicate analyses per sample. The only heavy metal identified for analysis was nickel. Nickel has been identified as possibly inhibitive in the landfill environment. It is of interest to examine the results from the control cell, and that of adjacent refuse, and compare these with the results of municipal solid waste excavated from Coastal Park Sanitary Landfill Site which was estimated to be of age 1 year.

It is difficult to compare results because of the variable composition of municipal solid wastes as received at landfill sites in different countries. However, the low percentage of volatile solids in the municipal solid waste excavated from Coastal Park Landfill Site is probably indicative that the solid waste was actually in excess of 1 year of age. The percentage volatile solids of the solid waste excavated from Coastal Park Sanitary Landfill site averaged 24 percent. The solid waste excavated from Mountain View Landfill was 43.5 percent in the control cell and 27 percent in the adjacent solid waste, after being deposited for 5 years.

(b) Additional analyses

TABLE 5.3 ADDITIONAL ANALYSES: MUNICIPAL SOLID WASTE SAMPLED AT COASTAL PARK SANITARY LANDFILL SITE

Sample No.	pH	Volatile solids (percent)	Total Kejldahl Nitrogen
3	7.7	32.6	20
6	8.0	19.2	10
9	7.8	23.5	40
12	7.7	16.4	20
15	8.2	24.9	10
18	8.4	27.6	10
Average	8.0	24.0	20
21	8.1	17.4	20

Except pH, results quoted above in ppm (w/w)

TABLE 5.4 CHARACTERISATION OF MUNICIPAL SOLID WASTE: MOUNTAIN VIEW AND COASTAL PARK

Component	Mountain View (control cell)	Mountain View (adjacent municipal solid waste)	Coastal Park (average values)
Moisture content (%)	40.0	22.0	20.4
pH	6.7	6.8	8.0
Volatile solids (%)	43.5	27.1	24.0
Kjeldahl Nitrogen (ppm [w/w])	0.4	0.3	20
Phosphorous (ppm [w/w])	279	185	53
Nickel (ppm [w/w])	6.3	3.7	13

5.4 COPPER-CHROMIUM-ARSENIC WOOD PRESERVATIVE

5.4.1 CHARACTERISATION OF THE COPPER-CHROMIUM-ARSENIC WOOD PRESERVATIVE

The copper-chromium-arsenic product employed in this investigation is marketed by Rentokil South Africa (Pty) Ltd., it is designated *Celcure A Paste*. The specification as supplied on the product is as shown overleaf:

Copper:	71g per kg
Chromium:	119g per kg
Arsenic:	128g per kg

The relative density of the solution is quoted as 1.85.

The method of data presentation employed by Rentokil South Africa (Pty) Ltd., tends to obscure the actual composition of the product. The composition as stated in the Material Safety Data Sheet is as shown below (Rentokil South Africa, 1994):

Component	Percent weight by weight
Arsenic pentoxide	24.63
Sodium dichromate	38.25
Copper sulphate	30.42

Analysis in the laboratory revealed the following mixture of the following composition:

Component	Grams per litre
Arsenic (as As)	270.2
Chromium (as Cr)	269.6
Copper (as Cu)	93.1

The solution was also analysed to determine speciation of the chromium and arsenic. Analysis revealed the chromium to be composed of 94.8 percent chromium(VI); the arsenic was composed of 97.1 percent arsenic(V). The European Economic Community Classification is Corrosive (Harmful); the Hazard Symbol employed is "Corrosive".

5.5 EVALUATION OF THE KINETICS OF ADSORPTION AND DESORPTION OF COPPER, CHROMIUM AND ARSENIC AT LABORATORY-SCALE

The kinetics of adsorption of the solution of copper, chromium and arsenic was examined by modifying the US EPA Method 1311 Toxicity Characteristic Leaching Procedure (TCLP). The procedure is described in detail in Appendix X of Ballard (1997).

5.5.1 MODIFICATION OF THE ENVIRONMENTAL PROTECTION AGENCY METHOD 1311 TOXICITY CHARACTERISTIC LEACHING PROCEDURE: KINETICS OF ADSORPTION

The TCLP was modified to enable the determination of the degree of adsorption, and the rate of that adsorption of industrial waste onto municipal solid waste. The extraction fluid used is composed of glacial acetic acid, sodium hydroxide and deionised water. The composition is shown below:

Component	Percent volume
Glacial acetic acid	0.57
Sodium hydroxide	4.00
Deionised water	95.43

This solution is termed Extraction fluid #1 in Appendix X of Method 1311. The solution's acetate buffered system would appear to provide a good approximation of leachate from a landfill in the acetogenic phase of stabilisation. The procedure for the preparation of the extraction fluid; addition of the copper-chromium-arsenic; pH adjustment, is described in depth below. Equivalent attention to detail in chemical procedures was practised

throughout. However, in the interest of brevity, the reader is referred to this section (Section 5.5.1) when similar chemical procedures are discussed. The modification of the EPA TCLP was effected in the following manner. The solution was formulated as shown above. Upon formulation, the pH was determined to ensure the fluid was correctly produced. If the procedure is followed correctly, the pH of the solution should be 4.93 +/- 0.05 pH units.

The copper-chromium-arsenic solution was available in a 25ℓ container. The contents of the container was firstly well mixed. From that container, an aliquot of volume 2.5ℓ was taken and placed in a glass winchester bottle. This bottle was subsequently used in all ensuing experiments. From this container, after ensuring the contents were well mixed, 10mℓ of the concentrated copper/chrome/arsenic solution was then transferred by pipette into a 100mℓ volumetric flask, deionised water was then added to the volumetric flask to the prescribed point. The reason for this exercise being, the copper-chromium-arsenic solution is viscous and dilution was necessary to maintain accuracy. Approximately 500mℓ of the extraction fluid was then transferred into a 2ℓ glass measuring cylinder, to this was added 10mℓ of the diluted copper-chromium-arsenic solution, the solution was then mixed with a glass rod. Further extraction fluid was then added to glass measuring cylinder until the solution was 1ℓ in volume. The solution was again stirred to assure uniformity. It had been previously calculated that this degree of dilution would provide a solution of composition:

copper, approximately 80mg;
chromium, approximately 300mg;
arsenic, approximately 260mg.

It is a requirement, when conducting adsorption studies, that sufficient heavy metals are available at the start of the study to ensure an excess of metal in solution at completion of the experiment.

A sample of volume 25mℓ was then taken. The pH of the solution was then measured. The pH of the solution was then adjusted with a 1N sodium hydroxide until the desired pH was achieved. Three pH values were chosen, pH5.5; pH6.4; and pH7.0. These pH values were selected as these values cover the usual range of pH encountered in full scale landfill operations. The measuring cylinder was then placed on the laboratory bench for approximately 30 minutes. This allowed any precipitation of the metals in solution to occur. After precipitation had occurred, the supernatant was then transferred into another measuring cylinder. A 25mℓ sample was then taken for analysis.

All 21 samples of the prepared municipal solid waste were available in the laboratory. To assure the results of the kinetic studies to be reproducible, and to eliminate any bias from the municipal solid waste it was decided to perform the experiments in triplicate at the three pH values. Another provision was made to assure reproducibility; at the three pH values one sample of the cumulative sample (sample 21) was used, the other two samples being differing sub-samples. This was done at every stage of the laboratory investigation.

A 50g portion of the prepared municipal solid waste was weighted and placed in the extractor vessel. The extractor vessel employed was a 2ℓ Schott bottle, fitted with a screw neck, with an internal teflon seal, within the plastic screw top. Exactly 1ℓ of the relevant pH-adjusted, dilute copper-chromium-arsenic solution was then added to the extractor vessel. The extractor vessel was then placed in the agitation device and agitation began. Samples of the dilute copper-chromium-arsenic solution, of volume 25mℓ, were then taken at designated time intervals throughout the duration of the experiment. These samples were taken at time zero, then subsequently after 0.5h, 1.0h, 2.0h, 4.0h, 8.0h, 16.0h, and 32.0h. From the examination of adsorption studies of conducted by soil scientists examining the adsorption of various metals onto soils it was thought an total experimental duration of 32 hours would be adequate. To confirm this, an initial trial was undertaken. After completion of the experiment the pH of the solution in the extractor vessel was determined.

The pH of the solutions was elevated during the experimental procedure. This elevation of pH is discussed in Chapter 8. The initial and final values of solution pH are shown below in Table 5.5.

5.5.2 MODIFICATION OF THE ENVIRONMENTAL PROTECTION AGENCY METHOD 1311 TOXICITY CHARACTERISTIC LEACHING PROCEDURE: KINETICS OF DESORPTION

On completion of the adsorption procedure, the contents of each extractor vessel were then filtered. Deionised water was added to the extractor vessel to ensure all solid particles were removed from the vessel, onto the filter paper. The filter paper plus solids was then removed from the Buchner funnel and placed in a stainless steel tray. The tray was then placed into a drying oven adjusted to a temperature of 50°C. The trays remained in the oven until all traces of moisture were removed.

TABLE 5.5 CHANGE IN pH DURING EXPERIMENTAL PROCEDURE

Coding	Initial pH	Final pH	Coding	Initial pH	Final pH
A	5.5	7.0	F	6.4	8.0
B	5.5	7.0	G	7.0	8.2
C	5.5	7.0	H	7.0	8.6
D	6.4	8.0	I	7.0	8.1
E	6.4	8.0			

The dried solids were then transferred into the extractor vessel. Approximately, 1ℓ of the relevant pH-adjusted extraction fluid was then prepared. A small aliquot was then taken for analysis, and exactly 1ℓ of the extraction fluid was added to the extractor vessel (a sample subjected to adsorption at a particular pH value was desorbed at the same pH value). The extractor vessel was then placed in the agitation device and agitation began. Samples of the extraction fluid of volume 25mℓ, were then taken at designated time intervals. Samples were taken at time zero, then subsequently after 0.5h, 1.0h, 2.0h, 4.0h, 8.0h, 16.0h, and 32.0h. On completion of the experiment the samples were preserved by the addition of the relevant quantity of 10M nitric acid (APHA Standard Methods, 1992).

5.6 LABORATORY-SCALE EVALUATION OF ADSORPTION ISOTHERMS

The kinetic studies commenced with initial concentrations of copper, chromium, and arsenic of approximately, 80; 300; and 260mgℓ^{-1}, respectively. To construct adsorption isotherms, additional data at lower concentrations is a requirement.

A similar procedure was then undertaken to that described previously in the evaluation of adsorption kinetic rate constants (Section 5.5.1). Again, three pH values were chosen, pH5.5; pH6.4; pH7.0. Differing amounts of the diluted copper-chromium-arsenic solution were then added to the pH adjusted extraction fluid. The concentration range was:

Copper (mgℓ^{-1})	80	50	40	15
Chromium (mgℓ^{-1})	300	200	150	60
Arsenic (mgℓ^{-1})	260	180	130	50

The samples taken during the evaluation of the kinetic rate constants for the adsorption of the various metals onto the municipal solid waste had already been analysed and the results partially evaluated. There did not appear to be any difference in the adsorption/desorption characteristics displayed by the various sub-samples of the municipal solid waste. However, it was decided to be prudent and to vary the sub-samples again. All 21 samples of the municipal solid waste were available in the laboratory. The cumulative sample (sample 21) was employed at each varying concentration of the copper-chromium-arsenic solution, the remaining two samples being differing subsamples from those employed in the kinetics investigation. Samples of the dilute copper-chromium-arsenic solution, of volume 25mℓ, were then taken prior to the commencement of agitation. A final 25mℓ sample of the solution was then taken for analysis after 32 hours had elapsed. On completion of the experiment, all samples were then preserved by the addition of the relevant quantity of 10M nitric acid (APHA Standard Methods, 1992).

5.7 ANALYTICAL PROCEDURES

Chemical analysis was performed at the Laboratory of the Department of Chemical Engineering of the University of Cape Town, and at the Laboratory of the Scientific Services Branch, City Engineer's Department, City of Cape Town. In some instances analysis was duplicated, being accomplished at both establishments to ensure accuracy. Analysis of the kinetics experiments was such an instance. The initial analysis of copper chromium, and arsenic was undertaken at the Department of Chemical Engineering. Copper and chromium analysis was then repeated at Scientific Services Branch on approximately 25 percent of the samples to ensure accuracy. In the case of copper agreement was excellent; some degree of instrument drift was noted in the analysis of chromium; the relevant samples were re-analysed were necessary.

TABLE 5.6 ANALYTICAL RESPONSIBILITIES

Component	Establishment
Characterisation of the municipal solid waste	Scientific Services Branch
Characterisation of the copper-chromium-arsenic wood preservative	Department of Chemical Engineering
Laboratory scale adsorption and kinetic trials	Department of Chemical Engineering, certain samples being repeated at the Scientific Services Branch

(a) Characterisation of the municipal solid waste

The municipal solid waste was analysed for the following:
Moisture content; copper; chromium; zinc; cadmium; nickel; lead; potassium; phosphorous; pH; percentage volatile solids; and total kejldahl nitrogen.

(b) Characterisation of the copper-chromium-arsenic wood preservative

The wood preservative was analysed for copper; chromium and arsenic.

(c) Laboratory-scale investigation into kinetics and adsorption properties of the CCA wood preservative

All samples taken were analysed for copper, chromium and arsenic

The analytical equipment employed is detailed below.

TABLE 5.7 ANALYTICAL EQUIPMENT

Analysis	Instrument
Conductivity	EDT Instruments BA 380
pH	Orion Research Model 601
Metal content	GBC Model 902 Atomic Adsorption Spectrophotometer

The analysis of metals was undertaken at the University of Cape Town, a Varian SpectrAA 30 Atomic Adsorption Spectrophotometer was employed.

5.8 SUMMARY

Municipal solid waste was excavated from Coastal Park Sanitary Landfill Site. The municipal solid waste was reduced in size and transported to the laboratory. The municipal solid waste was fully characterised in terms of moisture content, metal content, pH, volatile solids and Total Kejldahl nitrogen. The metals of concern in this investigation, copper, chromium and arsenic are in the form of CCA (or Tanalith), a chemical commonly employed for wood preservation. This chemical was also fully characterised.

The kinetics of adsorption and desorption of the solution of copper, chromium and arsenic onto municipal solid waste was examined. Equilibrium studies were also completed. Both adsorption/desorption and the equilibrium studies utilised a modification of the US EPA Method 1311 Toxicity Characteristic Leaching Procedure (TCLP).

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CHAPTER 6
MATERIALS AND METHODS: PILOT-SCALE LANDFILL COLUMN STUDIES

6.1 INTRODUCTION

Pilot-scale landfill columns were constructed at Athlone, Cape Town. Tracer studies were then undertaken at pilot-scale. Tracer studies enable the deviation from ideal flow to be determined. The combination of the results from the kinetic studies and the results from the tracer studies allow the computation of the exit stream composition. Heavy metals were then co-disposed at pilot-scale to evaluate the accuracy or otherwise of both the tracer studies and the chemical kinetics. The combination of the laboratory scale and pilot-scale studies should then allow the prediction of the amount of copper, chromium and arsenic which can be retained in a full-scale landfill operation.

6.2 PILOT-SCALE INVESTIGATION

This investigation advanced on two fronts:
Determination of the residence time distribution/deviation from ideal behaviour of the pilot-scale landfill columns.
Evaluation, at pilot-scale, of the kinetic rate constants determined at laboratory scale.

6.3 DESIGN OF PILOT-SCALE LANDFILL COLUMNS

Pilot-scale landfills have been utilised to observe and quantify phenomena occurring in landfills for over twenty five years. Many different types of experiments have been conducted, and their use is well documented. The column design of other researchers was thoroughly examined before construction of the Athlone pilot-scale columns commenced.

6.3.1 DESIGN AND CONSTRUCTION OF THE ATHLONE PILOT-SCALE LANDFILL COLUMNS

The initial step in the design of the pilot-scale landfill columns was to survey the literature and to review the constructional techniques employed by previous researchers. These are summarised in tabular form below. In evaluating the designs tabulated, one can observe a gradual simplification of the design of the pilot-scale columns, with the design Pohland pioneered (Pohland, 1975), becoming virtually a standard. The design of the University of

Cape Town pilot-scale columns was very similar to the column that originated in Atlanta, at the Georgia Institute of Technology, designed by Pohland.

TABLE 6.1 DESIGN ASPECTS OF PILOT-SCALE LANDFILL COLUMNS: I

Researchers	Number of columns	Height of columns (m)	Cross-sectional Area (m^2)	Configuration	Material of construction
Qasim & Burchinal (1970a, 1970b)	4	1.2, 2.4, 3.6, & 4.8	0.6362	Circular	Concrete
Fungaroli & Steiner (1971)	1	3.96	1.83	Square	Low carbon steel coated with fibreglass
Rovers & Farquhar (1973)	3	4.3	2.545	Circular	
Pohland (1975)	4	-	0.65	Circular	Steel
Newton (1977)	-		5.0	Rectangular	Concrete internally coated with epoxy
DeWalle *et al* (1978)	18	0.75	0.255	Circular	Steel walls with plastic liner
Raveh & Avnimelch (1979)	16	2.5		Circular	Poly Vinyl Chloride
Pohland (1980)	2	5.2	9.0	Square	Reinforced concrete coated with sealant
Tittlebaum (1982)	4	3.4	0.7854	Circular	Epoxy coated corrugated steel pipe

TABLE 6.1 DESIGN ASPECTS OF PILOT-SCALE LANDFILL COLUMNS: I (continued)

Researchers	Number of columns	Height of columns (m)	Cross-sectional Area (m^2)	Configuration	Material of construction
Ham & Bookter (1982)	8	1.5	165.62	Rectangular	One wooden wall, three concrete walls
Collins & Spillman (1982)	8	5.0 to 6.0	19.64	Circular	Poly ethylene flexible walls
Pohland *et al* (1985, 1986)	4	4.27	0.65	Circular	Corrugated steel pipe
Gould *et al* (1989)	10	4.27	0.65	Circular	Steel
Reinhart & Pohland (1991)	2	3.0	0.65	Circular	Steel
Pohland (1992)	5				
Pohland *et al* (1993)	3	3.25	0.65	Circular	Steel
Otieno (1994)	4	-	0.159	Circular	
Chapman & Ekama (1991); Novella *et al* (1996)	6	4.25	0.283	Circular	Galvanised steel coated with epoxy

TABLE 6.2 DESIGN ASPECTS OF PILOT-SCALE COLUMNS: II

Researchers	Underdrain	Distributor	Instrumentation	Environment	Insulation
Qasim & Burchinal (1970a, 1970b)	Size graded clinker,(8 - 13cm) 20mm steel outlet pipe	-	Thermocouples	Outdoor	None
Fungaroli & Steiner (1971)	Sand & glass beads	Perforated plastic pipe	Thermocouples	Indoor	Insul-ation plus heating tapes
Rovers & Farquhar (1973)		Perforated tubing	Thermocouples	Outdoor & Indoor	Indoor cell, Insulated
Pohland (1975)		Positioned in soil top cover			
Newton (1977)	-			Outdoor	
DeWalle *et al* (1978)	Gravel (15cm)	Sprinkler	Thermocouples	Indoor	None
Raveh & Avnimelch (1979)	Glass beads	0.3m sand		Indoor	None
Pohland (1980)		Positioned in gravel between MSW & top cover		Outdoor	Styro-foam
Tittlebaum (1982)	0.3m of sand	PVC pipe placed in sand layer		Indoor	None
Ham & Bookter (1982)		None	Thermocouples	Outdoor	None

TABLE 6.2 DESIGN ASPECTS OF PILOT-SCALE COLUMNS: II (continued)

Researchers	Underdrain	Distributor	Instrumentation	Environment	Insulation
Collins & Spillman (1982)			Thermocouples	Outdoor	
Pohland *et al* (1985, 1986)	Graded aggregate	Placed in aggregate layer between topsoil and MSW		Outdoor	None
Gould *et al* (1989)	Graded aggregate	Placed in aggregate layer between topsoil and MSW		Outdoor	None
Reinhart & Pohland (1991)				Indoor	
Pohland (1992)					
Pohland *et al* (1993)	Soil		Thermocouple		
Otieno (1994)	Gravel (100mm) placed on grate	Placed in 200mm gravel top layer		Indoor	None
Chapman & Ekama (1991): Novella *et al* (1996)	Graded pebbles, 20mm steel pipe	Perforated tubing	Thermocouple	Outdoor	40mm glass fibre

A diagram of the pilot-scale landfill columns constructed at Athlone is shown overleaf. Subsequently, the principal design considerations are discussed.

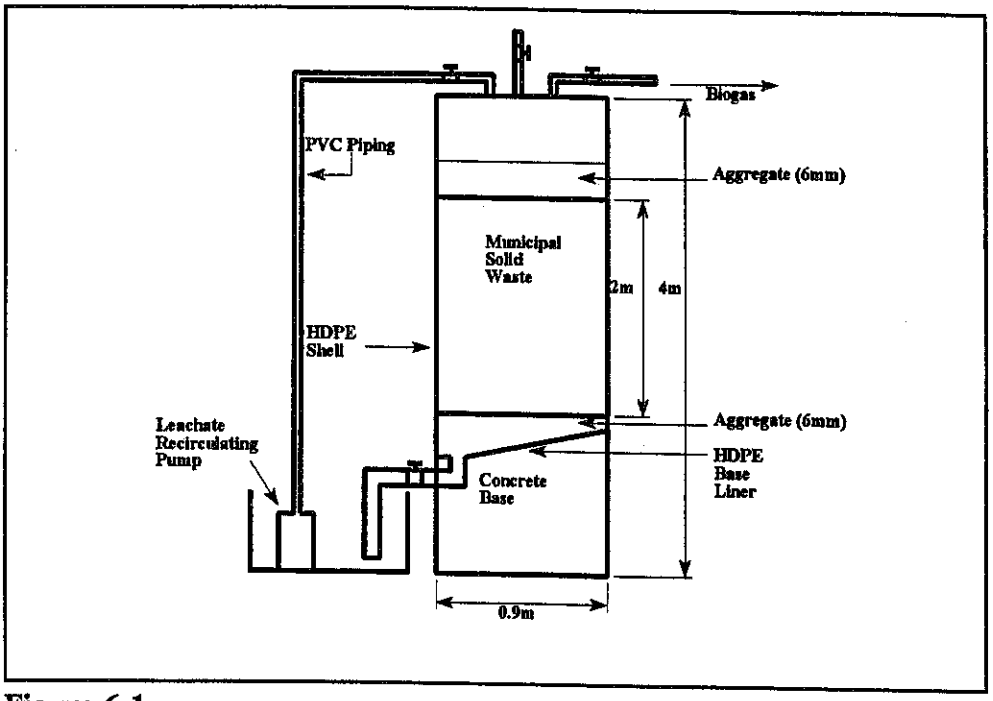

Figure 6.1
Diagrammatic representation of the Athlone pilot-scale landfill columns

(a) Column Shell

Problems had been experienced with the previous columns at the University of Cape Town. Attention had been paid to the durability of the columns, the 2mm gauge steel had been hot-dipped galvanised prior to an internal coating of epoxy paint. Corrosion problems occurred and Novella *et al* (1996) had difficulty in the latter stages of his experimental programme preserving the integrity of the columns.

The envisaged material should be inert to the products of decomposition of the municipal solid waste, such as the low pH leachate experienced; able to withstand the elements, as it was envisaged the pilot-scale columns would be outdoor; mechanically strong enough to hold the municipal solid waste. It was extremely important that chemical wall effects be avoided. A plastic type material was considered to be one of the better options available. Tittlebaum (1982) successfully constructed a pilot-scale landfill column shell from polyvinylchloride. Scrap High Density Poly Ethylene (HDPE) pipe became available from the City Engineers Department of the City of Cape Town. The dimensions of this pipe were internal diameter 0.70m, external diameter 0.90mm, the pipe was available in varying lengths. It was decided that five columns would be sufficient to meet the aims and objectives of the project. The pipes were firstly cut to a length of 4.1m.

(b) Underdrain

The next step in the design of the pilot-scale landfill columns was to determine the underdrain design. Again, the design of previous columns were surveyed. It was decided to cut the columns near to the base at an angle near to the base of the column, seal the base of the column with a HDPE plate, and to use a layer of 6mm aggregate as the underdrain.

(c) Column shell construction
The pipe was then cut 1m from the base at an angle approximating 30 degrees to the horizontal plane. The 0.9m base was then secured to a concrete plinth by means of steel tie-rods, the base being partially filled with concrete. A square notch was then cut into the HDPE base at the lowest point of the 30 degree cut. Shuttering was then placed around the notch and the remaining space within base filled with concrete.

The longer of the two lengths of HDPE pipe was then sealed with an elliptical plate of HDPE. Prior to sealing a 50mm hole was drilled in the sheeting at what was anticipated to be the lowest point of the column. A short stub of 50mm polyvinylchloride pipe was securely fixed into the hole, by means of a plastic securing lock-nut either side of the plate. An articulated crane lifted the 3.2m length of HDPE piping into the vertical position; the pipe was then lowered onto the base. The upper section was secured to the base by means of a steel collar, the column was further secured to the external wall of a single storey building located behind the column. On completion of the erection of the column shell, a 50mm polyvinyl chloride ball valve was affixed to the 50mm stub, leading to a U-bend, on the outside of the column. A plastic grid was then glued to the stub in the inside of the column. The columns were then filled completely with water to test their integrity.

(d) Distributor
Again the design of previous columns was examined, it was felt earlier designs could be simplified further. It was thought, if one placed a layer of aggregate of sufficient depth above the municipal solid waste within the column, adequate dispersion of any liquid added would occur before contact with the solid waste. A layer of 6mm aggregate of thickness 45cm would be sufficient.

(e) Associated pipework and tankage.
As mentioned, it was decided to use 50mm diameter polyvinylchloride pipe as the outlet pipe from the base of the column. This relatively large diameter pipe was used to discourage any blockages. To enhance landfill stabilisation, leachate recirculation is necessary. This was provided by placing a 80ℓ vessel at the base of the column. Within the vessel was placed a small submersible pump. All other associated pipework was 25mm diameter polyvinylchloride.

(f) Instrumentation
The design of previous columns was examined. Early columns were often fitted with a number of thermocouples, usually positioned with varying depth. Fugaroli and Steiner (1971) placed 4 thermocouples in a column containing solid waste of height 2.4m, while DeWalle and co-workers (1978) placed 3 thermocouples in a column containing solid waste of height 0.6m. Later columns were usually only constructed with one thermocouple in position (Chapman *et al*, 1991; Pohland *et al*, 1993). The Athlone pilot-scale columns employed one thermocouple per column, the thermocouple being positioned centrally in the solid waste.

g) Insulation
The wall thickness of the column shell is 50mm, the material of construction being HDPE, a material of low thermal conductivity. It was considered that in the Cape Town, with it's

Mediterranean climate, insulation was not required. The HDPE column shell was black in colour. When the columns were first erected it was mid-Summer, it was noticed that the outer skin temperature became relatively hot. Before the municipal solid waste was placed in the columns the outer column shell was painted white. This immediately alleviated the problem.

(h) Municipal Solid Waste

For the purposes of our investigation, the height of municipal solid waste in the column was to be 2m. This height was dictated by prevailing conditions used by the City of Cape Town in their full scale landfill operations. The landfill sites within the municipality are operated such that there is a 2m layer of waste, soil cover, another 2m layer of waste, soil cover, and so on. This also conformed to the configuration used by other researchers in the field. The solid waste was reduced in size to between 25-40mm before introduction into the column. Again, this conformed to methods pioneered by other researchers. The bulk density of the municipal solid waste at the full scale landfills in Cape Town approximates 1000kgm^{-3}. To model the full scale landfill at pilot-scale it is desirable to achieve densities of that order. Both Newton (1977) and Pohland (1975) were censured by Cope (1983) regarding the density of the municipal solid waste in their work. The average bulk density of the municipal solid waste in the pilot-scale landfill columns was 922kgm^{-3}.

After the 6mm aggregate drainer was placed in the column shell; the column was drained after hydraulic testing; the column was then measured internally and marked at a distance exactly 2m from the top of the underdrain. The shredded municipal solid waste was incrementally weighted prior to placing in the columns. The pulverised solid waste was then periodically compressed by hand to ensure the correct densities were achieved. The results are shown below.

TABLE 6.3 PILOT-SCALE LANDFILL COLUMNS: PHYSICAL CHARACTERISTICS OF THE MUNICIPAL SOLID WASTE

Column	Internal diameter (m)	Height of MSW (m)	Mass of MSW (kg)	Volume (m^3)	Density (kgm^{-3})
1	0.7	1.88	694	0.7235	959
2	0.7	1.94	669	0.7466	896
3	0.7	1.94	668	0.7466	895
4	0.7	1.94	676	0.7389	915
5	0.7	1.94	694	0.7351	944
Average					922

6.3.2 OPERATION OF THE PILOT-SCALE LANDFILL COLUMNS

In this section, the general operation will be discussed initially. Subsequently, detailed consideration will be given to the different aspects of the monitoring.

The operation and monitoring of the column temperatures commenced on Wednesday, February 8th, 1995; designated Day Zero (0). Soon thereafter, on Day 12, water was added to the pilot-scale columns, to bring the municipal solid waste to field capacity. Water was added at a rate of 30ℓ per day over a period of 5 days; Day 12, Day 13, Day 14, Day 15 and Day 16. A total of 150ℓ was added. There was no further addition of moisture for a period of one month. The temperature of the columns continued to be monitored daily, and every 7 days the outlet of the pilot-scale landfill was opened and examined for leachate. No excess moisture was found during this period. Addition of water again commenced on Day 44. Water was added at a rate of 30ℓ per day over a period of 5 days; Day 44; Day 45; Day 46; Day 47; Day 48; a total of 150ℓ was added, the total volume of water added to the pilot-scale columns now being 300ℓ.

After the addition of the additional water, monitoring the columns for biogas commenced. Monitoring of the pilot-scale landfills every 7 days continued. The next occasion the outlets were examined (after the second addition of water), no leachate was present. Leachate was present when the column drains were examined on Day 60. The columns were then drained until the flow of leachate ceased. The volume of leachate was measured, and a sample of leachate taken for analysis. The leachate was then pumped back to the top of the column and added to the municipal solid waste, to enhance the stabilisation process. The initial draining of the columns provided a relatively large quantity of leachate. With the second draining and subsequent recirculation the quantity of leachate was reduced substantially, this value is used in the table overleaf showing the field capacity of the municipal solid waste in the column. The volume of leachate drained is deducted from that added. Probably, the initial relatively large quantity of leachate drained from the columns was caused by a mixture of liquid by-passing and wall effects.

(a) Leachate recirculation

Leachate first became evident on Day 60. The following procedure was then followed. Leachate was drained until the flow diminished to a slow drip. While the leachate was flowing a sample was taken for analysis. On these samples the following analyses were performed:

pH;
Electrical conductivity;
Chemical Oxygen Demand (COD), unfiltered;
Chemical Oxygen Demand (COD), filtered;
Chloride content;
Total Alkalinity;
Bicarbonate Alkalinity;
Orthophosphate.

From the analyses of total alkalinity, bicarbonate alkalinity and orthophosphate, the volatile acid alkalinity was then calculated.

After the leachate flow diminished to a slow drip, the outlet valve from the pilot-scale column was then closed and the volume of leachate drained was measured. This was accomplished with a calibrated dip stick. The leachate was then pumped to the top of the column by means of the permanently located submersible pump. The recirculation procedure was performed every 7 days, until Day 118. Recirculation was ceased at this point as the temperature inside the columns had dropped to below 15°C, and there was no evidence of biogas production. The lower temperatures were due to the onset of the South African winter season.

Recirculation of leachate recommenced on Day 231, as ambient temperatures were beginning to rise, as the southern hemisphere summer season was beginning. The recirculation procedure then continued as before the procedure being repeated after a time interval of 7 days. The procedure ceased on Day 358, as there was no resumption of biogas production.

TABLE 6.4 PILOT-SCALE LANDFILL COLUMNS: FIELD CAPACITY OF THE MUNICIPAL SOLID WASTE

Column	Initial total mass (kg)	Initial mass of water present (kg)	Initial mass of bone dry MSW (kg)	Water added - Leachate drained (kg)	Total mass of water Day 67 (1995-03-16)	Percent moisture content (wet)
1	694	142	552	267	409	41.8
2	669	136	533	260	396	42.6
3	668	136	532	247	383	41.9
4	676	138	538	263	401	42.7
5	694	142	552	256	398	41.9
Average						42.2

(b) Volumetric biogas monitoring

Volumetric biogas monitoring commenced Day 54 prior to the addition of water, on Day 60. The instrument employed was a wet type gas flow meter manufacturer by Alexander Wright & Company (Westminster) Limited, model DM3A. One gas meter was used to monitor all 5 columns. The mode of operation was as outlined below.

The meter was placed within the building against which the pilot-scale landfill columns were secured. A hole was drilled through the building wall through which was placed a small bore plastic pipe. One end of the pipe was connected to the gas outlet positioned at the top of the columns, the other end being connected to the gas meter. The biogas from each column was measured every 5 days. The biogas vent from the columns being left open to atmosphere for the remaining 4 days. Leakage of biogas was noticed on Day 65.

The initial design of the columns featured a removable top cover, this was found to leak. Difficulties in effecting repair were experienced. It was then decided to treat the top covers in an identical manner to the base of the column and to heat weld the HDPE plates to the column shell. This was successful. The consequences of these problems was monitoring of the evolution of the biogas was severely curtailed. It should be noted the experimental study involved 5 columns and it was not known when biogas evolution would start, and the volume of biogas that would be evolved; this further complicated matters

The problems are shown chronologically below:

Day 65	Gas leakage first detected
Day 65 - Day 86	Repairs effected
Day 105	Repairs effected
Day 105 - Day 117	Only small amounts of biogas evolved, further leakage suspected
Day 117	HDPE heat welded onto the horizontal column shell
Day 118	Biogas monitoring resumed

Monitoring recommenced. but further problems were now experienced. Ambient temperatures began to fall with the onset of the southern hemisphere winter. Biogas production ceased completely from all of the pilot-scale columns on Day 128, the temperature of the columns had declined to below 10°C

When ambient temperatures began to rise at start of Spring, volumetric monitoring recommenced on Day 205. Monitoring continued until Day 348, biogas was not detected from any of the pilot-scale columns during this period. It was then decided to cease monitoring. It would appear the columns were now completely stabilised as no further evidence of biogas evolution was present. While biogas was present the maximum biogas volumetric flowrates were:

Pilot-scale landfill column No. 1	7.01 ℓday^{-1}
Pilot-scale landfill column No. 2	4.78 ℓday^{-1}
Pilot-scale landfill column No. 3	7.01 ℓday^{-1}
Pilot-scale landfill column No. 4	0.57 ℓday^{-1}
Pilot-scale landfill column No. 5	1.16 ℓday^{-1}

(c) Analysis of biogas composition

Samples were taken from the biogas outlets on three occasions. A small plastic inflatable container was employed for this purpose. The flexible vessel was secured to the gas outlet, the biogas allowed to fill the container by means of it's own pressure. The container was then evacuated prior to securing to the biogas outlet, then allowed to fill twice, on the third expansion, this sample was retained for analysis. The composition of the gas was then determined by means of a Varian 3300 Gas Chromatograph.

Samples were taken on Day 93, Day 124 and Day 127. The results are shown below. It should be noted, numerous attempts were made to sample biogas but as the biogas production from the columns was limited, only the results below can be shown.

TABLE 6.5 PILOT-SCALE LANDFILL COLUMNS: COMPOSITION OF GENERATED BIOGAS

Day	Sample	Percent methane	Percent carbon dioxide	Percent oxygen	Percent nitrogen
Day 93	Column 1	53.4	40.5	0.3	5.8
Day 124	Column 1	40.4	20.4	6.5	32.7
Day 127	Column 1	43.2	27.8	3.5	25.5
Day 93	Column 2	No gas production			
Day 124	Column 2	22.8	18.6	5.7	52.9
Day 127	Column 2	26.7	24.9	2.6	45.8
Day 93	Column 3	32.8	29.1	2.2	35.9
Day 124	Column 3	No gas production			
Day 127	Column 3	No gas production			
Day 93	Column 4	46.1	34.4	2.2	17.3
Day 124	Column 4	23.7	18.7	2.4	55.2
Day 127	Column 4	31.4	25.3	2.0	41.3
Day 93	Column 5	40.8	35.1	2.0	22.1
Day 124	Column 5	No gas production			
Day 127	Column 5	No gas production			

6.4 RESIDENCE TIME DISTRIBUTION: PILOT-SCALE LANDFILL COLUMNS

A continuous reactor may behave in a manner comparable to a plug flow reactor or as a perfect mixer, but it can never achieve these idealised states. In an ideal plug flow reactor, all reactant and product molecules move at the same rate in the direction of the bulk fluid flow, while in real flow reactors, fluid velocity profiles, turbulent mixing, and molecular diffusion cause molecules to move with a variety of speeds and directions. These inevitable deviations in ideal reactor conditions lead to several fundamental problems in reactor design and analysis (Dudukovic *et al*, 1983).

Tracer response analysis is a technique which is used to characterise the type of flow and mixing that takes place in a continuous process vessel. The technique is also applicable to biological systems, hydrological systems, and in general to any system through which a fluid flows continuously. In this case it is applied to the pilot-scale landfill columns.

The simplest method of determining the residence time distribution of a fluid within a reactor involves the use of a physical or non-reactive tracer. A number of different experimental techniques are available, the simplest to interpret are the pulse or the step experiment. For the purposes of this investigation it was decided to employ a non-reactive tracer with pulse input.

6.4.1 DETERMINATION OF NON-REACTIVE TRACER

It is of importance that the tracer utilised should behave in a manner identically to the fluid molecules within the reactor. No tracer should be lost within the system by reaction or adsorption with the reactor walls, or internal packing, if present. The internal packing within the pilot-scale landfill columns is municipal solid waste; it was relevant to investigate the adsorption characteristics of any tracer selected with that substance. A frequently used non-reactive tracer employed in aqueous systems are the various salts of lithium. Lithium chloride is commonly used as a non-reactive tracer. Lithium is readily detectable in aqueous solutions on an atomic adsorption spectrometer operating in the emission mode. The minimum lithium concentration detectable is approximately 0.2 $\mu g\ell^{-1}$ with a sensitivity of 0.04mgℓ , the optimum working range being 0.1 to 2mgℓ^{-1} (APHA Standard Methods, 1992).

As the chloride content of landfill leachate is often at elevated levels, it was consequently decided to investigate the adsorption characteristics of lithium sulphate. Potable water would be added to the columns to replace the leachate drained from the column. Potable water in the Cape Town municipal area has a chloride content of approximately 27mgℓ^{-1}. The decrease in chloride content in the leachate as the tracer response experiment progressed could well serve as an inverse tracer if problems were experienced with the lithium sulphate tracer.

The TCLP was modified to enable the determination of the degree of adsorption of lithium sulphate onto municipal solid waste. The extraction fluid, with it's acetate buffered system would appear to provide a good approximation of leachate from the pilot-scale landfill columns. The modification was effected in the following manner.

The solution was formulated, in the same manner as described previously (Section 5.5.1). The pH of this solution was then adjusted with 1N sodium hydroxide until the pH of the solution was 6.8. This pH was decided upon as it was the average of all pH measurements taken of the leachate from the pilot-scale landfill columns at that time.
Sufficient lithium sulphate was added to this solution for the lithium content to approximate $10mg\ell^{-1}$. To assure the results of the lithium sulphate adsorption studies to be reproducible, and to eliminate any bias from the municipal solid waste it was decided to perform the experiments in triplicate. Again, one sample of the cumulative sample (sample 21) was used, the other two samples being differing sub-samples.

A 50g portion of the prepared municipal solid waste was weighed and placed in the extractor vessel. A 25mℓ sample of the lithium sulphate solution was then taken from the measuring cylinder. Exactly 1ℓ of the relevant pH-adjusted, dilute lithium sulphate solution was then added to the extractor vessel. The extractor vessel was then placed in the agitation device and agitation began. Agitation continued for a period of 32 hours. After 32 hours had elapsed the agitator was stopped, another sample of volume 25mℓ was then taken for analysis. Details of the analysis, and degree of adsorption is shown below.

TABLE 6.6 ADSORPTION OF LITHIUM AT LABORATORY SCALE

Sample No.	Initial lithium concentration ($mg\ell^{-1}$)	Final lithium concentration ($mg\ell^{-1}$)	Percentage lithium adsorption
2	10.123	10.021	1.00
13	10.225	10.046	1.75
21	10.225	10.046	1.75

The percentage adsorption of lithium of less than 2 percent was considered acceptable and probably within experimental error for the analysis coupled with the degree of purity of the lithium sulphate employed.

6.4.2 MASS OF NON-REACTIVE TRACER UTILISED

A solution of approximately $1000mg\ell^{-1}$ of lithium, in the form of the sulphate salt was prepared. This solution was analysed in triplicate. The concentration of the solution was found to be $1027mg\ell^{-1}$. To determine the mass of lithium tracer to be added the following reasoning was applied. The total volume of water present in the pilot-scale columns approximated 400ℓ, the average weekly flowrates were approximately 35ℓ. There are two extreme *scenarios* to

consider: if perfect plug flow conditions existed; if perfect mixing conditions were prevalent. If 1000mg of lithium were added and the reactor functioned as a perfect mixer the outlet concentration would approximate $0.025mg\ell^{-1}$, if the reactor functioned as a perfect plug flow reactor the outlet concentration of lithium would approximate $29mg\ell^{-1}$. Both these concentrations are detectable by the analytical procedure employed.

6.4.3 METHOD OF INJECTION OF NON-REACTIVE TRACER

It was decided to use Column 4 for the residence time studies, this was an arbitrary decision. Leachate was withdrawn in the usual manner, the leachate being drained until the flow diminished to a slow drip. While the leachate was flowing a sample was taken for analysis. On these samples the following analyses were performed:

pH;
Electrical conductivity;
Chemical Oxygen Demand (COD), unfiltered;
Chemical Oxygen Demand (COD), filtered;
Chloride content;
Total Alkalinity;
Bicarbonate Alkalinity;
Orthophosphate;
Lithium content.

From the analyses of total alkalinity; bicarbonate alkalinity and orthophosphate, the volatile acid alkalinity was then calculated.

After the leachate flow diminished to a slow drip, the outlet valve from the pilot-scale column was then closed and the volume of leachate drained was measured. This was accomplished with a calibrated dip stick. The contents of the 80ℓ drainage tank were then pumped to waste. The same volume of potable water was then placed in the leachate drainage tank. At the top of the column exactly 1ℓ of the $1000mg\ell^{-1}$ lithium solution was poured onto the aggregate distributor. The pump was then started, the contents of the drainage tank pumped to the top of the column washing the tracer into the solid waste matrix.

6.4.4 MONITORING OF THE NON-REACTIVE TRACER

Every 7 days the leachate was drained; sampled; measured; and pumped to waste. The same volume of potable waste added to the drainage tank and pumped to the top of the pilot-scale landfill column. This exercise was repeated until chemical analysis revealed the lithium content of the sample of leachate diminished to a level similar to that of the first sample of leachate taken. The results were then examined to determine the residence time distribution of the landfill column, these are shown in Chapter 7.

6.5 PILOT-SCALE EVALUATION OF THE KINETIC AND TRACER STUDIES

After the completion of the laboratory-scale experiments and the pilot-scale tracer response study, the results were examined. A requirement was that sufficient copper-chromium-arsenic solution was co-disposed with the municipal solid waste in the column to obtain a response in the liquid effluent from the column. The following data were revealed from the laboratory-scale experiments:

the quantity of the metals adsorbed by the municipal solid waste;
the rate of that adsorption

The pilot-scale tracer study revealed the residence time distribution within the column. Results indicated adequate time for the adsorption reactions to reach completion. To estimate the mass of copper-chromium-arsenic solution the maximum adsorption was initially calculated. This was calculated in the following manner.

Mass of municipal solid waste in laboratory scale experiments = 50g
Mass of municipal solid waste in pilot-scale column ≈ 668kg

Example
Average mass of copper sorbed at pH7.0 = 23mg
Maximum mass of copper adsorbed at pilot-scale = (23/50)×668 = 308g

The calculation was completed for all relevant pH values, the results are shown in Table 6.7 overleaf.

Another factor that was considered before the addition of the solution was particle size. The municipal solid waste was reduced in size to below 1mm for the laboratory scale kinetic trials. The solid waste employed in the pilot-scale columns was reduced in size to between 25 and 40mm. The surface area presented for adsorption would consequently be vastly different.

The copper-chromium-arsenic solution is supplied by the manufacturer in the following composition (Section 5.4.1). Copper, is present at 93.1 $g\ell^{-1}$, chromium is present at 269.6$g\ell^{-1}$, and arsenic is present at 270.2$g\ell^{-1}$. It can be seen from Table 6.7, at pH7.0, the probable leachate pH, the expected masses of metal to be adsorbed were:

Copper = 307g
Chromium = 281g
Arsenic = 548g

TABLE 6.7 MAXIMUM ADSORPTION OF THE COPPER, CHROMIUM AND ARSENIC

Metal	pH	Average Mass sorbed (mg)	Average Mass sorbed (mg g^{-1})	Anticipated adsorption (g)
Copper	5.5	50.9	1.02	681
	6.4	14.1	0.28	187
	7.0	23.0	0.46	307
Chromium	5.5	53	1.06	708
	6.4	31	0.62	414
	7.0	21	0.42	281
Arsenic	5.5	70	1.40	935
	6.4	36	0.72	481
	7.0	41	0.82	548

It was anticipated that virtually all the copper would precipitate within the column, thus attention was focused upon the chromium and the arsenic. If the approximate minimum mass of arsenic was added (548g), then approximately the same mass of chromium would be added, from the calculations above this would greatly exceed the expected adsorption, and additionally no allowance had been made for particle size. It was then considered sufficient to add near the theoretical maximum of chromium (281g), the difference in particle size and hence surface area should allow both chromium and arsenic to be present in the leachate.

The volume of copper-chromium-arsenic added to the municipal solid waste was 950mℓ, the mass of metals added is shown below:

Mass of chromium added = 256.1g
Mass of copper associated = 88.4g
Mass of arsenic associated = 256.8g

6.5.1 EXPERIMENTAL PROCEDURE - CO-DISPOSAL OF COPPER-CHROMIUM-ARSENIC SOLUTION

It was decided to use Columns 3 and 5 for the co-disposal studies, these columns had exhibited the most consistent volumetric leachate flowrates. Leachate was withdrawn in the usual manner, the leachate being drained until the flow diminished to a slow drip. While the

leachate was flowing a sample was taken for analysis. On these samples the following analyses were performed:

pH;
Electrical conductivity;
Chemical Oxygen Demand (COD), unfiltered;
Chloride content;
Copper content;
Chromium content;
Arsenic content.

After the leachate flow diminished to a slow drip, the outlet valve from the pilot-scale column was then closed and the volume of leachate drained was measured. This was accomplished with a calibrated dip stick. The contents of the 80ℓ drainage tank were then pumped to waste. The same volume of potable water was then placed in the leachate drainage tank. At the top of the column exactly 950mℓ of the concentrated copper-chromium-arsenic solution was poured onto the aggregate distributor. The pump was then started, the contents of the drainage tank pumped to the top of the column washing the solution into the solid waste matrix.

6.5.2 MONITORING OF THE PILOT-SCALE CO-DISPOSAL EXPERIMENT

Every 7 days the leachate was drained; sampled; measured; and pumped to waste. The same volume of potable waste added to the drainage tank and pumped to the top of the pilot-scale landfill column. This exercise commenced on Day 567 and was repeated until Day 754. The results were then examined to determine the degree of agreement between the laboratory and pilot-scale studies. The results are shown in Chapter 7.

6.6 ANALYTICAL PROCEDURES

Chemical analysis was performed at the Laboratory of the Department of Chemical Engineering of the University of Cape Town, and at the Laboratory of the Scientific Services Branch, City Engineer's Department, City of Cape Town.

TABLE 6.8 ANALYTICAL RESPONSIBILITIES

Component	Establishment
Biogas analysis	Scientific Services Branch
Leachate analysis	Scientific Services Branch

(a) Biogas
Biogas was analysed for percentage: methane; carbon dioxide; oxygen and nitrogen.

(b) Leachate - tracer response study
Leachate was analysed for: pH; electrical conductivity; Chemical Oxygen Demand (COD), unfiltered; Chemical Oxygen Demand (COD), filtered; chloride content; total alkalinity; bicarbonate alkalinity; orthophosphate and lithium content.

(c) Leachate - pilot-scale co-disposal studies
Leachate was analysed for: pH; electrical conductivity; Chemical Oxygen Demand (COD), unfiltered; chloride content; copper content; chromium content; arsenic content.

The analytical equipment has been detailed in Table 5.14, the exception being the analysis of biogas. Biogas analysis was performed with a Varian 3300 Gas Chromatograph.

6.7 SUMMARY

The design of pilot-scale landfill columns constructed by previous researchers was reviewed to establish the design and construction for the Athlone pilot-scale landfill columns. Operation of the Athlone pilot-scale columns included leachate recirculation and biogas monitoring. Residence time distribution trials were undertaken at pilot-scale. A laboratory scale investigation established that lithium sulphate would be suitable for use as a tracer. A solution of copper, chromium and arsenic was then co-disposed at pilot-scale.

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CHAPTER 7
RESULTS AND CALCULATIONS: LABORATORY AND PILOT-SCALE STUDIES

7.1 INTRODUCTION

As reported in Chapters 5 and 6, the experimental programme comprised of two complimentary investigations:

(i) Laboratory scale investigation;
(ii) Pilot-scale investigation.

These two complimentary investigations were then further sub-divided into manageable, associated elements.

Laboratory scale investigation
The laboratory scale investigation was also constituted of two integral sections:
Evaluation of kinetic rate constants, adsorption and desorption;
evaluation of adsorption isotherms.

Pilot-scale investigation
This investigation advanced on two fronts:
Evaluation of the residence time distribution/deviation from ideal behaviour of the pilot-scale landfill columns.
Evaluation, at pilot-scale, of the kinetic rate constants determined at laboratory scale.

7.2 LABORATORY SCALE INVESTIGATIONS

7.2.1 RESULTS FROM THE ADSORPTION STUDIES

Adsorption studies were undertaken at three pH values; pH5.5, pH6.4, and pH7.0. Initial (0.0h) and final (32.0h) results from the kinetic studies were also utilised in the construction of the adsorption isotherms. The results are shown in Appendix B, Table B-1 (pH5.5); Table B-2 (pH6.4); Table B-3 (pH7.0) of Ballard (1997). Freundlich isotherms were successfully constructed for copper at pH values 5.5 and 7.0; for chromium and arsenic at all three pH values, 5.5, 6.4 and 7.0. The constructions are shown in section 7.4.2

7.2.2 RESULTS FROM THE KINETICS STUDIES

The kinetics experiments were undertaken in triplicate at three pH values, 5.5 (coded A, B and C) 6.4 (coded D, E and F) and 7.0 (coded G, H and I). As reported in section 4.5, the experimental method made available data for analysis of the kinetics of adsorption and desorption of the metallic ions. The adsorption results are reported as analysed in the laboratory and are shown in Appendix B, Table B-4 (pH5.5); B-5 (pH6.4) and B-6 (pH7.0) of Ballard (1997). The desorption results are reported Table B-7 (pH5.5); B-8 (pH6.4) and B-9 (pH7.0) of Ballard (1997). Graphical representations of the analytical results from the adsorption kinetic trials are shown overleaf (Figures 7.1 to 7.27). As with most experimental data, a degree of scatter can be observed in the experimental results, this is addressed in the interpretation of the data in section 7.4.3. The degree of scatter is however, most noticeable at the lower experimental time frames. Chemisorption is often preceded by physical adsorption, which is easily reversible (Section 3.8.1.3). This would explain the scattering of data points at short experimental times. The cationic ions being only loosely bound by physical adsorption to the solid waste matrix, at low experimental values of time.

In all cases, sorption of the metallic ions is characterised by a rapid initial sorption, the sorption rate decreasing with increased time. The analogy between the adsorption of solutes onto soils has been discussed (Sections 3.8.1.3(a) and 4.3.1). Rapid soil reactions are, in general, reactions which transport at the solid phase do not significantly influence the reaction rate. Conversely, slow reactions are often characterised by diffusional mass transfer limitations (Section 4.3.2). On initial inspection, these conditions would appear apparent. This phenomena, together with a proposed reaction mechanism is discussed fully in Chapter 8.

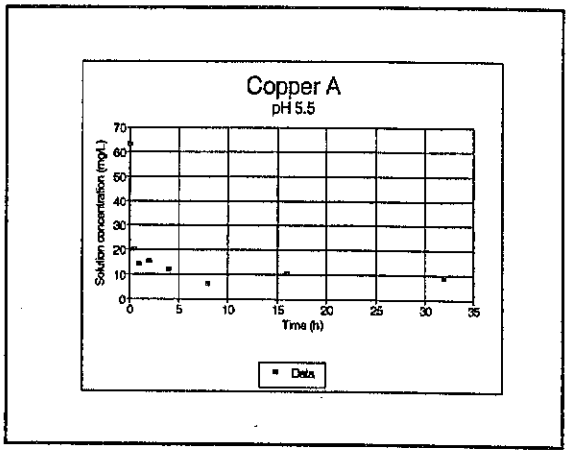

Figure 7.1
Adsorption of copper (A): pH 5.5

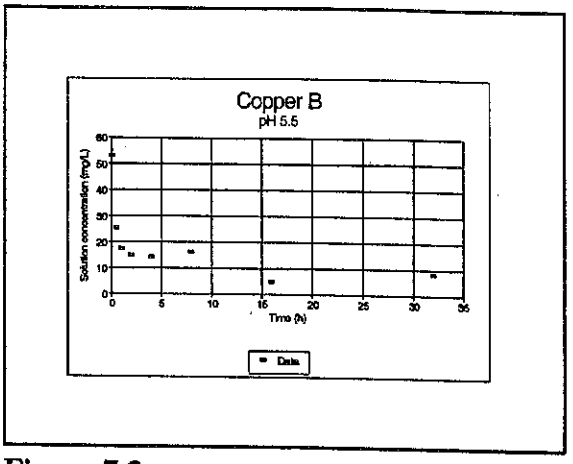

Figure 7.2
Adsorption of copper (B): pH 5.5

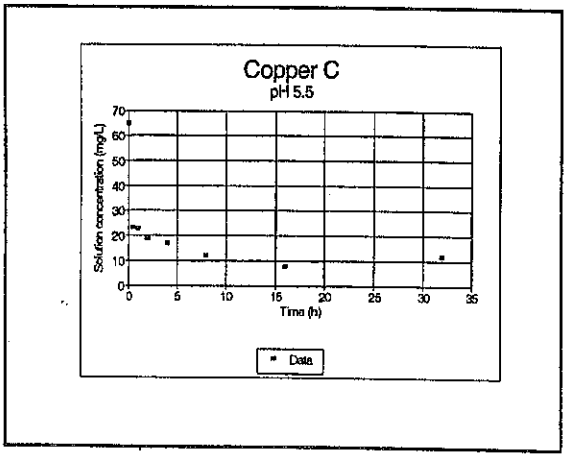

Figure 7.3
Adsorption of copper (C): pH 5.5

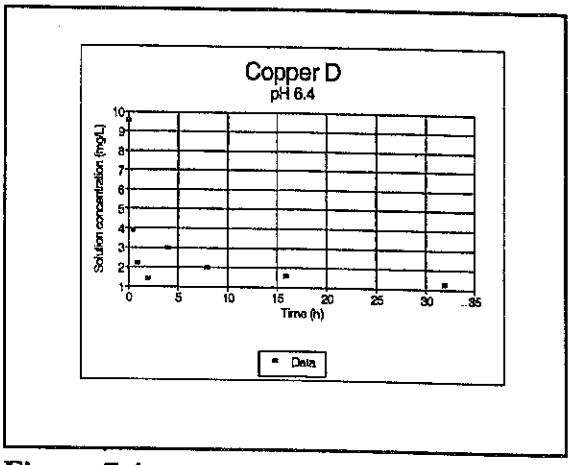

Figure 7.4
Adsorption of copper (D): pH 6.4

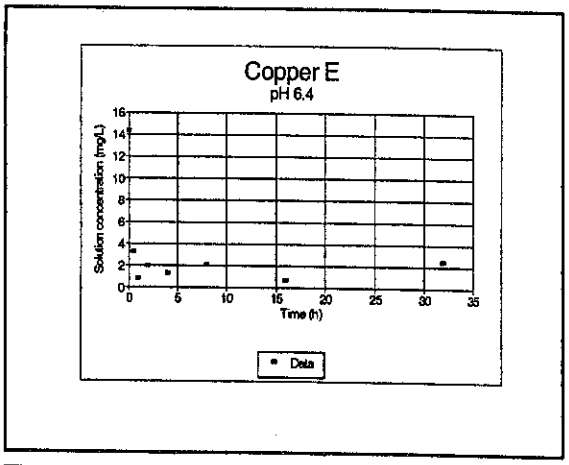

Figure 7.5
Adsorption of copper (E): pH 6.4

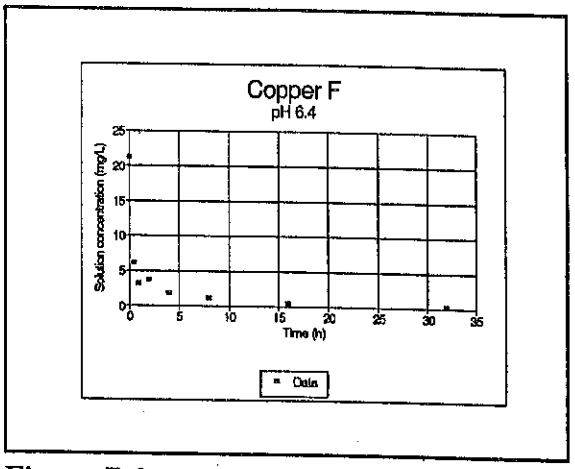

Figure 7.6
Adsorption of copper (F): pH 6.4

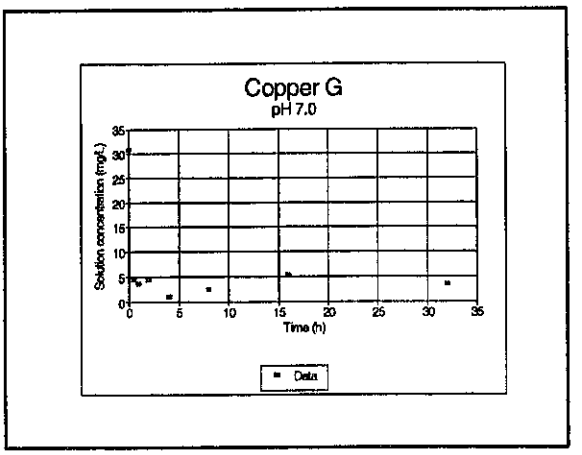

Figure 7.7
Adsorption of copper (G): pH 7.0

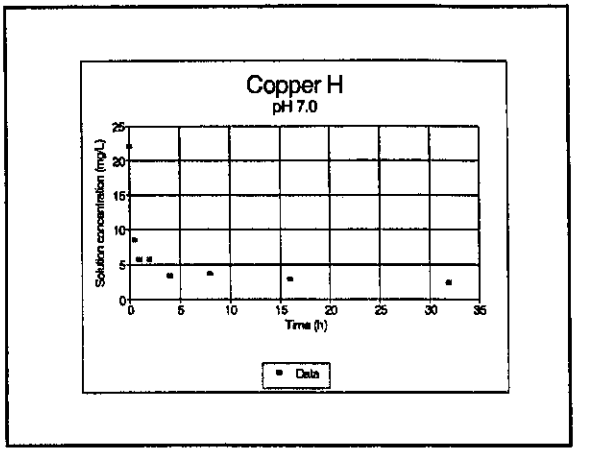

Figure 7.8
Adsorption of copper (H): pH 7.0

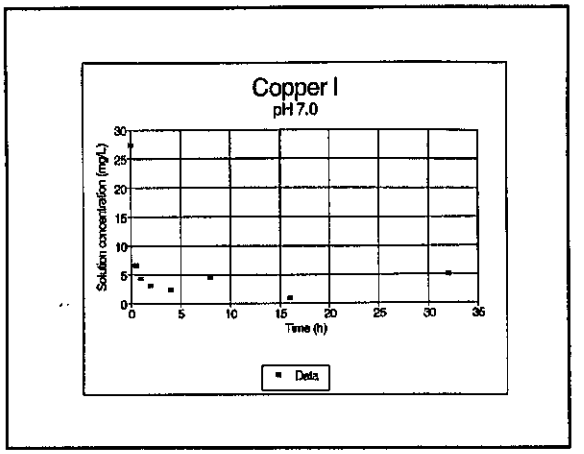

Figure 7.9
Adsorption of copper (I): pH 7.0

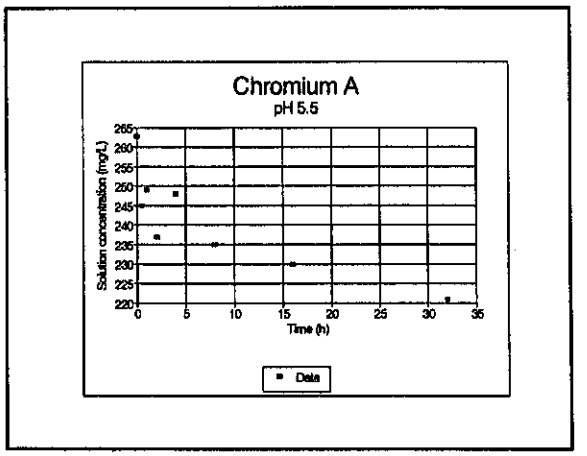

Figure 7.10
Adsorption of chromium (A): pH 5.5

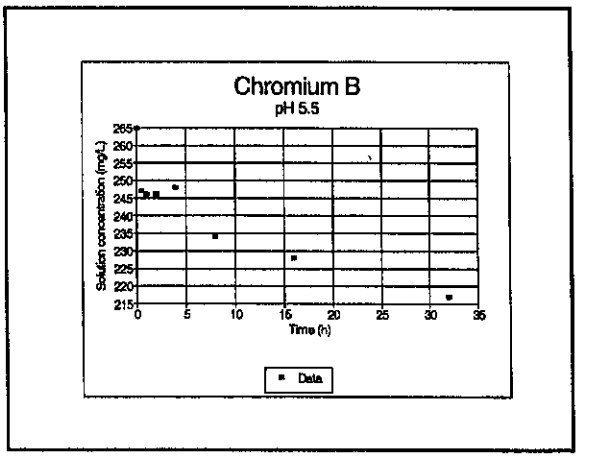

Figure 7.11
Adsorption of chromium (B): pH 5.5

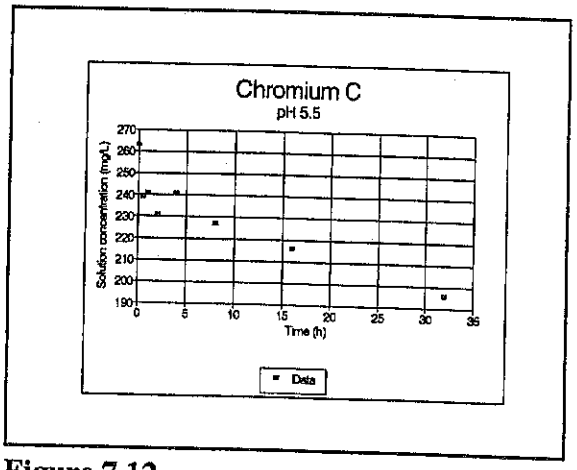

Figure 7.12
Adsorption of chromium (C): pH 5.5

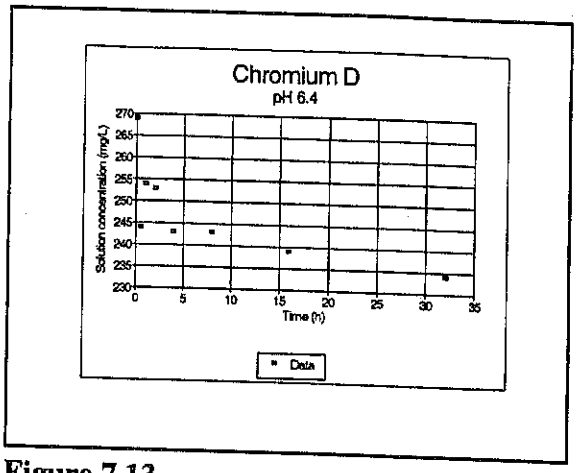

Figure 7.13
Adsorption of chromium (D): pH 6.4

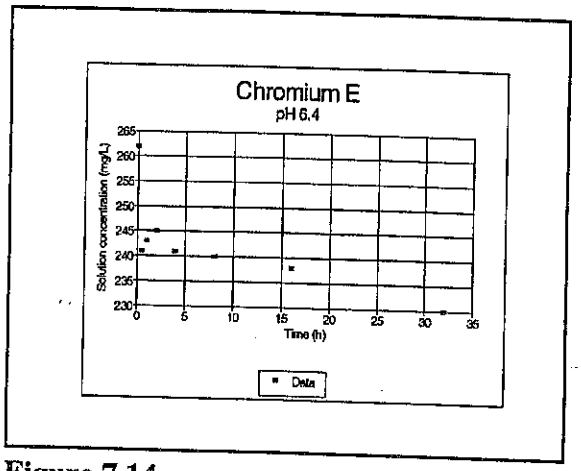

Figure 7.14
Adsorption of chromium (E): pH 6.4

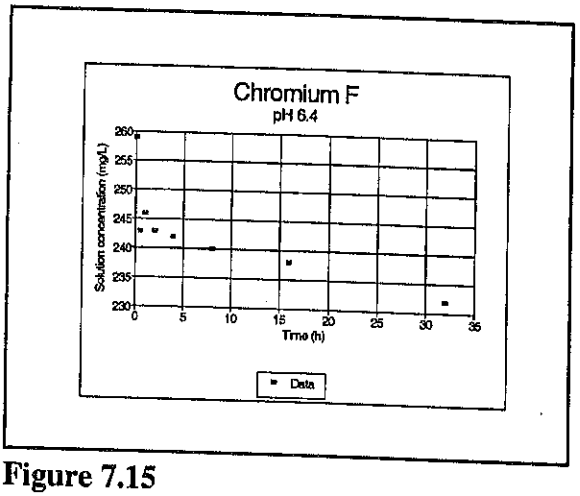

Figure 7.15
Adsorption of chromium (F): pH 6.4

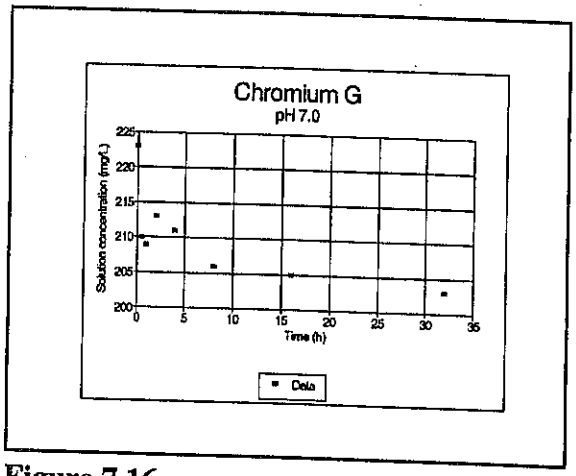

Figure 7.16
Adsorption of chromium (G): pH 7.0

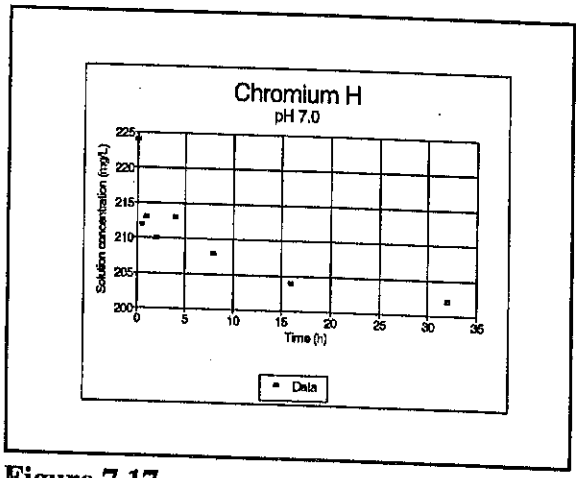

Figure 7.17
Adsorption of chromium (H): pH 7.0

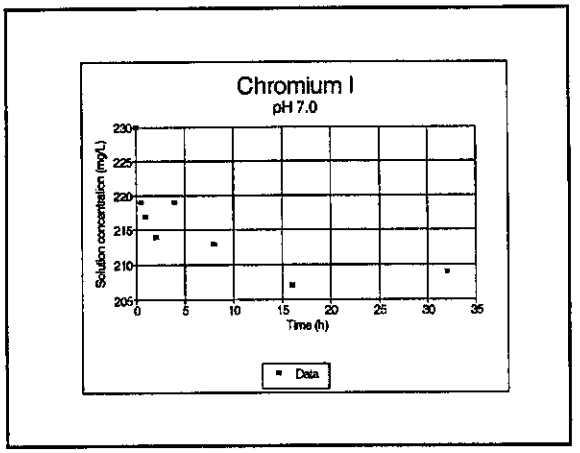

Figure 7.18
Adsorption of chromium (I): pH 7.0

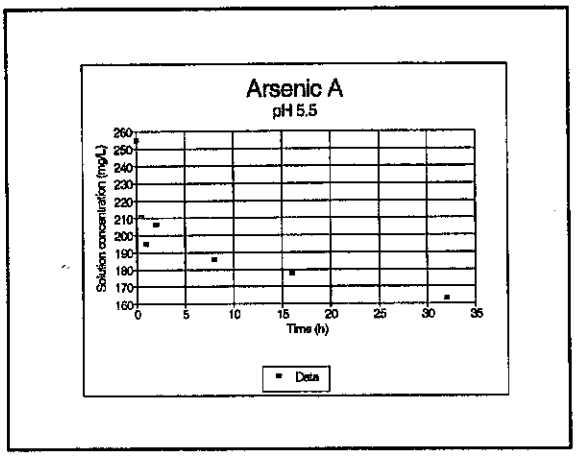

Figure 7.19
Adsorption of arsenic (A): pH 5.5

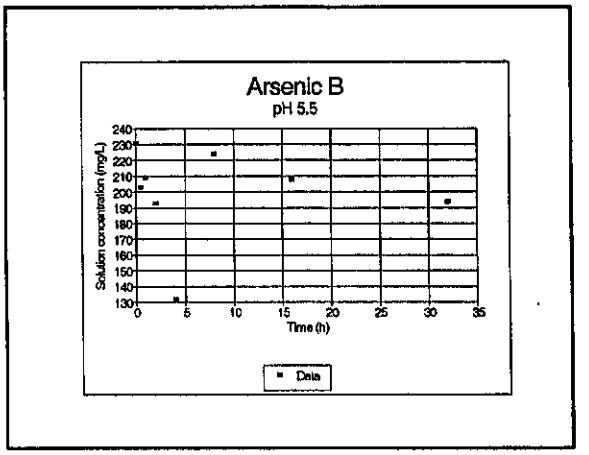

Figure 7.20
Adsorption of arsenic (B): pH 5.5

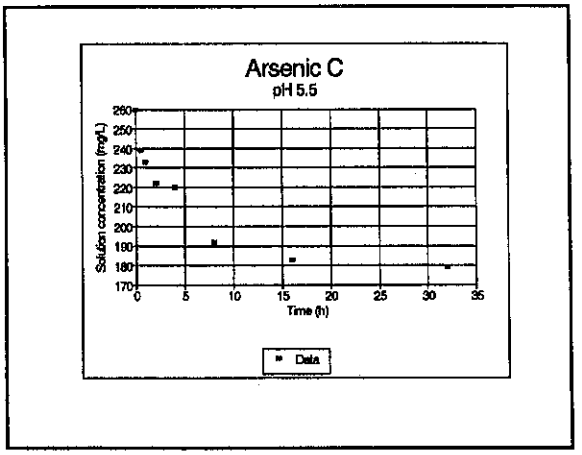

Figure 7.21
Adsorption of arsenic (C): pH 5.5

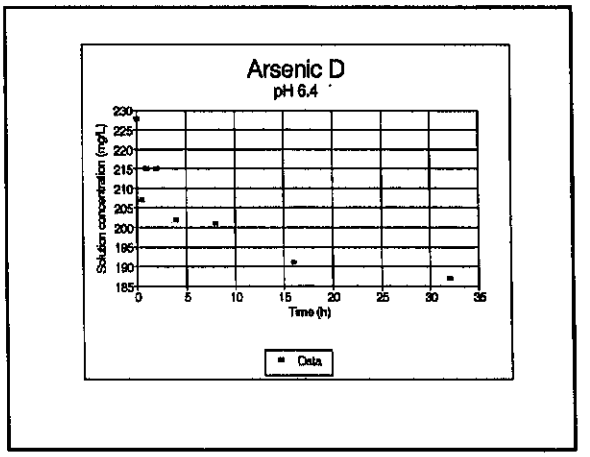

Figure 7.22
Adsorption of arsenic (D) : pH 6.4

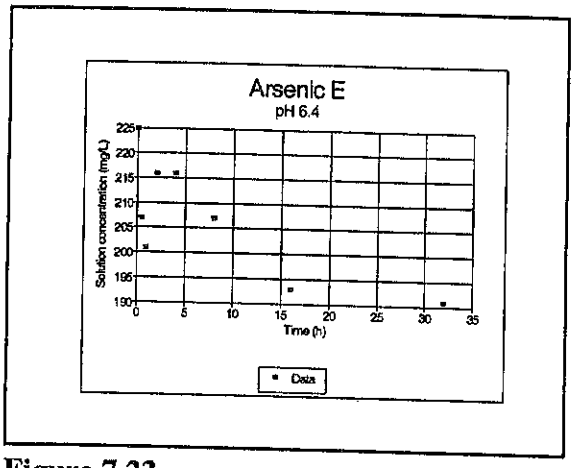

Figure 7.23
Adsorption of arsenic (E): pH 6.4

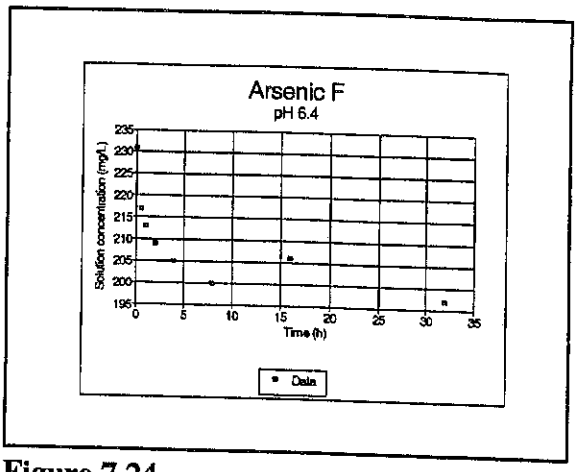

Figure 7.24
Adsorption of arsenic (F): pH 6.4

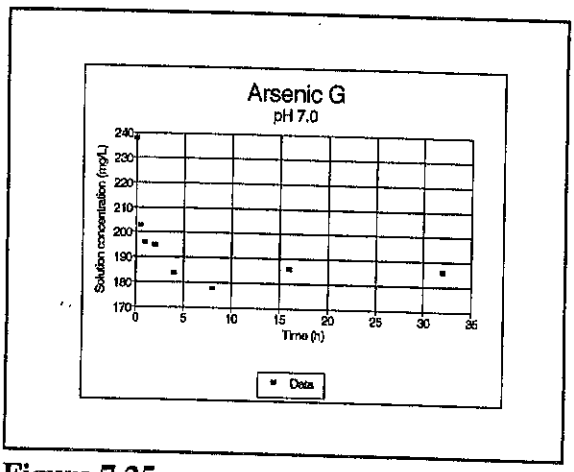

Figure 7.25
Adsorption of arsenic (G): pH 7.0

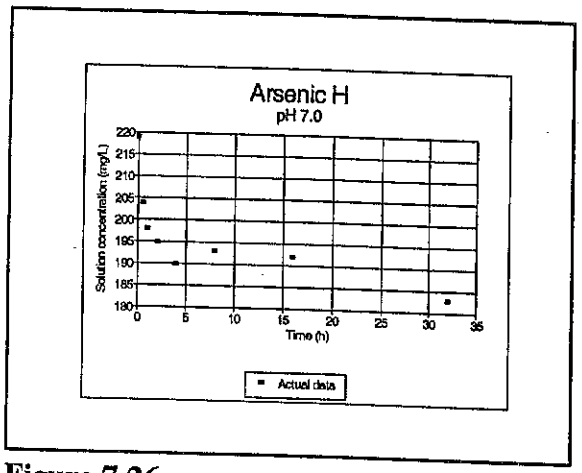

Figure 7.26
Adsorption of arsenic (H): pH 7.0

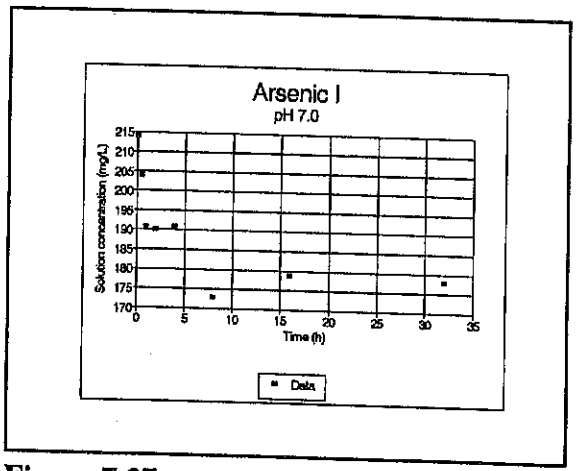

Figure 7.27
Adsorption of arsenic (I): pH 7.0

7.3 PILOT-SCALE INVESTIGATIONS

7.3.1 LEACHATE RECIRCULATION

As reported in Chapter 6, leachate first became evident on Day 60. Leachate was drained until the flow diminished to a slow drip. The volume of leachate obtained was measured on cessation of flow. While the leachate was flowing a sample was taken for analysis. On these samples the following analyses were performed:

pH;
Electrical conductivity;
Chemical Oxygen Demand (COD), unfiltered;
Chemical Oxygen Demand (COD), filtered;
Chloride content;
Total Alkalinity;
Bicarbonate Alkalinity;
Orthophosphate.

From the analyses of total alkalinity; bicarbonate alkalinity and orthophosphate, the volatile acid alkalinity was then calculated. Results of the chemical analysis, together with the volume of leachate drained are shown in Appendix C of Ballard (1997).

The recirculation procedure was performed every 7 days, until Day 118. Recirculation ceased at this point as the temperature inside the columns had dropped to below 15°C, and there was no evidence of biogas production. The lower temperatures were due to the onset of the South African winter season.

Recirculation of leachate recommenced on Day 231; ambient temperatures were beginning to rise, as the southern hemisphere summer season was beginning. The recirculation procedure then continued as before; the procedure being repeated after a time interval of 7 days. The procedure was discontinued on Day 358, as there was no resumption of biogas production. Column 4 was only recirculated until Day 118. From Day 231, column 4 was employed for tracer studies. The results obtained until Day 118 for column 4 are shown in Appendix C, Table C-5 of Ballard (1997). The results obtained from columns 1, 2, 3 and 5 are discussed briefly below.

The average pH of leachate from columns 1, 2, 3 and 5 averaged 7.0. The highest pH value recorded was 7.3, the lowest was 6.6. Initial measurements of electrical conductivity were performed on an undiluted sample. It was found the measurements varied and were inconsistent. This method of analysis continued until Day 110, thereafter leachate was diluted, and the value of electrical conductivity reported was adjusted to the degree of dilution. Electrical conductivity measurements (from Day 110) were relatively consistent from all the columns (apart from the occasional high or low value), and averaged 1068mSm^{-1} from column 1; 1050mSm^{-1} from column 2; 1042mSm^{-1} from column 3, and 1029mSm^{-1} from column 5.

Leachate was analysed for COD in the un-filtered and filtered, state. This was a precautionary

measure, as it was initially considered the presence of particulate matter would adversely affect data trend analysis. The COD content of the leachate showed an initial rapid reduction from approximately 6000mgℓ^{-1} to approximately 2000mgℓ^{-1} during the first 110 days. The COD continued to decrease until leachate recirculation ceased on Day 358. The COD then approximated 1200mgℓ^{-1} in the unfiltered samples. All of the columns exhibited similar behaviour.

Chloride levels remained consistent throughout the recirculation period; there was little difference in chloride measurements from individual columns. Chloride content averaged 1077mgℓ^{-1} from column 1; 1154mgℓ^{-1} from column 2; 1052mgℓ^{-1} from column 3; 998mgℓ^{-1} from column 5. Both Total Alkalinity and Bicarbonate Alkalinity gradually decreased throughout the duration of the recirculation, the Total alkalinity decreasing from approximately 4500mgℓ^{-1} to 3800mgℓ^{-1}. The bicarbonate alkalinity showed a similar trend the values being consistently lower by approximately 300mgℓ^{-1}. The volatile acid alkalinity of leachate from the columns showed an initial sharp decrease from approximately 550mgℓ^{-1} to 300mgℓ^{-1}, and stabilised at this value for the duration of the experiment. Levels of ortho-phosphate in the leachate showed a similar trend from all the columns. The results were extremely erratic over the duration of leachate recirculation, but decreased to very low levels (0.1mgℓ^{-1}) by Day 358.

Results from previous column studies conducted at the University of Cape Town employing "fresh" municipal solid waste are extremely well documented (Chapman *et al* 1991). After 50 weeks of recirculating leachate the researchers reported the following results: pH levels of 5.7; COD levels of 27000mgℓ^{-1} ; bicarbonate alkalinity of 120mgℓ^{-1} ; volatile acid alkalinity of 13000mgℓ^{-1} ; electrical conductivities approximating 1500mSm^{-1}; ortho-phosphate, 15mgℓ^{-1}. The columns did not generate biogas, acetogenic conditions were evident. The United Kingdom's Department of Environment (DOE, 1986) report values of leachate from "aged wastes". They report pH values of 7.5; COD levels of 1160mgℓ^{-1} and phosphate levels of approximately 1mgℓ^{-1}. This together with the low levels of biogas production from the columns (section 6.3.2) confirm the municipal solid waste was well stabilised prior to placement within the pilot-scale landfill columns.

7.3.2 LITHIUM SULPHATE PULSE EXPERIMENT

Results from the lithium sulphate pulse experiment are shown in Appendix D of Ballard (1997). Table D-1 details the volumetric displacement of leachate; the lithium concentration of the leachate; the mass of lithium obtained per sample, and the cumulative mass of lithium. Table D-2 characterises the leachate in terms of pH, COD, etc.. The mass of lithium sulphate introduced in the system was 1027.7mg, of this 954.3mg was successfully recovered, a recovery rate of 92.9 percent. The time duration of the experiment was 317 days, the average volumetric displacement of leachate was 36.5ℓweek^{-1} . Maximum lithium recovery occurred after 84 days, the lithium concentration of the leachate at that time was 2.003mgℓ^{-1}. Leachate was sampled and recirculated approximately every 7 days. The volumetric displacement of leachate from the column varied, and additionally, on occasion, sampling and recirculation could not be effected on the designated day. The conventional graphical representation reporting results of this nature is in terms of concentration-time, because of the variation in both volumetric displacement and on occasion time increments a far more satisfactory representation of the experimental data is mass (of lithium in leachate) versus time. This shown below in Figure 7.28

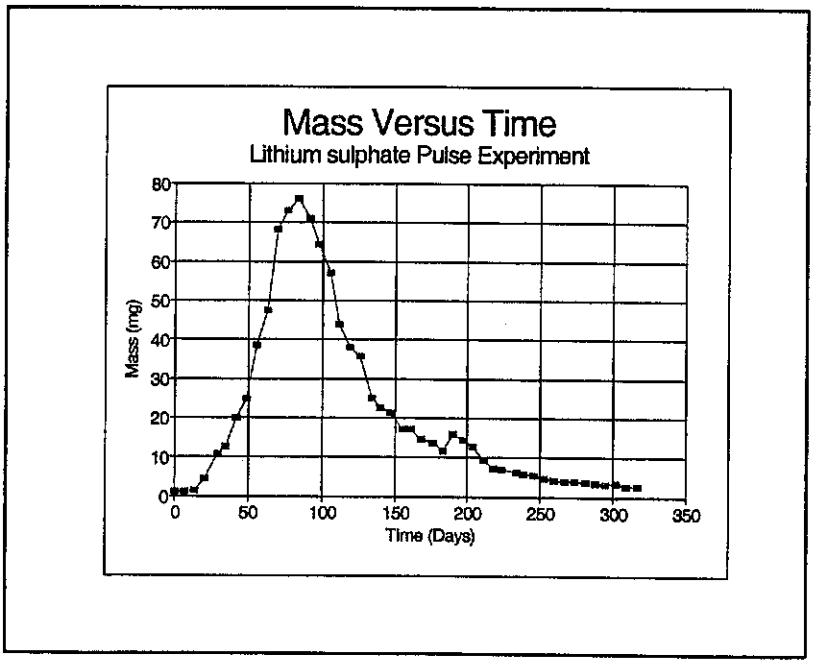

Figure 7.28
Results of lithium pulse experiment

The mass-time curve reveals a system that is non-ideal. In an industrial reactor of this nature i.e. a packed column, assuming ideal behaviour, one would anticipate plug flow, the graphical representation of the data should then resemble a thin spike located at maximum tracer concentration. The large base is indicative of axial dispersion of the fluid; the early initial commencement of the curve is a manifestation of channelling; the long tail is symptomatic of stagnant areas within the column. The curve is however consistent, except for a small secondary peak occurring around Day 200. This phenomena is indicative of stagnant flow areas within the column. The only deviation from ideality that one would not experience on a full scale landfill is the high degree of initial channelling. It is probable that wall effects from the column are a contributory factor. The curve is further examined in section 7.4.4.

*(a) **Chemical characteristics of leachate collected during the lithium pulse experiment***
As would be expected when draining leachate to waste, and replacing the leachate with an equal volume of fresh potable water, all the determined chemical parameters (except for pH) showed a steady decline. Initial COD levels approximated 2000mgℓ^{-1} reducing to just above 100mgℓ^{-1}, chloride levels diminished from 900mgℓ^{-1} to around 40mgℓ while electrical conductivity decreased from 1100mSm^{-1} to about 200mSm^{-1}.

7.3.3 CO-DISPOSAL OF COPPER, CHROMIUM AND ARSENIC AT PILOT-SCALE

As reported in section 6.5.1 a concentrated solution of copper, chromium and arsenic was co-disposed with the municipal solid wastes in columns 3 and 5. Analytical results are reported in Appendix E of Ballard (1997). Tables E-1 and E-3 tabulate leachate volumes and metal concentrations for columns 3 and 5 respectively; Tables E-2 and E-4 tabulate the associated chemical data (pH, COD, etc.,) for columns 3 and 5. The mass of metals introduced into both columns 3 and 5 was copper, 88.4g; chromium, 256.1g and arsenic, 256.7g. The time duration of the experiment with column 3 was 235 days, the average volumetric displacement of leachate was 19.2ℓweek^{-1}. The time duration of the experiment with column 5 was slightly shorter, 221 days. The average displacement of leachate was 18.5ℓweek^{-1} . The volumetric displacement of leachate, although similar to column 3, tended to vary slightly more.

(a) Copper content in leachate from columns 3 and 5

Results from the monitoring of copper concentration of leachate from columns 3 and 5 are shown graphically in Figure 7.29. The initial concentration of copper in the leachate from column 3 was 0.05mgℓ^{-1}, after 14 days the copper concentration in the leachate had risen to 0.11mgℓ^{-1}, the highest concentration recorded. This initial rise in copper concentration was probably caused by rapid liquid flow through the column symptomatic of a combination of preferential fluid channelling and wall effects. Subsequently, the copper concentration was lower at 0.04mgℓ^{-1}, slightly lower than the initial base-line reading of 0.05mgℓ^{-1}. From Day 170 to Day 202, the copper concentration stabilised at 0.06mgℓ^{-1}. At Day 235 the copper concentration was slightly elevated at 0.08mgℓ^{-1}. Over the entire period of monitoring (235days), the concentration of copper in the leachate from column 3 averaged 0.05mgℓ^{-1}, i.e. no higher than the initial reading at Day zero.

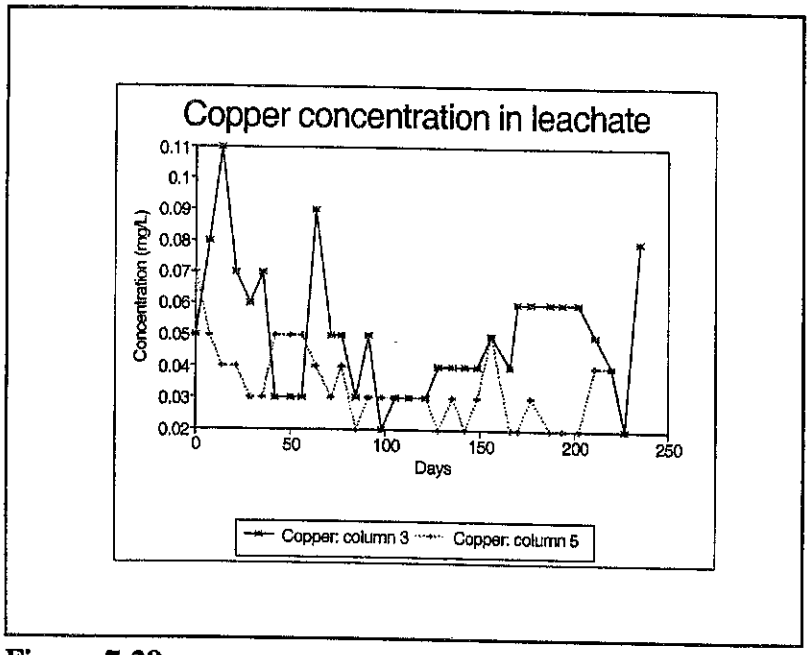

Figure 7.29
Copper concentration in leachate from columns 3 and 5

The initial concentration of copper in the leachate from column 5 was 0.07mgℓ^{-1} a value that was not exceeded for the entire duration of the experiment. The final copper concentration after 221 days was 0.04mgℓ^{-1}. Over the entire period of monitoring (221days), the concentration of copper in the leachate from column 3 averaged 0.03mgℓ^{-1}.

(b) Chromium content in leachate from columns 3 and 5

Results from the monitoring of chromium concentration of leachate from columns 3 and 5 are shown graphically in Figure 7.30. Initially, chromium in the leachate from column 3 was not detectable. The chromium content of the leachate rose steadily over the next 90 days to 0.04 mgℓ^{-1} , this value was not exceeded for the duration of the experiment, the final chromium concentration was 0.03mgℓ^{-1} on Day 235. The average chromium content in the leachate from column 3 over the entire duration of monitoring was 0.03mgℓ^{-1}

The initial chromium content of leachate from column 5 was 0.06mgℓ^{-1}, this dropped, and then steadily rose to 0.06mgℓ^{-1} by Day 90. The chromium concentration then stabilised at approximately this level until Day 180, whereafter metal content dropped very slightly. The final chromium concentration was 0.02 mgℓ^{-1} on Day 221. The average chromium content in the leachate from column 5 over the entire duration of monitoring was 0.04mgℓ^{-1}.

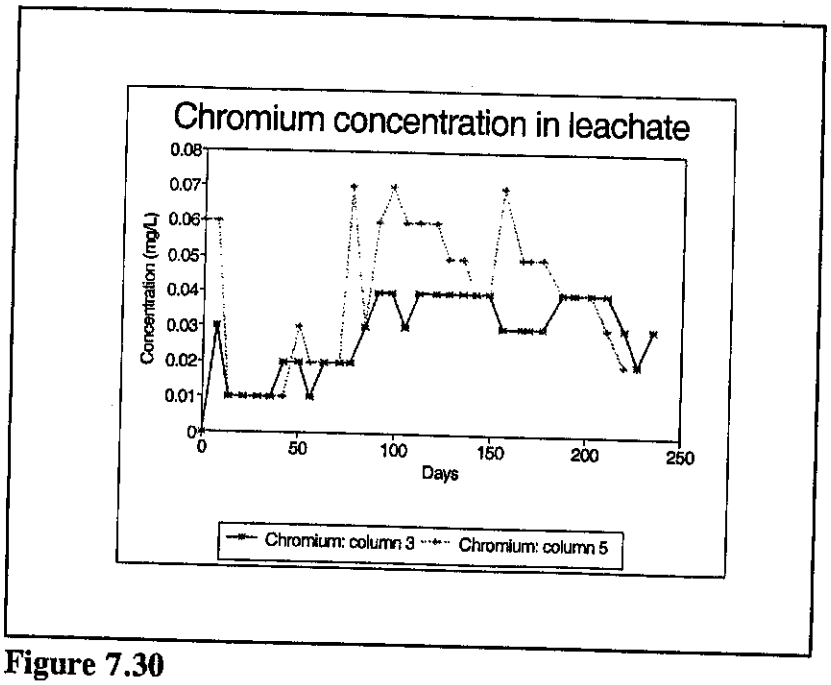

Figure 7.30
Chromium concentration in leachate from columns 3 and 5

(c) Arsenic content in leachate from columns 3 and 5

The behaviour of the co-disposed arsenic was by far the most interesting of the three metals. Results from the monitoring of arsenic concentration of leachate from columns 3 and 5 are shown graphically in Figure 7.31. The initial concentration of the arsenic in the leachate from column 3 was 17$\mu g\ell^{-1}$ rising in a near exponential manner to Day 135 where the arsenic concentration exceeded 1000$\mu g\ell^{-1}$. Subsequently, the concentration of arsenic in the leachate reduced to approximately 830$\mu g\ell^{-1}$ and stabilised at that level until Day 194 when the concentration exceeded 2000$\mu g\ell^{-1}$. Arsenic concentration in the leachate from column 3 remained at that level until the cessation

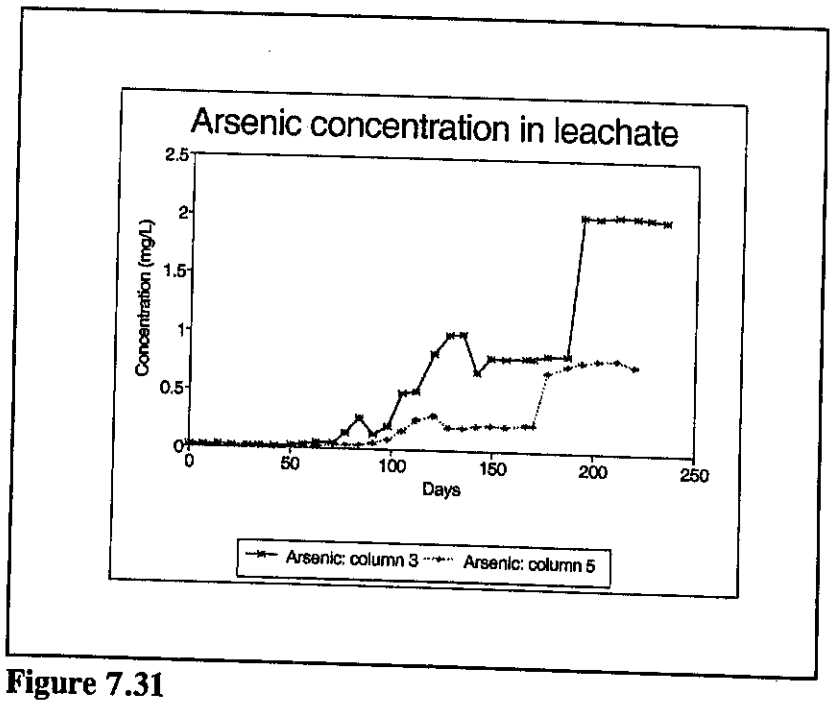

Figure 7.31
Arsenic concentration in leachate from columns 3 and 5

of monitoring on Day 235. Column 5 mirrored the behaviour of column 3 though at a reduced manner. The maximum arsenic concentration attained was 802$\mu g\ell^{-1}$ at Day 213; results were relatively constant from Day 188 at that level.

(d) Chemical characteristics of the leachate from columns 3 and 5

The chemical characteristics of the leachate from both columns 3 and 5 were very similar. Initial COD levels approximated 1200 reducing to 400$mg\ell^{-1}$, chloride levels diminished from 1000$mg\ell^{-1}$ to around 200$mg\ell^{-1}$ while electrical conductivity decreased from 500mSm^{-1} to about 300mSm^{-1}.

7.4 CALCULATIONS

7.4.1 ADSORPTION ISOTHERMS

(a) Freundlich Isotherm

The Freundlich or van Bemmelen equation may be expressed as:

$$q = K_F C_e^{\ M} \qquad 4.1$$

Where,

q	=	solute adsorbed per unit weight of solid adsorbent
K_F	=	Freundlich equilibrium distribution coefficient
C_e	=	Concentration of solute remaining in fluid at equilibrium
M	=	Freundlich power coefficient

Data are usually fitted to the logarithmic form of the equation:

$$\ln(q) = \ln(K_F) + M * \ln(C_e)$$

If the Freundlich adsorption isotherm is suitable, a logarithmic plot of solute adsorbed (q) versus equilibrium solute fluid concentration (C_e) results in a straight line with a slope equal to the Freundlich power coefficient (M) and an intercept equal to the value of the logarithmic form of the Freundlich equilibrium distribution coefficient (K_F)

(b) Method of examination of adsorption data

Initially, a logarithmic plot of solute adsorbed(mg) versus solute equilibrium concentration ($mg\ell^{-1}$) was constructed. This plot was then examined for any obvious outlying data points. As the numerical values obtained from the Freundlich Isotherm may only be considered as indicative, a more sophisticated form of statistical analysis (as undertaken for the kinetic studies) was not pursued. These outlying data points were then eliminated and the remaining results were examined by means of regression analysis.

7.4.2 FREUNDLICH ISOTHERM - COPPER, CHROMIUM AND ARSENIC

Freundlich Isotherms were successfully constructed for copper adsorption at two of the three pH values of 5.5, 6.4 and 7.0. The Freundlich isotherm was successful at the pH values of 5.5 and 7.0. Freundlich Isotherms were successfully constructed for chromium and arsenic adsorption at the three pH values of 5.5, 6.4 and 7.0. The graphical constructions are shown below, and subsequently tabulated are the total number of data points available, the number of data points utilised in the construction, the variance (R squared) between the actual results and the calculated isotherm, the value of the Freundlich equilibrium distribution coefficient (K_F) and the Freundlich power coefficient (M) for each metal at the various pH values.

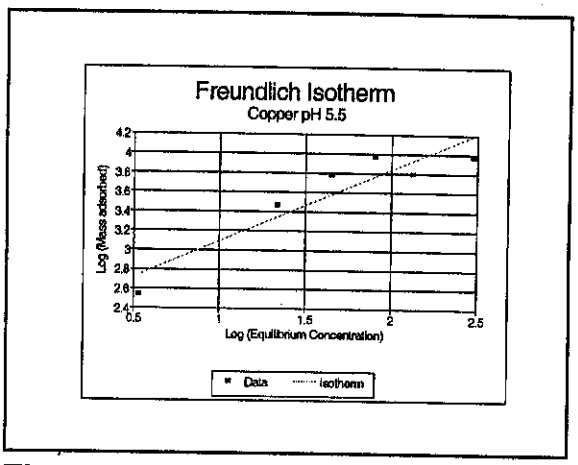

Figure 7.32
Freundlich Isotherm: copper @ pH 5.5

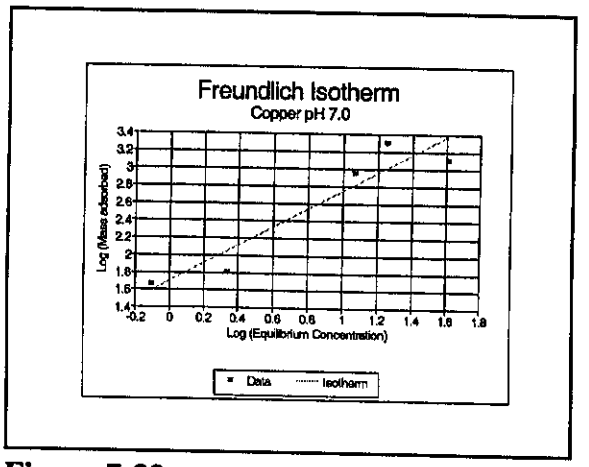

Figure 7.33
Freundlich Isotherm: copper @ pH 7.0

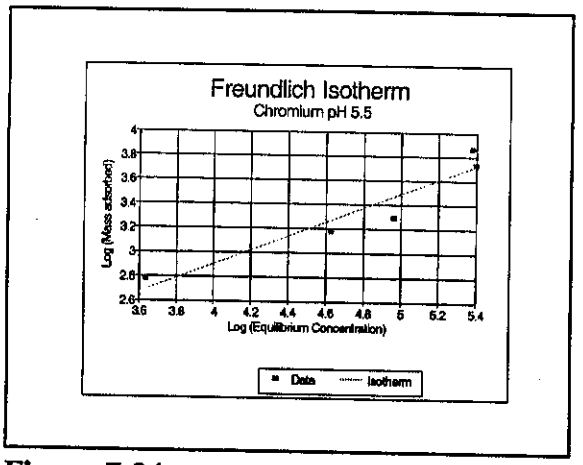

Figure 7.34
Freundlich Isotherm: chromium @ pH 5.5

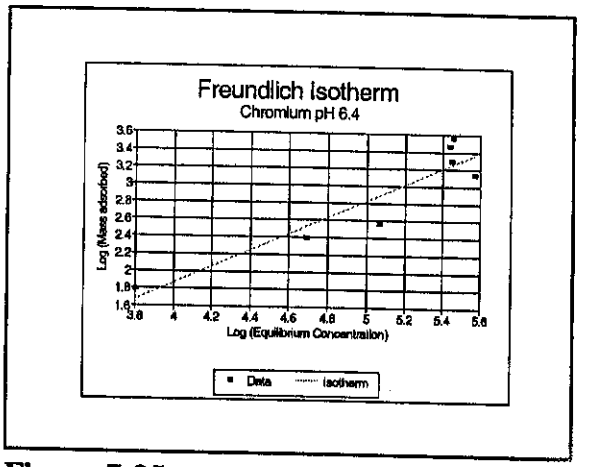

Figure 7.35
Freundlich Isotherm: chromium @ pH 6.4

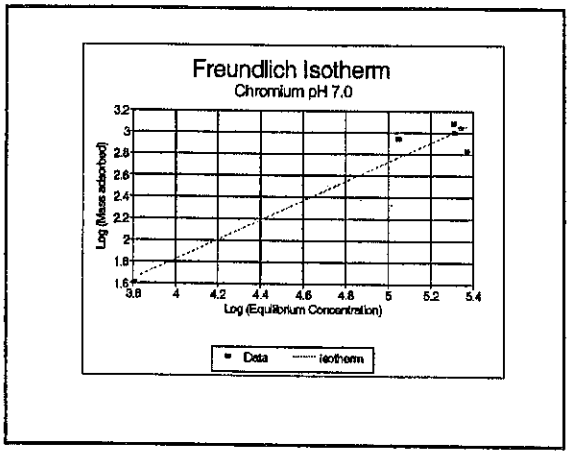

Figure 7.36
Freundlich Isotherm: chromium @ pH 7.0

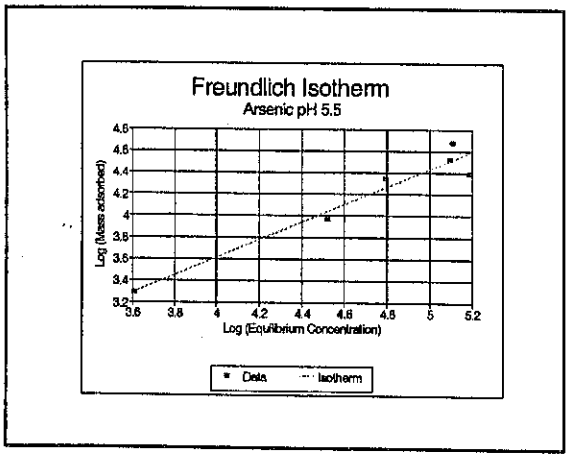

Figure 7.37
Freundlich Isotherm: arsenic @ pH 5.5

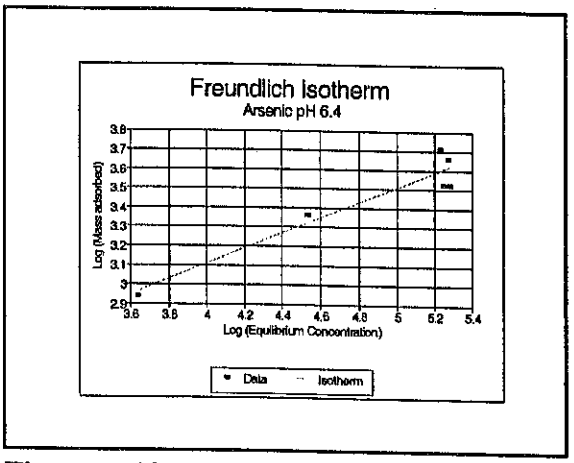

Figure 7.38
Freundlich Isotherm: arsenic @ pH 6.4

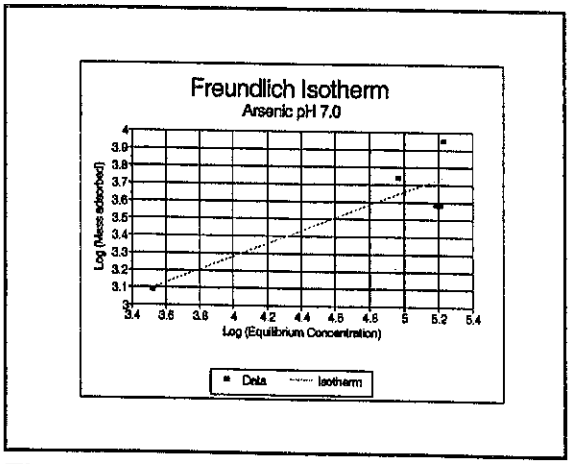

Figure 7.39
Freundlich Isotherm: arsenic @ pH 7.0

Consider Table 7.1 shown overleaf. The variance (R squared) ranged from 0.760 (arsenic at pH7.0) to 0.943 (chromium at pH7.0). As mentioned in section 5.7, copper and chromium analysis could be repeated in some instances. That facility was not available for arsenic. There appears to be no physical meaning of the exponent of the concentration term in the Freundlich equation (M) (Kuo *et al*, 1974). Researchers rarely comment these numerical values, usually reporting that analytical results conform to one type of adsorption isotherm and quoting the degree of agreement achieved. Therefore, there would not appear to be any great relevance in discussing at these numerical values at length.

However, if one considers soils, typically experimental data for power of the concentration term (M) approximates 1, an example being the adsorption of many pesticides at dilute concentrations (Tan, 1993). It can be seen that the power term for both copper and chromium conformed to this generalised rule. Arsenic adsorption only conformed at pH5.5. Elkhatib and fellow workers (1984) quote values of M obtained from arsenite (As(III)) adsorption on five West Virginian soils. The values range from 0.399 to 0.958. The calculated results shown in Table 7.1 range from 0.38 to 1.04.

Freundlich equilibrium distribution coefficient (K_F) may be considered as a measure of affinity between solute and adsorbent (Murali *et al*, 1983). The degree of affinity of the metals with municipal solid waste is copper > arsenic > chromium; a factor of 10 differentiating between the three metals, at pH5.5. At pH6.4, arsenic >> chromium. At pH7.0, copper ≈ arsenic >> chromium.

TABLE 7.1 CALCULATED RESULTS - FREUNDLICH ADSORPTION ISOTHERMS

Metal	pH	Maximum regression observations available	Utilised number of regression observations	R squared	Freundlich equilibrium distribution coefficient (K_F)	Freundlich power coefficient (M)
Copper	5.5	7	6	0.859	0.21	0.74
Copper	7.0	7	5	0.895	0.11	1.04
Chromium	5.5	7	5	0.911	$35E10^{-3}$	0.58
Chromium	6.4	7	7	0.871	$2.8E10^{-3}$	0.96
Chromium	7.0	7	6	0.943	$3.4E10^{-3}$	0.90
Arsenic	5.5	7	6	0.941	$2.8E10^{-2}$	0.82
Arsenic	6.4	7	6	0.915	$9.7E10^{-2}$	0.40
Arsenic	7.0	7	5	0.760	$12E10^{-2}$	0.40

7.4.3 INITIAL EVALUATION OF ADSORPTION AND DESORPTION OF COPPER, CHROMIUM AND ARSENIC ONTO MUNICIPAL SOLID WASTE

The results from the kinetic trials were first examined to appraise; the degree of variability of the results; the effect of pH, and the degree adsorption and desorption of the metallic ions. adsorption/desorption are shown (Figures 7.40, 7.41 and 7.42). The tabulated results are

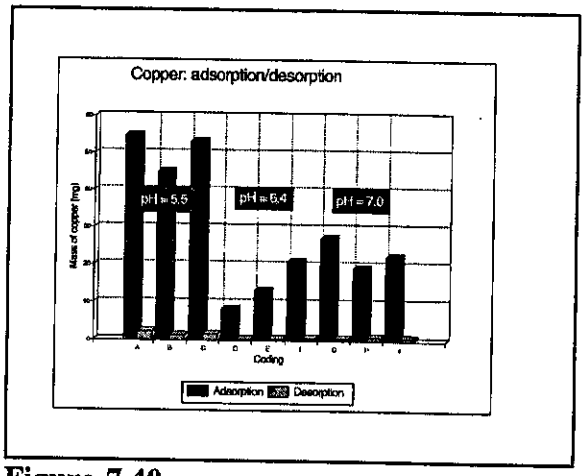

Figure 7.40
Mass of copper adsorped/desorped at pH 5.5, 6,4 and 7.0

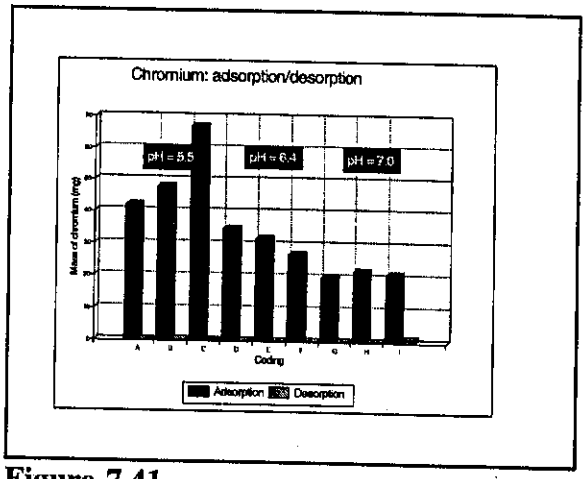

Figure 7.41
Mass of chromium adsorped/desorped at pH 5.5, 6.4 and 7.0

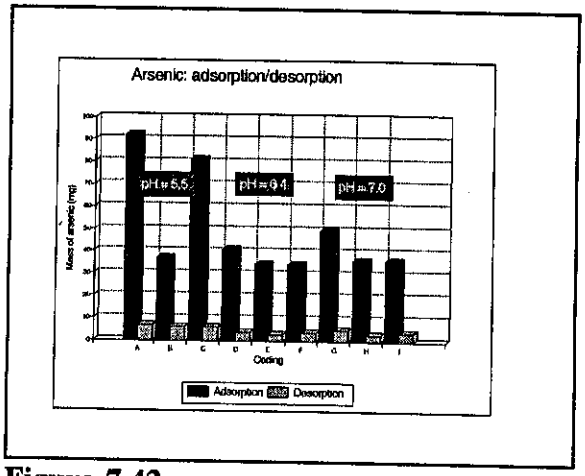

Figure 7.42
Mass of arsenic adsorped/desorped at pH 5.5, 6.4 and 7.0

assembled in Appendix F of Ballard (1997). It can be seen in Figures 7.40, 7.41 and 7.42 there is a degree of variability between samples especially when considering adsorption. This phenomena was not unexpected, municipal solid waste is an extremely heterogeneous solid. This was the primary reason that the kinetic experiments were completed in triplicate at the three pH values. In some cases there is however, a substantial anomaly in results. Considering Figure 7.41, the adsorption of chromium shows a large difference between the three samples designated A, B and C. The initial concentration of chromium in the sample was virtually identical at 263mg (A), 265mg (B) and 263mg (C). Nonetheless, sample C adsorped 70mg of chromium while sample A adsorped 42mg and sample B adsorped 48mg, the latter two exhibiting a similar degree of adsorption. This difference can only be explained by the differing composition of the adsorbent. A similar phenomena is present in Figure 7.42, the adsorption of arsenic at pH7.0 is extremely variable. There is a large difference between the initial arsenic concentrations but a reversal of the observations regarding chromium. Samples A and B with widely differing initial concentrations (225mg and 260mg, respectively) show a similar degree of adsorption (92mg. and 81mg, respectively). Sample B with an initial arsenic solution concentration of 231mg only adsorbs 37mg.

The effect of pH upon adsorption does not appear significant. Initial solute concentration is the primary variable. Figures 7.43, 7.44 and 7.45 show the effect of initial concentration on mass of solute adsorped. Initial concentration decreases with respect to the y-axis in all three figures. The pH value of that experiment is also shown together with the experimental coding.

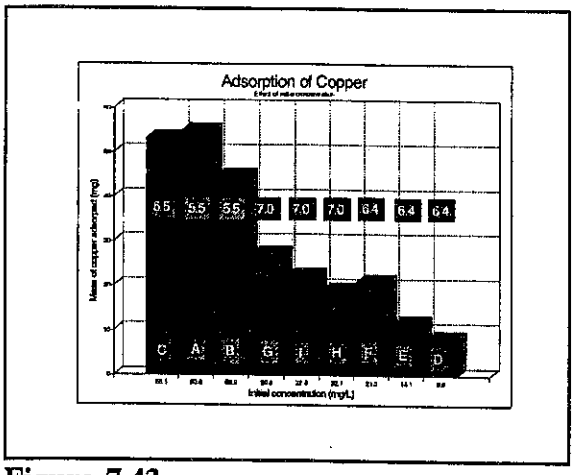

Figure 7.43
Copper adsorption with respect to initial solute concentration

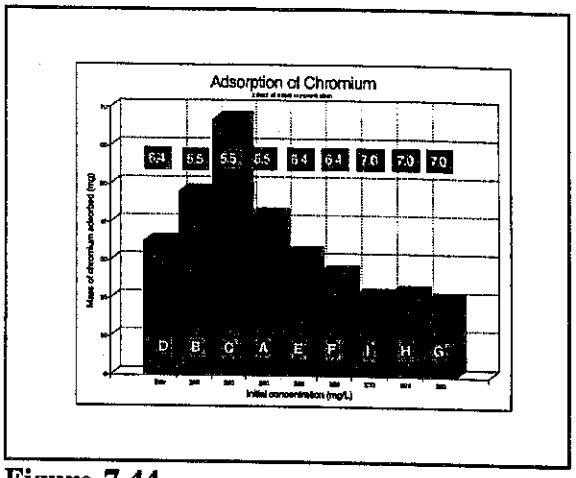

Figure 7.44
Chromium adsorption with respect to initial solute concentration

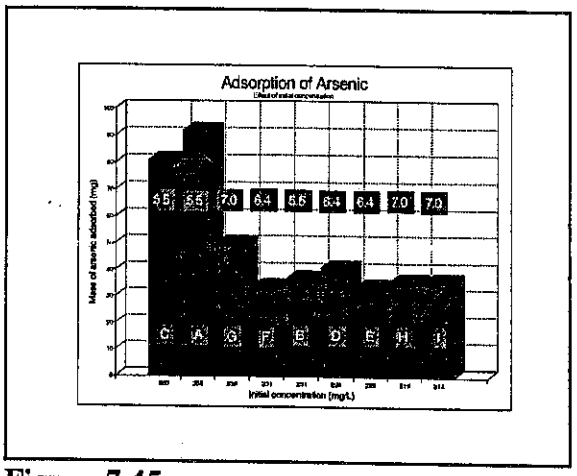

Figure 7.45
Adsorption of arsenic with respect to initial solute concentration

High rates of adsorption occur for copper at low pH levels (Figure 7.43) as a result of the experimental method (Section 7.4.3). Before commencement of the kinetic trials the pH of the solution was adjusted, after the addition of the metals to the solution. This allowed any precipitation to occur prior to evaluating adsorption. Therefore, at lower pH levels higher levels of copper were present due to solubility constraints. Lower adsorption rates for both chromium and arsenic appear to occur because the initial concentration of those metals was higher at the lower pH level. Again this may be attributed to the experimental method. When adjusting the pH precipitating copper entrained both chromium and arsenic resulting in lower concentrations of copper and arsenic at time zero of the kinetic trials. This may be seen in Appendix B, Table B-4 of Ballard, (1997). In all cases the original concentration (prior to pH adjustment) of chromium was approximately 270mgℓ^{-1} and between 270 and 280mgℓ^{-1} of arsenic. It may be clearly seen in the figures the initial concentration of both chromium and arsenic is substantially lower at the higher pH values. The effect of pH upon solute adsorption is further examined in Chapter 8.

The table below shows average values of adsorption and desorption at the various pH values for the three metals under consideration.

TABLE 7.2 COMPARISON OF MASS OF COPPER, CHROMIUM AND ARSENIC ADSORBED AND DESORBED AT PH 5.5, 6.4 AND 7.0

Metal	pH	Average Mass sorbed (mg)	Average Mass desorbed (mg)	Percentage of metal adsorbed that is desorbed
Copper	5.5	50.9	1.7	3.3
	6.4	14.1	0.5	3.5
	7.0	23.0	0.8	3.5
Chromium	5.5	53	0.2	0.4
	6.4	31	0.2	0.6
	7.0	21	0.5	2.4
Arsenic	5.5	70	6	8.6
	6.4	36	4	11.1
	7.0	41	4	9.8

The desorption of chromium was insignificant, the desorption of copper was less than 4 percent of that adsorped. Arsenic desorption was more significant, it did however, average less than 10 percent of the arsenic adsorped.

Analytical considerations of the method of analysis are of importance when appraising results at relatively low concentrations. The method of arsenic analysis employed to analysis of the leachate samples was hydride generation. Hydride generation is an extremely sensitive method allowing measurement in the parts per billion range. The limit of detection is $2\mu g\ell^{-1}$, accuracy is estimated at approximately 92 percent, within the optimum working range. This method was not available for analysis of the samples taken during the kinetic trials. The only analytical method available was flame atomic adsorption where the optimum working range was 50 - $200mg\ell^{-1}$, the sensitivity within the optimum range being $0.78mg\ell^{-1}$. This method was suitable for adsorption studies as the samples could be diluted to within the optimum range. However, at low concentrations (such as those experienced in the desorption trials) the degree of accuracy of the determination of arsenic can only allow the results to be utilised to examine trends. Calculation of kinetic constants from these results would be inaccurate. Levels of desorption were relatively low, especially in the case of copper and chromium, the kinetics of desorption were not investigated further, and attention was limited to the adsorption kinetics.

7.4.4 KINETICS CALCULATIONS

The rate of adsorption of all the metals onto the municipal solid waste was initially rapid and decreased with prolonged reaction time. The results from the kinetics experiments were examined extensively. An array of kinetic equations including zero-, first-, and second order and fractional power, were examined and found to be unsuccessful in describing the adsorption of the metallic ions on municipal solid waste. Attention was then directed to reversible orders of reaction. These were equally unsuccessful. A two-constant rate equation was found to be effective in describing the rate of metallic cation adsorption. Kuo and Lotse (1974) developed the two-constant equation to study the kinetics of phosphate sorption and desorption on hematite and gibbsite. The kinetic equation was developed by inserting a time-dependent expression into the Freundlich equation. The modified Freundlich equation used was in the form;

$$q = K_a C_o t^{1/m} \qquad 4.3$$

where,

q	=	metal adsorped per unit weight of solid (mg)
K_a	=	sorption rate coefficient (h^{-1})
C_o	=	initial metal concentration ($mg\ell^{-1}$)
t	=	reaction time (h)
1/m	=	constant

The results from the kinetic experiments were analysed in the manner shown below.

(a) Method of Kinetic data examination

Initially, a logarithmic plot of chromium adsorped (mg) versus time (h) was constructed. This logarithmic plot was then examined for any erroneous data points (see section (a) below). Erroneous data points were then eliminated and the remaining results were examined by means of regression analysis. Regression analysis principally supplied the following information:

Constant, or y-axis intercept of the regression;
R squared, or variance of the model;
X Coefficient (gradient of the linearised data).

Data generated by the regression analysis was then employed as shown.

$$q = K_a C_o t^{1/m}$$

Taking natural logarithms of both sides of the equation

$$\ln(q) = (1/m)\ln(t) + \ln(K_a C_o)$$

Plotting ln(q) versus ln(t):

(1/m)	=	X Coefficient
$\ln(K_a C_o)$	=	Constant, or y-axis intercept of the regression

The value of C_o, the initial concentration of the metal in solution is known, this allows the calculation of the sorption rate coefficient, K_a.

A plot was then prepared of the actual mass of metal sorbed (mg) and the calculated mass sorbed(mg) versus time (h), utilising all of the reported data (i.e. data points were not rejected). This plot allows the visual examination between the experimental data and that calculated from the regression analysis. To determine the degree of agreement between the measured data and the calculated data, the standard error of estimate (SE) was calculated (Steel and Torrie, 1960).

The standard error of estimate is defined as:

$$SE = [\sum (C_m - C_c)^2/(n-2)]^{1/2}.$$

Where,

C_m = measured metal sorbed by the soil at time, *t*
C_c = calculated metal sorbed by the soil at time, *t*
n = number of measurements

The lower the SE values the better the particular values calculated for the modified Freundlich equation describe the kinetics of the sorption of the metallic ions.

(b) Significance and rejection of experimental data

The method of data analysis described above, was repeated in an iterative manner. Where any doubt existed regarding the choice of any possible erroneous data points in the initial logarithmic plot, the logarithmic plot was then re-constructed releasing those of doubt and reinserting those initially disregarded. The SE was then recalculated again using all eight of the data points to ensure, ultimately, the minimum value of SE was obtained, and therefore the best representation of the experimental data.

To illustrate the method of kinetic data the analysis of chromium at pH7.0 is shown below (i.e. Chromium H).

TABLE 7.3 ADSORPTION OF CHROMIUM AT PH7.0 (CHROMIUM H)

Time (h)	Chromium concentration ($mg\ell^{-1}$)	Chromium sorbed (mg)	Ln (sorbed)	Ln (Time)
0.0	224	0		
0.5	212	12	2.485	-0.693
1.0	213	11	2.398	0.000
2.0	210	14	2.639	0.693
4.0	213	11	2.398	1.386
8.0	208	16	2.773	2.079
16.0	204	20	2.996	2.773
32.0	202	22	3.091	3.466

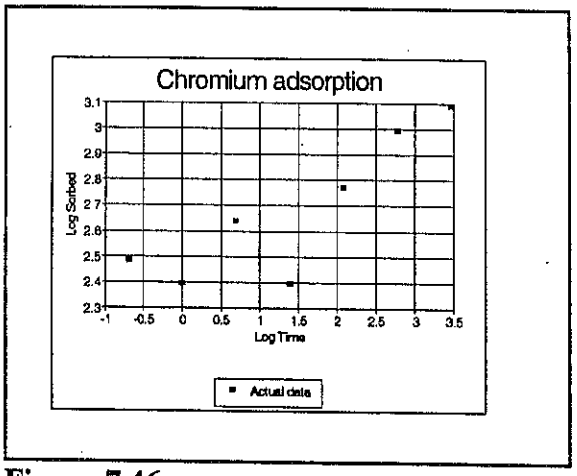

Figure 7.46
Logarithmic plot of measured data: Chromium H

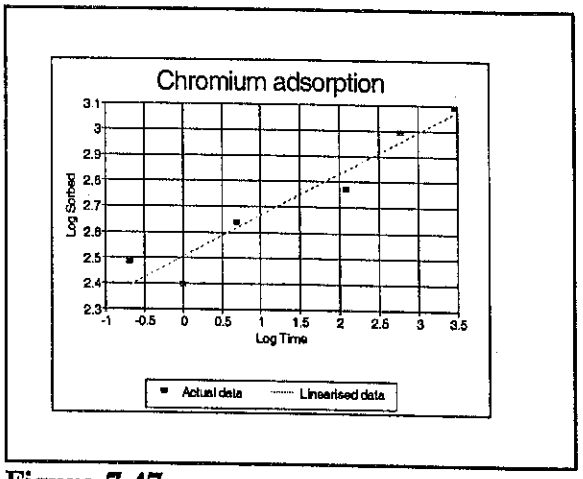

Figure 7.47
Linear regression: Chromium H

Examination of Figure 7.46 it would appear the chromium concentration at time = 4.0h (Log time = 1.386) is erroneous. Examining the remaining results by regression analysis.

Regression Analysis

Constant	=	2.5054
Standard error of Y estimate	=	0.0830
R squared	=	0.928
No. of observations	=	6
Degrees of freedom	=	4
X coefficient	=	0.1622
Standard error of coefficient	=	0.0226

The graphical presentation of these results is shown in Figure 7.44.

Now,				
(1/m)	=	X Coefficient	=	0.162
$\ln(K_a C_o)$	=	Constant, or y-axis intercept of the regression	=	2.5054
As,				
C_o	=	initial metal concentration ($mg\ell^{-1}$)	=	224
Then,				
K_a	=	sorption rate coefficient (h^{-1})	=	0.055

Substituting the measured values into the modified Freundlich equation gives the graphical presentation shown below (Figure 7.48).

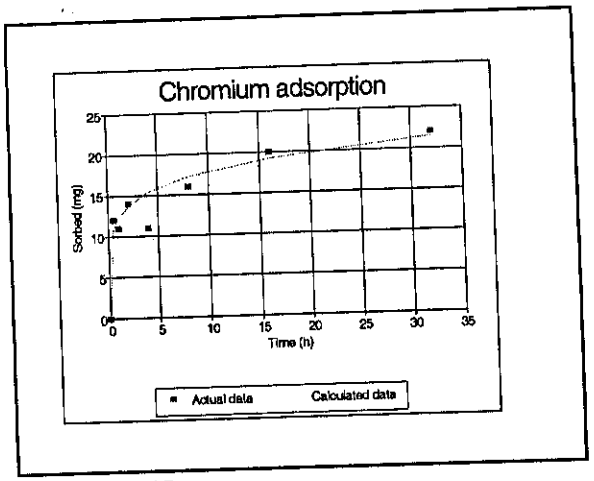

Figure 7.48
Calculated model & actual data: Chromium H

It can be seen by visual inspection the value obtained at time = 4h is probably erroneous. The final step of the analysis is the computation of the standard error, employing all eight data points. This is shown below in Table 7.4. It can be seen there is close agreement between the calculated results and the experimental values, except for the experimental data point at t= 4.0h, confirming that point to be erroneous. That point is the major contributor to the total standard error of 1.99. Graphical representation of all the kinetic trials are shown in Appendix G (Figures G-1 to G-25; of Ballard, 1997), together with details of the regression analysis (Tables G-1 to G-3).

Experimental data together with the modeled data for copper at all pH values is shown in Figures G-1 to G-8 of Ballard (1997). Visual examination, reveals in all cases, the adsorption rate of copper is extremely rapid, the rate of adsorption decreasing with time.

TABLE 7.4 STANDARD ERROR OF ESTIMATE (SE): CHROMIUM H

Time (h)	Measured chromium sorbed (mg)	Calculated chromium sorbed (mg)	SE
0	0	0	0.00
0.5	12	11	0.19
1.0	11	12	0.26
2.0	14	14	0.01
4.0	11	15	3.13
8.0	16	17	0.22
16.0	20	19	0.11
32.0	22	21	0.04
	SE =	square root of total =	1.99

Overall, the fit of the model to the experimental data is good, the experimental data points deviating from the model do not exhibit any trend in the manner of their deviation. The adsorption rate of chromium also has characteristic curve at all pH values (Figures G-9 to G-17; of Ballard, 1997). The initial rate of adsorption is slower than copper, absorption still continuing at extended time. For chromium adsorption at pH5.5 (Figures G-9 to G-11) the model under predicts, and for two (of the three) cases at pH6.4 (Figures G-13 and G-14). At pH7.0 (Figures G-15 to G-17) the model is well behaved. The adsorption rate of arsenic displays similar characteristics to that of chromium (Figures G-18 to G-25). There is again a slight tendency to over predict though this is in most cases near the degree of accuracy of the analytical method employed (see section 7.4.3). Again, as with copper, the experimental data points deviating from the model do not exhibit any trend in the manner of their deviation.

Table 7.5 tabulates the various calculated values obtained for the kinetic trials.

TABLE 7.5 CALCULATED RESULTS - KINETIC EXPERIMENTS

Coding	pH	Initial concentration [C_o] ($mg\ell^{-1}$)	Sorption rate coefficient [K_a] (h^{-1})	Constant [1/m]	Standard Error [SE]
Copper A	5.5	63.6	0.722	0.055	2.93
Copper B	5.5	53.2	0.677	0.063	3.95
Copper C	5.5	65.1	0.668	0.068	2.37
Copper D	6.4	9.6	0.629	0.096	0.92
Copper E	6.4	14.4	0.817	0.061	1.40
Copper F	6.4	21.3	0.766	0.081	1.00
Copper H	7.0	22.1	0.738	0.059	1.02
Copper I	7.0	27.4	0.825	0.064	2.74
Chromium A	5.5	263	0.080	0.182	5.93
Chromium B	5.5	265	0.076	0.237	4.98
Chromium C	5.5	263	0.096	0.243	7.18
Chromium D	6.4	269	0.057	0.252	5.55
Chromium E	6.4	262	0.065	0.152	3.07
Chromium F	6.4	259	0.051	0.189	2.03
Chromium G	7.0	223	0.062	0.099	2.59
Chromium H	7.0	224	0.055	0.162	1.99
Chromium I	7.0	230	0.057	0.162	2.58
Arsenic A	5.5	255	0.199	0.157	5.32
Arsenic C	5.5	260	0.107	0.347	8.84
Arsenic D	6.4	228	0.099	0.166	6.83
Arsenic E	6.4	225	0.096	0.138	10.33
Arsenic F	6.4	231	0.090	0.155	3.77
Arsenic G	7.0	238	0.167	0.089	6.48
Arsenic H	7.0	219	0.090	0.185	3.32
Arsenic I	7.0	214	0.101	0.149	6.38

7.4.5 LITHIUM SULPHATE PULSE EXPERIMENT

As mentioned in Section 6.3.2, leachate was sampled and recirculated approximately every 7 days. The time taken to displace the lithium from the column was 317 days. The experimental results are shown in Appendix D of Ballard (1997). The volumetric displacement of leachate from the column varied, and additionally, on occasion, sampling and recirculation could not be effected on the correct day. The conventional graphical representation and subsequent mathematical analysis of results of this nature is in terms of concentration-time, because of the variation in both volumetric displacement and on occasion, time increments, it was found to be more consistent to evaluate the data in discrete time increments, the mass of lithium discharged in the leachate being employed in the calculations. Utilising the concentration term would not make allowance for the variance in effluent volumetric displacement, and the differing time increment.

Firstly, the response curve of mass(m) versus time (t) was constructed (Figure 7.28). The area under the curve, the mean of the curve, and the variance are then evaluated with the formulae shown below. To maximise the accuracy of these calculations, the number of increments conformed to the number of measurements taken experimentally.
In terms of mass;

$$\text{Area under the curve} = \int_0^\infty m\,dt = \sum_0^\infty m_i \Delta t_i$$

$$\text{Mean of the curve } (\bar{t}) = \int_0^\infty t\,m\,dt \Big/ \int_0^\infty m\,dt$$

$$= \sum m_i t_i \Delta t_i \Big/ \sum m_i \Delta t_i$$

$$\text{Variance } (\sigma^2) = \left(\int_0^\infty t^2\,m\,dt \Big/ \int_0^\infty m\,dt\right) - \bar{t}^2$$

$$= \left(\sum m_i t_i^2 \Delta t_i \Big/ \sum m_i \Delta t_i\right) - \bar{t}^2$$

The calculated results should be then evaluated for consistency, by use of material balance computations. The equations are shown below.

$$\text{Area under the curve} = M/v \quad \text{(in terms concentration units)}$$

$$\text{Mean of the curve} = \bar{t} = V/v$$

Where,

M	=	mass of tracer added
v	=	volumetric flowrate (volume per unit time)
V	=	volume available for flow

Observation of the mass-time graph (Figure 7.28) reveal the graph to be consistent. The tabulated calculations for the evaluation of the area under the curve, the mean of the curve, and the variance are assembled in Appendix H of Ballard (1997).

(a) Graphical data

The calculations are shown in Appendix H, Table H-1 0f Ballard (1997).

Area under the curve = $\sum m_i \Delta t_i$ = 6709.1 mg day

Mean of the curve ($\bar{t}$) = $\sum m_i t_i \Delta t_i / \sum m_i \Delta t_i$ = 759738.6/6709.1
= 113.2 days

Variance (σ^2) = $(\sum m_i t_i^2 \Delta t_i / \sum m_i \Delta t_i) - \bar{t}^2$
= $(108428295/6709.1) - (113.2)^2$
= 3338

(b) Evaluation for consistency

Area under the curve = M/v (in terms of concentration units)

Mean of the curve = $\bar{t}$ = V/v

The concentration-time graphical representation was not employed in these calculations as discussed previously (Section 7.3.2); both time and volume increments were irregular. The area under the curve for concentration-time could not be calculated directly. Also the experimentally obtained mean of the curve could not be compared with the calculated value using the formula shown above. The actual volume available for flow within the packed bed of municipal solid waste cannot be determined as the solid waste is itself permeable. There is however a further means of evaluating consistency, the mass of tracer recovered may be compared with that initially added.

Mass of tracer added = 1026.7 mg
Mass of tracer recovered = 954.3 mg

Percent recovery = 92.95

The degree of recovery of the lithium sulphate tracer is satisfactory, showing the choice of tracer to be correct, and analytical methods to be adequate.

(c) Construction of the E(t) and E curve

The **E**(t) curve is constructed by use of the mass-time data. The area under the curve must equal unity. The mass of lithium in the liquid outlet is divided by the area under mass-time curve; the y-axis is still in units of real time. The **E** curve is then transposed from the **E**(t) curve. The **E** term (y-axis) is computed by multiplying **E**(t) by the mean of the mass-time curve($\bar{t}$). The dimensionless time function (x-axis) is computed by dividing the real time values(t) by the mean of the concentration-time curve($\bar{t}$). Again, the area under the curve must equal unity. The calculated data are assembled in Appendix H, Table H-2 of Ballard

(1997); the graphical representations are shown below (Figures 7.49 and 7.50).

The mean of the curve was calculated to be 113.2 days, this is conveniently represented on the E curve (Figure 6.50) as "1" on the reduced time x-axis. It can be seen the mean residence time in the column is displaced from the maximum value attained for "E". This phenomena is a sure indication of preferential areas of fluid flow (channelling) within the column.

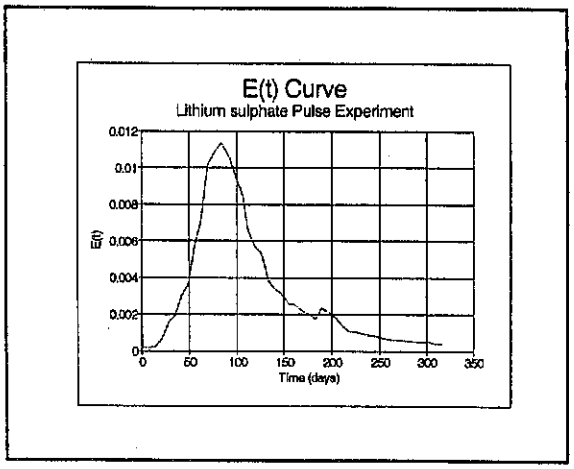

Figure 7.49
E(t) curve: Column 4

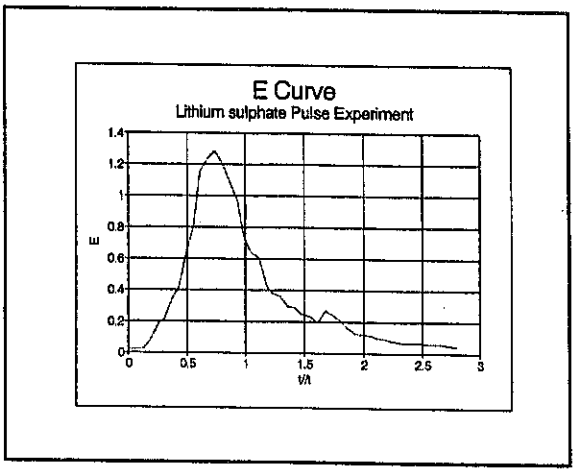

Figure 7.50
E curve: Column 4

The elongation of the base of the curve when compared with the usual thin spike expected for plug flow, is a visual representation of the high value of the variance obtained ($\sigma^2 = 3338$). This can be caused by many different flow phenomena, the consequences being either, longitudinal mixing and/or incomplete mixing in the radial direction. A small value of the variance indicates ideal plug flow, the larger the value the greater the deviation from ideality.

7.4.6 PILOT-SCALE CO-DISPOSAL EXPERIMENT

The calculated results from section 7.4.5, together with the kinetic constants calculated in section 7.4.4 are now employed to calculate the concentration of the three metallic ions in the outlet of the leachate from column 3. The analytical results from columns 3 and 5 are similar, but as the co-disposal experiment was marginally longer for column 3 attention is focused upon that column.

(a) Method of transforming residence time distribution data

The results from the lithium sulphate pulse experiment on column 4 are employed to supply residence time distribution data for column 3. This is a reasonable action as:

(i) the municipal solid waste employed in all the columns is from a common source;
(ii) the municipal solid waste was reduced to the same size range;
(iii) the degree of compaction obtained within the columns is similar for all;
(iv) the height of municipal waste is in the columns is virtually identical;
(v) the process of size reduction "homogenised" the municipal solid waste
(vi) the larger mass of municipal solid waste used in the pilot-scale studies (approximately 700kg) versus the 50g utilised in the laboratory scale experiments should minimise differences between individual columns.

However, the volumetric displacement of leachate employed during the tracer study averaged $5.21\ell day^{-1}$ whilst the volumetric displacement of leachate through column 3 averaged $2.75\ell day^{-1}$ therefore the residence time data from column 4 required mathematical manipulation to realise the conditions in column 3. Examining the data, a number of methods to achieve this objective were tried. The most successful was to adjust the number of days to correspond with the smaller volumetric displacement obtained from column 3. This was successful, the volume of liquid flowing in the initial increments i.e. 7 days remained the same but the time duration to obtain that volume was proportionally increased to 13.2 days ($7 \times 5.21/2.75$). This transformation was continued for all the data from the lithium pulse experiment. The characteristic curve is then maintained and no further calculation is required. A similar exercise was performed on the data obtained for the calculation of the mean for column 4, and the variance; new values may then be obtained for column 3. The tabulated calculations for the evaluation of the area under the curve, the mean of the curve, and the variance are assembled in Appendix I of Ballard (1997).

(b) Graphical data

The calculations are shown in Appendix I, Table I-2 (Ballard, 1997).

Area under the curve = $\sum m_i \Delta t_i$ = 12695.7 mg day

Mean of the curve ($\bar{t}$) = $\sum m_i t_i \Delta t_i / \sum m_i \Delta t_i$ = 2720477.6/12695.7

= 214.3 days

Variance (σ^2) = $(\sum m_i t_i^2 \Delta t_i / \sum m_i \Delta t_i) - \bar{t}^2$

= $(734706779/12695.7) - (214.3)^2$

= 11953

The time taken to displace lithium from the experimental system for the tracer study was 317 days. The total residence time is now calculated to be 600 days.

The transformed graphs are shown overleaf (Figures 7.51, 7.52 & 7.53), the calculations are shown in Appendix I, Table I-1 of Ballard (1997). It can be seen in Figures 7.51 to 7.53, that the method of transformation from the larger volumetric displacement in column 4 to the smaller volumetric displacement in column 3, retains the characteristic curve obtained in the

lithium sulphate pulse experiment (Figures 7.28, 7.49 and 7.50). The mathematical transformation extends the base of the curve to accommodate the longer residence time of the lower volumetric displacement.

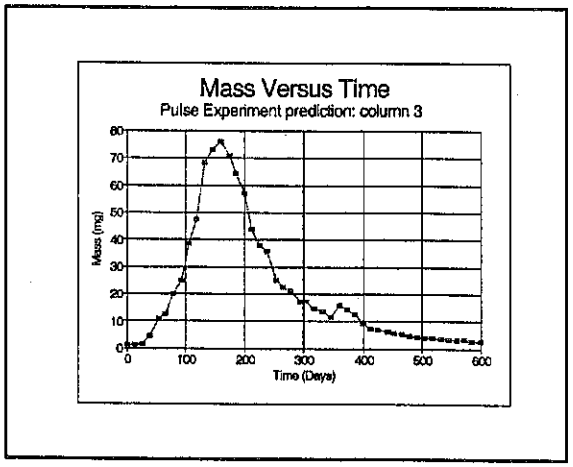

Figure 7.51
Predicted lithium mass versus time relationship for column 3

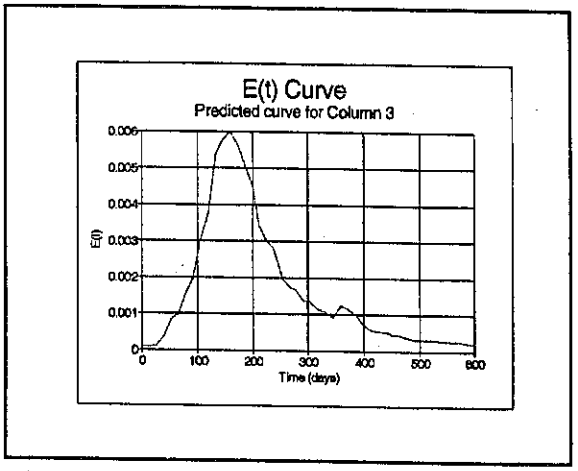

Figure 7.52
Predicted **E**(t) curve for column 3

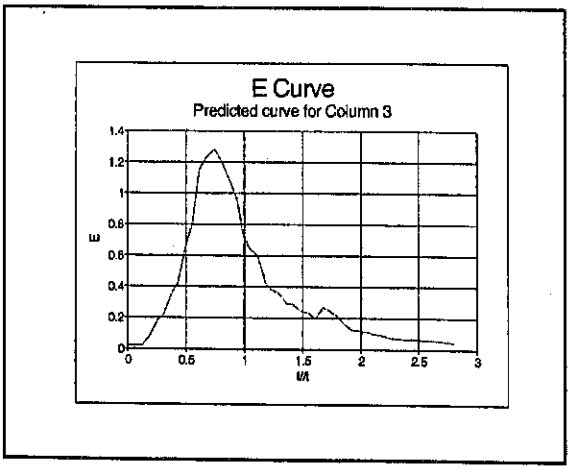

Figure 7.53
Predicted **E** curve for column 3

(c) Calculation of metallic ion concentration in leachate

Two mathematical methods were considered to calculate the concentration of the ions in the liquid effluent from the column. Both use the residence time data as a basis. The **E**(t) curve data allows one to calculate the volume of liquid leaving the column at any time increment during the total time. Both methods are dependent on the manner in which one envisages the liquid to behave in the column. One can view the column as a number of pipes of differing diameter through which the liquid of differing residence times flow, none of the elements of fluid hinder one another, and any metal adsorped does not affect any subsequent liquid of longer residence time.

Another method, is to consider that all the liquid passes through the column in the same path, leaving in its wake adsorped metal which then reduces the capacity of the adsorbate to adsorb metal contained in liquid elements of longer residence time. This adsorbed metal has to be allowed for in the calculation. It would appear probable that at short liquid residence times that the first *scenario* is correct whilst at longer residence times the latter scenario is the more accurate of the two proposed methods. Both methods of calculation were attempted. It was found that the latter method more accurately predicted the behaviour of the metal content in the leachate to the available data obtained from column 3, consequently this method is employed in the subsequent calculations.

The mathematical computation employs a conventional chemical engineering mathematical approach used to solve unsteady state conditions (Section 4.4.4) The calculation is performed incrementally allowing for the differing residence time frames of the various elements of fluid flowing through the column. Each incremental residence time is overlaid upon the previous shorter residence time until the longest residence time is the last time frame to compute.

As the rate of adsorption is initially rapid and decreases with time, the depth increment must be minimised to ensure the calculation accurately reflects the real situation within the column, where the low residence time elements of fluid flow rapidly and will not reach equilibrium with the solid waste. The depth increment was therefore minimised to 20mm. The time increment was also minimised (to ensure accuracy was maximised), to the minimum possible provided by the experimental procedure, approximately 13 days.

The method adopted for the formulation of the copper-chromium-arsenic solution at the various pH values made allowance for precipitation at the relevant pH (section 5.5.1). The solution employed during the kinetic trials was first formulated at a low pH, adjusted to the relevant pH by use of sodium hydroxide, and precipitation allowed to occur. The initial values of the kinetic trials where then the maximum concentration of the metal that would occur at that pH. When the combined copper/chromium/arsenic solution was prepared in the laboratory there was a substantial reduction of the copper in solution from approximately $80mg\ell^{-1}$ to $22mg\ell^{-1}$ due to precipitation. It would appear, that although 88.4g of copper are added, virtually all of this copper would precipitate upon introduction into the column.

With a full scale landfill water can only come from three sources; moisture provided by a precipitation event (rainwater); moisture from deposited solid waste, and moisture produced from anaerobic activity. The major source of moisture is rain water. Rainwater has a negligible alkalinity content and therefore would not raise the pH of the deposited copper solution. Additional rainwater would mobilise any soluble copper present. However, when water is in contact with stabilised municipal solid waste very high levels of alkalinity can be observed. This is evident in the results quoted in this chapter, where the alkalinity approximated $4000mg\ell^{-1}$ (section 7.3.1). It may be concluded that virtually all the copper deposited with municipal solid waste would precipitate as copper hydroxide at or near proximity to its place of deposition. Analytical results confirm these statements.

Extremely low levels of copper were detected in the leachate from columns 3 and 5. Copper concentration in the leachate from column 3 did not exceed $0.11mg\ell^{-1}$. Over the entire period

of monitoring (235 days), the concentration of copper in the leachate from column 3 averaged 0.05mgℓ^{-1}, i.e. no higher than the initial reading at Day zero. The initial concentration of copper in the leachate from column 5 was 0.07mgℓ^{-1} a value that was not exceeded for the entire duration of the experiment. The final copper concentration after 221 days was 0.04mgℓ^{-1}. Over the entire period of monitoring (221 days), the concentration of copper in the leachate from column 3 averaged 0.03mgℓ^{-1}. For these reasons the calculation of copper content was not computed.

The computation to predict chromium concentration employed the results obtained from the laboratory scale kinetic trail designated "chromium H". This outcome of this trial was the lowest standard error of the three trials at pH7.0 (1.99), the approximate pH of leachate exiting the pilot-scale columns. The values employed are:

K_a	=	sorption rate coefficient (day^{-1})	=	0.0916
1/m	=	constant	=	0.1622
Maximum sorption	=	21mg per 50g adsorbate	=	0.42gkg^{-1}

The calculation is shown in Appendix J of Ballard (1997). The predicted concentration of chromium over the total time period of 600 days (Figure 7.54) is extremely interesting, dispelling commonly held views.

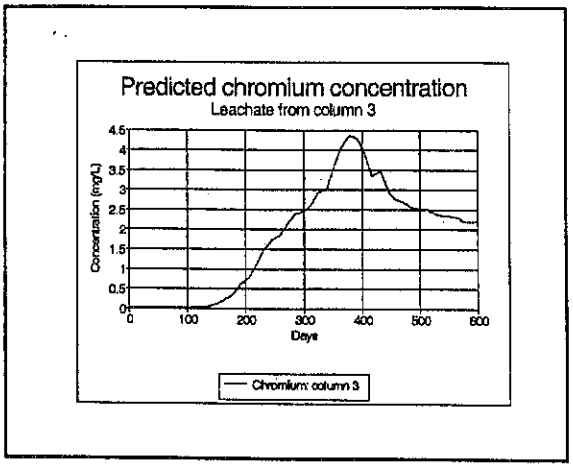

Figure 7.54
Predicted concentration of chromium in leachate from column 3

One would anticipate chromium concentration in the leachate to be initially high, as hydrodynamic factors such as fluid channelling and by-passing would convey chromium through the adsorbent. This does not occur, and the column behaves as a plug flow reactor, albeit a reactor with high degree of non-ideality. The maximum chromium concentration occurs on Day 390 at 4.4mgℓ^{-1} The secondary peak occurring at approximately Day 430 is a product of the smaller secondary peak which occurred in lithium pulse experiment.

For graphical scalar considerations, two figures are presented to illustrate the predictions of the computed model and that achieved in practice. Figure 7.55 shows predicted and actual results until Day 194; Figure 7.56 shows results until cessation of monitoring on Day 235. Considering Figure 7.55, until Day 142 the model realises actual measurements well, with very little deviation. From Day 142 the model begins to overpredict actual conditions. Results from monitoring continue in the region of 0.03mgℓ^{-1} whereas the model begins to predict chromium concentrations in excess of 2mgℓ^{-1} (Figure 7.56) in that time frame.

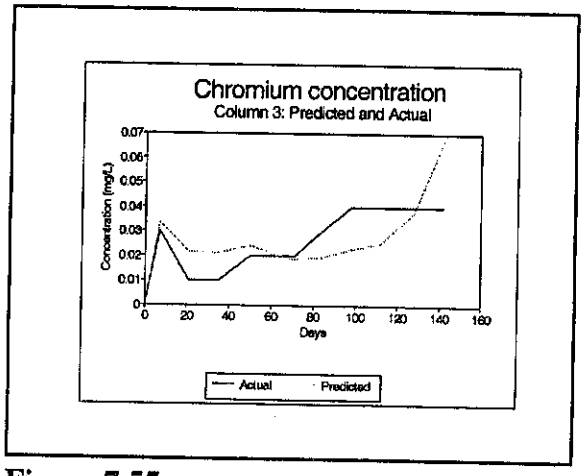

Figure 7.55
Predicted and actual concentration of chromium in leachate from column 3 until day 142

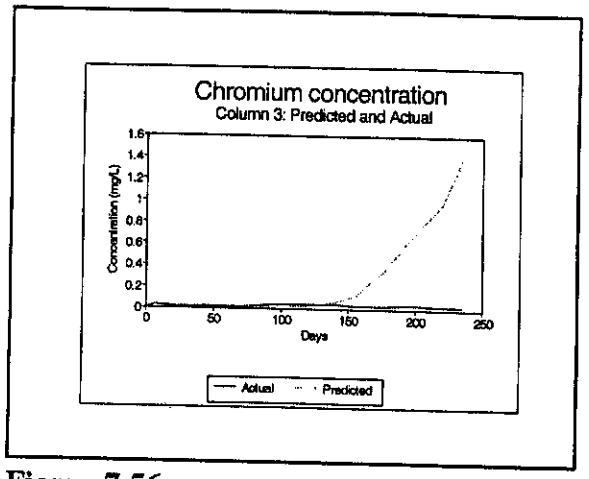

Figure 7.56
Predicted and actual concentration of chromium in leachate from column 3 until day 234

There are three obvious factors to consider:

(i) the affinity for chromium exhibited the solid waste in the pilot-scale landfill columns was not realised in the kinetic trials;

(ii) the method of computation does not model conditions in the pilot-scale columns with sufficient accuracy;

(iii) the transposing of the information obtained from the tracer studies undertaken on column 4 to column 3 could not be supported in practice.

The deviation of predicted values from that achieved in practice is only exhibited after a relatively long period of time has elapsed (160 days). It is therefore unlikely that comments (ii) and (iii) are the major contributory factor. It is probable that factor (i) is appropriate. Soil science researchers, Bartlett and James (1988) document similar occurrences. The drying and storage of soils can alter the surface characteristics of that soil. If this is applicable to soils, a similar analogy can be drawn from municipal solid waste. Another additional factor is the sample size utilised in the kinetic experiments. Only 50g was used, while the pilot-scale columns where packed with approximately 700kg of municipal solid waste. While sampling was exhaustive, solid waste is an extremely heterogeneous substance.

The predicted arsenic concentration employed the results obtained from the laboratory scale kinetic trial designated "arsenic H". This outcome of this trial was the lowest standard error of the three trials at pH7.0 (Section 7.4.4(a)), the approximate pH of leachate exiting the pilot-scale columns. The values employed are:

K_a	=	sorption rate coefficient (day^{-1})	=	0.1613
1/m	=	constant	=	0.1853
Maximum sorption	=	36mg per 50g adsorbate	=	$0.72gkg^{-1}$

The predicted outcome of the co-disposal of arsenic was calculated in the same manner as that of chromium. Calculations predicted there would be an absence of arsenic in the leachate from column 3 during the total time period of 600 days. The results quoted in section 7.3.3(c) showed a maximum arsenical content of the leachate of approximately $2mg\ell^{-1}$. The results from desorption kinetic trials (Section 7.4.3) showed that arsenic was the only metal of those under consideration that displayed any significant degree of desorption. This could not be allowed for in the calculation, and could account for the extremely low degree of error that is evident.

The method of computation allowed the graphical representation of the results in terms of metal saturation with depth and time. These are shown below in Figures 7.57 and 7.58.

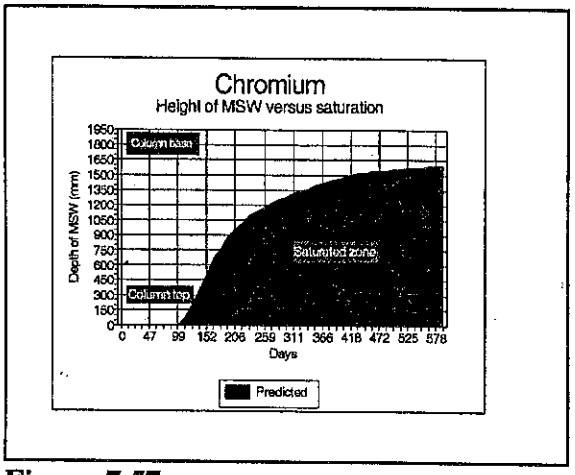

Figure 7.57
Chromium saturation versus column depth

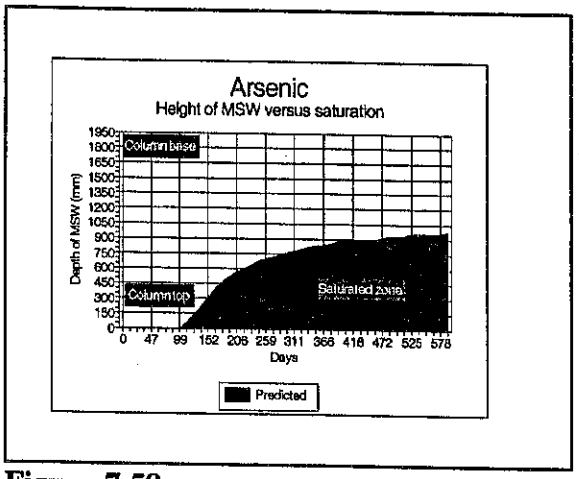

Figure 7.58
Arsenic saturation versus column depth

After 99 days both metals started to reach their equilibrium maximum value in the initial 20mm of municipal solid waste. The total height of municipal solid waste in column 3 was 1940mm. Chromium almost completely saturated the column and further addition of chromium would result in high levels of chromium in leachate. The mass of chromium added to the column was 256.1g. The degree of column saturation is due mainly to the low maximum chromium equilibrium value of 0.42g of chromium per kilogram of municipal solid waste. The final depth of saturation for chromium was 1600mm. The mass of arsenic added was 256.7g. The degree of arsenic saturation is far less than that of chromium reaching only 980mm, approximately half the column depth. The equilibrium saturation concentration is high in comparison with the other metals under consideration, at $0.72gkg^{-1}$. These graphical representations indicate the importance of the maximum saturation value. The rate of reaction is not dissimilar between chromium and arsenic however the high affinity of arsenic to the municipal solid waste results in far less mobility within the column. The mean residence time in the column was computed to be 214 days, at that time chromium 1020mm, and arsenic 600mm.

Analytical results are only available for comparison for the first 235 days of an anticipated 600 day residence time period. In this 235 day time frame the modelled results are an

excellent response to that experienced at pilot-scale. The results for copper cannot be compared as precipitation occurs. Both chromium and arsenic analytical results compare vary favourably with that predicted. There are additional factors to consider. These are discussed in Chapter 8.

7.4.7. APPLICATION OF THE PILOT-SCALE STUDIES TO THE FULL SCALE LANDFILL

In this sub-section the results obtained at pilot-scale are utilised to provide functional data that may be applied by the landfill practitioner. It was decided to employ a worst-case study. The assumptions of this worst-case study are detailed below.

(i) Precipitation occurring in the heaviest precipitation month proceeded to fall on a continual basis;
(ii) no loss of moisture from the landfill, such as evapotransportation or run-off;
(iii) the landfill was at field capacity prior to co-disposal;
(iv) metal content in leachate from the landfill should not exceed the most stringent requirements prescribed by current South African legislation.

The municipal solid waste utilised in this study was excavated from Coastal Park Sanitary Landfill Site (section 5.3). Therefore, to continue with a site-specific study, detailed precipitation data was available and was obtained for the Coastal Park Sanitary Landfill Site for the period 1991 to 1994 (City of Cape Town, 1994). During this period the greatest amount of precipitation occurred during June 1994. Rainfall approximated 290mm. In South Africa, the quality of water discharged into a catchment, where water in that catchment area will be subsequently purified to drinking water quality, is determined by The Water Act, 1956 (Act No. 54 of 1956) (DWA, 1956). The Water Act was originally promulgated in 1956, though there have been many subsequent amendments. The Special Standard (DEAF, 1984) defines the requirements of wastewater or effluent draining into a catchment area. The maximum allowable concentration of copper is $0.02mg\ell^{-1}$; the maximum allowable concentration of chromium is $0.05mg\ell^{-1}$; the maximum allowable concentration of arsenic is $0.1mg\ell^{-1}$.

As shown in section 7.4.6(c), predicted chromium concentration in the leachate from column 3 exceeded analytical measurements ($4.4mg\ell^{-1}$ *versus* $0.03mg\ell^{-1}$). Conversely, predicted arsenic concentration in the leachate from column 3 was exceeded by analytical measurements (zero *versus* $2mg\ell^{-1}$). It would appear reasonable to assume, if predicted chromium concentration is reduced to a maximum of $0.05mg\ell^{-1}$, actual concentration in arsenic in leachate would approximate zero. Attention is therefore focused on leachate chromium concentration.

Firstly, precipitation data were transposed into leachate volumetric displacement.

Maximum rainfall	=	290mm (June 1994)
Landfill column, cross-sectional area	=	$0.25 \times \pi \times 0.7^2$
	=	$0.3848m^2$

Volumetric flow = $0.29 \times 0.3848 \times 1000/30$
= $3.73\ell day^{-1}$

The residence time data obtained from the tracer studies (section 7.3.2) was then transformed in the same manner as reported in section 7.4.6(a). The same exercise was executed for the calculation of mean of the curve and the variance. The transformed graphs are shown below (Figures 7.59; 7.60 and 7.61) together with the calculated values for the mean and variance.

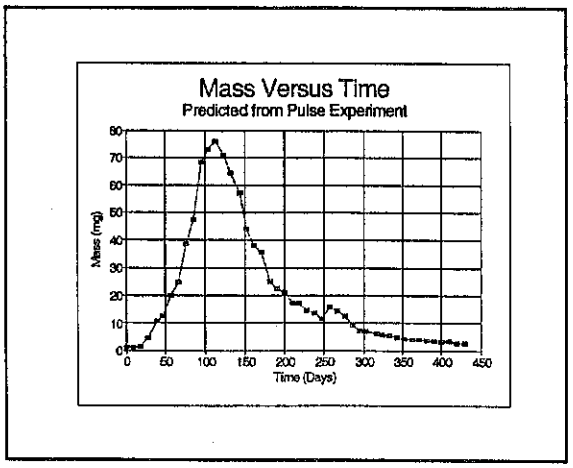

Figure 7.59
Predicted lithium mass versus time relationship: $3.73\ell day^{-1}$

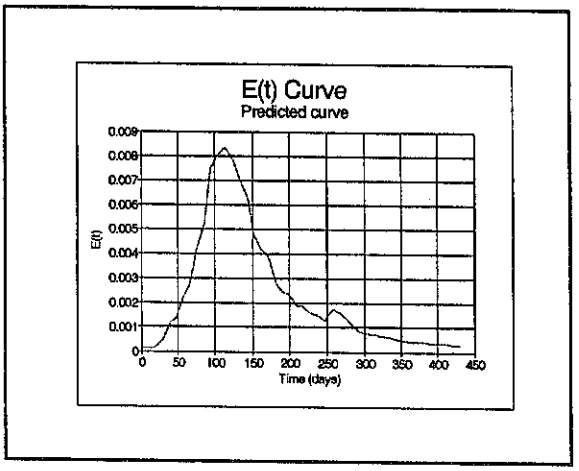

Figure 7.60
Predicted **E**(t) relationship: $3.73\ell day^{-1}$

Mean of the curve ($\bar{t}$) = 153.4days
Variance (σ^2) = 6123

The total residence time for the pilot-scale column at a displacement rate of leachate of $3.73\ell day^{-1}$ is 430 days.

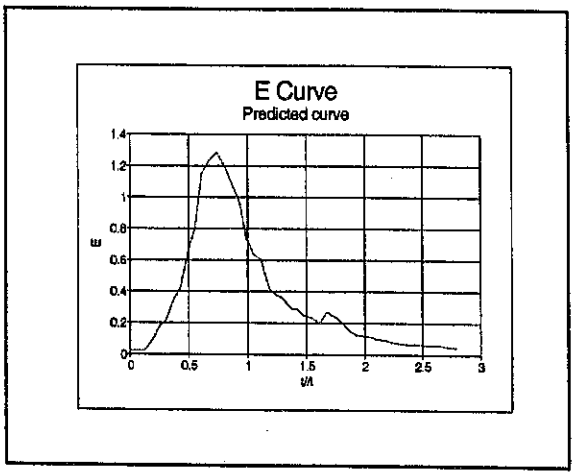

Figure 7.61
Predicted **E** relationship: $3.73\ell day^{-1}$

The computation to predict chromium concentration in leachate employed the same numerical values utilised in 7.4.6(c). The initial mass of chromium co-disposed at pilot-scale in column 3 was 256g. The

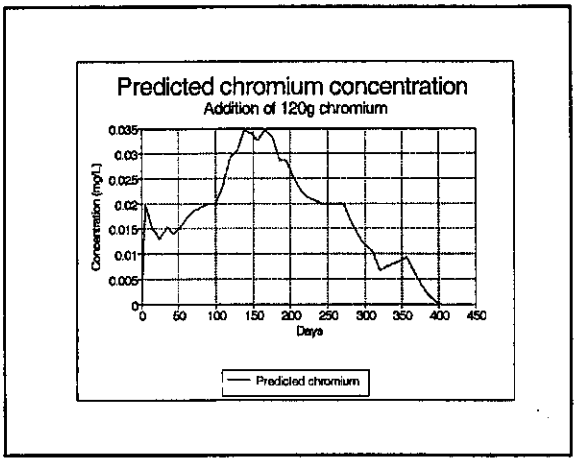

Figure 7.62
Predicted chromium concentration: Assumed addition of 120g of chromium

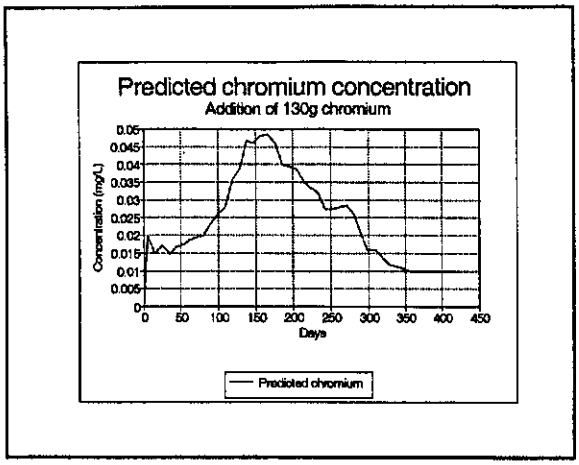

Figure 7.63
Predicted chromium concentration: Assumed addition of 130g of chromium

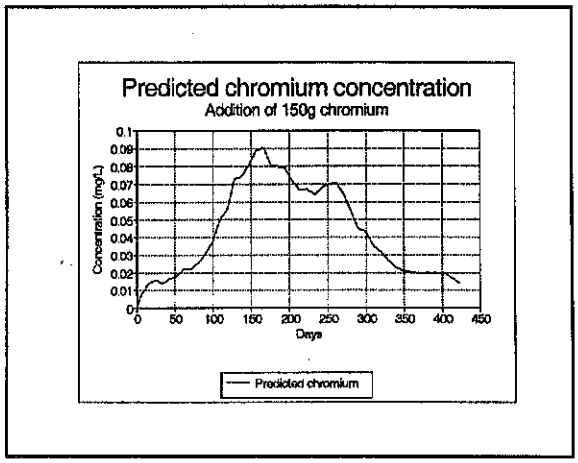

Figure 7.64
Predicted chromium concentration: Assumed addition of 150g of chromium

predicted maximum chromium concentration in leachate was then 4.4mgℓ^{-1}. Therefore, to have a predicted chromium concentration of 0.05mgℓ^{-1} in the leachate, the mass of chromium would have to be far less than 256g. Three modelled calculations were completed; 100g; 120g, and 150g of chromium, being assumed to be added to the column. The graphical representations are shown (Figures 7.62; 7.63 and 7.64). It can be seen that, with the assumed addition of 150g of chromium, predicted leachate chromium concentration reaches a maximum of 0.09mgℓ^{-1} (Figure 7.64) at Day 165. This exceeds the maximum allowable concentration of chromium of 0.05mgℓ^{-1}. With the assumed addition of 100g of chromium, predicted leachate chromium concentration reaches a maximum of 0.035mgℓ^{-1} (Figure 7.62) at Day 165. This concentration is within acceptable limits, but there is sufficient tolerance to add additional chromium. It can be seen from Figure 7.63 the assumed addition of 130g of chromium would result in a predicted chromium concentration of 0.048mgℓ^{-1}. Any further addition of chromium would result in the predicted concentration exceeding the maximum allowable chromium concentration of 0.05mgℓ^{-1}.

The mass of municipal solid waste contained in column 3 was 668kg. The maximum amount of chromium that could be co-disposed with acceptable risk of environmental damage is therefore 195gtonne^{-1}. This chromium would be co-disposed with the proportional amount of arsenic and copper, as dictated by the composition of the CCA solution. The laboratory scale equilibrium and kinetic studies and the pilot-scale co-disposal trials were conducted with the CCA solution. The CCA (Tanalith) solution has been characterised fully in section 5.4.1. The ratio of copper: chromium: arsenic is 1 : 2.9 : 2.9. Therefore, if 195g of chromium were co-disposed with municipal solid waste, there would be 195g of arsenic and 67g of copper associated with that amount of chromium.

7.5 SUMMARY

Adsorption equilibrium studies and kinetic studies were undertaken at laboratory scale, at three pH values; pH5.5, pH6.4, and pH7.0. The adsorbent being municipal solid waste, the adsorbate being copper, chromium and arsenic in aqueous solution. Data obtained at equilibrium was successfully described by the Freundlich Isotherm (section 7.4.2).

The kinetic studies revealed a reaction characterised by an initial rapid adsorption rate, the rate of adsorption subsequently decreasing at larger values of time. This reaction could be successfully described by a modification of the Freundlich equation (section 7.4.4) usually termed, the modified Freundlich equation, or the two-constant equation. The modified Freundlich equation was developed by Kuo and Lotse in 1974.

Tracer studies were undertaken at pilot-scale. The tracer employed was lithium sulphate. Tracer studies revealed (as expected) a system which conformed with a plug flow reactor, albeit with a great deal of non-ideality. Co-disposal experiments were then undertaken at pilot-scale. A solution of copper-chromium-arsenic was added to two of the pilot-scale columns. The effluent from the columns was closely monitored. Conventional chemical engineering reactor design allows the computation of reactor effluent composition from results from tracer studies in combination with kinetic results, together with details of the reactor feed.

The pen-ultimate phase of the investigation comprised of a comparison of the results obtained at pilot-scale with that predicted from the laboratory scale studies. Agreement was good between results obtained at pilot-scale with results predicted from the laboratory scale studies. Predicted chromium concentration in the leachate from column 3 exceeded analytical measurements ($4.4 mg\ell^{-1}$ *versus* $0.03 mg\ell^{-1}$). Actual arsenic concentration in the leachate from column 3 exceeded that predicted ($2 mg\ell^{-1}$ *versus* zero) (section 5.4.6(c)).

The final phase of the project employed the model developed from the laboratory scale results to compute the mass of copper-chromium-arsenic solution that could be added to municipal solid waste. A worst-case study was examined (section 7.4.7). Computation showed it is possible to co-dispose 195g of chromium together with 195g of arsenic and 67g of copper per tonne of municipal solid waste with the minimum of environmental damage to any receiving water body.

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CHAPTER 8
DISCUSSION: LABORATORY AND PILOT-SCALE STUDIES

8.1 INTRODUCTION

The results and subsequent calculations generated by the experimental study are examined and discussed in this chapter. The speciation and physical characteristics of the metals are scrutinised. The laboratory scale equilibrium and kinetic studies are examined and a sorption mechanism is proposed. The pilot-scale tracer studies and co-disposal trials are assessed and discussed. The computational method developed to model the pilot-scale studies is appraised and any deficiencies uncovered. The results established at pilot-scale, are applied to the full scale landfill. The effect of the co-disposal of copper, chromium and arsenic in an acetogenic, methanogenic and stabilised landfill assessed.

8.2 SPECIATION OF THE METALS PRESENT IN THE EQUILIBRIUM AND KINETIC TRIALS

It is advantageous to discuss firstly the speciation and the copper, chromium and arsenic under prevailing conditions. Chromium from the CCA wood preservative is present in the form of Chromium(VI), arsenic is in the form of arsenic(V) and copper is in the form of copper(II). Ionic equilibria for copper, chromium and arsenic in an aqueous solution are detailed below, together with their ionic structure in an aqueous medium.

8.2.1 COPPER(II)

The Cu^{2+} ion, at ordinary concentrations, begins to hydrolyse above pH4, and precipitation as the oxide (Cu_2O) or the hydroxide ($Cu(OH)_2$) begins soon after. The hydrated ion has the formula $Cu(H_2O)_6^{2+}$ and has a distorted octahedral structure (Jahn-Teller effect). This is a consequence of its d^9 configuration (Nicholls, 1974). Two of the water molecules are in the trans position, these are further removed from the Cu^{2+} ion than the other four, which are coplanar (Cotton *et al*, 1972). The ionic radii of the copper ion in aqueous solution is 0.87Å. The bond lengths are 1.94Å for the coplanar bonds and 2.4Å for the trans bonding ions (Burgess, 1988). It is important to note that copper is present in aqueous solutions in the form of a cation.

Structural details of the hydrated copper ion are shown in Figure 8.1.

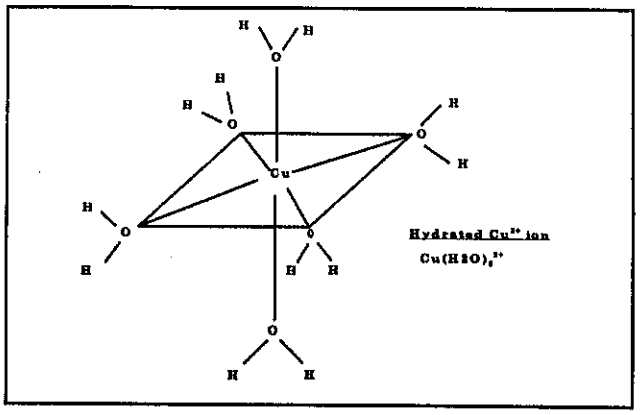

Figure 8.1
Structural details of the hydrated copper ion

8.2.2 CHROMIUM(VI)

Chromium(VI) hydrolyses extensively, so only neutral or anionic species occur in water. The speciation, well established by extensive data are $HCrO_4^-$, CrO_4^{2-}, and $Cr_2O_7^{2-}$. However $Cr_2O_7^{2-}$ is only dominant at chromium(VI) concentrations above 0.01M, in acidic media (Bates *et al*, 1976).

The equilibria for chromium(VI) in aqueous solutions is shown below,

$$H_2CrO_4 + H_2O \rightleftharpoons HCrO_4^- + H_3O^+ \quad pK_a = 0.74$$

$$HCrO_4^- + H_2O \rightleftharpoons CrO_4^{2-} + H_3O^+ \quad pK_a = 6.49$$

CrO_4^- (monohydrogen chromate ion) is the predominant species between pH0.75 and pH6.45, while CrO_4^{2-} (chromate ion) predominates at pH values greater than 6.45. The chromate ion has a tetrahedral structure, with four oxygen atoms bound to a central chromium atom. The mutual repulsion of the four electron clouds direct the oxygen atoms to the corners of an inscribed tetrahedron. Therefore, the monohydrogen chromate ion would have a distorted tetrahedron structure. The ionic radii of the chromium(VI) ion in aqueous solution is approximately 0.63Å. Structural details of the chromate ion are shown in Figure 8.2.

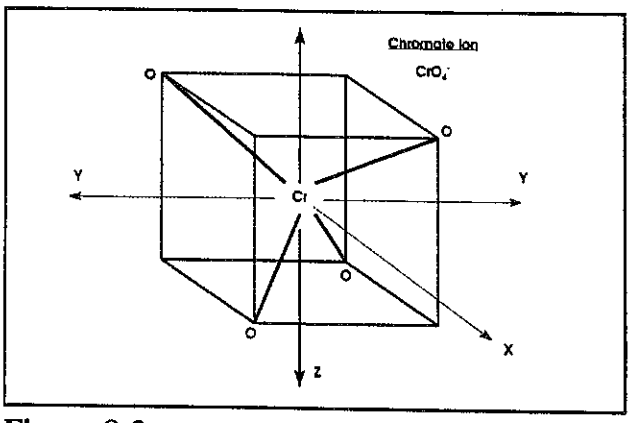

Figure 8.2
Structural details of the chromate ion

Metal to oxygen distances for metal ions in aqueous solutions parallel those obtained for crystal ionic radii and are very similar to those reported for analogous crystal hydrates (Burgess, 1988). This information is relevant. It is difficult to obtain bond lengths for every metal in combination with oxygen in aqueous solutions. The bond length quoted for Cr(III) in aqueous solution by Burgess (1988) is 1.94Å (X-ray diffraction), 1.98Å (EXAFS) and for a crystal hydrate 2.02Å. Wells (1975) quotes the following:

TABLE 8.1 BOND LENGTH: CHROMIUM(III) AND CHROMIUM(VI)

Cr(III) and Cr(VI)	Cr^{III}- 6O (Å)	Cr^{VI}- 4O (Å)
Cr_5O_{12}	1.97	1.65
KCr_3O_8	1.97	1.60
$LiCr_3O_8$	2.05	1.66
$CsCrO_8$	1.96	1.63

It would appear reasonable to estimate the chromium-oxygen bond length in aqueous solution to approximate 1.63Å.

8.2.3 ARSENIC(V)

Arsenic(V) in aqueous solution forms an oxyacid whose properties closely resemble dissolved phosphorous(V), which forms H_3PO_4. The dissociation constants and hence their dissociation

equilibria are extremely similar. The structure of both phosphoric and arsenic acid is better represented by formulas of the type $MO(OH)_2$.

The equilibria for arsenic acid (arsenic(V)) is aqueous solutions is shown below.

$$H_3AsO_4 + H_2O \rightleftharpoons H_2AsO_4^- + H_3O^+ \quad pK_a = 2.25$$

$$H_2AsO_4^- + H_2O \rightleftharpoons H_2AsO_4^{2-} + H_3O^+ \quad pK_a = 6.77$$

$$HAsO_4^{2-} + H_2O \rightleftharpoons AsO_4^{3-} + H_3O^+ \quad pK_a = 11.60$$

$H_2AsO_4^-$ (mono-ortho-arsenate ion) is the predominant species for pH values from 3.6 to 7.3, whereafter $HAsO_4^{2-}$ (di-ortho-arsenate ion) predominates. Arsenic achieves simple tetrahedral structures in the arsenate ion (Cartmell *et al*, 1961) by use of its sp^3 hybrid orbitals. The mutual repulsion of the four electron clouds direct the oxygen atoms to the corners of an inscribed tetrahedron (Toon *et al*, 1973). Therefore, the mono-ortho-arsenate ion and the di-ortho-arsenate ion would have a distorted tetrahedron structure. The ionic radii of the arsenic(V) ion, in aqueous solution, is approximately 0.70Å. Structural details of the arsenate ion are shown in Figure 8.3.

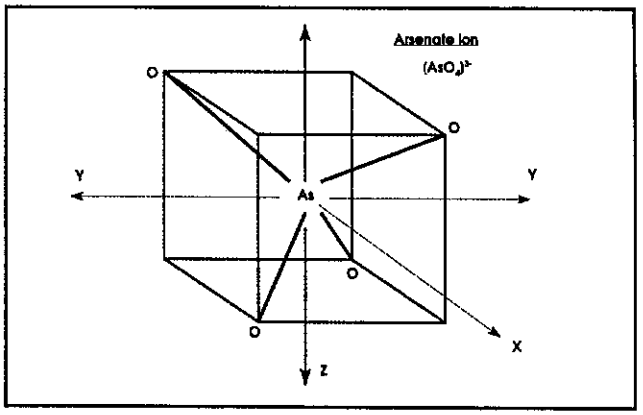

Figure 8.3
Structural details of the arsenate ion

For similar reasons to chromium(VI), the bond lengths relevant to the arsenate ion were not readily available. However, $HAsO_4^-$ has been studied in $(NH_4)HAsO_4$ and $Na_2HAsO_4.7H_2O$ and the bond lengths are As-O; 1.67Å and As-OH; 1.74Å (Wells, 1975).

8.3 ADSORPTION ISOTHERMS

The results obtained from the equilibrium studies were successfully described by the Freundlich isotherm. The Freundlich isotherm results from a consideration of the heterogeneity of the surface, when applied to the adsorption of vapours onto solid surfaces. If adsorption data fit the

equation, it is possible, but not proven, that the surface is heterogeneous (Adamson, 1982). If one considers the adsorbent being municipal solid waste there would appear to little doubt the surface is heterogeneous, and the suitability of the Freundlich isotherm, in this instance, is acceptable.

The numerical values of the constants, in addition to the degree of agreement or variance are shown in Table 8.2 below. The variance (R squared) ranged from 0.760 (arsenic at pH7.0) to 0.943 (chromium at pH7.0). As reported in section 5.7, copper and chromium analysis could be repeated in some instances. That facility was not available for arsenic. This could have affected the value obtained for the variance. As previously mentioned in section 7.4.2, numerical values obtained for the Freundlich constants do not appear to be of great value, and their significance was briefly discussed in that section. They do appear useful for the determination of trends, such as the degree of affinity for a solute for an adsorbent, this is discussed below.

TABLE 8.2 CALCULATED RESULTS - FREUNDLICH ADSORPTION ISOTHERMS

Metal	pH	R squared	Freundlich equilibrium distribution coefficient (K_F)	Freundlich power coefficient (M)
Copper	5.5	0.859	0.21	0.74
Copper	7.0	0.895	0.11	1.04
Chromium	5.5	0.911	$35E10^{-3}$	0.58
Chromium	6.4	0.871	$2.8E10^{-3}$	0.96
Chromium	7.0	0.943	$3.4E10^{-3}$	0.90
Arsenic	5.5	0.941	$2.8E10^{-2}$	0.82
Arsenic	6.4	0.915	$9.7E10^{-2}$	0.40
Arsenic	7.0	0.760	$12E10^{-2}$	0.40

Other forms of isotherms were examined and found unsuitable. However, detailed analysis of the equilibrium data revealed a very strong relationship between initial solute concentration in solution and final solute concentration in solution, irrespective of pH. This is displayed graphically below (Figures 8.4, 8.5 and 8.6).

The degree of agreement for this form of representation was surprising; regression analysis supplied the variance (R squared) and the X coefficient (gradient of the linearised data). These calculated values are shown below in Table 8.3. This form of relationship is not uncommon. The value obtained for the X coefficient allows direct calculation of the equilibrium solute concentration in solution and hence, computation of the mass adsorbed by the adsorbent, over the experimental range of initial solute concentrations (Equation 8.1).

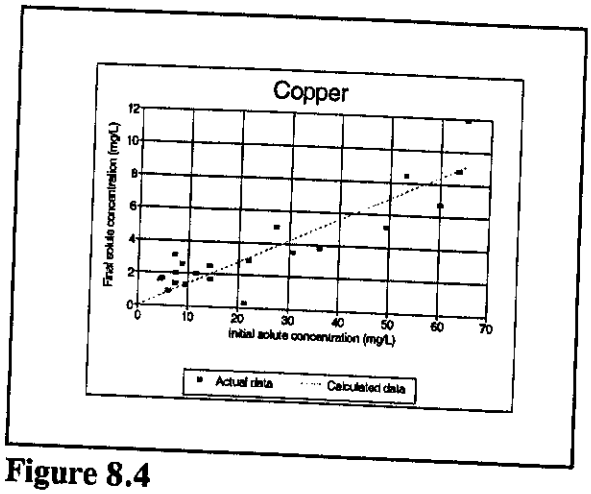

Figure 8.4
Copper: relationship between initial and final solute concentration

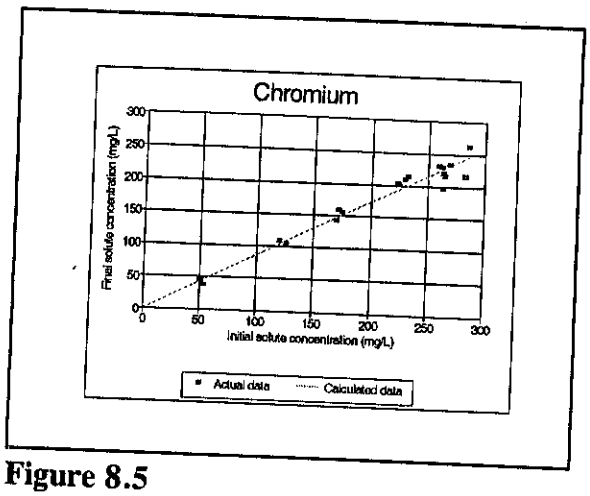

Figure 8.5
Chromium: relationship between initial and final solute concentration

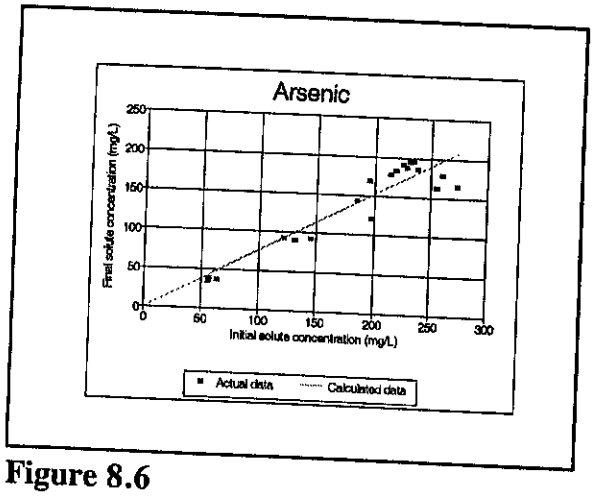

Figure 8.6
Arsenic: relationship between initial and final solute concentration

TABLE 8.3 DETAILS OF REGRESSION ANALYSIS: RELATIONSHIP BETWEEN INITIAL AND FINAL SOLUTE CONCENTRATIONS

Metal	R squared	X coefficient	No. of observations
Copper	0.807	0.140	21
Chromium	0.967	0.862	21
Arsenic	0.884	0.758	21

It is also of importance to examine the values of the X coefficient generated. The relationship can be expressed as shown below:

$$CAe = X.\,CAo \qquad 8.1$$

where,

CAe = Solute concentration at equilibrium
CAo = Initial solute concentration
X = X coefficient or gradient of the linearised data

In this case, the smaller the numerical value for the X coefficient, the greater the degree of affinity of the municipal solid waste to the metal in question. The degree of affinity is therefore; copper (0.140) > arsenic (0.758) > chromium (0.862).

By nature of a comparison, the Freundlich equilibrium distribution coefficient (K_F) may be considered as a measure of affinity between solute and adsorbent (Murali *et al*, 1983). The degree of affinity of the metals with municipal solid waste is copper > arsenic > chromium; a factor of 10 differentiating between the three metals, at pH5.5. At pH6.4, arsenic >> chromium. At pH7.0, copper ≈ arsenic >> chromium. There would appear to be good agreement between the degree of affinity reported by the Freundlich isotherm and the values quoted above. The discrepancy at pH7.0 is probably a result of the poor variance value (0.76) obtained for the Freundlich isotherm for arsenic.

Also evident from Table 8.3 is the *apparent* absence of the influence of pH on equilibrium solute concentrations, in the pH range measured. It is important to note the experimental pH range was narrow, being only 5.5 to 7.0, and the experimental technique adopted in this investigation was not entirely satisfactory to observe this phenomena. Often, the initial concentration of the adsorbing ions was not similar in each experiment trial, also three metals were simultaneously adsorbing from solution.

If a soil is reacted with a series of aqueous solutions with the same initial metal cation concentration but the aqueous solutions having an increasing value of pH, the degree of cationic adsorption will usually increase with increasing pH. A limitation can however be introduced, that of competing ligands in the soil solution. In the absence of competing ligands, a plot of metal cation adsorbed versus pH has a characteristic sigmoid shape known as an "adsorption edge" (Sposito, 1989). Anion adsorption onto soils is characterised by a plot termed an "adsorption envelope", and is a result of changes in the net proton charge on the soil particles, if the adsorptive anion does not protonate significantly. The decrease in hydrogen ion concentration with increasing pH produces a repulsion of the adsorptive anion from the soil particle. Therefore at low pH values, adsorption is high, rising to a maximum, then subsequently decreasing with increasing solution pH (Sposito, 1989).

To observe this adsorption phenomena directly from the analytical results was not possible (the results of the equilibrium studies are shown in Appendix B, Tables B-1, B-2 and B-3) of Ballard (1997). The analytical results are difficult to evaluate, as the initial concentrations differ

significantly for all of the metals, over the pH range. In the case of copper, solubility constraints were experienced. The initial concentration of copper in solution was the major influence on the mass of solute adsorped, and in the case of copper this value was determined by the pH. At pH5.5 copper in solution approximated 60mgℓ^{-1}, while at pH7.0, copper in solution approximated 27mgℓ^{-1}. In two instances in the kinetic trials, the maximum copper in solution at pH6.4 was lower than that at pH7.0. The probable cause of this oddity was the too rapid addition of sodium hydroxide whilst adjusting the pH, causing excess precipitation of copper, an effect of localised high pH. There is another form of representation of the effect of pH on adsorption, that is to evaluate the percentage adsorption with change in pH. This is a less sensitive method of data analysis, but can be used to examine trends. This is shown in Table 8.4. For all the metals under consideration, the highest percentage adsorption was achieved at pH5.5, while the percentage adsorption at pH6.4 and pH7.0 was very similar.

TABLE 8.4 VARIATION OF ADSORPTION WITH pH

Metal	pH	Percent adsorption	Metal	pH	Percent adsorption
Copper	5.5	86.9	Chromium	5.5	21.1
	6.4	78.9		6.4	10.3
	7.0	79.1		7.0	10.4
Arsenic	5.5	34.3			
	6.4	20.6			
	7.0	23.2			

8.4 KINETICS OF ADSORPTION

The kinetics of the adsorption of copper, chromium and arsenic onto municipal solid waste were successfully described by the modified Freundlich equation shown below.

$$q = K_a C_o t^{1/m}$$

where,

Co = initial solute concentration
t = time
K_a = constant
m = constant

The modified Freundlich equation is generally regarded as empirical (Aharoni *et al*, 1991b). However, the commonly used kinetic techniques are based on the assumption that the reactions are either unidirectional or discrete (Harter, 1991). The reaction under consideration involves three metals, themselves relatively complex in nature, reacting with a heterogeneous solid, municipal solid waste. It would seem probable that even if the reaction conformed to one of the simple kinetic orders of reaction it would only be fortuitous rather than an indication of the reaction mechanism. Chemical interactions between the solute and adsorbent may comprise of (Sparks, 1989):

(i) formation or rupture of a bond between sorbate and surface;
(ii) further reaction between adsorbed species; and,
(iii) rearrangements of the solid structure and formation or disappearance of solid species.

Sparks (1989) states that (with soils) it is often incorrect to apply simple kinetic models such as first- or second-order to activated adsorption, as reacting solid surfaces are rarely homogeneous, and because the effects of transport phenomena and chemical reaction are often experimentally inseparable. There would appear no reason why this statement should not equally apply to heterogeneous solids such as municipal solid waste.

The use of mechanistic rate laws to study adsorption phenomena assumes that only chemical kinetics are being studied, any physical aspects are ignored (Skopp, 1986). Most soil reactions of interest to soil scientists are heterogeneous solid-liquid reactions. These reactions usually take place by means of a multi-step mechanism that include mass transfer limitations, as well as chemical reactions (Aharoni *et al*, 1991a). The application of the simple kinetic relationships to complex systems is fraught with problems and caution should be exercised. Sposito discusses transport controlled adsorption kinetics in Chemical equilibria and kinetics in soils (1994) and states that *any surface reaction that involves chemical species in aqueous solution must involve a precursory step in which these species move toward a reactive site in the interfacial region.* He notes that *if the time scale for the transport step is comparable or much longer than that of the chemical reaction, the kinetics of adsorption will reflect transport control, not reaction control.*

Expressions such as the modified Freundlich equation are often successful when applied to various processes involving solid-fluid reactions, although initially developed by researchers investigating solute adsorption on soils. The characteristics of a reaction conforming to the modified Freundlich equation are rapid initial adsorption, the sorption rate decreasing with time. A generalised diagram is shown below.

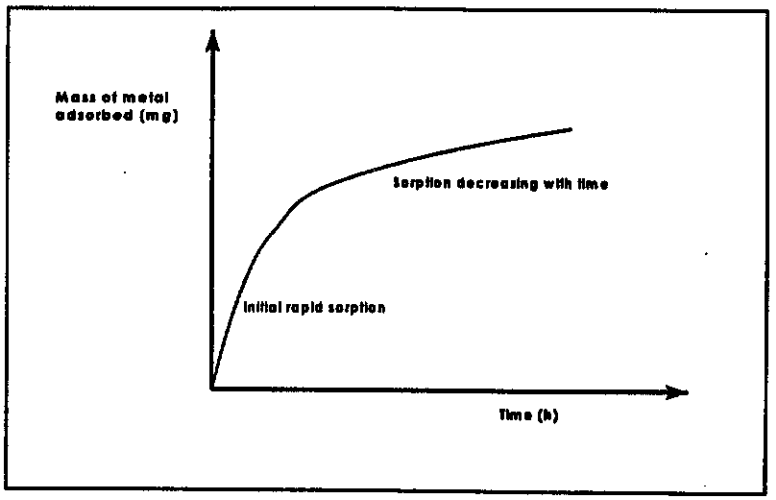

Figure 8.7
Characteristic curve of the modified Freundlich equation

8.4.1 KINETIC RATE CONSTANTS

The kinetic constants (K_a) for copper and chromium are consistent at the various pH values. The rate constants for arsenic show a greater variability. The results for copper and chromium were analysed in duplicate and any discrepancies in results were re-analysed. This ensured accurate reporting of these analytical results. This option was not available when analysing arsenic and probably accounts for the greater variability of the results. Rate constants for copper were the highest, arsenic intermediate, with chromium being the lowest. The relevant results are tabulated below in Table 8.5. Also tabulated is a parameter often reported by researchers; the half reaction time ($0.5t_{total}$). The half reaction time is indicative of the speed of the chemical reaction. It is defined as the time taken for 50 percent of the total reaction to occur. Copper is very strongly adsorbed, as can be seen by the extremely short times calculated for the half reaction time ($0.5t_{total}$). The half reaction times are longer for chromium and arsenic but still average only 1 hour. This method of data analysis is not sensitive. It does, however, provide an indication of the relative speeds of the adsorptive reaction.

A complete summary of the results from the kinetic trials is shown below in Table 8.5 as constant reference is made to these results during this chapter.

TABLE 8.5 SUMMARY OF RESULTS FROM KINETIC TRIALS

Coding	pH	Initial concn. [C_o] ($mg\ell^{-1}$)	Final concn. [Ce] ($mg\ell^{-1}$)	Mass sorbed (mg)	Sorption rate coefficient [K_a] (h^{-1})	Constant [1/m]	SE	Half reaction time [$0.5t_{total}$] (h)
Copper A	5.5	63.6	8.8	55.6	0.722	0.055	2.93	0.0001
Copper B	5.5	53.2	8.4	44.8	0.677	0.063	3.95	0.0000
Copper C	5.5	65.1	11.9	53.2	0.668	0.068	2.37	0.0000
Copper D	6.4	9.6	1.3	8.3	0.629	0.096	0.92	0.0223
Copper E	6.4	14.4	2.5	11.9	0.817	0.061	1.40	0.0000
Copper F	6.4	21.3	0.3	20.7	0.766	0.081	1.00	0.0039
Copper H	7.0	22.1	2.4	19.7	0.738	0.059	1.02	0.0002
Copper I	7.0	27.4	5.0	22.4	0.825	0.064	2.74	0.0000
Chromium A	5.5	263	221	42	0.080	0.182	5.93	0.8
Chromium B	5.5	265	217	48	0.076	0.237	4.98	1.8
Chromium C	5.5	263	196	67	0.096	0.243	7.18	1.8
Chromium D	6.4	269	234	35	0.057	0.252	5.55	1.9
Chromium E	6.4	262	230	32	0.065	0.152	3.07	0.5
Chromium F	6.4	259	232	27	0.051	0.189	2.03	0.9
Chromium G	7.0	223	203	20	0.062	0.099	2.59	0.04
Chromium H	7.0	224	202	22	0.050	0.174	1.99	0.9
Chromium I	7.0	230	209	21	0.057	0.162	2.58	0.4
Arsenic A	5.5	255	163	92	0.199	0.157	5.32	0.5
Arsenic C	5.5	260	179	76	0.107	0.347	8.84	4.3
Arsenic D	6.4	228	187	41	0.055	0.368	6.83	1.1
Arsenic E	6.4	225	191	34	0.024	0.567	10.3	0.4
Arsenic F	6.4	231	197	34	0.090	0.155	3.77	0.3
Arsenic G	7.0	238	186	52	0.167	0.089	6.48	0.01
Arsenic H	7.0	219	183	36	0.090	0.185	3.32	0.6
Arsenic I	7.0	214	178	36	0.070	0.286	6.38	0.6

8.5 RATE OF REACTION: ADDITIONAL CONSIDERATIONS

The modified Freundlich equation is often successful when applied to various processes involving solid-fluid reactions. In the case of soils, kinetic data obtained experimentally often do not conform to the rate laws, but often can be described by some simple semi-empirical equation, such as the modified Freundlich equation. At low values of time, the modified Freundlich equation is frequently germane, at intermediate values of time the Elovich equation is typically applicable, at high values of time the pseudo first-order equation being appropriate (Aharoni *et al*, 1991a).

Adsorption reactions on soils may be classed as slow or rapid. Slow reactions are those in which processes taking place at the solid phase are rate determining (section 4.3.2). These rate determining processes may include: surface diffusion; diffusion in micropores; penetration of the solute into micropores in the solid; diffusion into the bulk of the solid, etc. (Aharoni *et al*, 1991a).

Researchers in the soil science field have examined this phenomena (Aharoni *et al*, 1991b) and have found when processes taking place at the solid phase are rate determining, it is often observed that a plot of the reciprocal of the rate against time is S-shaped, and other semi-empirical equations may be applicable at different reaction times. The phenomena of the S-shaped curve is indicative that reactions at the solid phase are associated with activated diffusional processes, such as surface diffusion or bulk penetration, where chemical bonds are ruptured and formed along the diffusional path.

Analysis of the experimental results indicated the rate of the chemical reaction was determined by activated diffusion processes taking place on the solid phase. Further analysis of the data showed the data conformed to a generalised model indicative of heterogeneous adsorption. This is a process where a solute diffuses in solid media that has different properties.

Consider the modified Freundlich equation, where

$$q = kt^{v} \qquad 3.11$$

Then,

$$Z = (dq/dt)^{-1} = (1/vK)t^{1-v} \qquad 3.14$$

Plots of the reciprocal of the adsorption rate (Z) versus time(t) or q (amount sorbed) versus $\log_e t$, for various soil reactions and other solid-fluid processes are usually S-shaped: convex at small values of time, concave at large values of time, and linear at some intermediate range of time. The generalised expression, S-shaped Z(t) plots may be explained by models based on diffusion. Equations for diffusion in a heterogeneous medium lead to S-shaped Z(t) and q (amount sorbed) versus $\log_e t$ plots in which the intermediate linear part is dominant.

Consider the rate of adsorption of copper onto municipal solid waste at pH7.0, the coding being "copper H" (Figure 8.2). The adsorption of copper is initially extremely rapid. The rate of

reaction slows rapidly as the reaction progresses indicative in this case of diffusion control. Unfortunately measurements ceased after 32 hours therefore the latter part of the S-curve (convex at large values of time) is unavailable. Aharoni *et al* (1991b) reports the modified Freundlich is linear for times less than 50 hours when data is plotted as amount sorbed (q) versus the square root of time ($\sqrt{t}$), after the initial inflexion at low values of time. The linear relationship between the square root of time and mass of solute adsorped is a characteristic of intraparticle diffusion.

Consider the rate of adsorption of chromium onto municipal solid waste at pH6.4, the coding being "chromium D". The adsorption of chromium is rapid, diffusional control is evident by the beginning of the S-shaped curve. Again measurements ceased after 32 hours. Consider the rate of adsorption of arsenic onto municipal solid waste at pH7.0, the coding being "arsenic F". The adsorption of arsenic is rapid, diffusional control is evident by the beginning of the S-shaped curve. As mentioned, equations for diffusion in a heterogeneous medium lead to S-shaped Z(t) and q (amount sorbed) versus $\log_e t$ plots in which the intermediate linear part is dominant. It can be seen the linear part of the curve is dominant in all cases, though more pronounced with chromium and arsenic (Figures 8.11 and 8.13, respectively).

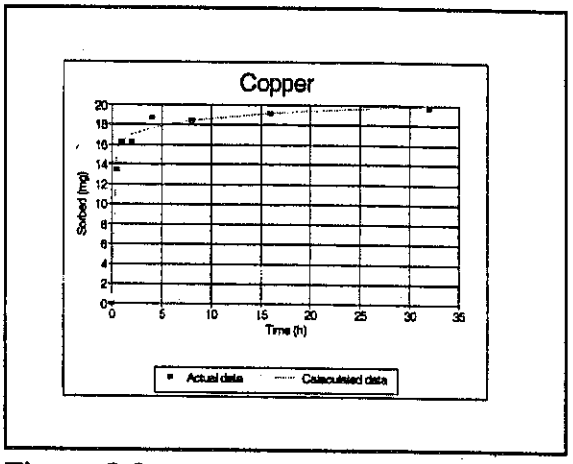

Figure 8.8
Adsorption of copper at pH 7.0 (copper "H")

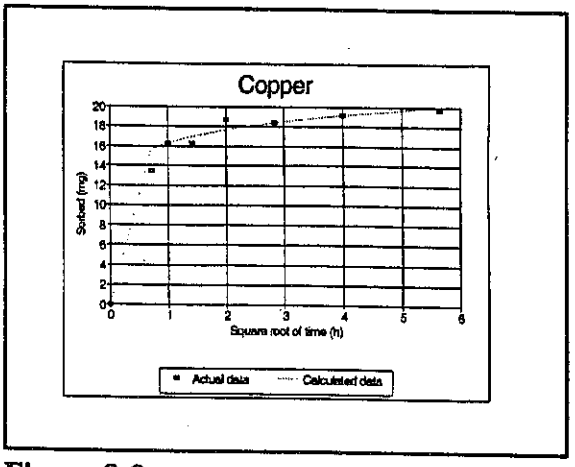

Figure 8.9
Mass of copper adsorbed (mg) versus square root of time (h)

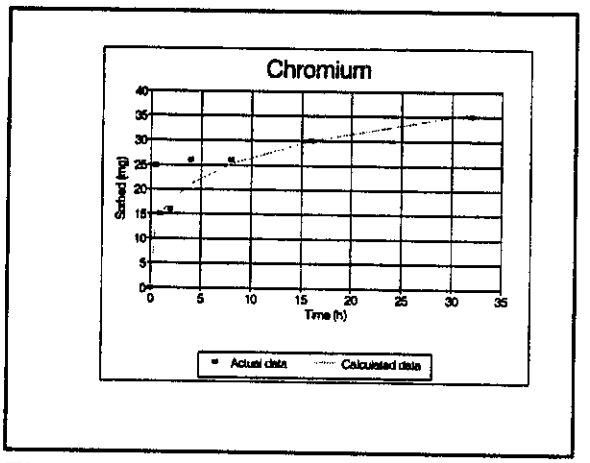

Figure 8.10
Adsorption of chromium at pH 6.4 (chromium "D")

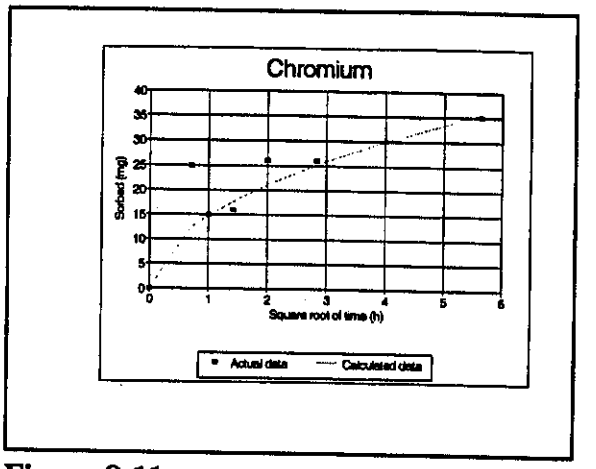

Figure 8.11
Mass of chromium adsorbed (mg) versus the square root of time (h)

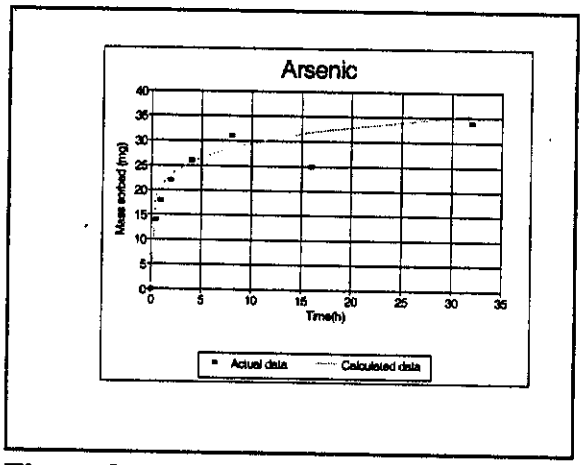

Figure 8.12
Adsorption of arsenic at pH 7.0 (arsenic "F")

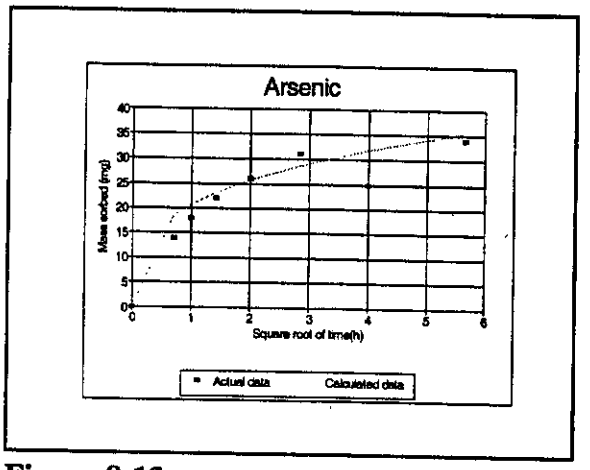

Figure 8.13
Mass of arsenic adsorbed (mg) versus the square root of time (h)

The results of this method of data analysis conformed to a generalised model indicative of heterogeneous adsorption. This confirms the results from the equilibrium studies, where the results obtained were successfully described by the Freundlich isotherm. Adherence to the Freundlich isotherm is generally considered to indicate adsorption onto a heterogeneous surface.

8.6 ADSORPTION RATE

The kinetic experiments were carried out at three pH levels; 5.5, 6.4 and 7.0. These pH values were adopted as they virtually cover the range which can occur in the full size landfill. It is important therefore, to examine the effect of pH on adsorption rate. The quantity of adsorption that occurs at these pH values has been examined in section 8.3. The three modelled fits are shown overleaf for each metal at the relevant pH values.

Adsorption of copper at all three pH values is characterised by a curve that rises sharply to a plateau (Figures 8.14, 8.15 and 8.16). The initial concentration of the solution plays a larger role than one would anticipate, accelerating adsorption rate. This can be immediately observed in Figure 8.14 where copper A and C are identical and copper B is displaced as the initial concentration was lower by $10mg\ell^{-1}$ (see Table 8.5). The characteristic curve is similar at all pH levels investigated. Also, the effect of initial concentration is consistent at the different pH levels. For copper, agreement is good between the different experiments at the same pH.

The characteristic curve depicting the adsorption rate of chromium is more rounded than that of copper, adsorption continuing at a faster rate than that of copper, at higher values of time (Figures 8.17, 8.18 and 8.19). At pH5.5 (Figure 8.17) there is close agreement between chromium A and chromium B, whereas chromium C differs substantially. The lack of agreement is caused by the unusually large degree of adsorption of chromium C when compared with the two other experiments conducted at the same pH. All three trials commenced with the virtually the same initial concentration. On completion of the trial, adsorbent A adsorped 42mg, adsorbent B adsorped 48mg, while adsorbent C adsorped 67mg. This discrepancy can only be attributed to the adsorbent. At pH6.4 (Figure 8.18), the higher the initial chromium concentration, the greater the mass of chromium adsorbed. Chromium initial concentrations were 269mg (D); 262mg (E) and 259mg (F). Chromium adsorbed was 35mg (D); 32mg (E) and 27mg (F). At pH7.0 (Figure 8.16) agreement between experiments is good, with only a slight dispersion at larger values of time. There is only a difference of 2mg between the final equilibrium values.

Arsenic adsorption at pH5.5 (Figure 8.20) gives widely differing characteristic curves. The characteristic curve for the adsorption of arsenic (in general) is similar to that of chromium. Arsenic A is similar to the characteristic curve at other pH values, has a lower standard error (5.32 *versus* 8.84) and is probably more representative than Arsenic C. At pH6.4 (Figure 8.21), agreement is excellent between arsenic E and F with arsenic D again varying at larger values of time. The effect of initial concentration is not evident with arsenic D. Arsenic D has the lowest initial concentration of the three trials (187mg) and shows the largest degree of adsorption (41mg). In comparison, Arsenic E and F initial concentrations were 225mg and 231mg respectively, the mass of arsenic absorbed being 34mg in both cases. At pH7.0 (Figure 8.22) agreement is also good for arsenic adsorption, with the larger initial concentration in experiment G displacing the rate curve.

Another factor to consider is the half reaction time ($0.5t_{total}$) (calculated values are shown in Table 8.5). The half reaction time is indicative of the speed of the chemical reaction. It is defined as the time taken for 50 percent of the total reaction to occur. The half reaction time, in this case, is not a particularly sensitive method of analysis, but it can be seen that the half reaction times did not differ substantially throughout the range of pH values employed. The effect of pH on reaction rate was not significant. The half reaction time for the adsorption of copper is almost instantaneous. For both chromium and arsenic the adsorption rate was slower. It is of interest to examine the experimental trials with the lowest standard error in each pH range. For arsenic the lowest standard error occurs for trials A, F and H. The average half reaction time for these three trials is 0.4h. For chromium the lowest standard error occurs for trials B, F and H; the average half reaction time for these trials is 1.2h.

In evaluating the information above, it is important not to underestimate the initial concentration

of solute in solution when considering the rate of adsorption and the mass of solute adsorbed. This has a radical effect on rate of adsorption. It is also evident that the rate of copper adsorption far outstrips both chromium and arsenic. The rate of adsorption may be categorised in the following order:

copper >> arsenic > chromium

With an heterogeneous adsorbent such as municipal solid waste there is a surprising degree of similarity in the results from the kinetic trials, especially when considering only 50g of solid waste was employed in each separate experiment. It is probable that, if larger sub-samples were employed in the experimental procedure, variances between individual experiments conducted at the same pH value could be minimised.

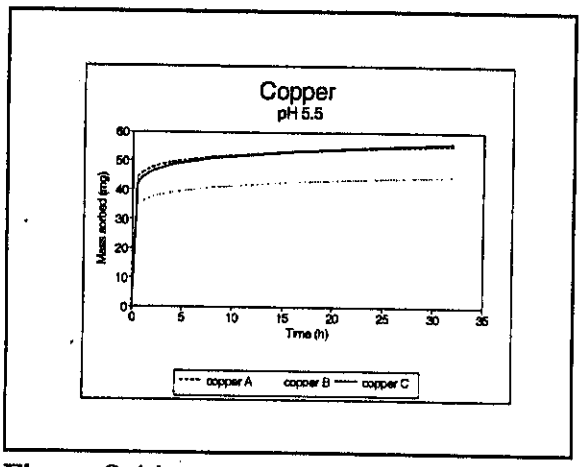

Figure 8.14
Copper: model fit at pH 5.5

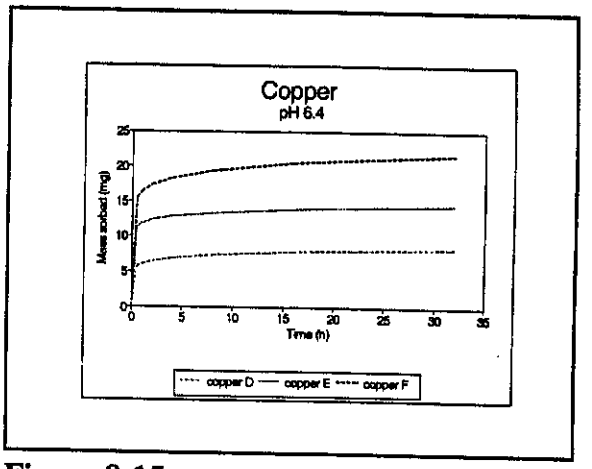

Figure 8.15
Copper: model fit at pH 6.4

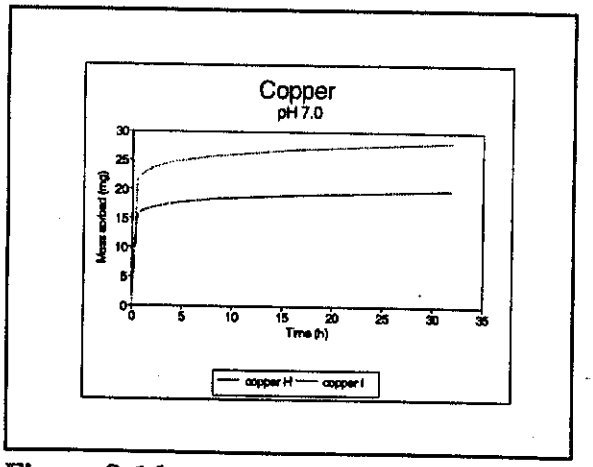

Figure 8.16
Copper: model fit at pH 7.0

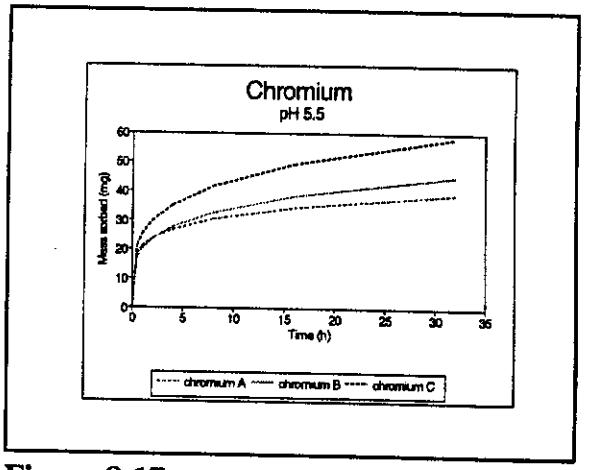

Figure 8.17
Chromium: model fit pH 5.5

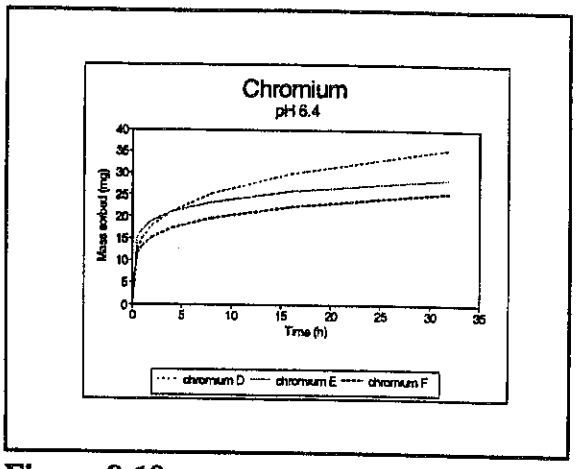

Figure 8.18
Chromium: model fit at pH 6.4

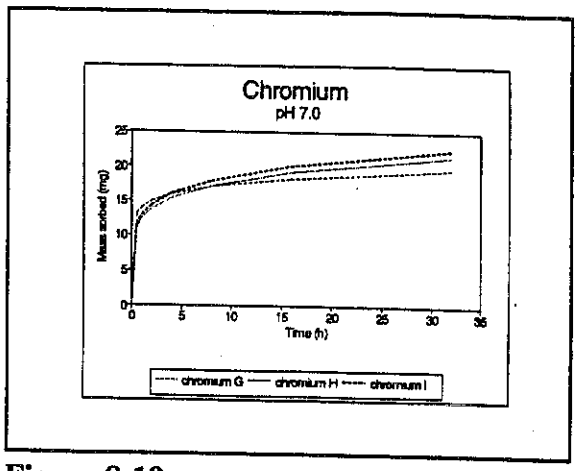

Figure 8.19
Chromium: model fit at pH 7.0

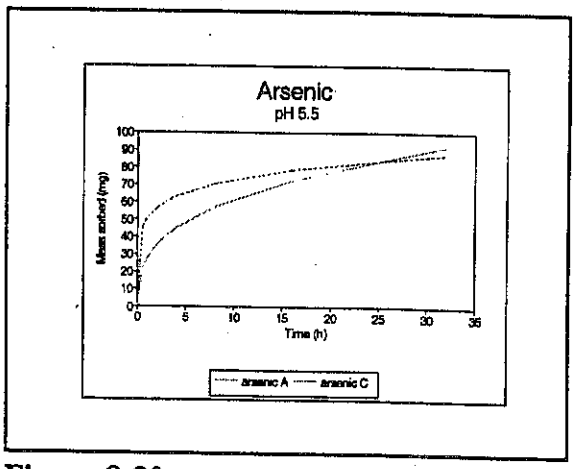

Figure 8.20
Arsenic: model fit at pH 5.5

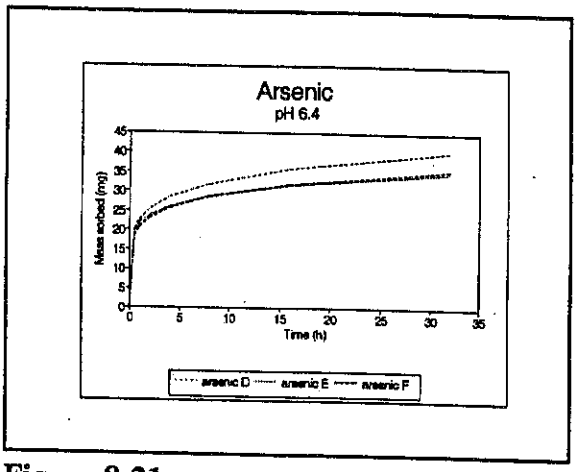

Figure 8.21
Arsenic: model fit at pH 6.4

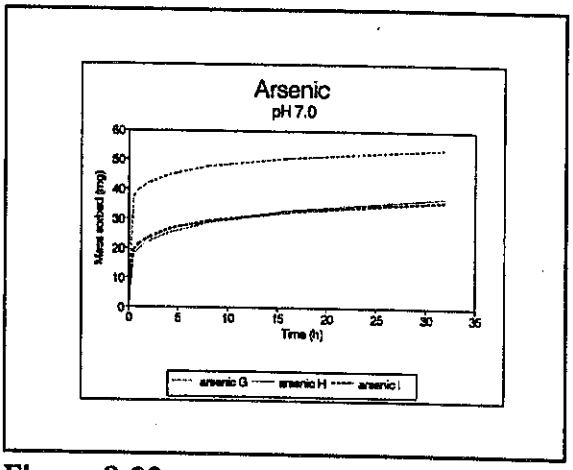

Figure 8.22
Arsenic: model fit at pH 7.0

8.7 ADSORPTION MECHANISM

The following items have been discussed; speciation of metals present, and their physical characteristics; the compliance of the metallic ions to the Freundlich isotherm, and the affinity of the various metallic ions to the adsorbent; the significance of the suitability of the modified Freundlich equation in describing the kinetics of adsorption and the rate of sorption of copper, chromium and arsenic. Information from the preceding sections will now be reviewed with the objective of characterising the solute adsorption mechanism. However, at the outset it should be noted that formulating reaction mechanisms for heterogeneous adsorbents can be tenuous (Harter, 1991). In principle, the requirements to investigate an adsorption mechanism include accurate adsorption data on well defined surfaces from well defined solutions at various temperatures, coupled with reliable thermodynamic data (Parfitt *et al*, 1983). All of the aforementioned are lacking.

In section 8.2 the speciation and size of the metallic ions was scrutinised. Copper is present in the form of a divalent cation. In aqueous solution, in the pH range under consideration, the hydrated ion is present as $Cu(H_2O)_6^{2+}$ and has a distorted octahedral structure. Chromium is present in the hexavalent form. The chromate ion (CrO_4^{2-}) predominates at pH values greater than 8.45. The chromate ion has a tetrahedral structure with four oxygen atoms bound to a central chromium atom. Arsenic is present in the pentavalent form. $H_2AsO_4^-$ (mono-ortho-arsenate ion) is the predominant species for pH values from 3.6 to 7.3. Mono-ortho-arsenate ion has a distorted tetrahedron structure.

In section 8.3 adsorption isotherms were discussed. Two important factors were revealed. Adherence to the Freundlich isotherm is generally considered to indicate adsorption onto a heterogeneous surface. Values obtained for the Freundlich equilibrium distribution coefficient (K_F) may be considered as a measure of affinity between solute and adsorbent. Over the pH range of the laboratory studies, the degree of affinity of the metals with municipal solid waste was copper > arsenic > chromium; this was confirmed by additional graphical analysis.

In section 8.5 the modified Freundlich equation was examined to determine reasons for its success in describing solid-fluid reactions. Researchers in the field of soil science have found the use of the modified Freundlich equation is indicative that reactions at the solid phase are associated with activated diffusional processes. Additional examination showed the data conformed to a generalised model indicative of heterogeneous adsorption. This examination confirmed observations from equilibrium studies, where adherence to the Freundlich isotherm is generally considered to indicate adsorption onto a heterogeneous surface.

In section 8.6 the rate of sorption was studied. It was found that the rate of copper adsorption was extremely rapid, the rate of adsorption of arsenic being intermediate, with chromium adsorption being the slowest of the three metals. The initial concentration of the metal in solution was of importance when examining both the mass of solute adsorbed and the rate of sorption.

The adsorption of small ions is strongly but not exclusively determined by electrical interactions (Lyklema, 1983). However, the relative size of the ions in solutions was investigated. As a first approximation, the presence of the hydrogen ions was neglected, if more stringent calculations

were required (i.e. if the relative size of the ions were close), they would be performed. Additionally, there are undoubtedly hydrogen ions clustered around both the chromate ion and the arsenate ion as in the case of copper ion, in an aqueous solvent. It can be seen below in Table 8.6, the copper ion is far larger than both the chromate and arsenate ions which are of a similar size. Copper is adsorbed far more rapidly than either chromium or arsenic, indicative that the adsorption in this case is determined by electrical interactions, and not the size of the relevant ions. Copper is present in the form of a cation while both chromium and arsenic are in the form of an anion.

TABLE 8.6 COMPARISON OF PHYSICAL DATA OF THE RELEVANT IONS

Ion	Formula	Ionic radii (Å)	Bond length (Å)	relative size to the chromate ion
Copper	$Cu(O)_6^{2+}$ (H ions neglected)	0.87	1.94 (x) 2.40 (y).	2.5
Chromium	CrO_4^{2-}	0.63	1.63.	1.0
Arsenic	AsO_4^{3-}	0.70	1.67	1.1

Unfortunately, a good fit of adsorption data to the less complex linear isotherms, such as the Langmuir or Freundlich isotherm does not in itself constitute any proof of any specific adsorption mechanism. Attempts were made to fit the equilibrium results to the system of isotherm classification, developed by Giles and co-workers (1974a; 1974b); the S, L, H and C isotherms. These isotherms can by used to assist in interpretation of adsorption mechanisms, and much useful information can be obtained. There were insufficient data points to for these isotherms to be properly constructed. However, the significance of the Freundlich isotherm to characterise adsorption onto a heterogeneous surface was reinforced by the applicability of the modified Freundlich equation in section 8.5, where equations for diffusion in a heterogeneous medium lead to S-shaped Z(t) and q (amount sorbed) versus $\log_e t$ plots in which the intermediate linear part is dominant. Also the applicability of the Freundlich power coefficient to determining the affinity of the various solutes to the adsorbent was confirmed by the additional graphical constructions in section 8.3.

In the determination of an adsorption mechanism there are a number of facts to consider, two of which are readily apparent. In aqueous solutions, adsorbents are usually charged as there is always ionic species present and typically there is preferential absorption/desorption of those species. At any solid/aqueous interface adsorption of these ions is the rule rather than the exception. Both the solution and the adsorbent must maintain electronic neutrality. If a cation is adsorped there is either the co-adsorption of an anion or the desorption of a corresponding cation (Lyklema, 1983). As shown in Table 5.5, there was a change in pH in the course of the

experimental procedure during the kinetic trials. The experiments conducted at initial solution pH5.5 furnished a final solution pH of 7.0; the experiments conducted at initial solution pH6.4 provided a final solution pH of 8.0 and the experiments conducted at pH7.0 showed a final pH varying from 8.1 to 8.6. There is an obvious increase in hydroxyl ions during the course of the experiment. This would appear to indicate an exchange of the anions, chromium and arsenic for hydroxyl groups. Lindsay suggested (cited by de Haan *et al*, 1976) that all copper reactions in soil could be summarised by the general equation,

$$Cu^{2+} + \text{soil} \rightleftharpoons \text{Cu-soil} + 2H^{+}.$$

This reaction with the municipal waste would maintain electroneutrality, the corresponding anion exchange between chromium and arsenic for hydroxyl ions would also maintain electroneutrality. Additionally, this postulated reaction mechanism is confirmed by the pH measurements, and the indications that the surface is heterogeneous, allowing hydrogen ions and hydroxyl ions to be present at the solid interface. There is far less copper in solution than either chromium or arsenic. Therefore the pH would rise during the course of the experiment as less hydrogen ions would be exchanged than hydroxyl ions. This analysis would be complimentary to the influence of diffusion. The diffusional influence is caused by the ions diffusing past each other in an effort to get to the surface of the adsorbent, not diffusion of ions into the inner recesses of the solid phase, as would be commonly encountered.

Adsorption of three metallic ions onto a heterogeneous substance such as municipal solid waste is a complex system. To definitively examine the adsorption mechanism is extremely difficult, especially considering the adsorptive medium in conjunction with the metallic ions. However, in the absence of further experimental data the above conclusions appear reasonable.

8.8 TRACER STUDIES

Initial laboratory work (section 6.4.1) indicated the suitability of lithium sulphate as a tracer in an environment where municipal solid waste is predominant. The percentage of lithium adsorbed was less than 2 percent (Table 6.6). This was confirmed in the pilot scale studies were the recovery of lithium bettered 92 percent. Of the 1027mg of lithium added, 954mg was recovered. The pilot-scale tracer studies ceased after 317 days, at that point lithium was still evident, albeit in a very low concentration. It is probable, that if monitoring had continued, the recovery of lithium would have been greater.

The characteristic curve of the tracer conformed to that expected. A high degree of non-ideality was exhibited, the variance was calculated at 3338, while the mean residence time was 113 days. Maximum lithium recovery occurred after 84 days, the lithium concentration of the leachate at that time was 2.003mgℓ^{-1}. The only departure from that expected on a full scale landfill is probably the initial rapid rise of lithium in the leachate, probably caused by a combination of preferential channelling and wall effects from the column. The characteristic curve, although not ideal, is not unlike commonly occurring E curves obtained from industrial equipment where the peak of the curve does not necessarily occur at the mean time and "tailing" does often occur (Denbigh *et al*, 1971). The rapid initial rise commented on earlier, is not a common phenomena.

8.9 CO-DISPOSAL AT PILOT-SCALE

As reported in section 6.5, a concentrated solution of copper, chromium and arsenic was co-disposed with the municipal solid wastes in columns 3 and 5. Analytical results are reported in Appendix E of Ballard (1997). Tables E-1 and E-3 tabulate leachate volumes and metal concentrations for columns 3 and 5 respectively; Tables E-2 and E-4 tabulate the associated chemical data (pH, COD, etc.,) for columns 3 and 5. The mass of metals introduced into both columns 3 and 5 was copper, 88.4g; chromium, 256.1g and arsenic, 256.7g. The time duration of the experiment with column 3 was 235 days, the average volumetric displacement of leachate was 19.2ℓweek^{-1}. The time duration of the experiment with column 5 was slightly shorter, 221 days. The average displacement of leachate was 18.5ℓweek^{-1}.

8.9.1 COPPER

Results from the monitoring of copper concentration of leachate from columns 3 and 5 are shown graphically in Figure 7.29. The initial concentration of copper in the leachate from column 3 was 0.05mgℓ^{-1}, the highest copper concentration was recorded was 0.11mgℓ^{1}. Over the entire period of monitoring (235 days), the concentration of copper in the leachate from column 3 averaged 0.05mgℓ^{-1}, The initial concentration of copper in the leachate from column 5 was 0.07mgℓ^{-1} this was not exceeded for the entire duration of the experiment. The final copper concentration after 221 days was 0.04mgℓ^{-1}.

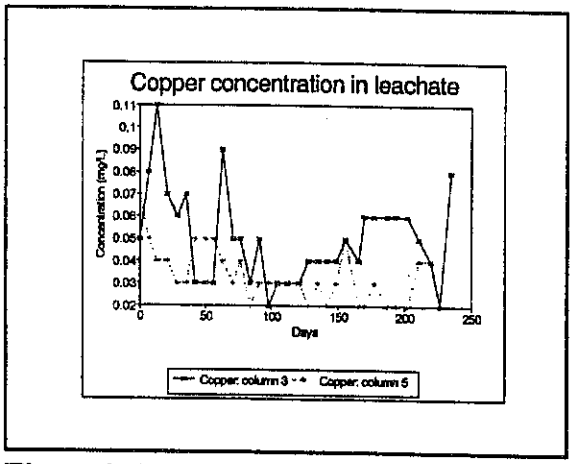

Figure 7.29
Copper concentration in leachate from columns 3 and 5

As stated in Section 7.4.6(c), although 88.4g of copper were added, virtually all of this copper would precipitate upon introduction into the column, a consequence of solubility effects. There was not any doubt concerning the lack of mobility of copper in the landfill environment, even an acetogenic landfill were pH levels approximate 5.5, at the outset of this investigation. The mobility of copper in various soils was reported in section 3.9.1.3(d) All the researchers reviewed (Korte *et al*, 1976; Aringhieri *et al*, 1985; Sapek cited by Aringhieri *et al*, 1985) commented on the low mobility of copper, even at low pH levels. Korte and co-workers (1976) examined the mobility of copper with an initial solution of landfill leachate at a pH of 3. Copper was immobile in all the soils except a sandy Wigram, even then, its mobility was low. The kinetic trials only served to confirm this, the rapid adsorption of copper has already been discussed in this chapter. Additionally, only 4 percent of the copper adsorbed was desorbed in the desorption trials. It is probable that desorbed copper would be re-adsorbed, as the liquid flows through the column contacting the remaining copper ions with adsorbent. The analytical results of the leachate from the pilot-scale columns confirms the work of previous researchers.

8.9.2 CHROMIUM

Results from the monitoring of chromium concentration of leachate from columns 3 and 5 are shown graphically in Figure 7.30. Initially, chromium in the leachate from column 3 was not detectable. The chromium content of the leachate rose steadily to a maximum of 0.04mgℓ^{-1}, this value was not exceeded for the duration of the experiment, the final chromium concentration was 0.03mgℓ^{-1} on Day 235. The average chromium content in the leachate from column 3 over the entire duration of monitoring was 0.03mgℓ^{-1}. The initial chromium content of leachate from column 5 was 0.06mgℓ^{-1}, The final chromium concentration was 0.02mgℓ^{-1} on Day 221. The average chromium content in the leachate from column 5 over the entire duration of monitoring was 0.04mgℓ^{-1}.

The predicted chromium concentration in the leachate from column 3 is shown in Figure 7.54. Until Day 160 the model realises actual measurements well, with very little deviation. From Day 160 the model begins to overpredict actual conditions. Results from monitoring continue in the region of 0.03mgℓ^{-1} whereas the model begins to predict chromium concentrations in excess of 2mgℓ^{-1} in that time frame, with predicted chromium concentration rising to a maximum of 4.4mgℓ^{-1} on Day 390.

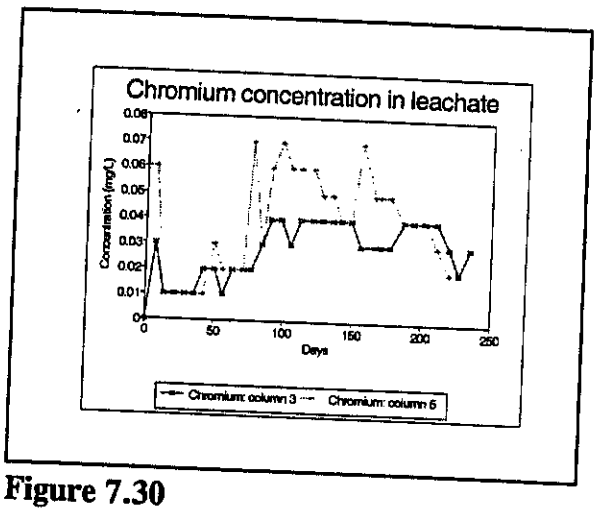

Figure 7.30
Chromium concentration in leachate from columns 3 and 5

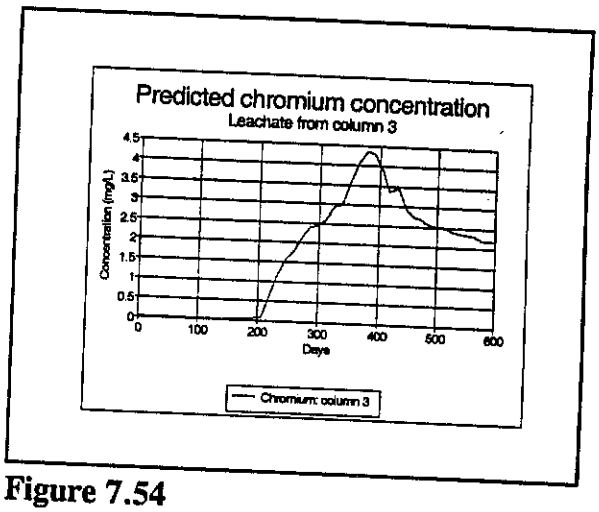

Figure 7.54
Predicted concentration of chromium in leachate from column 3

Some experimental considerations and the effect of the computational method were discussed briefly in section 7.4.6(c) and will not be repeated here. Although monitoring ceased on Day 235 and the calculations indicated a total residence time of 600 days this is not regarded as detrimental to a comparison of these results. It is extremely unlikely there would be any increase in actual chromium concentration in the column effluent. The computations assume the only attenuation mechanism to be adsorption. There are other possible attenuation mechanisms (such as precipitation) available to inhibit chromium mobility. Again, at the outset of the experimental work indications from the literature review indicated that chromium to be immobile in the landfill environment. A brief review of the work of other researchers confirms this.

Researchers in the field of soil science consistently reported a low mobility of chromium(VI) in soils (section 3.9.1.3(d)). Sheppard *et al* (1992) investigated the desorption of chromium from both a sandy and clay soil. The authors reported that if soil remediation was required, it would be less expensive to remove the soil that attempt any chemical treatment as the chromium was so firmly fixated. McGrath *et al* (1990) reported on a trial that had taken place over 19 years, where soils had received a sewage sludge containing chromium; there had been no significant movement of the chromium during that time period. Other researchers (Calder, 1988; Bartlett *et al*, 1976) reported the reduction of chromium(VI) to essentially immobile chromium(III) in the presence of organic matter, under anaerobic conditions, regardless of pH.

The composition of leachate from the columns (Appendix E of Ballard, 1997), the low percentage volatile solids of the municipal solid wastes (section 5.3.3(b)), plus the very low volume of biogas generated (section 6.3.2(b)) confirmed the municipal solid waste to be fully stabilised. The configuration of the columns, the length of time the columns have been at field capacity, the large volume of water present in the columns, are all factors that indicate that viable areas of anaerobic conditions would likely exist in the columns. The kinetic studies were completed in an aerobic environment. In that environment the behaviour of the metals under consideration can be regarded as ideal.

Conventional theory dictates the pilot-scale landfill column should be considered as a packed column. Traditional columns employed in industry are composed of adsorbents such as activated carbon, silica gel or activated alumina. Adsorbents are generally available as irregular granules, extruded pellets and formed spheres. The size of adsorbents rarely exceed 6mm, the size reflecting the need to pack as much surface area as possible into a given volume (Coulson *et al*, 1991). The municipal solid waste was reduced in size prior to placement in the column, increasing the surface area. This reduction in size did not approximate the reduction in size of the solid waste employed in the laboratory scale trials (section 5.3.2). A major difference between the solid waste and conventional columns is that liquid can flow through certain components of the waste such as paper, cardboard etc. It is probable the area available for adsorption is increased greatly by this mechanism, increasing adsorption. This analogy is given credibility by the nature of the characteristic curve obtained from the tracer studies. The liquid initially flows rapidly through existing channels, longer exit times are provided by fluid passing through the particles of solid waste. Here also an additional variable is introduced. A requirement of industrial adsorbents is structural integrity. In an aqueous environment components of the solid waste will lose structural rigidity and will start to collapse, delaying elements of the liquid.

As mentioned in section 7.4.6(c), an additional factor worthy of consideration is the sample size utilised in the kinetic experiments. Only 50g was used, while the pilot-scale columns were packed with approximately 700kg of municipal solid waste. While sampling was exhaustive, solid waste is an extremely heterogeneous substance.

8.9.3 ARSENIC

Results from the monitoring of arsenic concentration of leachate from columns 3 and 5 are shown graphically in Figure 7.31. The initial concentration of the arsenic in the leachate from column 3 was 17$\mu g\ell^{-1}$ rising in irregular steps to Day 194 when the concentration exceeded 2000 $\mu g\ell^{-1}$.

Arsenic concentration in the leachate from column 3 remained at that level until the cessation of monitoring on day 235. Column 5 mirrored the behaviour of column 3, though at a reduced manner. The maximum arsenic concentration attained was 802$\mu g\ell^{-1}$ at Day 213; results were relatively constant from Day 188 at that level.

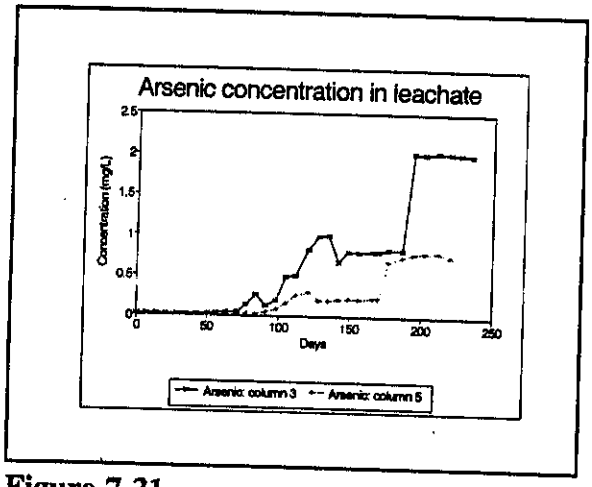

Figure 7.31
Arsenic concentration in leachate from columns 3 and 5

The predicted outcome of the co-disposal of arsenic was calculated in the same manner as that of chromium. Calculations predicted there would be an absence of arsenic in the leachate from column 3 during the total time period of 600 days. The results from desorption kinetic trials (section 7.4.3) showed that arsenic was the only metal of those under consideration that displayed any significant degree of desorption. This could not be allowed for in the calculation, and could account for the extremely low degree of error that is evident. There are not any significant solubility constraints with arsenic, whether it is in the form of arsenic(III) or arsenic(V), and if anaerobic conditions were experienced this would probably enhance the mobility of any arsenic present. In section 3.9.1.3(d) the behaviour of arsenic in soils under reducing conditions was reported. Reducing conditions convert arsenic(V) to arsenic(III). Arsenic(III) is 5 to 10 times more soluble than arsenic(V) increasing mobility.

In the case of arsenic it was unfortunate that the trials to did not proceed further, as reports of arsenic mobility are inconsistent (section 3.9.1.3(d)). However the degree of agreement between actual and predicted concentrations is excellent the maximum degree of error only being 2mgℓ^{-1} over the 235 day trial. Additionally, results appear to have stabilised at that level.

8.10 COMPUTATIONAL METHOD - GENERAL COMMENTS

The method employed to calculate the exit stream composition was reported in section 4.4.4 and section 7.4.6. The computation from the residence time data obtained from column 4 to provide suitable residence time data for column 3 and for the application of the pilot-scale studies to the full scale landfill proved to be successful. The calculated values for the mean, variance, total residence time and volumetric displacement of leachate are shown below in Table 8.7. The computational method retained the characteristic curve obtained in the lithium sulphate pulse experiment.

TABLE 8.7 SUMMARY OF ACTUAL AND COMPUTED RESULTS: RESIDENCE TIME DISTRIBUTION

	Volumetric displacement (ℓday^{-1})	Mean (t)	Variance (σ^2)	Total residence time (days)
Tracer studies (Column 4)	5.21	113.2	3338	317
Co-disposal trials (Column 3)	2.75	214.3	11953	600
Application of pilot-scale studies to the full-scale landfill	3.73	153.4	6123	430

The computational method employed to calculate the exit stream metal concentrations employs a conventional chemical engineering mathematical approach. The computational method is shown below in Figure 4.2

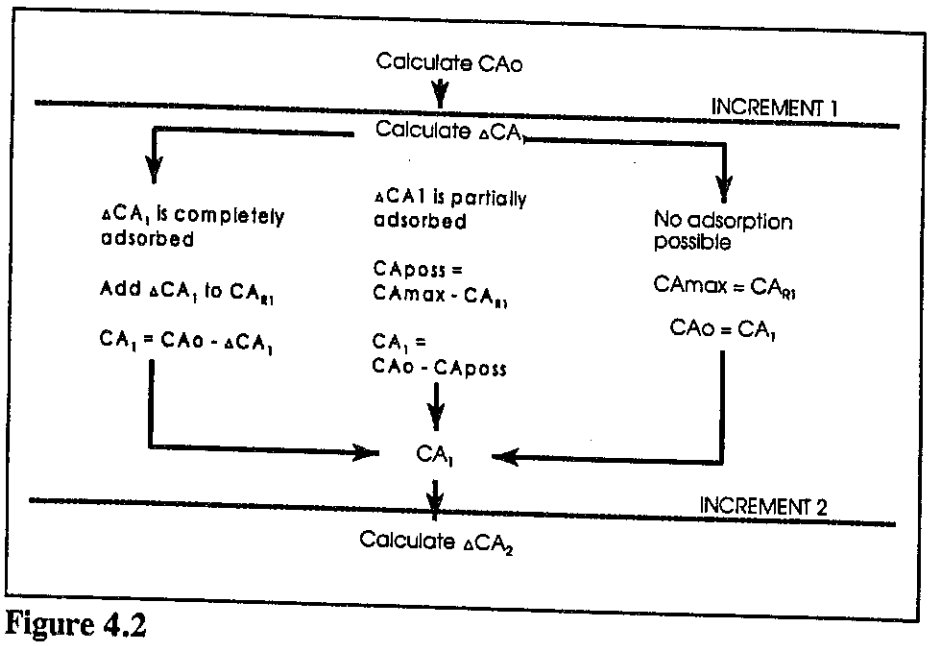

Figure 4.2
Illustration of computational method

Nomenclature

CAo	=	Solute concentration in fluid at t = 0 (gkg^{-1})
CA poss	=	Equilibrium solute concentration in adsorbent (gkg^{-1})
$\triangle CA_n$	=	Solute adsorbed in increment n (gkg^{-1})
CA_n	=	Solute concentration in fluid entering increment n (gkg^{-1})

The method is rigorous and accurate at low values of time. At larger time values the degree of accuracy is lowered. The incremental depth of the adsorbent is the problem area. The depth increment must be minimised for maximum accuracy, as the rate of adsorption is initially rapid and decreases with time. The depth increment must therefore be minimised to ensure the calculation accurately reflects the real situation within the column, where the residence time elements of fluid flow do not exceed the time required to reach equilibrium with the solid waste. The depth increment was minimised to 20mm. Using incremental depth of 20mm requires over 95 increments, as the column depth is 1940mm. This, together with the minimised time increment, requiring over 45 separate increments results in a spreadsheet in excess of 1.7Mb. At large values of time a smaller depth increment would ensure that each separate time increment of fluid would not spend excessive time in each increment of depth. Thus, at large values of time, it is possible the computed exit concentrations could be higher than that actually experienced.

8.11 APPLICATION OF THE PILOT-SCALE STUDIES TO THE FULL SCALE LANDFILL

As detailed in section 7.4.7 the application of the pilot-scale studies to the full scale landfill involved a worst-case study. The assumptions were:

(i) Precipitation occurring at Coastal Park Sanitary Landfill (from which the municipal solid waste was excavated) in the heaviest precipitation month falling on a continual basis;
(ii) no loss of moisture from the landfill, such as evapotransportation or run-off;
(iii) the landfill was at field capacity prior to co-disposal;
(iv) metal content in leachate from the landfill should not exceed the most stringent requirements prescribed by current South African legislation.

The assumptions are very stringent, and there is no doubt that the amounts of copper, chromium and arsenic determined to be suitable, would not cause any additional environmental damage to the area surrounding the landfill. The calculations revealed that when disposing of these metals in combination the mass of copper should not exceed $67gt^{-1}$; the mass of chromium in the form of chromium(VI) should not exceed $195gt^{-1}$; the mass of arsenic should not exceed $195gt^{-1}$. Rushbrook (1990) tabulated various maximum loading rates quoted in the United Kingdom by the various United Kingdom authorities. The values are shown in section 3.9.3, Table 3.16). The values for copper, chromium, and arsenic are shown below in Table 8.8, together with the proposed values obtained in this study. When considering the co-disposal of heavy metals, the United Kingdom's Department of the Environment state that *limited evidence suggests an initial loading of 100g of soluble chromium, copper, lead or zinc per tonne of mature household waste*

is unlikely to produce a significant change in leachate concentration 3 metres distance from the heavy metal waste (DOE, 1986). It should be noted that the DOE recommend, that if optimum attenuation is sought that co-disposal be practised with mature (that has been deposited between 1 and 5 years) municipal solid waste.

TABLE 8.8 CO-DISPOSAL LOADING RATES

Constituent	Loading rate	Proposed loading rate
Chromium	$100gt^{-1}$*	$195gt^{-1}$
Copper	$100gt^{-1}$*	$67gt^{-1}$
Arsenic	$10gt^{-1}$* $10kgt^{-1}$* (for As in sulphide form)	$195gt^{-1}$

* adapted from Rushbrook, 1990

The calculated loading rates compare favourably with that quoted by the DOE. It must be noted:

(i) the loading rates quoted by the DOE are for a total heavy metal loading of $100gt^{-1}$ whereas the proposed loading rate totals $262gt^{-1}$ for chromium and copper in combination;

(ii) the DOE quote a depth of 3m while the proposed loading rates were calculated with a depth of 2m of municipal solid waste.

Discussion of the loading rate quoted for arsenic is more complex. The value quoted by Rushbrook is not repeated in the DOE literature such as Waste Management Paper No 20, Arsenic-bearing wastes (1980) or Waste Management Paper No 26, Landfilling wastes (1986). Both publications express concern that the concentration of arsenic in leachate does not exceed $10mg\ell^{-1}$. Cossu *et al* (1989) reviewed the co-disposal of industrial wastes, including the disposal of arsenic wastes. The researchers affirm the value quoted by Rushbrook, that of $10gt^{-1}$, and refer to test work completed by Blakey (1984) (section 3.9.1.3(c)). It would appear that the leachate concentration is the controlling variable. If one does not exceed an arsenical concentration of $10gt^{-1}$ of municipal solid waste, the value of $10mg\ell^{-1}$ arsenic in leachate, will not be exceeded.

It is evident the loading rate values quoted by the DOE for arsenic are conservative. The DOE is concerned with additional factors such as the generation of arsine gas (section 3.9.3(c)). Arsine (AsH_3) is an extremely poisonous gas, with no effective antidote (DOE, 1980). Arsine is produced whenever a reaction generating nascent hydrogen occurs in the presence of arsenic.

Hydrogen generation can occur under anaerobic conditions, especially acetogenic conditions (section 3.7.2).

In general, loading rates proposed from experimental work undertaken in this study concur with loading rates employed in the United Kingdom, recommended by the United Kingdom's Department of the Environment.

8.11.1 FULL SCALE LANDFILL OPERATION - ADDITIONAL FACTORS

The life of a landfill may be classified into three primary time frames (section 3.7.1): the acetogenic or acid producing phase; the methanogenic or methane producing phase; the stabilised or final maturation phase. The pilot-scale studies together with the kinetic experiments explored the adsorption of the relevant heavy metals onto stabilised municipal solid waste. A stabilised landfill is characterised by a leachate comprising of a; neutral pH; high level of alkalinity; low level of carboxylic acids; low degree of organic contamination or Chemical Oxygen Demand (COD) and an extremely low production of biogas from the landfill. An acetogenic landfill is characterised by a leachate comprising of a; low pH; low level of alkalinity; high level of carboxylic acids; high degree of organic contamination with a virtual absence of biogas production from the landfill. A methanogenic landfill is categorised by leachate with a neutral pH; substantial generation of biogas with all other parameters being intermediate between the acetogenic and stabilised landfill.

Pohland *et al* (1986b) compiled data from a number of sources, indicative of the three primary stages of landfill life. This is shown in Table 8.9. Copper, chromium and arsenic are of primary interest. Other metals are also shown, for comparative purposes.

(a) Copper

It would be envisaged that copper would be relatively immobile in any age of landfill. The results collated by Pohland shown in Table 8.9 indicate copper to be mobile in an acetogenic landfill, less so in a methanogenic and a stabilised landfill. It is not unexpected that copper has a low degree of mobility in a methanogenic or a stabilised landfill. It is however surprising that it is mobile in an acetogenic landfill. Most researchers report the relative immobility of copper in organic soil, and report a tendency for copper to form stable organic complexes with organic matter in soil (section 3.9.1.3(d)). Also, soils having higher levels of organic matter are usually acidic in nature, as is the leachate from an acetogenic landfill. Other researchers report the mobility of copper in soils to be low, and describe the adsorption of copper onto organic matter, clay minerals, and even pure quartz. Soil scientists have conducted trials examining the movement of various metals in soils over extended periods. Lundblad and co-workers (1949) added over 250kg of copper (per hectare) to an acid peat soil. After 5 years had elapsed only 0.2 percent of the copper added was removed from the top 5cm of soil (section 3.9.1.3(d)).

Results from this current study are presented in Table 8.10. Copper is strongly adsorbed at all the pH levels shown, there is little evidence of significant desorption. (section 3.9.1.3(d)).

TABLE 8.9 **COMPOSITION OF LANDFILL LEACHATE AND BIOGAS FROM LANDFILLS OF DIFFERENT AGE**
(adapted from a review by Pohland *et al*, 1986b)

Constituent	Acetogenic landfill	Methanogenic landfill	Stabilised landfill
pH	4.7 - 7.7	6.3 - 8.8	7.1 - 8.8
Total Alkalinity ($mg\ell^{-1}$ as $CaCO_3$)	140 - 9650	760 - 5050	1460 - 4840
Total Volatile acids ($mg\ell^{-1}$ as CH_3COOH)	3000 - 18000	250 - 4000	Essentially absent
COD ($mg\ell^{-1}$ as O)	1500 - 71100	580 - 9760	31-900
Copper ($mg\ell^{-1}$)	0.005 - 2.2	0.03 - 0.18	0.02 - 0.56
Chromium ($mg\ell^{-1}$)	0.06 - 18	0.05	0.05
Lead ($mg\ell^{-1}$)	0.01 - 1.44	0.01 - 0.1	0.01 - 0.1
Nickel ($mg\ell^{-1}$)	0.03 - 79	0.01 - 1.0	0.07
Zinc ($mg\ell^{-1}$)	0.65 - 220	0.1 - 4.0	0.4
Cadmium ($mg\ell^{-1}$)	70 - 3900	76 - 490	76 - 254
Iron ($mg\ell^{-1}$)	90 - 2200	115 - 336	4 - 20
Methane (%)	< 1	30 - 60	0 - < 10
Carbon dioxide (%)	10 - 30	30 - 60	< 40
Nitrogen (%)	60 - 80	< 20	> 20
Oxygen (%)	0 - 5	0 - 5	> 5
Hydrogen (%)	0 - 2	< 0.1	Essentially absent

TABLE 8.10 MASS AND PERCENTAGE OF COPPER ADSORBED AND DESORBED AT PH 5.5, 6.4 AND 7.0

Metal and species	pH	Average mass sorbed (mg)	Percentage adsorption	Average mass desorbed (mg)	Percentage of metal adsorped that is desorbed
Copper(II)	5.5	50.9	86.9	1.7	3.3
	6.4	14.1	78.9	0.5	3.5
	7.0	23.0	79.1	0.8	3.5

The mobility of copper is severely restrained in both a methanogenic and a stabilised landfill. The solubility of copper is very limited in an aqueous solution, in an anaerobic reducing environment even more so. The subject of sulphate reducing bacteria was addressed in section 3.9.3(a). Hydrogen sulphide is produced by sulphate reducing bacteria. Hydrogen sulphide is a strong reducing agent, it can react with copper causing precipitation of the copper as insoluble copper sulphide.

Table 8.9 reveals copper to be one of the least mobile metals tabulated. The work of other researchers, together with results obtained in this study (Table 8.10), are in agreement.

(b) Chromium

It would be anticipated that the mobility of chromium(VI) would be limited in any landfill of any age. The kinetic trials showed that although mass of chromium adsorbed was proportionally less than copper or arsenic, chromium was strongly bound, and showed little evidence of desorption (Table 8.11).

Examination of Table 8.9 shows that the chromium content of a leachate from an acetogenic landfill to be relatively high when compared with a methanogenic or stabilised landfill. Leachate from an acetogenic landfill contains high levels of soluble organic acids enhancing the mobility of chromium. The pH of the leachate is low, adsorption of chromium(VI) was satisfactory in the kinetic trials at similar pH levels. The TCLP extraction fluid contains a carboxylic acid; acetic acid, which should approximate a leachate from an acetogenic landfill.
The degree of approximation was not adequate in this instance.

TABLE 8.11 MASS AND PERCENTAGE OF CHROMIUM ADSORBED AND DESORBED AT PH 5.5, 6.4 AND 7.0

Metal and species	pH	Average mass sorbed (mg)	Percentage sorbed	Average mass desorbed (mg)	Percentage of metal adsorped that is desorbed
Chromium (VI)	5.5	53	21.1	0.2	0.4
	6.4	31	10.3	0.2	0.6
	7.0	21	10.4	0.5	2.4

The low level of chromium in leachate from a methanogenic landfill is not surprising. By definition, a methanogenic landfill is anaerobic, and reducing conditions are prevalent. Chromium(VI) is readily reduced to chromium(III) in the presence of organic matter, especially at low pH. The solubility of chromium(III) decreases rapidly above pH4, with complete precipitation occurring above pH5.5. There are conflicting vectors however. The presence of soluble organic acids can maintain chromium(III) in solution at pH levels above 5.5.

It is envisaged that levels of chromium in leachate from a stabilised landfill would be low, possibly lower than that from a methanogenic landfill. The complete absence of carboxylic acids, the strong fixation of chromium to municipal solid waste shown in this study, indicate a low chromium mobility. Pohland *et al* (1983) expresses concern the more microbially recalcitrant materials could produce humic-like substances which could provide soluble organic material which could then remobilise any heavy metals present. There is the possibility of the occurrence of this phenomena, but this could only occur after a number of years, or even decades.

Soil scientists have evaluated vertical chromium movement in soils. In one experiment, chromium analysis of soils, which had received metal contaminated sludge treatment from 1942 to 1961, showed no evidence of significant movement below the depth to which the soil was cultivated (McGrath *et al*, 1990). Table 8.8 reveals chromium to be one of the least mobile metals tabulated. The work of other researchers together with results obtained in this study (Table 8.10) are in agreement.

(c) Arsenic

Unfortunately the review of leachate contaminants completed by Pohland *et al* (1986b) did not include arsenic. The behaviour of arsenic is the most complex of the three metals under consideration. The results from the kinetic trials are shown in Table 8.12. Arsenic is well adsorbed throughout the pH range under discussion. Arsenic is also the only metal which exhibits any significant desorption.

TABLE 8.12 MASS AND PERCENTAGE OF ARSENIC ADSORBED AND DESORBED AT pH 5.5, 6.4 AND 7.0

Metal and species	pH	Average mass sorbed (mg)	Percentage adsorption	Average mass desorbed (mg)	Percentage of metal adsorped that is desorbed
Arsenic(V)	5.5	70	34.3	6	8.6
	6.4	36	20.6	4	11.1
	7.0	41	23.2	4	9.8

The mobility of arsenic in soils is increased in anaerobic conditions. This increased mobility is a consequence of the reduction of arsenic(V) to arsenic(III). Arsenic(III) is estimated to be 5 to 10 timer more soluble, and hence more mobile then arsenic(V). The subject of sulphate reducing bacteria was addressed in section 3.9.3(a). Hydrogen sulphide is produced by sulphate reducing bacteria. Hydrowen sulphide is a strong reducing agent, it can react with arsenic (as with copper) causing precipitation of arsenic as insoluble arsenic sulphide. Another attenuation mechanism to consider is the co-precipitation of arsenic with iron sulphide. The iron content of leachates is generally high (see Table 8.9). Iron content is shown ac low in leachate from a methanogenic landfill as a consequence of attenuation mechanisms as just discussed.

The mobility of arsenic in the acetogenic landfill and the stabilised landfill are more difficult to envisage. Some of the attenuation mechanisms available in the methanogenic landfill would not be available. As reported in section 3.9.1.3(d) there is conflicting information regarding the mobility of arsenic(III) and arsenic(V). Sadler (1993) states that arsenic(III) has a high mobility in soils; while Elkhatib and co-researchers (1984) report arsenic(III) being irreversibly sorbed by the soils examined, only a small fraction of the arsenic(III) being desorbed from the soils. Korte and co-workers (1976) concludes that arsenic(III) (however at pH3) was more mobile than other metals examined. Frost and Griffin (1977) found arsenic(V) be mobile, especially at alkaline conditions, while arsenic(III) exhibited an increase in adsorption with rising pH.

It would appear there are substantial attenuation mechanisms available to reduce the mobility of arsenic in a methanogenic landfill. Adsorption would appear to be the principal mechanism in both the acetogenic and stabilised landfill. Arsenic adsorption was satisfactory throughout the pH range under scrutiny. There would not appear to be a great deal of difference in the behaviour of arsenic in an acetogenic landfill or that of a stabilised landfill, though adsorption of arsenic(V) is substantial at the lower pH values.

An additional problem that must be addressed when considering the co-disposal of arsenic on an acetogenic landfill is that of the generation of arsine gas (section 3.9.3(c)). Arsine (AsH_3) is an extremely poisonous gas, with no effective antidote (section 8.11). Arsine is produced whenever a reaction generating nascent hydrogen occurs in the presence of arsenic. Hydrogen can be generated in the acetogenic phase of landfill age. It is produced by hydrogen producing acetogenic bacteria (section 3.7.2). These hydrogen producing acetogenic bacteria convert the higher volatile acids to acetate and hydrogen. Pohand *et al* (1986b) reveals in Table 8.9 that hydrogen levels in gas from an acetogenic landfill have been recorded as high as 2 per cent by volume. For this reason it would appear that caution should be exercised in the co-disposal of arsenical waste in an acetogenic landfill.

(d) General

The calculations revealed that when disposing of these metals in combination the mass of copper should not exceed $67gt^{-1}$; the mass of chromium in the form of chromium(VI) should not exceed $195gt^{-1}$; the mass of arsenic should not exceed $195gt^{-1}$. A specific area which has not been addressed in the preceding section is that of the inhibiting effect of toxic industrial wastes on biological degradation of the municipal solid waste (section 3.9.3(a)). When practising co-disposal of industrial wastes with municipal solid wastes, avoidance of sterilising the landfill by exceeding the toxicity limit of the various microbial population groups and therefore inhibiting the degradation of the municipal solid waste is one of the two premier objectives. The other objective is that the emission of toxic substances in liquid and gaseous effluent from the landfill should not be greater than that from the disposal of only municipal solid waste. The latter objective was addressed in the initial assumptions of the calculation, were a worst case study was employed (section 7.4.7). The inhibition of anaerobic digestion was extensively examined in section 3.9.3(a), there is however, a number of interesting investigations deserving of further examination, for comparative purposes.

The work completed by Pohland and other workers (1985; 1986a; Gould *et al*, 1989) at the Georgia Institute of Technology, is one such study. A metal plating sludge containing zinc, chromium, nickel, cadmium, copper and iron, was co-disposed with municipal solid waste in pilot-scale landfill columns. In the control column (no addition of metal plating sludge) methanogenic conditions were established. In column 2 the onset of methanogenisis was delayed, addition of metal sludge was $84kgt^{-1}$. Where the sludge was added in a greater quantity, methanogenic conditions were not established.

Another investigation requiring further review is that undertaken by Yeates *et al* (1994). The researchers investigated the impact of copper, chromium and arsenic timber preservative on soil biological activity. Initially, the researchers visually graded areas of the pasture in terms of heavy metal contamination. Four levels of contamination were graded; uncontaminated, low contamination, medium contamination and highly contaminated. The researchers then sampled the site extensively in terms of degree of contamination and depth. The samples were then analysed for metal content and various biological parameters were measured to determine the whether there was evidence of repression of biological activities.

There was a close correlation between heavy metal contamination and the initial visual assessment. All the biological parameters measured in the contaminated area showed correlation with levels of copper, chromium and arsenic. The researchers concluded that contamination by

100mgkg^{-1} of copper, chromium and arsenic caused little depression of soil biological activity, there was some suppression at 400mgkg^{-1}, but at 800mgkg^{-1} normal biological processes were inhibited and herbage production was negligible. These results were comparable with other workers cited by Yeates and co-researchers.

The toxicity of heavy metals in the process of anaerobic digestion is well established and has been extensively investigated by various researchers principally investigating toxicity effects in waste water anaerobic digesters. Reid and fellow researchers (1968) evaluated the effects of metallic ions on a number of biological waste treatment processes, amongst them, anaerobic digestion at laboratory scale. They found that chromium (in the form, chromium(VI)) concentrations as high as 85mgℓ^{-1} reduced biogas production by 18 percent, and copper when added in concentrations up to 2mgℓ^{-1}, reduced gas production by 8 percent.

Hayes *et al* (1978) collated information concerned with the effect of metal addition on anaerobic digestion. The digesters were dosed with the metals in a step- and pulse-like fashion. Metal addition in a pulse-like mode is akin to shock loading, while metal addition in a step-like function allows microbial acclimation to the addition of the metal. The full results from the study are tabulated in Table 3.17. It was found that copper was more toxic than chromium. The shock loading toxic limit for; chromium(VI) was less than 200mgℓ^{-1}; copper was less than 50mgℓ^{-1}. The inhibiting concentration allowing microbial acclimation for; chromium(VI) was 110mgℓ^{-1}; copper was 40mgℓ^{-1}.

If one considers the work presented by Hayes and co-workers, it would appear there would not be any inhibition in anaerobic activity as the values quoted are high. Similarly, the value of 33.6kgt^{-1} (Pohland *et al*, 1985; Pohland *et al*, 1986a; Gould *et al*, 1989), would appear to be extremely high, a complete inhibition of anaerobic activity would have been expected, instead of only the delay of establishment of methanogenic conditions. The values presented by Reid and fellow researchers (1968) are of the same order as those presented by Hayes. Values for chromium are similar, but values presented for copper display variance. By far the most relevant of the work examined is that undertaken by Yeates and co-workers. There would appear to be some suppression at 400mgkg^{-1}.

To fully utilise the adsorptive capacity of the municipal solid waste, it would be required to co-dispose 457gkg^{-1} of copper-chromium-arsenic solution. It would appear possible that the co-disposal of the copper-chromium-arsenic solution at the proposed limits in a methanogenic landfill could inhibit methanogenic activity. The work of other workers does not absolutely confirm this, but the values quoted by Reid and fellow researchers (1968) where copper when added in concentrations up to 2mgℓ^{-1}, reduced gas production by 8 percent appear appropriate. It is conceivable that methanogenesis could be initially inhibited but it would be extremely unlikely that the anaerobic processes would not become acclimatised and proceed smoothly. This statement is confirmed by work carried out by Pohland and other researchers (1985; 1986a; Gould *et al*, 1989).

8.12 SUMMARY

The micro-physical characteristics of the metals under scrutiny, copper, chromium and arsenic were examined, and detailed. Results from the equilibrium studies were scrutinised. The Freundlich isotherm indicated the order of the degree of affinity of the metals to municipal solid waste was:

copper >> arsenic > chromium.

This was confirmed by additional graphical analysis. The effect of pH on adsorption was appraised. For all the metals under consideration the highest percentage adsorption was achieved at pH5.5 with percentage adsorption at pH6.4 and pH7.0 being similar.

Results from the kinetic trials were inspected, and reasons for the applicability of the modified Freundlich equation assessed. It was shown that diffusional effects at the solid phase were rate determining. The suitability of the Freundlich equilibrium isotherm in characterising adsorption is often taken to be indicative of adsorption onto a heterogeneous surface. Further analysis of the data showed agreement to a generalised model representative of heterogeneous adsorption. The rate of adsorption was also examined. Analysis showed the rate, and mass of adsorption increased as the initial solute concentration increased. Additionally, the rate of adsorption may be categorised in the following order:

copper >> arsenic > chromium.

Sorption mechanism was also investigated. It was evident that the relative size of the ions was not the controlling mechanism, but adsorption was probably determined by electrical interaction. Tracer studies were examined, together with the pilot-scale co-disposal trials. Results from the tracer studies showed the pilot-scale column to behave as a non-ideal plug flow reactor. Results from the co-disposal trial showed good agreement with that predicted from the modelled results from the laboratory investigation. Defects in the computational method were also discussed.

The application of the pilot-scale study to a full scale landfill were discussed, in conjunction with values promulgated by the United Kingdom's Department of the Environment. Loading rates predicted by computer model were of the same order as those utilised in the United Kingdom. The final sections of the Discussion centred around the behaviour of copper, chromium and arsenic in landfills of different age together with the effect of co-disposal of those metals at the proposed loading rates on anaerobic activity.

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SECTION B

FULL-SCALE LANDFILL CELL STUDIES

AT

COASTAL PARK

CHAPTER 9

FULL-SCALE LANDFILL CELL STUDIES AT COASTAL PARK

9.1 INTRODUCTION

The Coastal Park landfill is situated on the False Bay coastline above the Cape Flats aquifer. The landfill was commissioned in 1985 without a containment liner. The landfill site is underlain by approximately 20 m of fine silty sand and the regional water table is generally at a depth of 2,5 m below the ground surface.

Waste disposal activities were designed in accordance with the requirements as advocated at that time by the waste disposal regulations. These required a minimum two meter thick unsaturated zone between the waste body and the groundwater table.

Coastal Park is the only landfill in Southern Africa where the flow of leachate from the landfill can be sampled and measured. This was made possible by the construction of five research cells that have been installed in the landfill.

Since little was known about the production and possible attenuation of leachate in the unsaturated zone, the Cape Town City Council in co-ordination with the Foundation for Research and Development and the Water Research Commission negotiated several research projects at Coastal Park.

The Coastal Park landfill is possibly one of the most researched sites in the world. Measurements of rainfall and leachate outflow have enabled a water balance to be constructed together with developed models to predict water flow and leachate generation. It is recommended that should the details of this report be utilised elsewhere, cognisance be taken of the local conditions in the Western cape to assist in the adoption of the technology.

9.2 MATERIALS AND METHODS

9.2.1 LOCATION OF RESEARCH LANDFILL CELLS

The Coastal Park landfill is located in the south western portion of the Cape Flats, adjacent to the Cape Flats waste-water treatment works. The landfill is situated some 300 m from the False Bay coast line. The Cape Town central business district is situated some 30 km to the north of the landfill with the suburban area extending to some 3 km from the site. Figure 9.1 illustrates the location of Coastal Park in relation to the surrounding area.

The Coastal Park landfill is a general waste landfill which receives some 200 000 t/a of municipal waste, garden refuse and builders rubble. The classification in terms of the Minimum Requirements (DWAF, 1994) is GLB+ which implies a large general waste landfill which has the ability to produce significant volumes of leachate. It must be noted that the landfill is marginally B+ and therefore only small volumes of leachate are released.

The landfill covers an area of some 62 ha (refer Figure 9.2) and the research landfill cells are situated on the eastern side of the landfill.

9.2.2 CONSTRUCTION AND MAINTENANCE OF LANDFILL CELLS

The first collection sheet (1,5 mm thick HDPE geomembrane containment liner) with a surface area of 196 m^2 (14 m x 14 m) was successfully installed during 1986 (Cell 1). It was placed directly under the general waste body in order to be able to quantify and analyse the leachate. Leachate was sampled for analysis to establish quality trends and changes with refuse stabilisation.

In order to be able to verify the attenuation in a two meter thick unsaturated sandlayer of a calcareous nature, it was decided in 1987 to install a further four collection sheets (1,5 mm thick HDPE) in a position as indicated in Figure 9.2. and 9.3 (Cells 2, 3, 4 and 5). Each collection sheet was buried at a depth of 2 m below the original ground surface. The collection sheets each have an area of some 196 m^2 and they were placed 12 meters apart.

Each collection sheet had a central abstraction point which was covered with a pebble filter and additionally covered with a geotextile to prevent blockage by sand. A 50 mm diameter leachate drainage pipe lead to a collection manhole outside the fill area. The sheets were carefully covered with a layer of permeable Cape Flats sand of two meter thickness. There are no side walls separating the waste in each cell from the surrounding waste. Each cell is separated from its neighbour by 12 m of waste.

The entire area was thereafter covered with two layers of waste, each lift 2,5 m thick. The use of daily cover (150 mm thick) after the end of each day added permeable sand layers to the compacted waste. Construction of the landfill cells were completed by the addition of a 500 mm thick cover layer of permeable sand. The upper surface of the cells was identified by the construction of clay banks some 500 mm high. These banks ensured that the special wastes when applied remained on top of each specific cell.

Normal landfilling procedures were utilized when placing the refuse in order to ensure that results could be relevant to full-scale operations. No pre-sorting of the refuse took place. A bulk wet *in-situ* density of some 1 000 $kg.m^{-3}$ was achieved for the compacted waste.

Although accurate composition analyses of the general waste used was not carried out, it is assumed that the waste used was not significantly different to that which was tested during 1985 and 1986 (Futre, 1986). Table 9.1 gives average values of refuse composition assumed to have been used in constructing the cells.

Construction details of the cells is illustrated schematically in Figure 9.4.

TABLE 9.1: COMPOSITION OF GENERAL WASTE USED IN CONSTRUCTING THE CELLS AT COASTAL PARK

CONSTITUENT	AVERAGE
Kitchen	24,1
Garden	5,9
Cardboard	2,6
Paper	25,7
Glass	8,1
Plastics	10,4
Textiles	5,6
Beverage (Cans)	0,6
Other Metals	5,6
Fines	3,4
Unclassified	7,9

* All values are % by wet mass

Maintenance of the cells was limited to the continual rehabilitation of the upper surface. The clay banks had to be replaced every 6 months or so and the sand cover above the waste was kept free of litter and weeds by raking on a regular basis. The fact that these cells were subjected to the outside weather conditions made continual surface maintenance mandatory.

The following assumptions were made in calculating the mass of general waste in each of the research landfill cells 1 - 5.

Area of each cell	= 14 m x 14 m
	= 196 m^2
Depth of landfilled waste	= 5 m
Volume of waste per cell	= 980 m^3
Bulk density of landfilled waste	= 1 000 $kg.m^{-3}$
Mass of waste per cell	= 980 ton

9.2.3 TYPES AND DOSAGE OF SPECIAL WASTES

Three chemical wastes and tracers were identified for co-disposal with refuse, on cell surfaces, from 1988:

Cell 1: No additions - control cell

Cell 2: Wood preservative:
CCA powder: 9.5% copper, 16.0% chromium, 16.6% arsenic
CCA paste : 7.1% copper, 11.9% chromium, 12.8% arsenic

Cell 3: NaCℓ and LiBr were added as tracers of the movements of water and soluble salts: (control cell)

Cell 4: Phenolic waste effluents (mean phenol content 300 mg/ℓ) added in the form of gasworks effluent

Cell 5: Dried sludge from waste-water anaerobic digester:
TKN - about 80 g N/kg, zinc - about 250 mg/kg
Liquid sludge from waste-water anaerobic digester (2% solids):
TKN - about 1500 mg N/ℓ, zinc - about 5 mg/ℓ
Urea : 47 % N

Table 9.2 summarises these applications.

9.2.4 METEOROLOGICAL MEASUREMENTS

Records are available for rainfall and A-pan evaporation at the Coastal Park site for part of the period under consideration. However, because the site was not staffed on seven days of the week and because of theft of the evaporation pan there are gaps in the record.

Therefore, the rainfall and A-pan evaporation records from the adjacent Cape Flats Wastewater Treatment Plant have been used in preference. This plant operates 24 h/day, has complete records, and is an official DWAF rainfall gauging station, with rain recorder and check gauge. The topography of the two sites is similar, both being on the Cape Flats plain, 1 km apart and 0.4 to 0.9 km from the sea.

Data were taken from the primary records held at the treatment plant. The rainfall was for the most part taken to be the average of the recorder and check gauge figures, except in those few cases where there were gross discrepancies, which were resolved by comparison with figures for Coastal Park and the International Airport.

The scale on the A-pan was measured up and the figures for level change adjusted to read in millimetres (factor 0.55). The gross evaporation rate was then calculated by adding rainfall to the daily decrease in water level in the pan; allowance was made for the few occasions when the pan overflowed during heavy rain. As a final check, the increase in pan level on rainy days was plotted against rainfall; the two sets of figures were found to be consistent.

Figure 9.5 compares the rainfall figures for the Cape Flats works, Coastal Park and the International Airport for the period over which reasonably comprehensive records were available for Coastal Park. The pattern of monthly totals is very similar, with the Coastal Park values being slightly higher than those for Cape Flats. The overall difference is about

TABLE 9.2: CHEMICAL APPLICATIONS TO LANDFILL CELLS

DATE	CELL 2	CELL 3	CELL 4	CELL 5
1988-08-18	Nil	1 kg LiBr 114 ℓ water 700 mg/ℓ Li	Nil	650 kg dry sludge
1988-09-05	245 kg CCA powder. Water spray	Nil	Nil	Nil
11988-09-13 to 1988-10-05	Nil	Nil	116 kℓ phenolic effluent 300 mg/ℓ phenol	Nil
1989-04-27 to 1989-05-22	90 kg CCA powder Water spray	0.5 kg LiBr 114 ℓ water 350 mg/ℓ Li	30 kℓ phenolic effluent 300 mg/ℓ phenol	Nil
1991-05-04	220 kg CCA powder Water spray	1 kg LiBr 200 ℓ water 400 mg/ℓ Li	116 kℓ phenolic effluent 300 mg/ℓ phenol	610 kg dry sludge
1991-05-23 to 1991-05-30	Nil	Nil	Nil	56 kℓ wet sludge (2%)
1993-03-??	94 kg CCA paste 20 kℓ water 330 mg/ℓ Cu 560 mg/ℓ Cr 600 mg/ℓ As	50 kg NaCl 20 kℓ water 980 mg/ℓ Na	24 kℓ phenolic effluent 300 mg/ℓ phenol	50 kg urea 20 kℓ water 1150 mg/ℓ N
1993-09-24	94 kg CCA paste 20 kℓ water 330 mg/ℓ Cu 560 mg/ℓ Cr 660 mg/ℓ As	50 kg NaCl 21 kℓ water 940 mg/ℓ Na	24 kℓ phenolic effluent 300 mg/ℓ phenol	100 kg urea 20 kℓ water 2300 mg/ℓ N
1994-10-17	94 kg CCA paste 14 kℓ water 480 mg/ℓ Cu 800 mg/ℓ Cr 860 mg/ℓ As	50 kg NaCl 14 kℓ water 1400 mg/ℓ Na	22 kℓ phenolic effluent 300 mg/ℓ phenol	50 kg urea 14 kℓ water 1700 mg/ℓ N
1994-11-23		44 kℓ water		
1995-07-06 1995-07-07			3 kℓ phenolic effluent 300 mg/ℓ phenol	

7% but examination of the graph for cumulative totals shows that most of this difference arose during the second half of 1993. In any case, the conclusions of this report are not materially affected by these small differences and the figures for Cape Flats have been used in further calculations, except where otherwise indicated.

Figure 9.6 shows monthly and cumulative rainfall and evaporation rates at Cape Flats over the period 1989 to 1997.

9.2.5 MEASUREMENT OF LEACHATE VOLUMES FROM CELLS

Leachate was pumped up from the collection drums at the bottom of the manholes at intervals of 2 to 15 days, depending on the season, and the volume was measured to the nearest 10 litres.

The values for each cell were entered on computer and checked against the primary records. As far as possible, weekly values were then estimated by interpolation or summation of the measured values. There were some gaps, when the spacings between readings were inconvenient, but for the purposes of this work, these are unimportant.

9.2.6 SAMPLING AND ANALYSIS OF LEACHATE FROM CELLS

Sampling and analysis was carried out on a quarterly basis for the duration of the project.

In order to obtain a relatively fresh leachate sample, collection containers (10 ℓ) were placed beneath each outlet pipe from the cell for a period of 24 hours. A battery operated pump was utilised to pump the leachate from the sumps, thereby preventing staff from entering an area which could have contained methane gas. A 2½ ℓ bottle was filled (or a smaller volume if insufficient had accumulated) from the container and submitted to the laboratory for analysis. Where a particular analysis was delayed, a portion of the sample was preserved according to standard procedure.

The analysis of the samples was fairly comprehensive (Table 9.3) since besides the essential parameters chromium, copper and arsenic relevant to the study, it was felt that this was an opportunity to collect data which would reflect other processes occurring within the landfill cells. In this respect the stages of biological development within the cell would be of particular interest.

The chemical analyses were all carried out according to approved methods (American Public Health Association, 1992).

9.2.7 SUPPLEMENTAL WETTING OF CELLS

As the volumes of leachates collected during the project were small, a programme of supplemental wetting, of Cell 4, was embarked on in the closing stages, in an attempt to increase leachate flow rates.

Over a period of seven months, water from the adjacent Zeekoevlei outlet canal was brought in, firstly by pumping and later by tanker, and distributed over the cell surface (Table 9.4.)

TABLE 9.3: ANALYSES PERFORMED ON LEAHCATES FROM LANDFILL CELLS

DETERMINATION	UNITS
SOLIDS	
Total Solids @ 105 °C	mg/ℓ
Total Dissolved Solids @ 105 °C	mg/ℓ
Total Volatile Solids @ 600 °C	mg/ℓ
OXYGEN DEMAND	
COD	O mg/ℓ
NITROGEN	
TKN	N mg/ℓ
Ammonia	N mg/ℓ
Organic	N mg/ℓ
Nitrate + Nitrite	N mg/ℓ
PHOSPHORUS	
Total Phosphorus	P mg/ℓ
Ortho-Phosphate	P mg/ℓ
PHYSICAL	
pH	
Conductivity at 25 °C	mS/m
MINERAL	
Chloride	Cℓ mg/ℓ
Sulphate	SO_4 mg/ℓ
Sulphide	S mg/ℓ
Alkalinity	$CaCO_3$ mg/ℓ
Sodium	Na mg/ℓ
Potassium	K mg/ℓ
Calcium	Ca mg/ℓ
Magnesium	Mg mg/ℓ
Copper	Cu ug/ℓ
Chromium	Cr ug/ℓ
Zinc	Zn ug/ℓ
Cadmium	Cd ug/ℓ
Nickel	Ni ug/ℓ
Lead	Pb ug/ℓ
Mercury	Hg ug/ℓ
Arsenic	As ug/ℓ
Lithium	Li ug/ℓ
ORGANIC	
Phenols	C_6H_5OH mg/ℓ
Volatile acids (acetic acid)	mg/ℓ
Volatile acids (total)	mg/ℓ

TABLE 9.4: WATER APPLIED TO CELL 4 DURING SUPPLEMENTAL WETTING PROGRAM

DATE	WATER APPLIED mm
1995-12-30	100
1996-01-11	135
1996-02-08	100
1996-02-18	100
1996-02-22	100
1996-03-07	30
1996-03-19	100
1996-04-11	100
1996-05-16	100
1996-05-30	100
1996-06-06	100
1996-06-13	100
1996-07-03	40
1996-07-11	80
1996-07-18	100
1996-07-25	100
TOTAL:	**1485**

9.3 RESULTS OF FULL-SCALE STUDIES AT COASTAL PARK

9.3.1 VOLUMES OF LEACHATES FROM CELLS

Figure 9.7 shows the monthly leachate total volumes for each cell, divided by 200 m^2 to allow expression as mm. Note that the scales are mostly different to encompass the range of volumes encountered. Each point is plotted in the middle of a month.

Figure 9.8 gives the corresponding graphs for weekly leachate totals. In this case the values are more scattered. The solid line and shaded area have been derived by use of a finite-impulse digital smoothing filter designed not to introduce time lags. A constant scale has

been used to facilitate comparisons and the two large peaks for Cell 4 during 1996/97, which relate to the supplemental wetting program, are thus off the top of the graph. The two figures show essentially the same picture.

Figure 9.9 shows cumulative totals for each cell. Figure 9.10 gives the volumes of water added, either along with various chemicals, or as part of the supplemental wetting program.

The cumulative leachate graphs in Figure 9.9 show that the supplementary wetting program (end December 1995 to end July 1996) increased leachate volumes, not merely in Cell 4, but in all the other nearby cells. Cell 1, located far away, is free of this effect. Therefore, in the interpretation of these results, this needs to be borne in mind. Table 9.5 shows annual averages for the quantities involved.

TABLE 9.5: ANNUAL MEANS FOR LEACHATES, RAIN AND A-PAN EVAPORATION

	1989 to 1995 Rain : 542 mm Evaporation: 1775 mm		**1996 to 1997 Rain : 620 mm Evaporation: 1756 mm**	
	Leachate		**Leachate**	
	mm	**% of Rain**	**mm**	**% of Rain**
Cell 1	22.2	4.1	26.7	4.3
Cell 2	21.9	4.0	33.6	5.4
Cell 3	8.9	1.6	27.1	4.4
Cell 4	12.5	2.3	113.3	18.3
Cell 5	5.2	1.0	21.5	3.5
Mean	14.2	2.6		

Supplemental wetting, Cell 4: 1485 mm over January - July 1996 (refer Table 9.4)

It is not immediately clear why there should be a such a large range of leachate volumes for the various cells, particularly as the material for Cells 2 to 5 was laid down in a continuous strip. However, as the table shows and as discussed in more detail by Blight (Section 10.2), leachates at this site are only a small percentage of the rainfall, the remaining water perforce being removed by evapotranspiration. Leachate volumes are therefore dependent on small differences between the rates of two large-scale processes, and relatively minor variations in the conditions in each cell might therefore have a magnified effect.

It still remains to be established which the most important factors are in this regard, although it seems reasonable to assume that, as the necessary source of heat is solar radiation, the evaporation rate will be highest near the surface and that, the longer the residence time of

water in the surface layer, the smaller the proportion that will find it's way to the bottom, as leachate. The water-retaining properties of the wastes, including pooling in plastic bags, should therefore be important.

The effect of the supplemental wetting of Cell 4 is clearly shown in the figures and the table.

Cell 4 leachate, as a percentage of applied water (rainfall plus wetting), increased by a factor of 3.6 times during 1996/97. The relationship between water applied and leachate is thus non-linear, larger amounts of water giving rise to disproportionately greater amounts of leachate.

The concomitant increase in leachate production in nearby cells, may have three causes. Firstly, it may be the result of the extensive lateral movement of water reported by Blight (Section 10.3), on the basis on measurements of applied metal salts. Secondly, the application of water in one place only presumably created a pressure gradient and therefore, a flow, along the line of cells. Thirdly, as will later be seen, it is possible that the entire depth of Cell 4 became completely saturated during the winter rains after the supplemental wetting, thereby promoting lateral flow. As the supplementary wetting program was not designed to study lateral flows, these effects cannot easily be separated.

These leachate flow rates are far smaller than those obtained in the pilot column study, 2500 to 5000 mm/yr (refer Chapter 7). Even the peak flow in Cell 4 after supplemental wetting was only about 240 mm/yr. The difference is attributed to the near saturated conditions maintained, and the minimal opportunity for evaporation, in the pilot columns.

The seasonal relationship between leachates and rainfall is most easily studied in Cell 1, the oldest of the five. Not only had it the largest amounts of leachate but, in the last four years of the study, seasonal effects had become more marked, with volumes in late summer and autumn dropping nearly to zero, possibly as a result of the reducing organic content of the material. To facilitate the comparison, smoothed weekly rainfall and leachates for Cell 1 are plotted on the same graph in Figure 9.11. In general leachate peaks match those for rainfall, with a lag time, for the main peaks, that averages 2.0 months (range: 0.6 to 3.2). At the tail end of the annual peaks, the lags reduce nearly to zero and the responses, in terms of leachate per unit of rainfall, increase, a further example of the above-mentioned non-linear relationship.

An attempt was made to predict leachate volumes from rainfall and evaporation by means of a simple model based on the following assumptions:

1. All rain is first added to the store of water in the landfill. The stored water does not constitute leachate until it reaches the bottom.

2. Rate of water loss by evapotranspiration is equal to the A-pan evaporation rate multiplied by a constant factor, and limited by the available amount of stored water.

3. Rate of production of leachate is equal to the stored water volume multiplied by a constant factor ie leachate production is directly proportional to amount of stored water. Stored volume, when divided by surface area in order to express it as mm, has the dimension of length and is related to head of water.

4. Stored water volume is reduced by evaporation and leachate production, with a lower limit of zero.

The integration algorithm derived from these assumptions was applied to daily rainfall and evaporation figures and weekly leachate volumes calculated. The centre graph of Figure 9.11 compares the predicted weekly volumes with the measured leachates for Cell 1. The bottom graph shows the results for Cell 4; in this case the supplemental water and that used for dosing purposes were added to rainfall. The same evaporation and leachate production rate constants were used for both cells and were selected to give the best fit, as determined by eye; these were: evaporation rate constant, 0.35, and leachate production rate, 0.00035 mm/day/mm stored water.

The model is instructive, as much for it's deficiencies as it's successes. The 2-month lag between the onset of the rains and rising edge of the leachate peaks is largely accounted for and the areas of the main peaks in Cell 1 are fairly well represented, particularly in the last five years of the period. A non-linear response to applied water is, at least to a first approximation, provided by the use of stored water as a basis for calculation of leachate flow rates. The perturbation caused by the supplemental wetting of Cell 4 is largely predicted. The large peaks in 1996 and 1997 are shown to be the result of rainfall on top of the large amount of stored water remaining from supplemental wetting, rather than an overly delayed response to the latter.

However, the model under-estimates the amount of leachate generated at the tail end of the annual peaks for Cell 1, particularly in the earlier years. The response to minor rainfall peaks near the end of the rainy season is also muted. As regards Cell 4, generation of leachate during the years 1989 to 1995 is not well simulated, serving to highlight the curious pattern of leachate volumes for this cell; starting from a low base, there was a steadily increasing flow rate over the years with slight seasonal variations, and ending in 1995 with volumes as high as those for Cell 1. This suggests the presence of a relatively impervious layer, part way down, which gradually became more transmissive. The material below such a layer would be isolated from surface effects, having a low evapotranspiration rate and producing leachate mainly by release of water from decomposing organic material. It is possible that the 200 mm of sand, used to separate the two lifts of refuse, has had this effect; Harraway (Section 10.5) describes the paradoxical effect of sand layers in under-saturated conditions.

The deficiencies of the model are not removed by tinkering with the two constants. Reducing the evaporation constant eventually results in an upward trend in the annual peaks and valleys, while increasing it shortens peak duration with long dry periods between. A small leachate production rate constant gives peaks that are too small and a large one, peaks that are too big.

The volume of stored water predicted by the model, proportional to the leachate production rate, can be calculated from the graphs for the latter, in Figure 9.11, by dividing by the production rate constant (7 days/week x 0.00035 mm/day/mm). The maximum amounts of stored water for Cells 1 and 4 are thus shown to be 430 and 1620 mm respectively. The latter, which occurred during the late winter after the supplemental wetting, possibly approaches the field capacity. Blight (Section 10.2) has suggested a figure of 1500 mm for the latter, corresponding to a void space of 30%, while data obtained during the pilot column

studies (Chapter 6) correspond to a void space of 40 to 50%. It is thus possible that Cell 4 became near-saturated during this period. It may be expected that a different leachate production rate constant will apply under this condition - see Harraway's discussion in Section 10.5 and the pilot column flow rates discussed above.

Reduction of leachates - and also improvement of the model - would seem to depend on a better understanding of the factors influencing the movement of heat and water into the zone where evaporation takes place. The total amount of heat available is more than enough and, given that leachate production depends on a near-complete balance between water supply and loss by evaporation, a small increase in the latter would have a large effect.

9.3.2 ANALYSES OF LEACHATES FROM LANDFILL CELLS

Average concentrations, over the period September 1989 to 1996, were calculated for the various chemical substances applied to the cells and measured in the leachates. Additionally, the total mass of chemical substance in the leachate was obtained by numerical integration of the product of the weekly or monthly measured concentrations and leachate volumes; interpolation was used when the dates for the two sets of figures did not agree.

Measured concentrations have also been plotted, with smoothing, against time, along with plots for the most appropriate major constituent of the leachate. In most cases this was potassium, a good indicator of the presence of soluble material derived from garden wastes and vegetable matter in refuse (see Section 10.7). The dates of application of chemicals are indicated. The scales have been chosen to maintain a constant ratio, for each of the cells, between the constituent under discussion and the comparison substance.

The results for each category of added substance are discussed below:

a) **TRACERS - CELL 3:**

Lithium and, later, sodium salts were added to Cell 3 as indicators of the behaviour of soluble substances and the permeation of water. The application rates per tonne general waste were: 0,2 kg $Li.t^{-1}$ and 60 kg $Na.t^{-1}$. Table 9.6 shows that the measured average concentrations and masses of both in Cell 3 are amongst the lowest. Except for a possible small lithium peak in 1988/89, Figures 9.12 and 9.13 provide no evidence of a response to the applications of the chemicals. The measured concentrations of sodium and, to a lesser extent, lithium, closely mirror those of potassium.

These results suggest that the water in the leachate was originally part of the refuse with little contribution from the annual rainfall. The lithium peak in the pilot column tracer study (Section 7.3.2) occurred after 84 days. Allowing for the differences in refuse thickness and leachate flow rates, the peak in Cell 3 would thus be expected at about 290 years after application of the chemical, consistent with the absence of evidence of any break-through.

TABLE 9.6: TRACER CHEMICALS (Li and Na) ADDED TO CELL 3 AND FOUND IN LEACHATES OVER PERIOD 1989 TO 1996

SUBSTANCE	CELL	ADDED TO CELL		FOUND IN LEACHATE		FOUND AS % OF ADDED
		Concn. mg/ℓ	Mass kg	Concn. mg/ℓ	Mass g	
Lithium	1	0	0	0.159	4.2	-
	2	0	0	0.082	2.7	-
	3	350-980	0.2	0.032	0.7	0.35
	4	0	0	0.084	4.4	-
	5	0	0	0.030	0.3	
Sodium	1	0	0	1100	31	-
	2	0	0	930	37	-
	3	960	59	200	5	0.008
	4	0	0	910	55	-
	5	0	0	320	3	-

b) CCA - CELL 2:

Copper, chromium and arsenic are the constituents of interest in CCA, details for which are given in Table 9.7 and Figures 9.14 to 9.16. The overall application rates per tonne of general waste were: 74 g $Cu.t^{-1}$; 125 g $Cr.t^{-1}$; 131 g $As.t^{-1}$. These amounts are comparable with those considered to be safe as a result of the pilot-scale studies, namely 67 g $Cu.t^{-1}$; 195 g $Cr.t^{-1}$ and 195 g $As.t^{-1}$ (refer Section 7.4.7).

The mean concentrations of all three elements are less than the values given in Table 3.18 for leachates from other municipal solid waste landfills. The concentrations and masses of all three elements in Cell 2 leachates are not significantly greater than those for the remaining, undosed, cells. The total masses in the leachate are a very small percentage of the applied amount. The time plots show that while chromium concentrations quite closely follow those of the soluble ion potassium, those of copper and arsenic are much less correlated.

It thus appears that all three constituents of CCA were retained in the cell.

TABLE 9.7: METALLIC CHEMICALS (Cu, Cr, As) ADDED TO CELL 2 AND FOUND IN LEACHATES OVER PERIOD 1989 TO 1996

SUBSTANCE	CELL	ADDED TO CELL		FOUND IN LEACHATE		FOUND AS % OF ADDED
		Concn. mg/ℓ	Mass kg	Concn. mg/ℓ	Mass g	
Copper	1	0	0	0.032	1.0	-
	2	-	73	0.029	1.0	0.0014
	3	0	0	0.021	0.4	-
	4	0	0	0.028	1.2	-
	5	0	0	0.025	0.2	-
Chromium	1	0	0	0.070	1.8	-
	2	-	122	0.056	2.3	0.002
	3	0	0	0.019	0.4	-
	4	0	0	0.056	4.3	-
	5	0	0	0.015	0.1	-
Arsenic	1	0	0	0.012	0.4	-
	2	-	128	0.008	0.3	0.0002
	3	0	0	0.005	0.1	-
	4	0	0	0.011	0.4	-
	5	0	0	0.015	0.1	-

c) **PHENOLIC EFFLUENT - CELL 4:**

Table 9.8 and Figure 9.17 summarise the results for phenol, added in the form of gasworks effluent. The application rate per tonne of general waste was 103 $g.t^{-1}$.

Once again, the concentrations and masses, found in the leachates from Cell 4 to which the phenol was added, were lower than those in some of the other cells. The figure shows an interesting correlation between phenol and COD, which usually has a high concentration in the early, acid fermentation, stage of a landfill. It would seem that either this stage favours the formation of phenol or the later stages are conducive to it's destruction. In any event, there is no evidence of any break-through of applied phenol.

d) **DIGESTED SLUDGE AND UREA - CELL 5:**

The indicators for these materials are ammonia and zinc. The latter has the highest concentration of the trace metals in the digested sludge applied in these experiments. Application rates per tonne of general waste were 280 g $N.t^{-1}$ and 0.6 g $Zn.t^{-1}$, respectively.

According to Table 9.9 the ammonia levels in Cell 5 are in complete contrast to thosein the other cells. The time plots show that ammonia and potassium usually moved in unison, with a ratio of about 0.8. However, in Cell 5, the test cell,

ammonia levels were only about a fifth of those of potassium. Zinc concentrations were relatively high in 1988/89 in all the cells but generally low thereafter except for a minor peak in Cell 5 in 1993. The general concentration of zinc was considerably less than that given in Table 3.18, for leachates from municipal landfills. Average zinc levels in Cell 5 were the second lowest amongst the cells.

TABLE 9.8: PHENOLIC CHEMICALS ADDED TO CELL 4 AND FOUND IN LEACHATES OVER PERIOD 1989 TO 1996

SUBSTANCE	CELL	ADDED TO CELL		FOUND IN LEACHATE		FOUND AS % OF ADDED
		Concn. mg/ℓ	Mass kg	Concn. mg/ℓ	Mass g	
Phenol	1	0	0	0.0006	0.021	-
	2	0	0	0.0012	0.023	-
	3	0	0	0.0001	0.001	-
	4	300	101	0.0004	0.006	0.000006
	5	0	0	0.0000	0.0004	-

TABLE 9.9: NITROGENOUS AND ZINC CHEMICALS ADDED TO CELL 5 AND FOUND IN LEACHATES OVER PERIOD 1989 TO 1996

SUBSTANCE	CELL	ADDED TO CELL		FOUND IN LEACHATE		FOUND AS % OF ADDED
		Concn. mg/ℓ	Mass kg	Concn. mg/ℓ	Mass g	
Ammonia (in urea & sludge)	1	0	0	1110	33	-
	2	0	0	930	38	-
	3	0	0	200	5	-
	4	0	0	810	56	-
	5	-	279	50	1	0.0004
Zinc (in sludge)	1	0	0	0.197	4.8	-
	2	0	0	0.070	2.1	-
	3	0	0	0.041	0.8	-
	4	0	0	0.155	4.1	-
	5	-	0.6	0.048	1.4	0.2

e) **SUMMARY OF CHEMICALS APPLIED TO LANDFILL CELLS AND FOUND IN LEACHATES:**

The various chemicals applied to the landfill cells and recovered in the leachates from the landfill cells are summarised in Table 9.10.

TABLE 9.10: SUMMARY OF CHEMICALS APPLIED TO LANDFILL CELLS AND FOUND IN LEACHATES OVER THE PERIOD 1989 TO 1996:

LANDFILL CELL	MASS OF CHEMICALS ADDED TO CELLS	APPLICATION RATES OF CHEMICALS PER TONNE OF GENERAL WASTE*	CHEMICALS FOUND IN LEACHATE AS % OF THAT ADDED
Cell 2	73 kg Cu 122 kg Cr 128 kg As	74 g $Cu.t^{-1}$ 125 g $Cr.t^{-1}$ 131 g $As.t^{-1}$	0,0014 0,002 0,0002
Cell 3	0,2 kg Li 59 kg Na	0,2 g $Li.t^{-1}$ 60 g $Na.t^{-1}$	0,35 0,008
Cell 4	101 kg Phenol	103 g $Phenol.t^{-1}$	0,000006
Cell 5	280 kg N 0,6 kg Zn	285 g N.t-1 0,6 g $Zn.t^{-1}$	0,0004

* Assumed bulk wet *in-situ* density of general waste = 1 000 $kg.m^{-3}$
Assumed mass of general waste per cell = 980 tonne

According to the data in Table 9.10, there was no evidence of breakthrough of any of the applied chemicals, even soluble tracer salts, from the landfill cells over a period of 7 years. All applied chemicals were retained (attenuated) by the landfilled wastes.

9.4 CONCLUSIONS OF FULL-SCALE STUDIES AT COASTAL PARK

1. The most striking finding of these studies is the small amount of leachate that found it's way to the base of the cells, on average, 2.5% of the annual rainfall. It would appear that rain water was absorbed and mostly held by the refuse, subsequently being drawn near the surface by capillary action, where it evaporated during the course of the year. Given a void space of 40% and an annual rainfall of 600 mm, the thickness of the layer affected by rainwater would be about 1500 mm.

2. The average rate of accumulation of leachate, 14 mm/year, was far lower than that found in the associated pilot column studies, where saturated conditions and low evaporation prevailed. At this rate, soluble salts added at the surface might be

expected to take over one hundred and fifty years to pass through 5 m of refuse. Most of the liquid collected over the nine years of the project must therefore have been present in the material when laid down.

3. Seasonal variations in leachate flow rate were evident to varying degrees in all cells, becoming somewhat more marked as the material aged. There was an average lag of two months between early winter rainfall peaks and leachate peaks, but late in the rainy season the response to rainfall was both more immediate and more marked. As noted above, this does not necessarily mean that the some of the rain passed through the entire bed in one season. It is more likely that the presence of stored rain water in the upper layer of the bed increased the pressure and therefore the flow rate lower down.

4. It was possible to account for some of the features of the seasonal variations by assuming leachate production rate to be directly proportional to the amount of stored water. This model even gave a reasonable prediction of the much increased flow rate that resulted from the supplemental wetting program carried out on Cell 4 during the first seven months of 1996.

5. Evaporation plays such an important role in minimising the amount of leachate that it might be worthy of further study. For all except two or three months of the year, the evaporation rate in surface pans much exceeds rainfall, but leachate flows suggest that considerable volumes of stored water persist until late summer. The rate determining step is therefore probably the transport of stored water to the evaporation zone near the surface.

6. There is no evidence of breakthrough of any of the applied chemicals, even soluble tracer salts, into the leachates, over a period of 7 years. Not only were the total masses of chemicals found in the leachates a very small percentage of the applied amount, but the amounts and concentrations found in the treated landfill cells were no more than those in the untreated comparison landfill cells. This finding is consistent with the expectation of long residence times resulting from low leachate production rates.

9.5 REFERENCES

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Futre, H (1986) Cape Town waste analysis. Unpublished paper. City of Cape Town, City Engineer's Department, P O Box 1694, Cape Town, 8000 South Africa.

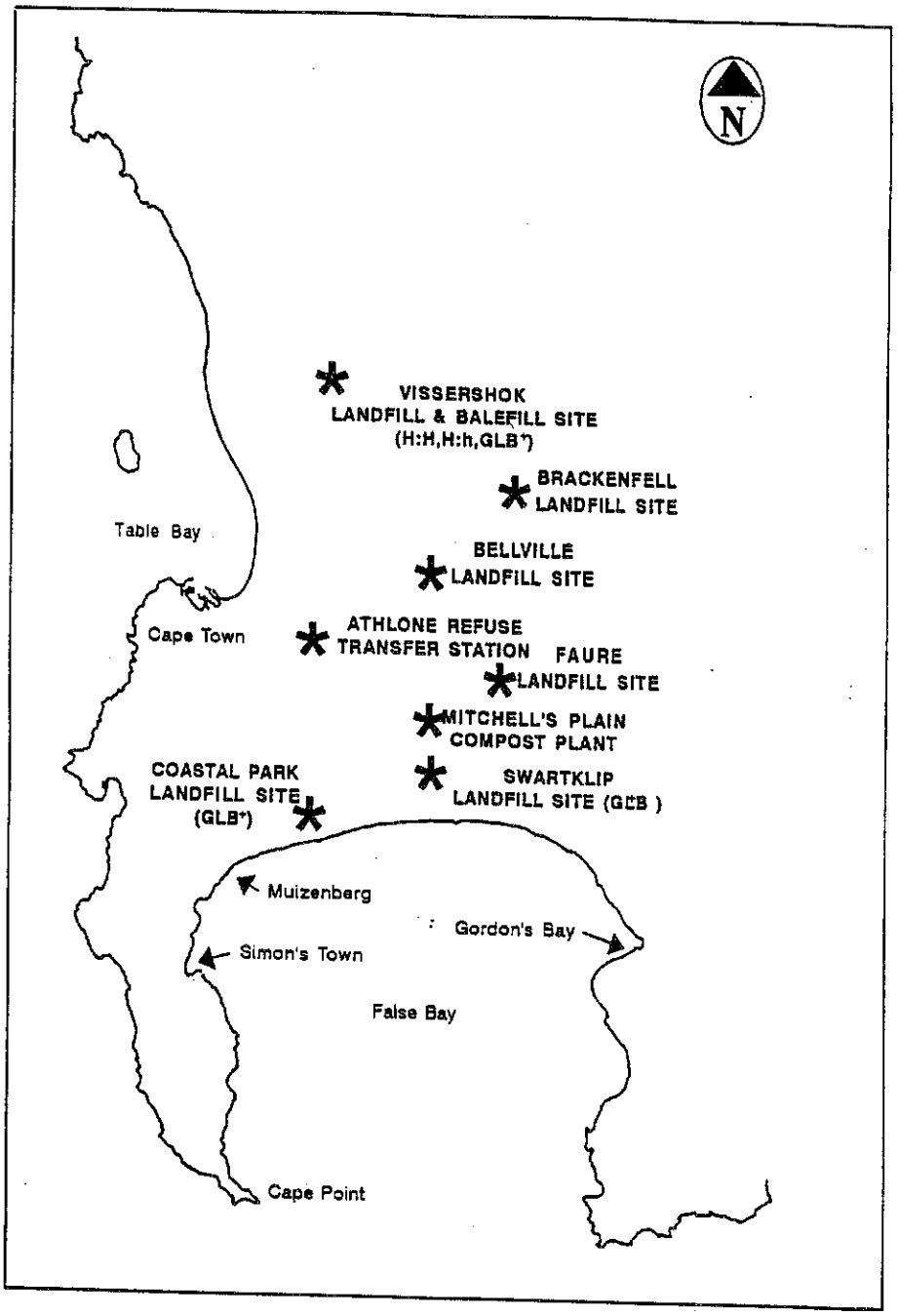


Figure 9.1 **Location of Coastal Park landfill within the Cape Metropolitan area**

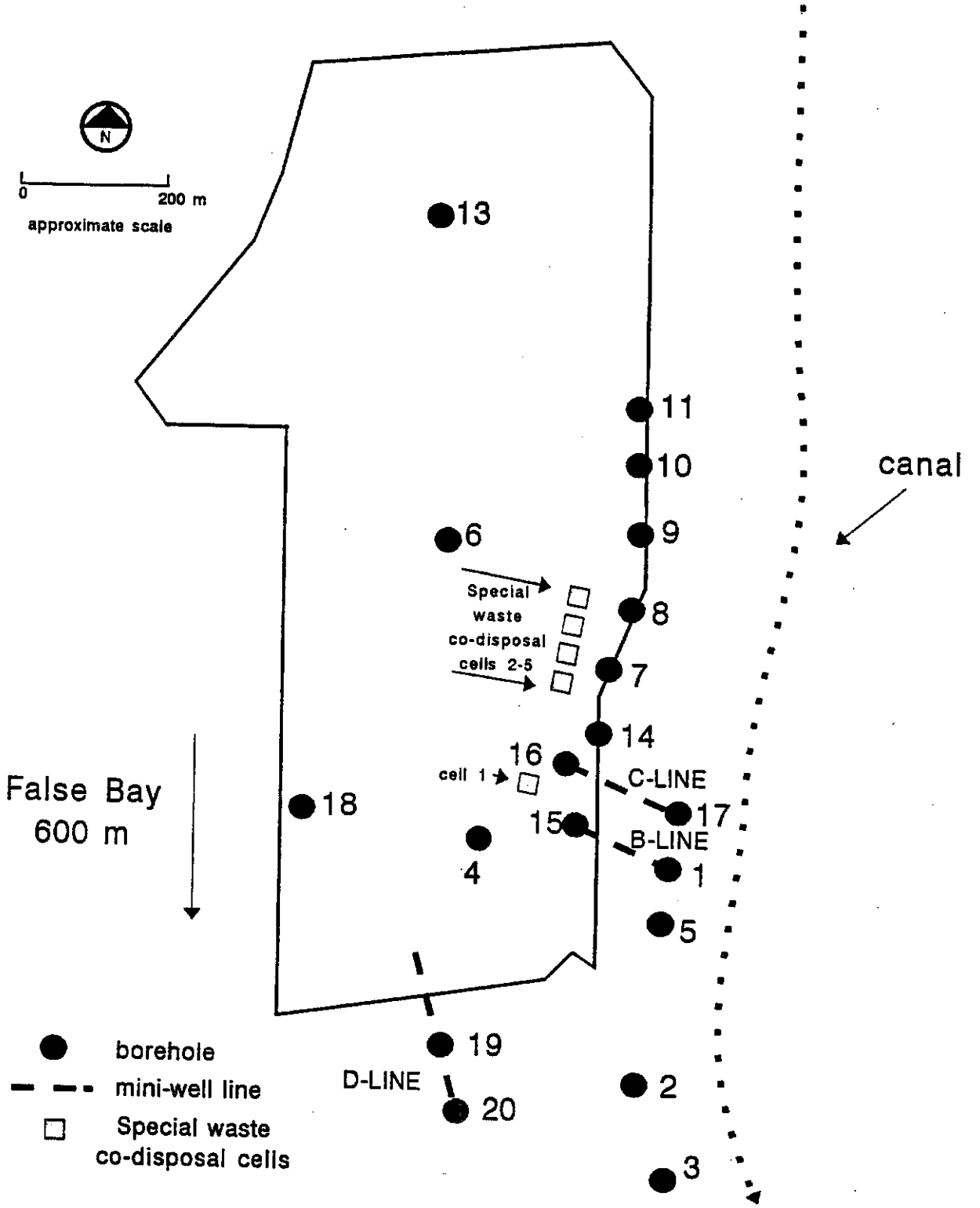


Figure 9.2 **Location of the special waste landfill cells at the Coastal Park landfill**

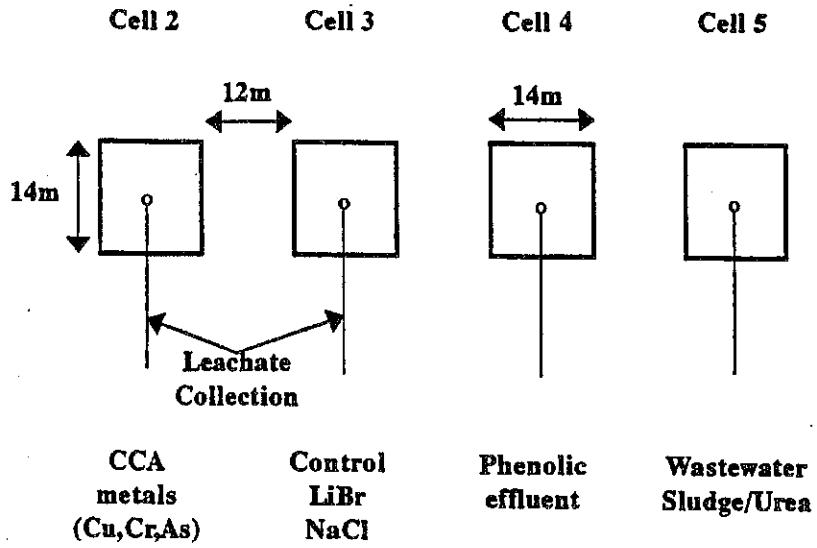


Figure 9.3 Layout of landfill cells 2 to5 and types of special waste applied

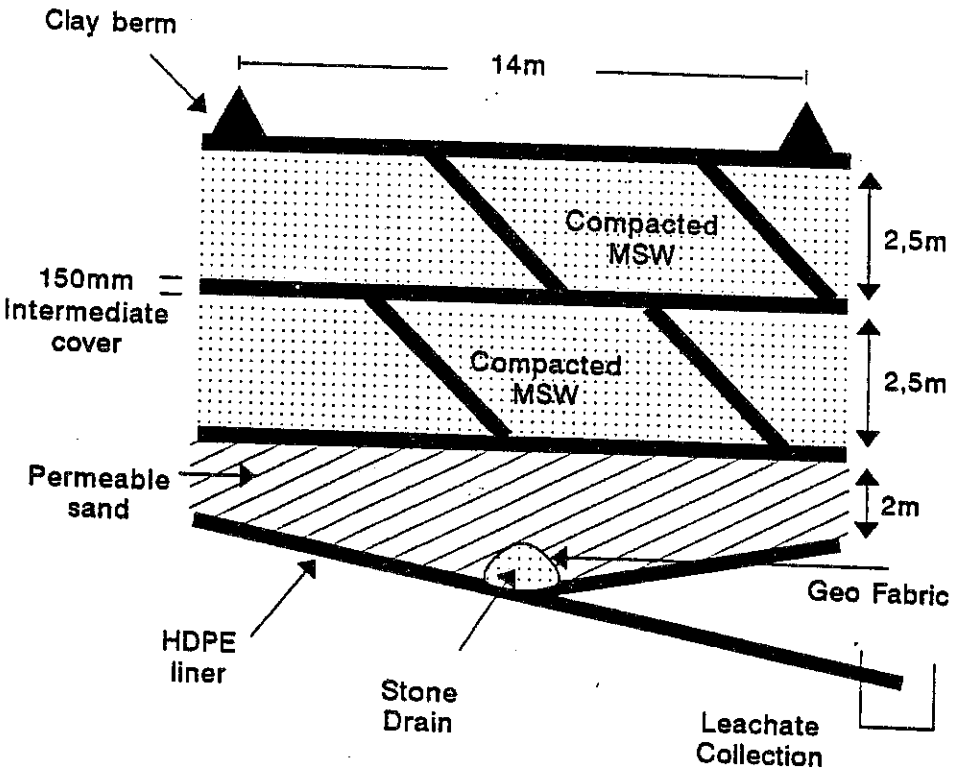
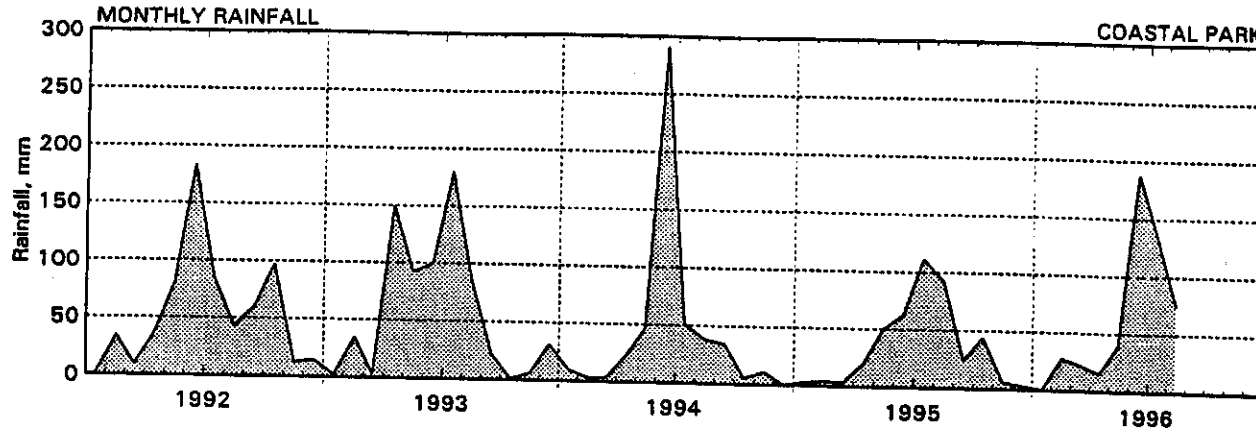
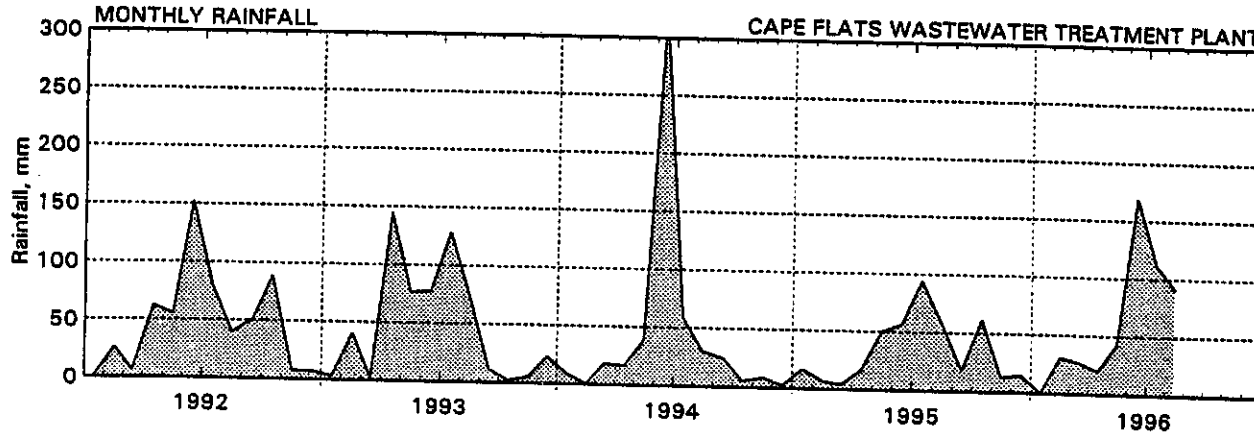
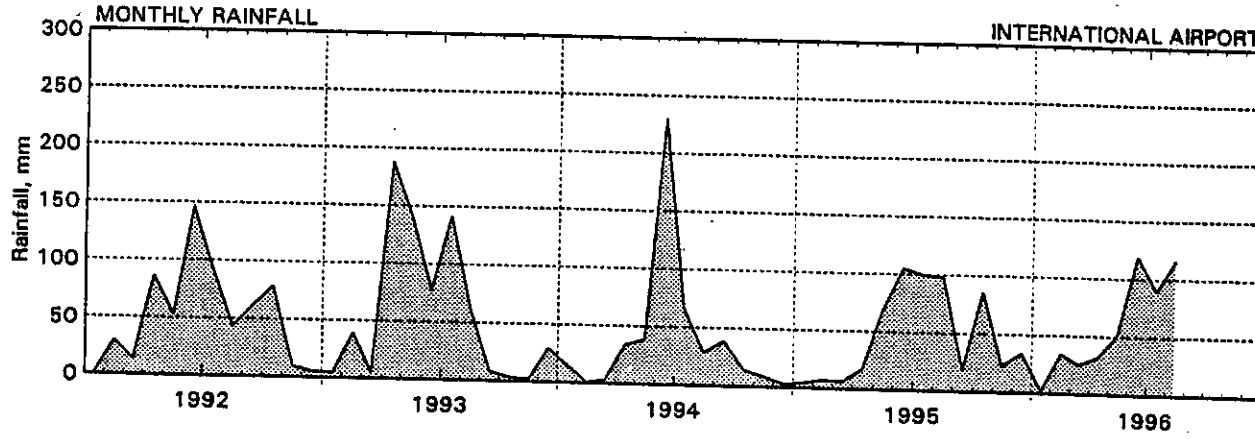
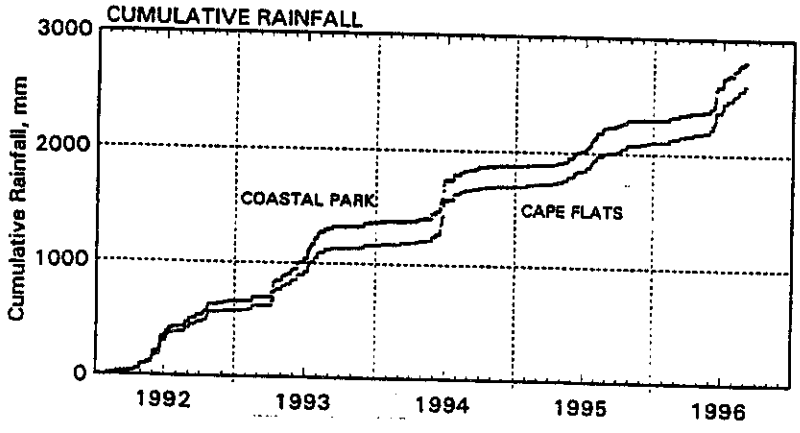


Figure 9.4 Construction details of the landfill cells 2 to 5









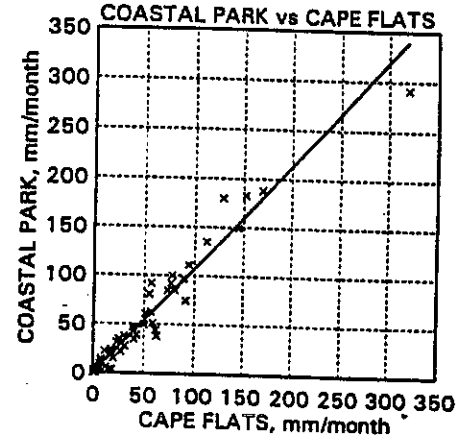


Figure 9.5 Comparison of rainfall figures

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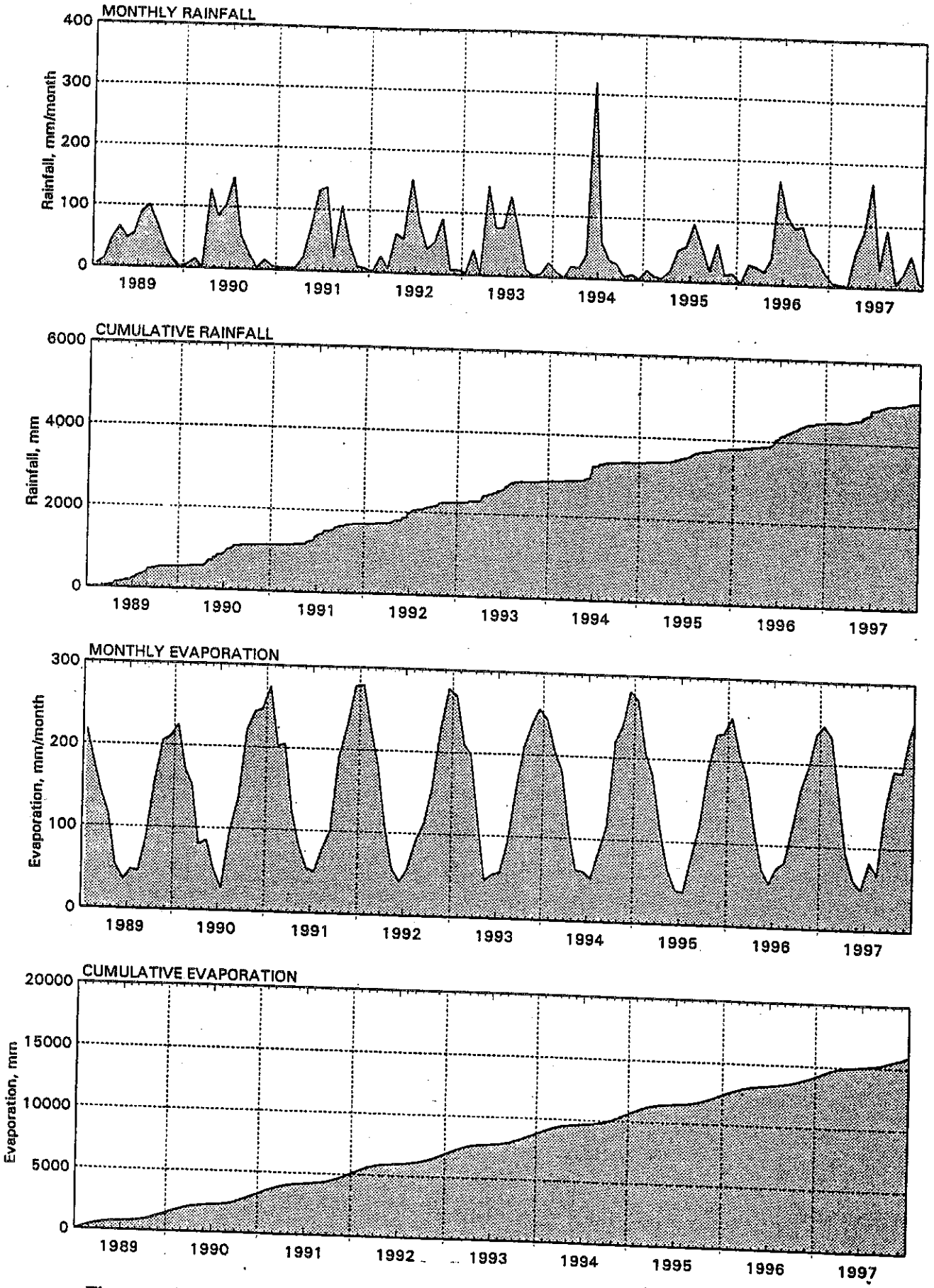

Figure 9.6 Rainfall and evaporation - Cape Flats

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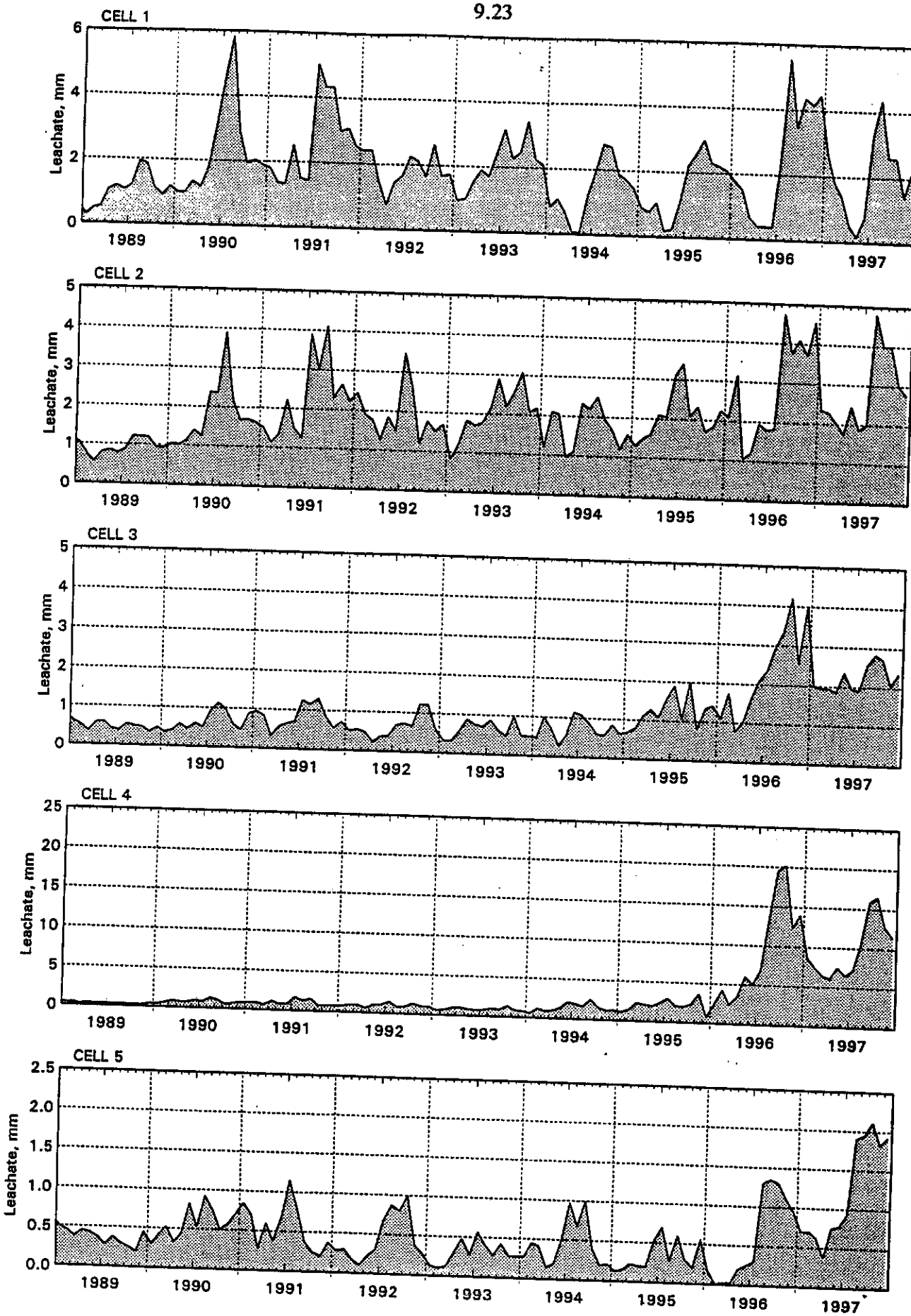

Figure 9.7 Monthly leachates

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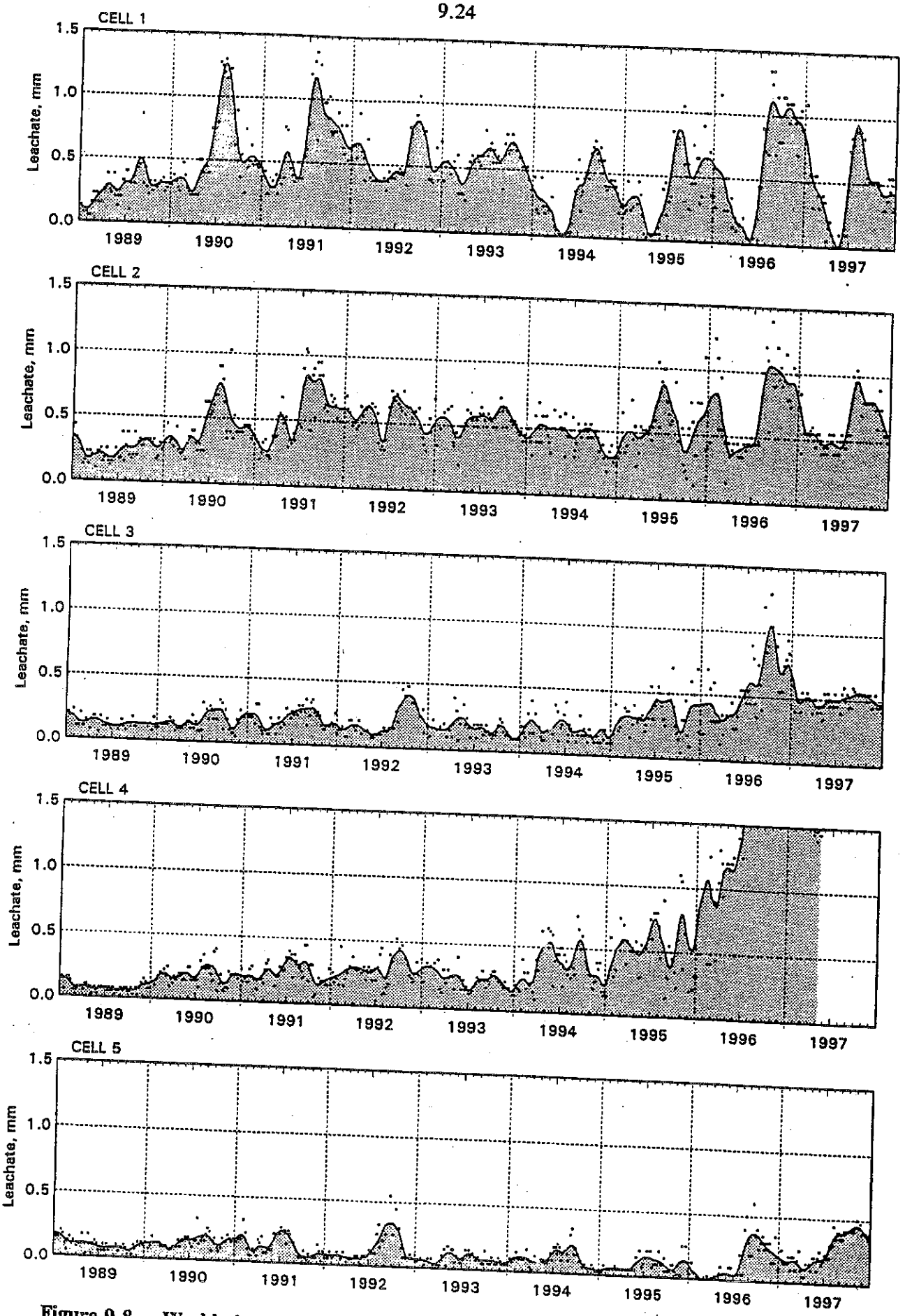

Figure 9.8 Weekly leachates

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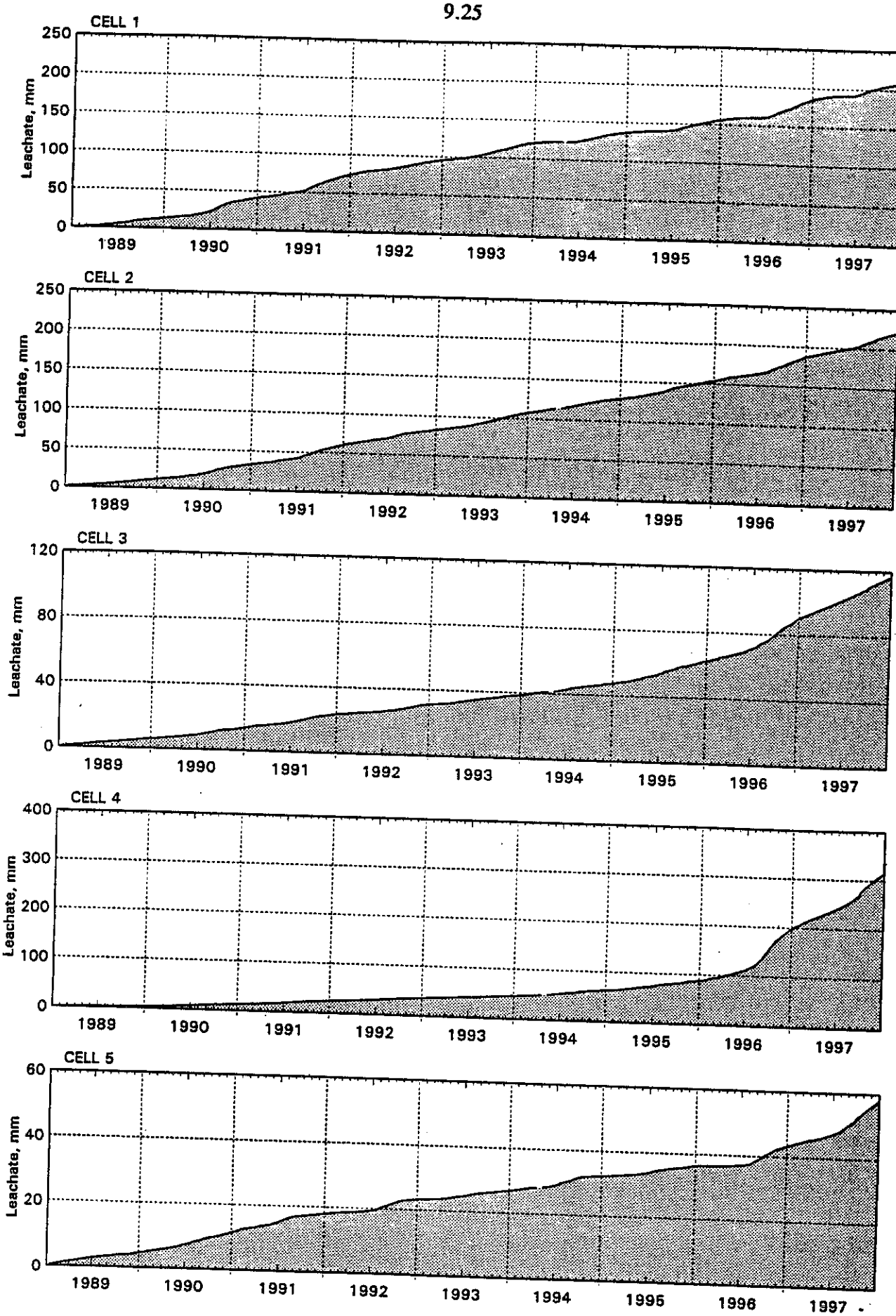

Figure 9.9 Cumulative leachates

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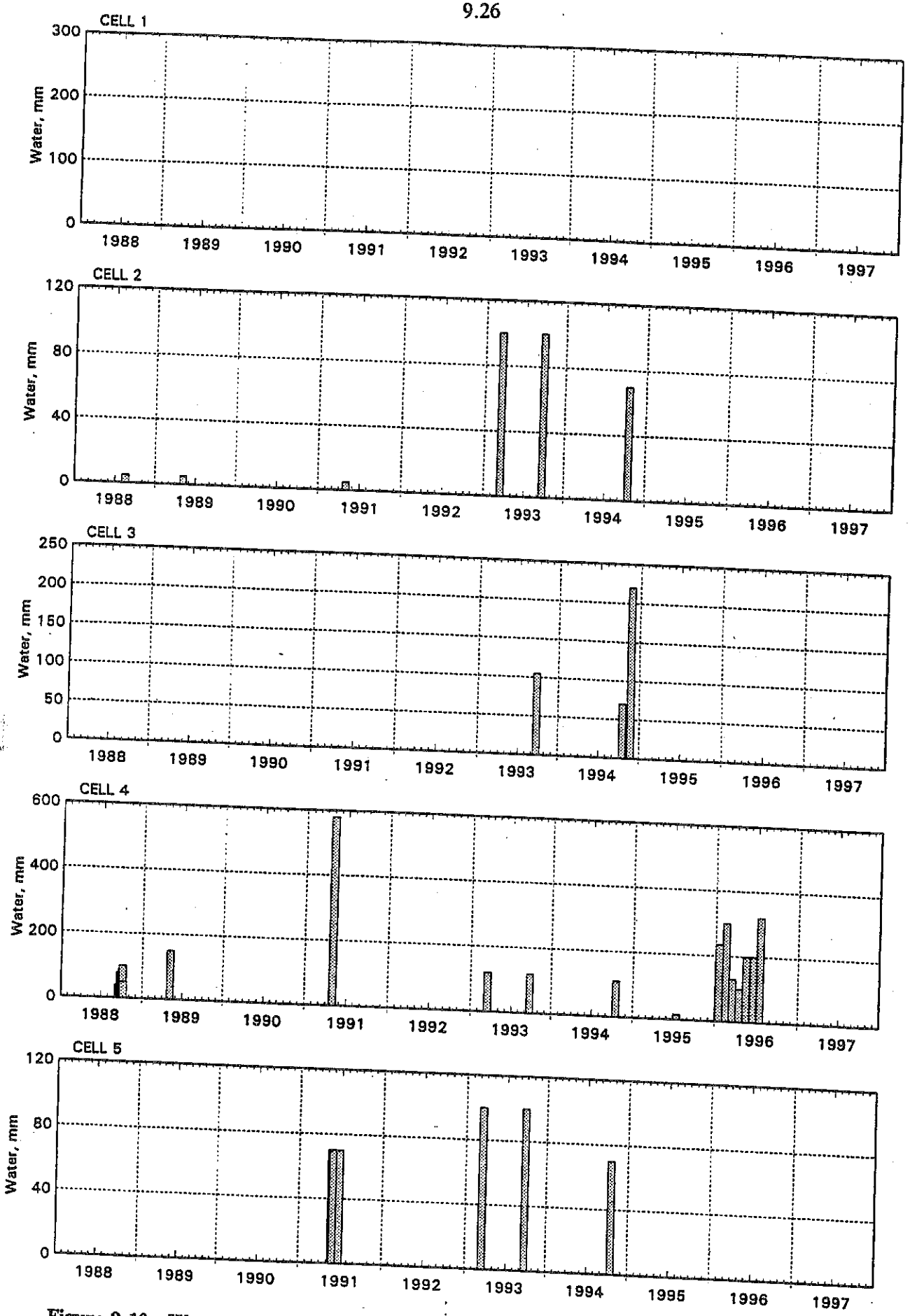

Figure 9.10 Water applications - monthly totals

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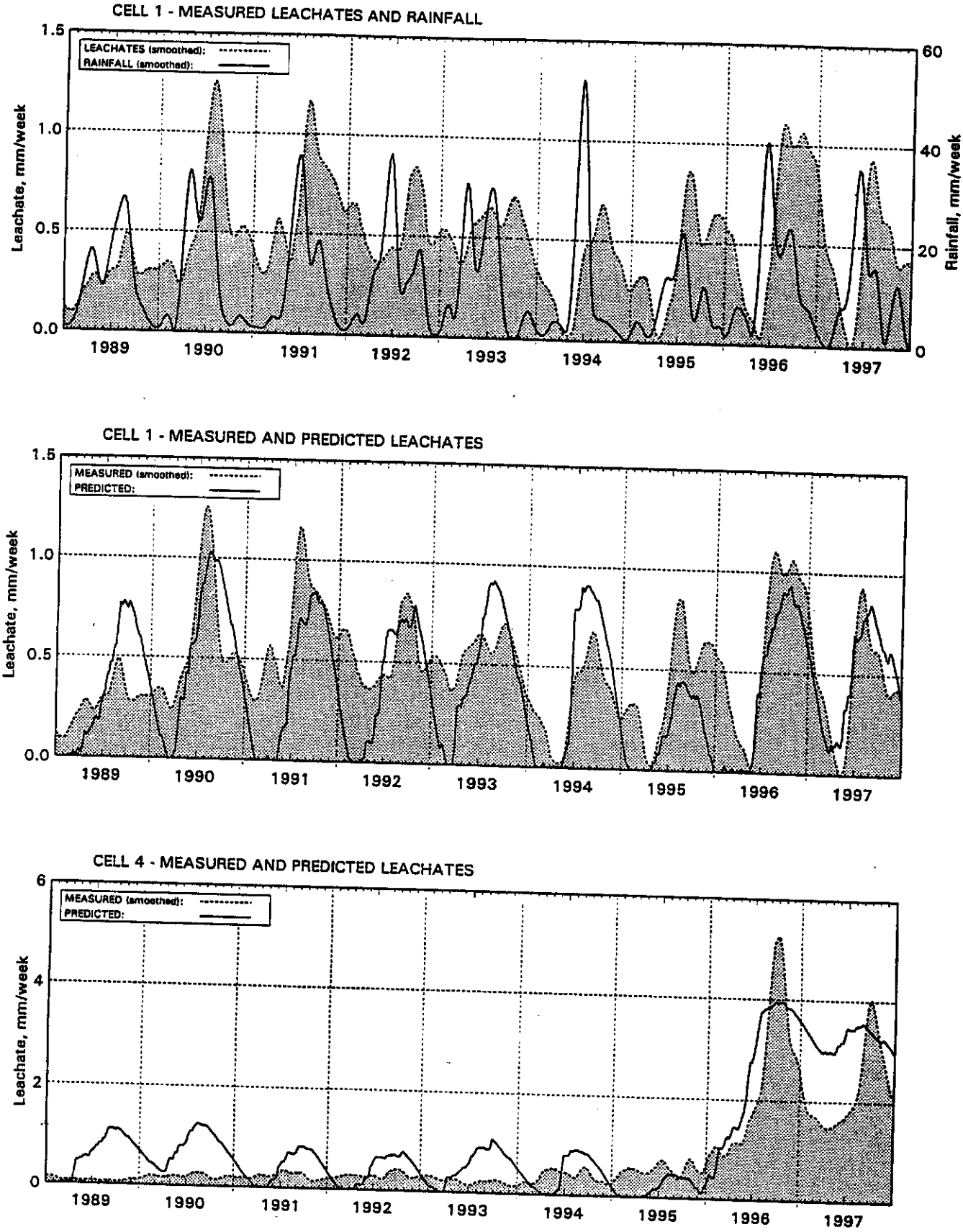

Figure 9.11 Seasonal effects

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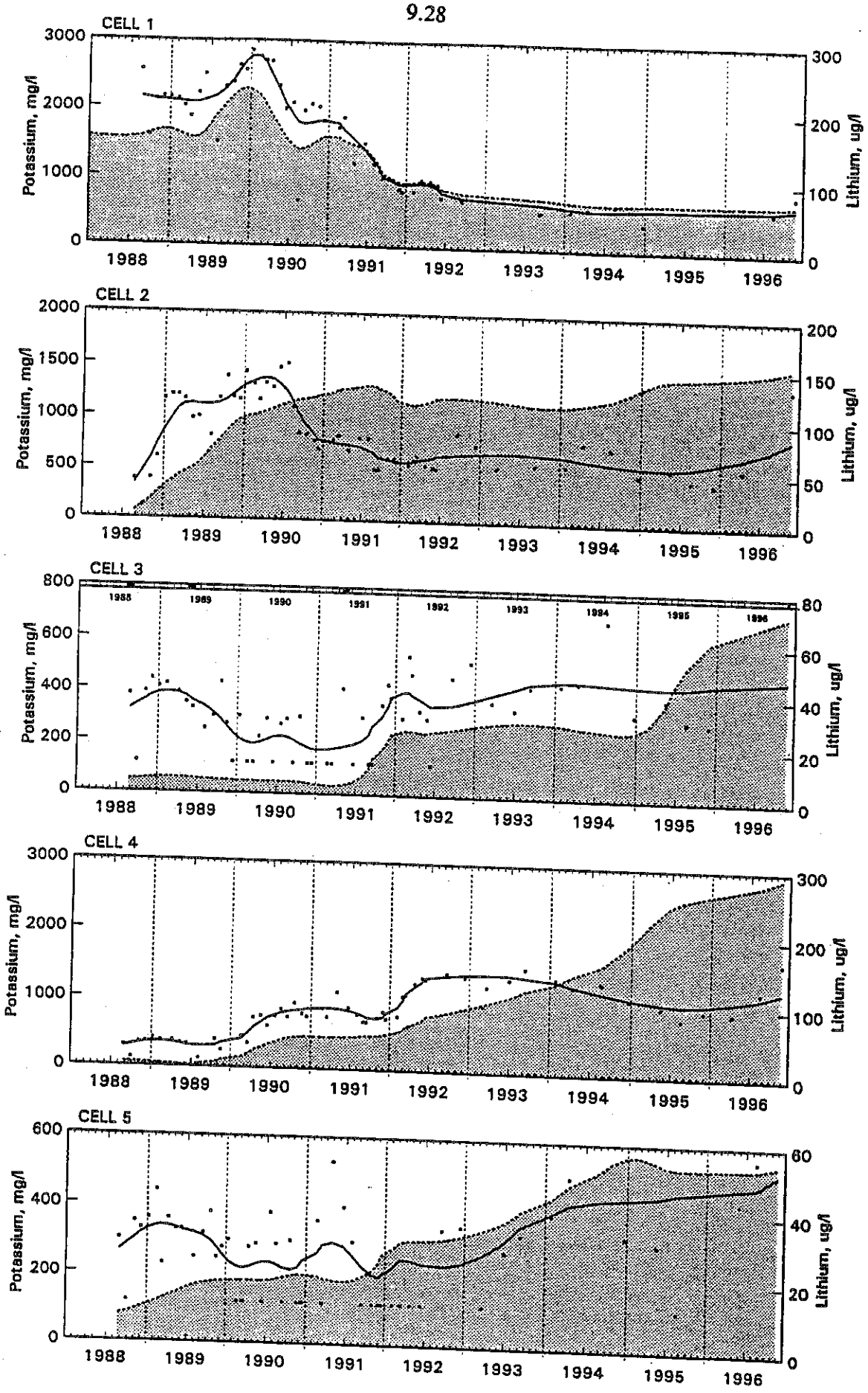

Dotted line - Potassium Solid line - Lithium Bar - Chemical applications

Figure 9.12 Lithium and potassium

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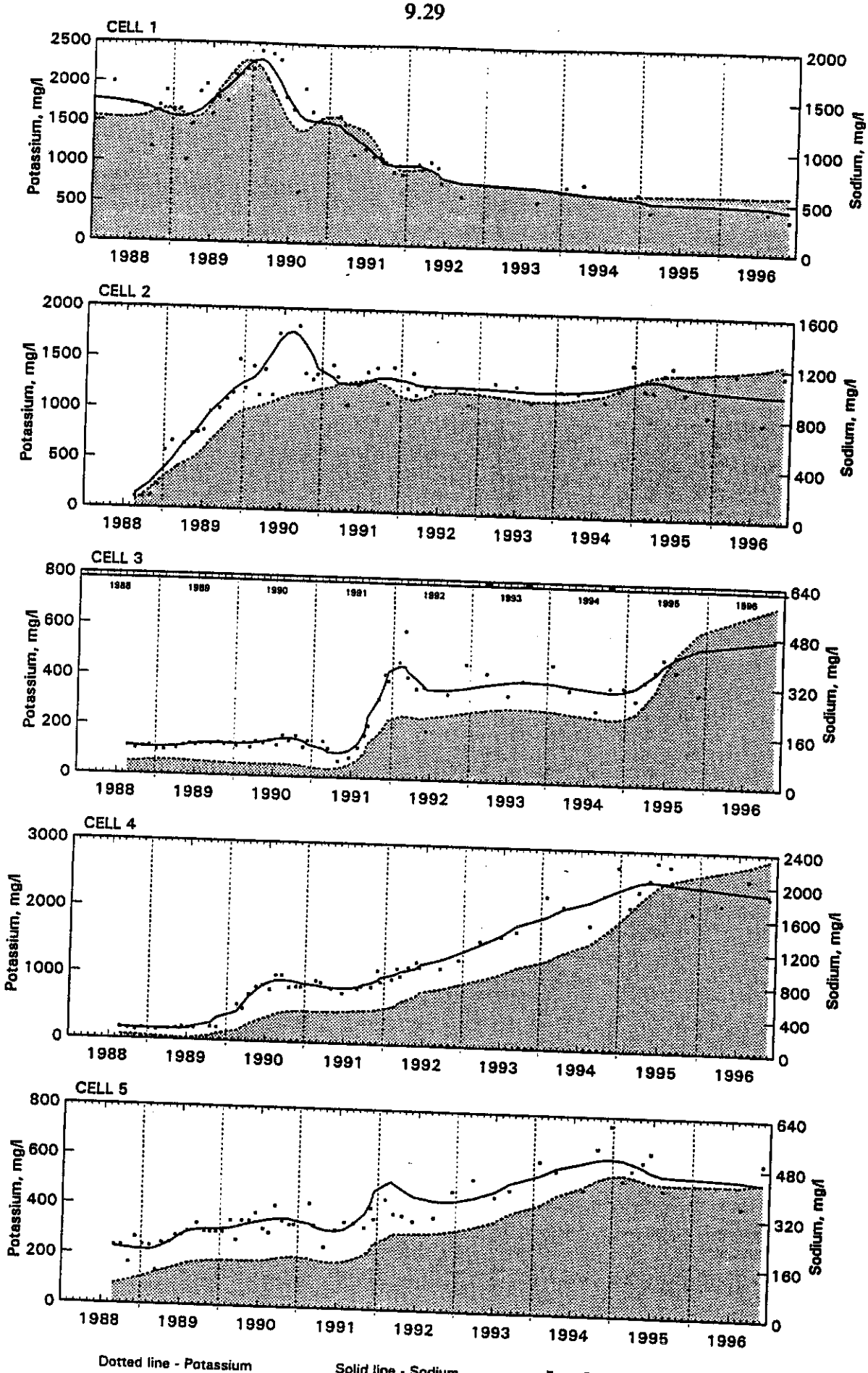

Figure 9.13 Sodium and potassium

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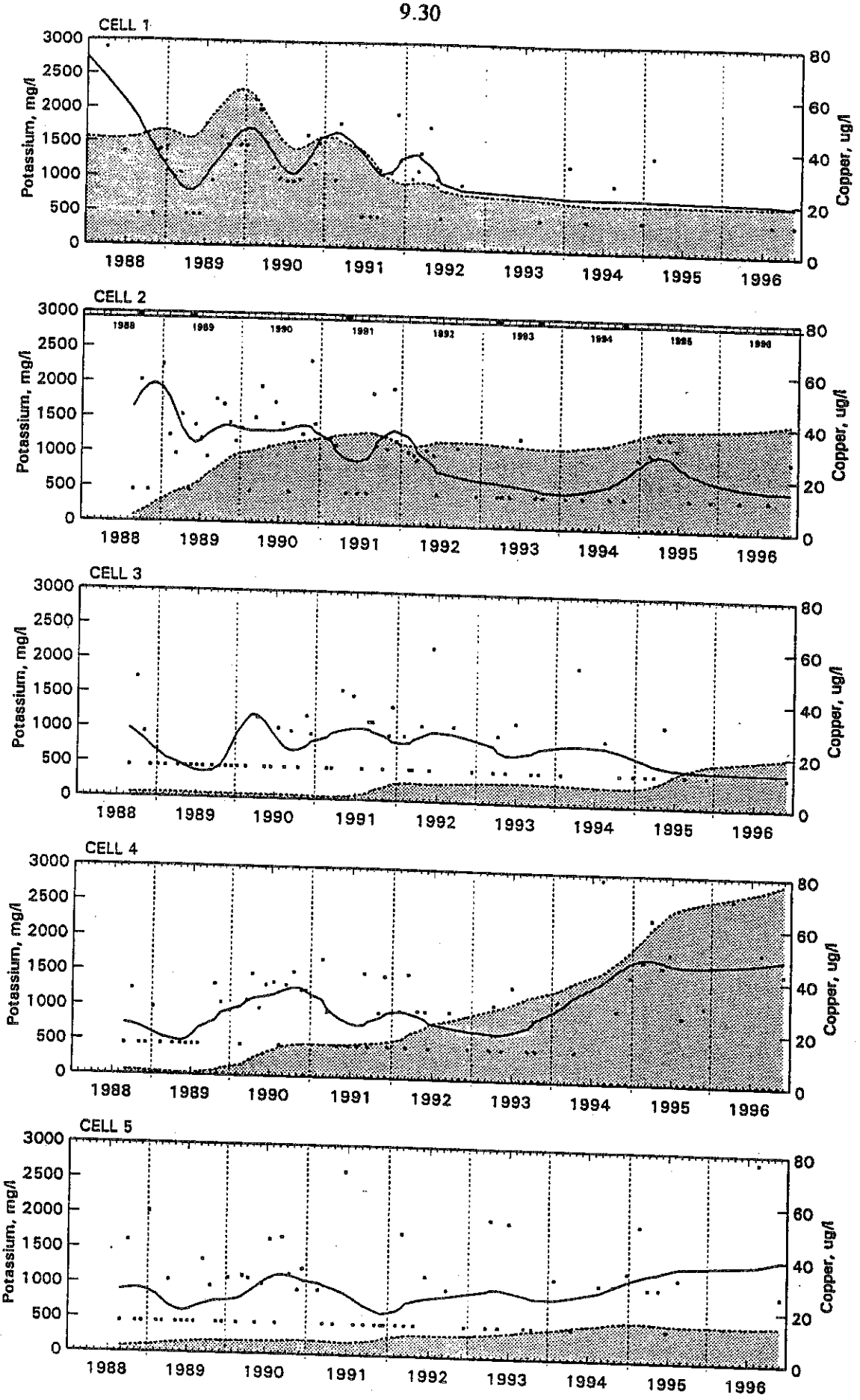

Figure 9.14 Copper and potassium

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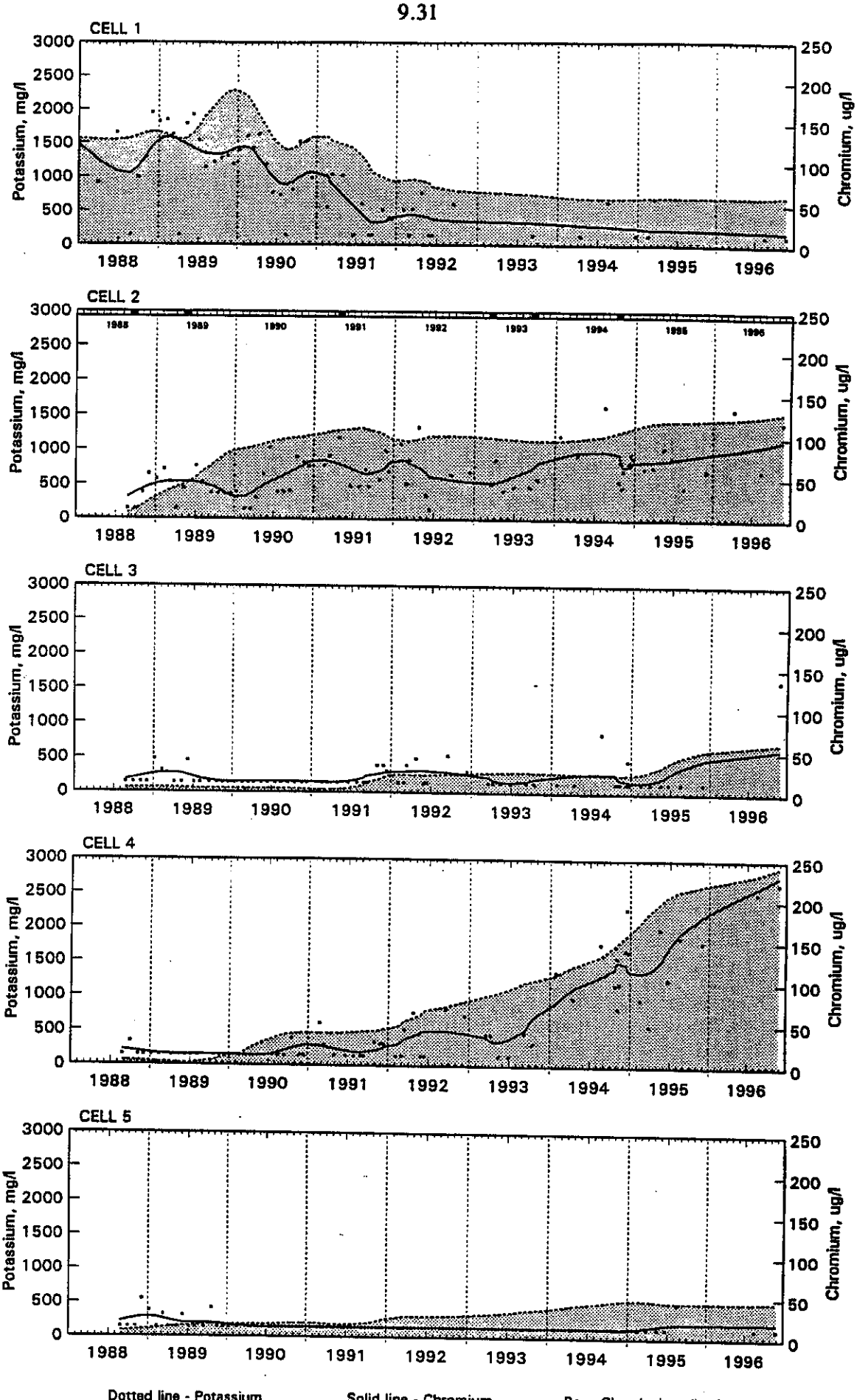

Figure 9.15 Chromium and potassium

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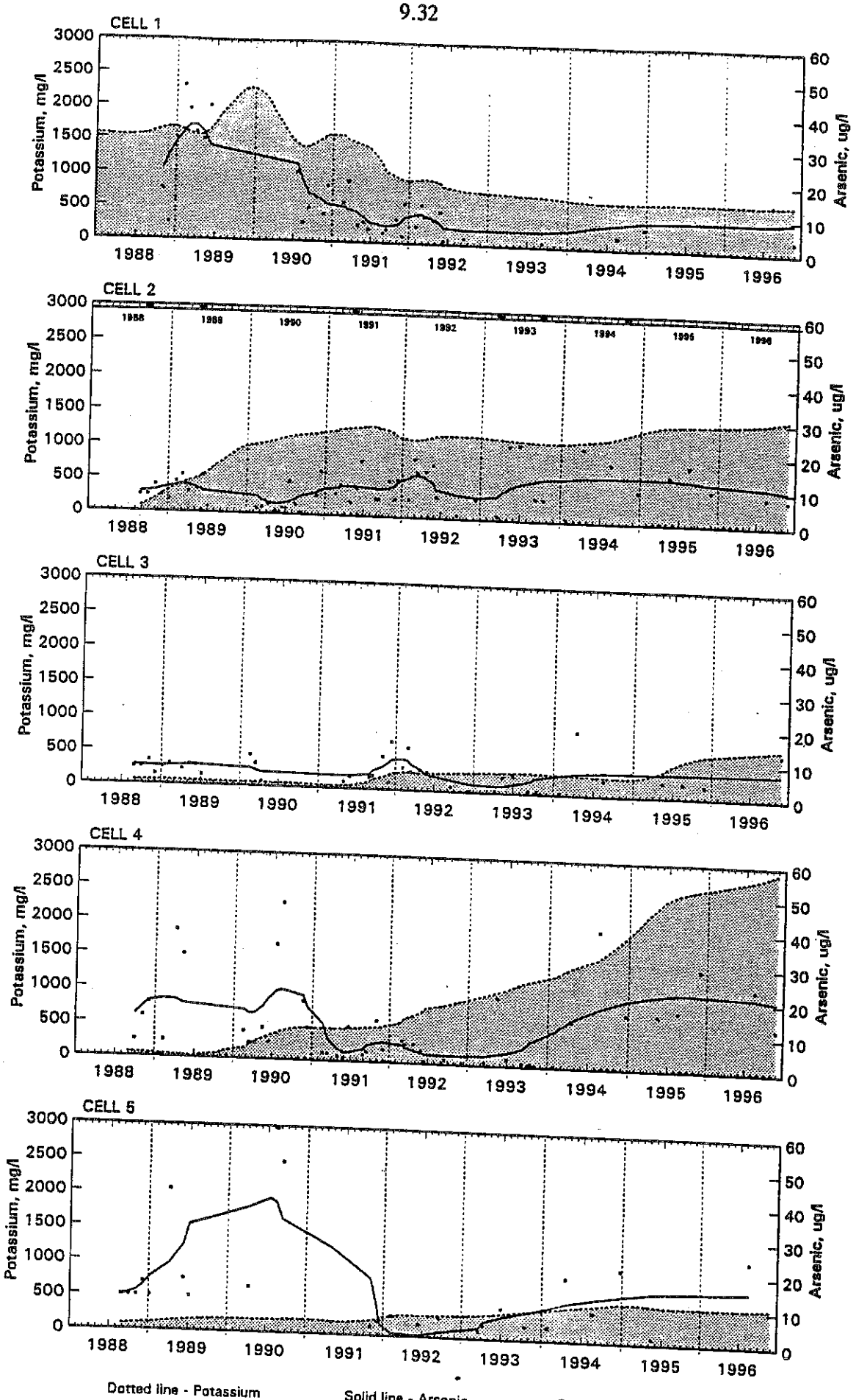
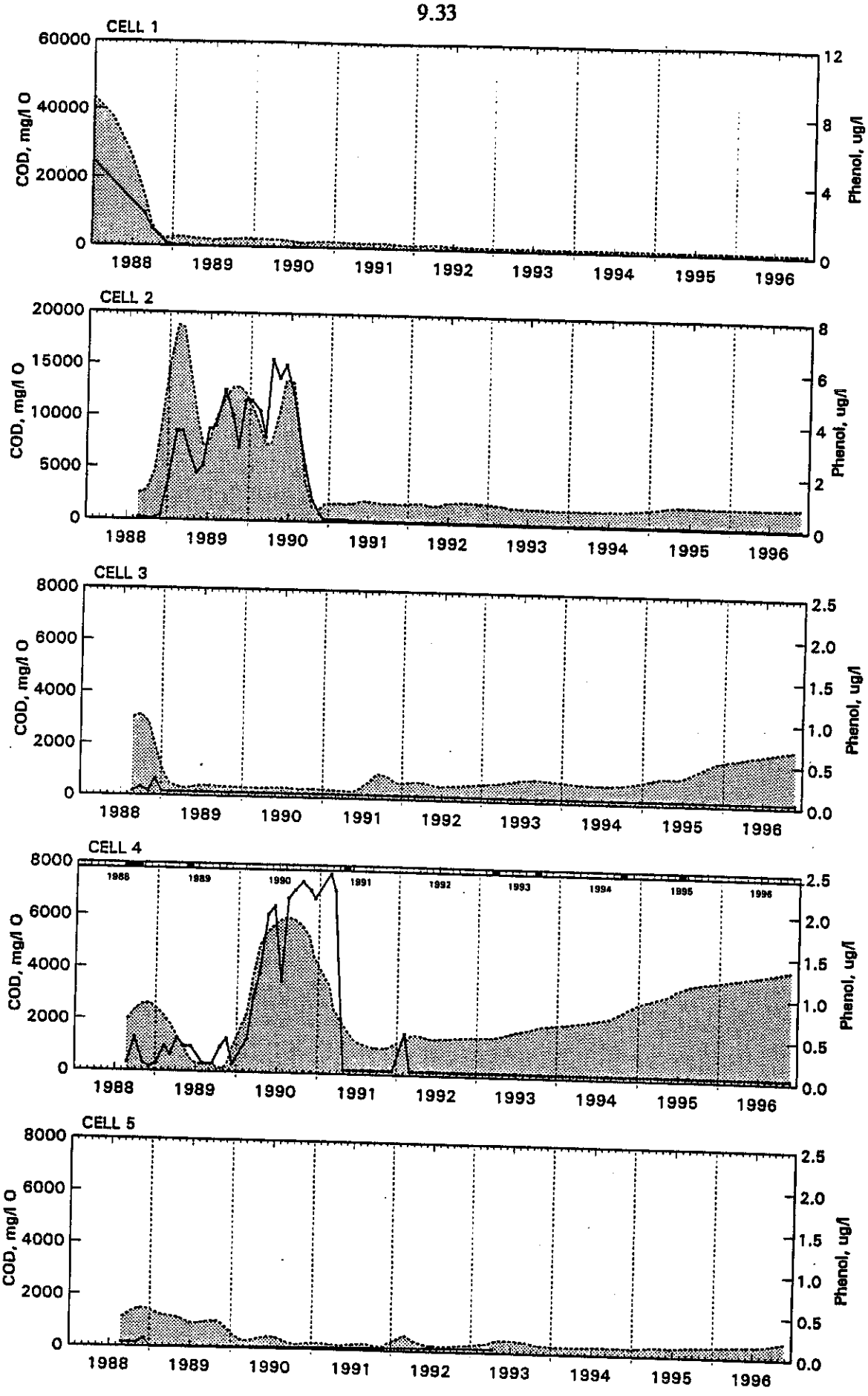


Figure 9.16 Arsenic and potassium

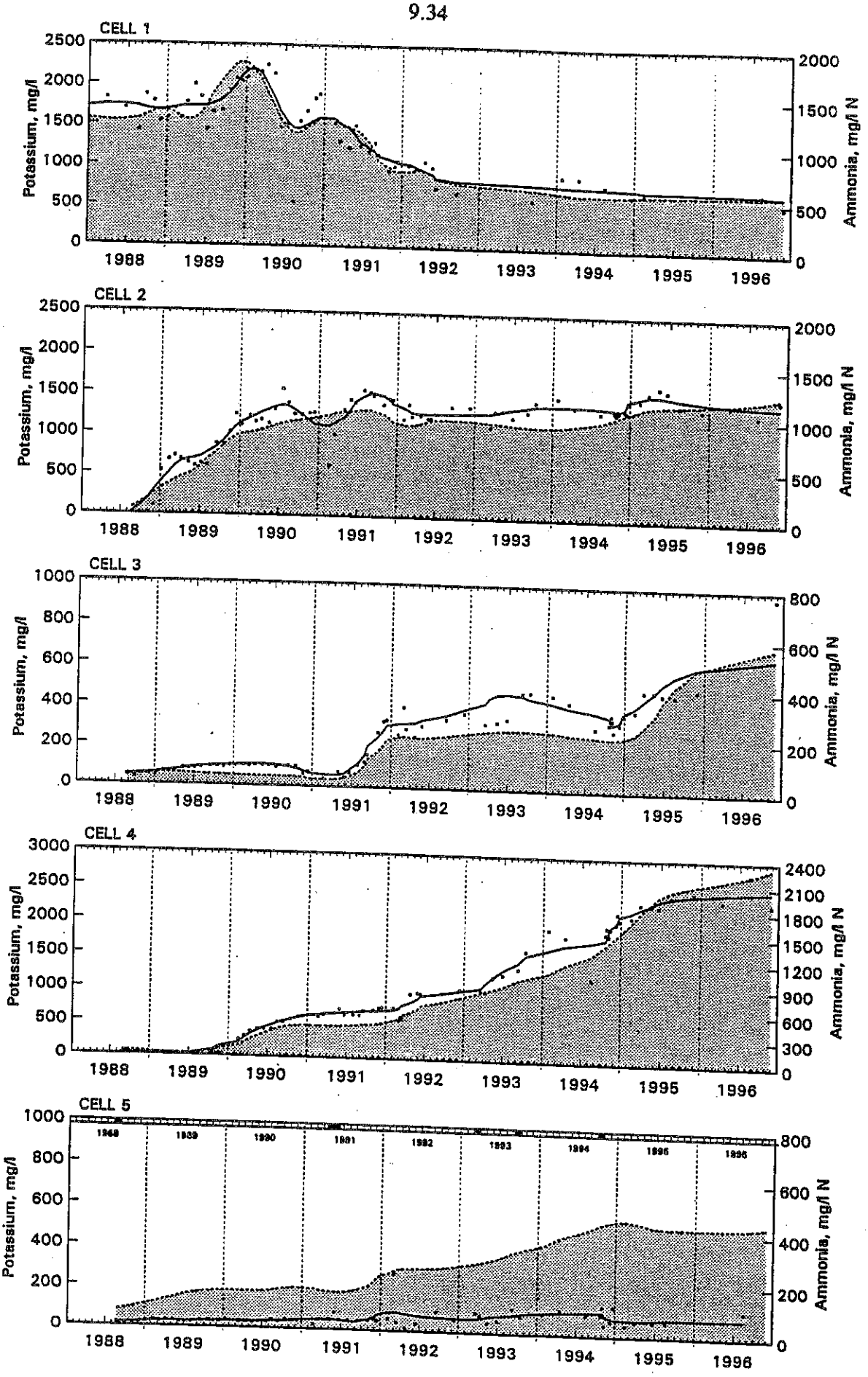
21MAY98



Dotted line - Potassium Solid line - Phenol Bar - Chemical applications

Figure 9.17 Phenol and COD

21MAY98



Dotted line - Potassium Solid line - Ammonia Bar - Chemical applications

Figure 9.18 Ammonia and potassium

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SECTION C

ASSOCIATED STUDIES

AT

COASTAL PARK

CHAPTER 10

ASSOCIATED STUDIES AT COASTAL PARK

10.1 INTRODUCTION

The two co-disposal research projects which were carried out by the Cape Metropolitan Council at the Coastal Park landfill site during the period 1991 - 1997 were instrumental in stimulating research into various other landfill matters. These associated studies at the Coastal Park landfill site provided supplemental information relating to a co-disposal operation and considerably broadened the scope of the project. For this reason, these associated studies are included in this report.

The associated studies were carried out by various research organisations and dealt with the following aspects:

a) Water balance, evapotranspiration, leachate flow and dilution at Coastal Park landfill;
Prof. G E Blight - Witwatersrand University

b) Lateral movement of soluble salts at Coastal Park landfill;
Prof. G E Blight - Witwatersrand University

c) Computer model to predict movement of leachate within a landfill;
Prof. K Vorster - Pretoria Technikon

d) Hydrological, geochemical and biological significance of the vadose zone and its role as a buffer in contaminated soil systems: A literature review;
Mr T J Harraway - University of Cape Town

e) Chemical characterisation of landfill leachate and its potential mobility through the Cape Flats sand: Abstract;
Mr T J Harraway - University of Cape Town

f) Evaluation of chemical composition of leachate and ground-water from the Coastal Park landfill site.
Mr J G Stow and Mr I Morrison - Cape Metropolitan Council

The following sections reflect the results from the associated studies.

SECTION 10.2

WATER BALANCE, EVAPOTRANSPIRATION, LEACHATE FLOW AND DILUTION AT COASTAL PARK LANDFILL

By

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10.2.1 INTRODUCTION

This Chapter will deal with three aspects of the hydrological performance of the Coastal Park landfill:

a) Measurements of rainfall and leachate outflow have enabled a complete water balance to be constructed for Coastal Park. This allows the actual evapotranspiration losses from the landfill surface to be evaluated.

b) Measurements of the radiation balance at Coastal Park have enabled independent calculations to be made of the component of evapotranspiration due to incoming solar radiation, on four occasions during the year. The results are compared with annual evapotranspiration derived from the water balance, and with A-pan evaporation.

c) A knowledge of the groundwater analysis upstream of the landfill, together with the analysis of leachate and leachate flow rate and estimated flow velocities in the ground water beneath the landfill, in principle allows the calculation of the dilution of the leachate outflow by the groundwater. This prediction can be compared with actual groundwater analyses downstream of the landfill to confirm the prediction.

10.2.2 THE WATER BALANCE AT COASTAL PARK

Coastal Park is the only landfill in South Africa where the flow of leachate from the landfill can be sampled and measured. This is made possible at Coastal Park by the five lysimeter cells that have been installed on the eastern side of the landfill. Rainfall and A-pan evaporation is also recorded at Coastal Park.

The water balance for the landfill can be written as:

Output = (Input + Production) - (Losses + change in Storage)..... (1a)
or Leachate = Precipitation - Runoff - Evapotranspiration - Change in Water Stored.. (1b)

Other terms, such as water produced by decomposition and the water exhaled with landfill gas could be included, but these terms are minor compared with those in equation (1b).

10.2.3 RUNOFF FROM LANDFILL SURFACE

Infiltration rates into the sand cover at the landfill were measured by means of double ring infiltrometers. Although the sand surface appears uniform, measured steady infiltration rates varied from 720mm/24h day to 25000mm/day with a mean of 5000mm/day. The permeability of the sand, measured in the laboratory, averaged 5500mm/day.

An analysis of daily rainfall at the landfill showed that 91per cent of rainfall events at Coastal Park total less than 10mm per 24 hour day, while only 9 per cent total more than 10mm/day. Hence, it appears unlikely that runoff from the landfill forms a significant term in the water balance. Hence, equation (1b) can be further simplified to:

Leachate = Precipitation - Evapotranspiration - Change in Water Stored . . . . . (1c)

10.2.4 PRECIPITATION AND LEACHATE FLOW

Figures 10.2.1a and 10.2.1b show the cumulative precipitation and leachate flow from the landfill recorded since July 1986. Both quantities have been expressed in mm, the leachate flows being the average for all five lysimeter cells.

Figure 10.2.1a shows the detail of the rainfall and leachate flow for the first two years of the landfill's existence, while Figure 10.2.1b shows information up to the end of 1995. It will be noted that the leachate flow has been virtually constant (if one ignores seasonal and annual variations) since late 1987. Hence the landfill has for all practical purposes, reached a steady-state balance with its environment. For the eight years from 1988 to 1996, the rainfall amounted to 5470mm, the A-pan evaporation to 12500mm and the leachate to 136mm (an average of 17mm per year).

10.2.5 EVAPOTRANSPIRATION DETERMINED FROM THE WATER BALANCE

If the landfill is in a steady-state, there will be no significant change in the water stored in the refuse, from year to year, apart from annual weather variations and seasonal fluctuations as the waste absorbs rain and then loses water by leachate flow and evapotranspiration.

If these changes are averaged out, then on average, the average evapotranspiration can be calculated from mid 1987 to the end of 1995 to be:

Cumulative evapotranspiration = Cumulative precipitation - Cumulative leachate ..... (1d)

Average evapotranspiration = Cumulative evapotranspiration ÷ time of accumulation
5470mm - 136mm
5334mm i.e. approximately 666mm/year

It is obvious from the numbers that almost the entire annual precipitation is re-evaporated, with a small percentage (2.5%) exiting the base of the landfill as leachate.

The average evapotranspiration can be related to the average A-pan evaporation by:

Evapotranspiration = 0.43 x A-pan Evaporation

Because the leachate flow is so small, this is virtually the same as the ratio of rainfall to A-pan evaporation. Hence effectively at Coastal Park, the annual rainfall is, on average, almost all re-evaporated.

10.2.6 EVAPOTRANSPIRATION DETERMINED FROM THE RADIATION BALANCE

The evapotranspirative process takes place by the consumption of energy. If the amount of energy consumed by evapotranspiration can be computed, the corresponding volume of water evaporated can be deduced. The evaporative energy is calculated by considering energy balance at the ground surface.

$$R_n = G + H + L_e \qquad \text{..... (2a)}$$

Where:
- R_n is the net radiation flux for the surface (incoming solar radiation, less reflected radiation and terrestial radiation)
- G is the soil heat flux
- H is the sensible heat flux for the air
- L_e is the latent heat flux of evaporation

R_n can be measured directly; and G can be estimated from the temperature gradient in the soil, together with the specific heat capacity for soil.

H may be expressed as:

$$H = \rho C_p k_h \frac{\delta T}{\delta z} \qquad \text{..... (2b)}$$

Where
ρ is the air density
C_p is the specific heat of air
T is the air temperature
z is the vertical height above the soil surface
k_h is the eddy diffusivity for heat in the air

The water vapour flux, E, may be expressed as:

$$E = k_v \frac{\delta \rho_v}{\delta z} \qquad \text{..... (2c)}$$

Where
ρ_v is the vapour density
k_v is the eddy diffusivity for water vapour in air

Applying the universal gas law to (2c), L_e may be written as:

$$L_e = \frac{\lambda \rho \varepsilon k_v}{P} \cdot \frac{\delta e}{\delta z} \qquad \text{..... (2d)}$$

Where
λ is the latent heat of evaporation of water
ε is the ratio of the molecular weight of water to the molecular weight of air
P is atmospheric pressure
$\delta e/\delta z$ is the vertical vapour pressure gradient above the surface

It is difficult to assess k_h and k_v, but over a uniform surface Bowen suggested that they may be assumed equal, thus:

$$\frac{H}{L_e} = \beta = \frac{PC_p}{\lambda \varepsilon} \cdot \frac{\delta T}{\delta e} \qquad \text{..... (2e)}$$

L_e may be calculated by combining equation (2e) with equation (2b), yielding:

$$L_e = \frac{R_n - G}{1 + \beta} \qquad \text{.....(2f)}$$

and hence:

$$H = \beta L_e \qquad \text{..... (2g)}$$

In practice δT and δe are replaced by finite differences - T and e being measured at two fixed heights above the surface. It will be seen from equation (2d) that the latent heat expended in evapotranspiration is directly proportional to the vapour pressure gradient above surface. Unfortunately, this applies mainly to still-air conditions. If the wind blows strongly, it can affect the vapour pressure gradient and even reverse it. Hence wind can seriously affect the results of evapotranspiration calculations based on the radiation balance.

At Coastal Park radiation measurements have been made on four occasions. These were:

23 April, 1996
02 July, 1996
05 November, 1996
01 February, 1997

Measurements were made by means of hand-held instruments (by the author) during daylight hours. This means that the derived evapotranspirations will be slight under-estimates of actual 24 hour evapotranspiration losses. Although in most cases, measurements were made over only 12 out of the 24 hours in a day, little evaporation occurs at night because of the absence of incoming solar radiation. The results for November and February have been extrapolated to allow for late afternoon radiation that was not measured. Figures 10.2.2a,b,c and d show the radiation balance measurements made on the four different occasions. In each of these diagrams, the net solar radiation R_n and its component parts G, H and L_e have been plotted. The area under the line for L_e represents the total latent heat of evaporation consumed during the day, from which the amount of evapotranspiration can be determined. Figure 10.2.3 shows the average daily A-pan evaporation rate E_A for the Cape Flats sewage works plotted by month. Also shown in the diagram is the line representing 0.43 E_A (0.43 is the factor relating A-pan evaporation to evapotranspiration from the landfill, as found from the water balance). The four points representing the evaporation rate, as found from the energy balance have also been plotted in Figure 10.2.3. Three of these points agree reasonably well with the line for 0.43 E_A. The measurement taken in February, however, does not. 11 February, 1997 was a warm day with a stiff breeze off the sea. The effect of this was to mix the air near the surface and give very low vertical vapour pressure gradients. As a result, the calculated evapotranspiration for the day was only 1mm, even though the net radiation exceeded that on 5 November, 1996, when the calculated evapotranspiration was 2.2mm. If the evapotranspiration for 11 February is adjusted in accordance will the received radiation, the evapotranspiration becomes 2.3mm, which is shown on Figure 10.2.3 as an adjusted value.

10.2.7 WATER STORED IN WASTE

Once the landfill has reached a steady-state and is in dynamic equilibrium with its surroundings, the water stored will fluctuate seasonally and annually as rainfall infiltrates and is re-evaporated. Hence the water content profile of the landfill represents the water stored in the waste at any stage of the year.

Figure 10.2.4 shows three water content profiles measured in April 1995, i.e. at the end of the dry season when moisture contents should be at their lowest ebb. The three profiles A, B and C are highly erratic, but if the sample descriptions are taken into account, it will be seen that the water contents fall into three rough groupings with main water contents (defined as mass of water divided by mass of dry solids) as follows:

sand cover and rubble	:	10%
paper and garden waste	:	25%
garden and food waste	:	45%

These water contents represent minimum annual moisture storage in the three components of the waste. In terms of mm of water stored in the 5m depth of the landfill, the moisture contents represents the following:

10% of 0.2m of sand and rubble at 1800kg/m^3	=	36mm of water
25% of 2.4m of paper and garden waste at 400kg/m^3	=	240mm
45% of 2.4m of garden and food waste at 400 kg/m^3	=	432mm
Total water stored is thus 708mm		708mm

As the dry densities of the three components of the waste have been guessed, this could be rounded off to, say 700mm of water. At the end of the of the wet season, the waste will hold this water, plus the infiltrated rainfall of, say, 700mm of water. Hence the field capacity of the waste must be about 1400 to 1500mm. in the 5m depth of waste. Hence an average overall working figure for the field capacity would be 300mm per m depth of waste. It is probably more useful to express the field capacity in these terms than as a water content of the waste.

It is apparent from the water balance that the body of the landfill that house the lysimeters is capable of absorbing and holding almost the entire annual rainfall, the small excess going to form the leachate flow. The obvious way of preventing the production of leachate entirely, is to add an additional lift of refuse to the landfill. This will have the effect of slightly reducing the field capacity of the existing 5m thickness of waste by compression, but the overall field capacity will be increased. The landfill will then be able to absorb the entire annual rainfall without any production of leachate.

It is proposed to prove this on a experimental basis as a extension of this project.

10.2.8 DILUTION OF LEACHATE BY GROUNDWATER FLOW

The leachate outflow from the Coastal Park landfill will be diluted by regional flow of the groundwater. Suppose that the aquifer under the landfill has a regional Darcy (i.e. superficial) velocity v_A and that the outflow from the landfill mixes into the upper layer of groundwater to a depth d below the phreatic surface. The downward velocity of the leachate flow will be denoted by v_L. Referring to Figure 10.2.5a the dilution of the leachate will be given by:

$$1 - \frac{\textit{Volume of leachate entering flow tube in time } t}{\textit{Volume of groundwater and leachate passing through flow tube in time } t}$$

$$= 1 - \frac{\textit{Volume of leachate in time } t}{\textit{Volume of groundwater + volume of leachate + sum of volumes of ground water flow entering and leaving in time } t}$$

$$\textbf{Dilution} = 1 - \frac{v_L\, Dt}{n\, Dd + V_L Dt + 2v_A dt} = 1 - \frac{1}{1 + d\left[\frac{n}{v_L t} + \frac{2v_A}{v_L D}\right]} \qquad \ldots\ldots\ldots (3)$$

where n = porosity of strata underlying the landfill

Note that if the ground water is stagnant, i.e. $v_A = 0$, the dilution becomes

$$\textbf{Dilution} = 1 - \frac{1}{1 + \frac{dn}{v_L\, t}} \qquad \ldots\ldots\ldots\ldots\ldots (3a)$$

In this case, the larger v_L is and the larger t becomes, the closer the dilution approaches zero, i.e. no dilution occurs, and the ground water composition will approach that of the leachate. Similarly, if v_L is zero

$$\textbf{Dilution} = 1 - \frac{0}{n\, Dd + 2v_A\, dt} = 1 \qquad \ldots\ldots\ldots\ldots\ldots (3b)$$

There is nothing to dilute in this case.

For Coastal Park, groundwater analyses are available for two upstream boreholes (Nºs 13 and 18) as well as a number of downstream holes (Nºs 1 (B9), 16 (C1) and 17(C9). The location of these boreholes is shown in Figure 10.2.5b. Parameters for calculating the dilution are:

$v_A = 4$m/y
$v_L = 0.016$m/y
and $n = 0.4$

The whole footprint of the landfill has not been covered with waste for the period 1986 to 1995. Hence for the present exercise, D will be taken as 100m. t should be taken as the time for which the flow tube has been exposed to leachate flow. In this case t = 10 years.

$$\text{Thus Dilution} = 1 - \frac{1}{1 + 7.5\,d}$$

The depth of mixing, d, is unknown but initially will be taken as either 1m or 2m.

Thus the rates of dilution are:

Dilution = 1 - 1/8.5 or 0.88 (for d = 1m) or 1 - 1/16 or 0.94 (for d = 2m)

Figure 10.2.6 shows profiles with depth below the water table of chemical oxygen demand, ammonia and chloride for upstream and downstream boreholes at Coastal Park. These profiles are compared with the range of corresponding values measured for the leachate extracted from the lysimeter cells.

The results of the dilution calculations are given in Table 10.2.1, which shows ranges of values, both for the groundwater analyses and for the leachate.

Note that water that passed BH13 and BH18 in 1986 will have travelled about 110m in the last 10 years. It will only emerge downstream of the landfill in about the year 2035.

TABLE 10.2.1: ANALYSES (in mg/l) OF BOREHOLE SAMPLES AND LEACHATE FROM COASTAL PARK

LOCATION	SOURCE OF SAMPLE	CHEMICAL OXYGEN DEMAND	AMMONIA	CHLORIDES
Upstream Groundwater	BH 13	5 to 25	0.5	65
	BH 18	55 to 75	0.5 to 1	400
Leachate	Experimental cells 1 to 5	200 to 2000	50 to 1000	1000 to 2500
Downstream Groundwater	BH 1	60 to 120	40 to 55	500 to 700
	BH 16	170 to 260	30 to 50	1250 to 1850
	BH 17	120 to 300	10 to 35	2400 to 2600
Calculated Diluted Leachate Analysis	d = 1m	29 to 310	7 to 118	182 to 694
	d = 2m	18 to 200	4 to 63	127 to 556

Allowing for the uncertainty in the given data for the upstream boreholes and the leachate, the calculated concentrations for COD, and ammonia seem to be reasonable (18 to 310 as compared with 60 to 300 for COD, and 4 to 118 as compared with 10 to 55 for ammonia). However, the results for chlorides appear to be too low, except for BH 1. It appears that for BH16 and BH17 there must be an increase in the chloride content from some source other than the leachate (possibly intrusion of sea water). One could, of course, get closer agreement by reducing the assumed depth of mixing. However, this would not be realistic, as it would not match up with the depth profiles for BH 1, BH16 and BH17 (see Figure 10.2.6).

10.2.9 DISCUSSION AND CONCLUSION

1: The complete pseudo steady state water balance for Coastal Park landfill is now known and hence the actual average annual evapotranspiration from the landfill is also known. This turns out to be 0.43 x A Pan Evaporation, as compared with the figure of 0.7 x A Pan Evaporation used in the Minimum Requirements for landfilling. Another limitation to evapotranspiration has been highlighted as a result of this study: annual evapotranspiration cannot, on average, exceed annual rainfall.

2: The surface radiation balance at Coastal Park has been used to make independent calculations of the rate of evapotranspiration from the landfill. These appear to confirm the conclusions drawn from the water balance.

3: A method has been suggested for evaluating the dilution of the leachate, leaving the landfill, by mixing with the groundwater flow. The results of this approach appear to be realistic provided there are no extraneous effects such as salt water intrusion from the sea.

10.2.10 REFERENCES

Blight, J.J. and Blight, G.E. (1996). The radiation balance for the determination of the landfill water balances. S A I C E Young Water, Environmental and Geotechnical Engineers' Festival, 15 pp.

Department of Water Affairs and Forestry (1994). Minimum Requirements for Waste Disposal by Landfill. The Department, Pretoria, South Africa.

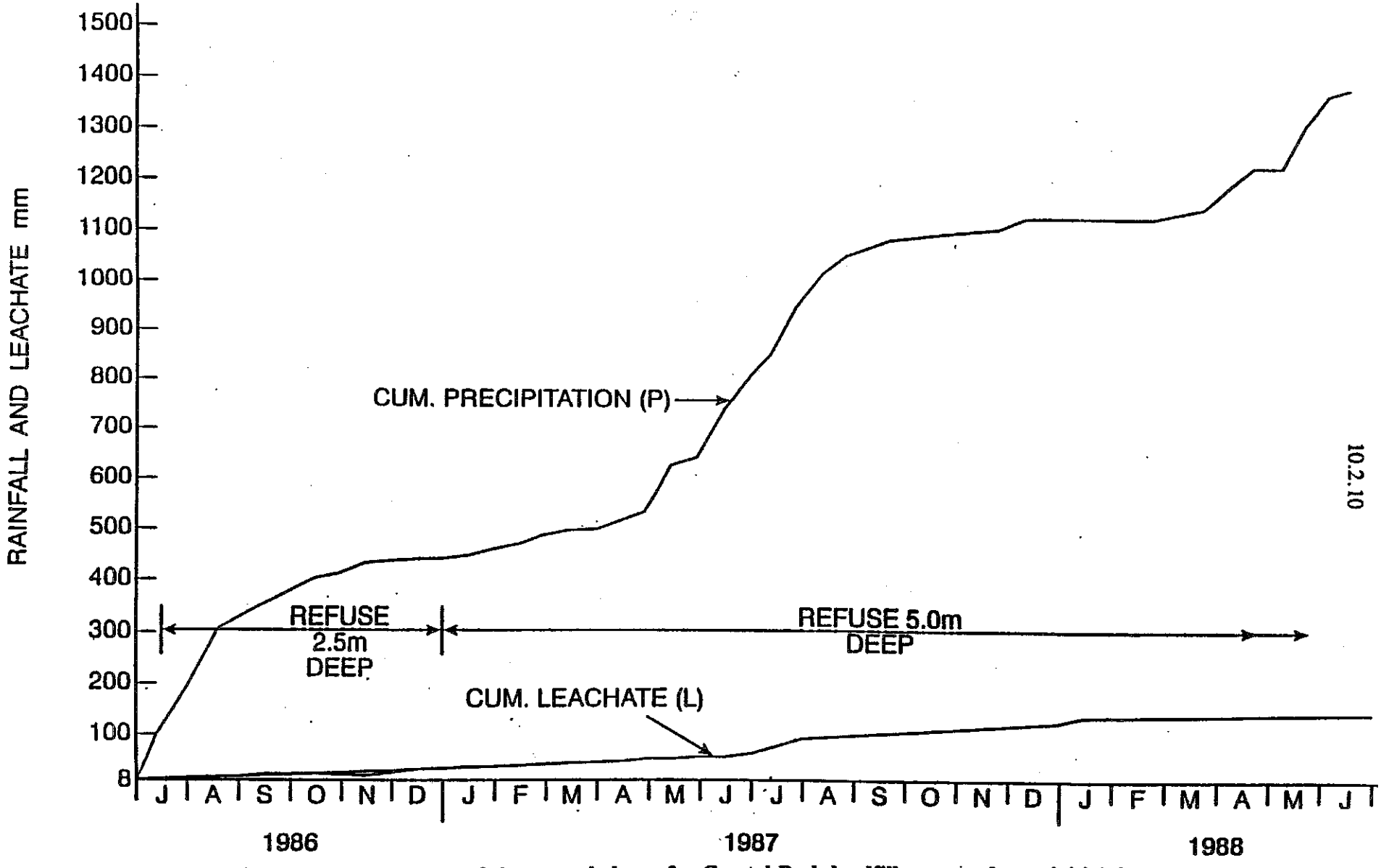

Figure 10.2.1a **Components of the water balance for Coastal Park landfill measured over initial 2 years**

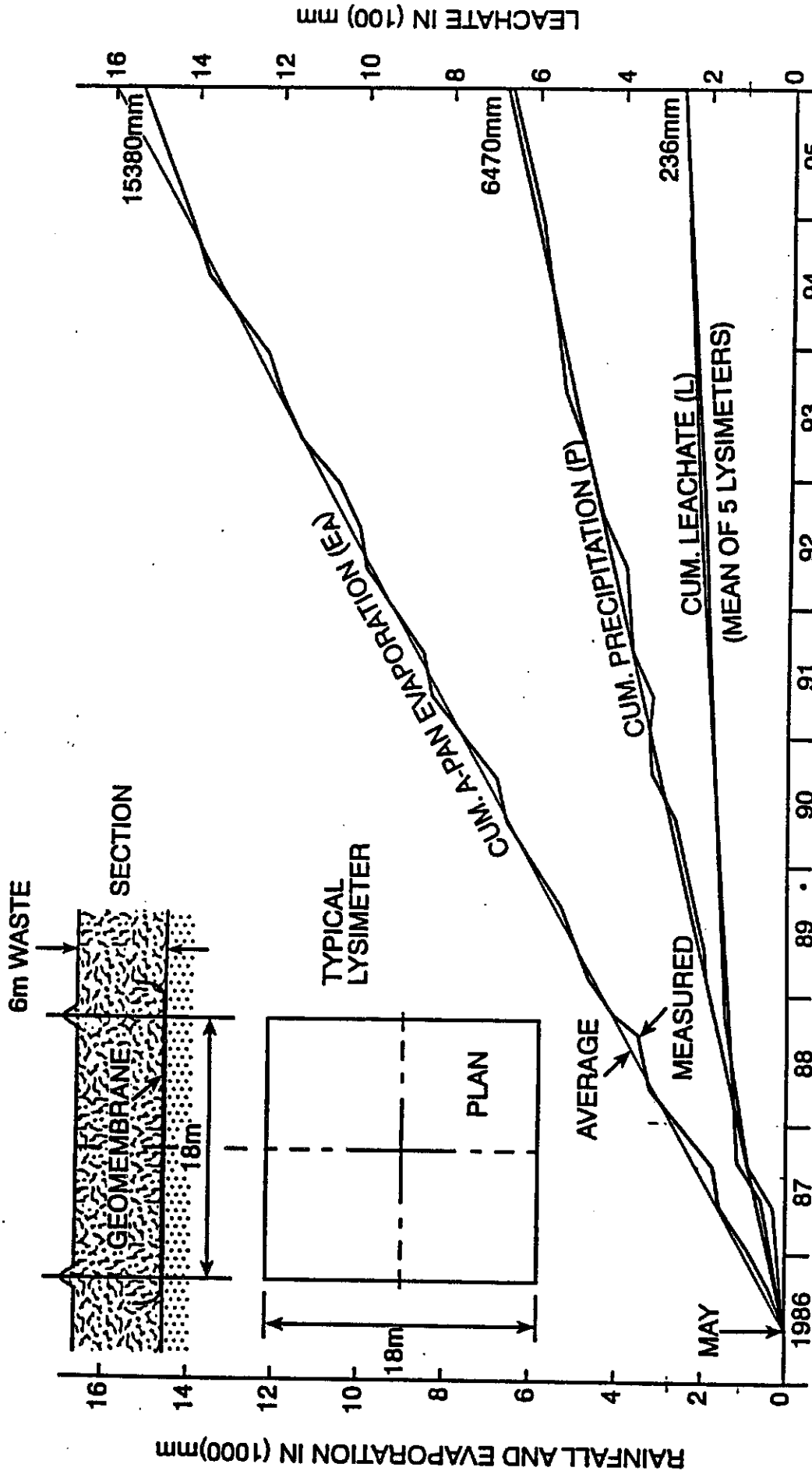

Figure 10.2.1b Components of the water balance for Coastal Park landfill, measured over 9.5 years

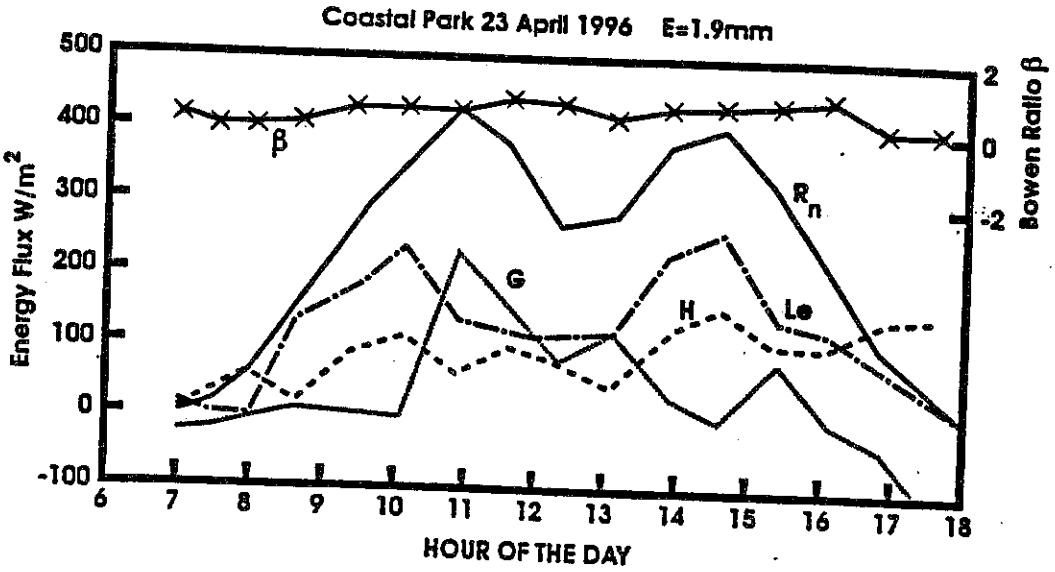

Figure 10.2.2a Radiation balance measured at Coastal Park landfill on 23 April 1996. E is the calculated evapotranspiration for the day, in each case

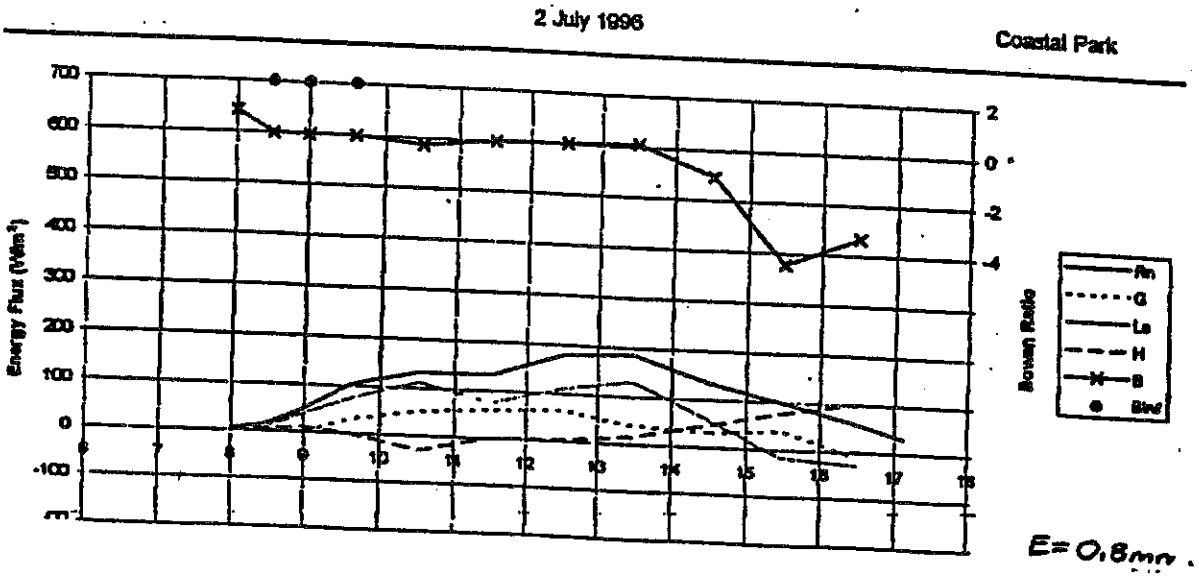

Figure 10.2.2b Radiation balance measured at Coastal Park landfill on 2 July 1996. E is the calculated evapotranspiration for the day, in each case

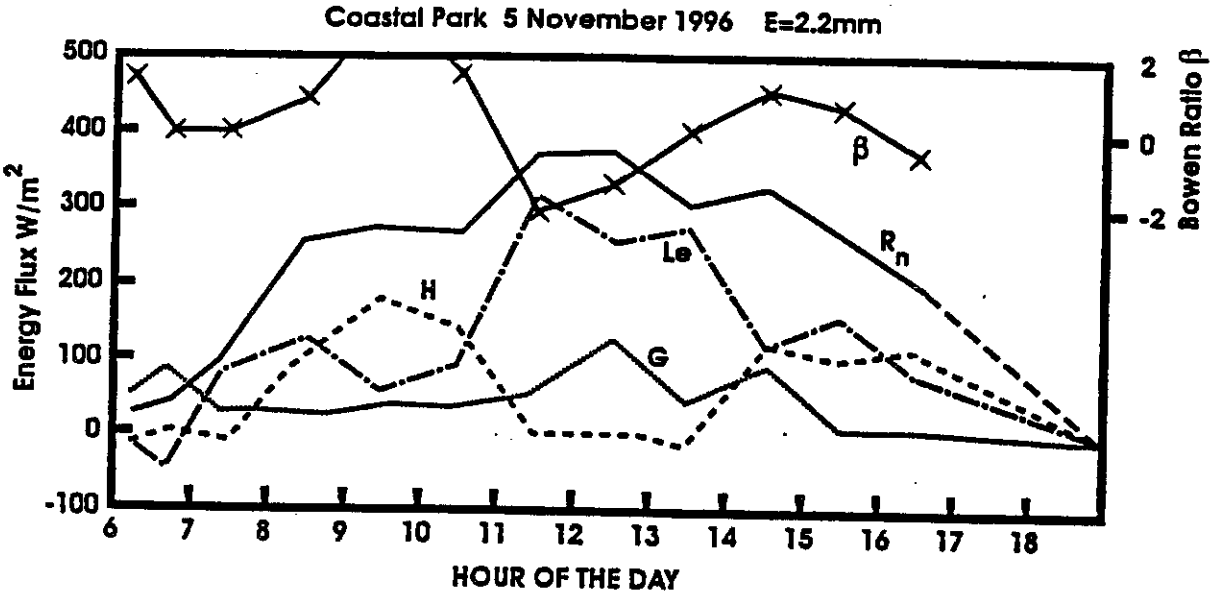

Figure 10.2.2c Radiation balance measured at Coastal Park landfill on 5 November 1996. E is the calculated evapotranspiration for the day, in each case

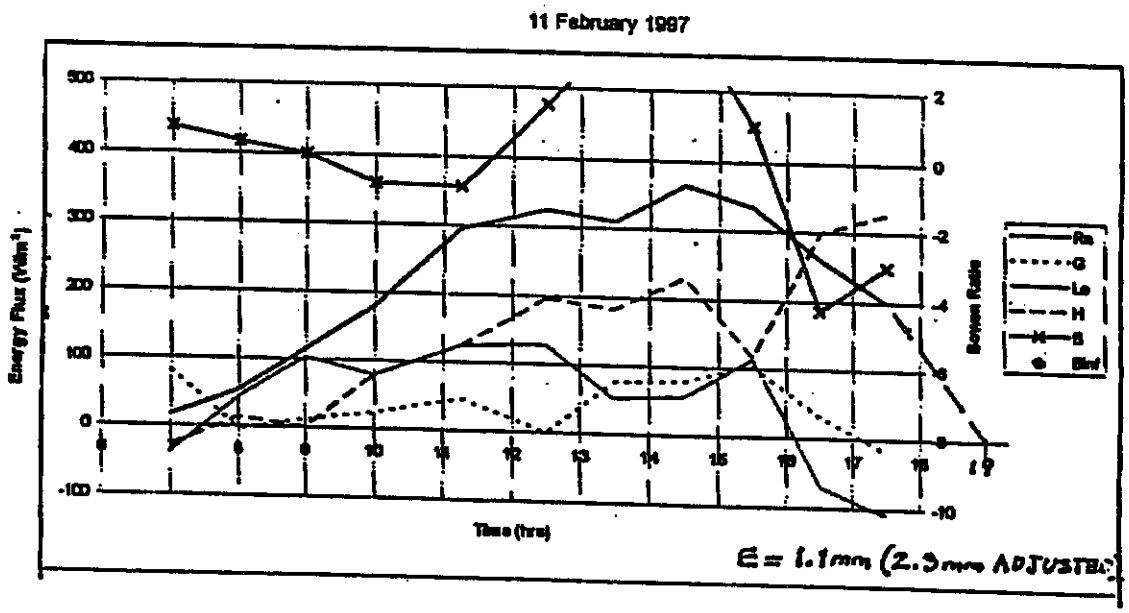

Figure 10.2.2d Radiation balance measured at Coastal Park landfill on 11 February 1997. E is the calculated evapotranspiration for the day, in each case

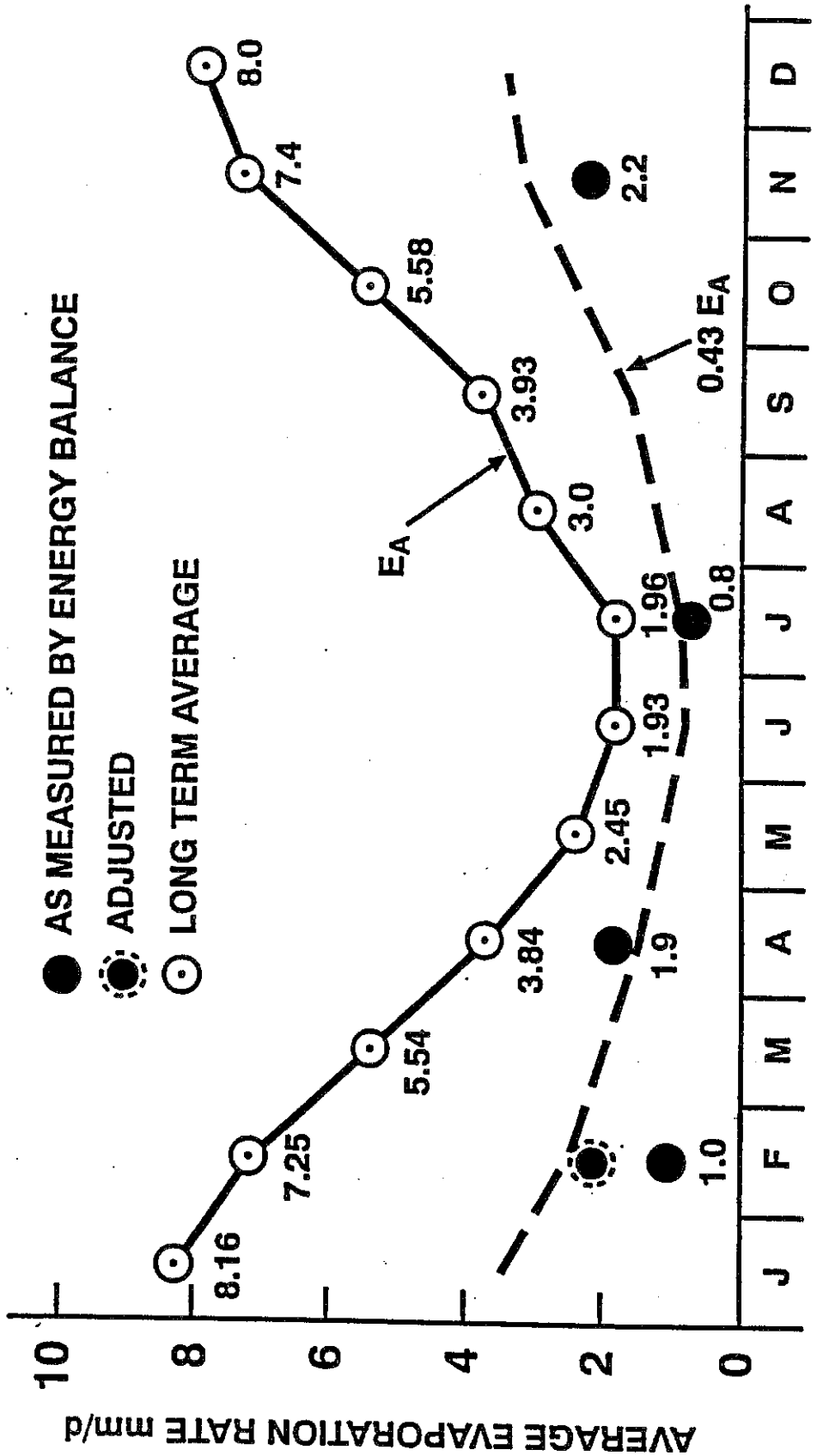

Figure 10.2.3 Comparison of evapotranspiration rates determined by energy balance with rates determined by water balance

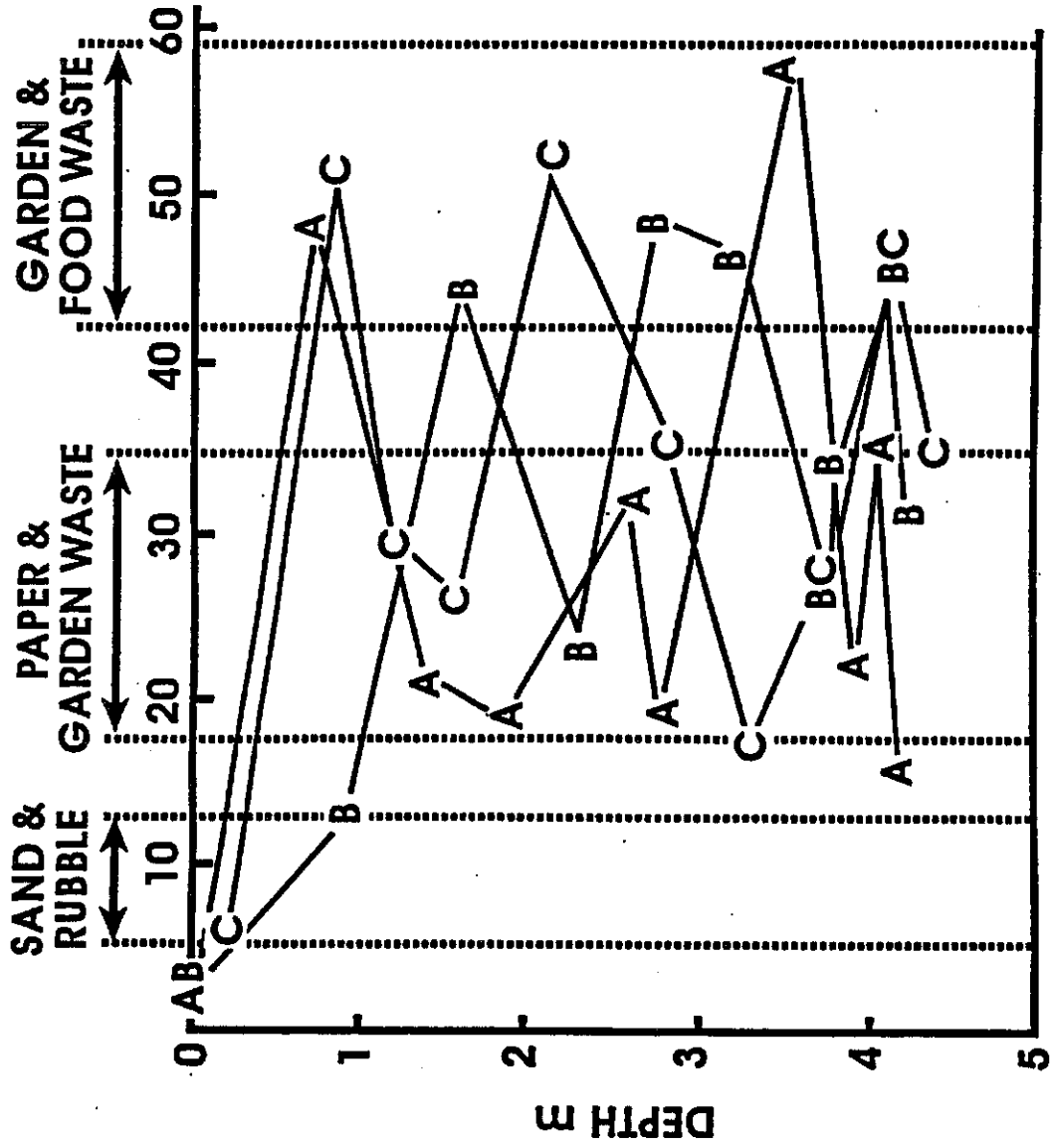

Figure 10.2.4 Water content profiles measured in April 1995 at Coastal Park landfill

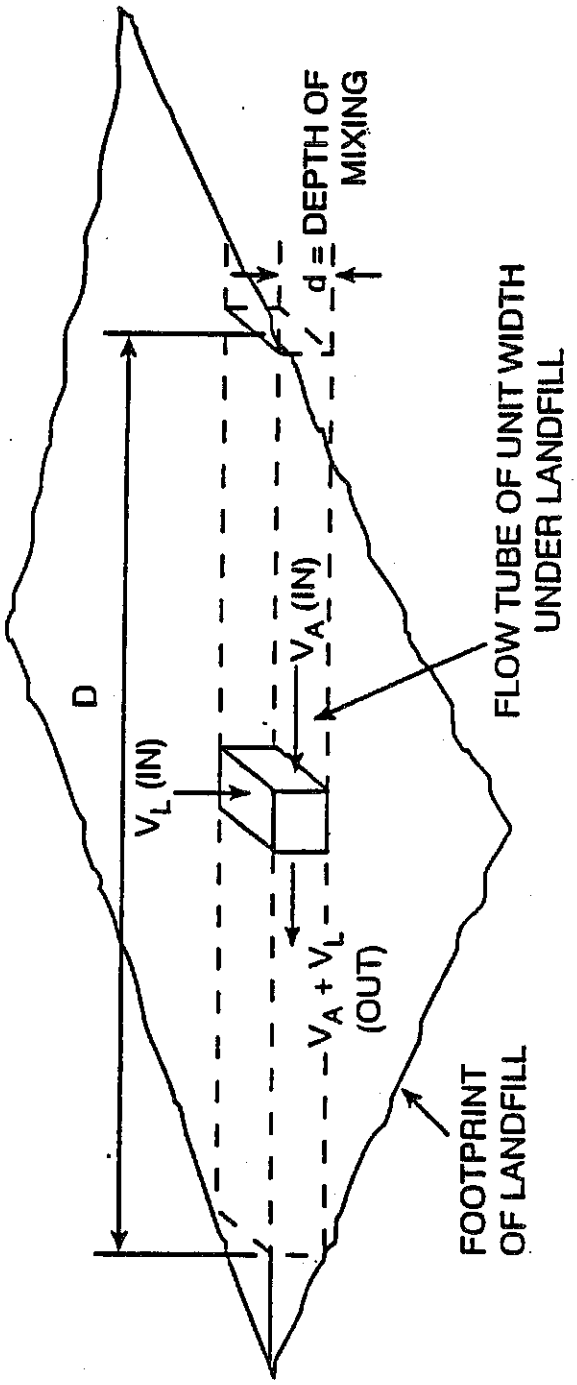

Figure 10.2.5a **Principle of calculating dilution of leachout outflow by groundwater through-flow**

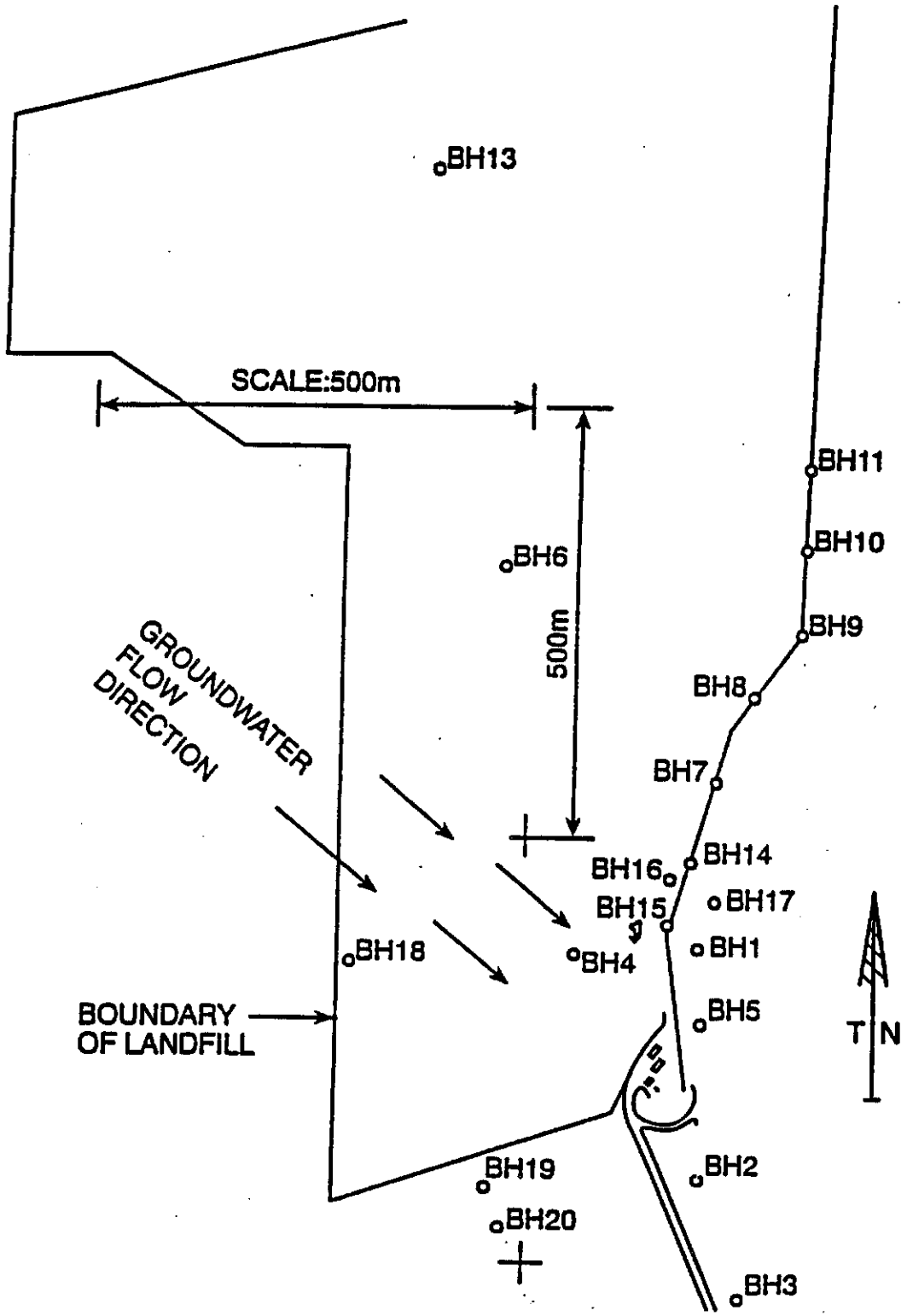

Figure 10.2.5b **Direction of groundwater flow and positions of monitoring boreholes at Coastal Park landfill**

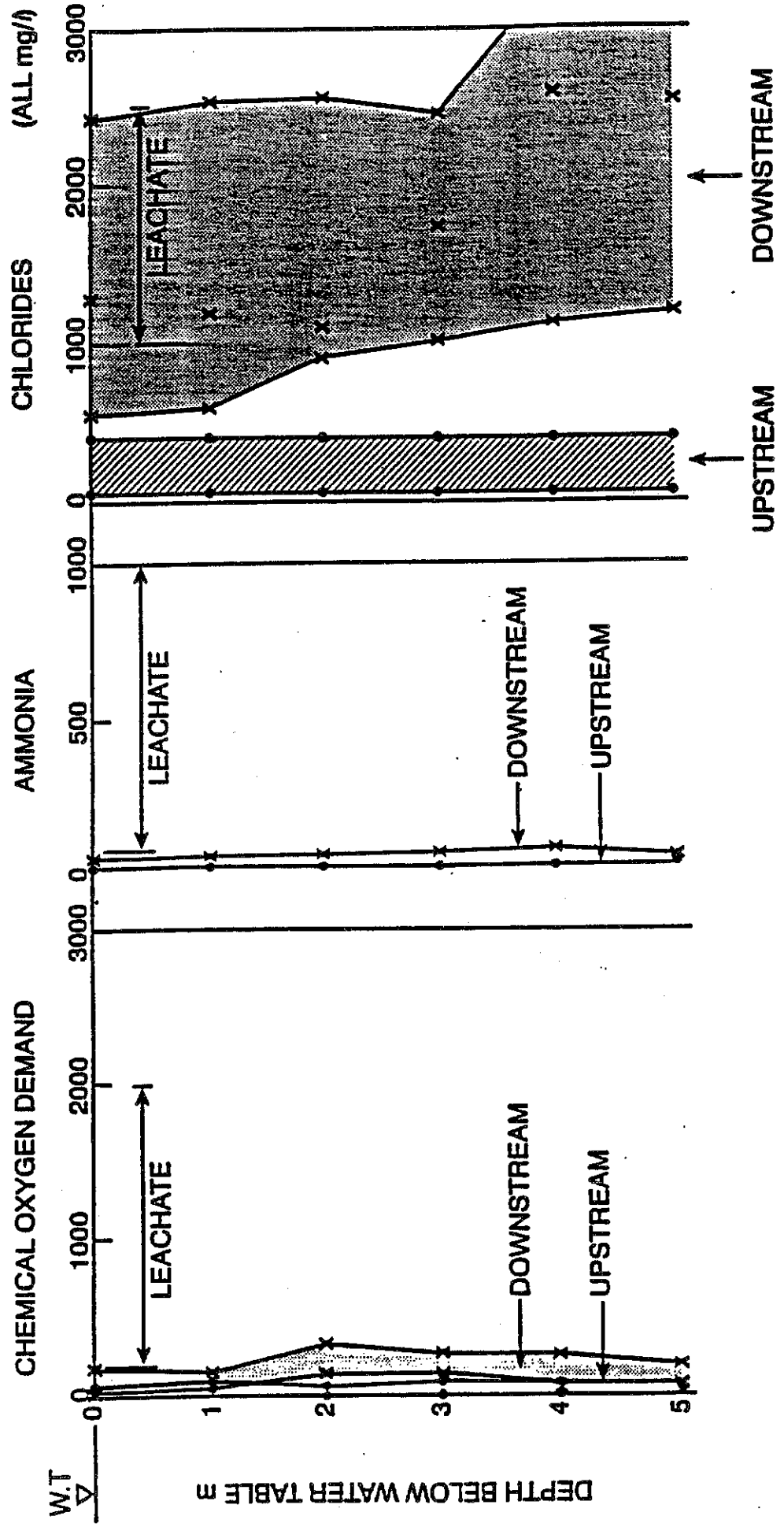

Figure 10.2.6 Summary of upstream and downstream ground-water analyses and analyses of leachate

SECTION 10.3

LATERAL MOVEMENT OF SOLUBLE SALTS AT COASTAL PARK

By

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10.3.1 INTRODUCTION

Although landfilled municipal solid waste is a heterogeneous material, it is often assumed to behave as if homogeneous on a macroscale when analyzing the flow of water through it. Thus, widely used computer-models (eg. Schroeder, 1983) that can be used to analyse moisture movement through landfills, usually assume that one-dimensional vertical flow takes place through a landfill under the influence of infiltrating precipitation. The results of an in situ experiment on the movement of soluble salts through the lysimers at Coastal Park landfill have shown that infiltration extensively spreads laterally and is not confined to vertical flow. The original object of the experiment was to see if various hazardous substances including the copper, chromium and arsenic salts used as a wood preservative, could be co-disposed with domestic refuse without adverse environmental consequences. Sampling of the refuse five years after starting the experiment showed that considerable lateral dispersion of the salts had occurred. This result was confirmed by additional sampling 3 years later. These observations lead to in situ and laboratory investigations of the anisotropic nature of the permeability of landfilled refuse. The results of these investigations are also reported here.

10.3.2 CO-DISPOSAL EXPERIMENT

The experiment took place at the co-disposal lysimeters at Coastal Park landfill. The main objectives and layout of the experiment have been reported in Chapter 9, but are resummarized here. A series of lysimeters was set up along the perimeter of the landfill. Each lysimeter consisted of a plastic geomembrane liner measuring 15m x 15m which was buried at a depth of 2m below the original ground surface at the landfill site. The site is underlain by approximately 20m of fine silty sand and the regional water table is generally at a depth of 2.5m. Each liner was laid with its edges turned up all round by 0.5m to form a lined

impervious basin. Each basin was graded to a corner from which a pipe lead to a collecting and measuring sump. In this way, all liquid percolating out of the bottom of the lysimeter could be recovered, its quantity measured and chemical analyses made. Figure 10.3.1 shows the layout of two of the lysimeters in both section (above) and plan (below).

After replacing the 2m of sand excavated to place the geo-membranes, refuse was placed and compacted to a depth of 5m, in two 2.5m lifts. The two lifts of refuse were separated by a 200mm layer of sand intermediate cover. After covering the surface of the 6m of refuse with a 0.5m cover-layer of sand, the area of landfill directly above each geomembrane was surrounded by a low bund of clayey soil. The soluble salts disposed on the surface of one of the lysimeters shown in Figure 10.3.1 was a wood preservative that contains copper (Cu), chromium (Cr) and arsenic (As) salts. The wood preservative (known as Tanalith or CCA) contains 8% copper, 15% chromium and 15% arsenic by mass, all in readily water-soluble form. The component salts, and their solubilities in water are as follows:

$Cu\ SO_4.5H_2O$ - 316g/1 at 10°C
$Na_2\ Cr_2\ O_7.2H_2O$ - 2380g/1 at 10°C
$As_2\ O5.2H_20$ - 1500g/1 at 10°C

CCA solution is oxidising in nature and in contact with reducing agents, e.g. organic matter, cellulose and H_2S (all common in landfills), forms low solubility products that are likely to be immobilized where they form. Examples of these compounds and their solubilities in water are as follows:

$Cu\ S$ - solubility 0.0003g/1 at 10°C
$Cr_2\ O_3$ - insoluble
$Cu\ HAs\ O_3$ - insoluble

The surface of the lysimeter was dosed to correspond to a nominal 100 mg of CCA/per dry kg of refuse contained vertically above the geomembrane liner.

On the surface of a second and adjacent lysimeter, lithium (Li) bromide, was applied as a tracer control at the same dosage as the CCA. No irrigation was applied, as it was decided to study the effects of infiltrating rain and subsequent evaporation on salt migration within the refuse. The lysimeters were completed and dosed with their soluble salts early in 1988.

10.3.3 PRELIMINARY RESULTS OF THE SALT MIGRATION EXPERIMENT

The lysimeters started producing leachate almost immediately. Concentrations of Cu, Cr, As and Li in the initial leachate and cold water extracts of refuse taken from a location adjacent to the lysimeters were, in round figures:

	Leachate:	Refuse:
Cu	0.02 mg/l	0.04 mg/dry kg refuse
Cr	0.02 mg/l	0.01 mg/kg
As	0.05 mg/l	0.01 mg/kg
Li	0.03 mg/l	0.02 mg/kg

The analyses for leachate from all of the lysimeters were similar, and the concentrations in the leachate and refuse reported above were thereafter regarded as background values for the salt migration study. The leachate analyses remained almost unchanged except for slight increases in Cu and Cr from the cell dosed with CCA. The concentration of As and Li in the leachate remained virtually unchanged throughout a monitoring period of over 7 years.

10.3.4 SAMPLING AROUND THE LYSIMETERS

Because there had been no change in the leachate analysis, it was decided to sample the area surrounding the lysimeters (after 5 years, in 1993) to see if the various substances, instead of migrating vertically down, had spread laterally.

Samples were taken at various points through the depth of the landfill and from the interface between the 0.5m sand surface-cover layer and the refuse. The layout in plan of these depth and surface samples is shown in Figure 10.3.1. Each sample was leached four times with cold distilled water to determine the content of water-soluble (and therefore water-mobile) salts within the refuse.

The results of the cold water-soluble analyses after 5 years are shown in Figure 10.3.2 in the form of profiles of concentration along the section lines AA and BB that are indicated in Figure 10.3.1. The numerical values of Cu, As, etc are given in units of mg/dry kg of refuse. The upper part of Figure 10.3.2 shows profiles of copper content along lines AA and BB. The lower limit of 0.2 mg Cu/dry kg of refuse is 5 times the background value quoted earlier. The limit of 0.1 mg As/dry kg of refuse indicated in the lower part of Figure 10.3.2 is about 10 times the background value.

The profiles along line AA show lateral mobility for both copper and arsenic. Profiles along line BB generally confirm the pattern shown by those along line AA. In 1993, substantial concentrations of Cu and As were be found at more than 15m from the edge of the CCA lysimeter throughout the full depth of the landfill. The corresponding concentrations of Li and Cr were similar to those for Cu and As, except that these two metals were apparently less laterally mobile although still moving considerable lateral distances.

Three years later (ie. In 1996 after 8 years) same additional samples wer taken, both to confirm the results of the earlier sampling and also to see if the lateral migration of the salts was continuing. Figure 10.3.2 also shows the results of 1996 sampling (marked with asterisks) superimosed on the results of the earlier sampling. The analyses confirmed that lateral migration was still continuing. Appreciable concentrations of copper and arsenic were now to

be found more than 20m from the edge of the CCA lysimeter and copper and arsenic contents seem generally to have increased relative to analyses carried out on the 1993 samples.

10.3.5 POSSIBLE MECHANISMS FOR LATERAL FLOW IN THE REFUSE

The results of the chemical analyses shown in Figure 10.3.2 indicate that lateral flow has occurred under infiltrating rainfall, that is, under what would be expected to be an essentially vertical flow regime. The percolating water must be deflected laterally during its passage through the landfill, and the obvious deflecting agent is the large quantity of plastic bags contained in the refuse. During the sampling, numbers of plastic bags were found that had entrapped infiltration and contained free water. If plastic bags can entrap water, they can obviously also deflect its seepage path.

Infiltration rates into the sand cover at the site were measured by means of double ring infiltrometers. Although the sand surface appeared uniform, measured long term infiltration rates varied from 720mm/24h day to 25000mm/day with a mean of 5000mm/day. The permeability of the sand, measured in the laboratory, averaged 5500mm/day. An analysis of daily rainfall at the site showed that over 60 per cent of rainfall events in the area of the site total less than 5mm per 24 hour day, while 98 per cent total less than 30mm/day. Hence, it appeared unlikely that prolonged ponding of water within the bunded areas could have driven the flow laterally.

10.3.6 ASSESSMENT OF LATERAL AND VERTICAL PERMEABILITIES OF REFUSE

The most likely cause of the lateral spreading of soluble salts appeared to be that the lateral permeability of the refuse might be several times greater than the vertical permeability. It was therefore decided to measure the permeabilities for vertical and horizontal flow in situ. The measurements were made using a method based on that developed by Matsuo *et al.* (1953).

A square hole or pit was excavated in the surface of the landfill close to the lysimeters. A falling head seepage test was then conducted by partly filling the hole with water and measuring the time taken for the water to seep away. The length of the hole was then extended, keeping the other two dimensions unchanged, and the falling head seepage test was repeated. In further stages the length of the hole was extended with the seepage test being repeated after each extension.

For a falling head test, the permeability k can be written as

$$k = A/FT \qquad \ldots\ldots\ldots\ldots\ldots \qquad (1)$$

where A is the plan cross-sectional area of the hole;

F is a shape factor (with dimensions of length);

T is the basic time lag. (See, eg. Hvorslev (1951) and Schmid (1967)).

The expressions for A/F and the method for obtaining T are given in Appendix 1.

For each shape of hole, the ratio of the area of the sides of the hole through which seepage was occurring, ie. the wetted side area (As) to the area of the base (A) could be determined. Figure 10.3.3 shows the observed relationship between the basic time lag T and As/A. This line could then be extrapolated to get the time lag corresponding to As/A=O, ie. when only vertical flow was occurring. From the values of A/F and the corresponding values of T, a permeability could be calculated for each value of As/A. These have also been plotted in Figure 10.3.3. The result shows no trend for k to change with changing As/A. The conclusion is thus that the refuse has a reasonably isotropic permeability and that the lateral spreading of the soluble salts cannot be ascribed to anisotropic flow on the macro-scale. Another mechanism therefore needs to be found.

It should be noted that the permeabilities shown in Figure 10.3.3 of about 1m/h or 9000 m/y, are considerably higher than other values reported in the literature. Oweis and Kera (1986) for example, quote 1500 m/y as a maximum permeability for landfilled refuse, and previous measurements in other areas of this landfill made by surface ponding tests (Blight, Ball and Blight, 1992) gave permeabilities of 700 to 1200 m/y. The discrepancy may arise because, in the tests described in Figure 10.3.3, flow entered the refuse through surfaces that had been disturbed by excavation, whereas the ponding tests took place at the surface of a layer of compacted refuse.

10.3.7 LABORATORY MODEL TESTS

As the macro-permeability of the refuse had been shown to be reasonably isotropic, a series of laboratory model experiments was started to try and identify possible mechanisms for lateral spread on a micro-scale. In these models, the refuse was represented by sand containing small strips and sheets of plastic film.

The most promising result was obtained from the model for which the results are sketched in Figure 10.3.4. In this model, sand was contained in a glass-sided tank with a pervious base. The sand was interrupted at vertical intervals, by plastic strips that each covered the full width of the tank, but had gaps of a predetermined width in them. The gaps were aligned vertically, one above the other. Figure 10.3.4 shows the results of models in which the gaps were 4mm and then 1mm wide. A potassium permanganate crystal was placed on the surface of the sand vertically above the gaps in the plastic strips and the sand surface was then subjected to a water spray to simulate rain. The dye streak from the potassium permanganate crystal moved vertically down to the first plastic strip, then spread laterally as the coloured water appeared to be dammed by the plastic. Part of the dye streak penetrated the gap in the plastic strip and the lateral spreading was repeated above the next strip. Figure 10.3.4 shows the steady-state dye patterns in these models.

This model illustrates a possible mechanism for the lateral spreading observed in the landfill.

Soluble substances moving through the refuse would be dispersed each time a narrow gap in a concentration of plastic sheets was encountered. The cumulative effect of such dispersion could have resulted in the lateral spreading observed in the landfill, even though the macro-permeability was reasonably isotropic. However, because the plastic strips in the models were all horizontal, the permeability of the models was, in reality, anisotropic. One would have to postulate similar dispersion of flow in a vertical direction as well as laterally in a model with the plastic strips arranged randomly to explain the field phenomenon completely. Attempts to observe the effect of randomly disposed plastic strips in sand model failed because the flow became too complex to interpret satisfactorily. The model is also unconvincing for other reasons, e.g. the observed flow phenomena took place under saturated conditions, whereas the dispersion observed in the landfill took place by unsaturated flow. The damming effect observed in the model is less likely to occur under capillary flow conditions, where flow quantities will be much smaller.

10.3.8 CONCLUSIONS

Soluble substances migrating downward through landfilled refuse have been observed to spread laterally to a considerable extent. Measurements in situ have shown that the macro-permeability of the refuse is reasonably isotropic, and the lateral spreading cannot be ascribed to lateral flow on a macro-scale. An investigation of the lateral spreading via laboratory models has shown that with saturated flow conditions, lateral dispersion can be induced by the damming effect of plastic sheets with a small gap between them. It is suggested that this is a possible partial cause of the observed lateral spreading. However, the observed lateral migration has not been adequately explained, and a full explanation must still be sought.

10.3.9 REFERENCES

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10.3.10 APPENDIX 1: IN SITU PERMEABILITY MEASUREMENTS

For a pit of circular cross-section with seepage taking place over a vertical depth of side L, the ratio A/F is given (Hvorslev, 1951) by:

$$A/F = D^2 \ln\frac{L}{D} + \left\{1 + \left(\frac{L}{D}\right)^2\right\}^{1/2} \quad \ldots\ldots\ldots\ldots (2)$$

For a pit of rectangular cross-section the diameter D is replaced by 4 times the hydraulic radius R where

$$R = A/P \quad \ldots\ldots\ldots (3)$$

and P is the perimeter of the pit.

The basic time lag T is found by plotting the log of the ratio of the depth of water L_t in the pit at time t to the depth of water at the start of the observations, L_o at t = O versus the time t to a linear scale. The resulting plot is a straight line, and T is the time corresponding to L_t/L_o = 0.37.

The above procedure gives a series of values of T for corresponding ratios of side area of seepage to base area, ie. of $LP/A = A_s/A$. Hence a plot of T versus A_s/A can be constructed. Figure 3 shows the T versus A_s/A relationship for the present series of tests. Extrapolating the line to A_s/A = O gives the value of T corresponding to seepage out of the base of the pit only. For this case, A/F for a circular area is given (Hvorslev, 1951) by:

$$A/F = \pi D/11 \quad \ldots\ldots\ldots (4)$$

The practical case of A_s/A = O would correspond to a very long trench with a very small depth of water in it for which R = B/2 where B is the breadth of the trench. Hence for As/A = O,

$$A/F = 2\pi B/11 = 0.57B \quad \ldots\ldots\ldots (4a)$$

Hence k_v for vertical flow can be obtained. Following this, k_h for lateral flow can be obtained from the original measurements of the mean permeability k via the expression

$$k = \sqrt{k_v . k_h .}$$

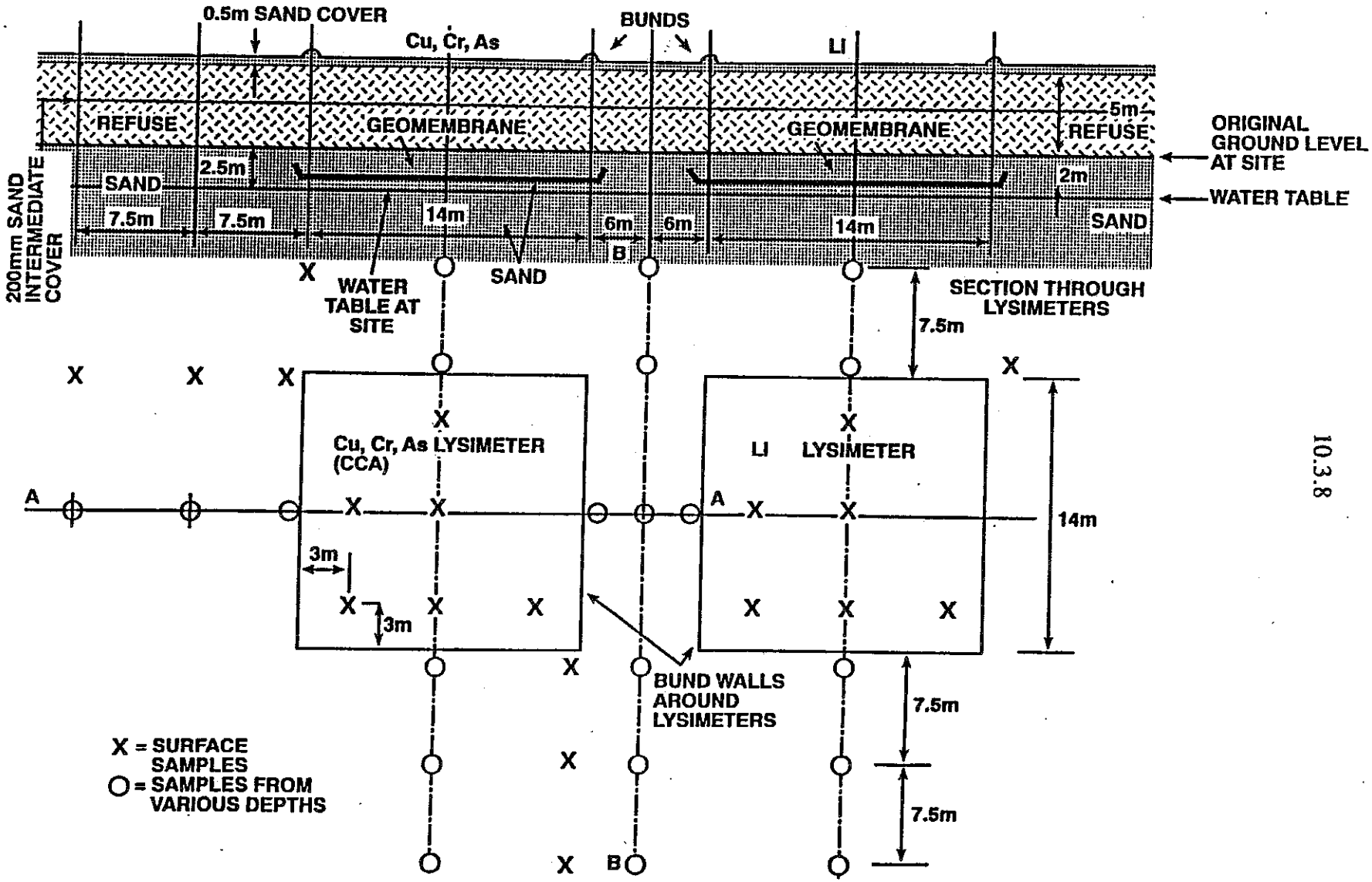

Figure 10.3.1 **Layout of lysimeters and sampling holes in plan**

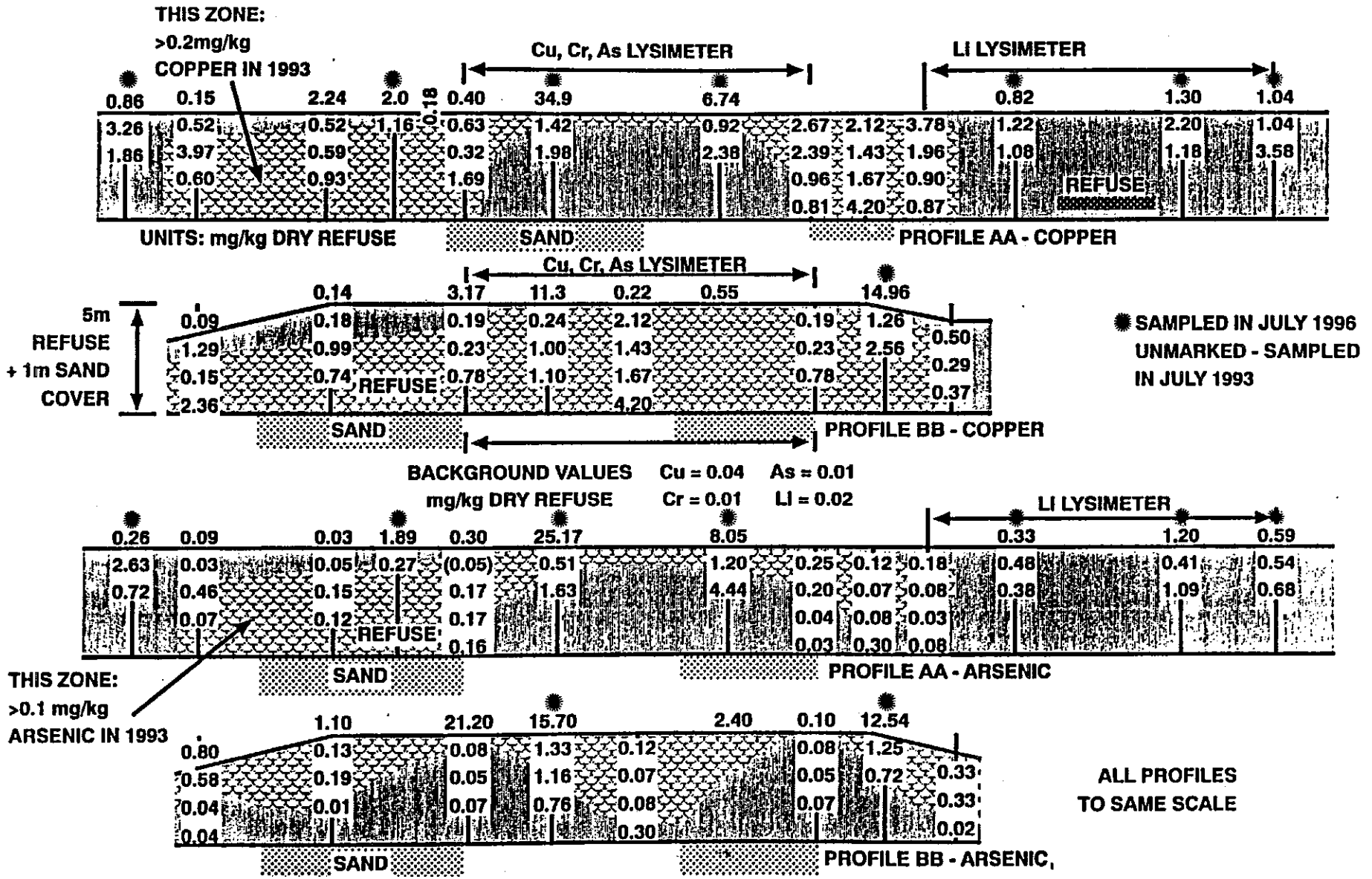

Figure 10.3.2 **Profile showing distribution of copper and arsenic in vicinity of lysimeters after 5 and 8 years**

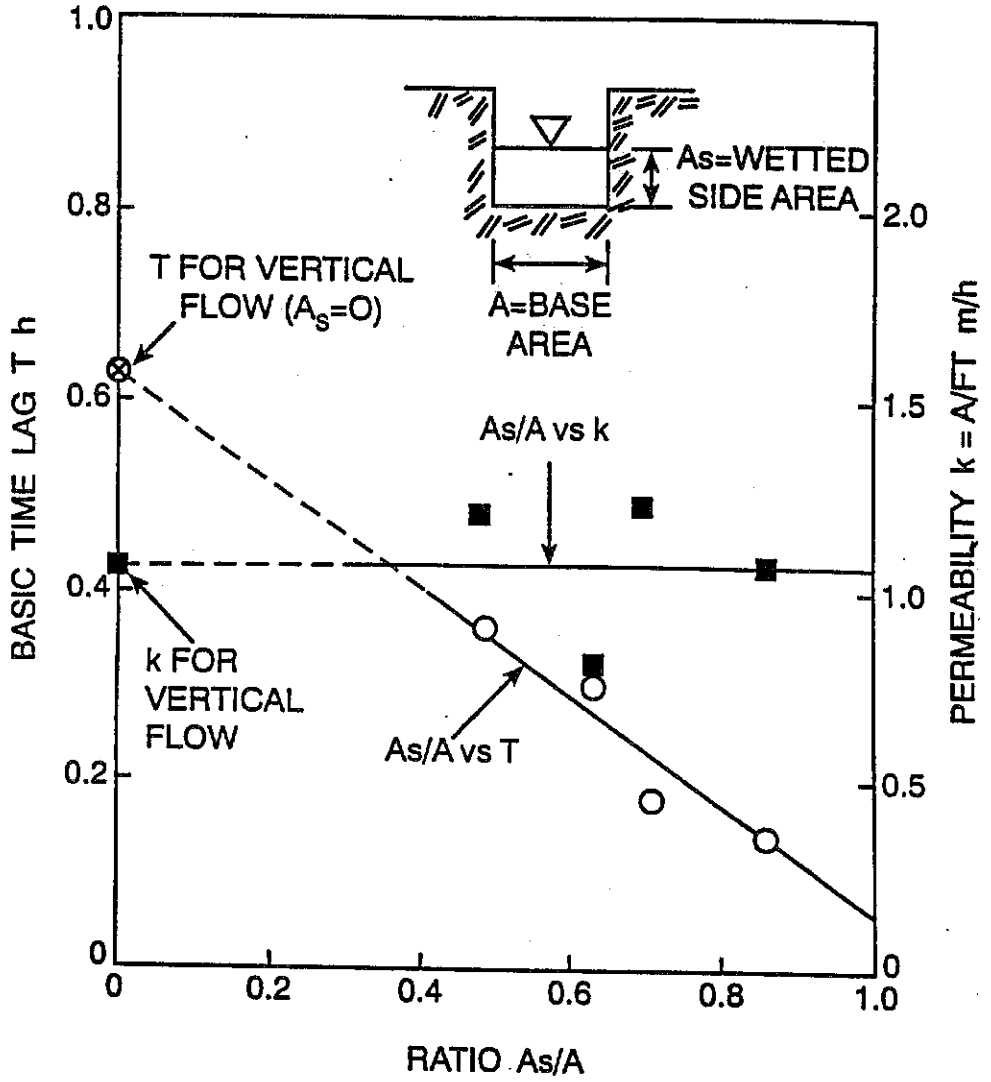

Figure 10.3.3 **Variation of basic time lag T with ratio As/A**

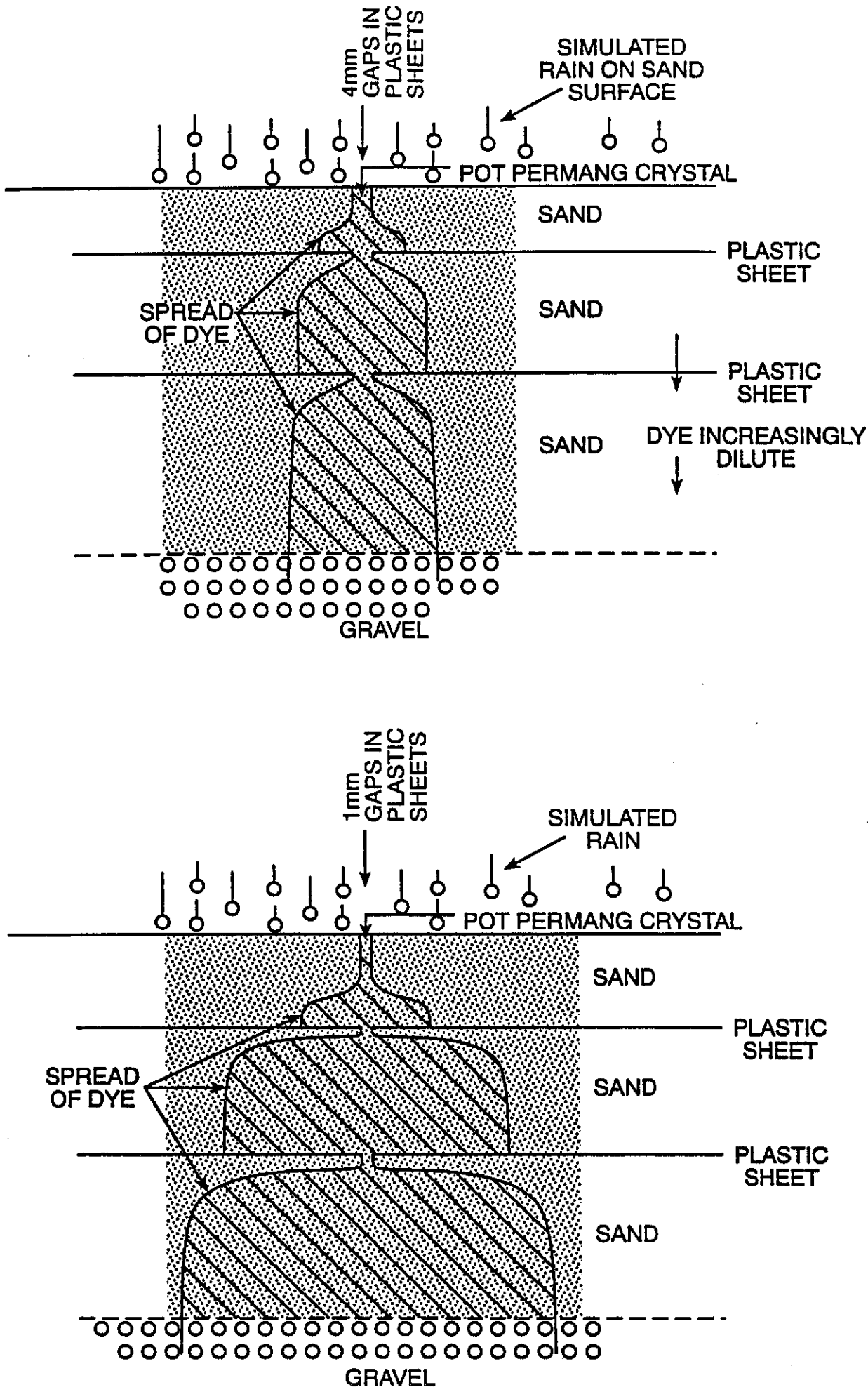

Figure 10.3.4 **Results of model tests to simulate the effect of the presence of plastic films in landfilled refuse**

CHAPTER 10.4

COMPUTER MODEL TO PREDICT MOVEMENT OF LEACHATE WITHIN A LANDFILL

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This section is extracted from a study carried out by Kobus Vorster (1994) in fulfilment of the requirements for the degree of Doctor of Philosophy at the University of the Witwatersrand.
Further details or copies of the program 'FLOW' can be obtained from the author at Technikon Pretoria, tel (012)-318 5120 or e-mail: kvorster@icon.co.za

10.4.1 STATEMENT OF THE PROBLEM

The purpose of this study was to develop a mathematical model which could be used to analyze water flow in a domestic waste disposal site in terms of the rate at which water accumulates in the landfill or leachate is released from the landfill. The elements considered by the model are shown in the following figure:

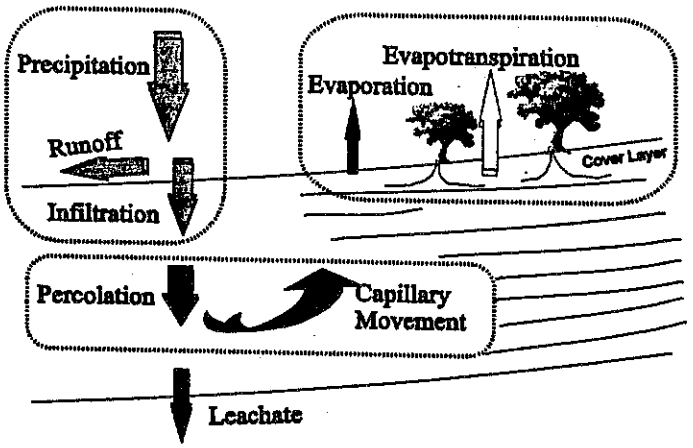

Figure 10.4.1 *Elements of the landfill water balance considered by the model FLOW*

The model considers the landfill to consist of a number of more or less horizontal layers, and makes provision for each of these layers to have different characteristics. It then does the necessary calculations for each of these elements to evaluate the overall effect of each element on the water balance of the landfill. Because these elements are often inter-related, the program uses iteration where required so that the effect of one element on another, or of one layer on another, may be taken into account.

The program also incorporates a rudimentary simulation of a horizontal drainage system to make provision for horizontal flow through a permeable layer immediately above a relatively impermeable liner. Should a perched water table develop above such a liner the program would allow (and make provision for) both horizontal flow towards the edge of the landfill as well as for vertical flow through the liner.

The computer implementation of the model resulted in a program which considers the landfill as a steady state model over a short period of time; over a longer period, the sum of the steady state models results in a pseudo-transient state model. It was found through experimentation that steady state periods of one week yielded results comparable to those of a model with one day steady state periods, with a sevenfold saving in computer time, but that longer steady state periods increased inaccuracies to an unacceptable level.

The way in which the model handles each of the elements of the overall water balance will now be briefly described.

10.4.2 PRECIPITATION

A landfill is typically sealed by a capping layer of natural soil. There is abundant evidence to show that the roots of any vegetation which may grow on the landfill surface will normally not penetrate the landfill below this capping layer. Surface vegetation will therefore extract moisture from the landfill's upper layer only, greatly increasing the landfill's ability to release some of its moisture into the atmosphere, which would happen mainly through evaporation in the absence of vegetation. Water which has passed this upper layer can be accounted for by one or more of the following mechanisms:

- as a chemical reagent (not considered by this model)
- as a biological reagent (not considered by this model)
- percolation to lower layers in the landfill
- upwards movement in the liquid phase because of pore suctions developing, termed *capillary movement* in the model FLOW
- movement in the gas phase (not considered by this model)

The model therefore treats the upper layer as a reservoir, with its water content being replenished by rain and capillary movement from the layer below, and being drained by surface evaporation and through extraction by vegetation, termed evapotranspiration. When this layer's water content

reaches a certain value, termed its field capacity, it is no longer able to hold the water to be extracted by evaporation and evapotranspiration, but releases it into the lower layers at the same rate as water is being fed into it. Although the sum of evaporation and evapotranspiration comfortably exceeds precipitation in most parts of Southern Africa if taken over a year, the rate at which water penetrates a landfill during a spell of rain exceeds the rate of evaporation and evapotranspiration by far; in addition, water extraction through evaporation and evapotranspiration slows down quite appreciably during extended dry spells. It becomes clear, therefore, that one should not only consider the total rainfall and evapotranspiration over extended periods when analyzing the water balance of a landfill, but that the short term **rainfall pattern** plays an extremely important role in the analysis of a landfill's water balance.

The program allows the user to supply monthly precipitation data to the computer, which it then converts into a series of weekly precipitations. This algorithm was developed in such a way that the generated weekly precipitations have similar statistical characteristics as actual weekly precipitations, and the program was shown to generate essentially similar results using actual weekly or generated weekly precipitations. Both of these sets of data also yielded results comparable to those generated using actual daily precipitation data.

This algorithm, and the program's outputs, were evaluated by using long term data provided by the Weather Bureau in Pretoria for four meteorological stations in different climatic regions of South Africa: Johannesburg, Durban, Cape Town and Kimberley.

Although it was found that the weekly data for these four regions had similar statistical characteristics, it is doubtful whether the same can be said about daily data. The advent of powerful microcomputers and the desire for greater accuracy means that this module of the program will eventually be revised.

10.4.3 RUNOFF

Descriptions of many infiltration models can be found in the literature, of which only two are given by way of examples:

Knight (1983) describes the formula due to **Philip** (1975):

$$i(t) = St^{1/2} + At + bt^{3/2} + ...$$

This series is believed to converge rapidly (Gish and Starr, 1983), so that only the first two terms are normally used.

Ahuja and Ross (1983) describes the following mathematical description of infiltration, due to **Morin and Benyamini** (1977) and **Morin and Cluff** (1980):

$$v_0 = (v_i - v_f)\, e^{-aR} + v_f$$

In this formula v_i is the initial infiltration rate and v_f the final steady state, and R is the cumulative rainfall.

The model uses the rational method, sometimes referred to as the Lloyd-Davies method, as described by Shaw, 1988. This method states that

$$Q_p = CiA$$

where Q_p is the peak flow resulting from a rainfall intensity i over a catchment area A, with C a coefficient of runoff which varies from 0,05 for flat sandy areas to 0,95 for impervious urban areas.

The program assumes that the first 10 mm of rain which falls in any given week will infiltrate the landfill with no runoff. Should more rain fall in the week under consideration, the runoff is determined by this formula using a coefficient of runoff specified by the user. Using data over several years for the Cape Town area it was found that, on average, more than 10 mm of rain fell in 17,7 weeks of each year.

The formulae proposed by Philip and by Morin and Cluff both yield essentially similar infiltration curves. A typical curve given by these three formulae is compared to the program's implementation of the Lloyd-Davies formula in figure 10.4.3.

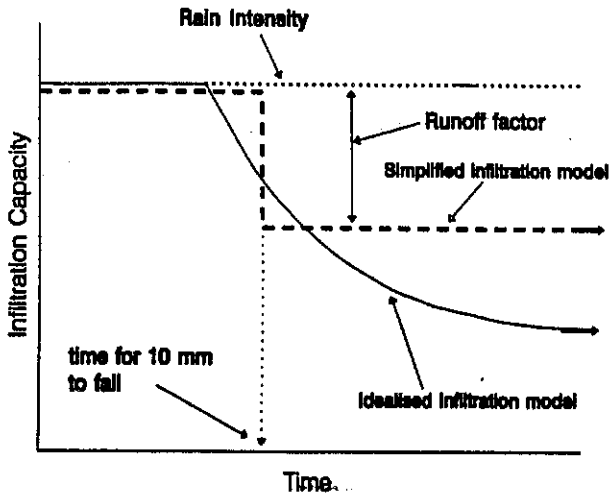

Figure 10.4.2: *Comparison of theoretical infiltration models to the simplified model used for this application.*

Infiltration tests on the Linbro Park landfill near Johannesburg by Blight and Blight (1993) showed

that runoff was extremely low for a variety of surface conditions investigated.

Based on the above, the program defaults to zero runoff unless instructed otherwise by the user, in which case it follows the method outlined above.

10.4.4 EVAPORATION

This module of the program is based on work done by Hojem (1988). He found that evaporation from bare soil surfaces was 30% of precipitation in case of sandy soils, and 50% of precipitation in case of heavy soils. The program defaults to 40%, unless the user supplies a different value when prompted to do so.

The user is prompted to give an estimate of the percentage of the landfill surface which is covered by vegetation. This calculation is then applied only to that fraction of the landfill surface which is not covered by vegetation.

10.4.5 EVAPOTRANSPIRATION

Many of the methods available to calculate evapotranspiration require data which are not readily available for specific sites. To obviate the need for meteorological testing, a simpler method which relied on data which would be either readily available or which could be obtained with relative ease was sought. It was eventually decided that the method proposed by Penman (1948), with a number of improvements as described by Shaw (1988) would be appropriate. The program uses the implementation of Penman's method used by Grindley (1969) to draw up a water budget for the landfill, as described by Shaw (1988).

Saturated soil relinquishes water until it reaches the moisture content at which it can just hold its moisture against the forces of gravity; it is then said to be at field capacity. As long as the moisture content is somewhere between saturation and field capacity, evapotranspiration occurs at the maximum possible rate, referred to as the potential evaporation, determined by meteorological conditions, and is taken as 70% of the rate of evaporation from a class A pan, after Hojem, 1988. In the early stages of his work, Penman used a factor of 60% in winter and 70% in summer (Shaw, 1988).

When the moisture content drops to less than field capacity, a soil moisture deficit (SMD), viz the amount of water required to restore the soil to field capacity, develops. As the SMD increases, evaporation slows down and vegetation extracts moisture with increasing difficulty, so reducing the rate of evapotranspiration. Penman, 1963, introduced the concept of a root constant, to quantify the amount of moisture, in mm depth, that can be extracted from a soil without difficulty by a given vegetation. This root constant varies from 75 mm for permanent grassland to 200 mm for woodland. It is assumed that evapotranspiration proceeds at the rate of the potential evaporation until the SMD reaches the appropriate root constant plus approximately 25 mm, after which evapotranspiration

slows down. For grassland, it is assumed that evapotranspiration occurs at the rate of potential evaporation until a SMD of 100 mm is reached, then slows down and ceases when the SMD reaches 125 mm, at which point permanent wilting occurs and evapotranspiration ceases. For trees, it is assumed that evapotranspiration equals potential evaporation if the SMD is less than 225 mm, then slows down until the SMD reaches 250 mm, assumed to be the wilting point of trees, where evapotranspiration is suspended. This is shown graphically in figure 10.4.2.

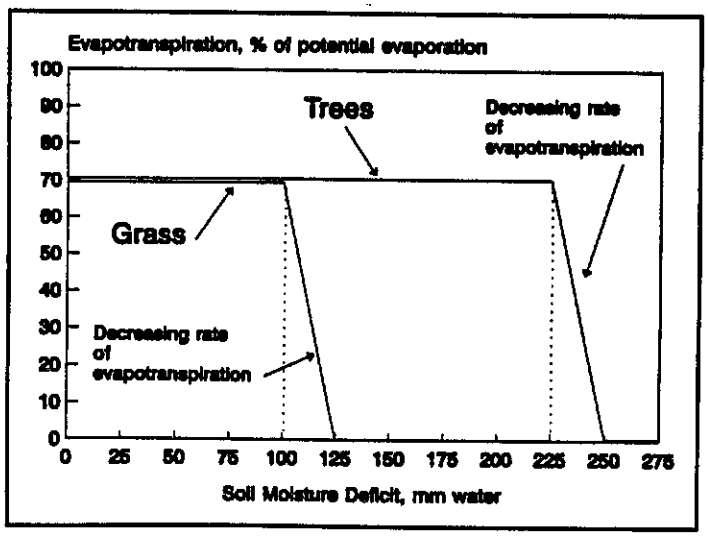

Figure 10.4.3 *Rate of evapotranspiration from grass and tree covered landfill surface as a function of Soil Moisture Deficit, expressed as a percentage of rate of potential evaporation*

The use of trees to increase the rate of evapotranspiration from landfills has been investigated by Ettala, 1992. Tests on a number of landfills in southern Finland indicate that a 100 mm cover layer is sufficient for grass vegetation, with 200 to 300 mm of rooting layer overlying a humus-rich layer of 200 to 300 mm being sufficient for growing willow trees. It was found that a mix of *Salix aquatica* and *Salix viminalis* could be established when the refuse was at least two years old

Because the thickness of the upper soil cover (typically 500 mm to 1 m) seems to be the maximum depth of root penetration of vegetation, it was decided to use the soil moisture deficit of the upper layer of material as the soil moisture deficit referred to by Penman to estimate the rate of evapotranspiration using the principle of the root constant.

To demonstrate how this module of the program works, the program was used to predict the total water content of the Linbro Park landfill to the end of the century, using measured data supplied by Hojem (1988), obtained by sampling a bore hole in the landfill in November 1988. It was also assumed, after Tyson (1986), that the dominant meteorological cycle in this area was of 11 years duration, so that the rainfall and evaporation for the year 1998, for example, would be similar to that

of the year 1987.

The program was run for the period 1989 to 2000, assuming that the landfill had no surface vegetation, or that respectively 10%, 30%, 50% or 70% of the surface area was covered by grass. For each case, the landfill's total water content was calculated, and compared to the landfill's overall water content of 5 250 mm when all the layers reached their field capacities and the landfill could be assumed to start leaking. The landfill's predicted total water content under the conditions as described is shown in figure 10.4.4a.

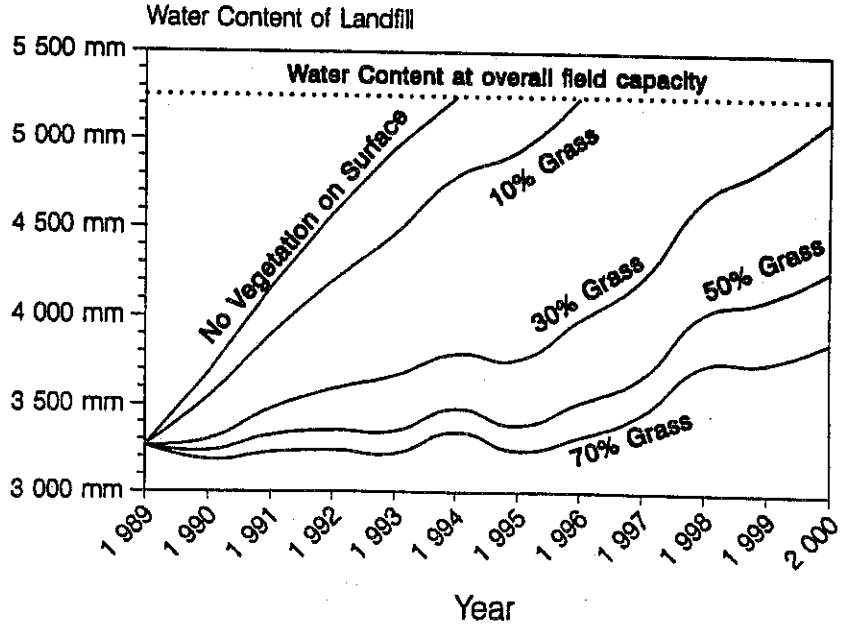

Figure 10.4.4a *Predicted water content of Linbro Park landfill using derived weekly data, for varying percentages of the surface covered by grass. It is assumed that leakage will commence as soon as the landfill reaches its overall field capacity.*

10.4.6 PERCOLATION

The program initially calculates, from data provided by the user, the volume of water in each layer. Thereafter it maintains a record of this volume for each week of the calculation period, by adding the volume of water entering from above through percolation and subtracting the volumes of water leaving the layer downwards through percolation (or seepage) or upwards through capillary movement.

To determine the volume each layer would release into the layer below, the program ads the volume the layer receives from above (through infiltration for the upper layer, and through percolation for

all other layers) to the volume of water it contained. If the new volume is less than the layer's field capacity it simply stores that water; if the new volume exceeds the layer's field capacity it releases a predetermined percentage of excess water (i.e. of the water in excess of its field capacity).

The percentage of excess water each layer would release was determined experimentally, using data from the Coastal Park landfill for 1989 and 1990. According to this data, each layer would release between 10,9% and 11,7% of excess water in each week.

It is now believed that the estimate of this percentage could be eliminated or, at least, improved upon by, applying the definition of field capacity more rigorously to the landfill (Vorster, 1997). This theory is presently (1998) still being investigated.

10.4.7 HORIZONTAL FLOW

Although the accumulation of water above a relatively impermeable liner would be rare under the arid conditions normally found in Southern Africa, a mechanism for such flow was incorporated into the program. The mechanism is best explained by reference to figure 10.4.4b.

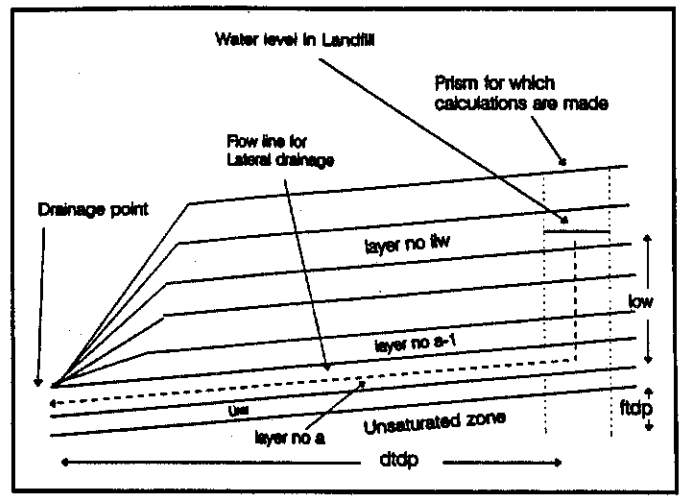

Figure 10.4.4b *Cross section through landfill to show how lateral water flow in the layer above the liner has been modeled*

The model considers a prism of accumulated water in the landfill, and uses the hydraulic gradient if would cause from that point to the edge of the landfill to calculate the horizontal seepage rate. The amount of water the program estimates to leave the landfill through this route is subtracted from the accumulated volume of water in the landfill for each calculation period, to maintain the landfill's water budget.

10.4.8 CAPILLARY MOVEMENT

It is well known that a suction develops in a soil as its moisture content drops. Typically, when a soil is near saturation, it will exercise a suction of approximately 100 Pa, increasing to about 10 kPa at field capacity and 1500 kPa (or pF = 4,2) at the permanent wilting point of vegetation (Marshall, 1959).

Marshall also provides curves of suction against moisture content for a number of materials ranging from coarse sands to slate dust and limestone. At the time when the model was developed, no such data was available for the landfill material in the Coastal Park landfill, but testing of this material is presently (1998) being done in the Technikon's laboratories.

Because no such data is available for either the cover material or the refuse at the Linbro Park landfill, hypothetical curves were drawn up to be roughly similar to the curves given by Marshall, bearing in mind the parameters given above and the known field capacities of the material in the Linbro Park landfill.

Using this data and the initial conditions (supplied by the user), the program calculates the pore suction in each layer. It then compares the suction in each layer with the suction in the layer below it and, if the upper layer has a higher pore suction, it calculates how much water should flow from the lower to the upper layer to equalize pore pressures in the two layers. This amount of water is, of course, limited by the volume of water actually present in the lower layer. The program then recalculates the landfill's water budget by assuming that a user specified fraction of this volume of water (required to equalize pore pressures between these two layers) is actually drawn from the lower to the upper of the two layers by the difference in pore suction. Naturally, this assumed water transfer upsets the pore suctions in the two layers above and below the two layers under consideration, so the process is repeated by iteration for all layers in the landfill until equilibrium is reached.

The fraction of water required to move between the two layers to equalize pore suction, referred to above, was found by experimentation to be between about 2,1% and 2,4% per week. These figures were found by comparing the program's predictions with actual leachate generation by the Coastal Park landfill in 1989 and 1990, as described in paragraph 10.4.9.4 below. Work is presently being carried out in the Technikon's laboratories to get a better approximation of these fractions.

10.4.9 APPLICATION OF THE MODEL TO THE COASTAL PARK LANDFILL

Although Coastal Park is located in a winter rainfall area with very little rain falling during the summer months the landfill continues to leak slowly throughout the year.

10.4.9.1 Initial Conditions

Because the landfill is fairly new, it was decided to run the program from 1986 (when the landfill was constructed) to 1990 (the last year for which data was available at the time), and to compare the actual measurement of leachate generated in 1989 and 1990 with the program's predictions. No data could be found on the moisture content of the landfill when it was first constructed, so again a range of values had to be tested and the one found which, in conjunction with the other parameters, caused the model's predictions to coincide with actual measurements. It was eventually found that the assumption of an initial degree of saturation of 66 % yielded acceptable results.

10.4.9.2 Surface Vegetation

The landfill's surface is not artificially vegetated after placement of the cover layer, but the grass seeds in the sand germinate quite easily and the surface becomes covered with the indigenous grass within a few months. It was therefore assumed that the landfill had no vegetation on its surface in 1986 (when the first layers were placed), that 40 % of the surface was covered with grass in 1987, and that 80 % of the surface was covered with grass thereafter. The figure is a realistic estimate, based on recent personal inspection of the surface and information gained from the staff working on the landfill. Although there are many trees growing all around the landfill, there are none on the landfill itself.

10.4.9.3 Downwards Flow Parameter

This model assumes that only a certain percentage, supplied by the user, of the excess water (i.e. water in excess of the field capacity) of each layer percolates downwards into the next layer during each week, as described in paragraph 10.4.6 above.

The program was run with this parameter being varied from 10% to 14% and all other parameters being kept constant. The predicted annual flows for 1989 and 1990 were then compared with the averages for the five test cells over these periods. The results of these computations are shown in figure 10.4.5.

These graphs show that a value of about 11,7% yields a correct prediction for 1989, and a figure of about 10,9% a correct prediction for 1990. It should be noted, however, that the actual measurements are scattered quite widely around the average values. These graphs nevertheless show that this parameter needs to be determined quite accurately before the model can be relied upon to provide reliable predictions, and emphasize the necessity of the continuation of research on the actual mechanisms controlling water movement in a landfill

so that the model can be properly calibrated, after which it could be used with confidence to evaluate landfill designs and landfill management.

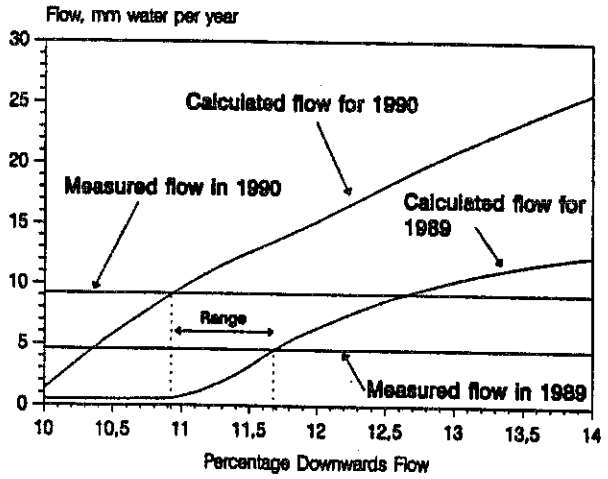

Figure 10.4.5 *Comparison of the results of actual measurements of leachate flow rates with those predicted by model FLOW when parameter for downwards flow is varied.*

10.4.9.4 Capillary Movement

As described in paragraph 10.4.8 above, this parameter had to be determined experimentally, by running the program with the parameter's value being varied between zero (no capillary movement) and 3%, and comparing the program's output with the measured data for Coastal Park in 1989 and 1990. Figure 10.4.6 summarizes the results of these trial runs.

As shown by these graphs, the program's prediction corresponds with the actually measured rate of leakage in 1989 if this parameter is given a value of about 2,1%, and with the 1990 data if the parameter has a value of about 2,4 %.

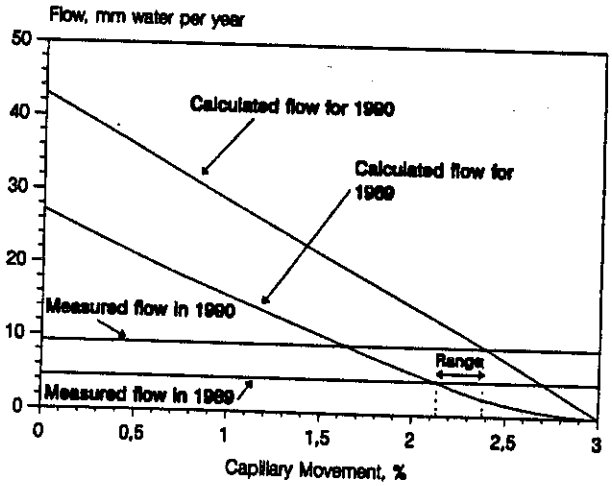

Figure 10.4.6 *Comparison of the results of actual measurements of leachate flow rates with those predicted by model FLOW when parameter for capillary movement is varied.*

10.4.9.5 Sensitivity of the Model for the Degree of Saturation of the Landfill When Constructed

The process of estimating the values for the program parameters by comparing with actual measurements at Coastal Park was repeated with the degree of saturation of the material when the landfill was constructed. Because no such data could be found, the program was run with this parameter being varied; figure 10.4.7 shows the results for initial degrees of saturation between 64 % and 68 %. This exercise shows that this parameter has to be determined or estimated very accurately if the model is to be reliable.

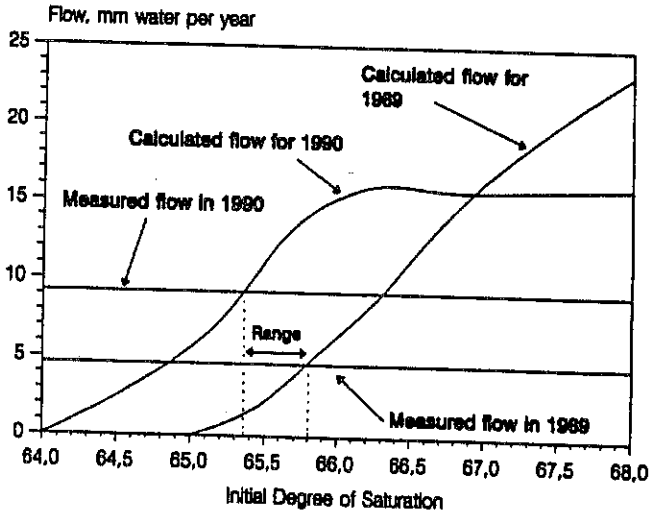

Figure 10.4.7 *Comparison of the results of actual measurements of leachate flow rates with those predicted by model FLOW when the assumed degree of saturation of the material when first placed is varied.*

10.4.9.6 Actual Leakage Measurements at Coastal Park

There are five leakage collection points in the Coastal Park landfill where leakage is collected over an area of approximately 14 m square each. A schematic presentation of such a collection point is shown in figure 10.4.8.

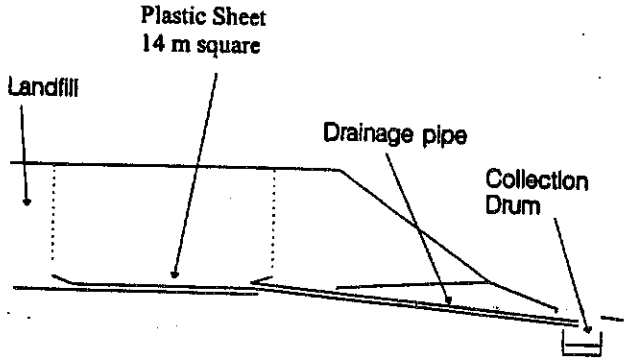

Figure 10.4.8 *Schematic presentation of a leachate collection point at the Coastal Park Landfill.*

The rate at which each the landfill leaked at each of these collection points was carefully measured over several years. There was quite a variation between the five points, as is shown by figure 10.4.9.

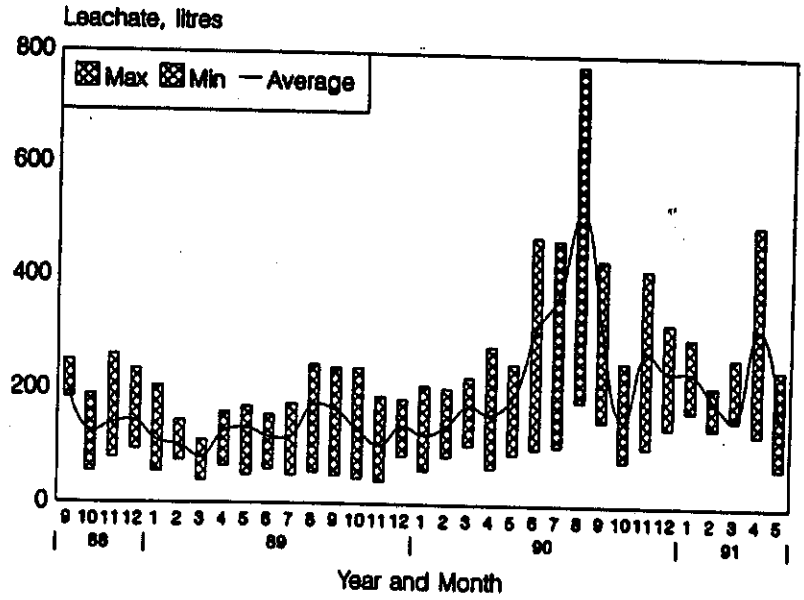

Figure 10.4.9 *Measured leachate production at Coastal Park Landfill, showing the lowest and highest measurements as well as the average of the measurements at five collection points.*

The bar for each month shows the range over the five collection points, and the line graph the average for the five points. There are very few landfills for which such data is available, and it proved extremely valuable to test the predictions generated by the model FLOW.

10.4.9.7 Predicted Rate of Leachate Generation at Coastal Park

The model was applied to the Coastal Park landfill using the parameters as outlined in the preceding paragraphs, and a graph was drawn to compare the model's "prediction" for 1989 and 1990 with the average measured leakage rates, all expressed in mm of water per month. The results obtained are shown in figure 10.4.10.

The two parameters which had to be found experimentally (the fraction of excess water released into the lower layers, and the fraction of water which should move upwards under capillary action to equalize pore suctions) emphasize the need for further research in these areas.

10.4.11 REFERENCES

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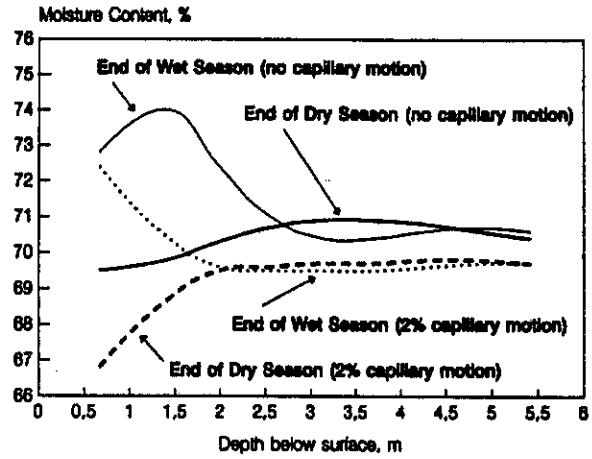

Figure 10.4.11 *Variation of moisture content of Coastal Park landfill with depth, at end of wet and dry seasons, with and without modelling for capillary movement of water in landfill.*

When no capillary movement is being modeled, FLOW predicts that the moisture content of the landfill will vary seasonally to a depth of about 2,5 m. Variation in moisture content below this depth is probably due to percolation.

The situation when capillary movement is modeled is as expected; the landfill is at an overall lover moisture content because a mechanism is now assumed to exist for water to escape from the landfill in an upwards direction in addition to downwards percolation. Because of the existence of this mechanism, the seasonal variation in moisture content does not go down as deep as without it: the upwards movement of water tends to stabilize the water content between depths of 2,0 m and 2,5 m.

10.4.10 CONCLUSION

It was shown that the model is capable of producing realistic values for the effect of surface vegetation, the moisture distribution in the landfill at the end of the wet and dry seasons, and the amount of leakage the landfill can be expected to generate.

It was also shown that the model is quite sensitive for the initial moisture content of the landfill material, which means that this data should be obtained as accurately as possible when the landfill is started, or that accurate estimates should be made from similar case studies.

SECTION 10.5
HYDROLOGICAL, GEOCHEMICAL AND BIOLOGICAL SIGNIFICANCE OF THE VADOSE ZONE AND ITS ROLE AS A BUFFER IN CONTAMINATED SOIL SYSTEMS: A LITERATURE REVIEW

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10.5.1 INTRODUCTION

Contaminant migration from shallow land burial sites most frequently involves unsaturated transport processes. Under unsaturated conditions, both chemical and hydrological factors control the subsurface transport of contaminants (Jardine *et al.*, 1993). Contaminant plumes emanating from waste sites are typically near neutral pH, anoxic, high in ionic strength and capable of dissolving reducible oxides from the sediments (Ryan & Gschwend, 1994). If no containment liner is in place, the leachate produced from a waste landfill will percolate through the vadose zone before entering and contaminating the groundwater. It is in the vadose zone where important attenuation mechanisms can significantly reduce the intensity of groundwater contamination. These attenuation mechanisms are physical, geochemical and biological in nature, and it is in the light of these processes that this literature review has been conducted.

Ferguson & Moolman (1994) carried out a literature review of the factors affecting contaminant mobility in soils. Their focus was on the chemical properties of the inorganic and organic contaminants, soil properties, climatic conditions and hazard assessment of contaminants. In this review more emphasis is placed on the flow of soil water and movement of contaminants in variably saturated soils and on the attenuation processes which influence the mobility and fate of contaminants, primarily in the vadose zone.

10.5.2 MOVEMENT OF WATER THROUGH POROUS MEDIA

The movement of water through soils, both saturated and unsaturated, is a fundamental process governing the migration of solutes and many pollutants in soils systems. In describing *saturated* hydraulic conductivity, the approach taken often involves the application of fluid flow theory through capillary tubes (Hillel, 1982), i.e., soil pores are assumed equivalent in structure to a set or bundle of straight, smooth tubes, each uniform in radius. However, this is a physically simplistic approach and becomes inadequate when predictions of soil water flow through complex soil media need to be made, since the walls of pores are not smooth, many of them have "dead-ends" and they do not possess uniform internal radii. A more thorough approach would be to describe flow through complex porous media in terms of a macroscopic *flow velocity vector*, which is the overall average of the microscopic velocities over the total volume of the soil. In this way detailed flow patterns are ignored, and the conducting body is treated as though it were a uniform medium, with flow spread out over the entire cross-section, solid and pore spaces alike (Hillel, 1982). Pursuant to this approach, the equation, referred to as Darcy's Law can be expressed as:

$$q = K\frac{\Delta H}{L} \qquad (1)$$

where q is the flux density (or simply the flux), and $\Delta H/L$ is the hydraulic head drop per unit distance in the direction of flow. K is the hydraulic conductivity and represents the proportionality constant. This is the basic form of the equation which is generally used in determining saturated hydraulic conductivity.

Although Darcy's Law and related equations describing saturated flow have been shown to be invaluable predictive tools (Hillel, 1982; Knox *et al.*, 1993; Daniel, 1993), their application is limited since most processes involving soil-water interactions in the field occur when the soil is in an unsaturated condition. Unsaturated flow processes are in general complicated and difficult to describe quantitatively, since they often entail changes in the state and content of soil water during flow. Such changes involve complex relations among soil wetness, suction and conductivity, the interrelations between which may further be complicated by hysteresis (Hillel, 1982; Kutílek & Nielsen, 1994). The formulation and solution of problems associated with unsaturated hydraulic conductivity very often require the use of indirect methods of analysis, based on approximations or numerical techniques (Hillel, 1982; Lorentz, 1993; Logsdon & Jaynes, 1993).

The concepts of saturated and unsaturated hydraulic conductivity (K_s and K, respectively) are well covered in a number of texts, including Hillel (1982), Klute (1986), Knox *et al.* (1993), Daniel (1993) and Kutílek & Nielsen (1994). The latter include probably the most mathematically comprehensive description of hydraulic conductivity available. What follows is a brief description of some of the concepts of unsaturated hydraulic conductivity, with some reference to saturated flow.

10.5.2.1 Unsaturated Flow

The simplest approach to describing unsaturated flow is to consider flow in rigid soils (i.e. soils which do not change their bulk volume with change in moisture content) in which the soil water content is invariant with time (Kutílek & Nielsen, 1994). In as much as the soil is not saturated and flow occurs primarily in those pores filled with water, the value of K will be smaller than that of K_s for the same soil. Equation (1) can be rewritten to allow the hydraulic conductivity to become a function of soil water potential head h, i.e.

$$q = -K(h)\frac{\partial H}{\partial z} \qquad (2)$$

and for two- and three-dimensional problems,

$$q = -K(h)\nabla H \qquad (3)$$

Equations (2) and (3) are called Darcy-Buckingham equations.

The unsaturated hydraulic conductivity is physically dependent on the soil water content Θ, because water flow is realized primarily in pores filled with water. Figure 1 demonstrates various soil water/flow relationships. Because the relationship $\Theta(h)$ (i.e. the relationship between volumetric water content and matric potential or soil water tension) is strongly influenced by hysteresis, K(h) is strongly hysteretic. On the other hand, it follows from percolation theory that $K(\Theta)$ is only mildly hysteretic (Kutílek & Nielsen, 1994).

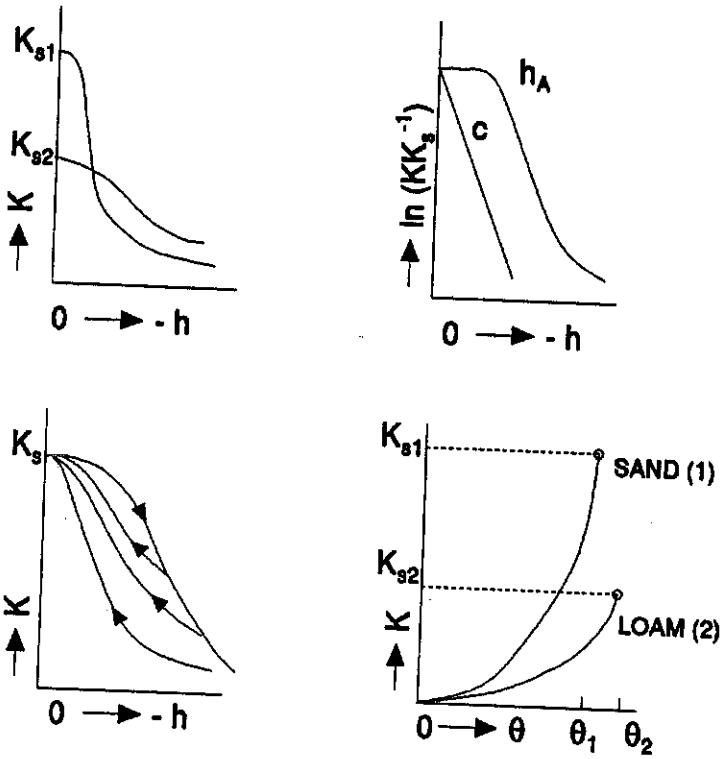

Figure 10.5.1 Dependence of unsaturated hydraulic conductivity K upon negative pressure head h (strongly hysteretic) and upon soil water content Θ.

Examples of K(Θ) and K(h) demonstrated in Figure 1 (where c is a coefficient and h_A is for soils manifesting a distinct air entry value), show that the more permeable soil at saturation does not necessarily keep its greater permeability throughout the entire unsaturated region. It is also evident in Figure 1 that the hysteretic behaviour of K(h) demands that, for a given value of h, the value of K is greater for drainage than for wetting (Kutílek & Nielsen, 1994).

Kutílek & Nielsen (1994) can be referred to for a more mathematical approach to describing unsaturated hydraulic conductivity under time-variant soil moisture conditions. They also present an in-depth study of the role of pore size distribution and total porosity on the physical interpretation of K(Θ) or K(h), as well as the derivation of the Richard's Equation for unsteady flow conditions, flow in non-rigid (swelling) soils, non-isothermal flow and flow at temperatures below zero.

Mualem (1986) presents mathematical formulae and methods for predicting hydraulic conductivity of unsaturated soils based on macroscopic and also statistical models. He also discusses hysteresis of the hydraulic conductivity, capillary head and water-content relations and how they depend on the history of wetting and drying processes to which the porous medium was subjected. The K(ψ) (where ψ is the capillary head) hysteresis is magnified by orders of magnitude relative to the Θ(ψ) hysteresis, while the K(Θ) hysteresis is much smaller. Mualem (1986) points out that it is preferable to use the K(Θ) relationship rather than the K(ψ) for any practical use in which wetting and drying processes are involved, if hysteresis is to be neglected.

10.5.2.2 Saturated Versus Unsaturated Flow

Unsaturated flow conditions are in general complicated and difficult to describe quantitatively, since they often entail changes in the state and content of soil water during flow. Such changes involve complex relations among the variables soil wetness, suction and conductivity, whose interrelations may further be complicated by hysteresis. In recent decades, unsaturated flow has become one of the most important and active topics of research in soil physics, resulting in significant theoretical and practical advances (Hillel 1982).

Soil water flow is caused by a driving force resulting from a potential gradient and flow takes place in the direction of decreasing potential. The rate of flow (flux) is proportional to the potential gradient and is affected by the geometric properties of the pore channels through which the flow takes place. These principles apply to both saturated and unsaturated flow (Hillel, 1982). The moving force in a saturated soil is the gradient of a positive pressure potential. On the other hand, water in an unsaturated soil is subject to a sub-atmospheric pressure, or suction, which is equivalent to a negative pressure potential, the gradient of which constitutes a moving force. Matric suction is due to the affinity of water molecules for soil particle surfaces and to capillary forces. Water will tend to move from a zone where the capillary menisci are less curved to where they are more highly curved, or from where the hydration envelopes surrounding the soil particles are thicker to where they are thinner. The moving force is greatest at the wetting front zone, where water is advancing into an originally dry soil, the region where the suction gradient is at its greatest (Hillel, 1982).

The hydraulic conductivity is perhaps the most important difference between saturated and unsaturated flow. All the pores are filled and conducting under saturated conditions, so that continuity and conductivity are maximal. There is a corresponding decrease in the cross-sectional area of the soil's conducting portion as the soil desaturates and some of the pores become air filled. In addition, it is the largest pores which are the most conductive, but which are also the first to empty. A consequence of desaturation is an increase in tortuosity because of the circumvention of empty pores (Hillel, 1982).

At saturation, the most conductive soils are those in which large and continuous pores constitute most of the overall volume, while the least conductive are the soils in which the pore volume consists of numerous micropores. Thus a saturated sandy soil conducts water more rapidly and with greater ease than a clayey soil. However, the opposite can be true for unsaturated conditions. In a soil with large pores, these pores empty quickly and become nonconducting as suction develops, thus steeply decreasing the initial high conductivity. On the other hand, in a soil with small pores, many of the pores retain and conduct water even at appreciable suction, so that hydraulic conductivity does not decrease as steeply and may actually become greater than that of a soil with large pores and subjected to the same degree of suction (Hillel, 1982).

In most instances the soil in the field is in an unsaturated state, and it often happens that flow is more appreciable and persists for longer in clayey than in sandy soils. For this reason a layer of sand in a fine-textured profile, far from enhancing flow, may actually impede unsaturated water movement. Only when water accumulates above the sand and suction decreases sufficiently for water to enter the large pores of the sand, can this impedance be overcome (Hillel, 1982).

10.5.2.3 Methods of Measuring Unsaturated Hydraulic Conductivity

Green, Ahuja & Chong (1986) present various field methods for the measurement of hydraulic conductivity of unsaturated soils. Short descriptions of these methods are presented below.

Unsteady drainage-flux method. This method of determining unsaturated hydraulic conductivity and diffusivity *in situ* is based on Darcian analysis of transient soil water content and hydraulic head profiles during vertical drainage following a heavy rainfall or irrigation. Isothermal conditions are assumed to exist in the soil profile during the course of the drainage, neglecting the effect of any temperature changes which might occur. When ponded infiltration has ceased, a plastic sheet is placed over the soil surface to prevent surface evaporation from occurring. The method was first used in the field by Richard *et al.* (1956). It was developed further by Nielsen *et al.* (1964), Rose *et al.* (1965) and van Bavel *et al.* (1968). Since then, the method has been used by many other investigators to determine hydraulic conductivity of well-drained soils. Typical field apparatus for the method would include tensiometers equipped with mercury manometers or pressure transducers, a calibrated neutron probe with access tubes and a double ring infiltrometer. An equation is used to calculate $K(\Theta)$ after analysis of Θ and H (hydraulic head) profiles measured at frequent time intervals at desired depths (z).

Simplified unsteady drainage-flux method. The simplified method determines $K(\Theta)$ using only the periodic measurements of $\Theta(z,t)$ (i.e. transient volumetric water content, where z is the vertical distance coordinate and t is time) during redistribution of water in the soil profile following ponded infiltration. In addition to the assumption of negligible lateral soil water flow, the simplified method assumes a unit hydraulic head (i.e., $\delta H/\delta z = -1$), during drainage. The method can be used for the calculation of hydraulic conductivity and soil water diffusivity (ratio of hydraulic conductivity to soil water capacity). The method is most useful when only $K(\Theta)$ is required.

Crust-imposed steady flux method. In contrast to the unsteady flow methods described in the previous sections, in which the downward flux of water past a given depth in the soil profile is calculated by invoking the conservation of mass as drainage proceeds, this steady flux method involves the establishment of a known flux of water through an isolated pedestal of soil by means of a crust at the soil surface. When the water flux through a soil horizon is maintained at a value below the saturated conductivity under steady flow with unit hydraulic gradient, the hydraulic conductivity is equal to the imposed flux. This conductivity is associated with a soil-water pressure less than zero, which is conveniently measured by a single small tensiometer inserted into the soil pedestal, giving one point on a K(h) curve. Successive measurement with different crusts, each with a different hydraulic conductivity, provide an *in situ* characterisation of the K(h) relationship over the range of pressures achieved.

Sprinkler-imposed steady flux method. This method differs from the crust-imposed steady flux method principally by the way in which the flux of water moving through the soil profile is maintained at a selected steady value below the infiltration capacity of the soil. Sprinkler application of water provides a means of controlling the flux of water entering the soil

surface; given sufficient time, the flux approaches a constant value throughout the profile. The hydraulic conductivity at a selected steady flux is given by the flux divided by the gradient in hydraulic head over the depth interval of interest. The method is therefore straightforward, requiring the establishment of steady water flux by sprinkler application of water and the measurement of Θ and h at the depths of interest for each flux.

10.5.2.4 Indirect Methods of Estimating Unsaturated Hydraulic Conductivity

Indirect methods can be used for the estimation of unsaturated hydraulic conductivity. One method described by Lorentz (1993) involves first establishing the liquid retention characteristic (relationship between matric potential or suction and water content) of the porous medium, then estimating the unsaturated hydraulic conductivity from this relationship. In this method the controlled outflow apparatus is used to establish a well defined retention characteristic shape by judicious control of the liquid outflow in a much shorter period, an advantage over more conventional methods (such as the pressure plate). The unsaturated hydraulic conductivity is then estimated using theoretical relationships defined by Hutson (1985; cited in Lorentz, 1993).

Another method of estimating unsaturated hydraulic conductivity involves the use of tension infiltrometers. In this field method, water is allowed to infiltrate the soil under a predetermined tension (or suction). Lorentz (1993) used this technique to estimate unsaturated flow of soils in the De Hoek experimental catchment in Natal. The method was also used in conjunction with other experimental apparatus by Lorentz *et al.* (1993) during soil water budgeting and modelling of some South African catchments. Logsdon & Jaynes (1993) investigated the different methodologies for estimating unsaturated hydraulic conductivity as a function of soil water pressure head (i.e. $K(h)$) using the tension infiltrometer apparatus. For good results, they recommend ponded infiltration should be run first followed by negative head infiltration runs on the same site. Nonlinear regression should be used to manipulate the data to estimate a value of K(h).

The unsaturated hydraulic conductivity, K, as a function of soil water tension, h, is a required input in many mathematical models of soil water flux. However, K(h) data for a given soil are not always available and often expensive to measure. There are a number of variations of pore interaction models to predict K(h) from the soil water characteristic, which is the relationship between the volumetric water content, θ, and h (i.e., $\theta(h)$). Alexander & Skaggs (1987) present a thorough investigation of 14 methods to predict K(h) from soil texture and/or other soil data. Soil textural data are available more often than θ(h) data, and are more easily obtained than either K(h) or θ(h). The authors list methods (with references) to predict K(h) from textural data. Another method also used to predict K(h) involves first using one of the methods presented in the literature (e.g., Gosh, 1976; Arya & Paris, 1981; Rawls & Brackensiek, 1982) to estimate θ(h), then predicting K(h) from θ(h). Alexander & Skaggs (1987) concluded that the method described by McCuen *et al.* (1981) gave the best predictions of K(h) (closest agreement with measured values) for all but the sandy soils tested. For sandy soils, the best prediction of K(h) was obtained by first predicting θ(h) by the method of Gosh (1976) and then applying the equation by Burdine (1953) to predict K(h).

10.5.3 THE VADOSE ZONE

The hydrogeologic profile extending from the ground surface to the upper surface of the principal water bearing formation is called the "vadose zone". The physical properties of the vadose zone associated with storage of water include (Daniel, 1993):

1. total thickness;
2. porosity;
3. bulk density;
4. water content;
5. soil/water characteristics;
6. field capacity (specific retention);
7. specific yield;
8. fillable porosity.

Technical information on each of these properties may be found in works by Davis and de Wiest (1966), Childs (1969), Hillel (1982), Colley *et al.* (1972), Bouwer (1978), Brakensiek *et al.* (1979), Freeze & Cherry (1979) and Everett *et al.* (1984).

Davis & de Wiest (1966) subdivided the vadose zone into three regions, designated as: the *soil zone*, the *intermediate vadose zone*, and the *capillary fringe* (Figure 10.5.2).

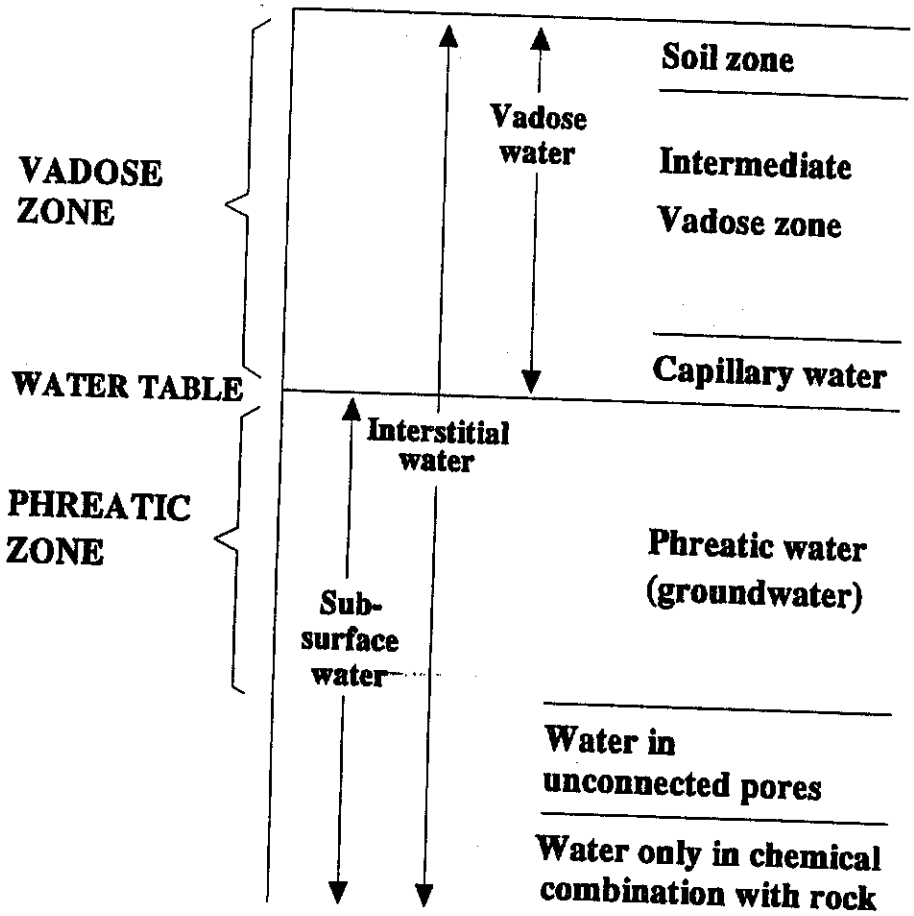

Figure 10.5.2 Classification of subsurface waters (Davis and de Wiest, 1966).

The movement of water in the *soil zone* occurs mainly as unsaturated flow caused by infiltration, percolation, redistribution and evaporation. Typically this zone varies in depth from 1-10 m and water is held by capillary forces (adhesion and cohesion). When the water-holding capacity of the capillary forces is exceeded, water begins to percolate downward in response to gravity.

As the weathered materials of the regolith grade into underlying strata, which are often unweathered, a transition is made to the *intermediate vadose zone*. In some regions this zone may not even exist, and the soil zone merges directly with the bedrock. The intermediate zone in alluvial basins, however, may be hundreds of meters thick. Often these very thick zones contain micro- and macro-lenses of clay and silt which can complicate the flow of moisture and solutes considerably. Water in the vadose zone exists primarily in the unsaturated state. Occasionally, perched groundwater may develop in the interfacial deposits of regions containing varying textures. Such perching may be hydraulically connected to ephemeral or perennial stream channels, wherein temporary or permanent water tables may develop (Daniel, 1993).

The *capillary fringe* is the base of the unsaturated zone that merges with underlying saturated deposits of the principal water bearing formation. The hydraulic conductivity of this zone and the height of the capillary fringe is dependent on the texture of the porous medium. The finer the pore structure of the zone, the higher the capillary movement of water will be. The height of the capillary fringe becomes important when understanding the hydrodynamics of the underlying zone of a wastepile.

In 1983 Bagchi published a paper on the design of natural, attenuation-type, sanitary landfills. He proposed the landfill be constructed on a natural thick clay stratum overlying a sandy aquifer. The clayey material would form the vadose zone and would be the medium in which primary attenuation mechanisms would operate in removing heavy metals and other contaminants from the leachate. Mundell (1983) responded to the proposed design and pointed out some potential flaws. The design method proposed assumes that the clay stratum is relatively intact and free of any secondary structure which may include pervious seams, fissures or fractures. The presence of a high percentage of these defects in a clay stratum brought about by the method of deposition, or volume changes during desiccation or geochemical processes, can greatly alter the stratum's ability to attenuate solutes, and may allow significant passage of relatively unaltered leachate, followed by subsequent groundwater pollution. The presence of such defects must be assessed during the hydrogeological study of the proposed site by conducting *in situ* permeability tests.

10.5.4 THE "BUFFER ZONE" CONCEPT IN POLLUTANT ATTENUATION

Various physical, chemical and biological processes can be responsible for the attenuation of landfill leachate. Attenuation refers to the immobilisation and retardation of the leachate and its constituents by the porous medium through which it passes. The *buffer zone* concept is based on the idea that a specified depth is allowed between the base of the landfill and the groundwater table in which these processes can act in attenuating the leachate seeping from the base of the landfill. Although sound in theory, natural attenuation processes are not sufficiently intense or sustainable to justify the exclusion of artificial barriers and attenuation systems in augmenting leachate attenuation for prevention of groundwater contamination. There seems to be no direct reference in the literature to "buffer zones" below landfills or

to the depth required to allow the leachate attenuation process to work efficiently. However, it is important to understand these processes because they do play a crucial role in the fate and subsurface transport of contaminants.

Two basic elements affecting the transport and fate of contaminants in the subsurface are properties of the subsurface materials or the subsurface environment and the physicochemical and biological properties of the contaminant. Knox *et al.* (1993) provide an overview of several subsurface and contaminant properties which may affect the transport and fate of the contaminants in the subsurface and indicate the impacts caused by these properties. The general categories of processes affecting subsurface fate and transport of contaminants are:

Hydrodynamic processes - affect contaminant transport by impacting the flow of groundwater (in terms of quantity of flow and flow paths followed) in the subsurface. Examples of these types of processes are advection, dispersion, preferential flow, etc.

Abiotic (nonbiological) processes - affect contaminant transport by causing interactions between the contaminant and stationary subsurface material (e.g., sorption, ion-exchange) or by affecting the form of the contaminant (e.g., hydrolysis, redox reactions).

Biotic processes - affect contaminant transport by metabolizing or mineralizing the contaminant (e.g. organic contaminants). Examples of these processes would include aerobic, anoxic and anaerobic biodegradation.

Knox *et al.* (1993) devote a full chapter to each of these processes. Tables 1 and 2 give an expanded list of subsurface processes and corresponding subsurface and contaminant properties influencing these processes.

It should be noted that hydrodynamic solute transport and multiphase flow are processes which would play a more important role under saturated conditions, whereas the abiotic and biotic processes would be equally important under unsaturated and saturated conditions in their effect on contaminant fate and transport.

TABLE 10.5.1: SUBSURFACE PROCESSES CORRESPONDING SUBSURFACE PROPERTIES AFFECTING THE FATE AND TRANSPORT OF CONTAMINANTS*

PROCESS	SUBSURFACE PROPERTY
Hydrodynamic Solute Transport	
Advection	Ground water gradient, hydraulic conductivity, porosity
Dispersion	Dispersivity, pore water velocity
Preferential flow	Pore size distribution, fractures, macropores
Abiotic Solute Transport	
Adsorption	Organic content, clay content, specific surface area
Volatilization	Degree of saturation
Ion exchange	Cation exchange capacity, ionic strength, background ions
Hydrolysis	pH, competing reactions
Precipitation/dissolution	pH, other metals
Co-solvation	Types and fraction of other solvents present
Redox	pE, pH
Colloid transport	pH, ionic strength, flow rate, mobile particle size, aquifer and particle surface chemistry
Biotic	
Metabolism/co-metabolism	Microorganisms, nutrients, pH, pE (electron acceptors), trace elements
Multiphase Flow	Intrinsic permeability, saturation, porosity

*from Knox *et al.* (1993)

TABLE 10.5.2: SUBSURFACE PROCESSES AND CORRESPONDING CONTAMINANT INTERACTIONS AFFECTING THE FATE AND TRANSPORT OF CONTAMINANTS*

PROCESS	CONTAMINANT PROPERTY	INTERACTIONS
Hydrodynamic Solute Transport		
Advection	Independent of contaminant	
Dispersion	Diffusion coefficient	Dispersion coefficient
Preferential flow		
Abiotic Solute Transport		
Adsorption	Solubility, octanol-water partition coefficient	
Volatilization	Vapour pressure, Henry's constant	
Ion Exchange	Valency, dipole moment	
Hydrolysis	Hydrolysis half-life	
Precipitation/dissolution	Solubility versus pH, speciation reactions	
Co-solvation	Solubility, octonal-water partition coefficient	
Redox	pK_a	
Colloid transport	Sorption, reactivity, speciation, solubility	Colloid stability
Biotic		
Metabolism/Co-metabolism	BOD, COD, degree of halogenation, etc.	
Multiphase Flow	Solubility, volatility, density, viscosity	Relative permeability, residual saturation, wettability, interfacial tension (surface tension), capillary pressure

*from Knox *et al.* (1993)

10.5.4.1 Physical Attenuation

Physical attenuation can occur through filtering of suspended particles from leachate which may coincide with a reduction in hydraulic conductivity of the soil. Column experiments with landfill leachate by Harraway (1996) in rigid-wall permeameters showed that suspended particles (concentration of 400 $mg.l^{-1}$) were becoming entrapped in the soil matrix. The subsequent blocking of pores resulted in a reduction of saturated hydraulic conductivity of the calcareous sand from a maximum of $10^{-1.5}$ to a minimum of $10^{-4.5}$ $cm.s^{-1}$ (i.e. a reduction of three orders of magnitude). However, it was found that the finer colloidal material was still capable of passing through the sand. Physical attenuation of coarser particles may therefore become unimportant since it is the finer material which constitutes the critical leachate fraction which is enriched with heavy metals such as Cr, Pb, Ni, and Cu (Gounaris *et al.* 1993). The latter may reach the groundwater and lead to contamination.

Contaminants adsorbed to colloid surfaces become mobilised through the transport of these colloids. In the vadose zone, interstitial water moves predominantly in the finer pores rather than the coarse pores, due to capillary forces. Moving in finer pores, the colloids are easily coagulated, filtered, and subsequently become less mobile. However, if the macropores do become active in fluid transport, then colloids may well find their way into the ground water, carrying with them the adsorbed pollutants, particularly heavy metals (Ruan & Illangasekare, 1995). Colloids can be mobilized from a natural sediment by increasing the electrostatic repulsion between the colloid surfaces. Ryan & Gschwend (1994) found evidence that surfactants may present an effective means of generating dispersed colloids capable of facilitating contaminant transport.

10.5.4.2 Geochemical Attenuation

Geochemical attenuation is probably the most important mechanism of leachate modification. Under the right conditions soils and sediments can act as efficient geochemical "traps". Clays, hydrous oxides of iron and manganese, and organic matter provide surfaces onto which contaminants are adsorbed. The main attenuation mechanisms include ion exchange processes, adsorption, precipitation and volatilisation.

If leachate intrudes the vadose zone, attenuation will proceed through a sequence of processes. The first stage of attenuation may cause the pH of the leachate-soil system to approach a near neutral value (Bagchi, 1993). Attenuation of Cu, Pb, Zn, Fe (in part), NH_4, Mg, K and Na, will occur during the first stage. According to Bagchi (1993), the following attenuation mechanisms may operate:

1. Copper, lead, and zinc: Likely attenuation mechanisms for these contaminants are precipitation, adsorption, cation exchange and dilution. In general, the concentration of these heavy metals will be low in the leachate solution. They will be strongly attenuated (mainly by adsorption) in a clayey environment.

2. Iron: Major attenuation mechanisms of iron are precipitation, cation exchange, adsorption, biological uptake and dilution. Beneath municipal landfills, iron most likely exists in the reduced state, and the mobility of divalent (ferrous) iron is higher than trivalent (ferric) iron. The redox status of the medium will thus also be important in governing attenuation.

3. Ammonium, magnesium, potassium and sodium: Attenuation occurs mainly through cation exchange, often increasing the hardness of soil water in the process. The total amount of NH_4, Mg, K and Na attenuated from leachate usually agrees closely with the amount of Ca eluted.

4. Biochemical oxygen demand (BOD) and chemical oxygen demand (COD): Unlike other pollutants, these do not represent ionic species. Major attenuation mechanisms for these constituents are biological uptake, dilution and filtration.

As early as 1976, Runnells proposed that discharge of wastewater to the vadose zone may be a safe means of disposal of wastes in arid regions. It is necessary to carefully test the suitability of a particular site for a particular waste. There is experimental evidence to indicate that soils from arid regions, such as New Mexico, are able to remove dissolved Mo and Cu, through physicochemical processes, from synthetic mill water, and they may retain these elements during subsequent leaching by fresh and metal-free mill waters.

Such attenuation, however, cannot always be assured. The Coastal Park landfill was established in 1985 on the coastline near Cape Town. The site is underlain by calcareous aeolian sands with a relatively high pH and buffering capacity. The site was built with the exclusion of a containment liner, but with an average depth of 2 m (referred to as the "buffer zone") separating the base of the wastepile from the phreatic surface. Authorities believed the calcareous sands (and the sea water) would attenuate any pollution by leachates (Blight *et al.*, 1994). It was subsequently shown (Harraway, 1996) that the sand contains negligible quantities of organic matter and clay content, which would render the sand almost incapable of any attenuation of leachate constituents.

a) Ion-exchange processes

Under appropriate conditions clay minerals, metal oxides and organic matter impart to natural earthy materials the capacity to scavenge and to concentrate cations and anions from seepage solutions or migrating groundwater (Dragun, 1988; Hornick, 1976; both cited in Daniel, 1993). Surface charge on these particles allows these ion-exchange reactions to take place. Ion exchange is not a chemical reaction in the usual sense, since the bonds broken and formed are long-range electrostatic bonds of low energy. However, the exchange process is written in the conventional form of a chemical equation. For example, the exchange of Mg^{2+} ions from a layer silicate clay surface by $CaCl_2$ can be expressed as:

$$CaCl_2\,(aq) + MgX_2\,(s) = MgCl_2\,(aq) + CaX_2\,(s)$$

where (aq) and (s) refer to the aqueous and solid (exchanger) phases, respectively.

In most applications, the ion exchange capacity of a soil refers to the maximum adsorption (positive surface excess) of *readily exchangeable ions*. These ions adsorb to the particle surfaces solely by outer-sphere complex formation and diffuse ion swarm mechanisms (Sposito, 1989). *CEC* (cation exchange capacity) is the quantity of cations reversibly adsorbed (expressed as moles of positive charge) per unit weight of mineral. Conventional units for CEC are centimols per kilogram ($cmol.kg^{-1}$), although millimols per kilogram ($mmol.kg^{-1}$) are more acceptable according to the International System of Units (McBride, 1994).

Structural (permanent) negative charge varies among layer silicate clays, from near zero in those possessing little or no isomorphous substitution to over 150 $cmol.kg^{-1}$ in vermiculites (in which extensive isomorphous substitution imparts high negative surface charge). However, the surface density of charge is much less varied because the specific surface area (area per unit weight of clay) tends to increase in proportion to the structural charge or CEC, as the data in Table 10.5.3 show. An obvious exception is seen in the micas, where the structural charge is very high yet the surface area and the CEC are low. In this particular case K^+ ions fixed in the interlayer region prevent the internal surfaces of the mica from becoming accessible to solution and cation exchange processes. It is necessary to conclude that structural charge and CEC are not always equal in magnitude, because some portion of the charged sites may be inaccessible (McBride, 1994).

TABLE 10.5.3: SURFACE AREA AND CEC OF SOME COMMON CLAY MINERALS

CLAY MINERAL	SPECIFIC SURFACE AREA ($m^2.kg^{-1}$)	CEC ($cmol.kg^{-1}$)
Kaolinite	5-20	1-15
Illite	80-150	10-40
Vermiculite	300-500	100-150
Smectite	700-800	70-120

b) Adsorption

Sposito (1989) defines adsorption as the net accumulation of matter at the interface between a solid phase and an aqueous solution phase. It differs from precipitation because it does not include the development of a three-dimensional molecular structure. The matter that accumulates in two-dimensional molecular arrangements at an interface is the *adsorbate*. The solid phase on which it accumulates is the *adsorbent*. A molecule or an ion in solution that potentially can be adsorbed is termed an *adsorptive*.

Soil particle surface functional groups (such as the carboxyl group or the phenolic hydroxyl group, both associated with soil humus), are able to complex with certain ionic, or

molecular, species in the soil solution. If a surface functional group reacts with an ion or a molecule dissolved in the soil solution to form a stable molecular unit, a *surface complex* is said to exist and the formation reaction is termed *surface complexation*. If no water molecule is interposed between the surface functional group and the ion or molecule it binds, the complex is *inner-sphere*. If at least one water molecule is interposed between the functional group and the bound ion or molecule, the complex is *outer-sphere*. As a general rule, outer-sphere surface complexes involve electrostatic bonding mechanisms and therefore are less stable than inner-sphere complexes, which necessarily involve either ionic or covalent bonding (Sposito, 1989). An example of a surface complex would be the K^+ ion forming an inner-sphere surface complex with the oxygen atoms of the siloxane layer at the vermiculite surface.

Sorption isotherms are linear or nonlinear equilibrium expressions defining the adsorption of solutes onto the adsorbant. The expression is presented as a plot q (mass of chemical sorbed, normalized with respect to mass of soil) versus C_e (liquid phase solute concentration at equilibrium). The Langmuir (i.e. non-linear plot) and Freundlich (linear plot) adsorption isotherms are just two of a number of isotherms which can describe the way in which adsorption sites on the adsorbant become occupied by solutes with increasing concentration of solute (McBride, 1994; Knox *et al.*, 1993; Sposito, 1989).

Elements that take the form of cations are retained in soils by cation exchange on clays and humus. However, more selective and less reversible sorption reactions such as complexation with organic functional groups and bonding on variable-charge minerals (e.g., oxides, allophane) can also retain and even immobilize metal cations. Elements having the form of anions in solution are retained in soils primarily by selective bonding (chemisorption) processes at variable-charge mineral surfaces and layer silicate particle edges. These types of cation and anion adsorption are collectively referred to as *specific adsorption* to distinguish them from ion exchange (McBride, 1994).

Noncrystalline aluminosilicates (allophanes), oxides, and hydroxides of Fe, Al and Mn, and even edges of layer silicate clays to a lesser extent, provide surface sites for the chemisorption of transition and heavy metals (McBride, 1994). All of these minerals provide a similar type of adsorptive site to the soil solution: a valence-unsatisfied OH^- or H_2O ligand bound to a metal ion (usually Fe^{3+}, Al^{3+}, or $Mn^{3+,4+}$). For example, on iron oxides, a trace metal, M, may bind according to the reaction:

$$>Fe\text{-}OH]^{-1/2} + M(H_2O)_6^{n+} = >Fe\text{-}O\text{-}M(H_2O)_5]^{(n-3/2)+} + H_3O^+$$

At least four features distinguish this reaction from cation exchange:

1. Release of as many as n H^+ ions for each M^{n+} cation adsorbed;
2. A high degree of specificity shown by particular minerals for particular trace metals;
3. A tendency toward irreversibility, or at least a desorption rate that is orders of magnitude slower than the adsorption rate;

4. A change in the measured surface charge toward a less negative value, which implies that the adsorbed metal and its charge become part of the mineral surface, thereby shifting the PZC (point of zero charge) to a higher pH value.

In a similar way to cations, anions are known to attach to the oxide and silicate mineral fraction of soils. However, certain anions are able to bond to soil organic matter as well. Borate, $B(OH)_4^-$, is notable in this regard. Some anions may bond indirectly to organic groups through a bridging metal ion such as Al^{3+} or Fe^{3+}. Most anions adsorb very little on humus, and it is safe to say that anion bonding at mineral surfaces accounts for most of the anion retention in soils (McBride, 1994).

Anion chemisorption occurs on soils minerals that possess surface hydroxyl groups. The most important minerals in this regard are the noncrystalline aluminosilicates (allophanes); oxides and hydroxides of Fe, Al, and Mn; and layer silicate clays (edge sites only). It is the H_2O or valence unsatisfied OH^- ligands bound to surface metal ions (usually Al, Fe, or Mn) that are the sites of anion chemisorption. In general terms, the surface reaction can be written as:

$$>S\text{-}OH + A^{n-} = >S\text{-}A^{(n-1)-} + OH^-$$

where A^{n-} is an anion of charge $-n$, and $>S\text{-}OH$ is a reactive metal hydroxyl group. This is termed a *ligand exchange reaction* because the anion displaces OH^- or H_2O from coordination positions of the metal ion at the mineral surface. This reaction is favoured by low pH, as is evident from the release of OH^- into solution. The low pH causes surface OH^- groups to accept protons, and since H_2O is an easier ligand to displace from metal bonding sites than OH^-, this facilitates the ligand exchange (McBride, 1994).

Anions may adsorb on positively charged mineral surfaces by anion exchange as well, a process involving nonspecific electrostatic forces. Ligand exchange is distinguished from anion exchange based on the following characteristics (McBride, 1994):

1. Release of OH^- into solution;
2. A high degree of specificity shown toward particular anions;
3. A tendency to be nonreversible, or at least for desorption to be much slower than adsorption;
4. A change in the measured surface charge to a more negative charge.

The abiotic process of sorption will slow down the movement of the contaminant as it accumulates on the subsurface medium. For neutral organic contaminants and subsurface materials with organic carbon present, sorption of hydrophobic substances is also possible. In such cases, as the solubility of the compound decreases, the potential to sorb at an interface is expected to increase. Also, as the organic carbon content of the subsurface material increases, the total capacity of the soil to sorb the hydrophobic contaminant increases (Knox *et al.*, 1993).

Griffin *et al.* (1981) found that the Freundlich isotherm best described the adsorption of PCB's (polychlorinated biphenyls), PBB's (polybrominated biphenyls) and HCB (hexachlorobenzene) by soils and carbonaceous adsorbents from aqueous solutions and organic solvents. All three persistent compounds were strongly adsorbed by these materials. There was a very strong, direct correlation between organic carbon content of the soil and the amount adsorbed. In general, highly chlorinated isomers were adsorbed more strongly than less chlorinated isomers. The authors concluded that these compounds would not move readily through earth materials leached with water or aqueous leachates, but that they would be highly mobile in organic solvents.

Large undisturbed columns were isolated from a proposed waste site consisting of fractured saprolite (weathered interbedded shale and limestone) by Jardine *et al.* (1993), and steady state non-reactive and reactive solute transport experiments were carried out at a number of pressure heads. Observed breakthrough curves (BTC's) for binary and ternary mixtures in the Co-Sr-Ca system were delayed relative to the non-reactive bromine BTC, indicating that the former tracers were adsorbed by the solid phase. The equilibrium convective-dispersive (CD) model predicted the transport of the binary mixtures Co-Ca and Sr-Ca reasonably well. Application of the non-equilibrium or kinetic CD model to the Sr and Co binary system resulted in an improved description of contaminant transport. Results suggested that preferential transport of reactive contaminants is negligible for the unsaturated conditions used in this study and the saprolite used was a chemically active constituent, in terms of adsorption, during reactive solute transport. Adsorption isotherms for the Sr-Ca and Co-Ca binary systems were linear and this supported the use of the transport model, which assumes linear exchange, for predicting Co and Sr mobility in soil. Jardine *et al.* (1993) found that use of the non-equilibrium (kinetic) CD model predicted the Co and Sr transport best.

Xu *et al.* (1994) examined the mechanisms and kinetics of adsorption of Zn^{2+} and Cd^{2+} on hydroxyapatite surfaces. Their sorption data followed Langmuir isotherms. Desorption data suggested that Zn^{2+} is held more strongly than Cd^{2+} on the mineral surfaces.

c) Precipitation

Chemical precipitation may participate in the removal of ions from water (McBride, 1994). The pH can affect the degree of precipitation. Precipitation ultimately removes all of the easily hydrolysed metals from solution as the pH is raised. As the pH is raised from an acid value, chemisorption is initially favoured, but even before adsorption sites become saturated, metal ions cluster into metal oxide or hydroxide nuclei at the soil mineral surface. Ultimately, precipitation as a separate phase of the metal oxide or hydroxide ensues. This sequence of processes usually appears as a "sorption continuum", which can be represented as a smooth sorption isotherm. Because the onset of metal chemisorption and the beginning of metal hydroxide precipitation are not often separated by a wide margin of pH, the chemisorption/nucleation/precipitation sequence is rarely resolved into discrete processes by clear discontinuities in sorption curves (McBride, 1994).

Generally, sorption of metals seems to be more nearly reversible at low than at high pH values. Studies of heavy metal bonding on pure oxides have indicated that the adsorption reaction step is fast and probably diffusion controlled, whereas the desorption reaction step has a rate constant that may be three orders of magnitude slower (McBride, 1994).

Precipitation (and coprecipitation) and complexation mechanisms can operate very closely in conjunction with other surface chemical processes. Xu *et al.* (1994) found that surface complexation and coprecipitation are the most important mechanisms, with possibly ion exchange and solid diffusion also contributing to the overall sorption of Zn^{2+} and Cd^{2+} to hydroxyapatite surfaces.

d) Volatilization

Volatilization in soil is a function of the vapour pressure of the chemical and the contact between the chemical in the soil and the gaseous phase or the atmosphere. Bioremediation systems are usually mixed and/or aerated to provide adequate oxygen input and aerobic conditions. As a result, such systems offer excellent opportunities for volatile compounds to be released (Daniel, 1993).

Groundwater at many Superfund sites in the USA have been contaminated by surface spills or leakage of organic compounds from storage tanks. These compounds include chlorinated, volatile organic compounds (CVOC's) and their movement through the vadose zone is often dependent on pore-size distribution and geometry, moisture content and flow hysteresis or wetting and drying history (Bales *et al.*, 1995).

Because PBB's are not degraded, are not leached in aqueous solutions, are not taken up by plants, and not readily volatilized (because of low vapour pressure), PBB's can be expected to be a relatively permanent component of soils they have contaminated. Highly chlorinated PCB's and HCB are also not easily degraded or leached through the soil by water to any significant extent. They are also apparently not taken up by plants because of their predominant absence from the aqueous phase. However, PCB's and HCB do have a moderate vapour pressure and their most likely path for redistribution or migration in soils may be by vapour phase transport through the unsaturated pores (Griffin *et al.*, 1981).

Sorption mechanisms also operate when vapours from VOC's pass through the soil. Smith *et al.* (1990) found that TCE (trichloroethene) sorption decreases as soil moisture content increases toward saturation. Their analyses suggested that adsorption of TCE by the mineral fraction of the vadose zone soil should be minimal relative to the partition uptake by the soil organic matter. TCE desorption from the solid phase is very slow relative to the dissipation from the soil gas by diffusion to the atmosphere, which indicates a strong disequilibrium condition in the contaminated zone.

Steinberg *et al.* (1993) differentiate between hydrogen-bonding and non-hydrogen bonding VOC's and they made use of Inverse Gas Chromatography (IGC) to determine vapour phase

sorption isotherms and kinetics. For dry soils, sorption isotherms are apparently nonlinear and finite desorption kinetics contribute to the chromatographic peak shapes. A small addition of moisture to the carrier phase in the column drastically decreases sorption of non-H bonding VOC's by soil, and eliminates the effect of finite sorption kinetics on chromatographic peak shapes. H-bonding VOC's exhibit nonlinear sorption isotherms and finite sorption and desorption kinetics in the presence of water.

e) Redox conditions

The redox environment of a soil is a function of the moisture status of the soil (i.e. the availability of free oxygen). Redox zones are believed to constitute an important chemical framework for the attenuation process in a leachate plume. The attenuation process in a plume will, for many pollutants, depend on the redox environment in the plume, and in some cases also contribute to the development of these redox zones. In an actual leachate plume, the redox environments are supposed to develop over a number of years as a result of interactions between, for example, redox processes, precipitation-dissolution processes, ion-exchange processes and dilution. Some areas of the plume may be dominated by one redox process while others may host several concurrent processes (Bjerg *et al.*, 1995).

Bjerg *et al.* (1995) review some of the redox processes which may take place in these redox zones in the plume:

1. Iron(III) reduction is considered mainly to be a microbially mediated process, but may occur through chemical reduction by sulfides (and may constitute an important sink for sulfides).
2. Significant manganese concentrations could be due to microbial reduction of Mn oxides by oxidation of organic matter, or by chemical oxidation of Fe(II) or of sulfide.
3. The presence of solid phases in the anaerobic zones of the plume, e.g. reduced Fe(II) or Mn(II), in high concentrations may cause precipitation of sulfides. This can reduce the concentration of sulfides in the aqueous phase. Bjerg *et al.* (1995) evaluated this aspect by means of the MINTEQA2 chemical speciation model.
4. Relatively low ammonium concentrations closer to the landfill indicate that cation exchange processes may attenuate ammonium in the anaerobic part of the plume.

10.5.4.3 Biological Attenuation - Biodegradation

A general approach is taken here in describing some of the factors involved in bio-degradation, with the main emphasis being placed on the fate of organic contaminants. The complexity of soil systems, and the dynamics and diversity of microbial populations, makes it particularly difficult to generalize on the typical biodegradation processes participating in soil contaminant attenuation, i.e. applications are, in most cases, highly case specific. The

vadose zone is characterised by variably saturated regions which will have an effect on the temporal and spatial distribution of certain microbial populations in response to redox fluctuations. Biodegradation will be discussed below in light of those processes involved in the attenuation of leachate invading a vadose zone below a landfill. Dodds (1993) carried out a comprehensive literature review on the factors influencing the fate of organic contaminants from which most of the ensuing information on biodegradation was extracted.

The biotic process of aerobic biodegradation may convert an organic contaminant to another form (metabolites) or to harmless end products (e.g., CO_2 and H_2O). For aerobic biodegradation (metabolism) to occur, aerobic microorganisms must be present in the subsurface system. The microorganisms require free oxygen as an electron acceptor (free oxygen is only present at high values of pE), nutrients such as nitrogen and phosphorus, certain trace elements and an acceptable environment (pH, temperature, etc.). These conditions must be satisfied in the subsurface system. For aerobic microorganisms to biodegrade organic contaminants, the process must be energetically favourable or biochemically advantageous for the microorganisms,and the pollutant must be present at sufficient quantities. In addition the contaminant must be readily metabolized (e.g., highly halogenated organic contaminants are typically refractory under aerobic conditions, making them difficult for microorganisms to metabolize). The biochemical oxygen demand (BOD) is a test that quantifies the biochemical oxygen equivalent of the organics present in a contaminant and thus indicates if the contaminant is susceptible to aerobic biodegradation. Thus, the aerobic biodegradation process is affected by the properties of the subsurface environment (presence of microorganisms, nutrients, free oxygen, etc.) and properties of the contaminant (concentration, BOD, etc.) (Knox *et al.*, 1993). Anaerobic biodegradation processes have received much attention, and are generally though to progress at slower rates than the aerobic process.

Soil microbes form an integral part of the soil system. Scow and Hutson (1992) maintain that in an environment as complex as soil, it is virtually impossible to manipulate chemical and physical properties without influencing microbial populations. The microbes need a source of carbon and energy, and in some instances this can be the soil organic matter (OM). The presence of this potential alternative source of organic carbon in soils with phenol degraders may cause a lag in phenol degradation time, since the microbes will preferentially utilize soil OM substrate as a carbon source (Rozich & Colvin, 1986). On the other hand, soil OM may even stimulate biodegradation as a result of cometabolism. Cork & Krueger (1991) defined cometabolism as the simultaneous but incomplete oxidation of a non-growth substrate (pollutant) during the growth of microbes on a utilizable carbon and energy source (e.g., soil organic matter).

A period of acclimation, or lag, often precedes pollutant biodegradation. The conditions of acclimation will have an important role in determining the kinetics of biodegradation, particularly in the case of mixed substrates. The presence of compounds which can be used in place of the contaminant concerned may influence the rate and extent of biodegradation. Rozich & Colvin (1986) showed how increasing amounts of glucose resulted in decreasing phenol utilization in a heterogeneous microbial population acclimated to phenol as a sole

carbon and energy source. The researchers also concluded from their work that the overall effect of toxic components on microbial growth rate would determine the population size of the degrading organisms.

Nutrient amendments, for example N or P fertilisers, can stimulate degraders. However, non-degrading microorganisms growth rates may simultaneously be stimulated, causing a rapid depletion of utilizable nutrients and a consequent inhibition of growth and activity of the degrading populations (Swindoll *et al.*, 1988). Manilal & Alexander (1991) found that nitrogen amendment in the form of KNO_3 resulted in reduced degradation rates of phenanthranene. This might be explained in part by the observed simultaneous pH decrease from 6.7 to 6.4.

Sorption phenomena are extremely important in determining the fate of xenobiotics in soils, since they govern the availability of contaminants for biodegradation, as well as their mobility and potential risk to groundwater. It is generally thought that biodegradation reactions are significantly slower for a sorbed-phase than for an aqueous-phase solute (Mihelcic & Luthy, 1988). However, if a compound is initially sorbed, it will be protected from intracellular degradation, but extracellular enzymes may become operative in which enzymatic cleavage can lead to pollutant biodegradation. Degradation products may also be adsorbed onto soil, thereby preventing complete mineralisation of pollution. Catechol, an intermediate in the degradation pathway of both phenol and naphthalene, was more strongly sorbed to soil than phenol or naphthalene in work conducted by Knezovich *et al.* (1988). They maintained that this rendered catechol less available for degradation, less mobile and more persistent in the soil environment. Such retention of metabolites may affect soil microbe populations negatively if the metabolites are more toxic than the initial substrate. There does seem to be some uncertainty, though, regarding the specific role of sorption in biodegradation. Guerin & Boyd (1992) state that separate evaluation of individual soil systems should be performed.

10.5.5 VADOSE ZONE MONITORING

Sampling solute concentrations in the vadose zone provides an early warning system for groundwater pollution. Fibreglass wick can be used for sampling water and solutes in the vadose zone (Boll *et al.*, 1991). The fibreglass wick acts as a hanging water column, drawing water from the undisturbed field soil without external application of suction. The wicks behave like a porous medium that could effectively apply a suction to the soil. Predetermined curves can be used to select optimal wick length and diameter for a given sampling configuration.

The most commonly used monitoring tool in the vadose zone is the suction lysimeter. Suction lysimeters may be divided into three categories (Daniel, 1993):

1. vacuum operated soil-water samplers;
2. vacuum-pressure samplers;
3. high-pressure vacuum samplers with check valves.

The instruments can be installed in the vadose zone beneath the landfill site prior to installation of the bottom, low permeability liner. Generally, lysimeters are located under leachate-collection sumps or other low points in the landfill bottom since these are the most likely place for potential leachate leakage after landfilling commences. Backup lysimeters are often installed beneath the primary lysimeters to assure that leakage is detected (Wright *et al.*, 1988).

10.5.6 MODELLING SUBSURFACE CONTAMINANT TRANSPORT

A number of models are available for the simulation of the fate and migration of pollutants in soils. To be able to mathematically simulate the movement of contaminants in the vadose zone, a holistic approach is required that integrates the interaction between the soil, water, contaminant and climate. Eigenhuis and Moolman (1996) used the CHAIN_2D model (developed by Suminek & van Genuchten) to predict the movement of water and dissolved contaminants in the upper part of a non-uniform soil profile for a single ring infiltration experiment. The relative importance and impact of contaminant attenuation processes and factors was investigated by performing a model sensitivity analysis. The results, in decreasing order of effect (values in parentheses), were summarised as follows: soil hydrological properties (20 - 40 %) > climate ≈ bulk density (20 %) > > adsorption isotherm (5 %) > first order kinetics > diffusion coefficient in water (1.5 %) > volumetric heat capacity of liquid > longitudinal dispersivity ≈ thermal conductivity coefficient > volumetric heat capacity of solid phase > volumetric solid phase fraction > adsorption isotherm coefficient ≈ transversal dispersivity > volumetric organic matter fraction ≈ transversal thermal dispersivity of material ≈ longitudinal thermal dispersivity of material ≈ Henry's coefficient = 0 %. Their results provide useful information for groundwater pollution control management, as well as risk assessment.

Mass (solute) transport is more difficult than flow modelling due to the mathematical character of the governing equations and the potential multiplicity of subsurface processes that can affect the concentration of the contaminant at any time in the subsurface environment. The many natural processes that affect transport in the subsurface can be divided into physical, chemical and biological categories as shown in Table 4 (from National Research Council, 1990, in Knox *et al.*, 1993).

Mirecki & Parks (1993) made use of the geochemical model PHREEQE (pH-redox equilibrium equations) to estimate the contamination of alluvial aquifer water near a leachate plume. The model is able to predict which pollutant constituents are involved in precipitation-dissolution reactions. The model is more suited to saturated conditions downgradient of the contaminant plume source, and for application to semi-conservative (i.e., semi-reactive) contaminants, such as Ba, B, Sr, and Cl.

TABLE 4: A SUMMARY OF THE PROCESSES IMPORTANT IN DISSOLVED CONTAMINANT TRANSPORT AND THEIR IMPACT ON CONTAMINANT SPREADING

PROCESS	DEFINITION	IMPACT ON TRANSPORT
Mass transport		
1. Advection	Movement as a consequence of groundwater flow	Most important means of transport away from source
2. Diffusion	Spreading due to molecular diffusion in response to concentration gradients	An *attenuation* mechanism of second order in most flow systems where advection and dispersion dominate
3. Dispersion	Fluid mixing due to effects of unresolved heterogeneities in the permeability distribution	An *attenuation* mechanism that reduces contaminant concentration in the plume; however, spreads to a greater extent than predicted by advection alone.
Chemical mass transfer		
4. Radioactive decay	Irreversible decline in the activity of a radionuclide through a nuclear reaction	An important mechanism for contaminant *attenuation* when the half-life for decay is comparable to or less than the residence time of the flow system; also adds complexity in the production of daughter products
5. Sorption	Partitioning of a contaminant between the groundwater and mineral or organic solids in the aquifer	An important mechanism that reduces the rate at which contaminants are apparently moving; makes it more difficult to remove contamination at a site
6. Dissolution/ precipitation	The process of adding contaminants to, or removing them from, solution by reactions dissolving or creating various solids	An important mechanism that can control the concentration of contaminant in solution; solution control is mainly controlled either at a source or at a reaction front
7. Acid/base reactions	Reaction involving transfer of protons	Mainly an indirect control on contaminant transport by controlling the pH of groundwater
8. Complexation	Combination of cations and anions to form a complex ion	An important mechanism resulting in an increased solubility of metals in groundwater, if adsorption is not enhanced; major ion complexation will increase the quantity of solid dissolved in solution
9. Hydrolysis/ substitution	Reaction of a halogenated organic compound with water or a component ion of water (hydrolysis) or with another anion (substitution)	Often hydrolysis/ substitution reactions make an organic compound more susceptible to biodegradation and more soluble
10. Redox reactions (biodegradation)	Reactions that involve the transfer of electrons and include elements with more than one oxidation state	An extremely important family of reactions in retarding contaminant spread through the precipitation of metals
Biologically mediated mass transfer		
11. Biological	Reaction involving the degradation of organic compounds, whose rate is controlled by the abundance of the microorganisms and redox conditions	Important mechanism for contaminant reduction, but can lead to undesirable by-products (metabolites)

Modelling fluid flow and solute transport in the unsaturated zone typically requires solution of the Richards' equation and an advective dispersive equation for contaminant transport as a function of time. Such numerical approaches and the non-linear nature of the Richards' equation are computationally demanding. Kandil *et al.* (1992), in their work on modelling long-term solute transport in drained, unsaturated zones, found that a simplified water balance approach to solve for the fluid flow in shallow, drained, unsaturated zones could be used to obtain solutions for the solute transport in these soils. Sample simulations showed good agreement between a Richard's equation-based transport model and a water balance-based model.

An important approach in modelling natural systems is to make use of physical models. Laboratory-scale microcosm studies can be used *in lieu* of, or supplementary to, field studies. In this context, a microcosm can be defined as a controlled laboratory system which attempts to simulate, on a small scale, a portion of a real world subsurface environment (within definable chemical and physical boundaries). Knox *et al.* (1993) classify four microcosm designs which include slurry, homogenised subsurface, incremented subsurface and subsurface core microcosms. The former is a test tube or serum bottle type of microcosm, which is static, whereas the latter three are flow-through, column-type microcosms.

It should be noted that results of the physical models show the great importance of the hydrologic conditions in the design, operation and modelling of solid waste disposal facilities. However, physical models are not, by nature, predictive tools, since they are restricted by the physical characteristics of the particular refuse and the mode of operation. Nevertheless, they can become useful when combined with an analysis of the mechanisms governing movement of moisture through the refuse.

Typically, microcosm studies focus on the relative importance of physical, chemical and biological processes for contaminants under a given set of subsurface media and environmental conditions. The information gained from microcosm studies can be used for several purposes:

1. Development of rate information for inclusion in groundwater flow and solute transport models;
2. Planning of source-oriented groundwater quality monitoring programmes;
3. Delineation of appropriate groundwater protection strategies for pollution source categories in specific hydrological settings;
4. Site selection for waste disposal operations;
5. Determination of potential plume management and groundwater pollution remediation measures for locations with contaminated soil and/or groundwater.

Lawrence *et al.* (1993) document the design and evaluation of a mesoscale physical model of the vadose and groundwater zones. The advantages of such a system include controlled fluxes, intensive sampling and instrumentation, high microbial diversity in a largely unaltered environment, and controlled, environmentally acceptable experimentation. They found that the mesoscale model preserved many of the features of natural systems while providing controlled conditions for studies such as evaluating the fate, and groundwater contamination potential, of agricultural and industrial chemicals in variably saturated soils.

Sand tanks were used by Johnson & Kreamer (1993) to investigate liquid and vapour migration characteristics of diesel fuel using a physically-based two-dimensional modelling approach. Mathematical modelling then provided estimation of vapour concentrations at discrete times and distances from the vapour source and compared to the physical experiment. The mathematical gaseous diffusion model accounted for sorptive effects of the media, and was calibrated using measured concentrations from the sand tank. A careful application of the method and values can be used to give a first approximation to the number of vadose zone monitors required at a field site as well as the optimal location of these monitors.

The theory of unsaturated flow through homogeneous porous media can be used to analyze physical processes governing moisture transport in solid waste landfills. Korfiatis *et al.* (1984) determined hydraulic properties of refuse from small scale experiments. This approach proved successful and comparisons of measured and mathematically modelled quantities of leachate discharged showed reasonable agreement.

Pantazidou & Sitar (1993) conducted physical model tests to simulate non-aqueous phase liquid (NAPL) spills in the unsaturated, two-dimensional domain above the water table. Fluctuations of the phreatic surface result in trapping the NAPL below the water table and in spreading the NAPL over a larger area. In layered soils, the behaviour is largely geometry dependent, although heterogeneities invariably result in extensive horizontal spreading. Simplified analytical relationships were developed to estimate the spreading rate of the contaminant during infiltration, and the thickness of the final immobilized oil lense during the experiments. These relationships are based on capillary pressure considerations, which have to be included in order to model the immobilization of the plume at saturations higher than the residual values, which typically occur in the vadose zone, when the NAPL encounters the capillary fringe in its migration downwards.

Vulnerability mapping is a recognised technique used in evaluating localised sites or regions for the suitability for waste disposal in terms of the potential for groundwater pollution. Knox *et al.* (1993) explain that the primary technical issue in vulnerability mapping is the subsurface transport and fate of potential pollutant chemicals, with often most emphasis placed on the vadose zone. Vulnerability mapping is a technique based on assigning indices to geographical areas which define their relative susceptibility to groundwater contamination. Developing these indices typically involves considering a multiple of physical and chemical factors along with their relative importance weighting. Caution is advised when using this and other similar techniques, since there is considerable need for professional judgement to interpret the information.

The vulnerability mapping technique may be categorised on the basis of whether they are developed to address point or non-point source pollution. Point source techniques or methodologies include: *surface impoundment assessment* (applied to pits, ponds and lagoons etc.); *landfill site rating method*; *waste-soil-site interaction matrix*; *hazard ranking system*; and *site rating methodology*. Non-point source based vulnerability techniques, mostly used in agriculture, include: *DRASTIC* i.e. Depth to ground water, Recharge, Aquifer media, Soil media, Topography (slope), Impact of vadose zone, Conductivity (hydraulic); and *SAFE* (Soil Aquifer Field Evaluation).

Kalinski *et al.* (1994) express confidence in the DRASTIC technique as a tool in land-use planning and management. Lynch *et al.* (1994) investigated the DRASTIC technique and outlined methods for preparing input data for a nation-scale groundwater vulnerability map of Southern Africa. The purpose of this map, for use within a GIS environment, is for presenting the concepts of groundwater vulnerability and groundwater protection to the layman.

Parsons & Jolly (1994) developed the WASP (Waste-Aquifer Separation Procedure) method to evaluate waste disposal sites based on geohydrological criteria. The WASP method differs from vulnerability mapping techniques in that vulnerability mapping does not consider the actual threat posed by the waste pile. The method defines a Threat factor, Barrier factor, and Resource factor, the values of which are derived from nomograms or graphs after the user has assessed certain physical and/or chemical properties of the site and waste. The method bypasses any attempts to model actual attenuation processes because of their complexity, but rather uses the time (calculated from Darcy's Law) that the leachate would take to reach the aquifer from the base of the waste pile. The Barrier factor rating curve, used to estimate the Barrier factor score, was constructed by the authors to include consideration of leachate chemistry on the chemical and hydraulic properties of the vadose zone.

10.5.7 SUMMARY

The vadose zone can be defined as the variably-saturated zone between the land surface and the phreatic surface, and includes the soil water, the intermediate vadose zone and the capillary fringe. During unsaturated conditions, both chemical and hydrological factors control the subsurface transport of contaminants. Unsaturated flow conditions are often complicated and difficult to describe quantitatively, since they often entail changes in the state and content of soil water during flow. Such changes involve complex relations among the variables soil wetness, suction and hydraulic conductivity, interrelations between which may further be complicated by hysteresis. Equations based on Darcy's Law can be used for determining unsaturated hydraulic conductivity (K). A number of techniques are available in the literature for measuring K, and these include: the unsteady drainage flux method; simplified unsteady drainage flux method; crust-imposed steady flux method; and sprinkler-imposed steady flux method. K can also be estimated from the measurement of the soil water retention characteristic using the controlled outflow cell using tension infiltrometer apparatus, or from soil texture and/or other soil data.

If a sanitary landfill site were unlined, then it is conceivable that the main effect of the vadose zone would be to attenuate the landfill leachate constituents. Attenuation processes may be broadly categorised into hydrodynamic processes, abiotic (nonbiological) processes, and biotic processes. The geochemical attenuation capacity of this zone would be a function of clay content, organic matter and metal oxides (mainly iron and manganese). An increase in clay, organic matter and metal oxide content would coincide with an increase in cation exchange capacity and adsorption processes and thus enhanced attenuation. Generally, an increase in pH from acid conditions would coincide with removal of heavy metals from solution by precipitation as hydroxides or sulfides. Colloid transport through the vadose zone could either be physically impeded by filtration, or may facilitate the migration of adsorbed chemicals, such as heavy metals like Cr, Cu, Zn, and Pb, which could ultimately find their way into groundwater. Redox conditions can fluctuate concomitantly with changes in water content in the vadose zone. In an actual leachate plume, the redox environments are supposed

to develop over a number of years as a result of interactions between, for example, redox processes, precipitation-dissolution processes, ion-exchange processes and dilution. Some areas of the plume may be dominated by one redox process while others may host several concurrent processes. Biological attenuation occurs through microbial degradation of contaminants. The degradation of these xenobiotics can be influenced by sorption phenomena, pE (redox conditions), pH, nutrient amendments, and the type of substrate available to the microbes as an energy and carbon source. Volatilization in a soil system is a function of the vapour pressure of the chemical and the contact between the chemical in the soil and the gaseous phase or the atmosphere. Bioremediation systems usually require aeration to promote aerobic conditions for enhanced biodegradation and volatilisation. Sorption phenomena may complicate the movement of VOC's from the soil to the atmosphere. Increases in soil moisture content can cause a decrease in TCE sorption. The kinetics of sorption phenomena will govern the fate of many solutes through the soil; often the rate of desorption is orders of magnitude smaller than that of adsorption.

Physical models (microcosms), such as sand tanks, are commonly constructed at a laboratory scale and used in conjunction with numerical models to model the fate and migration of solutes in a simulated vadose zone. These are intensely monitored and analyzed systems which are used to calibrate the numerical models for application at a field scale. Vulnerability mapping techniques are not models but empirical methods which can be used for waste site selection. In these techniques, the primary technical issue is the subsurface transport and fate of pollutant chemicals, with emphasis on the vadose zone and its attenuation capacity.

It is conceivable that the vadose zone is capable of attenuating, up to a point, the chemical constituents in a leachate plume emanating from a landfill. However, it is often likely that natural attenuation processes are not sufficiently intense or sustainable to justify the exclusion of artificial barriers and attenuation systems in augmenting leachate attenuation for prevention of groundwater contamination. The design and construction of natural attenuation landfills which are totally reliant on the attenuation capacity of the vadose zone would be exposing groundwater to too great a risk of contamination.

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SECTION 10.6
CHEMICAL CHARACTERISATION OF LANDFILL LEACHATE AND ITS POTENTIAL MOBILITY THROUGH THE CAPE FLATS SAND:

ABSTRACT

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Researchers and scientists involved with research over the previous decade at Coastal Park, a general waste landfill situated on the Cape Flats (Western Cape Province), have been concerned about the groundwater pollution occurring at the site. The landfill, constructed in 1985 without a containment liner, is situated on the False Bay coastline above the Cape Flats aquifer, with an average separation of 2 m between the base of the waste pile and the water table, forming a "buffer" zone. It was envisaged that the calcareous sand in this buffer zone and encroaching sea water would attenuate leachate discharged from the site. Previous chemical oxygen demand (COD) and ammonia measurements of the groundwater have shown that groundwater contamination is taking place.

This study was initiated as a result of uncertainties about hydrological and geochemical aspects, such as the hydraulic conductivity of the soil in the buffer zone below the landfill and the degree of leachate attenuation taking place in this zone. The use of suitable clays as soil amendments of the Coastal Park sands to form a liner has not previously been investigated. Previous application of a model (FLOW) and water balance studies have predicted that the landfill will generate leachate seasonally.

According to standard methods of soil analysis the soil at Coastal Park has been classified as an aeolian, calcareous, medium quartzitic sand with negligible organic carbon content. Extreme clay-depletion would render the soil almost incapable of leachate attenuation, although calcite and aragonite, found by X-ray diffraction (XRD) analysis, would impart a significant pH buffering capacity to the soil.

The solid phase of a locally sampled leachate (from Vissershok landfill, 35 km North West of Cape Town) was isolated by centrifugation, freeze-dried, and analysed by XRD. Halite was the only detectable crystalline phase in the dry power. XRD analysis of the same sample, this time not freeze-dried but rather dried as a paste, showed calcite to be the main crystalline phase. The presence of calcite in the leachate was attributable to CO_2 dissolving in the liquid which then reacted with Ca^{2+} ions. Freeze-drying tends to eliminate the opportunity for this process to take place and halite becomes the dominant crystallise phase. Freeze-drying also proved to be a good non-oxidative drying technique for the leachate solid phase. Similarity in colour, instability in air, and characteristic colour change from a dark green to an orange brown upon oxidation has led to the conclusion that, beside containing organic matter and amorphous sulfides of iron and other heavy metals , the leachate contains green rusts i.e. a mixture of Fe^{2+} - Fe^{3+} hydroxides belonging to the pyroaurite group of compounds. Distribution coefficients, calculated from solid phase concentrations determined X-ray fluorescence spectroscopy (XRF), and solution phase concentrations (from previous sample analyses provided by Vissershok landfill management) have shown that heavy metals such as Zn, Cr, Cu, Ni and Pb, have a high affinity for the colloidal fraction of the leachate, having severe implications if these colloids are mobile and capable of entering surface and groundwater environments.

A critical threshold hydraulic conductivity (K) of 1 x 10^{-7}cm.s^{-1} must be attainable if a material is to be used as a containment liner at a leachate generating landfill. Air dried samples of the Coastal Park soil were treated with 8% bentonite (swelling smectitic clay), 8% kaolinite (non-swelling clay) and 8% kaolinite plus a 4% gypsum (flocculant) treated middle layer, packed into rigid-wall perspex leaching columns and leached with landfill leachate after pretreatment with a 0,02 M $NaCO_3$ dispersant. The soil treatments were tested for their possible suitability as liner materials. The 8% kaolinite with 4% gypsum treated middle layer was the most effective sand amendment, maintaining a minimum K of $10^{-4,5}$cm.s^{-1}, which, however, is still higher than the requirement of 1 x 10^{-7}cm.s^{-1}. The 8% bentonite treatment achieved an initial minimum K value of $10^{-7,8}$cm.s^{-1}, but this rapidly increased to about $10^{-4,7}$cm.s^{-1} when leached with leachate. This enhancement was attribute to the high ionic strength of the leachate causing a diminish in the electric double layer thickness, a process described in terms of Gouy-Chapman theory. The untreated sand was capable of filtering suspended solids from the leachate, undergoing a reduction in K to a minimum of about $10^{-4,5}$cm.s^{-1}. However, this removal of solids did not include the finer colloids, implying that leachate mobility through the sands can be accompanied by transport of heavy metals associated with the solid phase into the environment which can subsequently undergo release if pH and redox conditions change.

The LEACHM model was used to predict the quantity of leachate which could be generated over the wettest and average rainfall conditions. A hypothetical capping system, comprising of sandy soil from the Coastal Park surroundings, was modelled with either a 1 or 2m depth and a 90, 70, 50 or 0% vegetation cover consisting of Acacia cyclops (commonly known as the Rooikrantz or Port Jackson plant). LEACHW (the water regime submodel of LEACHM) was used to simulate the water balance of this capping system, taking into account soil, vegetation, daily evaporation and daily precipitation data. It was assumed that a positive water balance in this layer would lead to moisture drainage into the waste pile and contribute directly to leachate discharge at the base of the landfill. The model predicted that under average rainfall

conditions and a 2 m soil cover depth, no leachate would be generated even with a 0% vegetation cover. However, under the wettest rainfall conditions, not even a 90% vegetation cover and 2 m soil depth is sufficient to prevent leachate generation over the period simulated, which suggests that under such conditions a more effective leachate management strategy, such as an efficient leachate drainage and collection system, should be implemented. The modelling exercise has demonstrated the use of LEACHM as an alternative approach to leachate generation predictions at landfills.

SECTION 10.7

EVALUATION OF CHEMICAL COMPOSITION OF LEACHATE AND GROUND WATER FROM THE COASTAL PARK SOLID WASTE DISPOSAL SITE

By

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10.7.1 INTRODUCTION

Ground water and leachate quality have been monitored at the Coastal Park solid waste disposal site since 1986. There are, on the site, five cells designed to allow collection of leachate and seventeen boreholes for sampling ground water.

This report summarises and reviews the results obtained. The main intention is to estimate the proportions of leachate in the ground water from the boreholes. No attempt has been made to interpret the values obtained in terms of spacial distribution or proximity to the landfill site.

10.7.2 UNPOLLUTED GROUND WATER

The sands of the Cape Flats have a marine origin reflected in the chemical composition of the ground water, the main constituents of which are varying amounts of sea salt and calcium bicarbonate, the latter derived from contact with fragments of shell contained in the sand.

Surveys[1] in connection with the Cape Flats aquifer have shown salinities varying from less than 500 to more than 3000. Water from test and production boreholes at Mitchells Plain is found to have alkalinity of 200 to 400 mg/ℓ, and is saturated with respect to calcium carbonate *in situ* but gives off carbon dioxide and deposits calcium carbonate on being brought to the surface. Ammonium and nitrate concentrations are low and potassium is low in relation to sodium and chloride.

In the present data similar results are found for samples early in the series or from boreholes remote from the filled area.

10.7.3 LEACHATE

Figures 10.7.1 to 10.7.5 contain time-series plots of COD and the main inorganic ions in samples taken from leachate cells 2 to 5. Figures 10.7.6 to 10.7.10 show the same results, expressed as fractions of the total number of equivalents of the ions ($me.\ell^{-1}$), as well as the difference between anions and cations as a fraction of the whole. Figure 10.7.11 gives a number of correlation plots for selected components.

It is usually found[2] that COD values are high during early, acid fermentation, phases of landfill stabilisation, then falling off fairly rapidly. All five leachate cells at Coastal Park show the expected pattern. COD was high in the first few years of testing and then declined markedly to a more steady state by mid 1991. COD is therefore potentially a useful leachate indicator early in the life of the landfill, but much less so later on. However, the peak values reached varied widely from one cell to the next.

In contrast ammonium, potassium, alkalinity, chloride and sodium increased as the COD declined, quite soon reaching a steady state, except in cell 1, the oldest, where these concentrations were high from the start of the monitoring, declining after 1991.

There is a strong correlation evident between these ions. The ratios between them, shown in the correlation plots of Figure 10.7.11, vary somewhat from cell to cell, with cells 1 to 3 being most similar and cell 5 usually the odd man out. Cell 5 is on the edge of the filled area and the quantity of leachate obtained from it is much below that from the others. It is considered to be a typical.

The amount of potassium - derived from vegetable and animal material - relative to chloride or sodium, far exceeds that in uncontaminated ground water as does ammonium. Alkalinity, mainly resulting from the combination of ammonia and carbon dioxide, also has a high value. The sodium to chloride ratio is a little less than that of sea water. These are all possible leachate indicators, the first two being the best as their background level in ground water is lower and better defined.

It is reported[2] that high calcium and magnesium concentrations are found along with elevated COD during the acid fermentation stage of decomposition of waste materials and subsequently declining. A similar pattern is shown in the present case. Consideration of the basic carbonic-species equilibria involved, suggests that deposition of calcium carbonate occurs when the pH and alkalinity are raised by production of ammonia. Figure 10.7.11 shows that low calcium concentrations go along with high alkalinities, in those samples with low COD.

The graphs (Figures 10.7.6 to 10.7.10) for the ionic fraction of magnesium in leachates, show that in the present case magnesium seems to peak later than calcium and shortly before the rise in potassium and ammonium concentrations.

Sulphate and nitrate were only present in small amounts relative to the other constituents and are not further considered.

Table 10.7.1 gives the mean concentrations of potential indicator ions and COD, during the period when the levels had steadied out at a maximum. These are approximate values, obtained by eye from the graphs; the variability from one cell to the next is such that a more exact procedure is not called for. With Cell 4 it is not clear that a steady state was reached and the final values have been used. Cell 5 has been excluded from the averages. COD can be seen to be far more variable than the other parameters.

Taking these concentrations into account, potassium, ammonium and alkalinity would seem to be the best indicators of leachate in the middle years of life of the site because of the greater contrast with the background levels in the uncontaminated ground water.

TABLE 10.7.1
CONCENTRATIONS IN LEACHATE DURING STEADY STATE PERIOD
All values mg/ℓ, ammonium as N

Cell	NH_4	K	Alk	Cl	Na	COD	Ca
1	1300	1800	7000	2800	1400	47000	480?
2	1100	1250	5800	2300	1000	11000	1200
3	350	300	2400	900	320	2600	700
4	1800	2500	10000	5000	1900	5000	900
5	70	500	1000	1600	450	1400	600
Mean excl. Cell 5	1100	1500	6300	2800	1200	16000	900

10.7.4 GROUND WATER NEAR LANDFILL

Figures 10.7.12 to 10.7.29 show the data obtained for water from boreholes 1 to 18 , on the edges of the disposal area.

In eight of the boreholes there are clear indications of increases in ammonium, potassium and alkalinity, the three chosen indicators of leachates. A steady state was mostly reached.

In borehole 3 only ammonium shows slight signs of leachate presence and borehole 16 is atypical in that ammonia rose steadily from 0 to 70 mg/ℓ N over three years without the other indicators showing any clear increases; monitoring in this latter case started very late.

Table 10.7.2 shows estimates of the percentage of leachate in the water from each borehole when an approximately steady state prevailed. These values were calculated using the concentrations in leachate from Table 10.7.1 and estimates of the concentrations in the ground water obtained from the graphs. Allowance was made for estimated baseline values, mainly of importance in the case of alkalinity.

TABLE 10.7.2

ESTIMATES OF PERCENTAGE OF LEACHATE IN WATER FROM EACH BOREHOLE UNDER STEADY STATE CONDITIONS

BH	PERCENT LEACHATE BASED ON				Start of rise	Steady state	Start of decline
	NH_4	K	Alk	Mean			
1	7	7	9	8	1988/9	1993/4	-
2	0	0	0	0	-	-	-
3	1	0	0	0.3	1992/3	1994	-
4	2	2	3	2	1989	1991	-
5	1	1	2	1.3	1990	1990/1	-
6	0.5	4	2	2	1987/90	1991	-
7	0	0	0	0	-	-	-
8	1	1	2	1.3	1990	1990?	-
9	0	0	0	0	-	-	-
10	4	3	5	4	1990/1	1990/1	-
11	0	0	0	0	-	-	-
13	0	0	0	0	-	-	-
14	17	15	14	15	1992	1993	1996?
15	5	4	7	5	1993	1993	-
16	?	?	?	?	1993	-	-
17	0	0	0	0	-	-	-
18	0	0	0	0	-	-	-

In almost all cases all three indicators gave similar results. Borehole 6, however has different values for each indicator and the concentrations also varied widely from one sampling occasion to the next. Further investigation seems to be required to interpret the results of this borehole, given its position.

A similar exercise was attempted for COD, with much less success, as the graphs are not easy to interpret. The problem arises mainly because sampling in many of the boreholes did not start until after disposal had commenced, thus precluding estimation of background values and

10.7.5 CONCLUSIONS

a) The composition of leachates and ground water from the Coastal Park solids wastes disposal site and it's pattern over time is consistent with that reported in the literature for other sites although the length of the phases may be different.

b) Potassium, ammonium and alkalinity levels can be used to estimate the proportion of leachate in ground water. The validity of these estimates depends on the degree to which the leachate from cells 1 to 4 is representative of conditions in the filled area as a whole.

10.7.6 REFERENCES

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10.7.7 APPENDIX: DATA VALIDATION

For those periods when calcium and magnesium figures were available, the concentrations of the cations and anions, expressed as equivalents were caculated for each sample. Figures 10.7.6 to 10.7.10 show these values, as fractions of the total ionic concentrations, for the leachates. The figures also show the differences between the sub-totals for anions and cations, a commonly used indication of the completeness and accuracy of the analyses.

Figure 10.7.30 gives frequency distribution plots for these differences for both leachates and ground water. These should approximate straight lines if the statistical distribution is nearly normal. The plot for leachates shows one outlier above the line and that for ground water, three outliers. For the ground water there is a small positive bias, not present with the leachates, suggesting either a bias in one or more of the methods or some neglected minor ionic component.

The original laboratory records for the outliers and some of the other samples were examined and a software error giving very infrequent errors was detected and corrected, along with some cases of injudicious use of dilutions, but otherwise no obvious sources of error were found.

Comparsion of the plots, in Figures 10.7.6 to 10.7.21, for the alkalinity fraction with those for anion-cation difference in the leachates shows a remarkable similarity of pattern, suggesting small errors in this determination; when high alkalinities are encountered it is possible to loose some carbon dioxide to the atmosphere during the titration.

The results for the outliers have been removed from the data set but all the others retained. The remaining differences are considered satisfactory for the intended purpose. The time and correlation plots show a considerable degree of consistency and because of the graphical approach, occasional outliers are easily spotted and allowed for.

There are a number of cases where unusual values may be seen to have occurred for several of the indicator ions, suggesting that those particular samples were different from the norm. One such case, that of borehole 18, was the result of the deliberate use of a very extended flushing period before taking the sample. Evidently water was drawn in from a different strata to the usual.

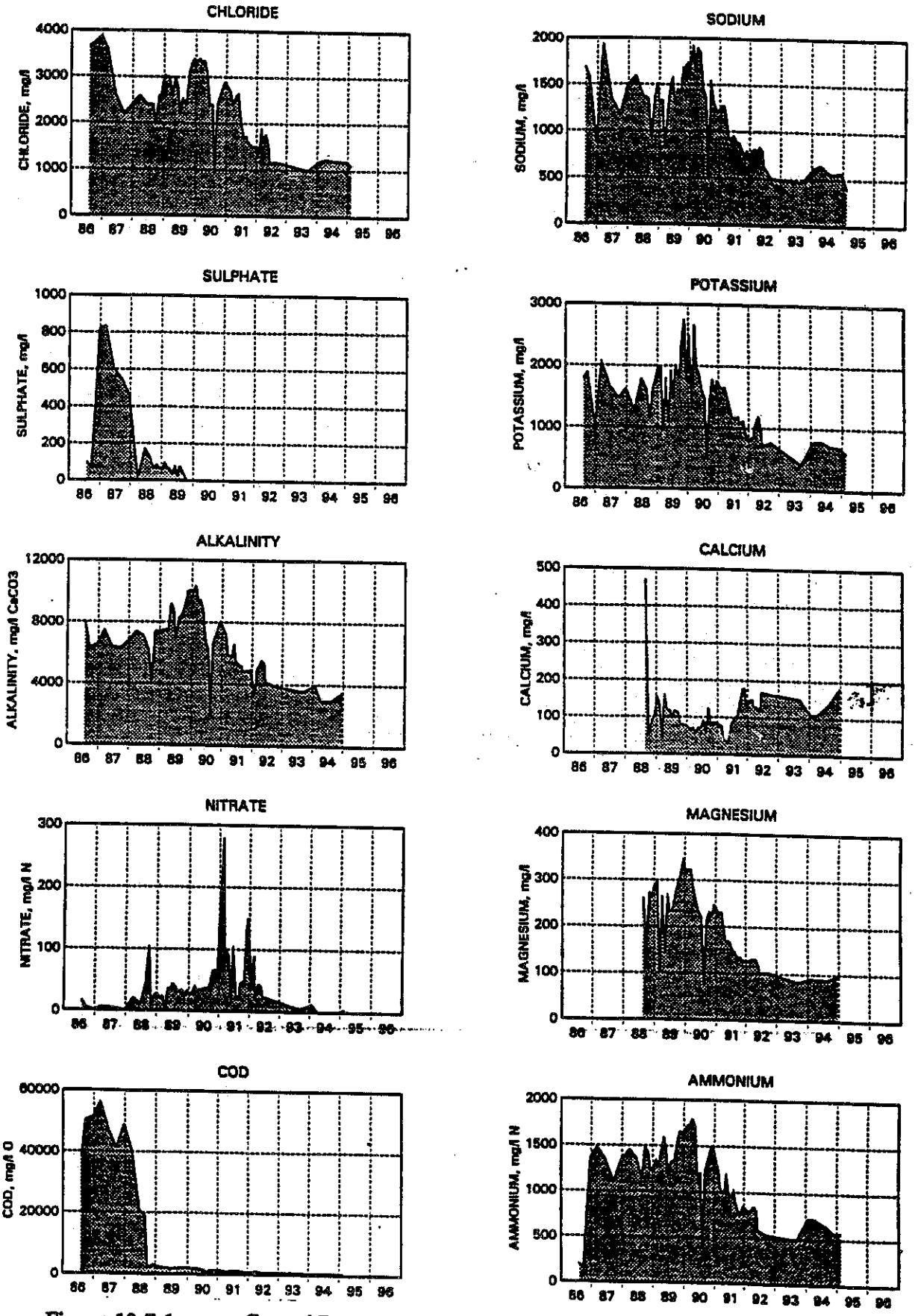


Figure 10.7.1 **Coastal Park leachate: Variation of ionic concentrations with time: Cell 1**

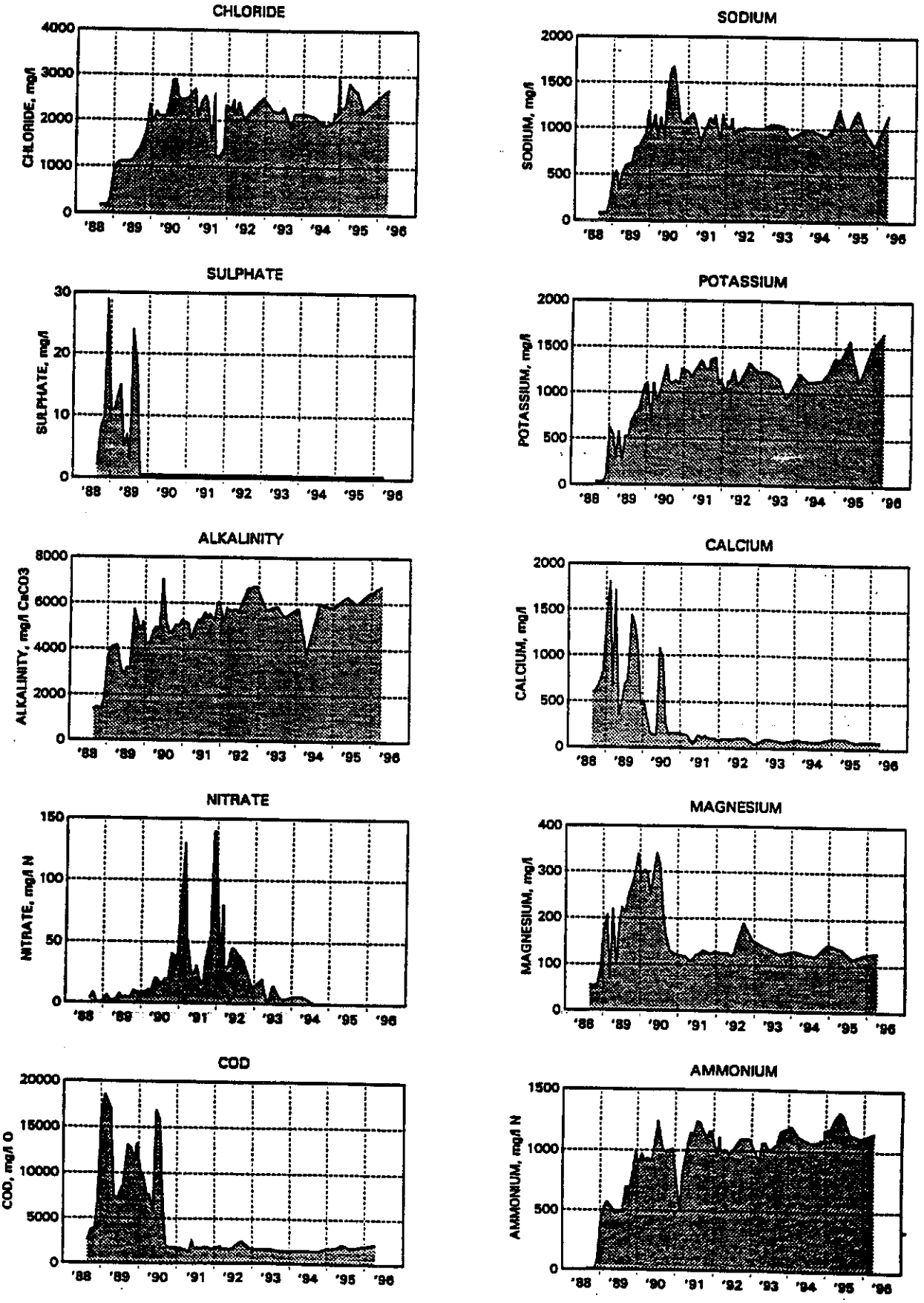


Figure 10.7.2 **Coastal Park leachate: Variation of ionic concentrations with time: Cell 2**

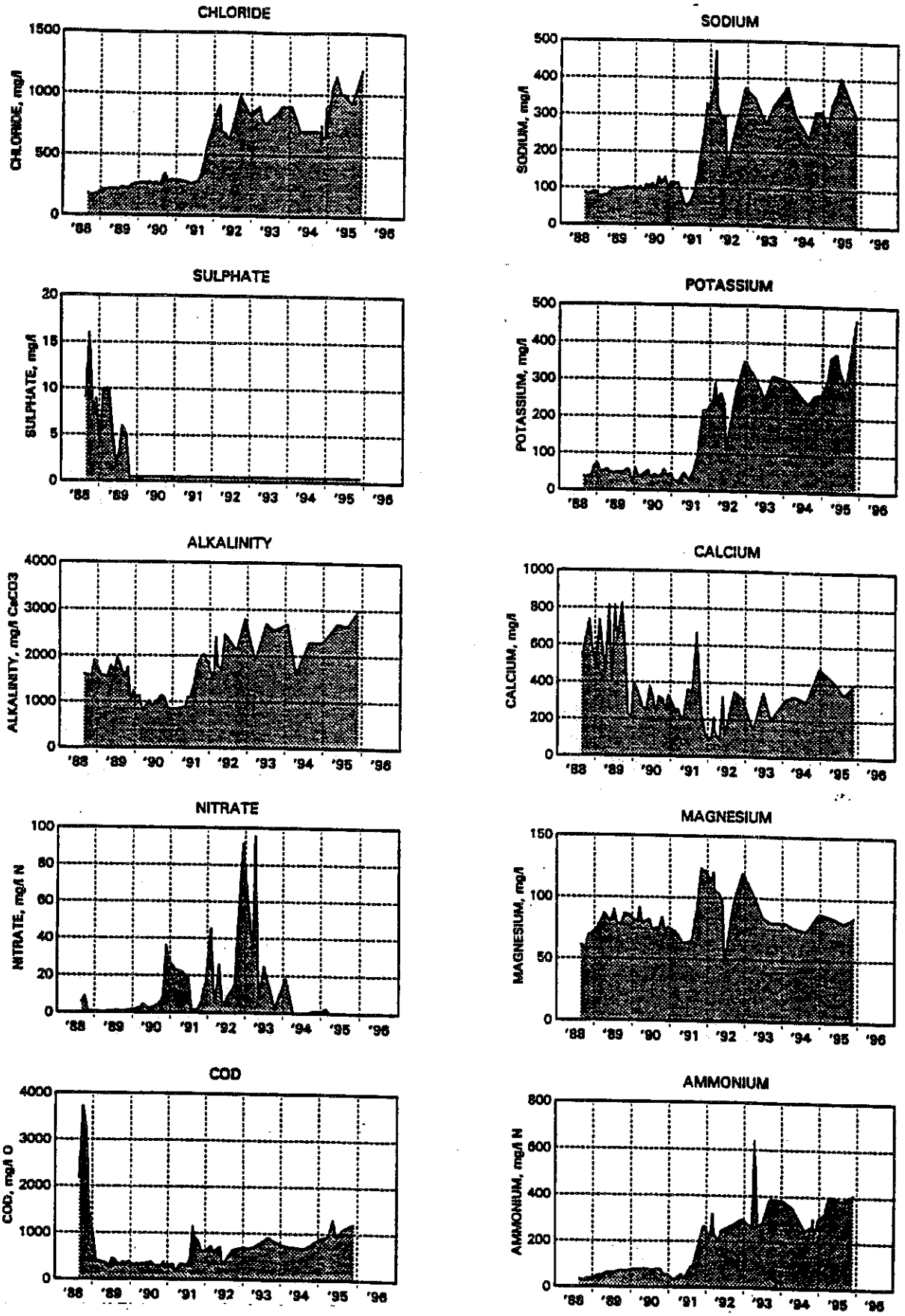


Figure 10.7.3 **Coastal Park leachate: Variation of ionic concentrations with time: Cell 3**

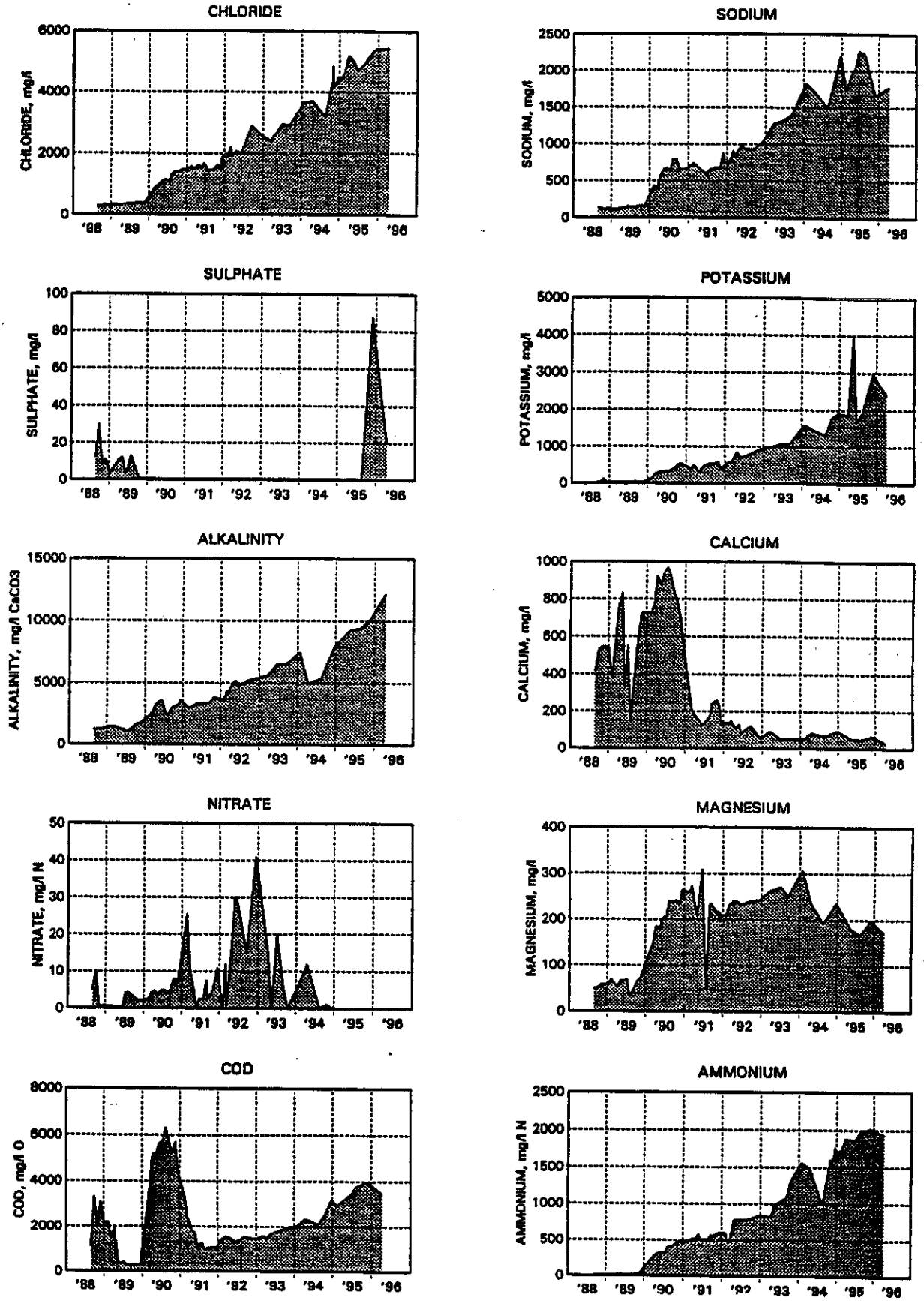


Figure 10.7.4 **Coastal Park leachate: Variation of ionic concentrations with time: Cell 4**

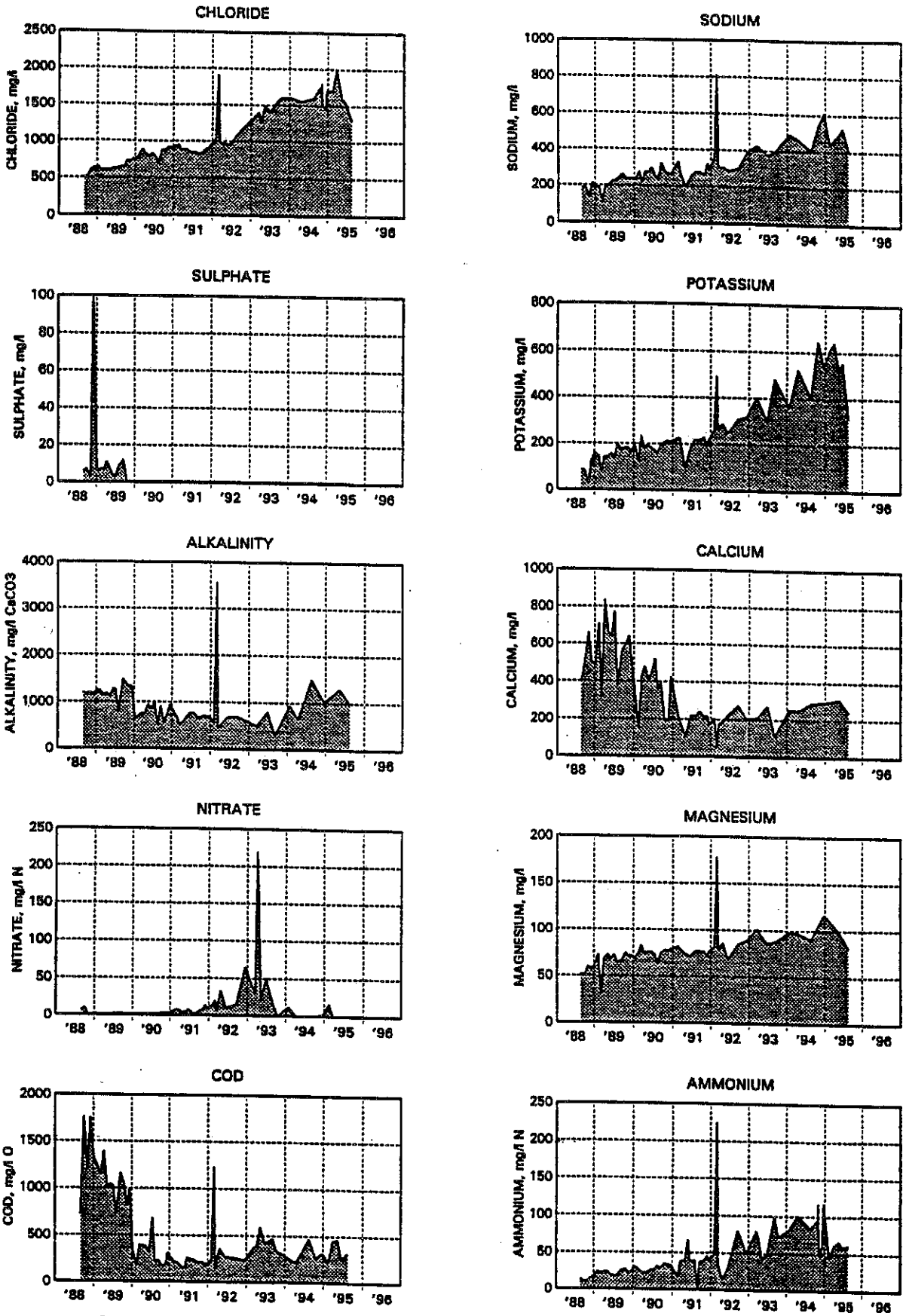


Figure 10.7.5 **Coastal Park leachate: Variation of ionic concentrations with time: Cell 5**

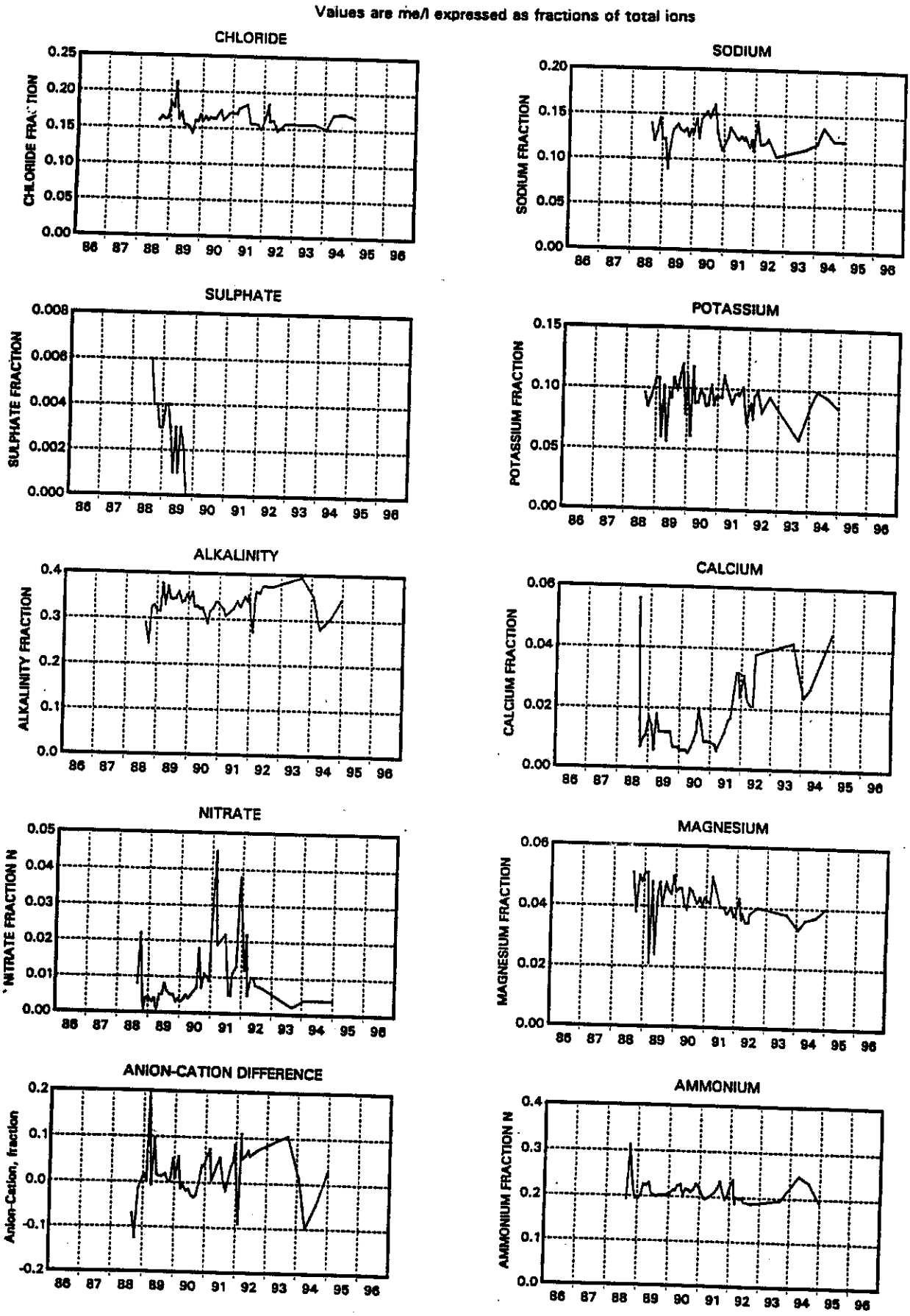


Figure 10.7.6 **Coastal Park leachate: Ionic fractions: Cell 1**

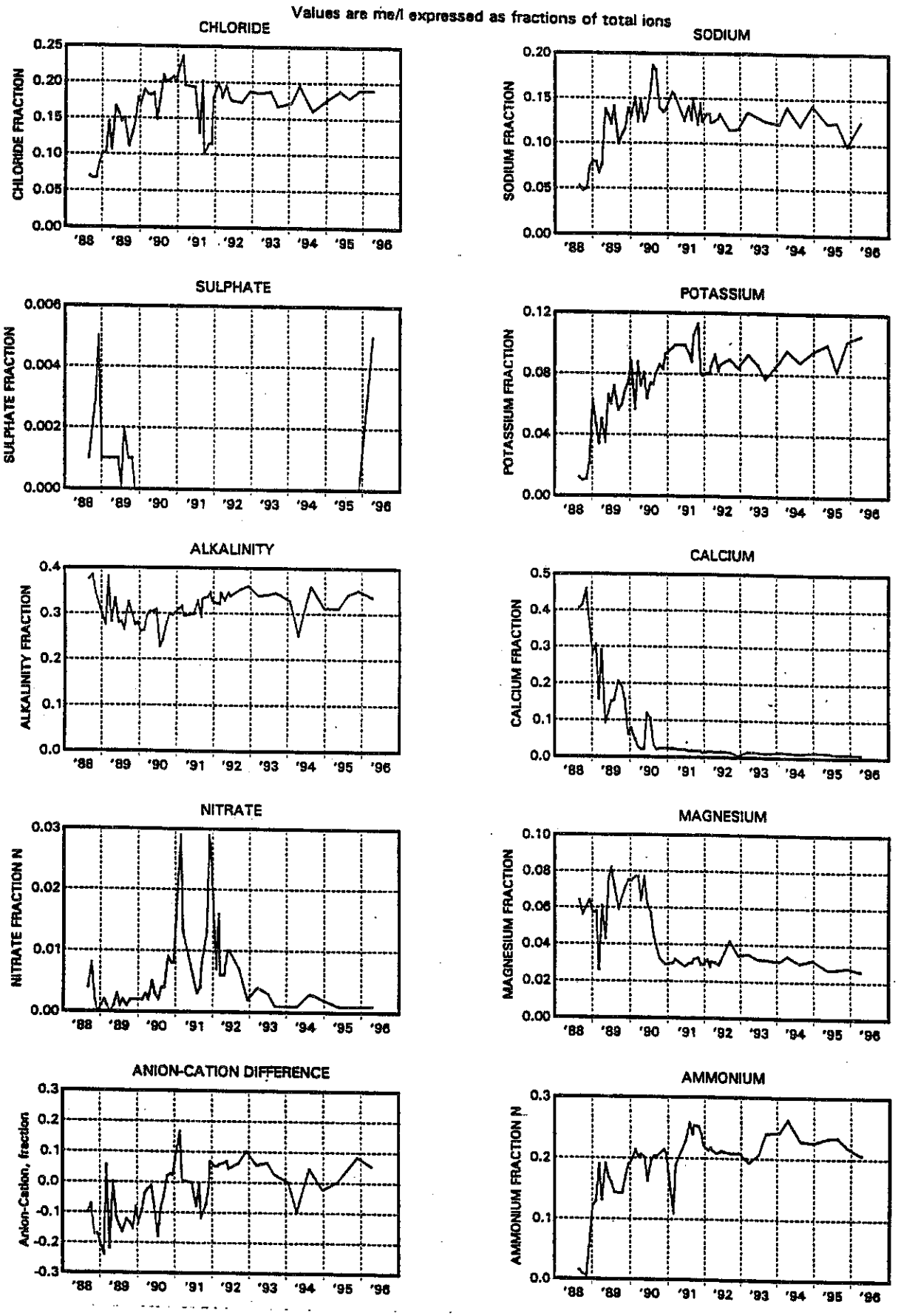


Figure 10.7.7 **Coastal Park leachate: Ionic fractions: Cell 2**

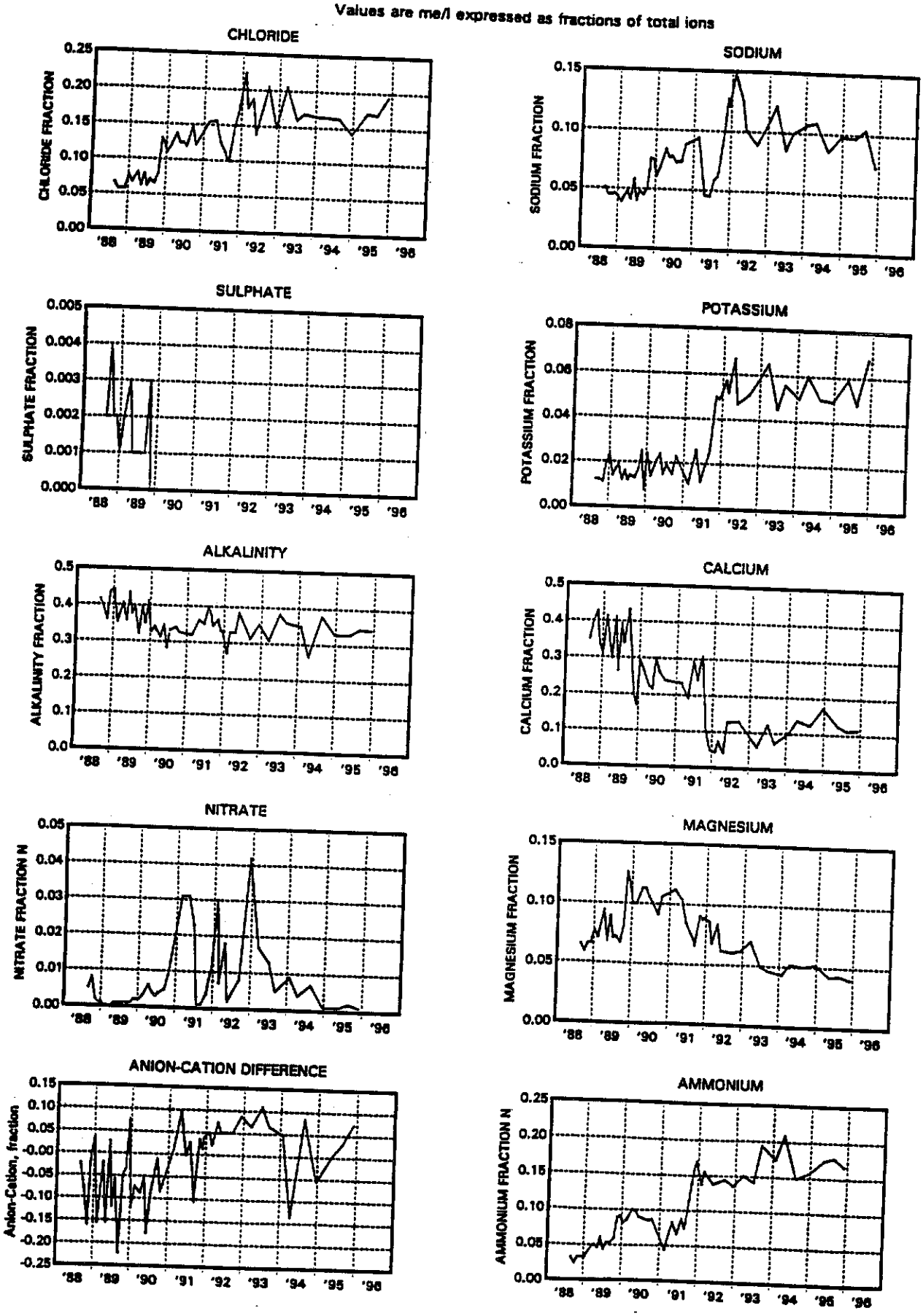


Figure 10.7.8 **Coastal Park leachate: Ionic fractions: Cell 3**

Values are me/l expressed as fractions of total ions

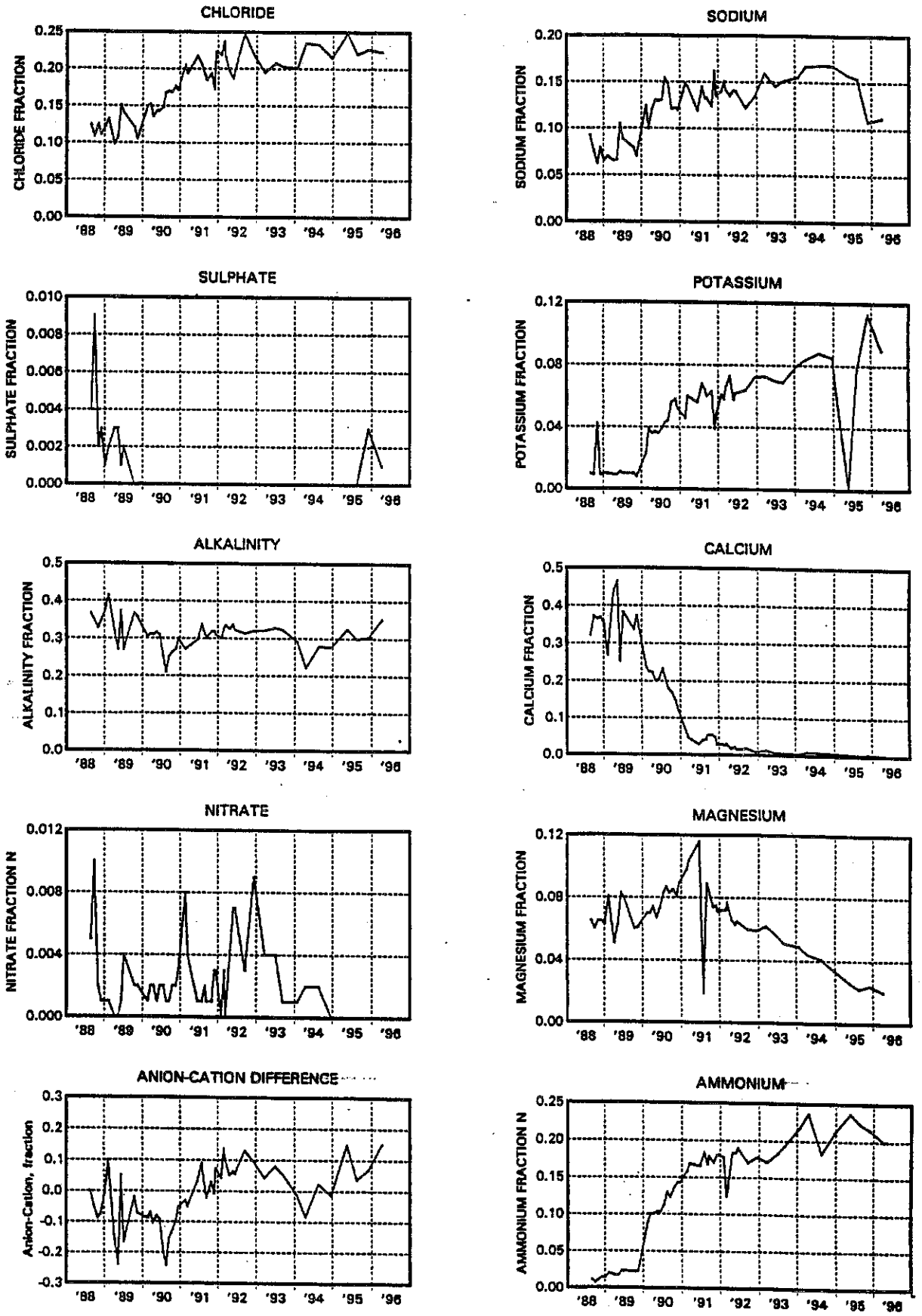


Figure 10.7.9 **Coastal Park leachate: Ionic fractions: Cell 4**

Values are me/l expressed as fractions of total ions

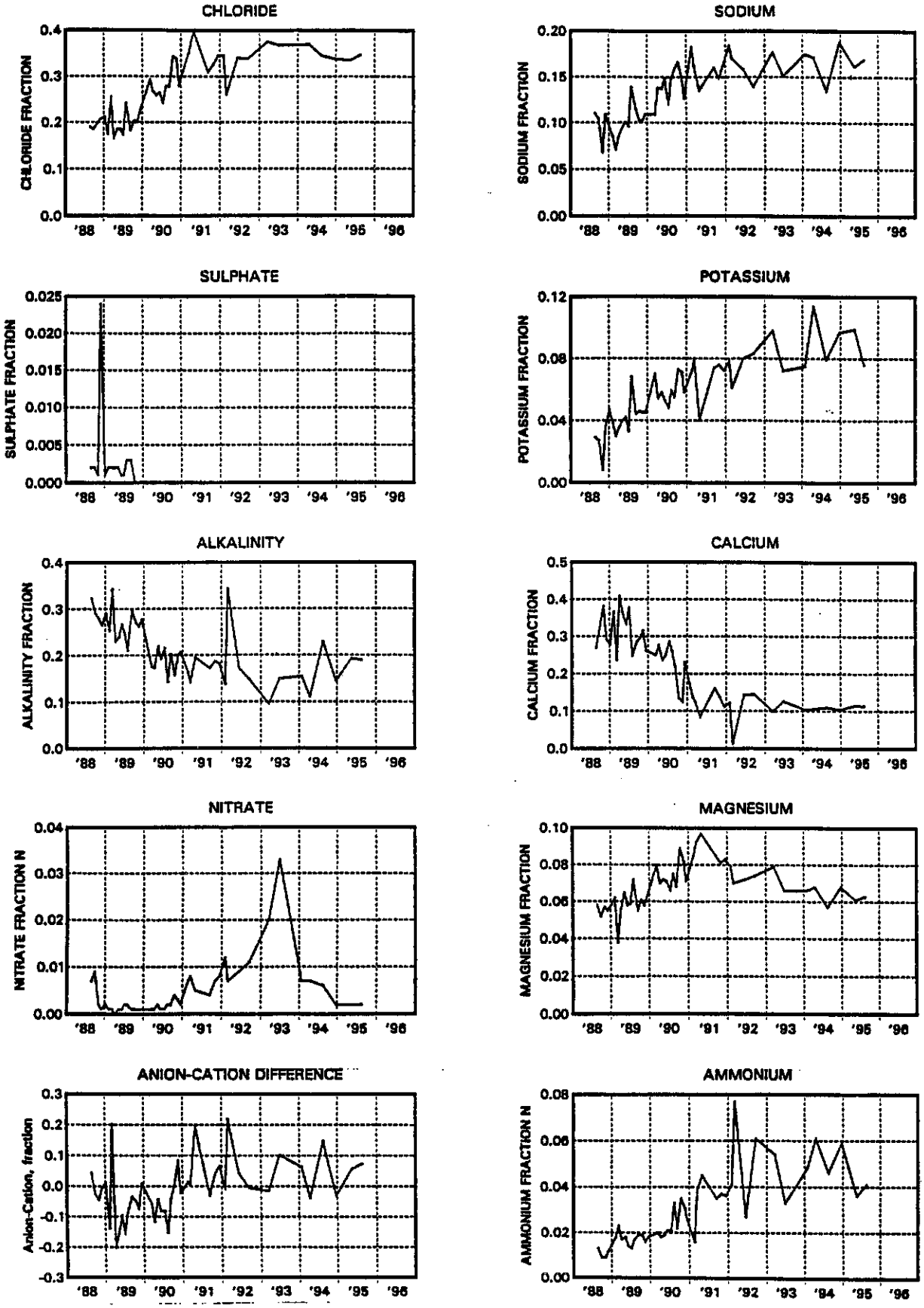
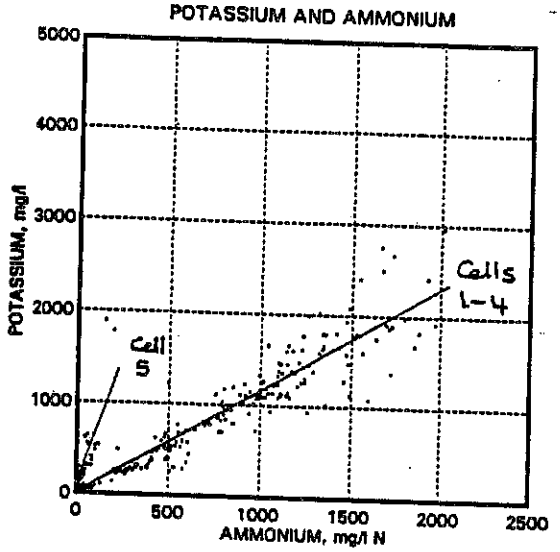
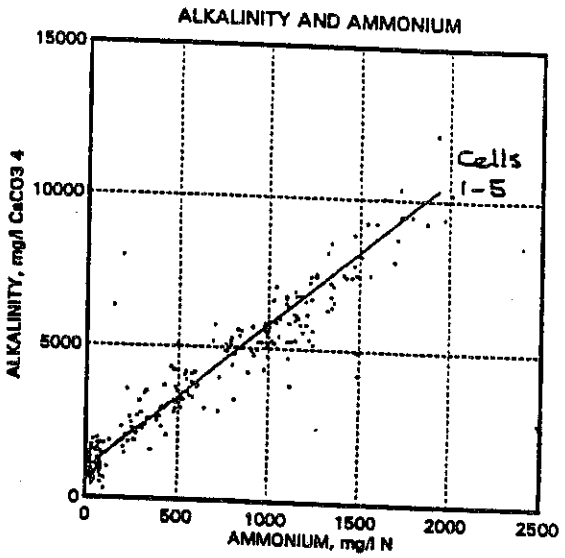
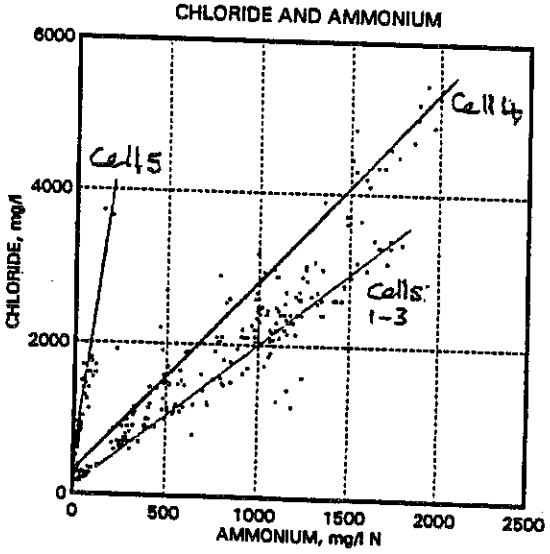
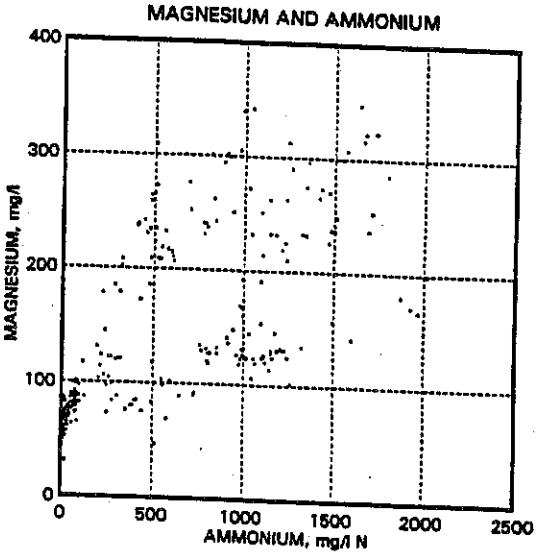


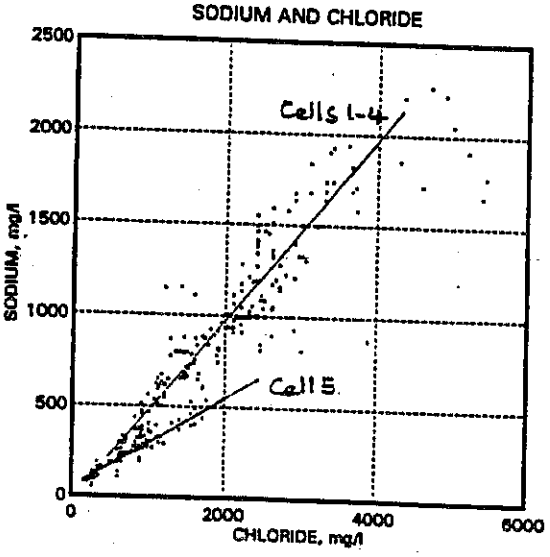
Figure 10.7.10 Coastal Park leachate: Ionic fractions: Cell 5











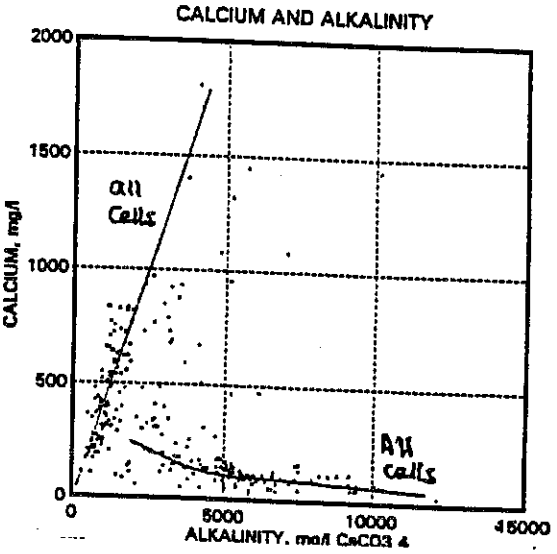


Figure 10.7.11 **Coastal Park leachate: Correlations between ionic concentrations: All Cells**

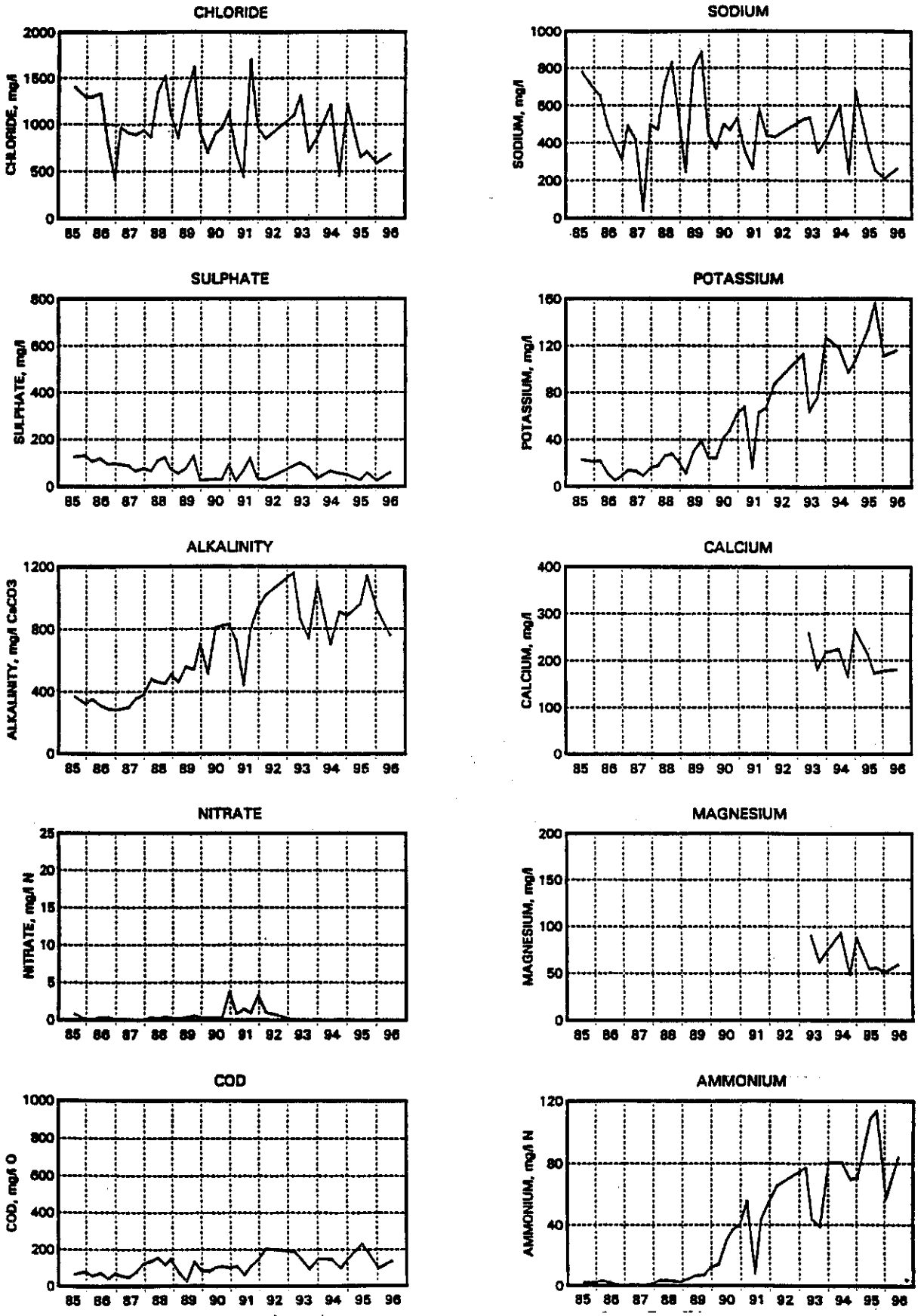


Figure 10.7.12 **Coastal Park ground water: Variation of ionic concentrations with time: Borehole 1**

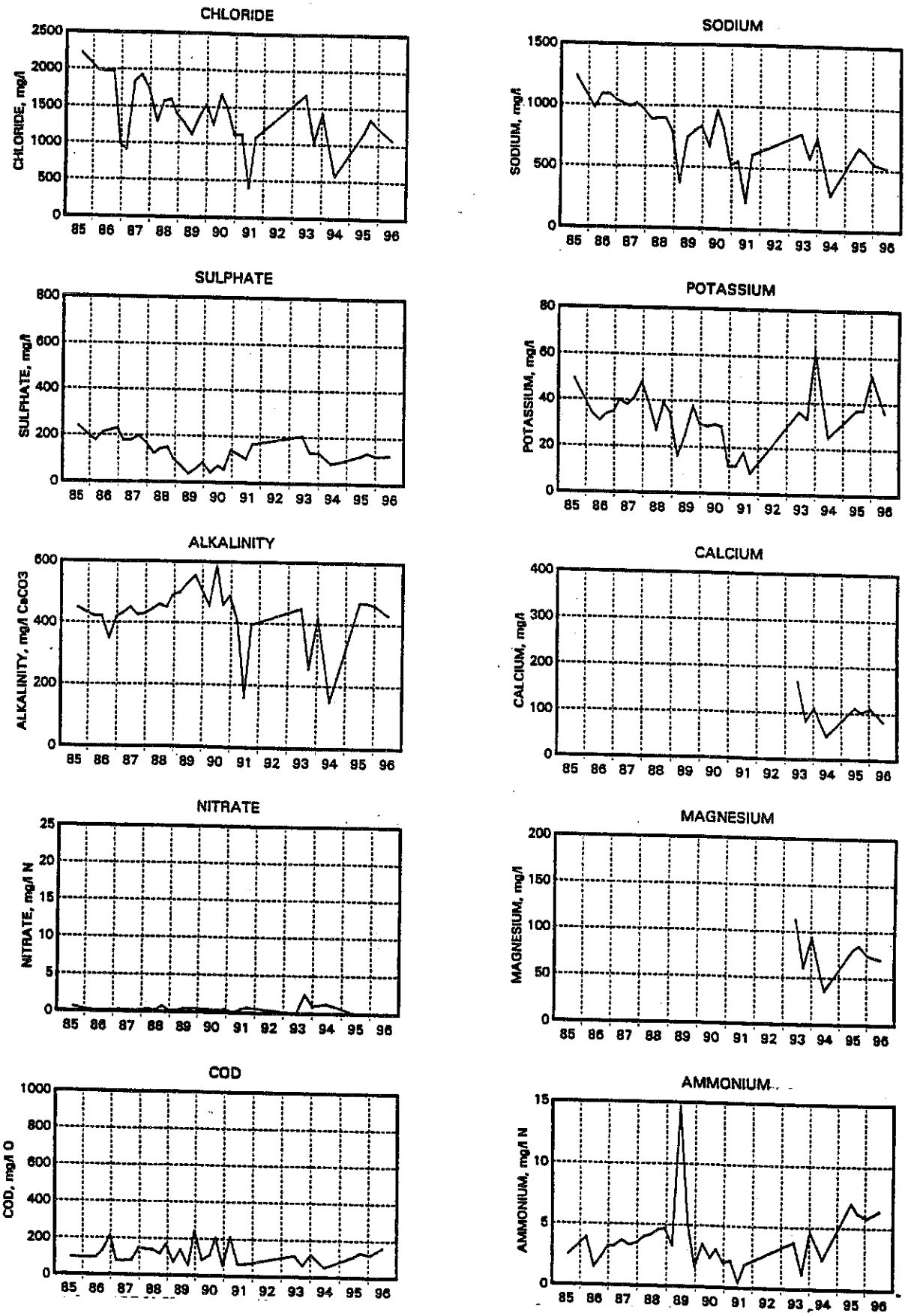


Figure 10.7.13 **Coastal Park ground water: Variation of ionic concentrations with time: Borehole 2**

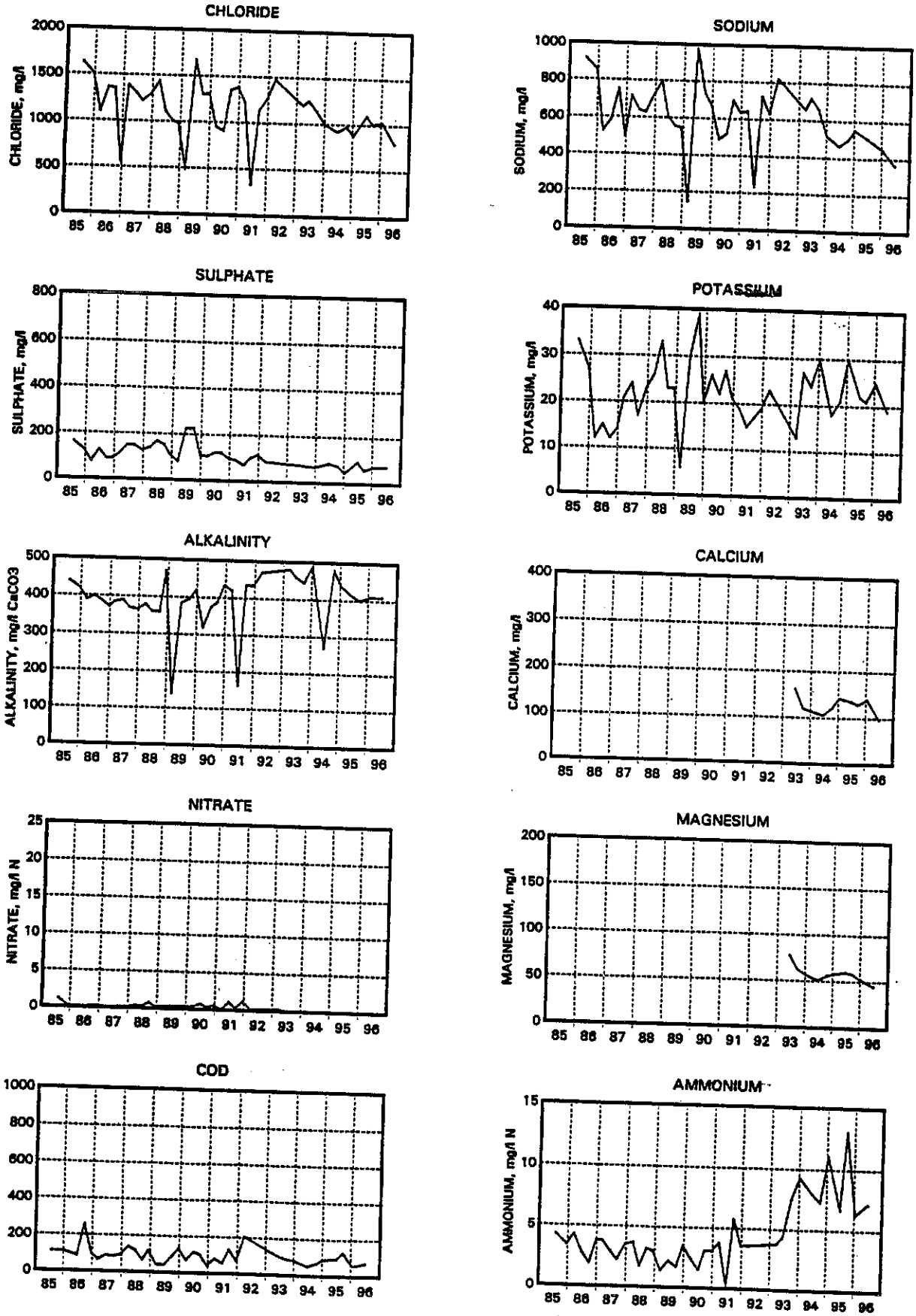


Figure 10.7.14 **Coastal Park ground water: Variation of ionic concentrations with time: Borehole 3**

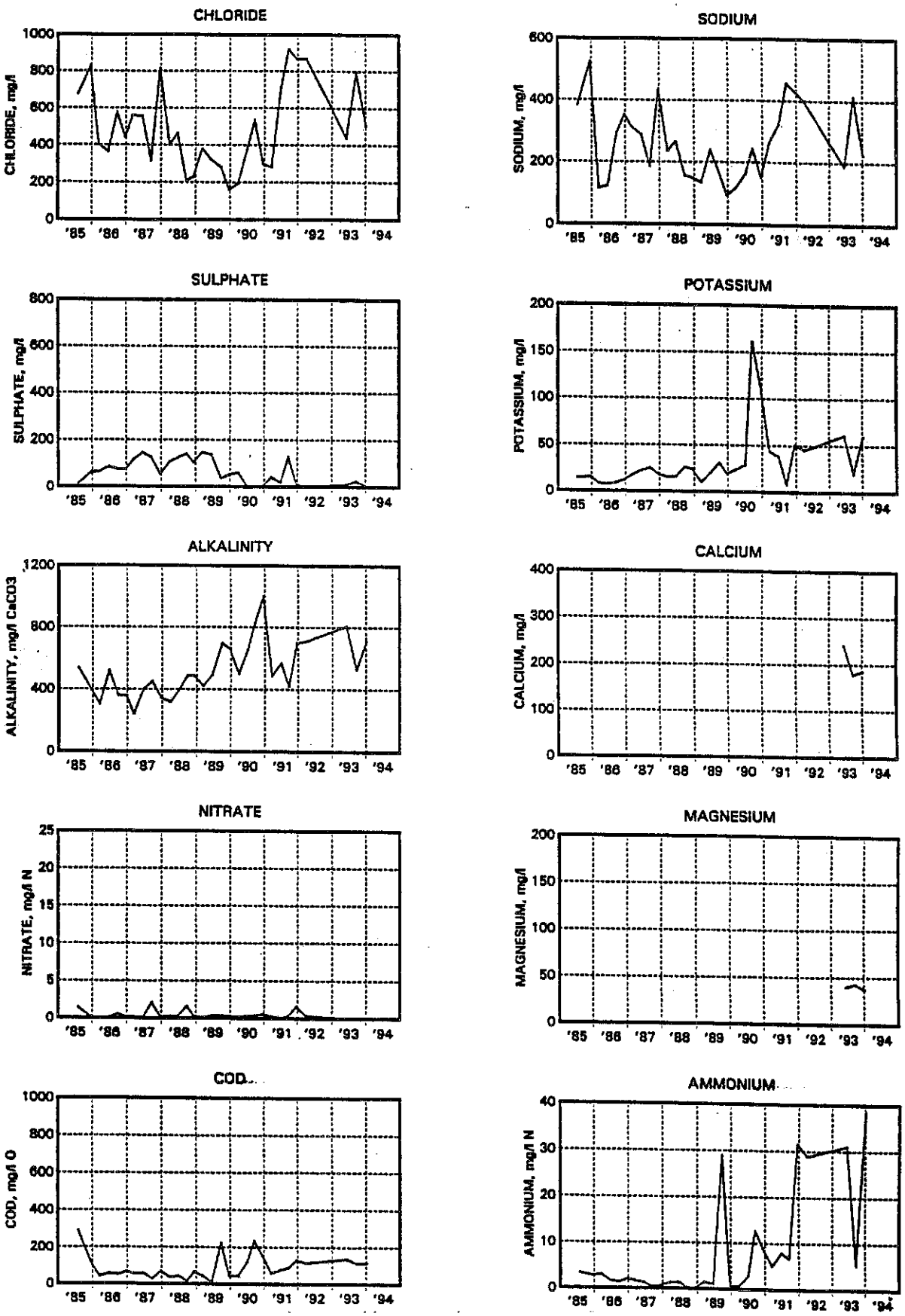


Figure 10.7.15 **Coastal Park ground water: Variation of ionic concentrations with time: Borehole 4**

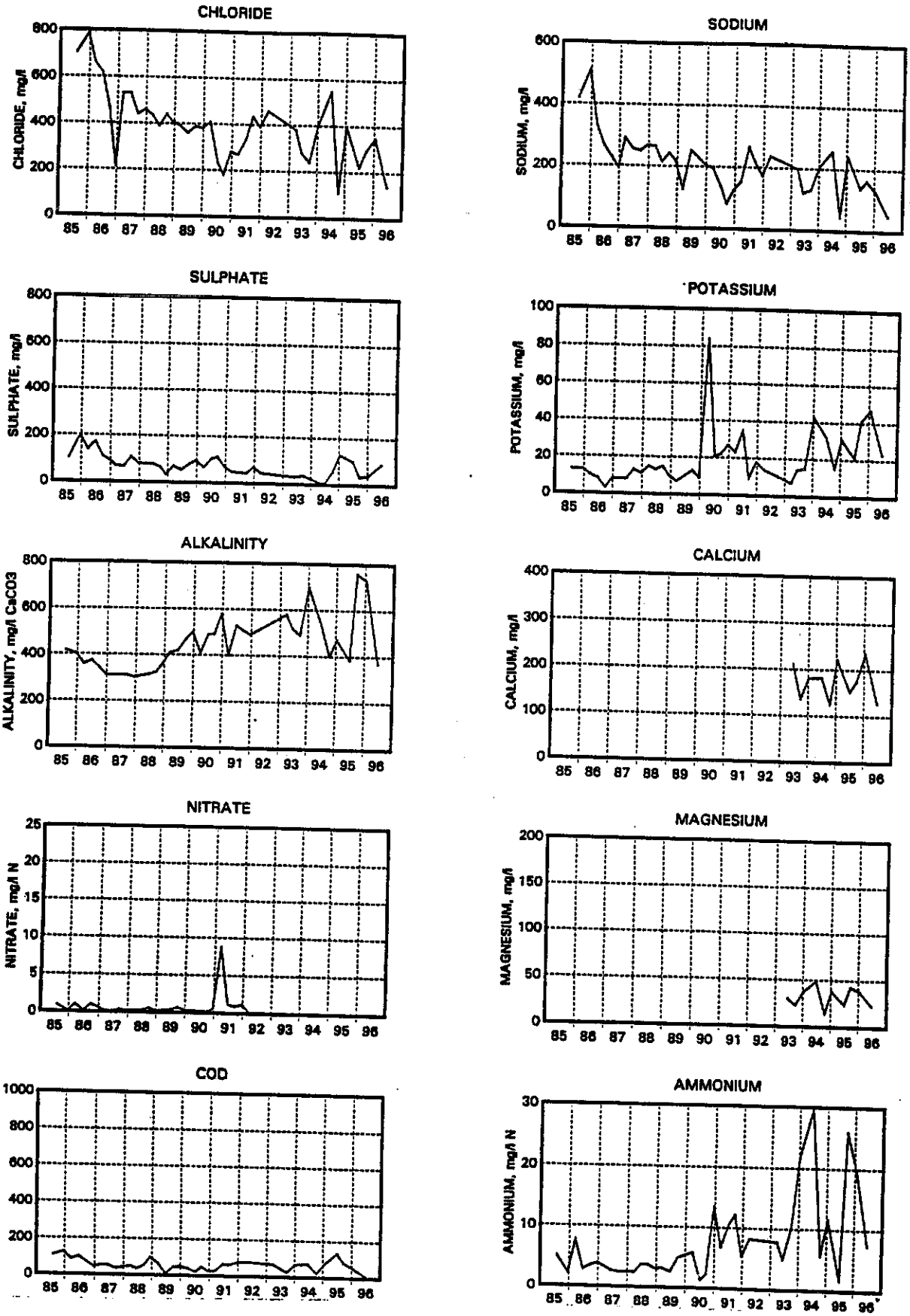


Figure 10.7.16 **Coastal Park ground water: Variation of ionic concentrations with time: Borehole 5**

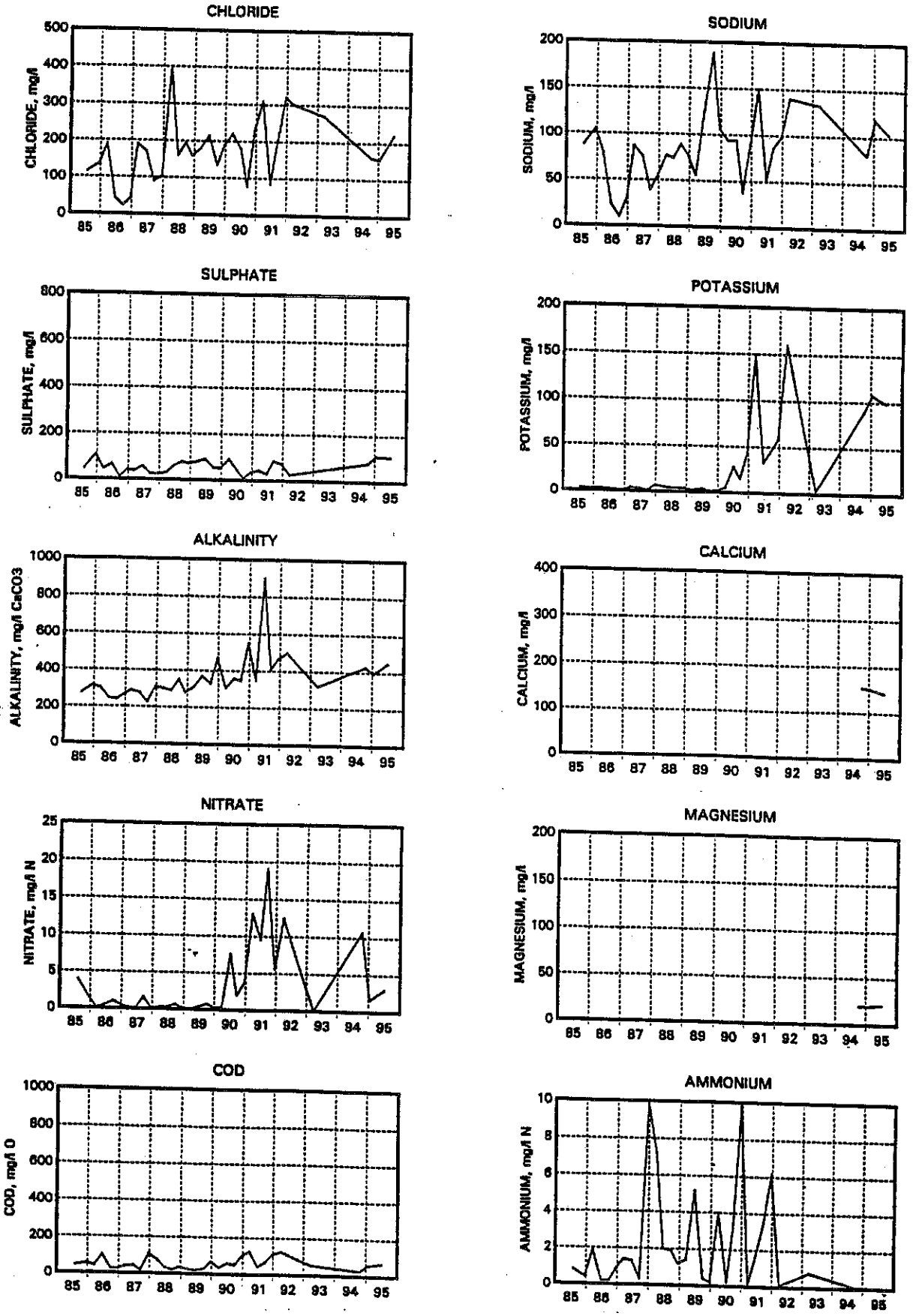


Figure 10.7.17 **Coastal Park ground water: Variation of ionic concentrations with time: Borehole 6**

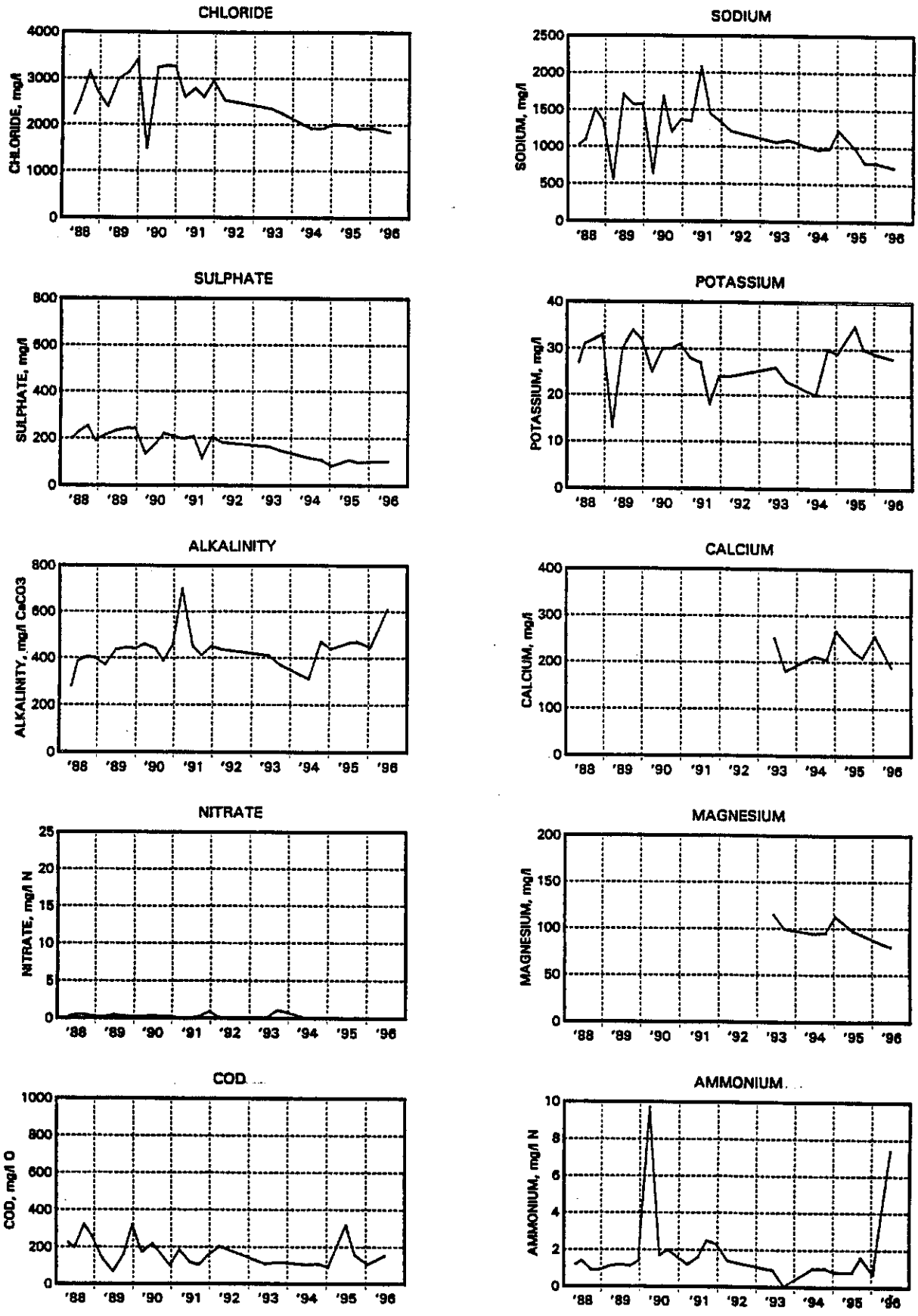


Figure 10.7.18 **Coastal Park ground water: Variation of ionic concentrations with time: Borehole 7**

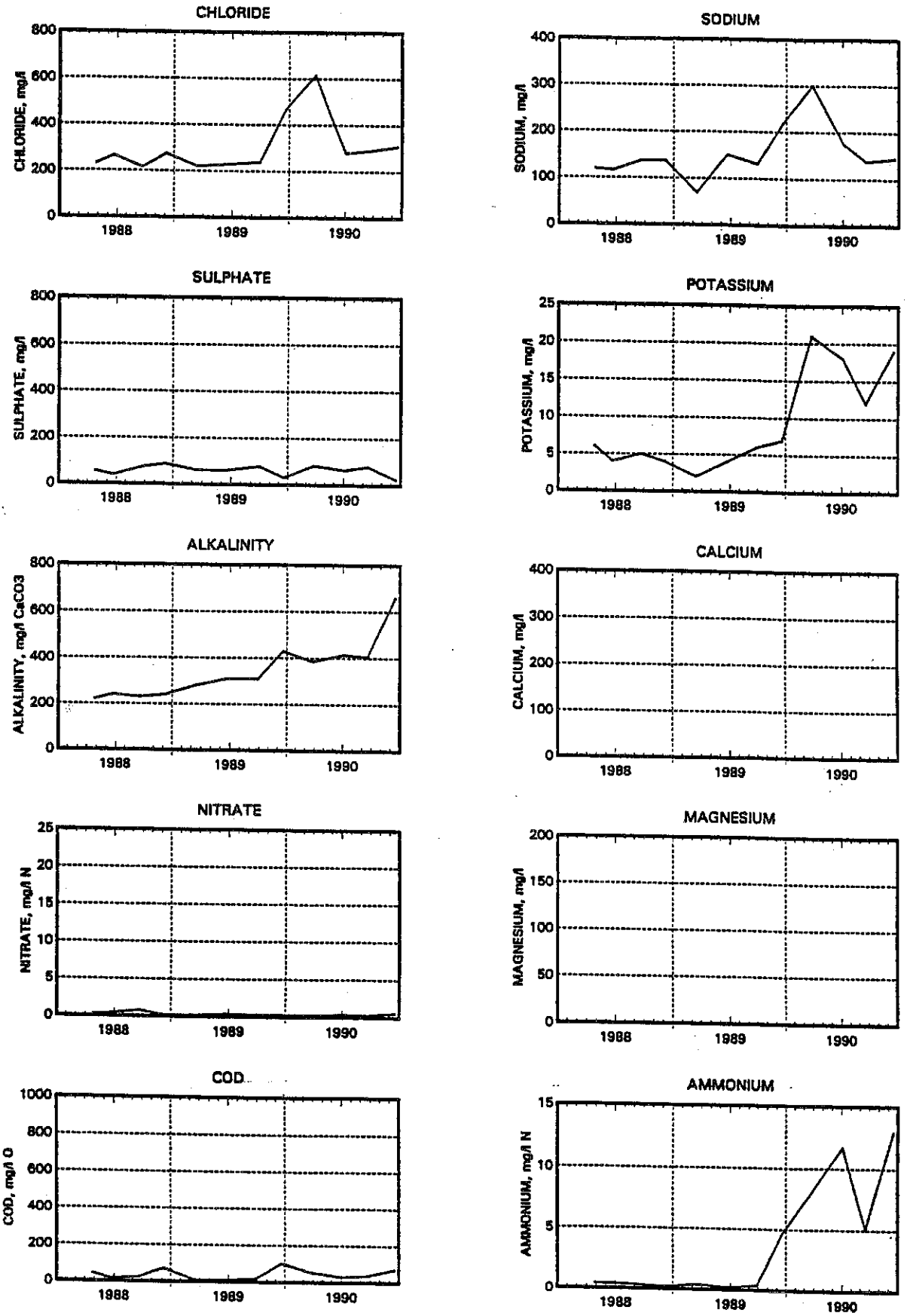


Figure 10.7.19 **Coastal Park ground water: Variation of ionic concentrations with time: Borehole 8**

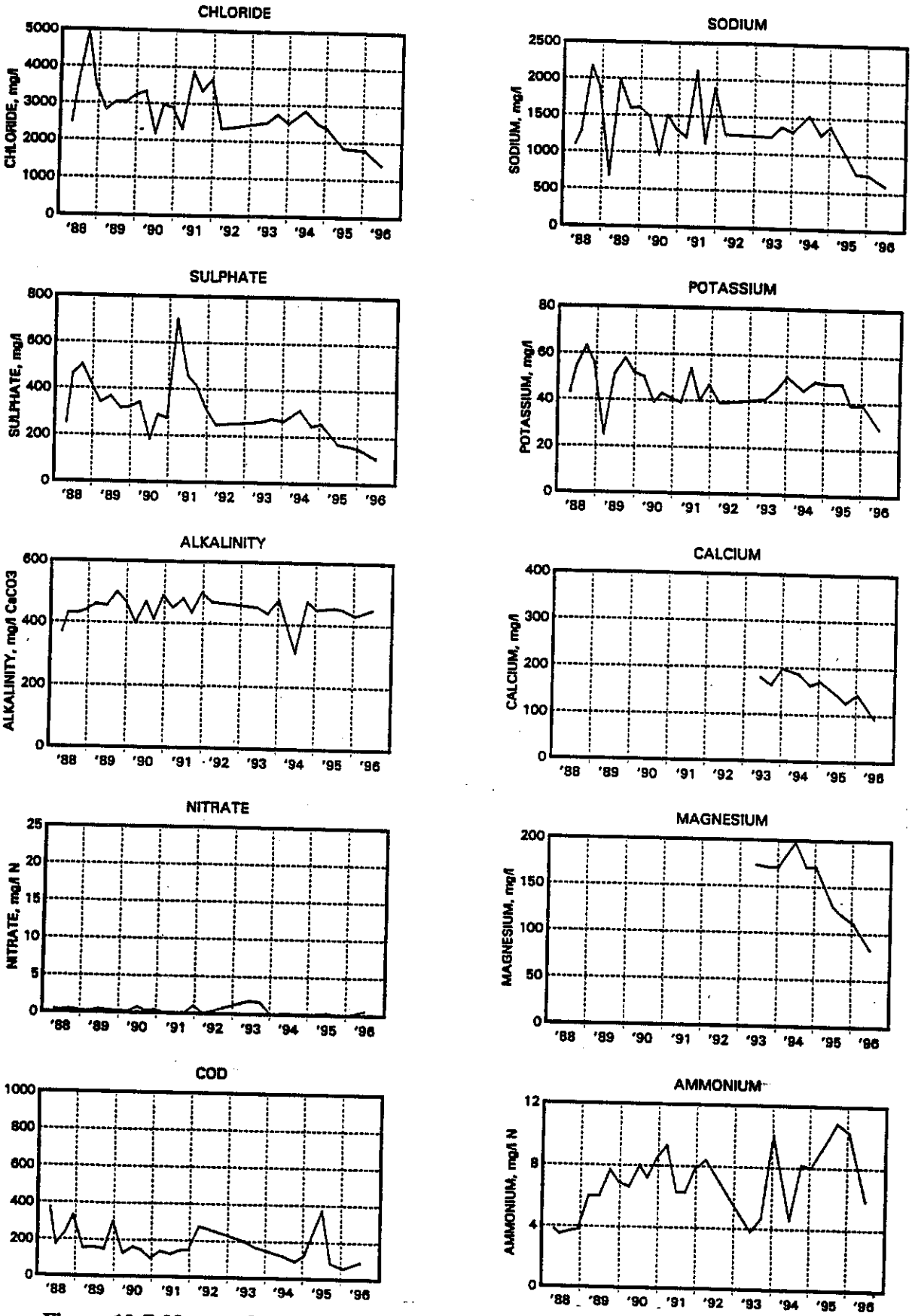


Figure 10.7.20 **Coastal Park ground water: Variation of ionic concentrations with time: Borehole 9**

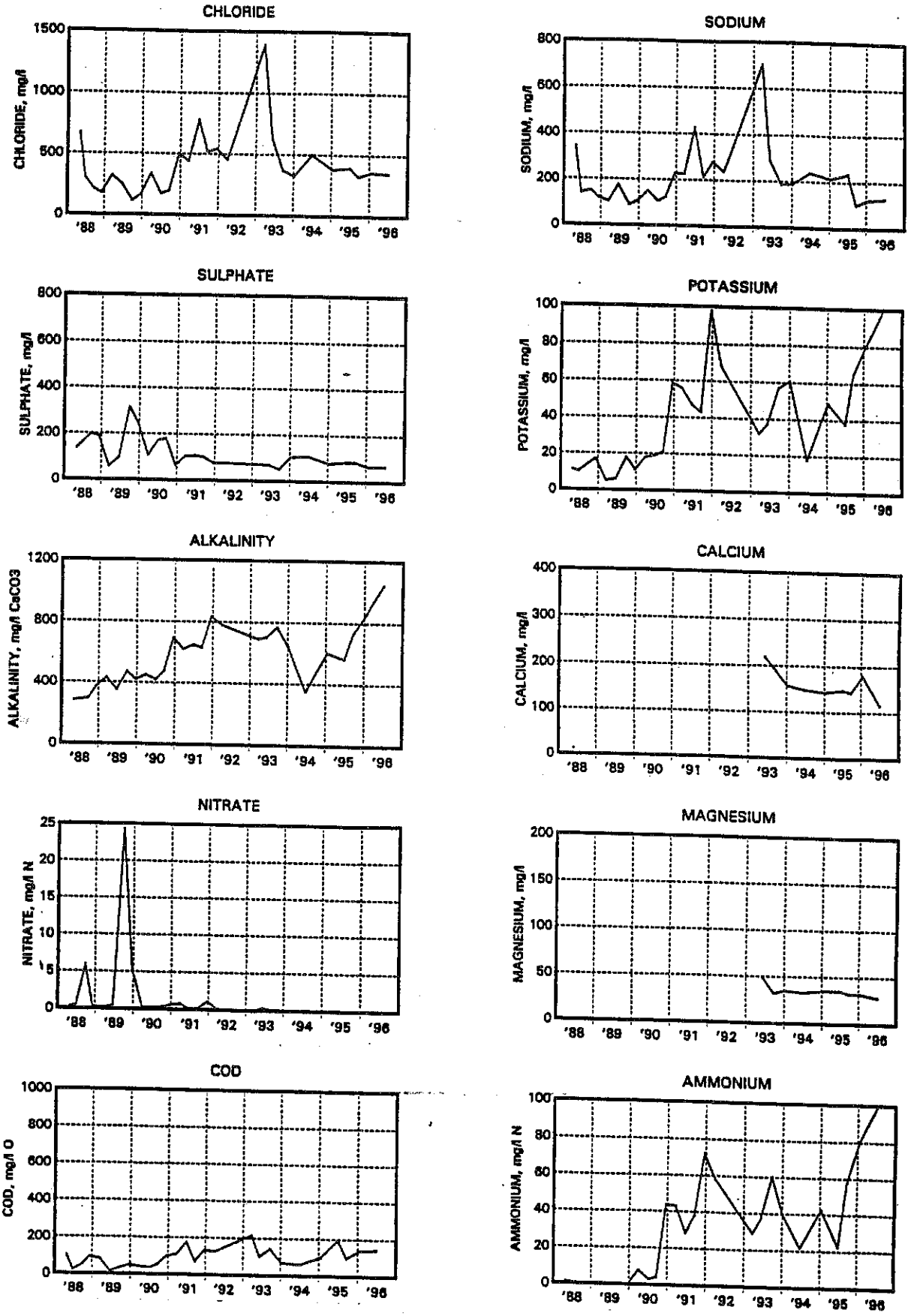


Figure 10.7.21 **Coastal Park ground water: Variation of ionic concentrations with time: Borehole 10**

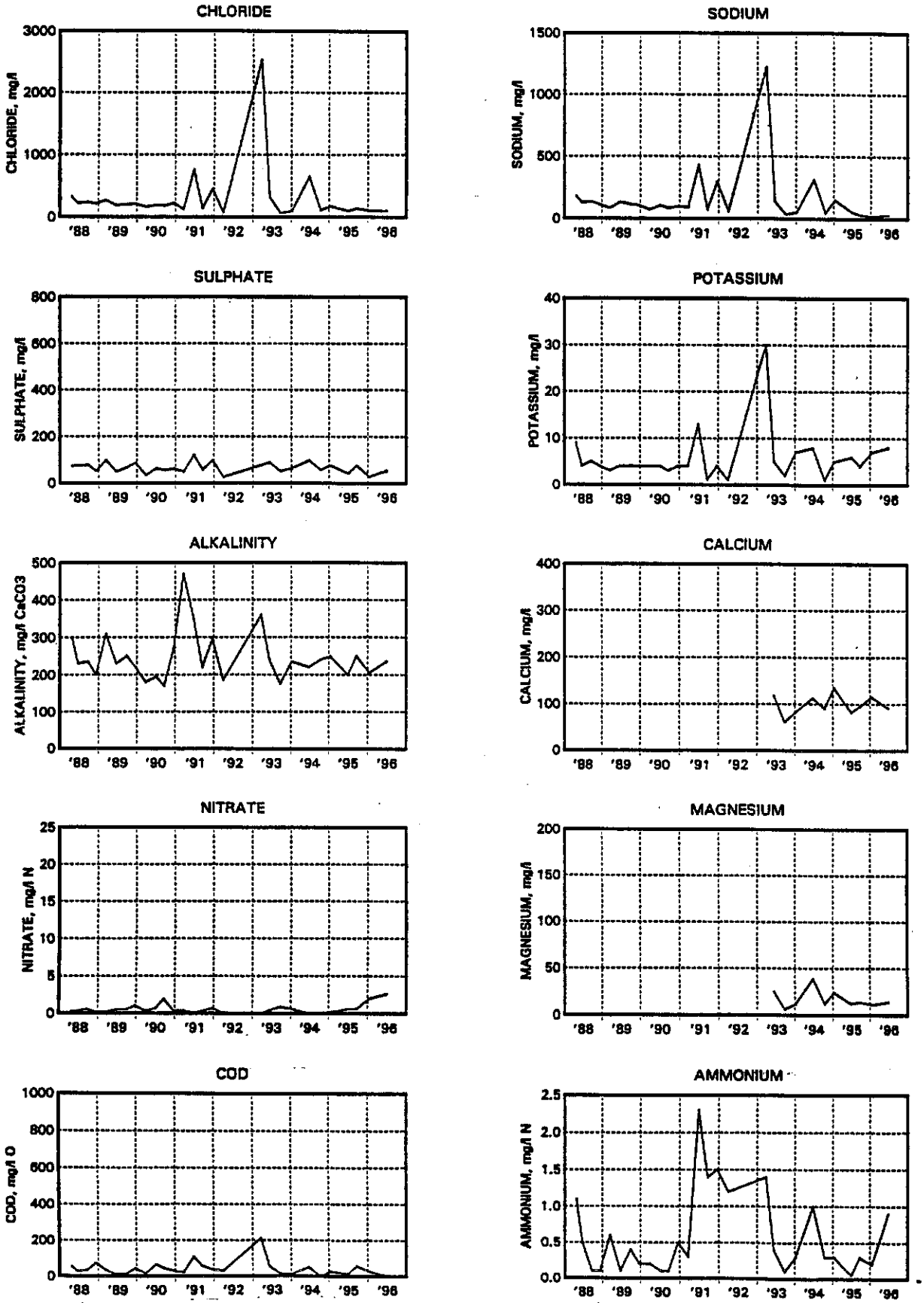


Figure 10.7.22 **Coastal Park ground water: Variation of ionic concentrations with time: Borehole 11**

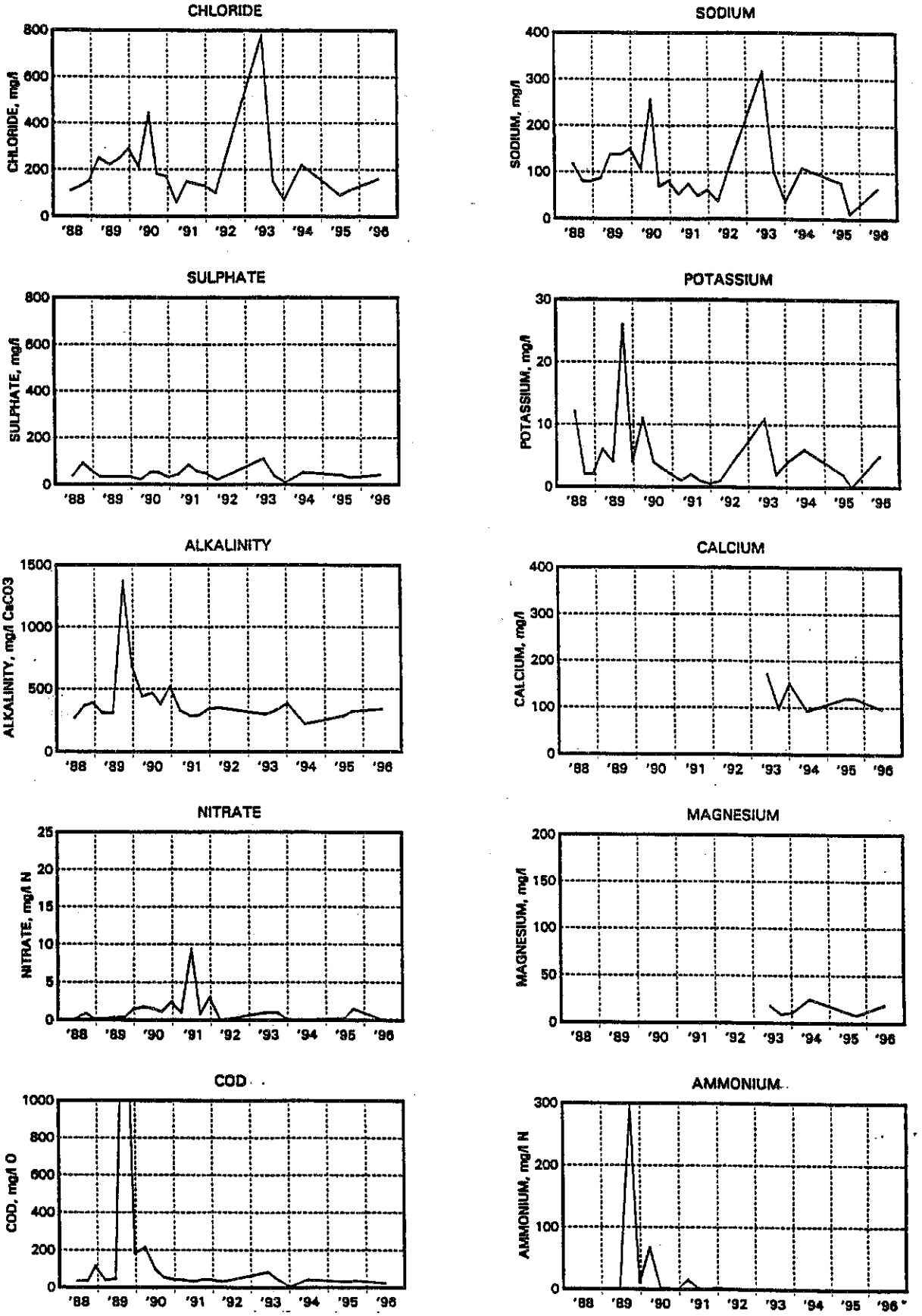


Figure 10.7.23 **Coastal Park ground water: Variation of ionic concentrations with time: Borehole 13**

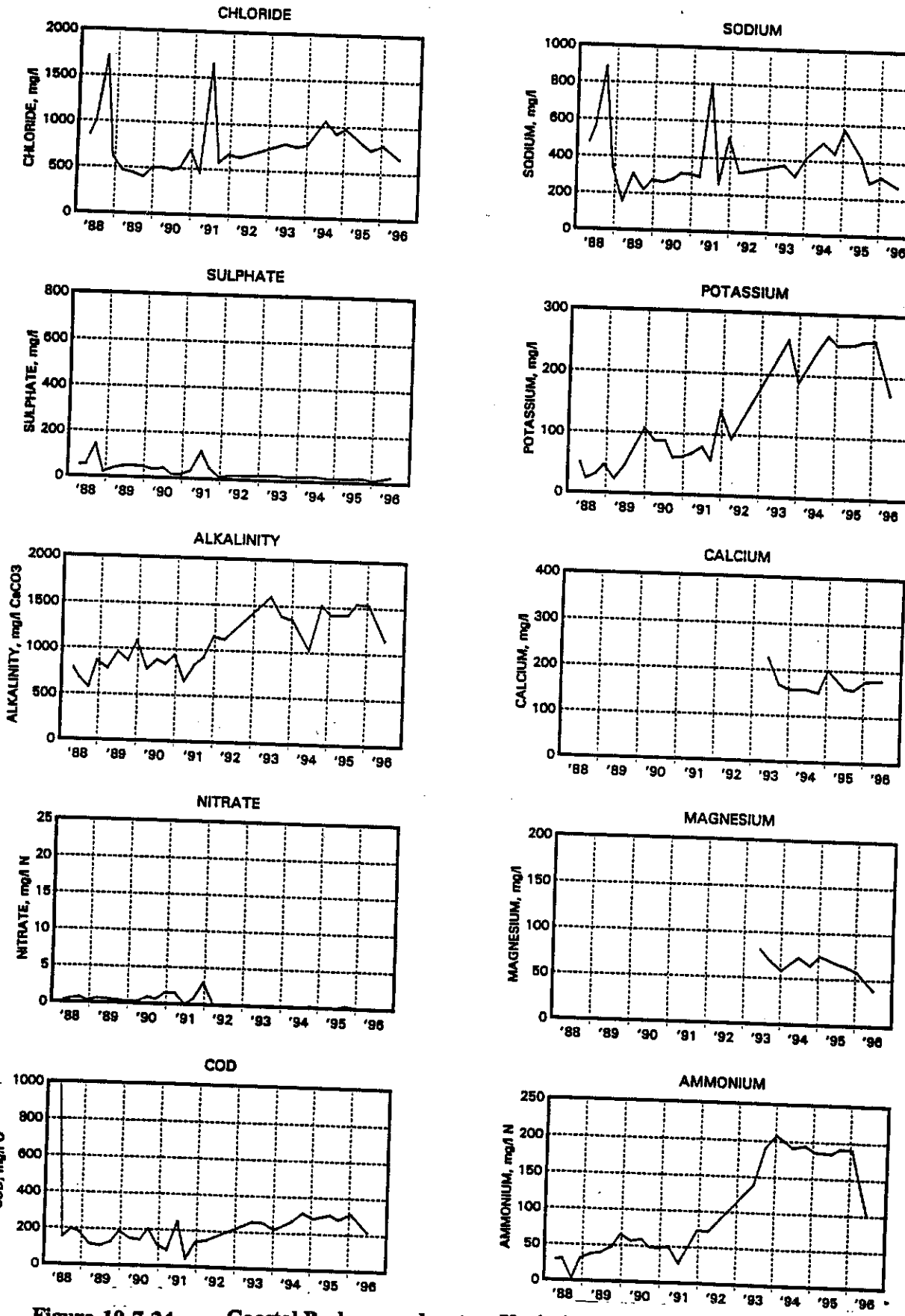


Figure 10.7.24 **Coastal Park ground water: Variation of ionic concentrations with time: Borehole 14**

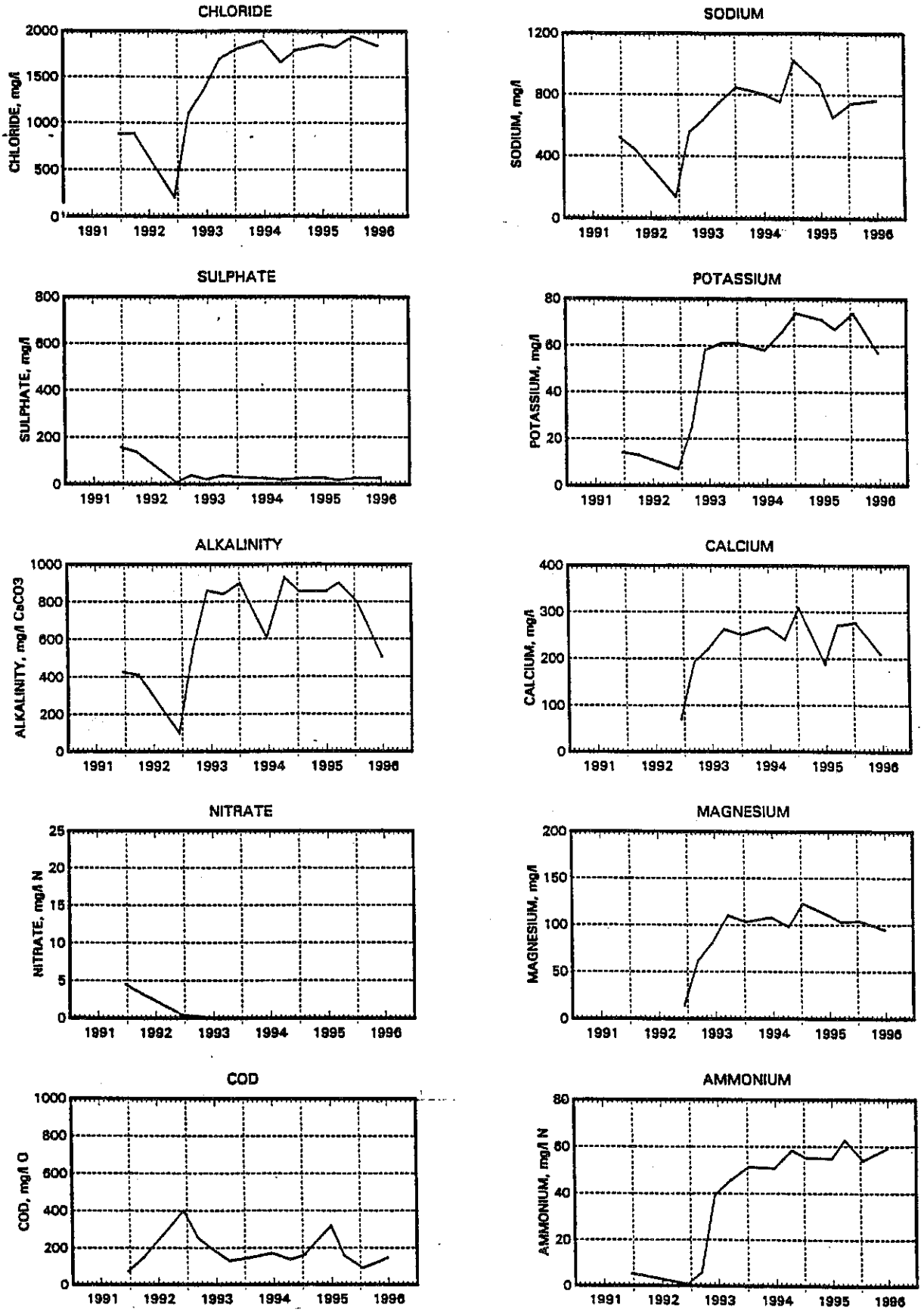


Figure 10.7.25 **Coastal Park ground water: Variation of ionic concentrations with time: Borehole 15**

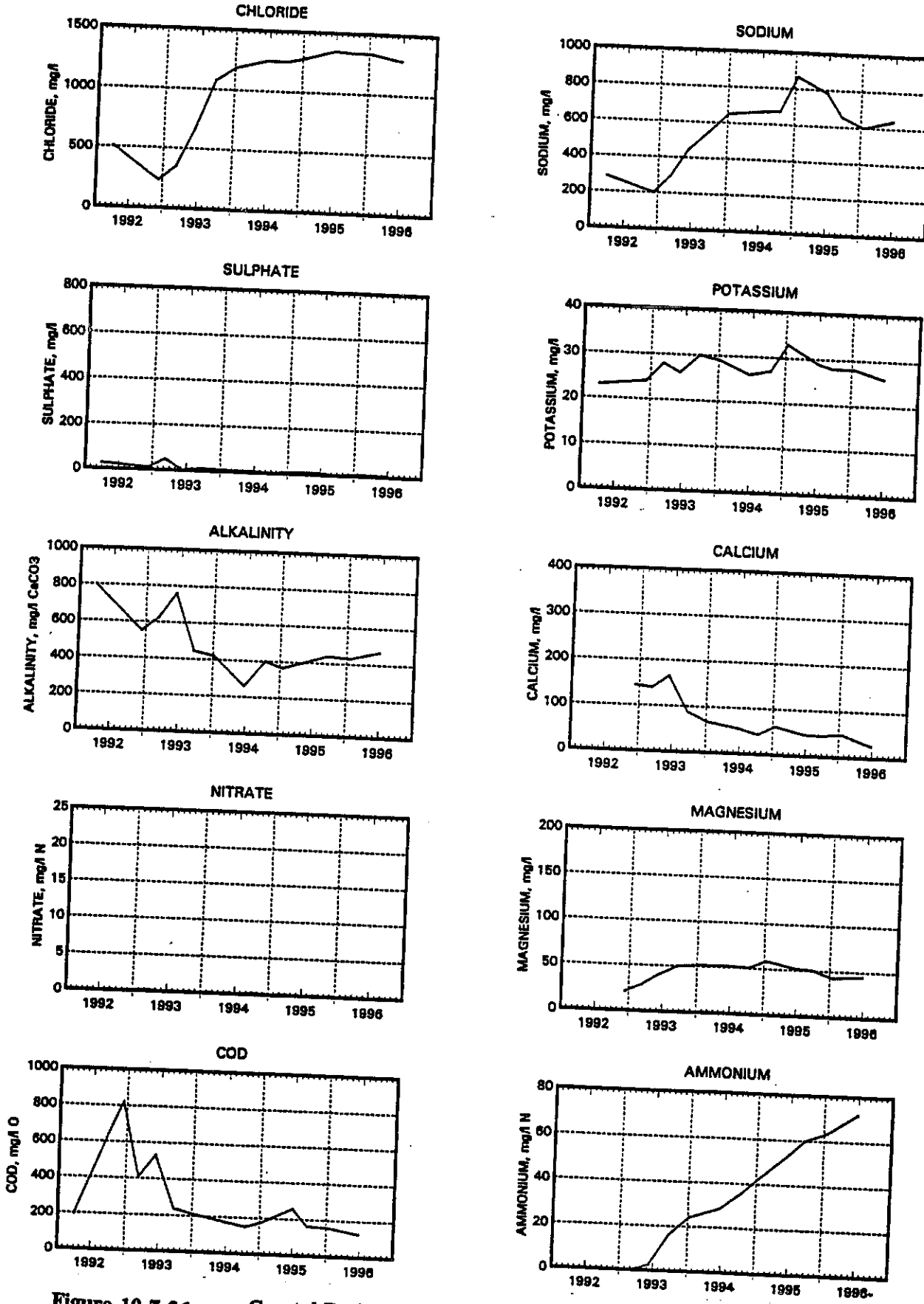


Figure 10.7.26 **Coastal Park ground water: Variation of ionic concentrations with time: Borehole 16**

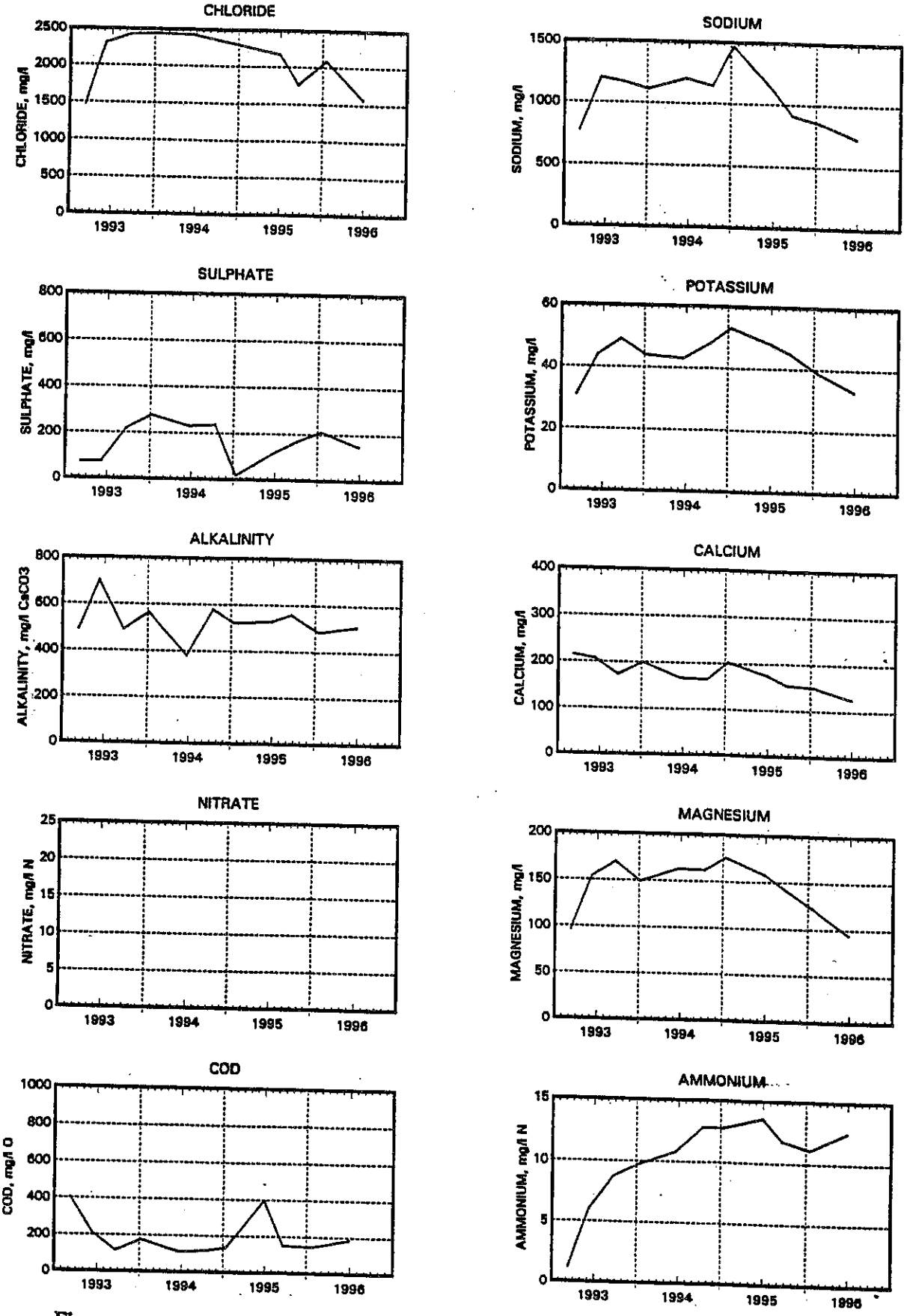


Figure 10.7.27 **Coastal Park ground water: Variation of ionic concentrations with time: Borehole 17**

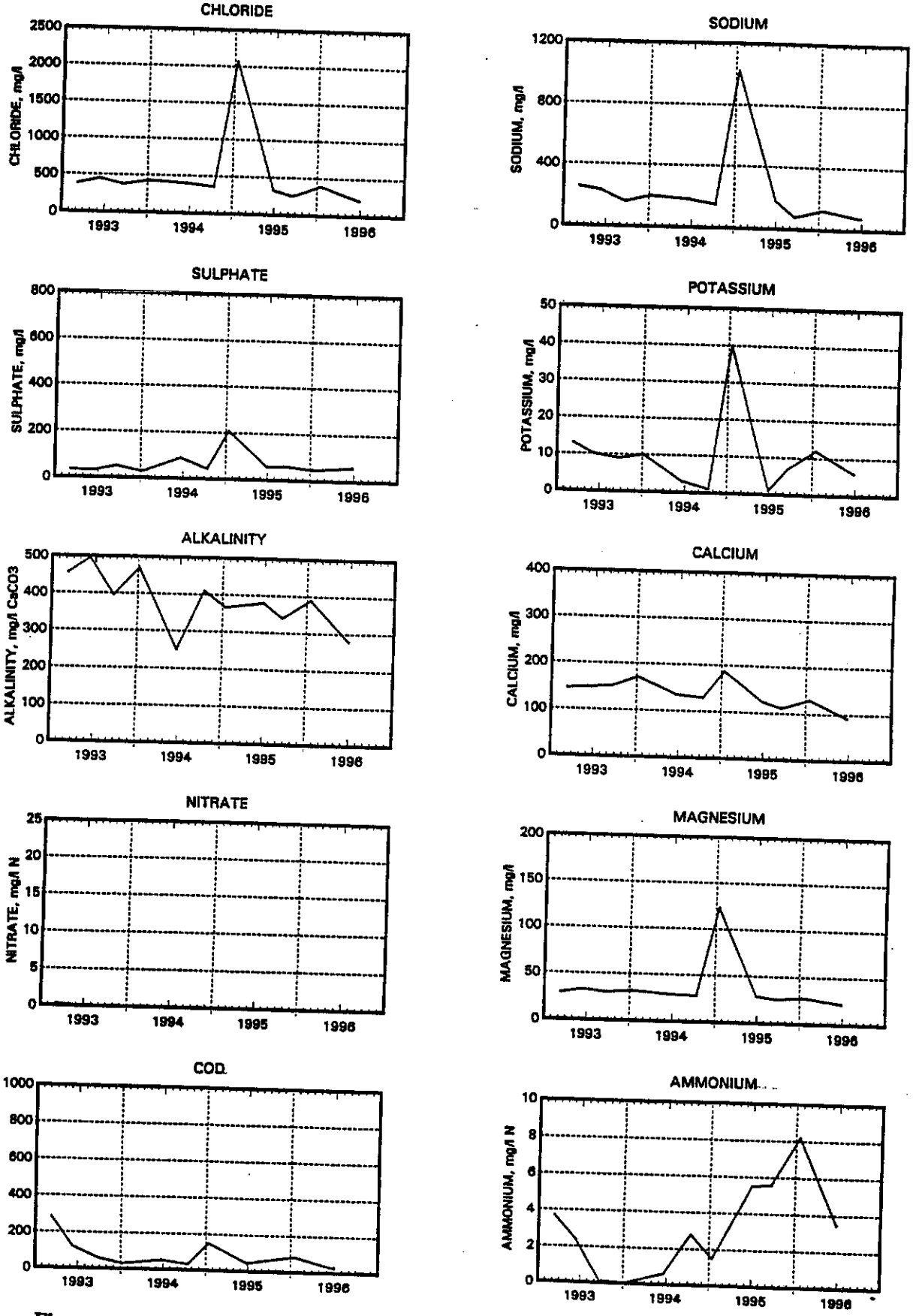
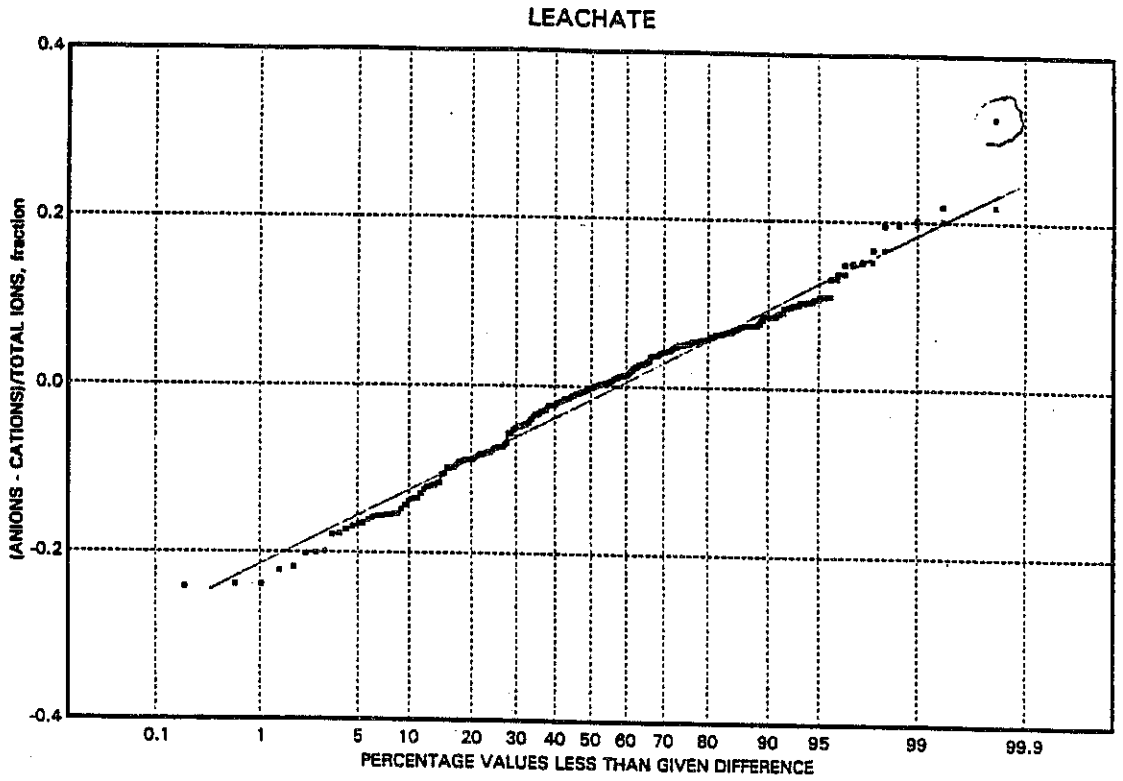


Figure 10.7.28 **Coastal Park ground water: Variation of ionic concentrations with time: Borehole 18**

Values are me/l expressed as fractions of total ions

Squares are with all samples included, crosses are with outliers removed



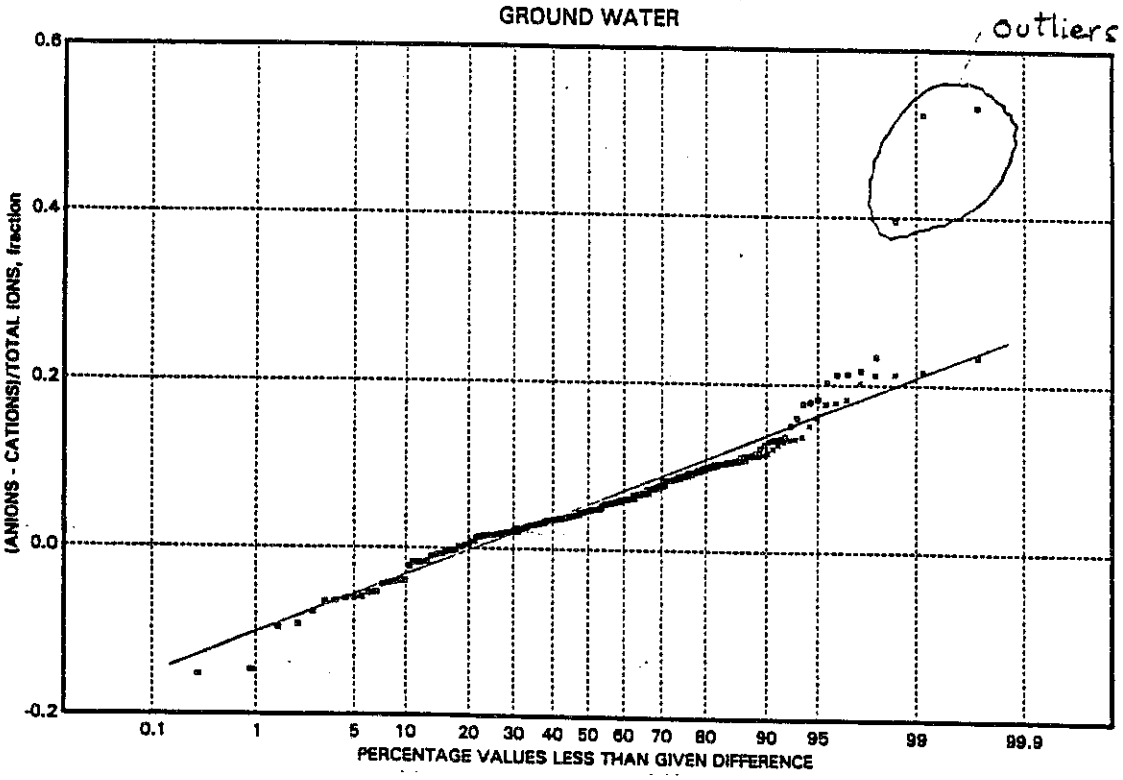


Figure 10.7.29 **Coastal Park: Frequency distributions for differences between anions and cations**

SECTION D

GENERAL

CHAPTER 11

GENERAL CONCLUSIONS

The research achieved the main objectives of the project in exploring the potential of landfill sites in South Africa to act as final depositories for metallic wastes at minimal environmental risk. The main conclusions to be derived from this research are summarised as follows:

11.1: The material of concern in this investigation is a wood preservative commonly called CCA. This preservative consists of a mixture of copper, chromium and arsenic. The disposal of these substances, both as a waste solution or in combination with wood at the end of its lifecycle has the potential to become a global problem.

The Industry and Environmental Programme Activity Centre (IEPAC) operating under the umbrella of the United Nations is concerned about the current disposal options of treated timber such as the uncontrolled burning or disposal to landfill. If industrial wastes are disposed to a landfill then the wastes must be securely bound within that landfill, without the potential to provide environmental damage in future decades.

11.2: The results of this research have proved that metallic ions in materials such as CCA can be effectively immobilised by the process of adsorption onto the general wastes in a landfill. The amount of copper - chromium - arsenic in combination that could be co-disposed with general waste without adversely affecting leachate quality was: copper at 67 g $Cu.tonne^{-1}$; chromium at 195 g $Cr.tonne^{-1}$ and arsenic at 195 g $As.tonne^{-1}$. The disposal ratio of these metals was dictated by the formulation of the CCA wood preservative. In general, the metal loading rates proposed from the experimental work and predicted by the modelling undertaken in this study, concurred with the metal loading rates employed in the United Kingdom as recommended by the Department of the Environment.

11.3: A significant aspect of this research was the emphasis placed upon adsorption as the only attenuation mechanism considered. The emphasis upon adsorption is a worst-case examination of co-disposal. Many previous researchers have concentrated upon strictly chemical affects such as reduction, precipitation and co-precipitation. Under anaerobic conditions other attenuation mechanisms are evident and are probably superior to adsorption in immobilising inherently non-biodegradable substances such as heavy metals. However, if none of the other attenuation mechanisms were present, this research has shown that adsorption has the capacity to immobilise the heavy metals under consideration.

CHAPTER 12

RECOMMENDATIONS FOR FUTURE RESEARCH

12.1: Very little information is available on how the landfill water balance would be influenced by increasing the height of the landfill. On theoretical grounds it is postulated that higher landfills leach less, because compaction by the overburden load reduces the permeability of the waste.

A proposal was submitted by the Cape Metropolitan Council for an extension of the current project at the Coastal Park landfill to research the abovementioned phenomenon.

The Water Research Commission has subsequently approved an extension of 2 years to the contract term of the project (1998 - 1999). The extended project will be printed as Volume 2 of the final report.

The extended project will entail raising the surface of that section of the Coastal Park landfill, where the underlined cells 2 to 5 are located, by an additional two lifts of waste of 2.5 m each. The objectives of the extended project will be:

a) to study the resultant outflow of leachate, as the 5 m of refuse already in place are squeezed by the additional overburden load;

b) to study the amounts and rates of settlement, both of the existing 5 m of refuse and of the two 2.5 m layers placed over it, and;

c) to study if and by how much the ultimate rate of leaching of this section of the landfill is affected by the increased height.

12.2: The use of the large pilot-scale columns employed in this study would not be warranted for further research. It would however be advantageous to maintain the laboratory-scale experimental methodology and determine the adsorption characteristics of other industrial wastes. Various other heavy metals should be examined in combination and individually. Even the use of smaller columns would accelerate the experimental programme to more acceptable time-frames.

12.3: An important matter requiring further research when considering the co-disposal of heavy metals with general wastes is the possible remobilisation of heavy metals.

12.4: Soluble substances migrating downward through landfilled general wastes have been observed to spread laterally to a considerable extent and are not confined to vertical flow. The observed lateral migration has not been adequately explained and a full explanation must still be sought.

CHAPTER 13

ARCHIVING OF DATA GENERATED BY THE PROJECT

13.1 SECTION A: LABORATORY AND PILOT-SCALE STUDIES

a) Mr R H Ballard, an employee of the Cape Metropolitan Council, utilised the laboratory-scale adsorption/ desorption studies and the pilot-scale landfill column studies for the purpose of obtaining a MSc (Engineering) degree through the Department of Chemical Engineering at the University of Cape Town, South Africa.

The MSc thesis titled "Immobilisation of copper, chromium and arsenic on stabilised domestic refuse (1997)" has been archived at the following address:

The Jagger Library, University of Cape Town
Private Bag, Rondebosch, 7701 SOUTH AFRICA

b) The raw analytical and monitoring data generated during the laboratory and pilot-scale studies (Chapters 5, 6, 7 and 8) have been archived at the following address:

Scientific Services Department, Cape Metropolitan Council
P O Box 16548, Vlaeberg, 8018 SOUTH AFRICA

13.2 SECTION B: FULL-SCALE LANDFILL CELL STUDIES AT COASTAL PARK

a) The raw analytical and monitoring data generated during the full-scale studies (Chapter 9) have been archived at the following address:

Head: Waste Management, Directorate: Water and Waste
Cape Metropolitan Council, P O Box 16548, Vlaeberg
8018 SOUTH AFRICA

13.3 SECTION C: ASSOCIATED STUDIES AT COASTAL PARK

The data generated during the Associated Studies (Sections 10.2 to 10.7) have been archived by the respective authors whose detailed addresses are provided on the title page of each section.