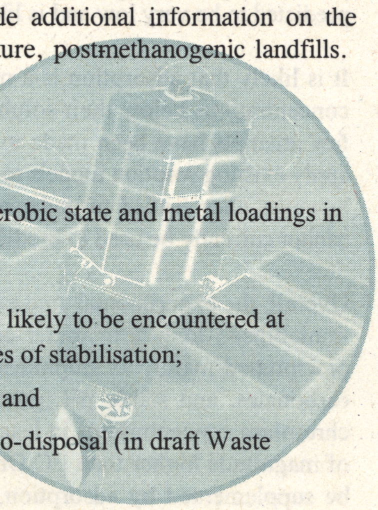
Long Term Fate of Metals in Landfill

ENVIRONMENT AGENCY

Background

This research was undertaken to address uncertainties regarding the long-term fate of heavy metals in landfill sites. A principal objective was to investigate the chemical stability of co-disposed metals under a range of conditions likely to be encountered at different phases of landfill stabilisation. This was to provide additional information on the stability of heavy metals under the more aerobic conditions that may prevail in mature, post-methanogenic landfills. The metals investigated were cadmium, chromium and zinc.

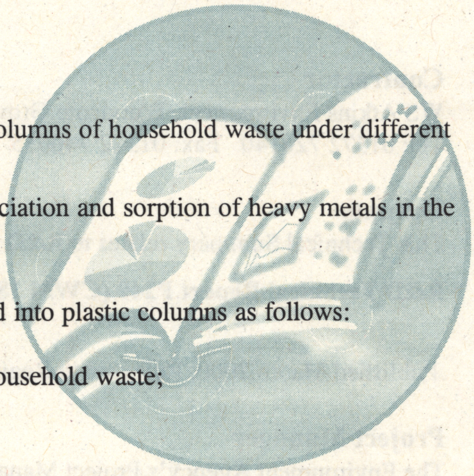
Objectives



The project objectives addressed the potential effects of a landfill site returning to an aerobic state and metal loadings in landfill. The key objectives at the outset of the project were to:

- determine the chemical stability of co-disposed metals under a range of conditions likely to be encountered at different phases of landfill stabilisation, particularly during the later and final stages of stabilisation;
- provide additional data on metal/waste loading ratios that may be safely disposed; and
- evaluate and discuss the results in the context of current UK guidelines for metal co-disposal (in draft Waste Management Paper 26F).

Approach



The project comprised two parallel, complementary components:

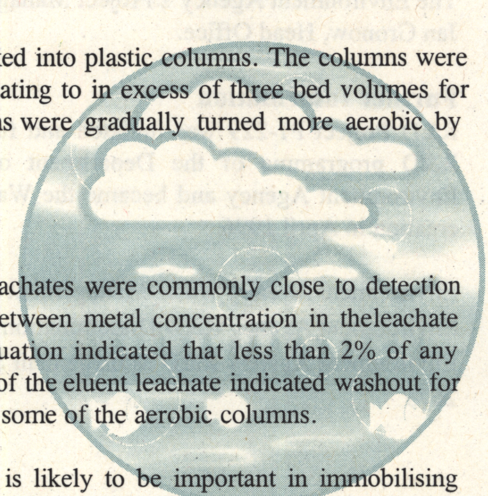
- laboratory experiments to investigate the retention of heavy metals in columns of household waste under different redox and chemical conditions; and
- computer modelling, undertaken by the contractor to determine the speciation and sorption of heavy metals in the landfill matrix.

For the laboratory experiments, three types of household waste were packed into plastic columns as follows:

- six columns containing previously well degraded, cadmium-enriched household waste;
- six columns containing waste from a co-disposal landfill; and
- six columns containing waste from a different area of the same landfill.

For the laboratory experiments, three types of household waste were packed into plastic columns. The columns were irrigated with synthetic rainwater over a period of 695 to 1035 days, equating to in excess of three bed volumes for all columns. After initial stabilisation, three of each set of six columns were gradually turned more aerobic by sparging moist air across the headspace.

Key Findings



In all columns, concentrations of cadmium, zinc and chromium in the leachates were commonly close to detection levels throughout the experiment and there was no consistent contrast between metal concentration in the leachate from anaerobic and predominately aerobic columns. Mass balance evaluation indicated that less than 2% of any metal was leached by the end of the experiment. In contrast, monitoring of the eluent leachate indicated washout for conservative species such as chloride, and enhanced sulphate release from some of the aerobic columns.

Computer modelling indicated that for cadmium, sulphide precipitation is likely to be important in immobilising cadmium in anaerobic landfill. Under aerobic conditions, predicted solubility limits for cadmium, with respect to a stable carbonate phase, are around an order of magnitude higher than measured leachate concentrations (generally below 0.01 mg/l), suggesting that other mechanisms are limiting cadmium release.

Research and Development
Technical Summary

R&D Technical Summary PS233

Solubility results for zinc also suggest that sulphide precipitation is likely to be an important retention mechanism in anaerobic landfill but that zinc carbonate will predominate under aerobic conditions. The predicted solubility limits for zinc carbonate are close to measured leachate concentrations (generally below 1 to 2 mg/l) suggesting that precipitation may be limiting zinc release.

Results for chromium indicated that, irrespective of redox conditions, in immature leachates solubility is enhanced due to organic complexation. In contrast, in mature leachates with low organic contents, chromium hydroxide solubility is predicted to be very low and is likely to contribute to the immobilisation of chromium in landfill.

It is likely that adsorption is a major component of metal retention in landfill and prevents the release of metals at concentrations below their solubility limits. Perhaps due to the highly heterogeneous nature of landfill material, very few attempts have been made to model sorption processes in landfill. A pilot study was carried out to translate and apply existing sorption models to landfill systems. The models provided reasonable results at low metal concentrations, however, they tended to under-predict the capability of landfill to immobilise high loadings of metals and therefore cannot currently be used to predict "safe" operational metal loading ratios.

Overall, the experimental studies indicate that cadmium, zinc and chromium at concentrations up to 100 $mg.kg^{-1}$ are immobilised long-term under aerobic and anaerobic conditions. Computer models indicate that the metals are precipitated mainly as sulphides under anaerobic conditions. In the longer term, assuming adequate buffering by carbonates, and stable pH, precipitates such as hydroxides and carbonates, have the potential to limit zinc and chromium concentrations in leachate to close to EC Drinking Water Standards, and for cadmium to around an order of magnitude higher than EC Drinking water standards. In aerobic landfill, it is likely that solubility processes will be supplemented by adsorption, particularly to newly formed iron and manganese oxyhydroxides, to limit metal release.

Contractor

WS Atkins Environment, Woodcote Grove, Ashley Road, Surrey, KT18 5B
Tel: 01372 726140 Fax: 01372 740055

Outputs

This Technical Summary relates to R&D Project P1-229 and the following output:

R&D Technical Report P249 (CWM 184/99)	*'Long term fate of metals in landfill: a combined experimental and modelling study'*

.Published March 2000. Released to Regions and Public Domain.

Project Manager

The Environment Agency's Project Manager for R&D Project P1-229 was:
Jan Gronow, Head Office.

Further Information

R&D Project P1-229 was initiated and funded by the Environment Agency. The Controlled Waste Management R&D programme of the Department of the Environment's Waste Technical Division transferred into the Environment Agency and became the Waste Regulation and Management Research Programme on the Agency's creation in April 1996.

Environment Agency Waste Management & Regulation Policy Group Tel: 01454 624071 Fax: 01454 624470
Environment Agency R&D Dissemination Centre (WRc) Tel: 01793 865000 Fax: 01793 514562
Environment Agency R&D Management Support Officer (Waste Programme) Tel: 0117 914 2783 Fax: 0117 914 2673

Long Term Fate of Metals in Landfill
A Combined Experimental and Modelling Study

R&D Technical Report P249

Long Term Fate of Metals in Landfill
A Combined Experimental and Modelling Study

R&D Technical Report P249

D Ross[1], C Harries[2], A Revans[1], C Cross[2] and P Nathanail[3]

Research Contractor:

[1] WS Atkins Environment
[2] Minton Treharne & Davies Limited
[3] Land Quality Management Limited

Further copies of this report are available from:
Environment Agency R&D Dissemination Centre, c/o
WRc, Frankland Road, Swindon, Wilts SN5 8YF

tel: 01793-865000 fax: 01793-514562 e-mail: publications@wrcplc.co.uk

Publishing Organisation:
Environment Agency
Rio House
Waterside Drive
Aztec West
Almondsbury
Bristol BS32 4UD

Tel: 01454 624400 Fax: 01454 624409

ISBN: 1 873160 83 6

ISBN 1 85705 327 3 CWM 184/99

Dissemination status
Internal: Released to Regions
External: Released to Public Domain

Statement of use
This report summarises the findings of combined experimental and computer modelling study investigating the long term fate of metals in landfill. The study provides an insight into the processes controlling metal mobility in landfills. The conclusions have implications for the definition of appropriate loadings for metals in household waste and are relevant to the debate regarding the long-term sustainability of landfill.

Research contractor
This document was produced under Contract EPG 1/7/46, R&D Project P1-229 by:

WS Atkins Environment
Woodcote Grove
Ashley Road
Surrey
KT18 5BW

Tel: 01372 726140 Fax: 01372 740055

Environment Agency Project Leader
The Environment Agency's Project Leader for R&D Project P1-229 was:
Dr Jan Gronow – Environment Agency, Head Office, Bristol

CONTENTS

Page

LIST OF FIGURES

LIST OF TABLES

ABBREVIATIONS

BMP	Biochemical Methane Potential
CAMR	Centre for Applied Microbiology Research
COD	Chemical Oxygen Demand
ECDWS	EC Drinking Water Standards
GC	Gas Chromatography
LQM	Land Quality Management at the University Of Nottingham
VFA	Volatile Fatty Acid
WMLR 1994	Waste Management Licensing Regulations (1994)
WMP26F	Draft Waste Management Paper 26F

EXECUTIVE SUMMARY

WS Atkins was contracted (in November 1995 under contract EPG 1/7/476), initially by the Department of the Environment and then by the Environment Agency for England and Wales to undertake research directed at addressing uncertainties regarding the long-term fate of heavy metals in landfill sites. A principal objective was to investigate the chemical stability of co-disposed metals under a range of conditions likely to be encountered at different phases of landfill stabilisation. This was to provide additional information on the stability of heavy metals under the more aerobic conditions that may prevail in mature, post-methanogenic landfills. The metals investigated were cadmium, chromium and zinc.

The project comprised two parallel, complementary components:

- laboratory experiments (carried out by sub-contractor Minton Treharne and Davies), to investigate the retention of heavy metals in columns of household waste under different redox and chemical conditions; and
- computer modelling to determine the speciation and sorption of heavy metals in the landfill matrix.

For the laboratory experiments, three types of household waste were packed into plastic columns as follows:

- six columns containing previously well degraded, cadmium-enriched household waste;
- six columns containing waste from a co-disposal landfill; and
- six columns containing waste from a different area of the same landfill.

The columns were irrigated with synthetic rainwater over a period of 695 to 1035 days, equating to in excess of three bed volumes for all columns. After initial stabilisation, three of each set of six columns were gradually turned more aerobic by sparging moist air across the headspace.

In all columns, concentrations of cadmium, zinc and chromium in the leachates were commonly close to detection levels throughout the experiment and there was no consistent contrast between metal concentration in the leachate from anaerobic and predominately aerobic columns. Mass balance evaluation indicated that less than 2% of any metal was leached by the end of the experiment. In contrast, monitoring of the eluent leachate indicated washout for conservative species such as chloride, and enhanced sulphate release from some of the aerobic columns.

Computer modelling indicated that for cadmium, sulphide precipitation is likely to be important in immobilising cadmium in anaerobic landfill. Under aerobic conditions, predicted solubility limits for cadmium, with respect to a stable carbonate phase, are around an order of magnitude higher than measured leachate concentrations (generally below 0.01 mg/l), suggesting that other mechanisms are limiting cadmium release.

Solubility results for zinc also suggest that sulphide precipitation is likely to be an important retention mechanism in anaerobic landfill but that zinc carbonate will predominate under aerobic conditions. The predicted solubility limits for zinc carbonate are close to measured leachate

concentrations (generally below 1 to 2 mg/l) suggesting that precipitation may be limiting zinc release.

Results for chromium indicated that, irrespective of redox conditions, in moderately mature leachates solubility is enhanced due to organic complexation. In contrast, in mature leachates with low organic contents, chromium hydroxide solubility is predicted to be very low and is likely to contribute to the immobilisation of chromium in landfill.

It is likely that adsorption is a major component of metal retention in landfill and prevents the release of metals at concentrations below their solubility limits. Perhaps due to the highly heterogeneous nature of landfill material, very few attempts have been made to model sorption processes in landfill. A pilot study was carried out to translate and apply existing sorption models to landfill systems. The models provided reasonable results at low metal concentrations, however, they tended to under-predict the capability of landfill to immobilise high loadings of metals and therefore cannot currently be used to predict "safe" operational metal loading ratios.

Overall, the experimental studies indicate that cadmium, zinc and chromium at concentrations up to 100 $mg.kg^{-1}$ are immobilised long-term under aerobic and anaerobic conditions. Computer models indicate that the metals are precipitated mainly as sulphides under anaerobic conditions. In the longer term, assuming adequate buffering by carbonates, and stable pH, precipitates such as hydroxides and carbonates, have the potential to limit zinc and chromium concentrations in leachate to close to EC Drinking Water Standards, and for cadmium to around an order of magnitude higher than EC Drinking water standards. In aerobic landfill, it is likely that solubility processes will be supplemented by adsorption, particularly to newly formed iron and manganese oxyhydroxides, to limit metal release.

KEY WORDS

Landfill, heavy metals, household waste, leachate.

1. INTRODUCTION

1.1 Background

Landfill sites containing domestic and/or commercial/industrial wastes may contain elevated levels of heavy metals. Initial reviews of the impact of landfill leachates on groundwater quality in the UK focused on leachate parameters such as ammonia, chloride and chemical oxygen demand (COD) (Blackley et al., 1995). More recently, more comprehensive studies of UK landfill leachates have been carried out that indicate that heavy metals are present at relatively low concentrations, both at sites receiving household waste and at sites receiving industrial waste (Robinson, 1995). In addition, laboratory studies have investigated the partition of metals in landfill based on physical and chemical abstraction techniques (Reynolds et al., 1993). Overall, both field monitoring data and laboratory studies indicate that the reducing conditions prevailing in anaerobic landfill result in heavy metals being substantially "locked" within the waste.

In order to assess the sustainability of the landfill option, it is important to investigate whether metals continue to be immobilised within landfill in the long term. In particular, as anaerobic degradation is completed, more aerobic conditions may become established, and it has been argued by some that this may lead to the release of heavy metals.

WS Atkins was contracted (in November 1995, under contract EPG 1/7/476) by the Wastes Technical Division of the Department of the Environment, now part of the Environment Agency for England and Wales, to undertake research directed at addressing uncertainties regarding the long-term fate of heavy metals in landfill sites.

At the time this project was commissioned, guidance in Draft Waste Management Paper 26F, for the practice of co-disposing industrial waste with domestic refuse was being re-assessed by the Department of the Environment in the context of the proposed European Commission (EC) Landfill Directive (DoE, 1992). One of the initial purposes of the project was therefore to provide additional information to support, or otherwise, the proposed loading limits for different metals and to address some of the uncertainties identified in a review of technical aspects of co-disposal by Knox (1989).

Since the project started the European Council has adopted a Common Position (EC, 1998) on the proposed Landfill Directive. If adopted by the UK (as seems likely) key articles of the Directive will limit the amount of biodegradable waste landfilled and ban the mixing of hazardous and non-hazardous waste. This will effectively end the practice of co-disposal.

The issues addressed in this project are still relevant, however. Firstly it is important to understand the likely long-term leaching behaviour of metals from existing co-disposal and other landfill sites in order to inform site monitoring, closure and completion strategies. Secondly, "non-hazardous waste" such as municipal waste contains significant quantities of heavy metals. This will continue to be landfilled, although with some form of pre-treatment, and a better understanding of the long term behaviour of the metals in this waste will help inform landfill design and management strategy.

In addition, this research is relevant to the control of ongoing waste disposal operations through the Waste Management Licensing Regulations 1994. In particular, Regulation 15 of WMLR 1994 implements the EC Groundwater Directive (EC 80/68/EEC). Draft guidance for the interpretation and application of Regulation 15 (EA, 1999) requires, amongst other things, that risk assessments are carried out for the potential for release to groundwater of List I and List II substances. Again, research reported here is relevant and some of the techniques and results could be used to aid in the definition, and identification of uncertainties in source terms for metals in landfill risk assessments.

1.2 Project objectives

The project objectives addressed the potential effects of a landfill site returning to an aerobic state and metal loadings in landfill. The key objectives at the outset of the project were to:

1. determine the chemical stability of co-disposed metals under a range of conditions likely to be encountered at different phases of landfill stabilisation, particularly during the later and final stages of stabilisation;

2. provide additional data on metal/waste loading ratios that may be safely disposed;

3. evaluate and discuss the results in the context of current UK guidelines for metal co-disposal (in draft Waste Management Paper 26F).

In recognition of the evolving regulatory context, the objectives were refocused during the course of the project, to ensure that the research was relevant to issues such as landfill sustainability and Regulation 15 of the WMLR 1994. Objectives 1 and 2 remained unchanged but Objective 3 was modified to include wider evaluation of metal stability in the context of the long term sustainability of landfill disposal of household waste.

1.3 Approach and methodology

The work programme comprised experimental and modelling components and was carried out in two phases. Phase 1 involved a review of the theoretical controls on metal mobility in landfill and the setting up of a first set of column experiments on metal rich waste. Phase 2 encompassed field sampling, and laboratory and modelling studies of metal mobility under hydrodynamic conditions leading to a statistical analysis and final assessment of long term metal mobility. The proposed programme was discussed with a Project Steering Committee at the outset of the project and reviewed after six months once pilot studies had been carried out.

The Project Steering Committee comprised the Agency's Project and Programme managers, representatives from the landfill industry, particular companies carrying out co-disposal, and representatives from the Centre for Applied Microbiology Research (CAMR), Porton Down who carried out the previous, related Department of the Environment contract.

As is often the case in research projects, it was necessary to review and adapt the detailed approach as the project progressed. This process took account of the Steering Committee comments. A number of modifications to the scheduled tasks were agreed with the Agency during the course of the project. The final approach is summarised below, with reference to specific tasks. Additional details of the approach are included in the experimental and modelling chapters.

Task 1 - Prioritise controls on metal mobility in late stage waste and leachate

This task reviewed research on landfill maturation and on metal mobility in the environment. The review informed the detailed design of the experimental and modelling studies. Collated information was presented in an Interim Report.

Task 2 - Phase 1 mature waste sampling

Mature waste for the pilot column experiments was obtained from CAMR. This waste was well degraded and enriched in heavy metals.

Task 3 - Pilot study of metal release under accelerated aerobic return

The purpose of the pilot study was to investigate whether, under accelerated conditions, any evidence existed for changes in metal mobility in landfill waste when aerobic conditions were established.

Metal-rich waste obtained in Task 2 was sampled and characterised to assess its degradation. The waste was then homogenised and transferred to experimental columns in the laboratory with minimal air exposure during transfer. The columns were leached using synthetic rainwater and, once landfill gas production was minimal, aerobic conditions were introduced to half of the columns. Leachate emerging at the column base was sampled and analysed for selected heavy metals and other key parameters.

The pilot study was used to optimise the design of Phase 2 column experiments, but because useful results continued to be generated after the initial phase, the time scale was extended from 6 months to 34 months. Thus the pilot study continued in parallel with Phase 2.

An Interim Report was produced six months into the project to draw together the results of the theoretical review and pilot study and to finalise the forward programme through consultation with the Steering Committee.

Task 4 - Phase 2 field waste sampling

The Phase 1 study used household waste enriched with metals in the laboratory. Phase 2 used household waste that has been co-disposed with industrial wastes, as this waste should be representative of metal loaded waste in the field. Samples of waste were obtained from boreholes in Pitsea landfill site, Essex. A total of 10 samples were taken from boreholes in different areas of the site known to have received either acidic or alkaline wastes added in trenches in the placed household waste. The industrial waste stream at this site contains a considerable proportion of metal bearing liquid wastes. After laboratory analysis of metal loadings, two samples were selected for further column studies.

Task 5 - Phase 2 metal release experiments

Based on the pilot study results, additional column experiments were carried out using the two new waste types selected from the Pitsea landfill sampling. To permit sufficient bed volumes of rainfall to leach the columns, the columns were shortened from 50 cm to 30 cm. Six new columns were set up for each of the two new waste types and once the columns had stabilised, half the columns for each waste type were gradually turned more aerobic. To ensure that results for different waste types, and for aerobic versus anaerobic conditions, could be compared, synthetic rainwater was used as the leaching solution throughout. Monitoring was carried out for 23 months, by which time three to five bed volumes had passed through he columns.

Task 6 - Evaluation of column experiments using models

Modelling techniques developed in research on metal mobility in soils and aquifers were applied to aid the interpretation of the experimental studies and to address the broader objectives of the project. The geochemical models and databases utilised in this project are all well established, are in the public domain, and have been widely used in studies of metals in groundwater and soil.

The evaluation of the column experiments addressed a number of fundamental questions including the following.

1. What are the dominant aqueous metal complexes (e.g. organic complexes, chlorides, carbonates, hydroxides) likely to be present in the column leachates?
2. What are the most insoluble metal precipitates likely to be present in the columns and are these precipitates likely to limit metal concentrations in leachate?
3. Is sorption important in immobilising metals, and if so, can this process be understood and predicted?

Task 7 - Statistical evaluation

In order to facilitate statistical comparison of the experimental results, all experiments were carried out in triplicate. Metal release trends from the different waste types and differences between the anaerobic and aerobic columns were evaluated using a statistical approach.

Task 8 - Implications for waste management guidance

The original objective of this project was to provide further data to support, or otherwise, the UK guidelines for metal loadings in co-disposal in Draft Waste Management Paper 26F. The implications of the results on broader issues, such as landfill sustainability and Regulation 15 of the WMLR 1994 are also discussed.

Task 9 - Project management and reporting

The project was managed by WS Atkins. Regular progress reports were submitted during the course of the project. An Interim Report was completed six months into the project and consultation was held with the Steering Committee at this stage to finalise the forward programme.

Contract Variation

A Contract Variation was agreed to allow the column leaching experiments to continue for a further 300 days. The objective was to carry out the following additional tasks.

1. The monitoring and analytical programme for the Pitsea waste columns was extended for a further 300 days. SO_4^{2-} was added to the monitoring suite to provide information on the possible leaching of metal sulphates as the columns turned more aerobic.

2. Batch experiments were set up to investigate in more detail uptake of metals by waste. Cadmium, chromium and zinc were added at three different loadings related to WMP 26F; each metal was added individually and in a 'cocktail' with the other two. Metal uptake was monitored by analysing leachate samples that were obtained via a dip tube, without opening the flasks.

3. The modelling programme was extended to include an evaluation of the batch experiments and an evaluation of chloride washout trends for the columns.

1.4 Report structure

This final report summarises the methods and results of the experimental and modelling programmes and discusses the significance and implications of the results. Experimental aspects of the study are reported in Chapter 2, which contains details of the overall approach, techniques and results. Chapter 3 summarises the modelling programme. Chapter 4 assesses the significance of the results and discusses the implications of the study as a whole in the context of UK waste management guidance. Conclusions are provided in Chapter 5.

Additional details of the experimental programme and modelling programme are included in Appendices A and B respectively.

2. EXPERIMENTAL PROGRAMME

2.1 Introduction

The experimental programme of this contract has studied the uptake and re-release of heavy metals from landfilled wastes with particular emphasis on the effect of changes in redox conditions within the waste on mobility and leaching of metals. In particular, the heavy metals cadmium, zinc, chromium, iron, nickel and lead often found in co-disposed industrial wastes have been the focus of attention. The objective has been to study the stability of heavy metals arising in waste either naturally in components of the waste stream or artificially as a result of co-disposal of industrial wastes. The retention of these metals within the waste mass has been studied while the waste has been subject to leaching and the conversion to aerobic conditions such as might be expected to occur late in the life of a landfill site. The major question at the start of the experiment was whether changes in the redox conditions within the waste would initiate transformations such as sulphide and ammonia oxidation, pH falls and mobilisation of metals.

There were three main elements of practical experimentation in the contract:

- the leaching of metals from household waste, artificially enriched with cadmium, under both anaerobic and aerobic conditions;
- the leaching of heavy metals and other species from household waste, under both anaerobic and aerobic conditions, after enrichment with heavy metals as a result of co-disposal in real landfill conditions; and
- a study of the uptake and re-release of heavy metals from leachate by household waste in batch experiments with anaerobic and aerobic phases.

The first two elements of the experimental work were long term leaching studies using columns of waste leached with a simulated rainfall from which the emergent leachate was retained for analysis. The columns were designed such that they could be operated as anaerobic gas tight vessels or the headspaces purged with air to initiate aerobic conditions as required. These two experiments lasted a total of 1035 and 695 days (Table 2.1.1)

Table 2.1.1 Summary of column experiment programme

Waste type	Condition	Months from start of column experiment					
		6	12	18	24	30	36
Cadmium-loaded municipal waste	Anaerobic	■	■	■	■	■	■
	Aerobic	▨	▨	▨	▨	▨	▨
Metal-rich co-disposal waste	Anaerobic			■	■	■	■
	Aerobic				▨	▨	▨

The third element of the experimental work, the batch experiments, involved studying the uptake of heavy metals from solution by samples of old household waste and subsequent re-release or retention of these metals during a period of aerobic conditions. These batch experiments were short term lasting a few weeks only.

Appendix A contains the detailed experimental procedures and full results obtained during this experimental work but in the following sections we give experimental outlines and summary results only.

2.2 Experimental work

2.2.1 Experiment 1 - Leaching of cadmium amended household waste(CAMR waste columns)

Column design, establishment and operation

For this experiment six experimental columns were custom fabricated out of clear perspex tubing, as shown in Figure 2.2.1. These were 500 mm tall x 100 mm diameter. The design allowed provision for uniform addition of liquids to the top, release and sampling of gas leaving the columns, basal drainage and removal of leachate. For some columns of waste, into which air was subsequently introduced, this was added via the rainwater addition port and exhausted through the gas outlet port. Shortly after establishing the experiment, the column pipework was modified such that a pipe connected the basal drain pipe to the headspace. This allowed gas escape from the column base and encouraged leachate drainage to the base from where it could be removed. Prior to this, gas accumulation in the void beneath the basal drainage geotextile seemed to retard liquid drainage from the waste.

Six of the columns were filled with refuse from some completed experiments undertaken on another Department of Environment study, (DoE project ref. EPG 1/7/08) at the Centre for Applied Microbiological Research (CAMR), Porton Down. This waste was understood to be substantially decomposed and had been deliberately loaded with cadmium, as cadmium nitrate, as part of a study of microbial inhibition by metals.

The cadmium loaded waste was obtained from CAMR in a number of experimental pots which had received different cadmium loadings. The material was amalgamated and mixed thoroughly to give a uniform cadmium rich waste. Samples were retained for analysis and the remainder used to fill the six columns. As the quantity of material was barely sufficient, the gravel/waste mix recovered from the basal drainage layer of the CAMR pots was used to fill the lower 100 mm of each of the new columns above the geotextile drainage layer. The total waste filled depth in the columns was 440 mm (100 mm gravel/waste, 340 mm waste). The waste was transferred to the six columns under a stream of 70 % nitrogen : 30 % carbon dioxide to minimise air exposure and the column headspaces flushed out with this gas mix prior to closure of the tops. They were then left to re-establish anaerobic conditions. Columns were wrapped in aluminium foil to minimise any photosynthetic bacterial activity during the experiment. Columns were maintained at 30 °C in a constant temperature room throughout the experiment.

After closure the cumulative gas production was recorded on a daily basis using a Triton P181 gas meter connected to the gas outlet port of each column. This gave a measure of the methanogenic activity of the waste in the columns. Occasional analysis of the headspace gas quality was carried out by gas chromatography (GC). Gas flow from the columns passed through a trap containing 10 g/l zinc acetate solution to scrub hydrogen sulphide which has a deleterious effect on the gas meters.

The retained sub-samples of the waste were analysed for water content, selected heavy metals and biochemical methane potential (BMP). The cadmium added during the CAMR experiments had been substantially retained within the waste mass. Analysis of the combined waste from the CAMR experimental pots showed a mean cadmium content of 102 mg/kg dry weight (53 mg/kg wet weight).

After closure, the columns showed a rapid resumption of methanogenic activity with headspace gas composition reaching 52-58% methane after a few days and gas production reaching a specific rate of 11-23 m^3 landfill gas/tonne wet weight.year. These are relatively high rates of methanogenesis by landfill standards given the history of the waste and the enrichment with cadmium.

During the first 129 day anaerobic period, gas production from the waste was monitored and confirmed anaerobic methanogenic decomposition processes were established. After 129 days, three of the six columns were 'turned aerobic' by passage of a slow stream of air through the headspace of the columns. All other conditions were unaltered. Monitoring of air flow and composition through the aerobic columns and gas production from the anaerobic columns was continued thereafter.

The three 'anaerobic' columns acted as controls for the three 'aerobic' ones and the period from 0-129 days acted as an anaerobic control period for specific columns.

During the aerobic period, the waste in the three aerobic columns (nos. 1, 3 and 6) was observed to gradually turn from a black colour to an ochre colour, the change progressing from the top downwards. The rate of change differed in the three columns and black inclusions lasted for variable periods within the otherwise ochreous waste. The colour change is believed to be due principally to the conversion of ferrous iron to ferric forms. This is a good indication of the gradual conversion from anaerobic, reducing conditions to more aerobic, oxidising conditions.

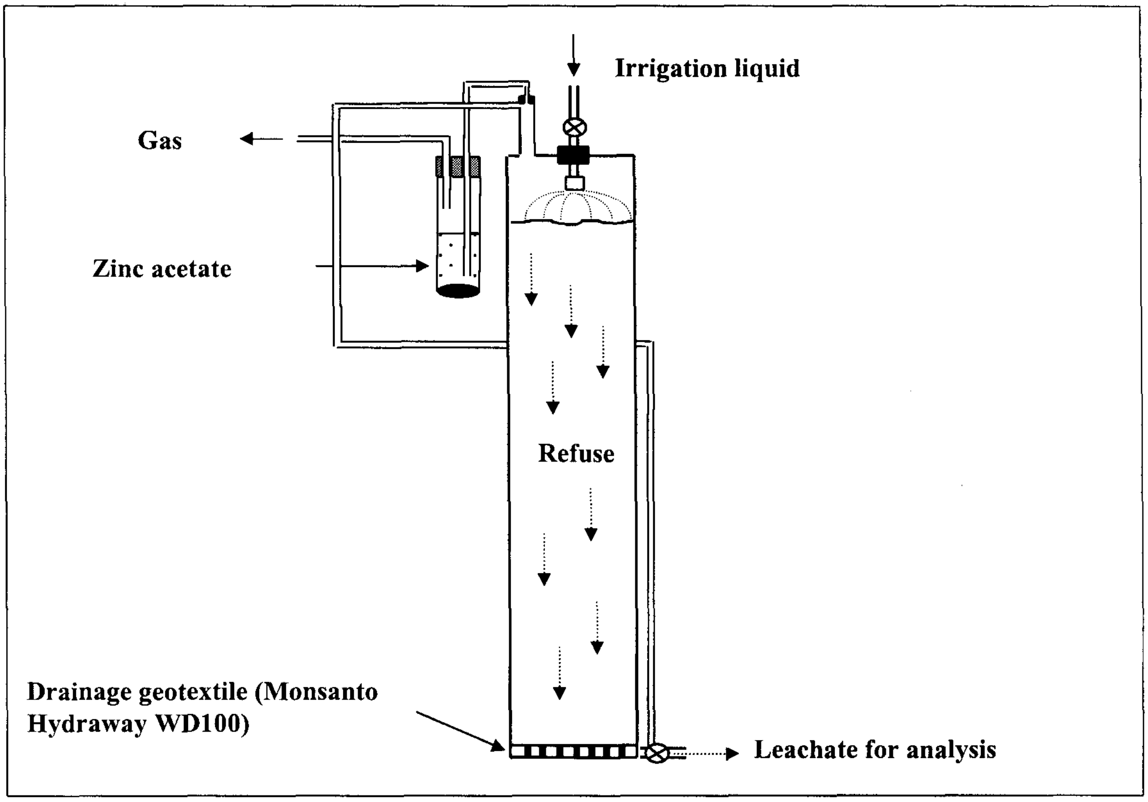


Figure 2.2.1 Schematic showing set up of column experiments

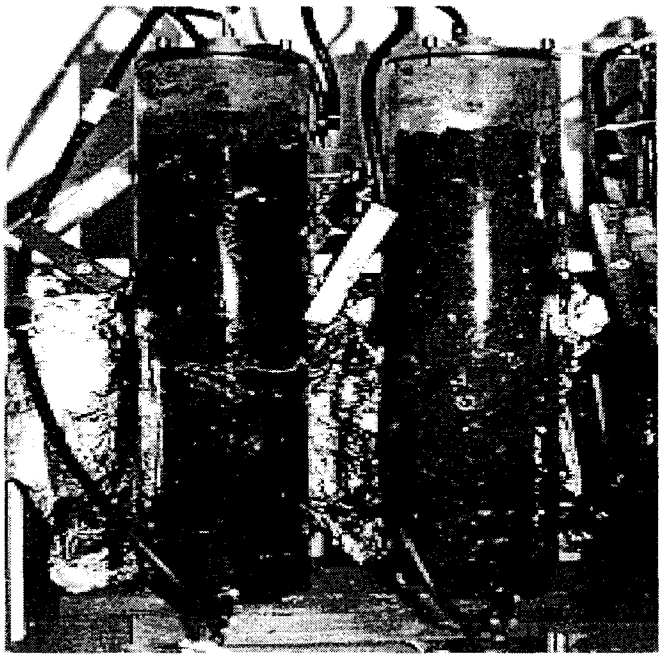


Figure 2.2.2 Photograph of two waste columns showing differing penetration of aerobic conditions (indicated by brown colouration)

Rain water addition

A synthetic rain water was used to irrigate the columns to simulate a typical annual rainfall. This was added weekly as a single slug of 50 ml/week. The artificial rain water was made to a recipe obtained from National Power Research and Engineering to have a similar composition to a 'dirty' UK rain from a typical location affected by moderate airborne pollution. Rain water was introduced to the columns via a clamped tube through the column top-plates without compromising the anaerobic status of the refuse and headspace. These tubes had luer fittings to enable syringes to be connected for dispensing rain water to the columns. Irrigation jets attached to the end of these tubes assisted with dispersal of rain water over the entire surface of the waste. Rain addition was carried out weekly after removal of drainable leachate from the base of the columns. Rain water addition was constant throughout the experiment, during both anaerobic and aerobic phases, except in some cases where poor drainage within the columns caused ponding on the waste surface. In such cases, rain water addition had to be suspended for periods to ensure sufficient space in the column headspaces.

Records of volumes of added rain and removed leachate were kept and these show when the waste was accumulating water, or losing it by evaporation in some cases after the commencement of aeration. These are shown graphically in Appendix A2. Records of the quantities of ponded liquid were also made upon final destruction of the columns.

Watering was continued, as far as possible, at the original rate until termination of the experiment after 1035 days.

Leachate removal and handling

Removal of drained leachate from the column bases was generally achieved by simple drainage into centrifuge tubes whilst purging with a 70:30 nitrogen:carbon dioxide gas mix. Leachates were weighed to record the volume and analysed for pH and Eh under a headspace of this gas mix. Samples were centrifuged at 5000g for 15 minutes in sealed tubes with the same headspace and then sub-samples of supernatant were transferred immediately into nitric acid for subsequent analysis of heavy metals. This procedure was employed to ensure that analysis was for dissolved metal concentrations and samples did not include fine particulates from the waste. In practice little centrifugable solid matter was apparent after the first few weeks of leachate collection. After collection, samples were maintained under the N_2:CO_2 gas mix in order to minimise oxidation and possible precipitation of metals, and stored at 4°C prior to analysis.

For much of the time, space beneath the geotextile layer in the column bases allowed accumulation of liquid and the leachate samples could be drained readily from the columns. However, some columns showed poor drainage characteristics at times and leachate was forcibly sucked by syringe from the drain pipes in order to obtain samples and encourage movement of liquid through the columns.

Leachate samples were analysed for pH, electrical conductivity, Eh, ammoniacal-N, chloride, and selected heavy metals on a regular basis. Volatile fatty acids were also analysed near the start of the experiment until these declined to undetectable concentrations. Total sulphur was analysed on selected samples of acidified leachate as an approximate measure of sulphate-S. Occasional analysis of other inorganic ions was also undertaken.

Air sparging

In order to initiate a progressive transformation to aerobic conditions in selected columns (columns 1,3 and 6) air sparging was initiated after a period of monitoring all columns under anaerobic conditions. This involved the introduction of a slow stream of air through the column headspaces.

Air flows through the column headspace could not be controlled accurately as this was regulated by simple clamping of delivery tubing. In practice, air flow rates fluctuated but were adjusted to give a similar rate as adjudged by the rate of bubbling in the zinc acetate traps on the exhaust line leaving the columns. Air flow rates were recorded to be an average of 183 litres/day (range 98-261 litres/day) which gives a corresponding turnover time for the column headspaces of about 15 turnovers/hour. Analysis of gas samples from the column headspaces indicated that the gas composition in the aerated columns was close to that of air.

After a period of air sparging it became apparent that drainable leachate volumes were declining from the aerobic columns despite a constant rain water addition regime. This is evident as a divergence of the lines of cumulative rain addition and leachate removal contained on the graphs in Appendix A 2.3. It was suspected that evaporation of water from the waste surface and resultant water loss in the air stream was occurring. This theory was reinforced by the slower decline in chloride concentration observed in the aerobic columns than the anaerobic columns over this period indicating reduced washout of solutes. In order to remedy the problem steps were taken to humidify the air prior to introduction into the column headspaces. This was achieved by passage of the air through three Drechsel bottles of water in series each equipped with a sintered glass sparger to achieve fine bubbling of the air flow through the water. This modification resulted in a gradual resumption of normal drainable leachate volumes.

Gas samples were also analysed from the base of the columns on day 684 and confirmed methane present in the column bases of the anaerobic columns and high oxygen levels in the aerated columns indicating good penetration of the air to the column bases. Methane was only detected in the base of column 1, the slowest of the aerobic columns to turn aerobic.

Lithium bromide tracer study

In order to study the hydrodynamics of the leachate movement through the waste in the columns, a tracer study was undertaken with two columns (number 5, anaerobic and number 6, 'aerobic'). Lithium bromide was included in one of the regular additions of synthetic rainwater to the columns at day 796 of the experiment. Monitoring of both lithium and bromide in the emergent leachate drained from the columns was carried out from this date until the end of the experiment using ICP and ion exchange chromatography techniques respectively. Lithium was also analysed in the refuse solids at the end of the experiment.

Column dismantling and destructive analysis

At day 888 of the experiment, watering with the synthetic rain water was ceased in columns 1, 2, 3 and 4 but continued in 5 and 6 which had been the subject of the LiBr tracer study. Drainage of all columns continued until day 1033 but they had not drained completely by this time and in fact columns 2 and 4 still had ponded water on top at the end. Columns 5 and 6 were watered with 'rain' right up to day 1033. At the end of the 1035 day duration of the experiment, the columns were opened and the contents removed for final analysis. The waste was removed as three discrete depth samples from each column, designated top, middle and bottom, each representing an equal depth range of the column contents. These were then dried for final analysis and water content determination. In addition, columns were washed with water to recover adhering solids and then acid rinsed with 1 molar nitric acid. These water and acid washings were retained pending analysis of the solids in case questions regarding sorption of metals to the column walls arose.

Analysis

Methods for analysis of solid waste, leachate and gas samples are in Appendix A1.

2.2.2 Experiment 2 - Leaching of landfilled co-disposed waste (Pitsea waste columns)

Samples of waste were obtained by drilling boreholes in Pitsea landfill site, Essex. A total of 10 samples were taken from boreholes in different areas of the site known to have received either acidic or alkaline wastes added in trenches in the placed household waste. The industrial waste stream at the site contains a considerable proportion of metal bearing liquid wastes. After laboratory analysis of these waste samples, two samples were selected for further column studies. These were selected on the basis of high metal contents and also different pH values indicating the different, acid or alkaline, waste disposal areas of the landfill. Columns designated numbers 7 to 12 received alkaline area waste and columns 13 to 18 received acid area waste. Deionised water was added to the acid area waste prior to putting it in the columns (nos.13-18) to bring it to approximately 60% water content to avoid a lengthy waste wetting period prior to production of emergent leachate.

Establishment and operation of the columns was broadly as described in section 2.2.1 with an anaerobic period of 283 days after column filling followed by an aerobic period until the end of the experiment at day 965. This was brought about by passage of an air stream through the column headspace. Due to leaks arising from methods of construction of the columns, the experiment was interrupted after 83 days, the waste removed to individual sealed containers and the waste replaced 45 days later after modifications to the column design. This interruption is evident as the plateau in the cumulative gas production graphs for this experiment. Apart from this interruption, the columns remained sealed, with waste in place, throughout the experiment. After 283 days, half of the columns i.e. three of each waste type, were sparged with air as described in section 2.2.1 by passage of a slow stream of air through the column headspaces to initiate aerobic conditions.

Watering of columns with artificial rain water and sampling of leachate and air sparging was carried out as described in 2.2.1.

Column dimensions were shortened compared to Experiment 1 to reduce leachate turnover times. The poor drainage characteristics of the waste meant that modifications to the leachate drainage method were needed after 245 days. Permanent leachate traps were fitted to the base of the columns to allow free drainage of leachate into the glass receivers for later removal.

2.2.3 Experiment 3 - Uptake and re-release of heavy metals in leachate exposed to household waste(Flask experiments)

A series of short term flask experiments were established to look at the uptake of metals from artificial leachate solutions by aged methanogenic household waste. These experiments were initially in sealed anoxic flasks which, after a period of incubation were then bubbled with a slow stream of air to create aerobic conditions. Metal concentrations in solution were studied by repeated sampling of leachate during the anoxic period and after a period of aeration. Flasks were maintained under sealed anoxic conditions for a month during which approximately weekly samples of leachate were recovered for analysis. After this, slow aeration of all flasks commenced for two weeks and a final leachate sample was taken at the end of this period.

The waste used for the experiment was anaerobically degraded wet pulverised household waste obtained from a landfill site in Buckinghamshire. A large amount of this material had been used for another DoE/EA contract (EPG 1/7/66), as a source of methanogenic waste. Methanogenic conditions had been initiated in this waste by the addition of anaerobically digested sewage sludge and leachate recirculation. This waste had been gassing in an experimental lysimeter for a considerable period and was thought to be substantially degraded. Incubation of sub-samples revealed a very low rate of methane production. This was an essential condition as the batch culture flasks remained completely sealed until the start of the aerated phase. The expected gas production from the 200g wet weight of waste in each batch culture was about 2 ml biogas/day so there was no risk of hazardous gas pressures.

One litre of a synthetic leachate, designed to mimic leachate from an old methanogenic landfill, was added to each flask after addition of the 200g of waste. The leachate recipe was created to mimic the ionic concentrations determined for Cell 3 of Compton Bassett landfill site, an example of an old methanogenic landfill as reported in Robinson (1995). The composition of the synthetic leachate is detailed in Appendix A1.

Leachate samples were obtained without opening the flasks, by sucking them up a dip tube extending through the top bungs into the leachate/waste suspension.

Leachate samples were centrifuged and analysed as described in Section 2.2.1 and Appendix A1.

Aeration was carried out by passage of a slow stream of air through the dip tube immersed in the liquid and released through a second port in the bung closure. During the period of aeration there was a notable loss of liquid volume from the flasks due to evaporation. This may have been as much as 50% in some cases. At the end of the aeration period, flask contents were made up to the original volume with deionised water, mixed and final samples taken.

Batch experiments were set up to give different additions of heavy metals relative to the waste solids present in the flasks. All permutations were set up in triplicate, replicates A, B and C. Each metal was used individually and in a 'cocktail' with the other two. Cadmium, chromium and zinc were the three metals studied. Metals were added as chloride salts to the synthetic leachate prior to dispensing this into the flasks containing the waste. Flasks were pre-gassed with 70:30 nitrogen : carbon dioxide gas mix with the waste in place. Then the metal amended or control (no added metals) leachates were added to each flask, the flasks swirled to mix the contents and the headspace further gassed out with the same gas mix. Leachates were prepared under a stream of the same gas mix and sealed prior to dispensing to the flasks.

Metal concentrations used were based on the guideline levels for heavy metal co-disposal to landfill, contained in Draft Waste Management Paper 26F. These guide levels give limits for the quantities of each metal that may be accepted at a landfill site in the hazardous waste stream relative to the amount of household waste being received at the site. Guideline levels are defined in g metal/tonne household waste This is based on tonnes wet weight of received household waste.

In order to standardise the metal addition rate used in these batch experiments with the WMP26F loading rate guidelines, the guideline concentrations were converted from g/tonne wet weight to g/tonne dry weight on the basis that the 'as received' water content of waste arriving at a landfill would be 30% by weight. The WMP 26F guideline levels for Cd, Cr and Zn are 10, 100 and 100 g/tonne wet weight respectively for these metals which equates to 14, 143 and 143 g/tonne dry weight when recalculated on this basis.

The batch tests were set up to give equivalent metal loadings on a dry weight basis to the guideline levels or multiples of these levels. The water content of the experimental waste was determined for individual batches of waste used for each group of tests. Slight differences were found between the water content of waste in the batches of waste used for each group of flasks set up at a time. This varied between 55.7 and 64.2%. Therefore, although the metal loading was standardised on the dry weight of waste present in each flask the amount of metal added per flask for a given loading varied slightly between batches. This is because a fixed 200g wet weight of waste and 1 litre of leachate was used in each flask.

Table 2.2.1 Summary of flask experiment programme

	Metal loadings as a function of waste mass (headings = nominal loadings, numbers = actual loadings used {mg/kg dry weight})			
Solution	0.1 x WMP26F	1 x WMP26F	10 x WMP26F	100 x WMP26F
Cd-loaded leachate		14	143	
Cr-loaded leachate	14	143		
Zn-loaded leachate	14	143		
Cd+Cr+Zn loaded leachate -Cd	1.4	14		1429
-Cr	14	143		14286
-Zn	14	143		14286

2.3 Summary of results

The full tabulated and graphically presented results are contained in Appendix A2 and discussion and statistical evaluation of results in section 4.2 but the main experimental observations are described below.

2.3.1 Experiment 1 - CAMR waste columns

Waste composition

Analysis of the waste used to pack the columns was principally for selected heavy metals and water content. The results obtained for the principal metals of interest are shown in Table 2.3.1 in comparison with the guideline loading rates defined in draft Waste Management paper 26F.

Table 2.3.1 Summary of metal concentrations (in mg/kg wet waste) in the CAMR cadmium amended waste in comparison with WMP26F guidelines

	CAMR Cd amended waste	WMP26F loading rate guidelines
Cd	53	10
Zn	470	100
Cr	123	100
Pb	285	100
Ni	42	100

Anaerobic/aerobic transformations

The results indicate a successful progressive transformation of conditions within three of the columns from anaerobic conditions to aerobic conditions after the start of air sparging in the 'aerobic' columns (Nos. 1, 3 and 6). Although the Eh analysis of the emergent leachates were subject to considerable variation and in general were difficult to interpret, the analysis of headspace and column base gas samples indicated biogas (50-60% methane, balance carbon dioxide) in the 'anaerobic' columns and air (20+% oxygen) in the 'aerobic' columns. The waste colour became progressively more ochreous, from the top down, in the 'aerobic' columns but remained black in the 'anaerobic' ones. The gas composition and waste colour change observations were evidence of the progressive transformation of redox conditions within the waste. Upon dismantling the columns and removal of the waste solids for analysis, it was apparent that the appearance of the waste from the outside was representative of its condition right through the waste mass. i.e. where the waste appeared ochreous from the outside it was found to be ochreous through the full depth of waste at that level in the column and likewise where the waste appeared black. This suggests that the colour change was not simply an edge effect caused by preferential air or water flow down the sides of the column.

The three aerobic columns appeared to change state at different rates, apparently affected by the drainage characteristics of the waste in each column. Notably, column 1 which showed poorest drainage, to the extent of some ponding on the waste surface, was slowest to change colour and retained some grey-black zones at the base of the column, within the otherwise ochreous waste, at the end of the experiment. Columns 3 and 6 turned completely ochreous before the end of the experiment.

The waste in the anaerobic, control columns remained predominantly black with perhaps only a superficial ochreous change in the top 1 mm of waste in one column. This may have resulted from oxygen introduced with the rain coupled with the advanced state of decomposition of the waste, particularly by the end of the experiment. Biochemical methane potential (BMP) analyses of the waste at the start of the experiment indicated that the waste at this time was already highly decomposed (BMP = 2 m^3 CH_4/tonne dry weight).

The appearance and evidence of ponding at the end of the experiment was recorded and is shown in Table 2.3.2.

The redox measurements (Appendix A.2.3), which began on day 516, did not show the values expected in the emergent leachates. Also differences between the aerobic and anaerobic columns were not clear cut. It was found that the interval between leachate sampling and redox measurement was important. After day 782, redox measurements were taken as soon as practically possible after collection of the individual column leachates. Previously all leachate samples had been recovered before Eh measurements were made. After this transition to 'immediate' Eh measurement, they appeared to show some difference between the aerobic and anaerobic columns and values were generally more negative but prior to this, results seemed erratic and indistinguishable. After the change in methodology, Eh values in leachates from columns 3 and 6, the first to turn 'aerobic' were notably higher than the other columns. It seems that the Eh measurements were affected by sample handling procedures possibly by interaction with the nitrogen:carbon dioxide gas mix to which they were exposed after removal from the columns. For future experiments of a similar nature we would advise in-situ redox measurements.

Despite the problems discussed above, we assume that the columns were predominately anaerobic or aerobic as described by other indicators (such as colour, ammonium concentration and gas composition at the column bases).

Table 2.3.2 Final appearance of CAMR waste columns prior to destruction

Column No.	Column treatment	Final coloration	Leachate ponding
1	aerobic	Waste all ochreous but for a few black patches near base.	None
2	anaerobic	Waste all black	2 cm ponded liquid
3	aerobic	Waste all ochreous, some grey patches at base.	None
4	anaerobic	Waste all black	1 cm ponded liquid
5	anaerobic	Waste all black	None
6	aerobic	Waste all ochreous, some grey patches at base.	None

Gas production

Gas production (Appendix A.2.1) from all columns showed a high initial rate, possibly stimulated by the mixing of waste prior to introduction into the columns and the liquid addition thereafter. This rate declined steadily over the duration of the experiment and had virtually ceased by the end, presumably due to depletion of the organic content of the waste. Records of gas production from the aerobic columns ended after day 129 when aeration started and gas meters were used to quantify the air flows.

By day 200 of the experiment gas production rates had declined considerably and low daily gas volumes (typically <20 ml/day) meant that identification of problems with gas metering devices was difficult. Data after this period may reflect some losses of data due to unspecified periods of gas meter failure. However it is clear that the gas production had declined to extremely low rates by the end of the experiment.

Leachate composition

Leachate composition (Appendix A.2.3) showed a combination of changes through the course of the experiment believed to have resulted from the effects of dilution, washout, sorption/desorption and microbial transformations.

Dissolved heavy metal concentrations in the leachate (Appendix A.2.3) were in many cases close to the detection limits of the analytical methods employed. Changes over time and differences between columns were more apparent amongst the non-metal solutes.

Chloride, generally considered a particularly unreactive ion, showed a decline attributable to washout (Appendix A.2.2). The reduced leaching rate resulting from drying out of the aerobic columns resulted in a slower decline in both electrical conductivity and chloride concentrations in the leachate from these columns after approximately day 250 of the experiment.

The ammoniacal nitrogen (Appendix A.2.3) showed primarily simple washout under anaerobic conditions. However there was a rapid decline in the aerobic columns presumably as a result of bacterial conversion to nitrite and nitrate. All columns showed a gradual decline in NH_3N due to washout but the aerobic columns showed a much more sudden decline following the penetration of aerobic conditions through the waste mass. It was notable that the major reduction in ammoniacal-N concentrations in the leachate from the aerobic columns did not occur until the redox front (as adjudged by the ochreous/black colour interface) had reached the base of the columns.

pH values (Appendix A.2.3) remained predominantly in the range 6.5-7.5. No sustained change in leachate pH was observed through the course of the experiment but for a period between days 275 and 500 the average pH of leachates from the aerobic columns was consistently lower than that from the anaerobic columns. This period was also the period of greatest sulphate release, (as adjudged from total S in acidified leachates, from the aerobic columns (Appendix A.2.10). This suggests that differences in pH may have been caused by the oxidation of sulphides in the aerobic conditions following the transformation to aerobic conditions. However other such reactions would also have been occurring at the same time, including the oxidation of ammoniacal-N proposed above.

It is notable that in columns 3 and 6 leachate sulphate concentrations seem to have peaked and declined during the course of the experiment, yet the depression of pH has only been slight. It appears that the pH buffering capacity of the waste remains sufficient to protect it from severe pH destabilisation during sulphide oxidation for example. However this might not be the case if leaching by a greater number of bed volumes of water occurred prior to the change in redox conditions. This is because, under anaerobic conditions, washout of some of the soluble components of the waste such as ammoniacal nitrogen will occur but sulphides present as metal precipitates will probably be mainly retained in the waste mass. Extended leaching during the anaerobic phase may result in loss of potential pH buffering species such that subsequent development of aerobic conditions after extended leaching could result in a more dramatic pH drop than observed in this study. A greater understanding of buffering properties of waste and the solubility of different species under different conditions is needed in order to predict potential pH effects associated with leaching and redox changes in the waste.

Initial and final waste analysis

The results of the analysis of the waste solids from the Experiment 1 - CAMR waste columns are shown in Appendix A.2.4. along with tables showing the mass balance calculations for the heavy metals. These show the weight of each metal present at the end of the experiment compared to that present at the start. Examination of these figures avoids the confusion possible when comparing metal concentrations. Waste weight per column and water content are different at start and finish due to weight losses through gas formation or leached solutes or changes in waste water content.

In some cases anomalies exist where there is an apparent increase in total weight of metals and this can only be explained by analytical errors. The high levels of iron in the waste presented problems for analysis of the iron itself and some of the other metals.

Another error has arisen from the use of waste containing some gravel in the bottom of the CAMR waste columns. This was necessitated by the shortage of material to fill the columns but this material was not the subject of an independent water content determination. A single water content value was used for all the waste put in the columns and this figure was based on the gravel-free CAMR waste. The inclusion of some gravel in the waste forming the 'bottom' sample has meant that the initial water content of the waste in the column bottoms was probably lower than that of the majority of the waste which did not contain any gravel. This is believed to have lead to the apparent slight increase in dry weight of material in the columns between the start and finish of the experiment. This resulting from an underestimate of the initial dry weight of material present. It will also have introduced an error into the heavy metal balance calculations as the gravel will probably have diluted the cadmium in the bottom of the column. The effect on the other metals is uncertain without knowledge of the gravel composition.

Lithium bromide tracer study

The addition of lithium bromide to the artificial rain added to columns 5 and 6 at day 796 was monitored by analysis of emergent leachate and inclusion of lithium in the final suite of analyses undertaken during the final destructive analysis of the waste solids. The actual amount of lithium bromide added to the columns was small so that the pH of the added rain was not severely lowered. The actual amount of lithium and bromide added to the two columns was 1.4 mg and 16.1 mg respectively.

Against the background concentration of lithium in the waste, as demonstrated by the final analysis of waste solids, the lithium addition proved to be very small compared to that naturally present in the waste (approx. 20 mg/column). Analysis of the leachate did not show any evidence of increased lithium following the addition of the lithium bromide tracer. However the bromide showed a clear rise in concentration following the addition of the tracer in both columns but with slightly different patterns of emergence.

In column 5 - anaerobic, the bromide did not begin to appear until approximately 60 days after addition of the tracer. In column 6 - aerobic, the bromide concentration in the emergent leachate began to rise straight after addition indicating some short circuiting of the flow resulting in rapid transit of bromide to the drainage zone at the column base. The column 5 results indicate a more gradual passage of the tracer through the waste solids in this column.
The reason for the difference in behaviour in the two columns is believed to be a result of partial drying out of the waste in the aerobic columns, particularly near the surface, resulting in shrinkage away from the column sides. It was noted that, in some of the columns exhibiting more obvious shrinkage, added rain had a tendency to flow between the waste and the column walls, at least in the upper third of the column. This would result in an element of short circuiting of the liquid flow, more rapid appearance of rain as leachate and reduced leaching of solutes from the waste.

However, although there was some relatively rapid tracer flow, the concentration of bromide in the leachate was still increasing in both columns at the end of the experiment. This suggests that the majority of irrigated water was passing through the waste matrix in a behaviour close to plug flow. Importantly, this indicates that the minimal leaching of metals in the experiments was not due to the irrigated water byassing the waste but rather, was due to the retention capacity of waste.

2.3.2 Experiment 2 - (Pitsea waste columns)

Waste composition

Analysis of the waste used to pack the columns was principally for selected heavy metals and water content. The results obtained for the principal metals of interest are shown in Table 2.3.3 in comparison with the guideline loading rates defined in draft Waste Management paper 26F.

Table 2.3.3 Summary of metal concentrations (in mg/kg wet waste) of Pitsea waste samples in comparison with WMP26F guidelines

	Pitsea BH1 (columns 13-18) acid waste area	Pitsea BH3 (columns 7-12) alkaline waste area	WMP26F Loading rate guidelines
Cd	1.21	1.86	10
Zn	183	742	100
Cr	66	51	100
Pb	262	101	100
Ni	18	14	100

Anaerobic/aerobic transformations

The Pitsea waste columns, designated columns 7 to 18 showed similar characteristics to the CAMR waste columns in terms of a transition from black to ochreous coloration after the change to 'aerobic' conditions in columns 8, 9 ,10 ,14 ,15 and 16. Other columns remained black.

The waste which had been obtained by rotary drilling rig was substantially macerated and of fine fibrous texture with few discernible items of waste visible. This was believed to be a consequence of the drilling technique. The resultant waste had poor drainage characteristics and ponding on top of several columns was a constant problem which necessarily affected the watering regime. As with the CAMR waste columns, aerated columns showing better drainage characteristics turned ochreous more rapidly than those with a tendency to surface ponding.

At the end of the experiment only columns 8, 14 and 16 had turned almost completely ochreous. Of the other aerobic columns, 9 and 10 had only a 5mm ochreous waste layer overlain by ponded liquid. Column 15 had only a superficial ochreous tinge to the waste surface beneath the ponded liquid.

The appearance and evidence of ponding at the end of the experiment was recorded and is shown in Table 2.3.4.

For the purposes of data analysis, those columns treated aerobically, i.e. with an air stream through the headspace have been regarded as the aerobic group and the others as an anaerobic group, though in reality, most of the aerobic columns were in some sort of transition state as adjudged by the colour of the column contents. It can be seen that from the final appearance of the columns only column 16 was in fact completely ochreous in nature.

Table 2.3.4 Final appearance of Pitsea waste columns prior to destruction

Column No.	Column treatment	Final coloration	Leachate ponding
7	anaerobic	Waste all black.	Ponded to column top-plate, liquid pale yellow.
8	aerobic	All ochreous except 3 cm layer of black near column base.	None
9	aerobic	5mm ochreous layer on otherwise black waste.	2cm ponded yellow liquid.
10	aerobic	5mm ochreous layer on otherwise black waste.	1cm ponded yellow liquid.
11	anaerobic	Waste all black	Ponded to column top-plate, liquid yellow.
12	anaerobic	Waste all black	Ponded to column top-plate, liquid yellow.
13	anaerobic	Waste all black	5 cm ponded almost clear liquid.
14	aerobic	Waste ochreous with odd black patches	None
15	aerobic	Black waste with ochreous surface only	2 cm ponded brown/orange liquid
16	aerobic	Waste all ochreous, crystallisation on surface	None
17	anaerobic	Waste all black	3 cm ponded clear liquid.
18	anaerobic	Waste all black	Ponded to column top-plate, liquid clear.

Gas production

All columns produced biogas soon after sealing of columns, with methane content rapidly reaching 50-60%. The waste in columns 7 to 12 showed an initial production of mostly carbon dioxide which seemed to have a significant hydrogen sulphide content judging by the unusually rapid formation of precipitate in the zinc acetate traps on the gas lines leaving the columns.

Gas production rates in all columns (Appendix A2.6) started rapidly and tailed off during the course of the anaerobic phase and afterwards in the case of the anaerobic control columns.

Rainwater addition/leachate removal

Due to poor leachate drainage and accumulation of ponded liquid in the top of the columns, watering had to be suspended at times and forcible suction of leachate employed to enable samples to be obtained from many columns. Accumulation of ponded leachate is evident on the graphs of cumulative water addition/removal as a divergence of the removal lines relative to the water addition lines. This can be seen with the acid waste columns (nos. 13-17) after day 400. Watering was suspended at times after day 570 due to excessive ponding.

The alkaline waste columns also needed suspension of watering due to ponding in many of the columns. The drainage characteristics of the aerobic columns seemed to improve after the start of aeration, a situation which makes the interpretation of leachate quality data difficult. The effects of washout are different in the two groups of columns , i.e. the aerobic and the anaerobic groups thus it is difficult to distinguish the effects of the redox differences from those of differential rain water volumes.

Leachate composition

Methods of analysis and handling of leachates were similar to those used in Experiment 1.

pH values (Appendix A.2.8) of the column leachates confirmed a difference between the two waste types. The acid waste leachate had a pH of about 6.3, rising to 7.1 before falling again towards the end of the experiment. A similar pattern was observed in the alkaline waste columns but initial pH was 6.7, rising to 7.3 before falling back again towards the end of the experiment.

Eh results (Appendix A.2.8) show some grouping between replicate columns particularly after the change to 'immediate' redox testing. However, there is not a clear difference between the 'aerobic' and 'anaerobic' columns and the results seem generally inconclusive. The use of in-situ redox electrodes permanently installed in the base of each column might offer a better means of redox measurement than the spot readings on drained leachates employed here.

Alkaline waste columns produced leachates with considerably higher ammoniacal nitrogen concentrations (Appendix A.2.8) (approx. 1000 mg/l at the start) than the acid waste columns (approx. 200 mg/l at the start). Ammoniacal nitrogen analysis of the leachate samples showed the effects of washout as well as probable microbial oxidation in the aerated columns. Aerobic columns with the alkaline waste (8, 9 and 10) showed a decline relative to the anaerobic controls (7, 11 and 12) from day 370 whereas aerobic acid waste columns (14,15 and 16) showed a reduction in ammoniacal nitrogen relative to the anaerobic controls only after day 600.

Electrical conductivity (Appendix A2.8) showed a decline related to washout of solutes during the experiment but there is a suggestion of a more rapid decline in the aerobic columns in the case of the alkaline waste columns. At least part of the difference between the aerobic and anaerobic columns with the alkaline waste is due to increased washout effects with the aerobic columns due to increased volumes of added rain water. The three replicate anaerobic columns with the alkaline waste (nos. 7,11 and 12) showed poor drainage characteristics compared to the aerobic ones and this is believed to be related in some way to the redox conditions either through decomposition processes affecting permeability or waste drying and shrinkage effects in the aerobic columns. On average these columns received approximately 800 ml less rain water (approx. 25% less) than the aerobic equivalents (columns 8, 9 and 10) because surface ponding necessitated suspension of watering on a number of occasions.

Chloride results show very similar trends to the electrical conductivity suggesting simple washout characteristics and little reaction with the waste solids.

Dissolved heavy metal concentrations in the column leachates were generally low and fluctuated around the limit of detection in most cases without showing any obvious trends or differences between anaerobic and aerobic columns. The exception was zinc which showed higher levels in all columns in the earlier part of the experiment than during the later stages though concentrations did not seem to be linked to anaerobic or aerobic conditions.

Initial and final waste analysis

The fate of the heavy metals in the waste has been assessed by comparison of analytical results for waste at the start and finish of the experiment and also by calculation of the total amount leached. The amount of metals leached has been over-estimated as many results were below detection limits. In such cases, concentrations were assumed to be at the detection limits thus giving rise to a degree of over-estimation.

Appendix A.2.9 contains results of the waste analysis and Appendix A.2.3 the analysis of leachate and calculated amounts of metal leached.

It can be seen from the results of the solid waste analysis that very little metal appears to have been leached. This is also supported by the leachate analysis which shows that very little of the heavy metal can be accounted for in the leachate.

2.3.2 Flask experiments

Leachate samples from the flask experiments were analysed for similar determinands as the leachates from the column experiments.

The full results are shown in graphical and tabular form in Appendix A2 but the main observations are included here. It should be noted that the day 0 values for the various analytical determinands are in fact concentrations determined in sub-samples of the artificial leachate, with or without added metals, taken prior to adding the leachate to the flasks.

It was also noted that precipitate often occurred in these metal amended samples and it was clear that some of the metals were prone to precipitation when added to the artificial leachate. No chelating agents were added to assist with metal solubility.

pH results (Appendix Table A2.10.1) were variable between different groups of tests set up at different times indicating that there seemed to be some variation in the batches of waste used for setting up each group of tests even though this originated from the same source. Control flasks showed variation between those set up in different groups of tests. The level of added metal salts also seemed to have an effect on pH as did the different salts used.

In general the pH rose by up to 1.5 units after aeration of the flasks but this was variable and possibly influenced by the added metal salt concentrations which would have affected the pH buffering capacity.

Eh values measured in the removed leachate (Appendix Table A.2.10.2) were variable, slightly above or below 0 mV. If these values are a true reflection of the redox conditions within the flask contents, then it appears that reducing power of the waste had not achieved strictly anaerobic conditions, neither did the aeration initiate completely aerobic conditions. The visible presence of iron sulphides in the flasks and the later presence of iron oxides after aeration suggests a greater redox transition than is recorded by the redox measurements.

Chloride concentrations were observed to fall significantly after aeration, a result which was not anticipated and is difficult to explain given chloride is generally considered both highly soluble and notably unreactive.

Ammoniacal nitrogen concentrations fell significantly after aeration as in the column experiments presumably due to microbial oxidation. Alkalinity showed a similar change after aeration.

The soluble metal concentrations were low in all but the cocktail of metal additions at the highest level. Cadmium and zinc showed a decline in concentration over the course of each batch test. Changes in chromium concentrations were less predictable.

Dissolved iron concentrations showed a rise during the anaerobic period followed by a decline after aeration. This is consistent with our understanding of iron solubility in relation to redox potential, ferrous iron being more soluble than ferric.

Total sulphur in acidified leachates analysed by ICP showed a rise indicating probable sulphide oxidation to sulphate. This was supported by Ion Exchange chromatographic analysis of sulphate which also showed a rise after the aeration period.

2.4 Overview of waste maturities and metal leaching

2.4.1 Maturity of experimental waste

During the design of the experimental programme, careful consideration was given to ensuring that the laboratory studies represented a wide range of landfill stabilisation phases.

Considering the CAMR anaerobic columns first (Experiment 1), the original waste was known to be in an advanced stage of maturity before loading into the columns. Although handling of the waste led to rejuvenation of methanogenesis, gas production gradually declined during the experiment and had virtually ceased by the end. Thus, the anaerobic CAMR columns can be considered to represent landfill in an advanced, anaerobic, post-methanogenic state of maturity. For the aerobic CAMR columns, some differences were noted in the rate of advance of the visible oxic front through the columns. However, by the end of the experiments, the oxic front had progressed to the base of all the columns.

Waste sampled from Pitsea landfill was also reasonably mature. This is supported by the biochemical methane potential (BMP) analysis of the waste. The Pitsea samples had BMP values in the range 10.9 to 34.8 m^3CH_4/tonne dry weight, with figures of 19.7 and 10.9 m^3CH_4/tonne dry weight for the samples from holes 1 and 3 used in columns 13 to 18 and 7 to 12 respectively. Volatile fatty acid (VFA) concentrations in both field sampled leachates were greater than 1000 mg/l. This compares with values for the CAMR waste of 2.2 m^3CH_4/tonne dry weight. The relatively high concentrations of volatile fatty acids (greater than 1000 mg/l) and particularly chloride were probably due to the proximity of the samples locations to liquid co-disposal sites and should not be taken as an indication of immaturity.

Aerobic conditions were introduced to the Pitsea columns in the same manner as for the CAMR ones, however, due to the relatively poor drainage properties of the waste, the oxic front only progressed to the base (or close to the base) of one out of three aerobic columns for the borehole 3 waste and two out of three of the aerobic columns for the borehole 1 waste.

The CAMR columns were leached at a relatively consistent rate for over 1000 days and by the end of the experiments in excess of 5 bed volumes of leachate had passed through all of the columns. The Pitsea columns were leached for 695 days and by the end of the experiments had been leached by in excess of 3 bed volumes.

Selected parameters for the different waste types at the beginning and end of the experiments are summarised in Table 2.4.1 and compared with generic values for UK leachates, based on Robinson (1995) to show that the experiments were representative of a range of landfill maturities.

Table 2.4.1 Summary of leachate parameters for the experimental wastes.

	PitBH3F	PitBH3L	PitBH1F	PitBH1L	CAMRE	CAMRL	UK Mean Aceto-genic	UK Mean Methano-genic
pH	6.73	6.9	6.3	6.7	7.1	7	6.7	7.52
Ammoniacal-N	2040	210	889	109	207	76	922	889
Chloride	11525	1349	1125	241	1564	83	1805	2074
Fatty acids as (C)	3427	400est	1058	<50	103	20	8197	18

CAMRE leachate based on early concentrations from column experiments (first 3 months)
CAMRL leachate based on late concentrations from column experiments (last 3 months)
PitBH1F and PitBH3F based on mean analysis of waste porewaters from field sampling from boreholes 1 and 3 respectively
PitBH1L and PitBH3L based on late concentrations from column experiments (last 3 months)

2.4.2 Overview of metal leaching

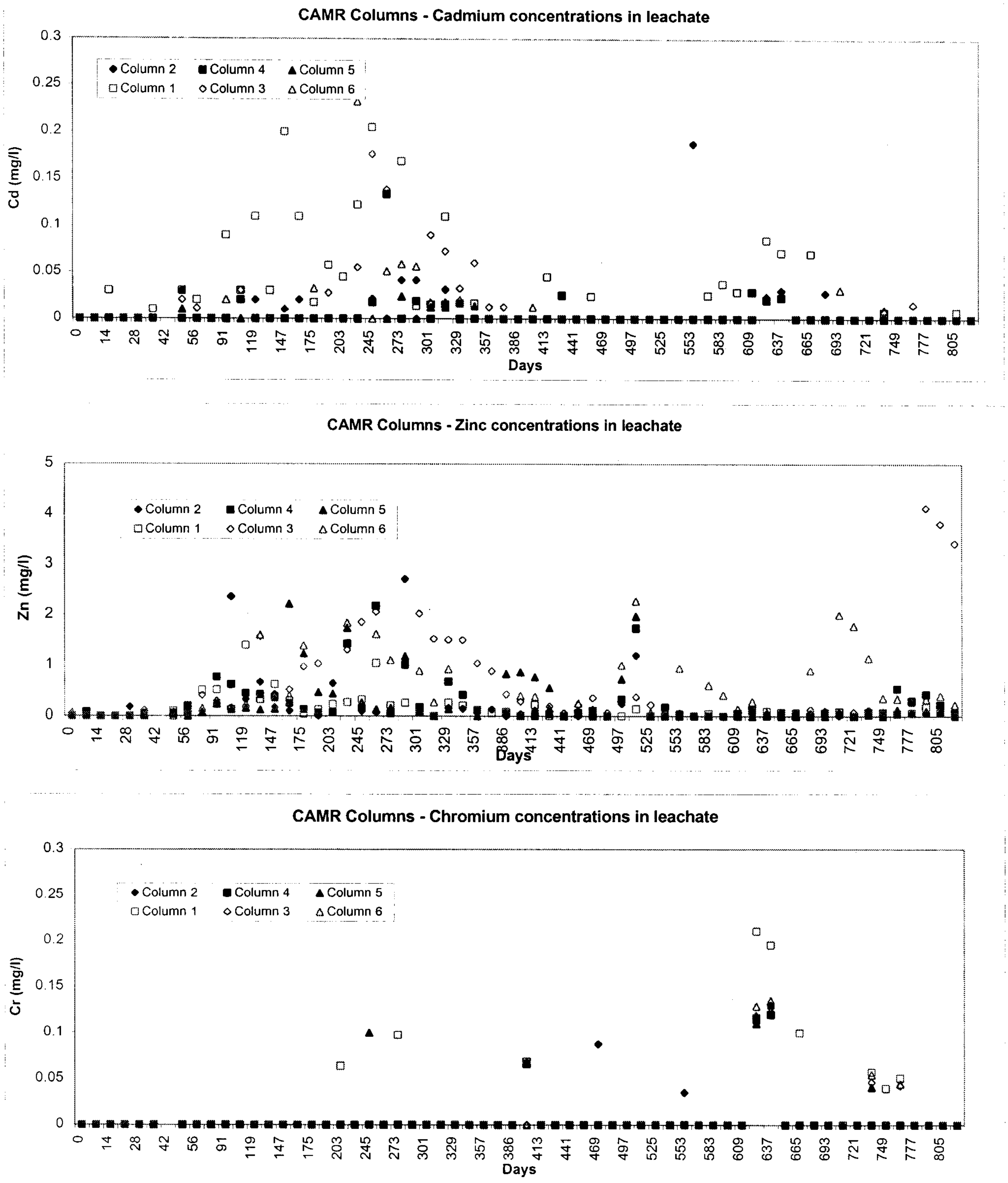
The project aimed to investigate metal leaching from waste with a range of metal loadings. Waste from the CAMR experiments was selected as it was known that this had been enriched with cadmium in excess of the WMP 26F guidelines of 10 mg/kg. Pitsea wastes were below guideline levels for cadmium. Zinc was enriched in all wastes in excess of the guideline levels. Efforts were made, particularly following the Pitsea sampling programme to select waste with a range of chromium loadings. However, in all wastes, chromium was found to be close to or below guideline levels. Overall, the experimental waste had a reasonable range of metal loadings. (Table 2.4.2).

When interpreting analytical data relating to heavy metal concentrations in relation to guideline loading rates it should be understood that the guideline loading rate defines the amount of each heavy metal which can be added to a given tonnage of household waste. This is different from the actual concentration in the ultimate waste mix as clearly, for many metals, the household waste itself will contain a significant 'natural' concentration. This is particularly the case with relatively abundant elements such as zinc which may already exist at levels above the loading rate in household waste. In such cases addition of extra metal by co-disposal up to the guideline loading rate may result in only a modest increase in the concentration present.

Table 2.4.2 Summary of metal concentration in experimental columns (in mg/kg wet waste) and comparison with WMP26F guidelines

	CAMR Cd amended waste	Pitsea BH1 (columns 13-18) acid waste area	Pitsea BH3 (columns 7-12) alkaline waste area	WMP26F Guidelines
Cd	53	1.21	1.86	10
Zn	470	183	742	100
Cr	123	66	51	100
Pb	285	262	101	100
Ni	42	18	14	100

The aerobic phase of the experiments was most complete in the case of the CAMR columns where all 3 air sparged columns were oxic to the base. If there was any overall trend of increased metal release as a result of the air sparging, it should be present for these experiments. Summary metal plots for the three metals for each of the six CAMR columns are shown in Figure 2.4.1 to 2.4.3. These plots show some evidence for higher metal concentrations for zinc and cadmium during the first year of the experiments (possibly due to slow washout of initial porewaters with synthetic rainwater).



Analytical data at detection limit plotted as zero

Closed symbols are anaerobic columns, open symbols are aerobic columns

Note: anomalously high experimental data excluded

Figure 2.4.1 Summary of leachate metal concentrations for the CAMR columns

For cadmium it appears that leachate concentrations were higher for the air sparged columns than for the anaerobic columns between approximately day 100 and day 350. Air sparging started on day 129. However evidence from visual inspection, supported by ammonia monitoring, indicates that aerobic conditions did not reach the base of the columns until around day 275 for column 6, day 325 for column 3 and even later for column 1. It is therefore unlikely that the apparent contrast between the air sparged and anaerobic columns was due to the advance of aerobic conditions

Some of the erratic zinc and VFA results in the CAMR column leachate were due to suck back of zinc acetate from the gas traps due to imbalances in gas pressure on the gas outlet side of the columns. This resulted on some occasions where power to the constant temperature (CT) room was temporarily lost and columns cooled to ambient temperature. It may also have happened as a result of rising barometric pressure coupled with a low gas production from the waste.

This effect has, not surprisingly, resulted in occasional high peak zinc concentrations notably in columns 2, 3, 4, 5 and 6. As the zinc acetate concentration was equivalent to 2979 mg Zn/l any suck back of this into the column could have a severe effect on observed zinc concentrations. In some cases where the cause of this effect was apparent such as loss of power to the CT room, a rapid, though short lived, appearance of zinc in the emergent leachate was observed. An example of this is on day 432 when leachates drained from columns 4 and 5 showed greatly elevated zinc concentrations (to 33 mg/l) this being the first leachate sampling date after a CT room failure over the weekend between days 426 and 429. It is probable that other zinc peaks (up to 160 mg/l) resulted from similar suck back events.

These events have complicated the interpretation of results with respect to zinc. It is unclear whether the rapid appearance of zinc in the leachate after some events and subsequent return to previous levels suggests a high degree of fissure flow in the waste or whether the zinc acetate found its way via the vent pipe directly to the column base without passing through the waste.

As a result of this problem being detected in the course of Experiment 1, slight modifications to the downstream pipework were made when the Experiment 2 (Pitsea waste) columns were constructed. The modification trapped any zinc acetate sucked back in this manner before it could enter the columns.

As discussed in section 2.3, there is no consistent evidence for increased metal release from the aerobic columns in any of the waste types.

Graphs showing metal leachate concentrations for all columns are included in Appendix A.2.3 and A.2.8.

To provide a summary of metal release from the columns, a mass balance evaluation has been carried out. By combining the monitoring data for leachate concentrations and volumes, the cumulative mass of metals leached from each of the columns has been calculated. Where metal concentrations were below detection limits, the loading has been calculated based on the detection limit. In addition, all analytical results have been retained in the evaluation, including some potentially spuriously high one-off concentrations. The mass balance evaluation therefore represents a worst case assessment of metal leaching from the columns.

The results of the mass balance evaluation are one of the key findings of this study. They indicate that, even based on the worst case assumptions outlined above, less than 2% of any metal was leached by the end of the experiment (Table 2.4.3). In considering the significance of this result, there are several facts that should be borne in mind.

- Initial metal loadings were quite high and some columns were above draft WMP26F guideline levels (Cd = 10 g/tonne; Zn 100 g/tonne and Cr 100 g/tonne) for each metal.
- By the end of the experiments, each of the columns had been leached by more than three bed volumes of synthetic rainwater.
- Monitoring of parameters such as chloride demonstrated that the columns showed classical washout trends for conservative, non-reactive species.

The only results showing more than 1% leaching were for cadmium in the Pitsea columns, where initial loadings were very low, at around 1 g/tonne. Many of the leachate analyses for cadmium for these columns were below detection limits and it is likely that by assuming concentrations were *at* detection limits, the evaluation has overestimated release. Considering the results as a whole it is probable that less than 1% of any metal was leached in the long term experiments.

When considering the leaching of metals from the waste in the columns the proportion leached can be determined in two ways using the data available. This is either (i) from the initial analysis of the waste solids and the leachate analysis or (ii) from the difference between the initial and final analysis of the waste solids.

Tables 2.4.3 to 2.4.5 show the summary data for the proportion of the metals leached derived from the leachate analysis and the initial analysis of waste solids. These results suggest that in all cases less than 2% of the metals have been accounted for in the leachate and in the large majority of cases, less than 1%. Even with zinc, where contamination of the CAMR columns/leachate by zinc acetate is thought to have occurred, the total in the leachate represents less than 1% of the initial amount in the waste solids.

Table 2.4.3 (a-f) Summary of metal leaching from the Experiment 1

(a) CAMR waste - Total Cadmium leached as a percentage of initial metals present

Column No.		Initial (mg)	Leached (mg)	Leached (%)	Average
1	aerobic	247	0.20	0.08	0.05
3	aerobic	251	0.09	0.03	
6	aerobic	235	0.07	0.03	
2	anaerobic	250	0.09	0.04	0.03
4	anaerobic	244	0.07	0.03	
5	anaerobic	241	0.07	0.03	

(b) CAMR waste - Total Chromium leached as a percentage of initial metals present

Column No.		Initial (mg)	Leached (mg)	Leached (%)	Average
1	aerobic	575	0.35	0.06	0.06
3	aerobic	584	0.29	0.05	
6	aerobic	547	0.31	0.06	
2	anaerobic	581	0.58	0.10	0.07
4	anaerobic	567	0.30	0.05	
5	anaerobic	562	0.40	0.07	

(c) CAMR waste - Total Zinc leached as a percentage of initial metals present
N.B. leached zinc includes contamination from zinc acetate traps.

Column No.		Initial (mg)	Leached (mg)	Leached (%)	Average
1	aerobic	2196	0.56	0.03	0.37
3	aerobic	2229	12.87	0.58	
6	aerobic	2088	10.75	0.51	
2	anaerobic	2217	14.29	0.64	0.52
4	anaerobic	2164	4.05	0.19	
5	anaerobic	2143	15.61	0.73	

(d) CAMR waste - Total Lead leached as a percentage of initial metals present

Column No.		Initial (mg)	Leached (mg)	Leached (%)	Average
1	aerobic	1333	0.05	0.00	0.01
3	aerobic	1352	0.05	0.00	
6	aerobic	1267	0.07	0.01	
2	anaerobic	1345	0.05	0.00	0.00
4	anaerobic	1313	0.05	0.00	
5	anaerobic	1300	0.06	0.00	

(e) CAMR waste - Total Nickel leached as a percentage of initial metals present

Column No.		Initial (mg)	Leached (mg)	Leached (%)	Average
1	aerobic	196	0.68	0.35	0.36
3	aerobic	199	0.73	0.37	
6	aerobic	187	0.66	0.35	
2	anaerobic	198	0.51	0.26	0.31
4	anaerobic	193	0.60	0.31	
5	anaerobic	192	0.67	0.35	

(f) CAMR waste - Total Iron leached as a percentage of initial metals present

Column No.		Initial (mg)	Leached (mg)	Leached (%)	Average
1	aerobic	53120	32.88	0.06	0.04
3	aerobic	53905	9.70	0.02	
6	aerobic	50502	12.66	0.03	
2	anaerobic	53630	27.99	0.05	0.05
4	anaerobic	52348	21.01	0.04	
5	anaerobic	51836	25.77	0.05	

Table 2.4.4 (a-f) Summary of metal leaching from the Experiment 2

(a) Pitsea BH1 - Total Cadmium leached as a percentage of initial metals present

Column No.		Initial (mg)	Leached (mg)	Leached (%)	Average
14	aerobic	3	0.04	1.27	1.26
15	aerobic	3	0.03	1.15	
16	aerobic	3	0.04	1.37	
13	anaerobic	3	0.05	1.70	1.53
17	anaerobic	3	0.04	1.46	
18	anaerobic	3	0.04	1.42	

(b) Pitsea BH1 - Total Chromium leached as a percentage of initial metals present

Column No.		Initial (mg)	Leached (mg)	Leached (%)	Average
14	aerobic	147	0.19	0.13	0.14
15	aerobic	147	0.20	0.14	
16	aerobic	147	0.22	0.15	
13	anaerobic	147	0.23	0.16	0.16
17	anaerobic	147	0.23	0.16	
18	anaerobic	137	0.22	0.16	

(c) Pitsea BH1 - Total Zinc leached as a percentage of initial metals present

Column No.		Initial (mg)	Leached (mg)	Leached (%)	Average
14	aerobic	413	0.42	0.10	0.08
15	aerobic	412	0.30	0.07	
16	aerobic	412	0.26	0.06	
13	anaerobic	413	0.31	0.08	0.08
17	anaerobic	412	0.32	0.08	
18	anaerobic	388	0.31	0.08	

(d) Pitsea BH1 - Total Lead leached as a percentage of initial metals present

Column No.		Initial (mg)	Leached (mg)	Leached (%)	Average
14	aerobic	589	0.56	0.09	1.10
15	aerobic	589	0.51	0.09	
16	aerobic	589	0.63	0.11	
13	anaerobic	589	0.65	0.11	0.11
17	anaerobic	588	0.63	0.11	
18	anaerobic	554	0.61	0.11	

(e) Pitsea BH1 - Total Nickel leached as a percentage of initial metals present

Column No.		Initial (mg)	Leached (mg)	Leached (%)	Average
14	aerobic	41	0.24	0.57	0.83
15	aerobic	41	0.37	0.91	
16	aerobic	41	0.42	1.02	
13	anaerobic	41	0.26	0.64	0.73
17	anaerobic	41	0.27	0.67	
18	anaerobic	38	0.34	0.89	

(f) Pitsea BH1 - Total Iron leached as a percentage of initial metals present

Column No.		Initial (mg)	Leached (mg)	Leached (%)	Average
14	aerobic	17663	27.54	0.16	0.11
15	aerobic	17655	13.11	0.07	
16	aerobic	17660	20.10	0.11	
13	anaerobic	17668	25.67	0.15	0.16
17	anaerobic	17649	30.62	0.17	
18	anaerobic	16621	26.20	0.16	

Table 2.4.5 (a-f) Summary of metal leaching from the Experiment 2

(a) Pitsea BH3 - Total Cadmium leached as a percentage of initial metals present

Column No.		Initial (mg)	Leached (mg)	Leached (%)	Average
8	aerobic	4	0.04	1.12	0.99
9	aerobic	4	0.04	0.95	
10	aerobic	4	0.04	0.91	
7	anaerobic	4	0.15	3.76	1.91
11	anaerobic	4	0.04	0.90	
12	anaerobic	4	0.04	1.07	

(b) Pitsea BH3 - Total Chromium leached as a percentage of initial metals present

Column No.		Initial (mg)	Leached (mg)	Leached (%)	Average
8	aerobic	116	0.50	0.43	0.41
9	aerobic	116	0.45	0.39	
10	aerobic	116	0.48	0.41	
7	anaerobic	116	0.58	0.50	0.40
11	anaerobic	116	0.42	0.36	
12	anaerobic	116	0.40	0.34	

(c) Pitsea BH3 - Total Zinc leached as a percentage of initial metals present

Column No.		Initial (mg)	Leached (mg)	Leached (%)	Average
8	aerobic	1669	0.64	0.04	0.04
9	aerobic	1670	0.67	0.04	
10	aerobic	1669	0.52	0.03	
7	anaerobic	1670	0.31	0.02	0.01
11	anaerobic	1670	0.20	0.01	
12	anaerobic	1669	0.21	0.01	

(d) Pitsea BH3 - Total Lead leached as a percentage of initial metals present

Column No.		Initial (mg)	Leached (mg)	Leached (%)	Average
8	aerobic	227	0.65	0.29	0.26
9	aerobic	227	0.56	0.24	
10	aerobic	227	0.58	0.25	
7	anaerobic	227	0.55	0.24	0.21
11	anaerobic	227	0.39	0.17	
12	anaerobic	227	0.47	0.21	

(e) Pitsea BH3 - Total Nickel leached as a percentage of initial metals present

Column No.		Initial (mg)	Leached (mg)	Leached (%)	Average
8	aerobic	31	0.29	0.95	0.80
9	aerobic	31	0.22	0.70	
10	aerobic	31	0.23	0.75	
7	anaerobic	31	0.33	1.08	0.80
11	anaerobic	31	0.20	0.64	
12	anaerobic	31	0.21	0.67	

(f) Pitsea BH3 - Total Iron leached as a percentage of initial metals present

Column No.		Initial (mg)	Leached (mg)	Leached (%)	Average
8	aerobic	22959	26.53	0.12	0.11
9	aerobic	22968	30.34	0.13	
10	aerobic	22958	20.95	0.09	
7	anaerobic	22972	32.82	0.14	0.11
11	anaerobic	22972	22.01	0.10	
12	anaerobic	22958	17.30	0.08	

In addition to the analysis of leachate, leached metal quantities has been determined by difference between that present at the start and finish of the experiment. In calculation of these figures full regard has been taken of changes in waste water content and the total amount of dry matter present in the columns over the period of the experiment. Weight loss due to leaching and gasification of organic matter has resulted in a loss of dry matter of typically about 10 % from the columns. The actual figures compared are the calculated mass of each individual metal present in the columns at the start and end of each experiment.

The summarised results from this mass balance calculation are shown in Tables 2.4.6-2.4.8 below.

Table 2.4.6 Change in metals present in columns - Experiment 1 - CAMR waste columns

Column		**Total metals present (mg)**											
		Cd	% Loss	**Cr**	% Loss	**Pb**	% Loss	**Zn**	% Loss	**Ni**	% Loss	**Fe**	% Loss
1	Initial	247	7	575	9	1333	-11	2196	-10	196	2	53120	59
	Final	**231**		**526**		**1481**		**2407**		**193**		**21767**	
2	Initial	250	-19	581	18	1345	-25	2217	5	198	12	53630	60
	Final	**296**		**474**		**1680**		**2110**		**175**		**21690**	
3	Initial	251	-41	584	3	1352	-33	2229	-18	199	-10	53905	48
	Final	**354**		**568**		**1799**		**2619**		**219**		**27919**	
4	Initial	244	11	567	6	1313	-23	2164	-34	193	-5	52348	56
	Final	**217**		**531**		**1610**		**2909**		**203**		**23275**	
5	Initial	241	11	562	5	1300	-3	2143	4	192	-41	51836	58
	Final	**214**		**534**		**1338**		**2063**		**271**		**22022**	
6	Initial	235	-12	547	12	1267	-39	2088	-17	187	-13	50502	42
	Final	**263**		**480**		**1757**		**2451**		**210**		**29257**	

Table 2.4.7 Change in metals present in columns - Experiment 2 - Pitsea BH 1 columns

Column		Total metals present (mg)											
		Cd	% Loss	Cr	% Loss	Pb	% Loss	Zn	% Loss	Ni	% Loss	Fe	% Loss
13	Initial	3	-74	147	10	589	21	413	-40	41	-53	17668	32
	Final	**5**		**133**		**465**		**577**		**63**		**12077**	
14	Initial	3	-57	147	-9	589	-496	413	-18	41	8	17663	25
	Final	**4**		**161**		**3510**		**486**		**37**		**13197**	
15	Initial	3	3	147	20	589	-44	412	-60	41	30	17655	56
	Final	**3**		**118**		**847**		**659**		**28**		**7843**	
16	Initial	3	-25	147	10	589	14	412	-31	41	23	17660	40
	Final	**3**		**133**		**509**		**541**		**31**		**10621**	
17	Initial	3	-10	147	4	588	14	412	2	41	18	17649	34
	Final	**3**		**142**		**504**		**402**		**34**		**11650**	
18	Initial	3	-1744	139	-9	554	-101	388	-107	38	-155	16621	23
	Final	**47**		**151**		**1114**		**804**		**98**		**12808**	

Table 2.4.8 Change in metals present in columns - Experiment 2 - Pitsea BH 3 columns.

Column		Total metals present (mg)											
		Cd	% Loss	Cr	% Loss	Pb	% Loss	Zn	% Loss	Ni	% Loss	Fe	% Loss
7	Initial	4	44	116	2	227	-58	1670	-44	31	18	22972	40
	Final	**2**		**114**		**360**		**2409**		**26**		**13845**	
8	Initial	4	38	116	6	227	-38	1669	-42	31	9	22959	41
	Final	**3**		**109**		**313**		**2367**		**28**		**13452**	
9	Initial	4	38	116	-11	227	-43	1670	-52	31	1	22968	37
	Final	**3**		**129**		**324**		**2532**		**31**		**14401**	
10	Initial	4	23	116	2	227	-28	1669	-47	31	11	22958	41
	Final	**3**		**114**		**292**		**2446**		**28**		**13488**	
11	Initial	4	38	116	-1	227	-26	1670	-48	31	8	22972	41
	Final	**3**		**117**		**287**		**2463**		**29**		**13609**	
12	Initial	4	19	116	-31	227	-33	1669	-51	31	6	22958	38
	Final	**3**		**152**		**301**		**2519**		**29**		**14272**	

The results tabulated in Tables 2.4.6 to 2.4.8 create an unclear picture of metal leaching from the columns. Generally, the observed change in metal accounted for by the comparison of before/after analysis of solids represents a far greater amount of metal than that accounted for in the leachate. However, with the exception of iron, the metals show as many gains as losses over the course of the experiments. This can only really be accounted for by analytical variation in the waste as it would seem impossible for the metal present in the waste to increase.

Given the level of variability in the results obtained for replicate columns for each metal it seems that the over-riding observation from the before/after analysis is that because of the heterogeneity of metal distribution in the waste solids, it is difficult to draw conclusions from this type of calculation about the leaching of relatively small quantities of metal. It suggests that greater trust should be placed in the quantification of leached metals by leachate analysis than any determinations based on solids analysis given the size of samples available for analysis from small lab scale experiments. On this basis the metal loss from the columns through leaching represents a very small percentage of the total.

3. MODELLING PROGRAMME

3.1 Introduction

The processes by which metals are retained in landfill are poorly understood. However, extensive research on soils and groundwater has provided some considerable insights into the processes that control metal mobility in the environment. Precipitation/dissolution reactions and the interaction of metals with matrix via adsorption have been identified as important processes in soils (Alloway, 1990; Ross, 1994) and groundwaters (Domenico and Schwartz, 1990; McKinley & Scholtis, 1991). Research on surface waters (Tipping & Hurley, 1992), soils (Sposito, 1994) and groundwaters (Read, 1997) has also drawn attention to the enhancement of metal mobility due to complexation with organic compounds. However, as yet relatively few such studies have been carried out on landfill.

In recognition of the need for close integration of the modelling and experimental studies, the programmes for the two aspects of this project were closely linked. The modelling studies therefore focus on the same metals (zinc, cadmium and chromium) and were used to investigate metal behaviour in the mature landfill wastes from the Centre for Applied Microbiology Research (CAMR), and the two field sampled wastes from Pitsea Landfill.

Modelling studies addressed a number of fundamental questions.

1. What are the dominant aqueous metal complexes (e.g. organic complexes, chlorides, carbonates, hydroxides) likely to be present in landfill leachates?

2. What are the most insoluble metal precipitates likely to be present in landfill over a range of conditions and are these precipitates likely to limit metal concentrations in leachate?

3. Is sorption important in immobilising metals in landfill, and if so, can this process be understood and predicted?

4. What are the likely metal concentrations in leachate for different metal loading ratios?

5. How is the potential for metal release likely to change as a landfill matures?

In order to address these questions, it was important to build understanding from the simple to the complex. The techniques used in this study are described in Section 3.2. Following this, the types of aqueous complexes likely to be present in landfill are investigated using speciation models in Section 3.3. Results of solubility modelling and sorption modelling, which investigated the roles of precipitation and adsorption in controlling metal retention in the experimental columns are given in Sections 3.4 and 3.5 respectively. The modelling results are summarised in Sections 3.6.

3.2 Modelling techniques

In this project, techniques developed in research on metal mobility in soils and aquifers have been integrated with research on landfill and applied to aid in the interpretation of the experimental studies and to address the broader objectives of the project. The geochemical models and databases utilised in this project are all well established, are in the public domain, and have been widely used in studies of metals in groundwater and soil.

Modelling has been undertaken predominantly using the speciation-solubility model PHREEQC (Parkurst, 1995) which is available on the internet and can be run on a PC. The PHREEQE suite is one of the most widely used geochemical models and can be used to assess both the solubility and sorption of metals in groundwaters and leachates.

Geochemical modelling relies on the availability of high quality and comprehensive thermodynamic data to describe the range of reactions that may occur in the system being studied. For the purposes of this study, thermodynamic data are based on the MINTEQA2 (Allison et al., 1991) database. Supplementary data have been derived from the CHEMVAL database Version 6.0 (Falck and Read, 1996), which was developed over 8 years in a multi-country EC R&D programme.

In most groundwater contaminant transport models, the concept of a distribution coefficient (Kd) is used to represent sorption, where the Kd is defined as the ratio of adsorbed metal to metal in solution.

However, Kds for individual metals vary over many orders of magnitude, depending on a range of factors including the concentrations of metals and ligands, pH and the nature of the matrix material. For example in a regional study of cadmium sorption in soils in Denmark it was found that Kds generally double for each increase in pH of 0.5 units or in organic matter corresponding to 2% weight percent (Christensen, 1989). The use of inappropriate distribution coefficients in contaminant transport modelling and groundwater risk assessment therefore has the potential to lead to grossly misleading predictions of contaminant migration.

In this study, a more rigorous approach to sorption has been adopted, based on the concepts of surface complexation modelling. In this approach, the sorption of metals is sensitive to the leachate concentrations, pH and the nature of the matrix material. The approach is compatible with the thermodynamic equilibrium assumptions that are also applicable to the speciation and solubility modelling and has been widely applied and tested in studies of soils and groundwater (Sposito, 1994; Dzombak & Morel, 1990; Read, 1997). The thermodynamic data for modelling surface complexation in this study were derived largely from a literature search and from previous publications by the authors.

3.3 Metal speciation in leachates

3.3.1 Basis for speciation modelling

In the natural water environment, metals occur as a wide range of aqueous complexes. The types of complexes vary depending on the metal being considered and the types and concentrations of ligands in the solution. In landfill leachates, that have near neutral pH, quite high alkalinities and high chloride and organic contents, aqueous complexes are likely to include hydroxides, carbonates, chlorides and organic complexes. The principal reasons why metal speciation needs to be understood are:

- the toxicity and uptake of some metals is dependent on speciation;
- the mobility, solubility and sorption of metals are controlled by interactions with aqueous complexes.

In standard water analyses e.g., for leachate, surface and groundwaters, metals are reported as dissolved and/or total concentrations. Metal speciation can be analysed in the laboratory but this is time consuming and expensive. It is therefore far more common to assess speciation using geochemical models. These models take analytical data for dissolved concentrations and, by referencing databases of equilibrium constants, calculate the distribution of aqueous species by iterating between multiple equilibria. Additional theoretical background is provided in Appendix B.

In order to investigate metal speciation over a range of landfill maturities, four leachate analyses have been modelled:

1. leachate from Pitsea Borehole 3 which had high concentrations of fatty acids and chlorides, probably due to its proximity to co-disposal sites;

2. leachate from Pitsea Borehole 1 which had moderate to high concentration of fatty acids and chlorides;

3. leachate from CAMR waste at the beginning of the column experiments which had moderate fatty acid and chloride concentrations and is representative of methanogenic phase leachate; and

4. leachate from CAMR waste at the end of the column experiments which had low fatty acid and chloride concentrations and is representative of post-methanogenic phase leachate.

Because of the small volumes of leachate generated in the experiments, not all parameters were analysed. Where necessary, the analytical suite has been supplemented by generic data for mean UK methanogenic landfill based on Robinson (1995). The input parameters used for the modelling of the CAMR and Pitsea wastes are summarised, and compared with generic UK leachates in Table 3.3.1.

Table 3.3.1 Summary of input parameters for metal speciation modelling and comparison with generic UK leachates

	PitBH3F	PitBH1F	CAMRE	CAMRL	UK Mean Acetogenic	UK Mean Methanogenic
pH	6.73	6.3	7.1	7	6.7	7.52
Ammoniacal-N	2040	889	207	76	922	889
Chloride	11525	1125	1564	83	1805	2074
Fatty acids as (C)	3427	1058	103	20	8197	18
Alkalinity as CaCO3	(3191)	3191	*5376*	1013	7251	5376
Nitrate-N	*0.86*	*0.86*	*0.86*	*0.86*	1.8	0.86
Sulphate-SO4	(6299)	6299	*67*	*67*	676	67
Sodium	(3153)	3153	*1480*	*1480*	1371	1480
Magnesium	(321)	321	*250*	*250*	384	250
Potassium	(1088)	1088	*854*	*854*	1143	854
Calcium	(1858)	1858	*151*	*151*	2241	151
Cadmium	0.12	0.04	0.01	0.01	0.02	0.015
Zinc	1.3	0.75	0.1	1.78	17.4	1.14
Chromium	0.2	0.16	0.05	0.05	0.13	0.09
Iron	242	218	25	67	654	27.4

CAMRE leachate based on early concentrations from column experiments (first 3 months)
CAMRL leachate based on late concentrations from column experiments (last 3 months)
PitBH1F and PitBH3F based on mean analysis of waste porewaters from field sampling from boreholes 1 and 3 respectively
Where no analyses available from Pitsea BH3 (due to small sample volume), data transposed from BH1 – denoted by ()
Analyses in italics retained from generic UK data based on Robinson (1995)

It should be noted that the high fatty acid and particularly chloride values were probably due to the proximity of the samples to liquid co-disposal sites and should not be taken as an indication of immaturity.

3.3.2 Results of speciation modelling

The results of the speciation modelling indicate that a wide range of metal complexes occur in landfill leachates and that the types of complexes evolve as a landfill matures. Modelling results for metals investigated in this study, cadmium, zinc and chromium, are summarised below.

Predicted speciation of cadmium in leachates

Modelling results show that particularly for the mature leachates, speciation is dominated by carbonate complexes and the divalent metal ion Cd^{2+} (Table 3.3.2). In the high chloride, high VFA leachates from Pitsea, chloride and acetate complexes are significant. Additional multiple sulphates and chlorides are present in very low amounts and account for the small deficit in total percentage in the two Pitsea wastes. Hydroxides are insignificant.

Table 3.3.2 Predicted speciation of cadmium in leachates (components > 20% shaded)

Cd	PitBH3F	PitBH1F	CAMR Early	CAMR Late
Cd+2_m	4	18	11	42
CdHCO3+_m	7	28	37	30
CdCO3_m	2	4	34	23
CdCl+_m	34	14	15	4
CdCl2_m	19	1	2	0
CdSO4_m	2	11	0	1
CdAcetate+_m	18	18	1	1
CdAcetate2_m	8	3	0	0
Total	95	96	100	100

The strong complexation of cadmium by chloride has been noted previously (Alloway, 1990; Ross, 1994). In immature landfill leachates, formation of chloride and organic complexes will tend to compete against immobilising processes such as precipitation and sorption. Based on speciation considerations alone, this could potentially lead to higher metal concentrations in immature landfill leachate compared with mature leachates. This issue is discussed further, in the context of other potential controls on metal mobility, in Section 4.

Predicted speciation of zinc in leachates

The results for zinc show some similarities to those for cadmium. Speciation in all of the leachates is dominated by carbonate complexes and the divalent metal ion Zn^{2+} (Table 3.3.3) In the leachate from Pitsea BH3, with very high VFAs, organic complexation is also significant. As for cadmium, the small deficit in total percentage for the two Pitsea wastes is accounted for by multiple sulphate and chloride complexes. Hydroxides are insignificant. The overall similarity in complexes in immature and mature leachates indicates that, with the exception of very organic-rich leachates, zinc speciation does not change greatly during landfill maturation.

Table 3.3.3 Predicted speciation of zinc in leachates (components > 20% shaded)

Zn	PitBH3F	PitBH1F	CAMR Early	CAMR Late
Zn+2_m	22	27	7	41
ZnHCO3+_m	28	42	26	32
ZnCO3_m	8	4	19	20
Zn(CO3)2-2_m	6	1	47	6
ZnCl+_m	5	1	0	0
ZnSO4_m	7	13	0	1
ZnAcetate+_m	20	8	0	0
ZnAcetate2_m	2	0	0	0
ZnAcetate3-_m	0	0	0	0
Total	97	97	100	100

These results are in good agreement with speciation studies of metals in soils that predict zinc speciation to be dominated by Zn^{2+}, carbonates, and sulphates (Sposito, 1994; Alloway, 1990).

Predicted speciation of chromium in leachates

Chromium in the natural environment occurs primarily in two oxidation states, Cr(VI) and Cr(III). Cr(VI), the more toxic form, only occurs under highly oxidising conditions, with the critical Eh for transformation being around +8000 mV at pH 8 (Sposito, 1981). In landfill, where Eh values are typically between –500 to 0 mV, chromium will be entirely present as Cr(III).

Chromium (III) is a trivalent ion and has a different speciation to zinc and cadmium. In immature leachates, although some hydroxides occur, speciation is strongly dominated by organic complexes (represented here as acetates). The formation of these organic complexes could contribute to chromium mobility in immature landfill. In mature leachates where VFAs concentrations are lower, organic complexes are insignificant and only hydroxides, which are also dominant in soil systems (Ross, 1994) remain.

Table 3.3.4 Predicted speciation of chromium in leachates (components >20% shaded)

Cr	PitBH3F	PitBH1F	CAMR Early	CAMR Late
Cr+3_m	0	0	0	0
Cr(OH)2+_m	1	3	56	60
Cr(OH)3_m	0	0	39	35
Cr(OH)+2_m	0	1	4	5
CrOHSO4_m	0	1	0	0
CrO2-_m	0	0	0	0
CrAcetate3_m	92	72	0	0
CrAcetate2+_m	6	15	0	0
CrAcetate+2_m	1	7	0	0
Total	100	100	100	100

Summary of metal speciation in leachates

Modelling of the speciation of cadmium, zinc and chromium in landfill leachates representative of a range of maturities demonstrates that speciation is likely to evolve as leachates mature. The main results of the speciation modelling are as follows.

1. In immature leachates cadmium complexes strongly with the high concentrations of chlorides and organics. As the concentrations of these components decline cadmium complexation becomes dominated by $Cd^{2+}$and carbonates.

2. Zinc complexation for all leachate types is dominated by $Zn^{2+}$and carbonates. In immature leachates organic complexes may be significant.

3. Chromium complexation is dominated by organics in immature leachates and hydroxides in mature leachates.

4. Overall, reducing concentrations of organics and chloride as leachates mature will tend to lead to weaker aqueous complexation and this may favour immobilising processes such as precipitation and sorption.

3.4 Metal solubility in leachates

3.4.1 Basis for metal solubility modelling

Heavy metals in the natural environment can occur as solid precipitates. The solubility and stability of these preciptates, which may include sulphides, carbonates, hydroxides etc., depends upon, among other factors, the concentration of the metal and associated ligands and the prevailing pH and redox conditions.

Under the anaerobic, strongly reducing, conditions present in landfill, it is likely that most heavy metals are immobilised as insoluble sulphides. However, if conditions become more aerobic, the potential exists for sulphides to become soluble and for metals to be released. An initial aim of the modelling was therefore to investigate the stability of metal precipitates in a typical landfill leachate over a range of redox conditions. As a representative range for mature and potentially aerobic landfills, modelling trials were based on varying the Eh potential from -300 mV to +200 mV.

In the first stage of modelling, mineral saturation indices were calculated for a range of leachates. Saturation indices provide a measure of the tendency of a mineral to precipitate. The tendency of a mineral to precipitate is indicated by the saturation index as follows:

- below zero means that the solution is undersaturated and the mineral phase is unlikely to be present;
- close to zero - the mineral is approximately in equilibrium with the solution and is likely to be present as a precipitate; and
- above zero means that the solution is supersaturated, i.e. the mineral will tend to precipitate.

In the second stage of the solubility modelling, having identified the most insoluble mineral phase likely to be present in aerobic landfill, the model was used to calculate metal solubility limits for a range of leachate types. These results are then compared with typical metal concentrations in landfill leachates and conclusions drawn of the likely role of precipitation in immobilising metals in landfill. This approach was used to assess whether mineral solubility alone can explain the leachate heavy metal concentrations for both early and late stages of waste degradation in the three sets of columns.

The majority of leachate parameters are included in Table 3.3.1. Full details of input parameters for the solubility modelling are given in Appendix B.

Prior to reporting the results for heavy metals, the likely ranges of Eh in the columns are established with reference to experimental measurements of Eh and visual observations of precipitation in the columns.

3.4.2 Results of solubility modelling

Eh ranges in the experimental columns

One of the main aims of this project was to compare metal release from anaerobic and aerobic waste. As described in Section 2, despite the precautions taken, Eh monitoring showed quite strong fluctuations within individual columns (See Appendix A) and showed minimal contrast between the anaerobic and aerobic columns for any of the wastes.

Although Eh monitoring showed little contrast between the aerobic and anaerobic columns, visual inspection of the columns indicated that in the air sparged columns, an ochreous oxidation front progressed down the columns. The rate of progress of the aerobic front varied between individual columns, however the front had progressed to the base of all of the CAMR columns and half of the Pitsea air sparged columns by the end of the experimental programme.

The ochreous colour change observed in the columns represents a changeover in iron minerals from sulphide dominated to oxyhydroxide dominated. Modelling of the CAMR leachates over a range of Ehs indicates that iron sulphide (pyrite) would be expected to become soluble above Ehs of around –200 mV. Above this Eh the iron oxyhydroxide minerals goethite and lepidocrocite have the potential to precipitate. However, it is not until Eh rises to above +20 to +40 mV that dominant ochre minerals ferrihydrite and jarrosite have the potential to precipitate. These latter minerals have been widely reported in natural ochreous deposits, for example associated with mine drainage and are likely to be cause of the red colouration in the waste columns.

The modelling results in Figure 3.4.1 demonstrate that as aerobic conditions become established, the solubility limiting phase for iron changes from sulphide to oxyhydroxide. Confidence in the modelling approach is provided by comparison with the colour changes observed for iron in the experimental columns. In the following sections, similar principles are used to investigate the role of precipitation in limiting the concentration of heavy metals in landfill leachates.

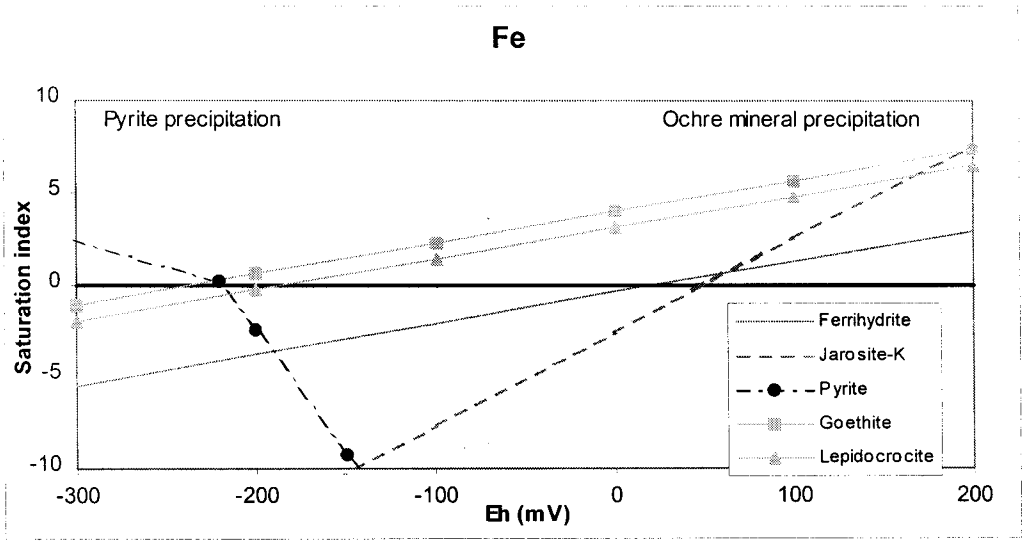


Figure 3.4.1 Saturation indices for iron minerals in CAMR column leachates

Solubility of cadmium in leachates

Modelling results indicate that cadmium sulphide is oversaturated under reducing conditions (Figure 3.4.2). The Eh at which cadmium sulphide is predicted to become undersaturated varies between the different leachates (Appendix B), but is around –80 to –150 mV. In methanogenic landfill where Eh is likely to be lower than –200 mV it is likely that sulphide precipitation is important in reducing cadmium mobility.

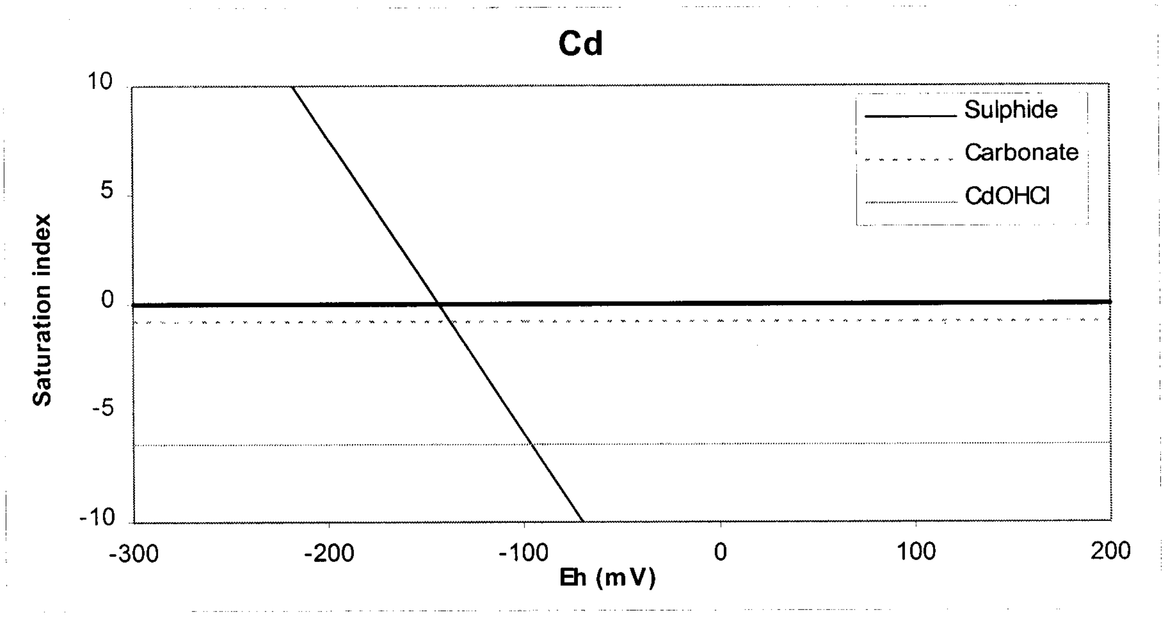


Figure 3.4.2 Saturation indices for cadmium minerals in CAMR column leachates

Under more aerobic conditions, cadmium sulphide will become undersaturated. Overall, the laboratory measurements supported by modelling and interpretation of iron mineralisation, suggest that positive Ehs were established in the majority of the air-sparged columns. Under these conditions, cadmium sulphide is likely to become soluble and cadmium carbonate (otavite) will become the solubility limiting phase. Lindsay (1979) showed that otavite is also likely to be the main mineral to control cadmium concentrations in soil solutions.

Having identified cadmium carbonate as the likely solubility limiting phase for cadmium in aerobic landfill leachate, the second stage of modelling has been carried out, in which equilibrium is imposed between cadmium carbonate and the three leachates under investigation. The model has been used to predict the solubility limits for cadmium in each leachate. Cadmium concentrations in leachate below the predicted limits will be soluble, and therefore precipitation is unlikely to contribute to metal retention.

The results of this solubility modelling indicate that in immature leachates with high chloride and VFAs, cadmium solubility limits are between 170 and 840 µg/l whereas in mature post methanogenic leachates such as the mature CAMR waste, carbonate precipitation is likely to prevent cadmium concentrations rising above 60 to 90 µg/l (Table 3.4.1). Laboratory results indicate that even for the aerobic columns, cadmium concentrations generally remain below 10µg/l. Overall, the results of the experimental and modelling studies in combination suggest that cadmium is retained in landfill under aerobic conditions, but that the retention mechanism is probably not precipitation alone.

Table 3.4.1 Predicted solubility limits for cadmium carbonate in a range of landfill leachates

	Cd solubility limit in Initial column leachates (mg/l Cd)	Cd solubility limit in Final column leachates (mg/l Cd)
Pitsea BH3 (high chloride and VFAs)	0.84	0.14
Pitsea BH1 (moderate chloride and VFAs)	0.55	0.17
CAMR (mature waste)	0.06	0.09

Solubility of zinc in leachates

Modelling results for zinc indicate that solubility trends are similar to those for cadmium (Figure 3.4.3). Zinc sulphide is oversaturated under reducing conditions at Ehs lower than −100 to −180 mV. As for cadmium it is likely that in methanogenic landfill, zinc sulphide precipitation is important in reducing zinc mobility.

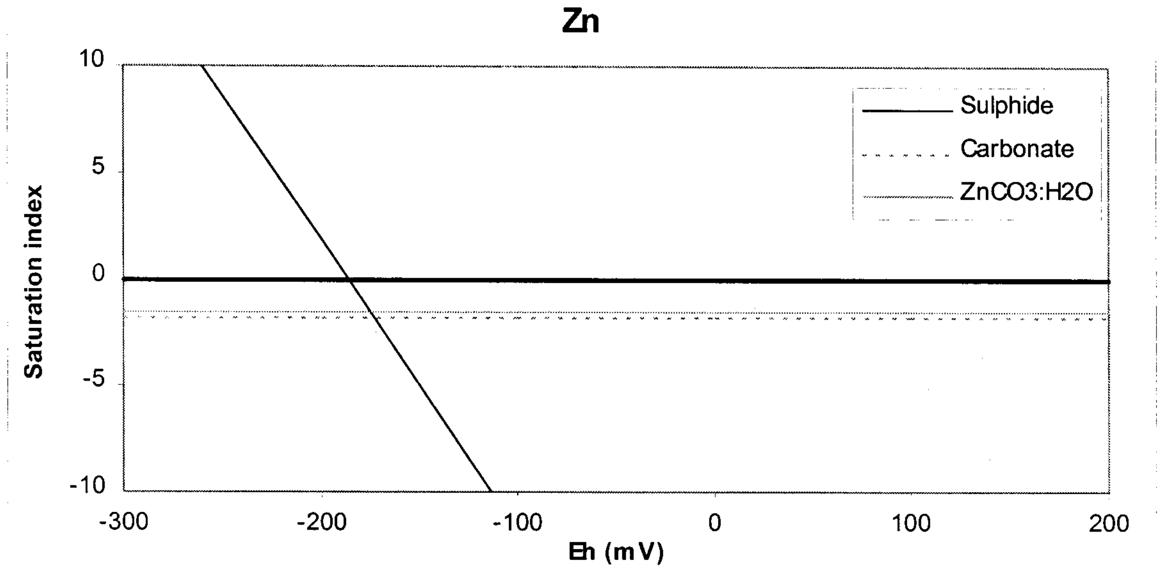


Figure 3.4.3 Saturation indices for zinc minerals in CAMR column leachates

Under more aerobic conditions, the two most likely precipitates are $ZnCO_3$ (smithsonite) and its hydrated equivalent $ZnCO_3.H_2O$, with the latter having a slightly higher saturation index. Investigations into zinc solubility in soil suggest that willemite (Zn silicate) and franklinite (Zn-ferric oxide) may also be important in limiting solubility (Lindsay, 1979). However, solubility products for the formation of these minerals were not available in the thermodynamic databases used in this study, therefore, they have not been included. Such limitations need to be borne in mind when evaluating modelling results and it is likely that the solubility modelling for zinc may be pessimistic in terms of the predicted solubility limits in leachates (i.e. predict unduly high zinc concentrations in leachate).

For the positive Eh values implied for the majority of the air sparged columns, zinc sulphide is likely to become soluble and, based on the available thermodynamic data, the two zinc carbonate phases will become solubility limiting phases. Having selected zinc carbonates as the likely solubility limiting phases in aerobic landfill leachate, the model has been used to predict the solubility limits for zinc in each leachate. The results of this solubility modelling indicate that in immature leachates with high chloride and VFAs, zinc solubility limits are between 14.7 and 4.7 mg/l whereas in mature post methanogenic leachates such as the mature CAMR waste, the solubility limits are around 3.6 mg/l (Table 3.4.2).

Laboratory results indicate that even for the aerobic columns, zinc concentrations remain below 1 to 2 mg/l. Measured zinc concentrations in the mature leachates are therefore quite close to the predicted zinc solubility limits, even for carbonate phases. Overall, the results of the experimental and modelling studies in combination suggest that zinc is retained in landfill under aerobic conditions and that precipitation of carbonates, or potentially less soluble silicate and iron oxide phases, may be a contributing process.

Table 3.4.2 Predicted solubility limits for $ZnCO_3.H_2O$ in a range of landfill leachates

	Zn solubility limit in Initial column leachates (mg/l Zinc)	Zn solubility limit in Final column leachates (mg/l Zinc)
Pitsea BH3 (high chloride and VFAs)	8.11	4.73
Pitsea BH1 (moderate chloride and VFAs)	14.77	6.22
CAMR (mature waste)	3.66	3.59

Solubility of chromium in leachates

As discussed in Section 3.3, chromium in landfill leachates will be present as Cr(III) which is relatively immobile. Solubility modelling results for chromium indicate the most likely precipitates are Cr_2O_3 and $Cr(OH)_3$ (Figure 3.4.4). Particularly for the CAMR waste columns, the measured chromium concentrations imply that Cr_2O_3 and amorphous $Cr(OH)_3$(A) would be supersaturated in the leachates.

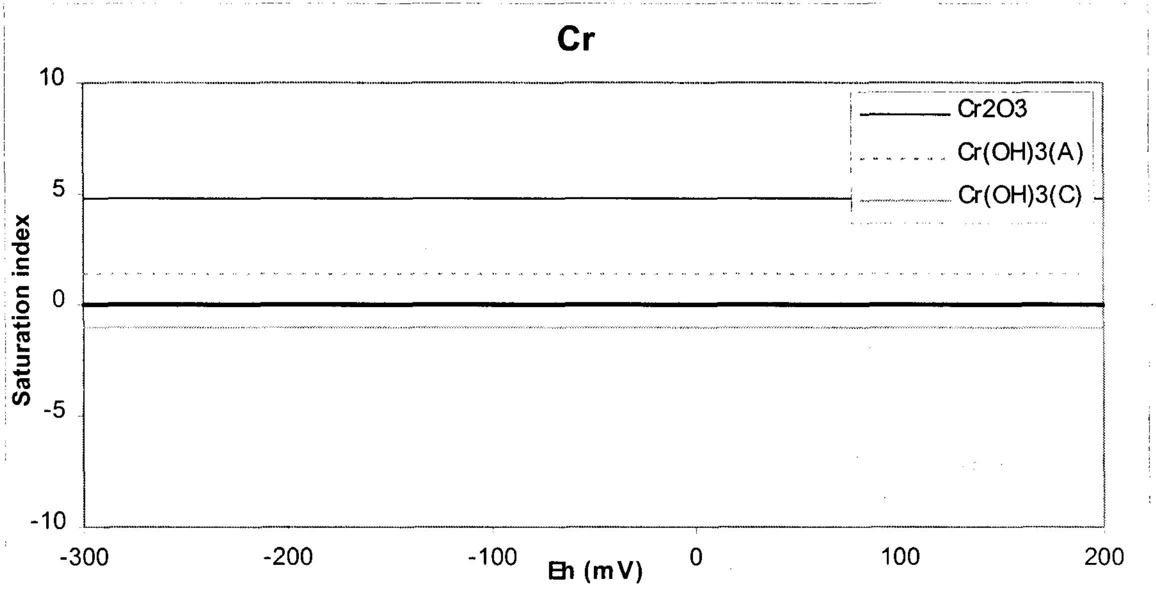


Figure 3.4.4 Saturation indices for chromium minerals in CAMR column leachates

Studies of chromium at contaminated sites indicate that chromium typically precipitates as amorphous $Cr(OH)_3$(A) and that, under different conditions, this amorphous form can crystallise as $Cr(OH)_3$ (C) or Cr_2O_3 (Palmer and Puls, 1994).

Geochemical modelling studies carried out by the US Environmental Protection Agency investigating $Cr(OH)_3$(A), concluded that chromium concentrations in groundwater contaminant plumes should be less than 0.05 mg/l, based on $Cr(OH)_3(A)$ solubility considerations in an entirely inorganic model (Palmer and Puls, 1994). In our study, organic complexation is included, with acetate being used as a generic organic ligand. Based on this slightly more sophisticated model, chromium solubility in leachate is predicted to be in the order of 0.23 to 0.37 mg/l for the VFA rich Pitsea leachates compared with measured values of around 0.1 to 0.5 mg/l. For the CAMR leachates the model predicts very low solubilities of 0.002 mg/l compared with measured concentrations in leachates generally below 0.1 mg/l.

The combined experimental and modelling results of this study suggest that in landfill leachates, organic complexation of chromium is important and may cause chromium solubility to be significantly elevated above values predicted by geochemical models based on inorganic complexation. In mature leachates with low organic contents, chromium hydroxide solubility is predicted to be very low and is likely to contribute to the immobilisation of chromium in landfill.

Table 3.4.3 Predicted solubility limits for chromium in a range of landfill leachates

	Cr solubility limit in Initial column leachates (mg/l Cr)	Cr solubility limit in Final column leachates (mg/l Cr)
Pitsea BH3 (high chloride and VFAs)	0.37	0.003
Pitsea BH1 (moderate chloride and VFAs)	0.23	0.004
CAMR (mature waste)	0.002	0.002

Summary of solubility modelling results

By comparing the modelling results with measurements from the experiments and with research on metals in soils and at contaminated sites, the following conclusions can be drawn from the solubility studies.

- metals such as iron, cadmium and zinc (and other metals such as lead and nickel) are likely to be present as insoluble sulphides in landfill under reducing conditions below about -150 mV to -200 mV. If aerobic conditions become established in landfill, sulphides will tend to be oxidised to soluble sulphates;

- under more aerobic conditions solubility limiting phases vary for different metals, but include carbonates and hydroxides;

- for cadmium, the modelling studies suggest that under aerobic conditions, the measured leachate concentrations (generally below 0.01 mg/l) are around an order of magnitude below predicted solubility limits for cadmium carbonate, and therefore that other mechanisms are limiting cadmium release;

- for zinc, the modelling studies suggest that under aerobic conditions, the measured leachate concentrations (generally below 1 to 2 mg/l) are close to predicted solubility limits, and therefore that precipitation of carbonates or less soluble silicate or iron oxide phases may be a controlling factor limiting zinc release; and

- modelling results for chromium indicate that organic complexation is important and may cause chromium solubility to be significantly elevated above values predicted by geochemical models based on inorganic complexation - in mature leachates with low organic contents, chromium hydroxide solubility is predicted to be very low and is likely to contribute to the immobilisation of chromium in landfill.

3.5 Modelling metal sorption in landfill

3.5.1 Basis for sorption modelling

The adsorption of metal ions to solid phases exerts a strong control on the concentrations of metal ions in solution and their movement through a solid matrix. Adsorption is recognised as being a major component of natural attenuation in aquifers, particularly those rich in organic material, and is the main cause of the long term retention of metals in soils (Alloway, 1990).

Mechanisms for removing ions from solution include ion exchange and specific adsorption. Ion exchange relates to the removal of ions from solution by permanent charge sites on silicate minerals and organic material. However, since heavy metal ions such as Cd^{2+} and Zn^{2+} must compete for exchange sites with much more abundant ions such as Ca^{2+} and Mg^{2+}, strong electrostatic sorption of heavy metals onto these sites is rarely expected (Ross, 1994). Instead, more specific mechanisms are needed to explain the retention of trace metals in soils, aquifers and waste. In PHREEQC, sorption is simulated as an equilibrium reaction, based on user specified sorption surface parameters and equilibrium constants (Appendix B).

Although sorption is a key process in controlling metal mobility in natural waters, it is complex and cannot generally be predicted in natural systems with the same degree of confidence as more simple chemical processes such as aqueous complexation and solubility. In landfill, where the matrix material is highly heterogeneous and alters in composition as the landfill matures, sorption processes are likely to be particularly complex and this may explain why very few attempts have been made to model sorption processes in landfill. The modelling study reported here makes some significant steps in translating and applying existing models to landfill systems but should be considered as a pilot study.

Parameters for the sorption of trace metals to surfaces such as iron hydroxide, silica and soils can be found in the literature. However, due to the variability of sorption processes between different media, it is common practice to carry out flask or batch tests to study metal uptake on the matrix being studied and to use the results to calibrate sorption models. This approach has been adopted in this study and the calibrated models have then been tested against the column experiments.

3.5.2 Sorption modelling of the batch experiments

Triplicate batch experiments were carried for out over a range of concentrations equating to 1, 10 and 100 g/tonne household waste(wet wt.) loadings for Cd, Zn and Cr on their own and for a combined case (Appendix A). Experiments at the higher loadings were prone to precipitation, which masked the effect of sorption, whereas experiments at lower loadings resulted in aqueous metal concentrations commonly below the standard detection limits of the analytical techniques. Therefore, following a review of the results, data from the 10 g/tonne individual metal experiments were selected for modelling.

In order to model sorption processes based on the surface complexation approach it is necessary to know the ratio of solid to liquid; to estimate surface parameters of solid phase; and to estimate the metal to surface complexation constant. Sorption models for the batch experiments were initially set up using the generic literature values and experimental parameters summarised in Table 3.5.1.

Table 3.5.1 Initial parameters for modelling batch sorption experiments

Parameter	**Value**	**Reference**
Mass of waste / litre of solution (g/l)	140	Experimental data
Specific surface area of waste m^2/g	500 to 5000	Tipping & Woof (1990) for organic rich soils
Site density of sorption sites eq/m^2	1×10^{-6} to 1×10^{-5}	Based on Tipping & Woof (1990) for organic rich soils
LogK $Cd^{2+} + SOH^0 = SOCd^+ + H^+$	-6.0	Brady (1992) for sorption to silica
LogK $Zn^{2+} + SOH^0 = SOZn^+ + H^+$	-3.0	Ivanovich et al. (1996) for sorption to silica/sandstone
LogK $Cr(OH)_2^+ + SOH^0 = SOCr(OH)_2 + H^+$	-4.0	Ivanovich et al. (1996) for sorption to silica/sandstone

For a particular solution, the positions of sorption equilibria are determined primarily by the concentration of sorption sites and the surface complexation, logK. Each of these parameters needs to be scoped in the optimisation procedure. As can be seen from Table 3.5.1, surface parameters vary over quite a wide range. Therefore, initial bounding cases to derive equilibrium constants runs were carried out using the maximum and minimum literature values for site densities and specific surface areas. In addition, there was some analytical variability in the measured final aqueous concentrations in the batch experiments and sorption calibration was carried out against both extreme high and low values.

As would be expected, the calibration runs using extreme literature values and experimental results produce a wide range of logK values (Appendix B). In order to impose some constraints on the selection of appropriate sorption parameters, an assumption was imposed: that the surface complexation constants for cadmium, zinc and chromium to household waste should be close to, or stronger than the literature values for sorption to silica/sandstone. Taking this assumption into account, the preferred surface parameters are at the low end of literature values for site densities and specific surface area. The parameters selected are detailed in Table 3.5.1.

3.5.3 Sorption modelling of column experiments

The sorption model calibrated against the batch experiments has been applied to the column experiments. Experimentally determined metal loadings for the Pitsea and CAMR wastes have been entered into the model and predictions made of leachate concentrations. The predictions are then compared with experimental measurements of leachate concentrations.

Table 3.5.2 Summary of input parameters and validation results for modelling column experiments

Sorption model parameters			
Surface area m2/g	500	Cd eqm coef.	-3
Site dentisy Eq/m2	1.00E-06	Zn eqm coef.	-2.25
Mass matrix g/dm3	2300	Cr eqm coef.	-4.05
Total sites Eq/dm3	1.2		
Validation Results			
CAMR	Cd	Zn	Cr
Loading mg/kg wet waste	70	735	113
Measured leachate concentration mg/l	0.01 to ~ 0.25	0.18 to ~3.0	0.05 to ~ 0.2
Modelled concentration mg/l	0.11	0.19	0.81
Pitsea BH1			
Loading mg/kg wet waste	1.1	311	84
Measured leachate concentration mg/l	0.02 to ~ 0.08	0.04 to ~1.0	0.14 to ~ 0.3
Modelled concentration mg/l	0.01	0.40	1.22
Pitsea BH3			
Loading mg/kg wet waste	1.8	1353	52
Measured leachate concentration mg/l	0.01 to ~ 0.15	0.1 to ~1.0	0.2 to ~ 0.5
Modelled concentration mg/l	0.01	1.28	0.61

The validation results in Table 3.5.2 demonstrate that the sorption model developed from the batch experiments provides a reasonable representation of measured metal concentrations in the column leachates. In the experimental data, for a specific metal in a particular waste type, there was a considerable range of leachate metal concentrations. It should be noted that very high concentrations, that are considered likely to be anomalous, have been excluded from the ranges quoted in Table 3.5.2.

The pilot sorption model approach represents an improvement on the use of dissociation constants (Kds), in particular where predictions are required across a range of loadings. For example, for cadmium, loadings are around 60 to 70 times higher in the CAMR columns than in the Pitsea BH1 columns, but measured leachate concentrations were only slightly higher in the CAMR columns. A simple Kd approach assumes a constant ratio between loading and leachate concentrations and would predict leachate concentrations to be 60 to 70 times higher for the high loading case. By contrast, the pilot sorption model predicted concentrations to be around 11 times higher in the CAMR leachates.

Because of the ranges in experimental data, it is difficult to rigorously test the sorption model. However, for cadmium and zinc, the model predictions are within, or very close to, the range of experimental data. For chromium, the sorption model tends to over-predict leachate concentrations. This may be a result of poor calibration against the batch experiments, where VFA concentrations (which are an important control on chromium speciation) were poorly constrained.

In translating the sorption model from the batch experiments to predict leachate concentrations from metal loaded waste in the columns, there are four main factors that need to be taken into account.

1. In batch tests, metal sorption is generally investigated under conditions in which the ratio of waste to liquid was relatively low. In the experiments conducted by Minton, Treharne & Davies Ltd (MTD) (EPG 1/7/66), 200g wet waste was added to 1 litre of metal loaded leachate. By contrast, in column experiments, which are more representative of real landfill conditions the ratio of waste to liquid is much higher with solid waste forming 60 to 70 % of the bulk volume. Therefore, the concentration of sorption sites per unit volume of leachate is far higher in the columns and higher Kds would be expected.

2. In batch tests it is rarely possible to investigate metal soprtion under high metal concentrations because the low solubilities of trace metals causes precipitation to occur. In the Minton, Treharne and Davies experiments, extensive precipitation occurred for loadings greater than 10 g/tonne household waste (wet wt.). By contrast, analysis of the column waste demonstrates loadings in excess of 1000 g/tonne MWS (wet wt.) for zinc in some columns. The validity of the low concentration sorption models at higher loadings/concentrations therefore needs to be assessed.

3. In batch tests, the regular agitation, and slurry consistency of the waste will encourage reasonable mixing and, therefore, relatively homogenous conditions. By contrast, waste-leachate equilibria in the columns will be highly heterogeneous, with leachate being distributed between isolated impermeable areas and interconnected preferential flow paths.

4. Differences in leachate chemistry (e.g. pH, alkalinity, VFA concentrations) between the batch and column experiments.

The factors above may well be very important in controlling metal concentrations in leachate. Although this pilot study shows some cause for encouragement, it is therefore considered unwise to attempt to use this relatively simple sorption model to predict metal leachate concentrations in landfill based on different metal loadings.

3.6 Summary of modelling programme

The primary purpose of the modelling studies was to improve understanding of the controlling processes and to predict whether landfill maturation, and in particular the potential return of aerobic conditions, might lead to a significant release of metals from landfill. The main results of the modelling studies are summarised below.

- This study represents one of the first attempts to apply the well-established modelling techniques developed through research into metal behaviour in soils and groundwaters to the landfill context.

- Modelling has been carried out on a range of leachates from the experimental programme. The leachates included: leachates rich in chloride and VFAs from Pitsea landfill; mature methanogenic leachates from the initial CAMR columns and "supermature" post-methanogenic, low chloride leachates from the late stages of the CAMR experiments.

- Aqueous speciation controls the toxicity of some metals and, by influencing processes such as precipitation and sorption, also controls metal mobility. For zinc and cadmium, speciation was found to be dominated by carbonates and the divalent metal ion for all leachate types, with chloride complexation being important for cadmium in immature leachates. Chromium was found to be strongly complexed with organics in immature leachates, potentially leading to enhanced mobility compared with hydroxide dominated speciation in mature leachates.

- Solubility modelling studies for cadmium indicates that sulphide precipitation is likely to be important in immobilising cadmium in anaerobic landfill. Under aerobic conditions, predicted solubility limits are around an order of magnitude higher than measured leachate concentrations (generally below 0.01 mg/l), suggesting that other mechanisms are limiting cadmium release.

- Solubility results for zinc also suggest that sulphide precipitation is likely to be an important retention mechanism in anaerobic landfill. Under aerobic conditions, the predicted solubility limits for zinc carbonate are close to measured leachate concentrations (generally below 1 to 2 mg/l) suggesting that precipitation of carbonates or a less soluble silicate or iron oxide phases may be limit zinc release.

- Chromium does not form a simple sulphide precipitate. Modelling results for chromium indicate that irrespective of redox conditions, in immature leachates solubility is enhanced due to organic complexation whereas in mature leachates with low organic contents, chromium hydroxide solubility is predicted to be very low and is likely to contribute to the immobilisation of chromium in landfill.

- It is likely that adsorption is a major component of metal retention in landfill and prevents the release of metals at concentrations below their solubility limits. Perhaps due to the highly heterogeneous nature of landfill material, very few attempts have been made to model sorption processes in landfill. The pilot study reported here makes some significant steps in translating and applying existing models to landfill systems. Although the models provide reasonable results at low metal concentrations, they tend to under-predict the capability of landfill to immobilise high loadings of metals and therefore cannot currently be used to predict "safe" operational metal loading ratios.

4. DISCUSSION OF RESULTS

4.1 Introduction

The main objectives of this project were: to determine the chemical stability of co-disposed metals under a range of conditions likely to be encountered at different phases of landfill stabilisation, particularly during the later and final stages of stabilisation; and to provide additional data on metal/waste loading ratios that may be safely disposed.

In the experimental programme, a range of leachate types were investigated. These included very mature leachates from CAMR experiments and leachates from Pitsea co-disposal landfill with elevated chloride and fatty acid concentrations. In addition, the experimental waste had a reasonable range of metal loadings, with some columns containing metals at more than 10 times WMP26F guideline levels, as detailed in Section 2.4.

The following discussion focuses on the role of precipitation and sorption in immobilising metals in landfill and draws implications for metal loadings and metal leachate concentrations from landfill.

Particular attention was paid to any change in metal leachability following a transformation of the waste from anaerobic to aerobic conditions. This transformation is anticipated to occur gradually in aged landfills but for purposes of simulating the chemical changes in a realistic time scale, this effect was artificially stimulated in the lab experiments. Various sample handling and analytical issues have become apparent as a result of undertaking this type of work on real waste and the experimental work should be viewed as an initial screening for 'gross' wash out of heavy metals following a redox change in the waste rather than an accurate assessment of leached metal concentrations which may or may not arise in a field situation.

4.2 Discussion of controlling processes

In order to assess the stability of heavy metals in landfills, it is important that the full range of processes controlling metal retention and mobility are understood and accounted for. Extensive research has demonstrated that there are a number of competing processes that, in combination, control metal within the environment. Precipitation/dissolution reactions and the interaction of metals with matrix via adsorption have been identified as the most important processes in controlling metal mobility in soils and groundwater (Alloway, 1990; Domenico and Schwartz, 1990; Ross 1994).

The results of the modelling studies indicated that precipitation is likely to be an important process in immobilising metals in landfill. Under anaerobic conditions, metals that form sulphides (e.g. zinc, cadmium, nickel and lead) will tend to be immobilised as sulphides. Because sulphide solubility is highly dependent on Eh, and Eh cannot be reliably measured and is likely to vary spatially, it is not possible to predict theoretical concentrations of metals in anaerobic leachate based on sulphide solubility constraints.

A further important result from the modelling studies was the identification of additional solubility limiting phases for the studied metals, including carbonates and hydroxides. Presuming that other factors such as alkalinity and pH remain reasonably stable, these phases should not be affected by redox changes associated the development of aerobic conditions in landfill. This implies that these phases have the potential to retain metals in landfill in the long term.

It is likely that adsorption is a major component of metal retention in landfill, as it is in soils and groundwaters (Alloway, 1990; Domenico & Schwartz, 1990; Ross, 1994) and that sorption prevents the release of metals at concentrations below their solubility limits. The pilot study reported here makes some significant steps in translating and applying existing models to landfill systems. However, validation of the model against column experiments indicated that although the models provide reasonable results at low metal concentrations, they tend to under-predict the capability of landfill to immobilise high loadings of metals.

There are a number of reasons that make modelling sorption processes in landfill difficult. These include:

- the high organic content of waste compared with the better studied soil and aquifer systems;
- the high concentrations of inorganic and organic ligands in landfill leachates; and
- the highly heterogeneous nature of landfill material and, the wide range of surface types available for sorption.

The modelling studies in this project were based on the principles of adsorption by surface complexation, which have been widely applied to soil and aquifer systems, and essentially involves sorption to specific sites on mineral surfaces such as iron and manganese oxides, hydroxides and amorphous aluminosilicates. Other adsorption processes, such as cation exchange, which involve sorption to the charged surfaces of clays and the pH dependent charge sites of organic matter, are generally considered to be less important for immobilising trace metals in soils. This is due to the excessive competition with more abundant ions such as Ca^{2+} and Mg^{2+} (Ross, 1994).

Models have also been developed to simulate the specific sorption of metals to organic humic and fulvic acids (Tipping & Hurley, 1992; Read, 1997). However, in surface and groundwater studies, these organics are typically considered to be part of the mobile fraction. By contrast, in landfill the abundant organic matrix will act as a surface for adsorption and will contribute to metal retention.

It is likely that additional adsorption processes, relating largely to the organic content of landfill material, are the probable explanation for the under-prediction of sorption model in the validation against column experiments in this study. The model was calibrated against batch experiments at relatively low metal concentrations (to avoid precipitation). It is possible that at higher concentrations in the columns, competition by heavy metals with more abundant ions for organic cation exchange or immobile humic acid type sites becomes much more important.

An additional cause of the under-prediction of the simple sorption models may be the heterogeneous nature of the columns. For example, it is quite likely that both in the columns and in landfill, immobilising processes are in reality a combination of precipitation, in hydrodynamically isolated portions of the waste, and sorption along preferential flow paths.

Overall, this pilot study provides an indication of the likely complexity of sorption processes in landfill. Clearly, further carefully designed experimental and modelling studies, including careful consideration of heterogeneity and preferential flow paths, are required before sorption models can be used to inform waste management guidelines. Nonetheless, the pilot study has provided a useful insight into potential controlling processes and, even as it stands, represents a significant advance on the use of simple distribution coefficients (Kds) that do not account for the influence of varying metal concentrations, aqueous complexation, pH controls or variability of surface types.

4.3 Implication of results for UK waste management guidance

4.3.1 Implications for metal loadings

The solubility limiting phases identified in this study for aerobic landfill were carbonates for cadmium and zinc and hydroxide for chromium. These are in general agreement with research into soils and contaminated sites, although for zinc in soils additional more insoluble silicate and iron oxide phases have also been identified. Predictions in this study of solubility limits for zinc may therefore portray an unduly pessimistic picture.

Solubility limits were calculated for each of the three metals studied in each of the leachate types at the beginning and end of the column experiments. In general, solubilities were predicted to be highest in the Pitsea wastes, due to the high concentrations of organics and chloride, and low in the CAMR wastes. Therefore, the solubility limits of metals in Pitsea BH1 and CAMR leachates are used to provide benchmarks against which to compare guideline metal loadings in the draft of WMP26F. Solubilities are represented as concentrations of metals in mg/dm^3 for the specified leachate composition. Therefore, for comparative purposes, the draft WMP26F guideline values based on mg/kg wet waste have been converted into an equivalent mg/l for leachate, based on an assumed waste density of 1 kg/tonne and a porosity of 30%.

Table 4.3.1 Comparison of modelled solubility limits for aerobic precipitates in moderately mature and mature leachates with WMP23F guidelines

	Moderately mature waste, E.g. Pitsea BH1	Mature waste E.g CAMR columns	WMP26F Guidelines (assuming waste 1kg/t and porosity 30%)
Cd mg/l	0.55	0.09	33
Zn mg/l	8.1	3.5	330
Cr mg/l	0.23	0.002	330

The comparison in Table 4.2.1 indicates that the guideline loadings of each of the metals studied are likely to cause precipitation metal salts under aerobic conditions, assuming equilibrium with landfill leachate. In reality, equilibrium will not be attained immediately, particularly in settings such as co-disposal trenches. However, assuming that reasonable mixing and buffering occurs, significant precipitation is expected. Under the anaerobic conditions present in young landfill, sulphide precipitation will also occur for most metals as the leachate percolates through the landfill.

4.3.2 Implications for metal concentrations in landfill leachate

In addition to acting as an immobilising process for metals in immature landfill, precipitation is also likely to limit metal mobility in mature landfill, if aerobic conditions become re-established. In mature landfill, the leachate will have lower concentrations of complexing ligands such as VFAs and chloride, and this will tend to favour precipitation.

As indicated by modelling studies on the experimental columns, some of the measured leachate concentrations were close to values predicted by the solubility models for aerobic conditions. For cadmium, measured leachate concentrations were generally lower than solubility predictions whereas for zinc, there was a reasonable agreement between measured and predicted concentrations based on carbonate solubility. Organic complexation emerged as an important factor for chromium, leading to potentially significantly higher concentrations in moderately mature leachates than in mature leachates.

The prediction of leachate concentrations is important when considering groundwater protection. In particular Regulation 15 of the WMLR 1994 requires that operators demonstrate that adequate measures have been taken to prevent discharges of List I and List II substances, which include heavy metals, to groundwater.

Predicted leachate concentrations for moderately mature and mature leachates, based on the Pitsea BH1 and CAMR columns respectively, and based on solubility constraints under aerobic conditions, are compared with EC Drinking Water Standards in Table 4.2.2 .

Table 4.3.2 Comparison of modelled solubility limits for aerobic precipitates in moderately mature and mature leachates with EC Drinking Water Standards

	Moderately mature waste, Eg Pitsea BH1	Mature waste Eg CAMR columns	EC Drinking Water Standards
Cd mg/l	0.55	0.09	0.005
Zn mg/l	8.1	3.5	5.0
Cr mg/l	0.23	0.002	0.05

Table 4.2.2 indicates that in moderately mature landfill, assuming only aerobic precipitates, leachate concentrations of all metals studied are likely to be significantly above ECDWS. However, in moderately mature landfill, redox conditions will be very reducing throughout the acetogenic and methanogenic phases, and under these conditions sulphide precipitation is likely to be an important immobilising processes. Given the focus of this project on the later stages of landfill stabilisation, the more important figures are those for the CAMR leachate. Here, the leachate concentrations based on solubility considerations are predicted to be below ECDWS for zinc and chromium, but above ECDWS for cadmium.

The discussion above suggests that solubility is a potentially important mechanism in limiting metal release from landfill under aerobic, as well as anaerobic conditions. Model predictions always need to be applied with caution. However, the results of this project demonstrate how models can be used to predict conservative/worst case leachate concentrations for source terms in risk assessments, in this case assuming that aerobic precipitation is the only metal retention mechanism. Having identified solubility as an important control, and one that lends itself to experimental and modelling investigation, scope may exist to carry out further studies to expand and develop confidence in the findings of this study.

4.3.3 Implications for long term sustainability of landfill

One of the key issues in landfilling is how to achieve environmental protection in the long term and thus to address the aims of sustainable development, as discussed in Waste Management Paper 26B (DoE 1995). Over recent years there has been considerable debate regarding the best design and operational practices to minimise the long term pollution potential from landfill. In the UK extensive research has investigated the concept of the "flushing bioreactor", where water ingress and moisture movement are actively promoted to optimise microbial degradation of waste organic fractions (Harris et al., 1994; Walker et al., 1997) and a number of studies have investigated ways to accelerate water circulation, and therefore degradation (Blakey et al., 1996; Powrie & Beavan, 1998).

Much of the debate regarding landfill sustainability has focused on the potential for pollution from the major leachate pollution parameters such as COD, ammonia and chloride. Metal concentrations in leachate are usually low, and tight controls on metal releases to groundwater from operational landfills are in place under Regulation 15 of WMLR 1994. However, this study aimed to investigate landfill sustainability from the perspective of potential metal release, in the long term.

Experimental studies were successful in simulating mature landfill conditions and leaching waste with several bed volumes of synthetic rainwater within manageable experimental timescales of around 1000 days. The results showed that less than 1% of metals were leached from the columns, indicating that metal release is maintained at very low levels. However, it is clear that metal levels cannot be minimised in the same way as biodegradable leachate pollutants. Therefore, it is important that the potential impacts of long term landfill maturation on metal release are understood.

Based on the results of the modelling studies, some of the key controls on long term metal mobility, and therefore landfill sustainability, are discussed below.

Influence of organic and organic complexation

Due to effects such as the decline of microbial activity and washout, both the organic and inorganic composition of leachates evolve as landfills mature. Modelling in this study has demonstrated that complexation with organic ligands (particularly for chromium) and inorganic ligands such as chloride (particularly for cadmium) is important in moderately mature leachates. For chromium, solubility studies indicated that complexation with organic ligands could cause chromium solubility to be as much as two orders of magnitude higher in moderately mature VFA-rich leachates than in mature leachates. This is because aqueous complexation is "competing" against precipitation and causing solubility to increase. Sensitivity studies were not carried out using the sorption model, however, it is likely that similar considerations will apply, and that overall, the high concentrations of inorganic and organic ligands in moderately mature leachates will tend to enhance metal mobility. Conversely as landfills mature, it is reasonable to assume that the reduction in concentration of complexing ligands will tend to favour immobilising processes and lead to reduced metal mobility.

Influence of Aerobic Return

The solubility of many metal precipitates is known to be strongly redox sensitive. In particular sulphides that are stable under reducing conditions, become more soluble as Eh rises, potentially leading to an increase in metal mobility.

Experimental and modelling results in this study confirmed that metal sulphides could become solubilised in aerobic waste. In particular, the colour change from black to red and the flush of sulphate from the air sparged columns confirmed that sulphide oxidation was occurring. However, the rate of metal release from the columns did not increase, indicating that additional processes, probably a combination of precipitation of carbonates/hydroxides and sorption, were immobilising the metals.

Another dramatic feature of the change to aerobic conditions in the waste was the sudden disappearance of ammoniacal nitrogen in the emergent leachate, this effect becoming apparent only when the black front of the anaerobic waste zone had progressed virtually to the bottom of the column.

Experimental evidence also confirmed that aerobic return would lead to iron and manganese oxyhydroxide precipitation. These ochre minerals have a strong affinity for heavy metals cations which they scavenge by adsorption and co-precipitation. Aerobic conditions may therefore lead to enhanced sorption properties in landfill waste and it is possible that sulphide solubilisation could be substantially offset by increased co-precipitation and sorption with ochre minerals.

Influence of pH

There are two main processes by which pH controls metal mobility. First, the solubility of some metal precipitates is pH sensitive. For example, carbonate minerals will tend to be more soluble under acidic conditions, whereas, metal oxides tend to be less soluble under acidic conditions. Secondly, increasing acidity can significantly reduce the proportion of metals adsorbed, i.e. increase mobility.

Experimental results indicated that pH in the columns was relatively stable and in general rose slightly through the course of the leaching experiments. A reduction in pH was noted when the oxic front reached the base of the columns in first two CAMR columns to become entirely aerobic. This may have been caused by proton release associated with the precipitation of $Fe(OH)_3$ as noted with acid mine drainage. However, presumably due to the buffering potential of the landfill waste, the observed pH drop was small (from pH 7 to pH 6.8) and temporary (~150 day) and was not associated with any obvious metal release.

Data from a review of landfill leachate compositions in the UK (Robinson 1996) and long term monitoring data from landfills in Germany (Ehrig, 1991) both indicate that the pH of the landfill leachate varies in a predictable way. During the early stages of landfill history, leachates exhibit a relatively wide spread of pH, in some cases as low as pH 5. With time, pH tends to rise slightly and have a narrower range of values. UK data from methanogenic landfills ranges from 6.8 to 8.2 with a mean value of 7.35 (Robinson, 1996). The stabilisation and gradual rise of pH in landfills will tend to be beneficial with regard to metal retention in landfill.

5. CONCLUSIONS

This study represents one of very few detailed investigations into the long term fate of metals in landfill. The project combined long term column experiments and modelling studies.

For the laboratory experiments, three types of household waste were packed into plastic columns and irrigated with synthetic rainwater. Six columns of each waste type were set up and, after stabilisation, three of each set of columns were turned more aerobic by sparging moist air across the headspace. For the majority of air-sparged columns, a change in colour from black to brown and indicators such as ammoniacal-N concentrations in the leachate confirmed that more aerobic conditions had been established in the waste. For all columns, at least 3 bed volumes of synthetic rainwater had passed through the waste by the end of the experiments

Detailed monitoring of the leachate confirmed that heavy metals such as cadmium, zinc and chromium are retarded effectively in methanogenic household waste and continue to be retarded in well-degraded, more aerobic waste. There was no consistent contrast between metal concentrations in leachate from the anaerobic and predominantly aerobic columns, and mass balance evaluation indicated that less than 2% of any heavy metal was leached by the end of the experiment. By contrast, monitoring of the leachate indicated washout for conservative species such as chloride and enhanced sulphate release from some of the aerobic columns.

Modelling studies have helped to identify the likely mechanisms for metal retention. The results indicate that precipitation is likely to be an important process in immobilising metals in landfill. Under anaerobic conditions, metals that form sulphides (e.g. zinc, cadmium, nickel and lead) will tend to be immobilised as sulphides.

A further important result from the modelling studies was the identification of additional solubility limiting phases for the studied metals, including carbonates and hydroxides. Presuming that other factors such as alkalinity and pH remain reasonably stable, these phases should not be affected by redox changes associated the development of aerobic conditions in landfill. This implies that these phases have the potential to retard metals in landfill in the long term.

Overall, the experimental studies indicate that cadmium, zinc and chromium at concentrations up to 100 mg.kg^{-1} (10 to 100 times EC guideline levels) are immobilised long-term under aerobic and anaerobic conditions. The modelling studies indicate that the metals are precipitated mainly as sulphides under anaerobic conditions. In the longer term, assuming adequate buffering by carbonates, and stable pH, precipitates such as hydroxides and carbonates, have the potential to limit zinc and chromium concentrations in leachate to close to EC Drinking Water Standards, and for cadmium to around an order of magnitude higher than EC Drinking water standards. In aerobic landfill, it is likely that solubility processes will be supplemented by adsorption, particularly to newly formed iron and manganese oxyhydroxides, to limit metal release.

6. REFERENCES

Allison, J. D., Brown, D.S. and Novo-Gradac, K. J., (1991) MINTEQA2/PRODEFA2 A geochemical assessment model for environmental systems. Version 3.0 User's Manual, US Environmental Protection Agency Report EPA/600/3-91/021.

Alloway, B. J. (1990) Heavy Metals in Soils, Blackie and Son, Glasgow.

Arthur, D.J. and Read, D. (1996) PHREEQE 96 Theoretical Overview. UK Department of the Environment/Her Majesties Inspectorate of Pollution Draft Report.

Blakey, N.C., Reynolds, P.J. Bradshaw, K and Young C.P. (1996) Landfill 2000 – A field trial of accelerated waste stabilisation. UK Department of the Environment Waste Technical Division, Report CWM 050/96.

Blackley, S., Hodgson, J. and Wootton, N. (1995) The effects of old landfill sites on groundwater quality – Phase 1. R&D Note 415 National Rivers Authority, Bristol.

Brady, P. V. (1992) Silica surface chemistry at elevated temperatures. *Geochimica et Cosmochimica Acta*, **56**, 2941-2946.

Christensen, T.H. (1989) Cadmium soil sorption at low concentrations: VIII. Correlation with soil parameters. *Water, Air and Soil Pollution* **44,** 71-82.

Council of the European Communities (1980), Council Directive of 17 December 1979 on protection of groundwater against pollution caused by certain dangerous substances (80/68/EEC), Official Journal of the European Communities, L20 43-47.

Department of the Environment (1992) EC draft directive on the landfill of waste. The Government's response to the seventh report from the House of Commons Select Committee on the Environment. Presented to Parliament by the Secretary of State for the Environment by Command of Her Majesty, Cm 1821, London HMSO.

The Waste Management Licensing Regulations 1994, SI 1056/1994, HMSO, London.

Department of the Environment (1995) Landfill Design, Construction and Operational Practice – Draft for consultation. UK Department of the Environment Waste Management Paper 26B, HMSO, London.

Domenico, P.A. and Schwartz, F.P. (1990) Physical and Chemical Hydrogeology, John Wiley & Sons, Toronto.

Dzombak, A. and Morel, MM. (1990) Surface complexation modelling: Hydrous Ferric Oxide, Wiley, New York.

Environment Agency (1999) Interim internal guidance on the interpretation and application of Regulation 15 of the Waste Management Licensing Regulations, 1994 (The Protection of Groundwater) with respect to Landfill. Draft for Consultation. Environment Agency, Bristol.

Falck, W.E. and Read, D. (1996) CHEMVAL II: A co-ordinated research initiative for evaluating and enhancing chemical models used in radiological risk assessment. Final report on the thermodynamic database. CEC EUR Report 16897.

Harris R.C., Knox, K and Walker, A.N. (1994) A strategy for the development of sustainable landfill design. Proceedings of the Institute of Waste Management, January 1994, 26-29.

Ivanovich, M., Gardiner, M.P., Baumann, T., Delakowitz, B., Fruhstrofer, P., Klein, T., Niessner, R., Kim, J., Tellam, J.H., Lloyd, J.W., Kleinert, U., Read, D., Wilcox, D., Ross, D. and Thomas J.T. (1996) The role of colloids in the transport of pollutants in shallow groundwaters: development of monitoring and assessment procedures. CEC Contract EV5V-CT-92-0228 Draft Report.

Knox, K. (1989) A review of technical aspects of co-disposal. UK Department of the Environment Waste Technical Division Research Report No. CWM 007/89.

Lindsay, W. L. (1979) Chemical equilibria in soils. Wiley, New York.

McKinley, I.G. and Scholtis, A (1991) A comparison of radionuclide sorption databases used in recent performance assessments. Paper presented at the NEA Sorption Workshop, Interlaken, 14-18 October 1991.

Palmer, C.D. and Puls, R.W. (1994) Natural attenuation of hexavalent chromium in groundwater. US Environmental Protection Agency Ground Water Issue EPA/540/s-94/505.

Parkhurst, D.L., Thorstenson, D.C. and Plummer, L.N. (1980) PHREEQE - a computer programme for geochemical calculations. US Geological Survey Report No. PB81 167801.

Parkhurst, D.L. (1995) User guide to PHREEQC – A computer program for speciation, reaction-path, advective transport, and inverse geochemical calculations. US Geological Survey, Water Resources Investigations Report 95-4227.

Powrie W. and Beavan, R. (1998) Hydraulic conductivity of waste – current research and implications for leachate management. Wastes Management, November 22-23.

Read, D. ed. (1997) CHEMVAL II: A co-ordinated research initiative for evaluating and enhancing chemical models used in radiological risk assessment. Final report. CEC EUR Report 16648.

Reynolds, P., Juggins, P., Oliver, R. and Blakey, N.C. (1993) Heavy metal co-disposal to landfill: physico-chemical factors affecting the metal binding capacity of refuse. UK

Department of the Environment Waste Technical Division Contract PECD 7/10/263, Draft Report.

Robinson, H.D., (1995) A review of the compostion of leachates from domestic wastes in landfill sites. Report No CWM/072/95 UK Department of the Environment Waste Technical Division, London.

Ross, S. M. (1994) Toxic metals in soil-plant systems. John Wiley & Sons, Chichester, UK.

Sposito, G. (1981) The thermodynamics of soil solutions. Oxford University Press, Oxford.

Sposito, G. (1994) Chemical Equilibria and Kinetics in Soils, Oxford University Press, New York.

Tipping, E. and Hurley, M.A. (1992) Modelling the binding of cations by humic substances, UK Department of the Environment/Her Majesties Inspectorate of Pollution Report No. RR/089.

Waste Management Paper No 26.F, (1994) Landfill Co-disposal. A draft for External Consultation, UK Department of the Environment.

APPENDIX A THE EXPERIMENTAL PROGRAMME

CONTENTS

A.1 EXPERIMENTAL METHODS.

A.2 EXPERIMENTAL RESULTS

LIST OF FIGURES

LIST OF TABLES

A.1.1 Artificial rainwater recipe

The recipe for the artificial rainwater given below is based on a moderately dirty UK rain obtained from Loose How, North Yorkshire Moors. Recipe obtained from National Power Research and Engineering.

Table A1.1.1 Artificial rainwater recipe

Salt	**Salt conc. (mg/l)**	**Ion concentration (mg/l)**							
		Na^+	**K^+**	**Ca^{2+}**	**Mg^{2+}**	**NH_4^+**	**NO_3^-**	**SO_4^{2-}**	**Cl^-**
NaCl	3.7577	1.48							2.28
$CaCl_2.2H_20$	1.4847			0.40					0.72
$(NH_4)_2SO_4$	0.3634					0.10		0.26	
NH_4NO_3	3.4017					0.77	2.64		
KCl	0.2013		0.11						0.10
$MgCl_2.6H_20$	1.0470				0.13				0.37
$MgSO_4.7H_20$	0.8873				0.09			0.35	
H_2SO_4	5.6488							5.53	
Total		**1.48**	**0.11**	**0.4**	**0.22**	**0.87**	**2.64**	**6.14**	**3.47**

A.1.2 Artificial leachate recipe

Artificial leachate recipe designed to mimic the typical analysis of a methanogenic leachate from cell 3, Compton Bassett landfill, Wiltshire. Taken from Robinson and Gronow 1997.

Table A1.2.1 Artificial leachate recipe

		Ion concentration (mg/l)										
Salt	**Salt conc. (mg/l)**	**Ammoniacal -N (as N)**	**Chloride**	**Nitrate-N (as N)**	**Nitrite-N (as N)**	**Sulphate (as SO_4)**	**Carbonate**	**Phosphate-P (as P)**	**Sodium**	**Magnesium**	**Potassium**	**Calcium**
NH_4Cl	3700.0	968.22	2455.14									
$NaNO_3$	3.0			0.49					0.81			
$NaNO_2$	0.4				0.08				0.13			
NaH_2PO_4	3.5							0.90	0.67			
$MgSO_4.7H_20$	66.0					25.76				6.44		
$MgCl_2.6H_20$	1280.0		443.56							152.08		
KH_2PO_4	8.0							1.80			4.53	
KCl	1600.0		761.39								838.61	
$CaCl_2.2H_20$	343.0		164.45									93.97
$NaHCO_3$	4800.0						3428.57		1314.29			
Total Concentration (mg/l)		**968.22**	**3824.55**	**0.49**	**0.08**	**25.76**	**5714.29**	**2.69**	**1315.90**	**158.52**	**843.14**	**93.97**

A.1.3 Sample preparation

Bulk solid waste samples were coned and quartered prior to sub-sampling. Sub-samples were dried at 105°C to constant weight and ground to < 1mm prior to analysis. Final analysis of column contents involved drying and grinding the entire quantity of waste present.

Column leachates were centrifuged at 500g for 15 minutes in sealed tubes with a headspace of 70:30 nitrogen:carbon dioxide.

A.1.4 Analytical methods - heavy metals and sulphur

Dried, ground solid waste samples for metal analysis underwent an acid digestion of 2.5g of dried, ground, material with 40 mls of acid mixture containing 3 parts, 50% hydrochloric acid and 1 part concentrated nitric acids. Analysis of the digest was by ICP-OES for the heavy metals and sulphur. Lithium and other cations were also analysed by this method.

Analysis of heavy metals in leachate was undertaken on sub-samples of centrifuged leachate. 5 mls of 50% HNO_3 was added to 20 mls of the centrifuged leachate supernatant immediately after centrifuging.

A.1.5 Analytical method - ammoniacal nitrogen

Ammoniacal nitrogen was carried out by steam distillation into 10% boric acid and titration with 0.02N H_2SO_4 using a Buchi 339 Distillation/titration unit according to Buchi standard method.

A.1.6 Analytical method - chloride

Analysis of chloride was carried out by titration with silver nitrate using potassium chromate indicator according to MEWAM 51.

A.1.7 Analytical methods - pH and Eh

pH of leachate samples was measured by combination pH electrode and a Hanna Instruments 8417 pH meter taking readings soon after sampling the leachates from the anaerobic environments. Measurements were taken while under a stream of 70:30 nitrogen:carbon dioxide gas mixture. The pH meter was calibrated using standard buffer solutions prior to use. Eh determinations were made using a standard platinum redox electrode coupled to The Hanna 8417 meter. Redox calibration was checked using standard buffers saturated with quinhydrone.

A.1.8 Analytical method - Electrical conductivity

Electrical conductivity was determined according to MEWAM 14 using a Kent EIL 5007 conductivity meter with a EIL 2000 conductivity cell.

A.1.9 Analytical method - gas analysis

Gas analysis was undertaken using a Perkin Elmer 8310 GC equipped with a thermal conductivity detector and helium carrier gas with a 5 m Poropak N and 1 m molecular sieve columns. The GC method was isothermal at 30 °C with carrier gas flow rate of 55 mls/min. 0.5 ml gas samples were used for the 10 minute run to quantify hydrogen, oxygen, nitrogen, methane and carbon dioxide.

A.1.10 Analytical method - Biochemical methane potential (BMP)

Solid waste samples were analysed for BMP according to the draft methodology developed by MTD for the Environment Agency under research contract EPG 1/7/25 - CLO 219.

A.1.11 Analytical method - Volatile fatty acids

Volatile fatty acids (C2 to C7) were analysed by GC equipped with flame ionisation detector. Leachate samples were acidified with an equal volume of 25% phosphoric acid and 1 ul samples injected on to the column. The GC was equipped with a 1.6 m 5% FFAP on Teflon packed column using nitrogen carrier gas at a flow rate of 40 mls/min. The temperature was programmed to increase from 100 to 190°C in a 30 min. run time.

A.1.12 Detection limits of analytical methods employed

Where sample dilution was required as part of the preparation for analysis, the actual detection limits would be higher. This occurred in cases of limited available sample volume or through dilution with preservatives such as acids in the case of the metals analyses.

Table A1.12.1 Detection limits

Determinand	Detection limit
Cadmium	0.005 mg/l
Chromium	0.03 mg/l
Lead	0.1 mg/l
Zinc	0.03 mg/l
Nickel	0.015 mg/l
Iron	0.008 mg/l
Sulphur	0.05 mg/l
Ammoniacal-nitrogen	1 mgN/l
Chloride	1mg/l
pH	+/-0.01
Eh	+/- 1mV
Electrical conductivity	0.05 uS/cm
Hydrogen	1%
Oxygen	0.10%
Nitrogen	0.10%
Methane	0.10%
Carbon Dioxide	0.10%
Biochemical Methane Potential	1 m^3 CH_4/tonne dry weight
Volatile Fatty Acids	20 mg/l

Fig. A2.1.1 Gas Production from CAMR Cd Amended Waste Columns

Columns 1,3 and 6 sparged with air from day 129

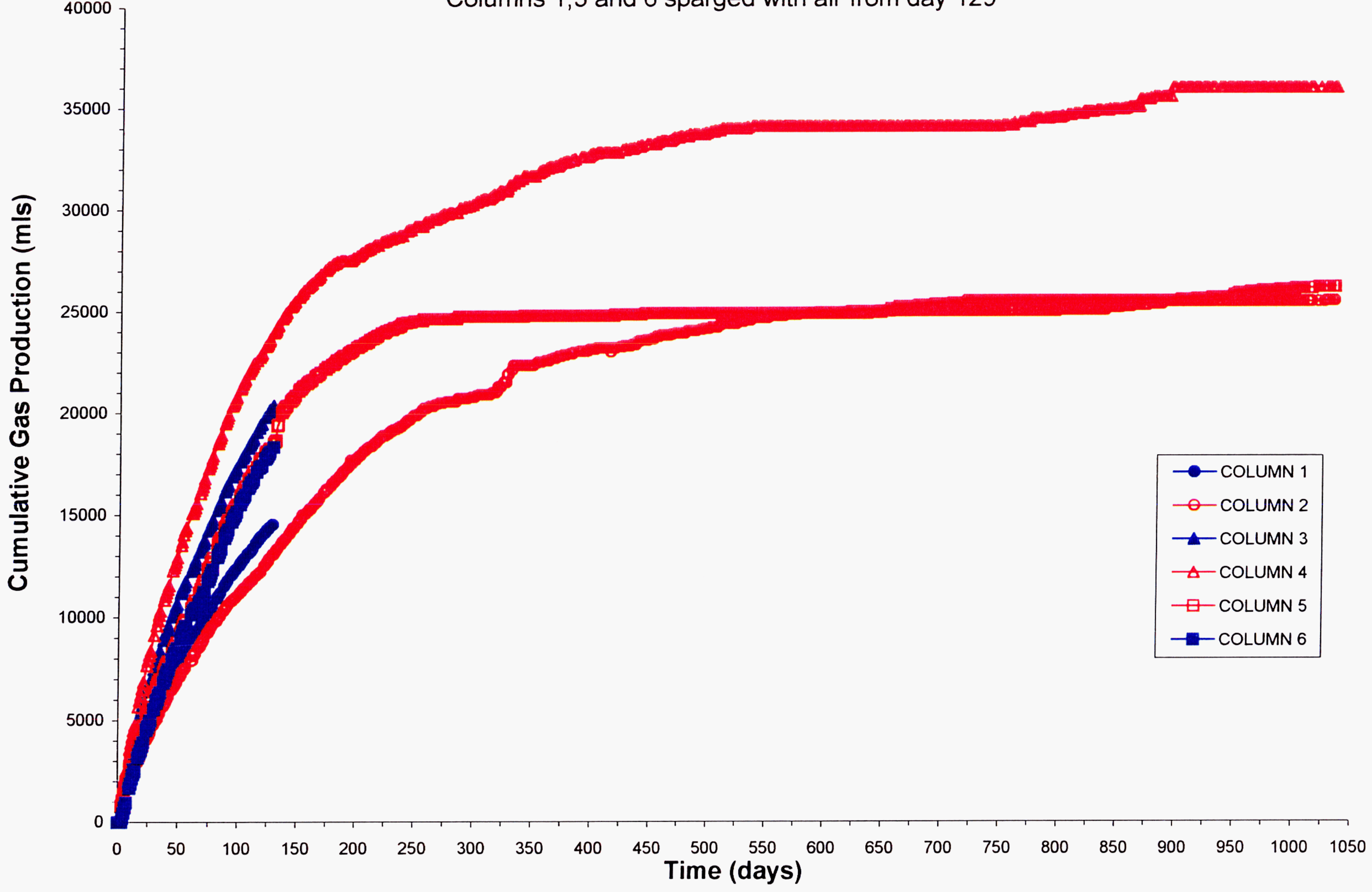


Fig. A2.2.1 'Rain' Addition and Removal from Cadmium Amended Refuse Column 1
Column sparged with air from day 129

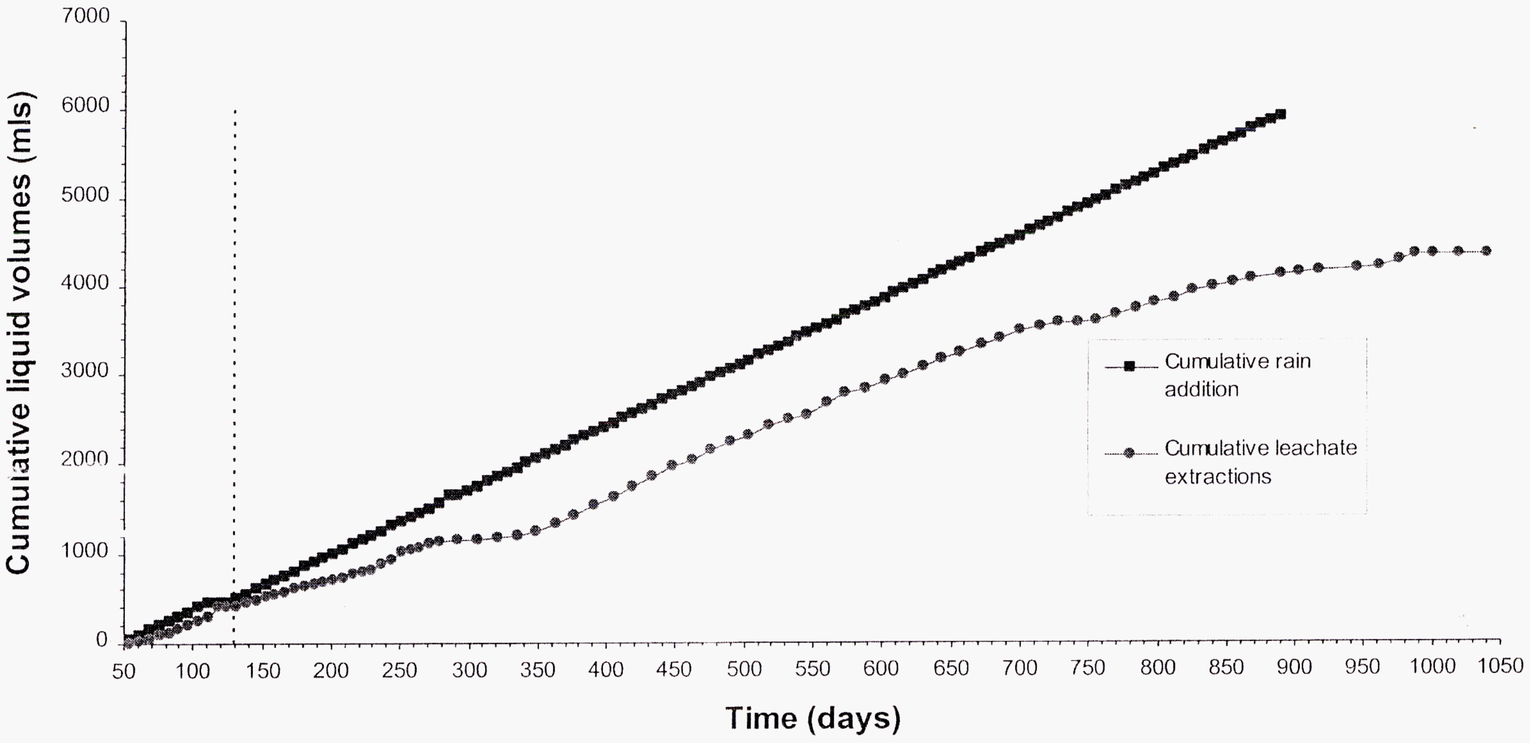


Fig. A2.2.2 'Rain' Addition and Removal from Cadmium Amended Refuse Column 2

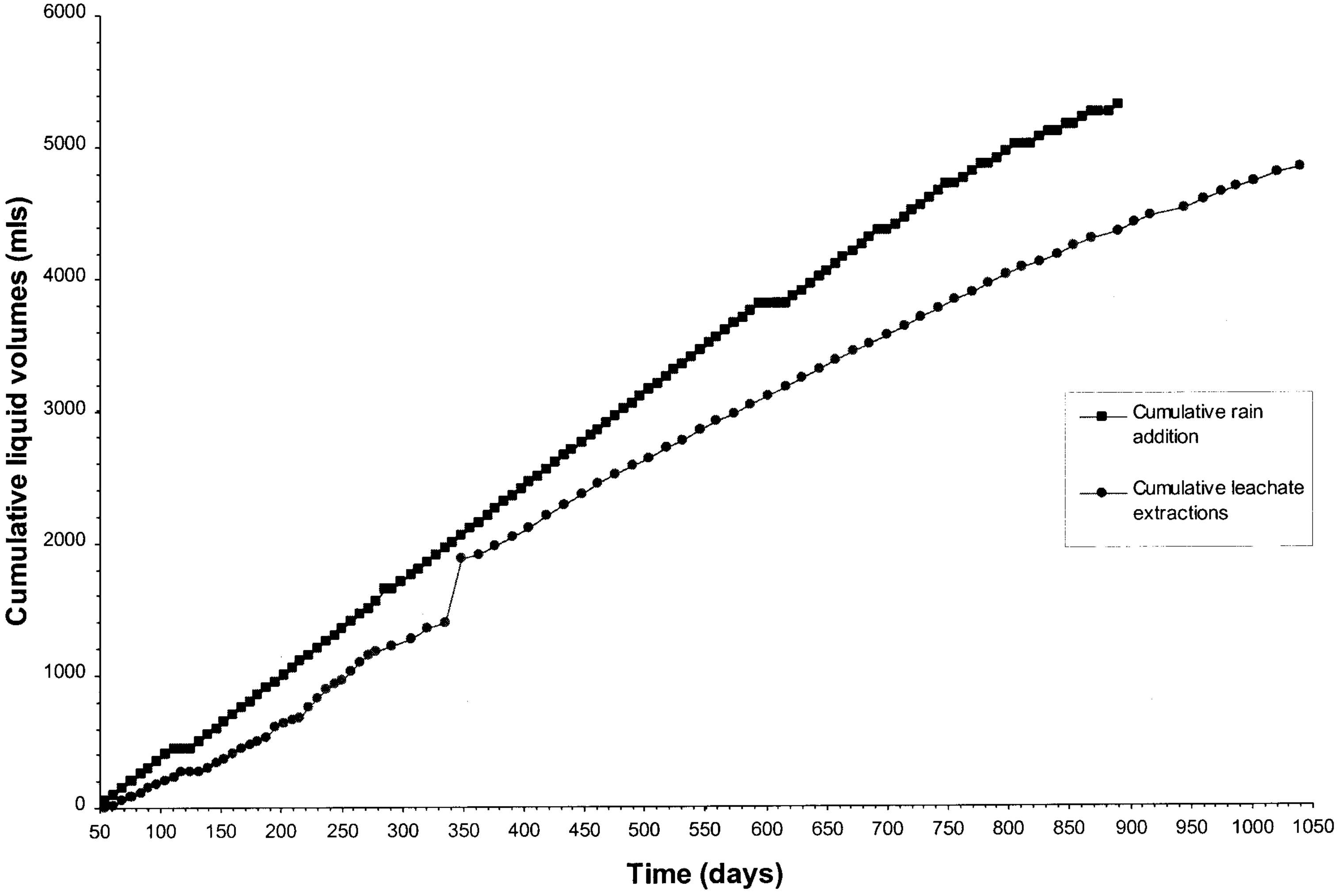


Fig. A2.2.3 'Rain' Addition and Removal from Cadmium Amended Refuse Column 3

Column sparged with air from day 129

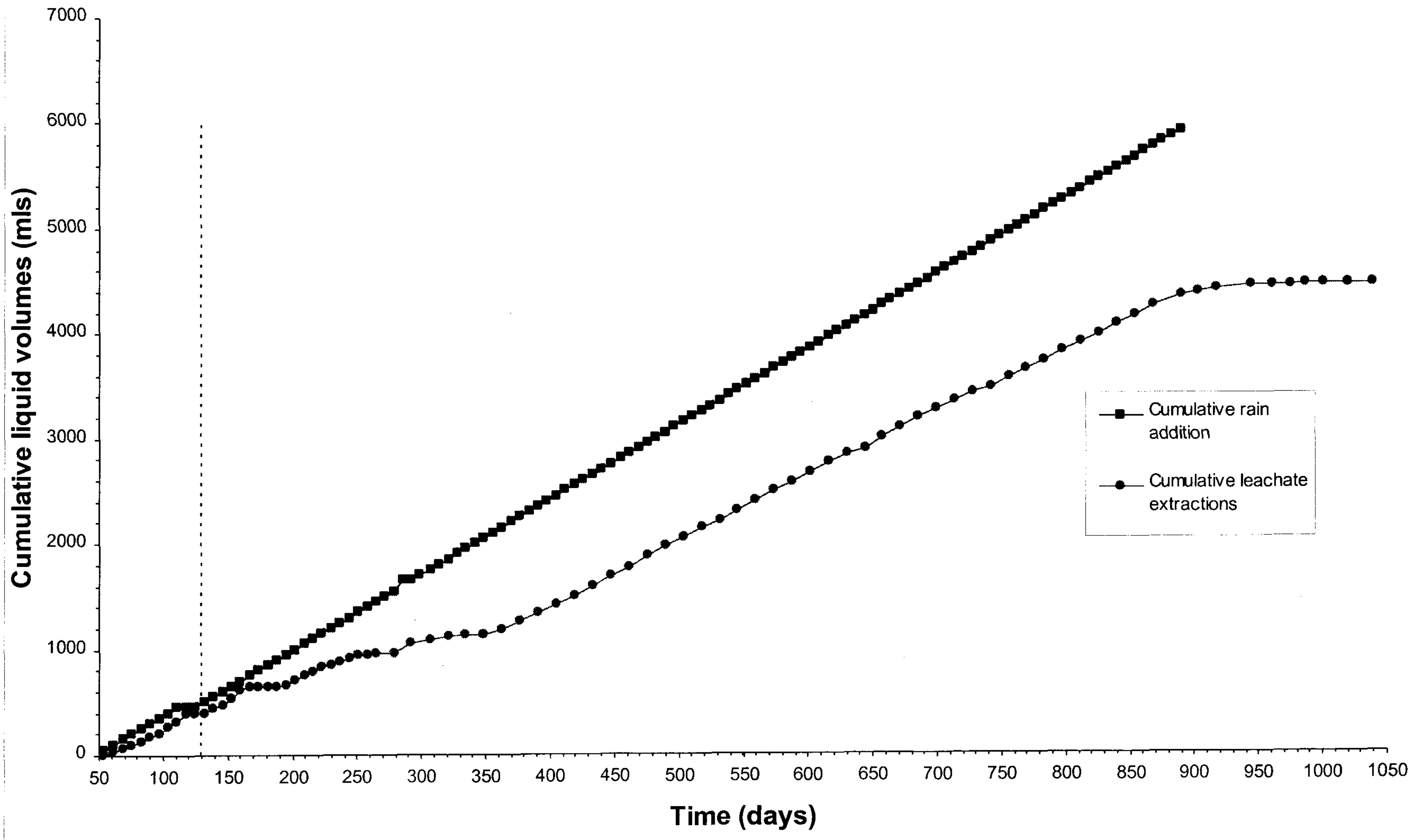


Fig. A2.2.4 'Rain' Addition and Removal from Cadmium Amended Refuse Column 4

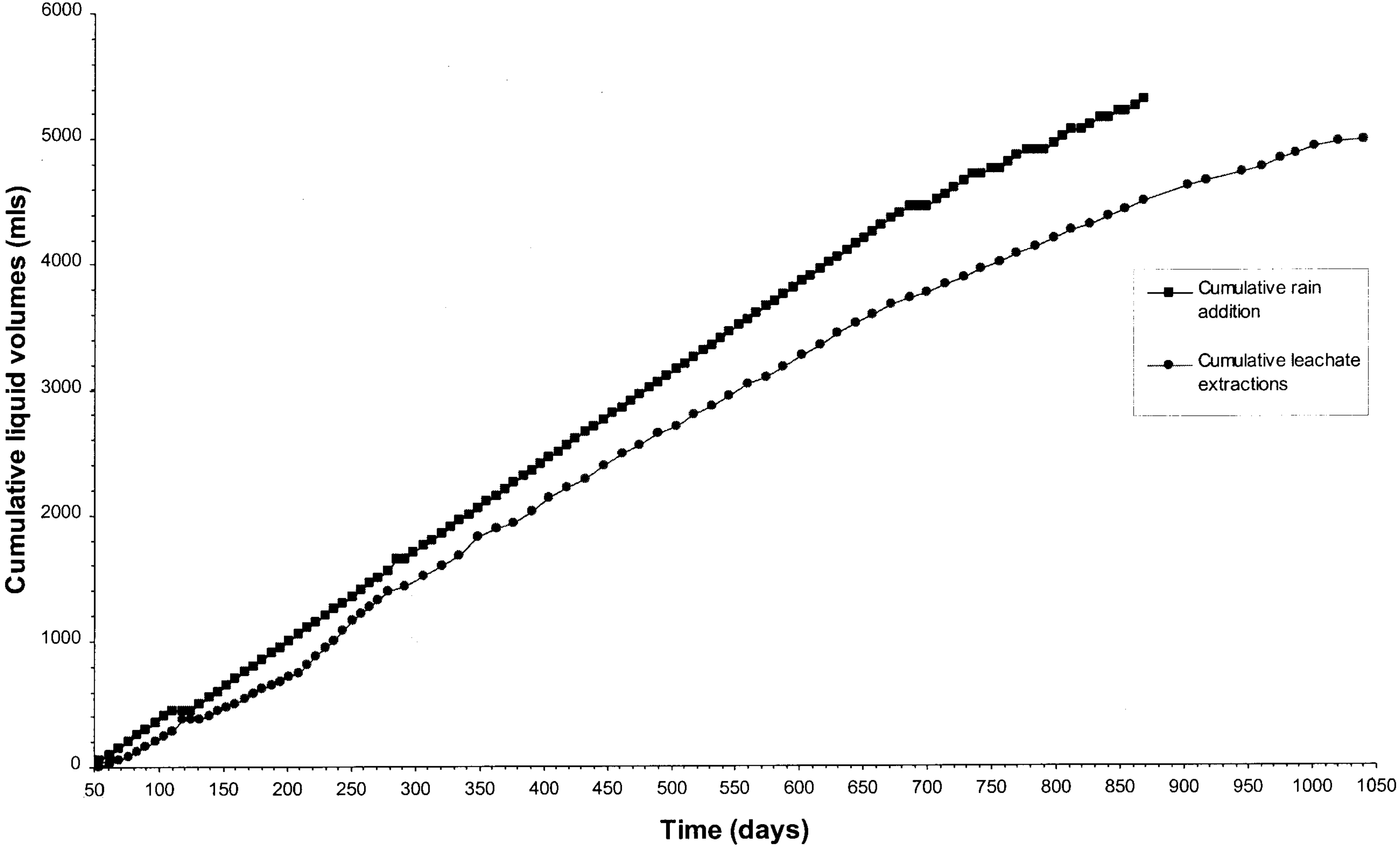


Fig. A2.2.5 'Rain' Addition and Removal from Cadmium Amended Refuse Column 5

LiBr added with rain for tracer study day 796

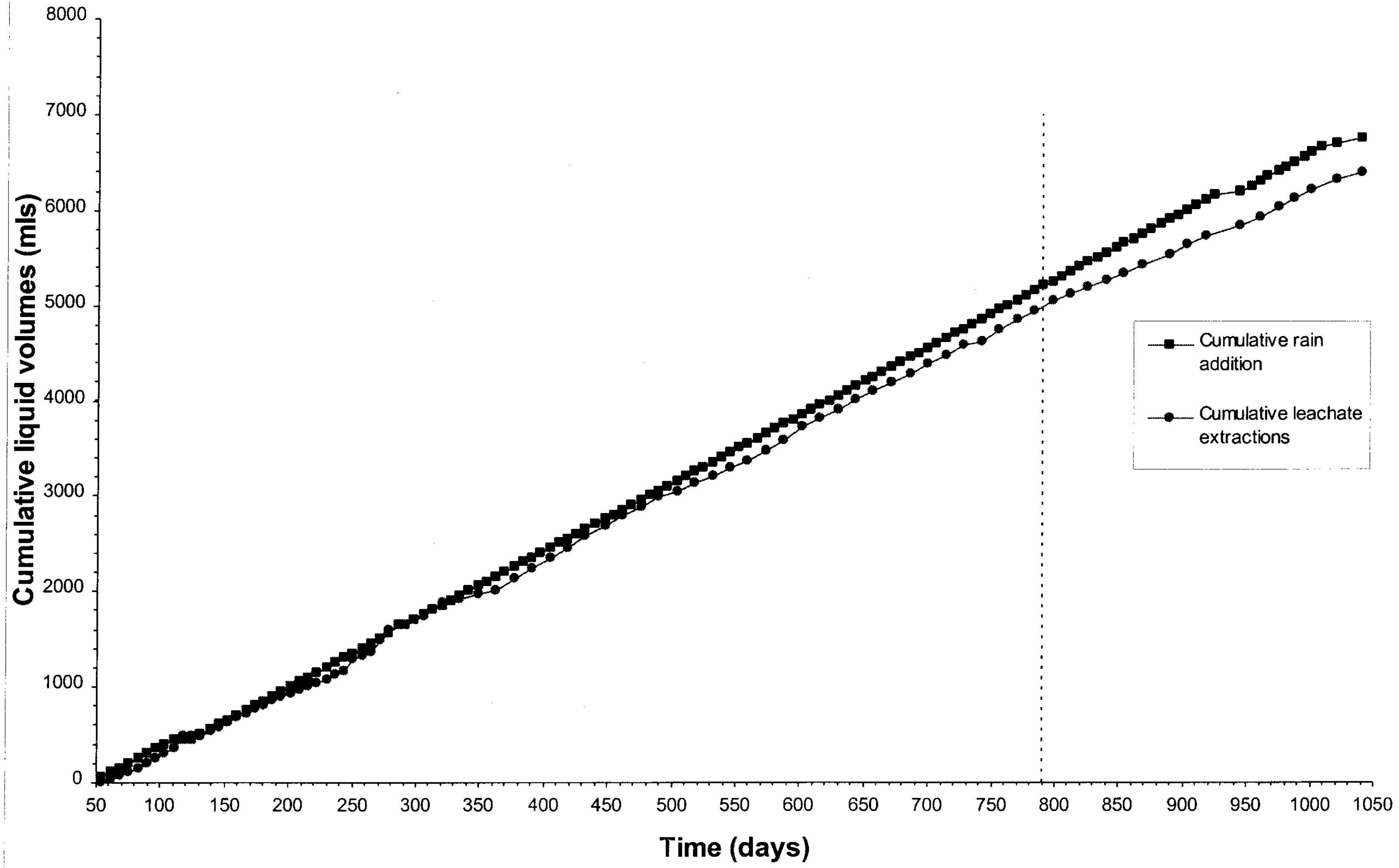


Fig. A2.2.6 'Rain' Addition and Removal from Cadmium Amended Refuse Column 6

Column sparged with air from day 129

LiBr added with rain for tracer study day 796

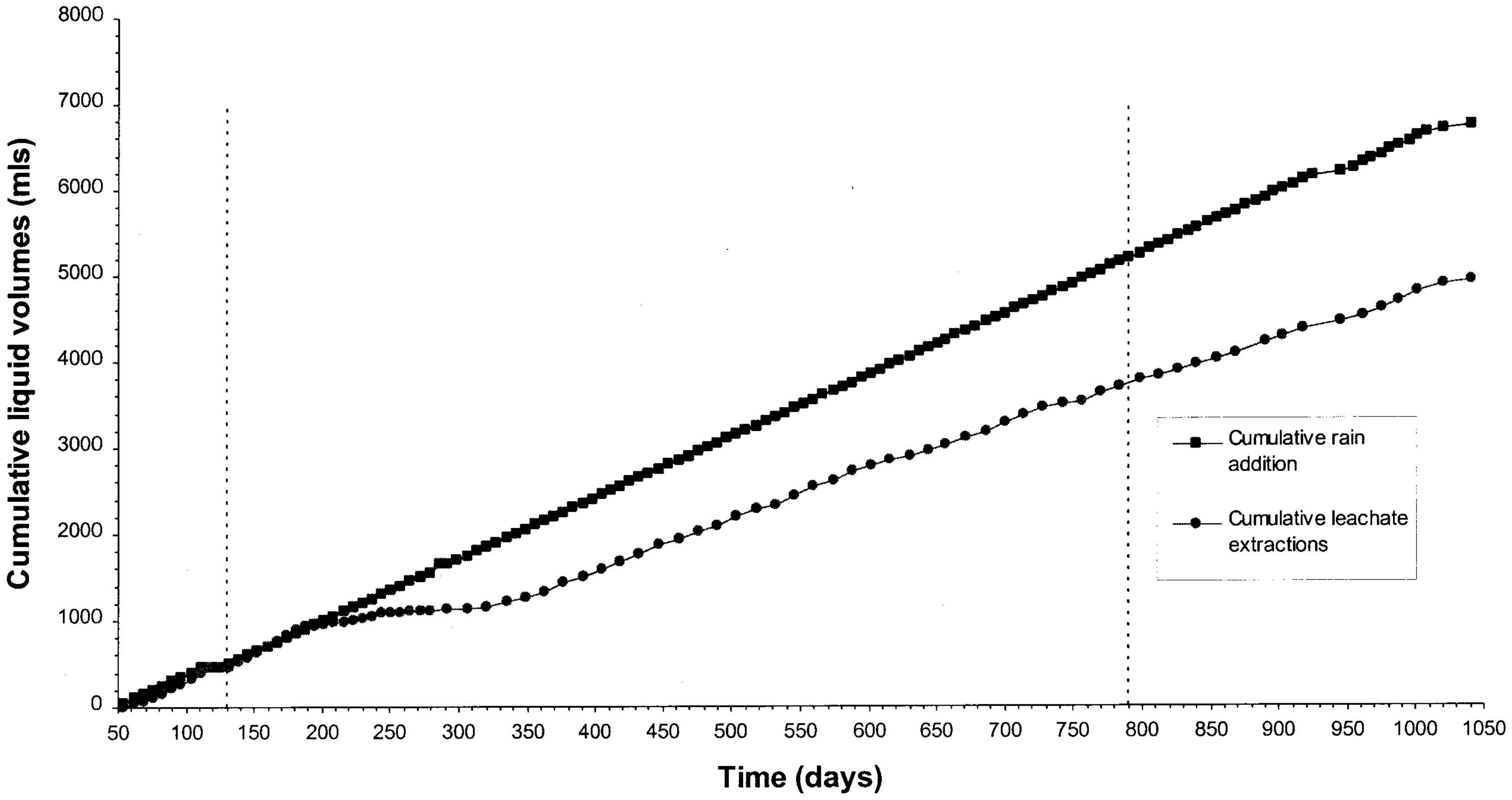


Fig. A2.3.1 Ammoniacal-Nitrogen Analysis of Cadmium Amended Refuse Column Leachates.

Columns 1, 3 & 6 sparged with air from day 129

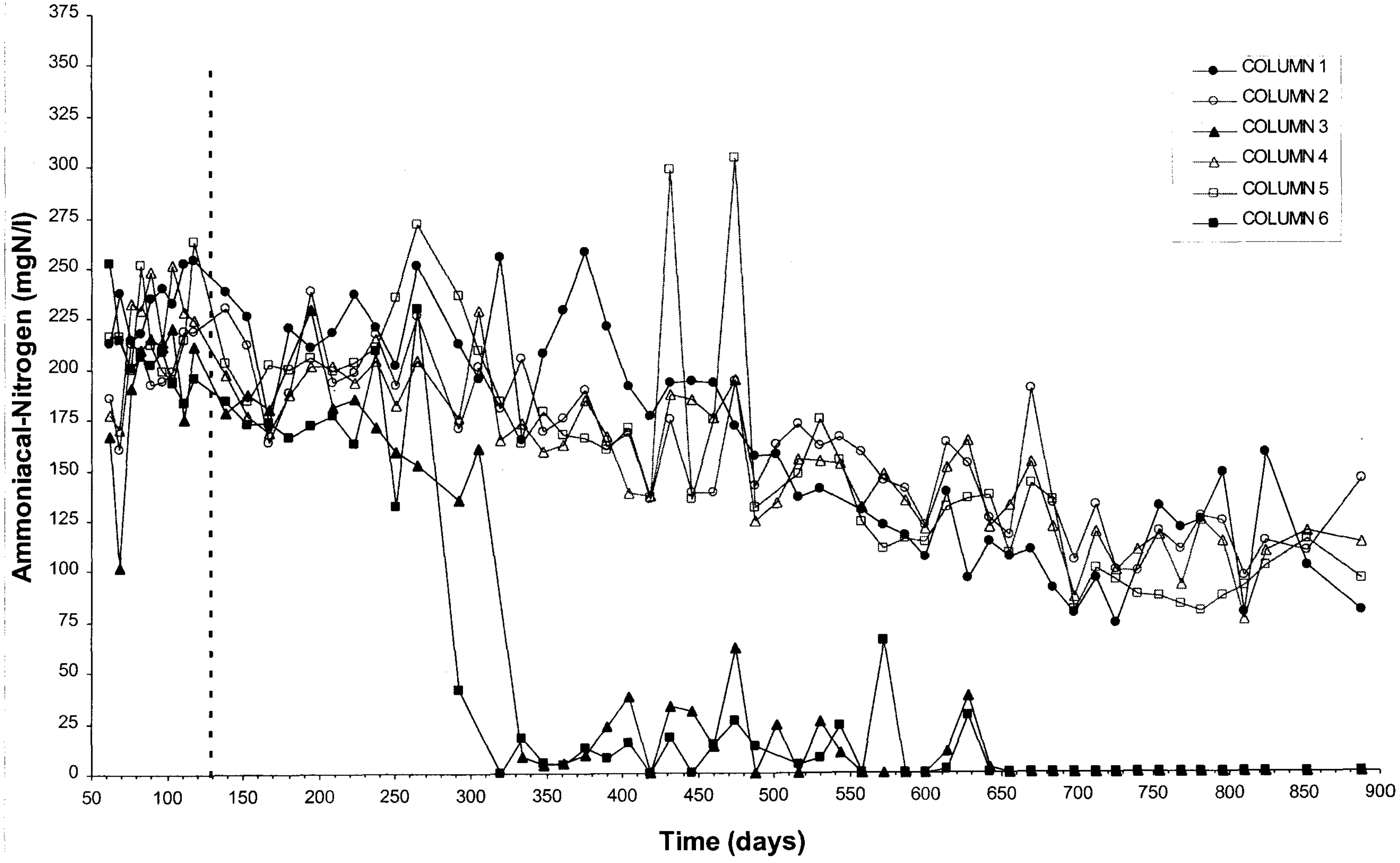
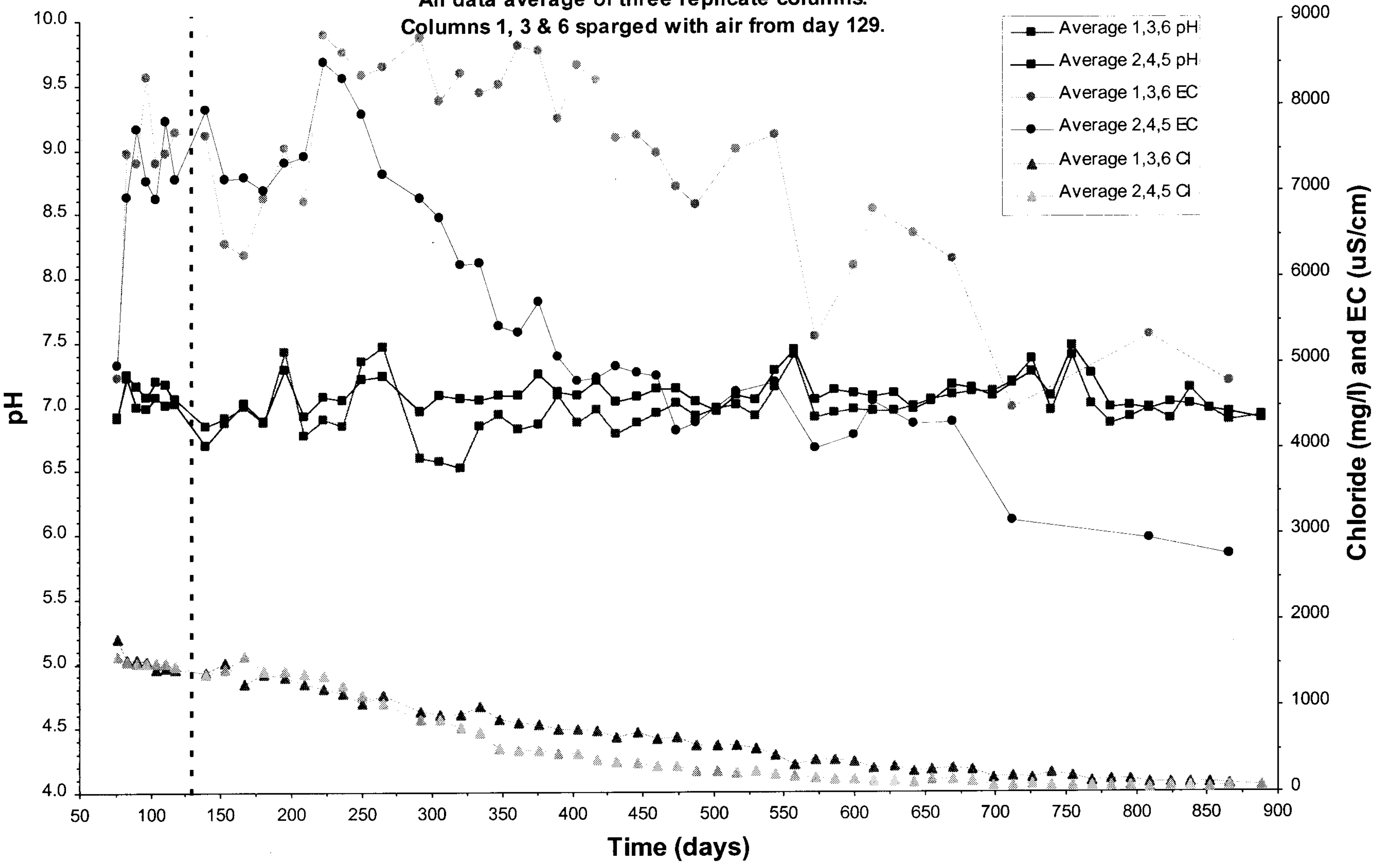


Fig. A2.3.2 pH, EC and Chloride Concentrations of Leachates from Cadmium Amended Refuse Columns

All data average of three replicate columns.
Columns 1, 3 & 6 sparged with air from day 129.



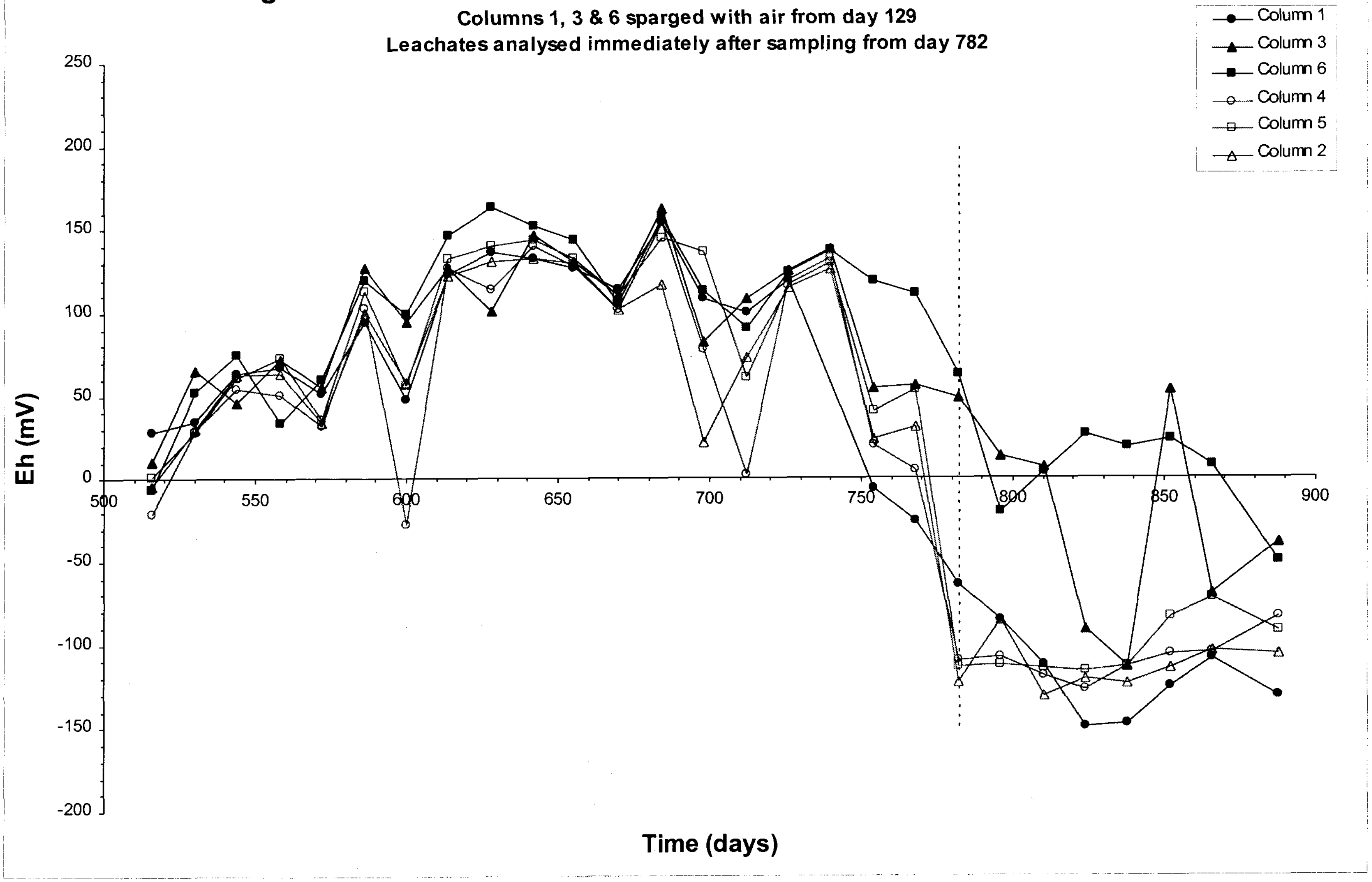


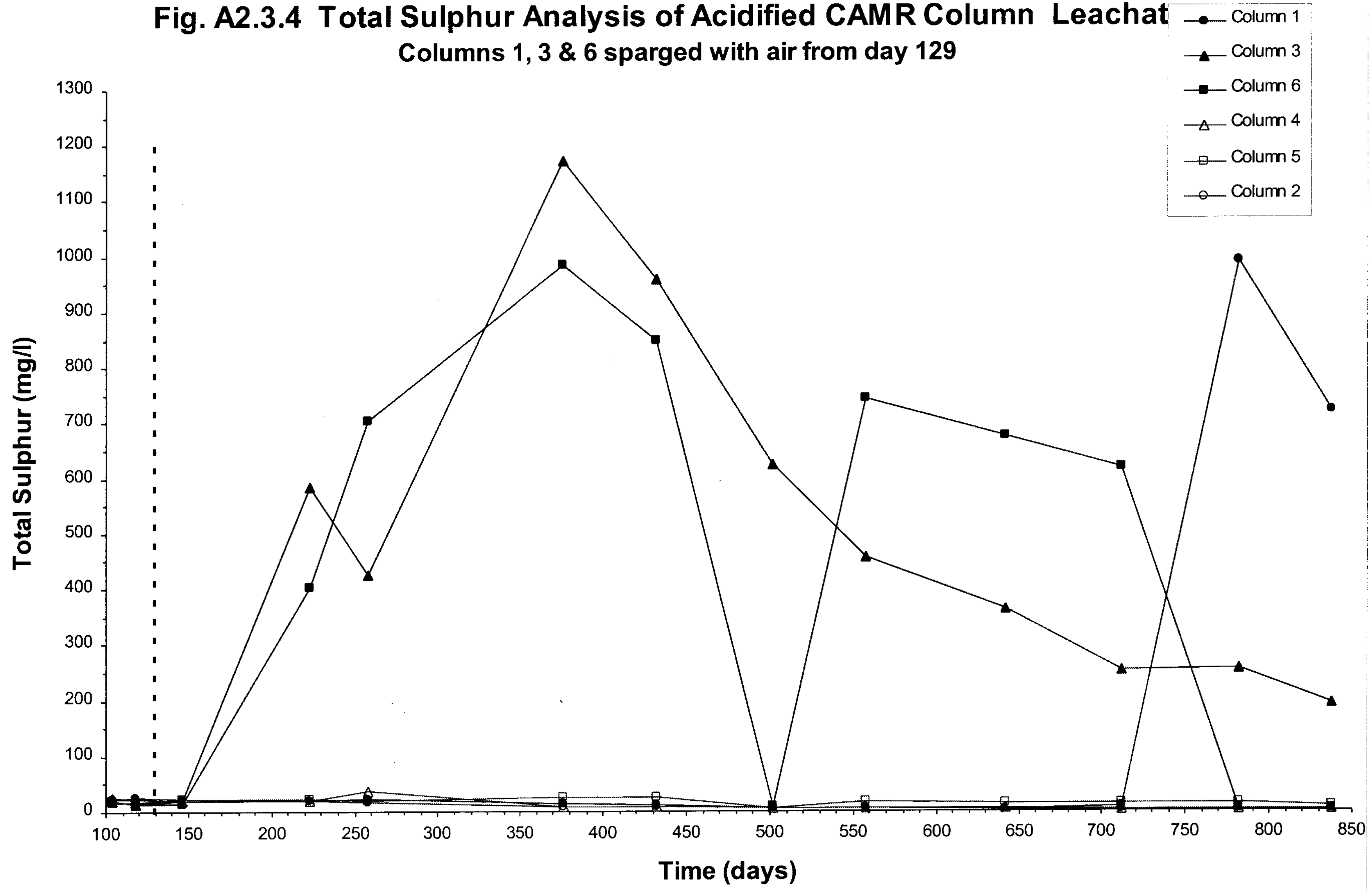
Fig. A2.3.3 Eh of Cadmium Amended Refuse Column Leachates

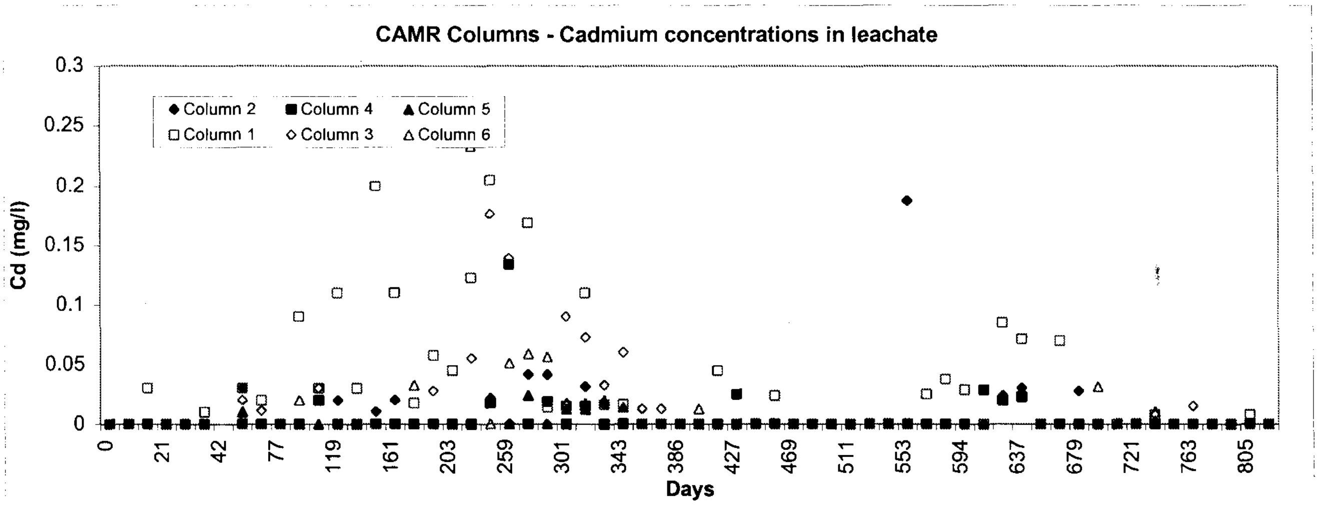
Columns 1, 3 & 6 sparged with air from day 129

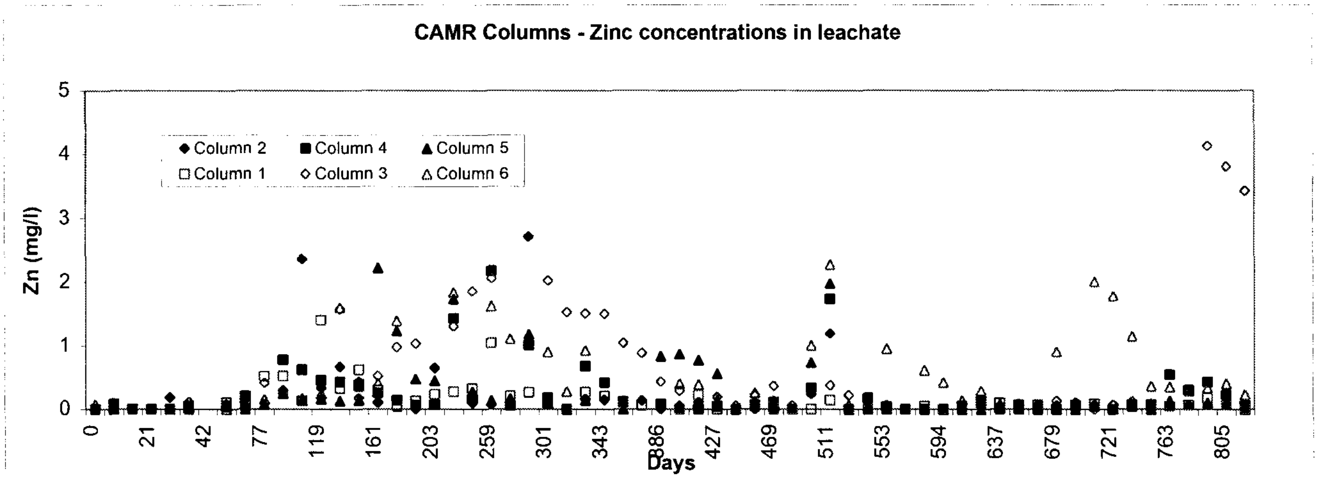
Leachates analysed immediately after sampling from day 782

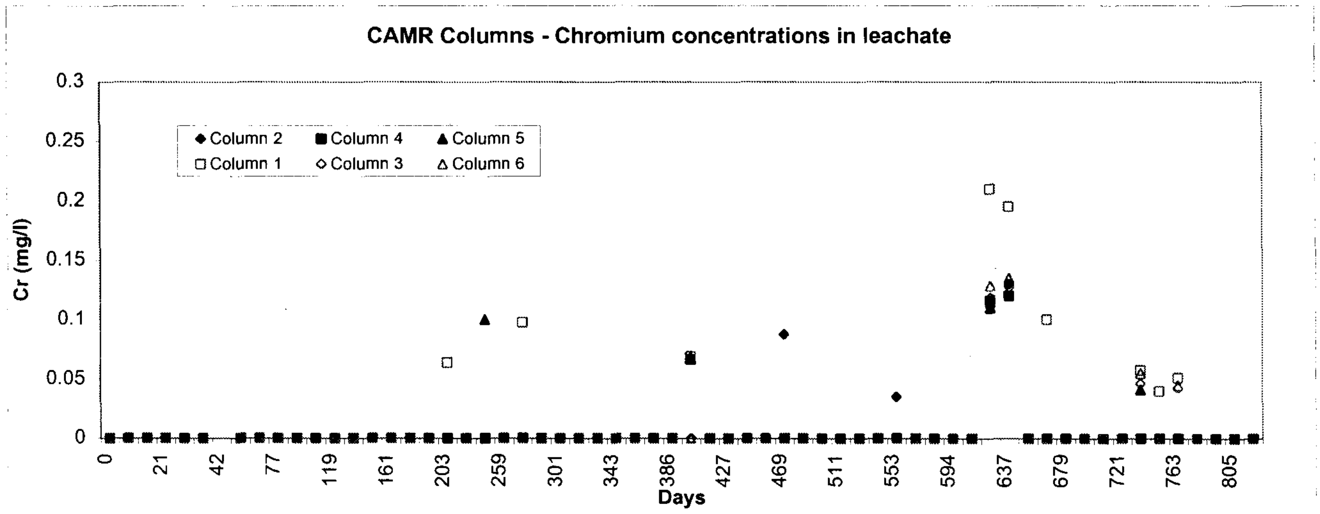
Fig. A2.3.4 Total Sulphur Analysis of Acidified CAMR Column Leachat

Columns 1, 3 & 6 sparged with air from day 129









Analytical data at detection limit plotted as zero
Closed symbols are anaerobic columns, open symbols are aerobic columns
Note: anomalously high experimental data excluded

Figure A.2.3.5 Summary of dissolved metal concentrations in CAMR column leachates

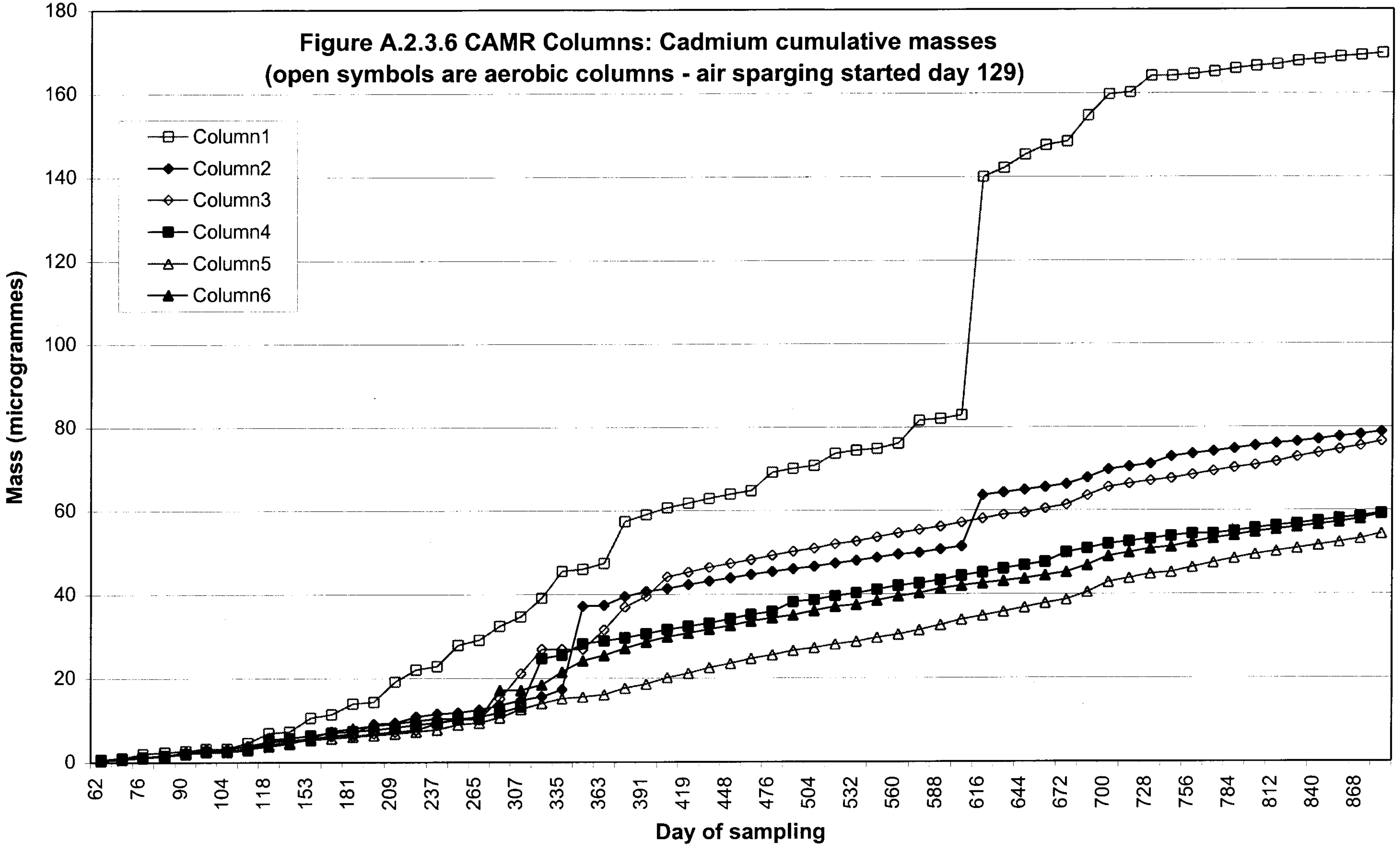


Figure A.2.3.6 CAMR Columns: Cadmium cumulative masses (open symbols are aerobic columns - air sparging started day 129)

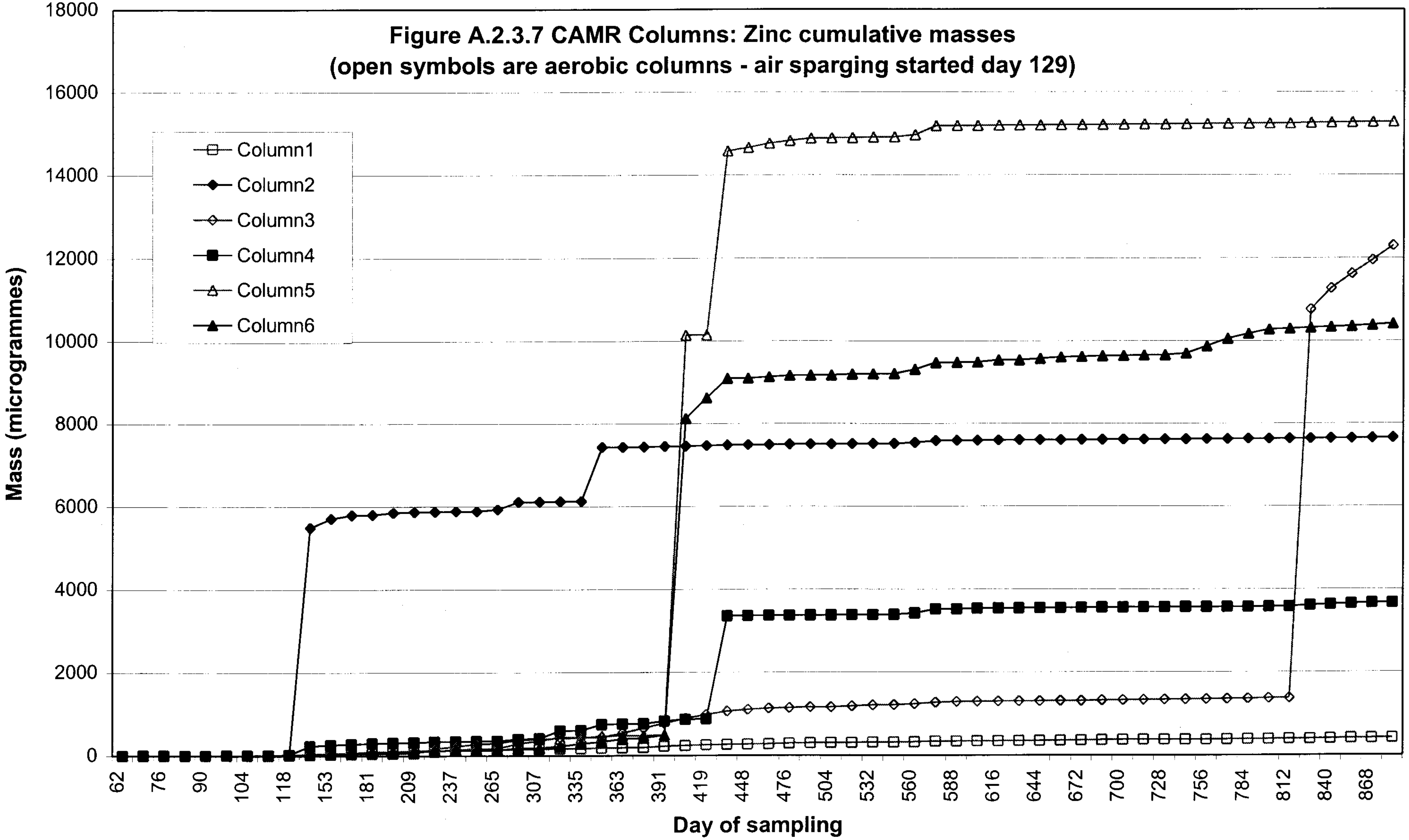


Figure A.2.3.7 CAMR Columns: Zinc cumulative masses
(open symbols are aerobic columns - air sparging started day 129)

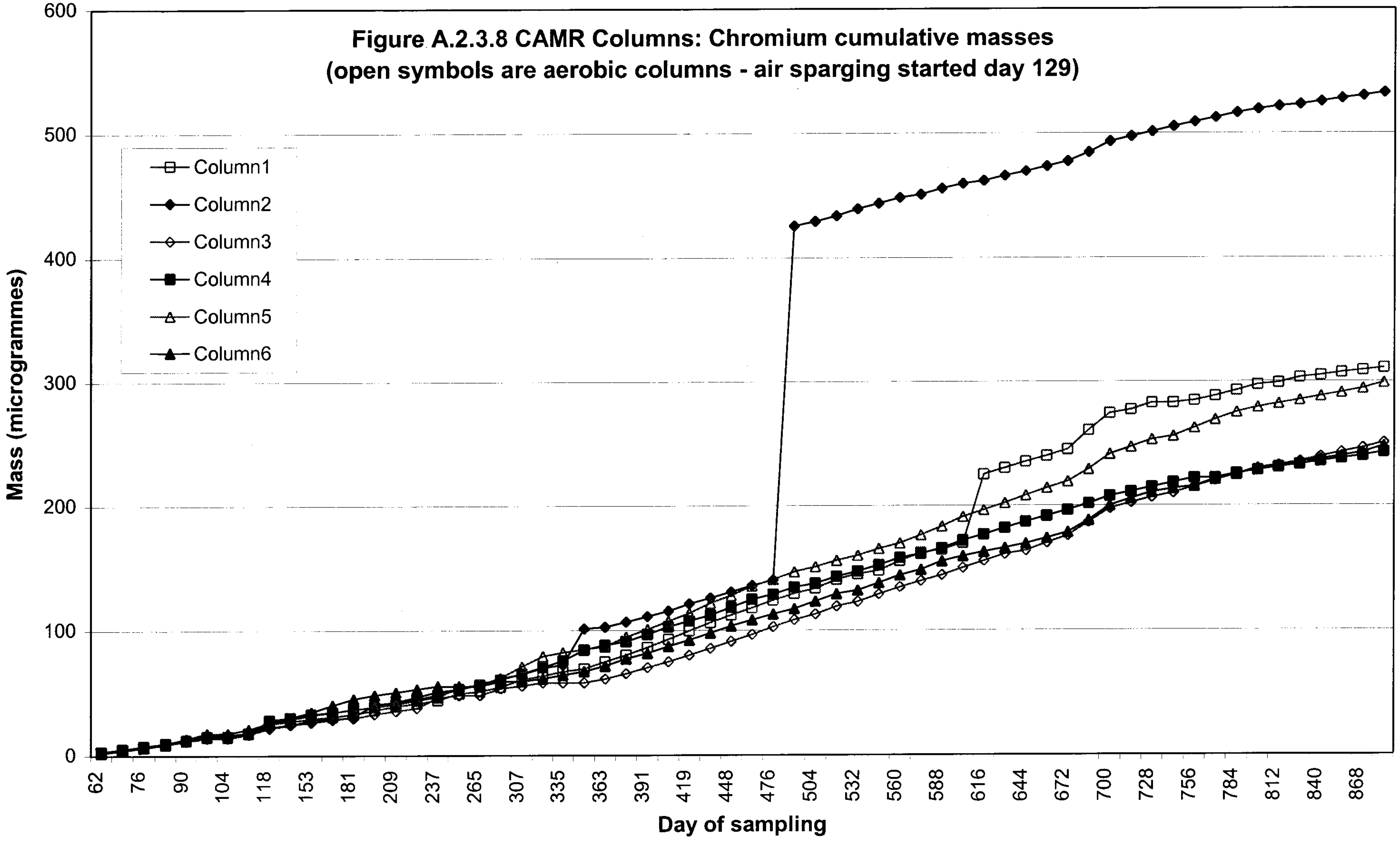


Figure A.2.3.8 CAMR Columns: Chromium cumulative masses
(open symbols are aerobic columns - air sparging started day 129)

Fig. A2.5.1 Lithium Bromide Tracer Study:
Lithium and Bromide Concentrations in Leachate Emerging from the base of CAMR Column 5
(anaerobic)
322 mg/l Br- and 28mg/l Li+ added to top of column on day 796

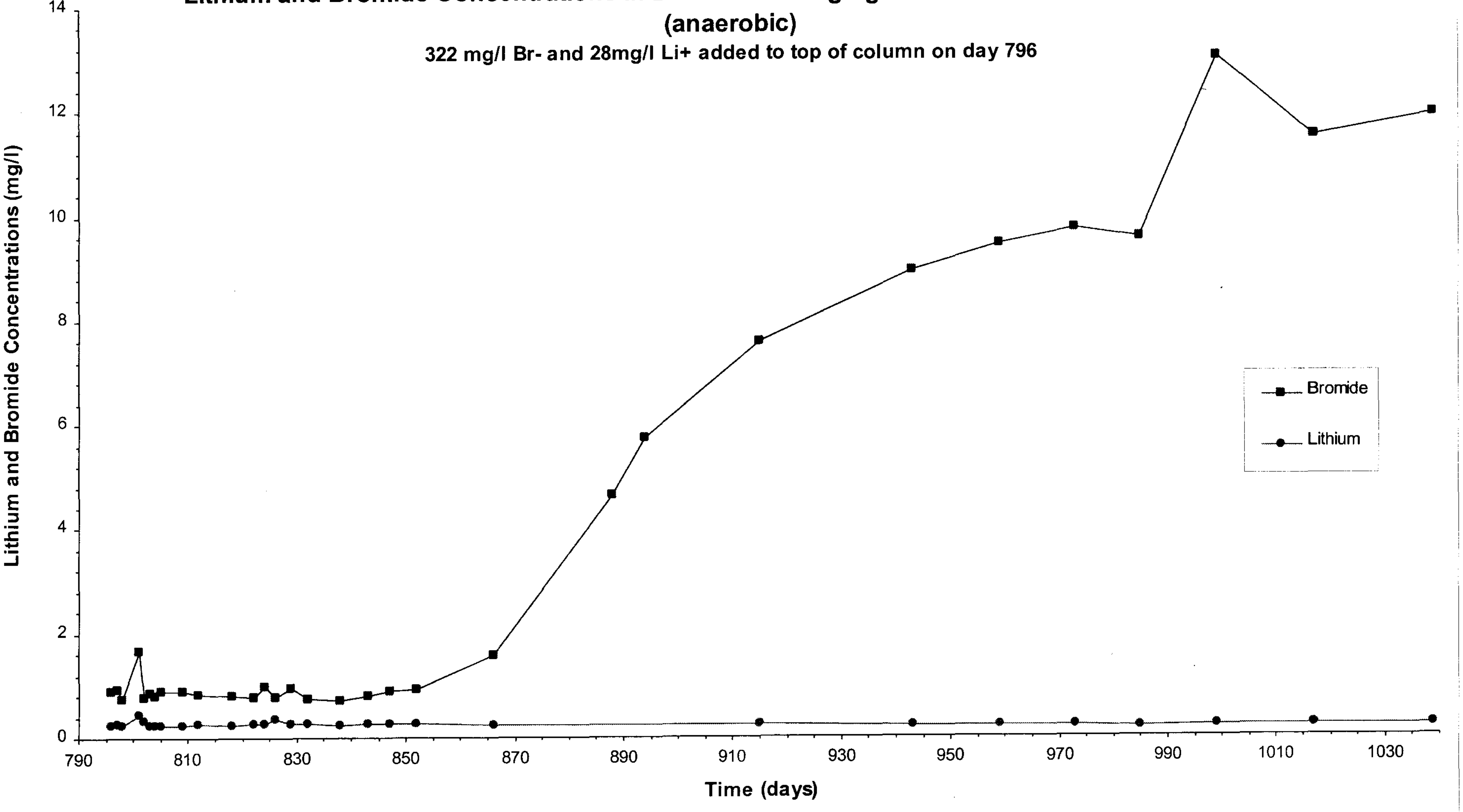
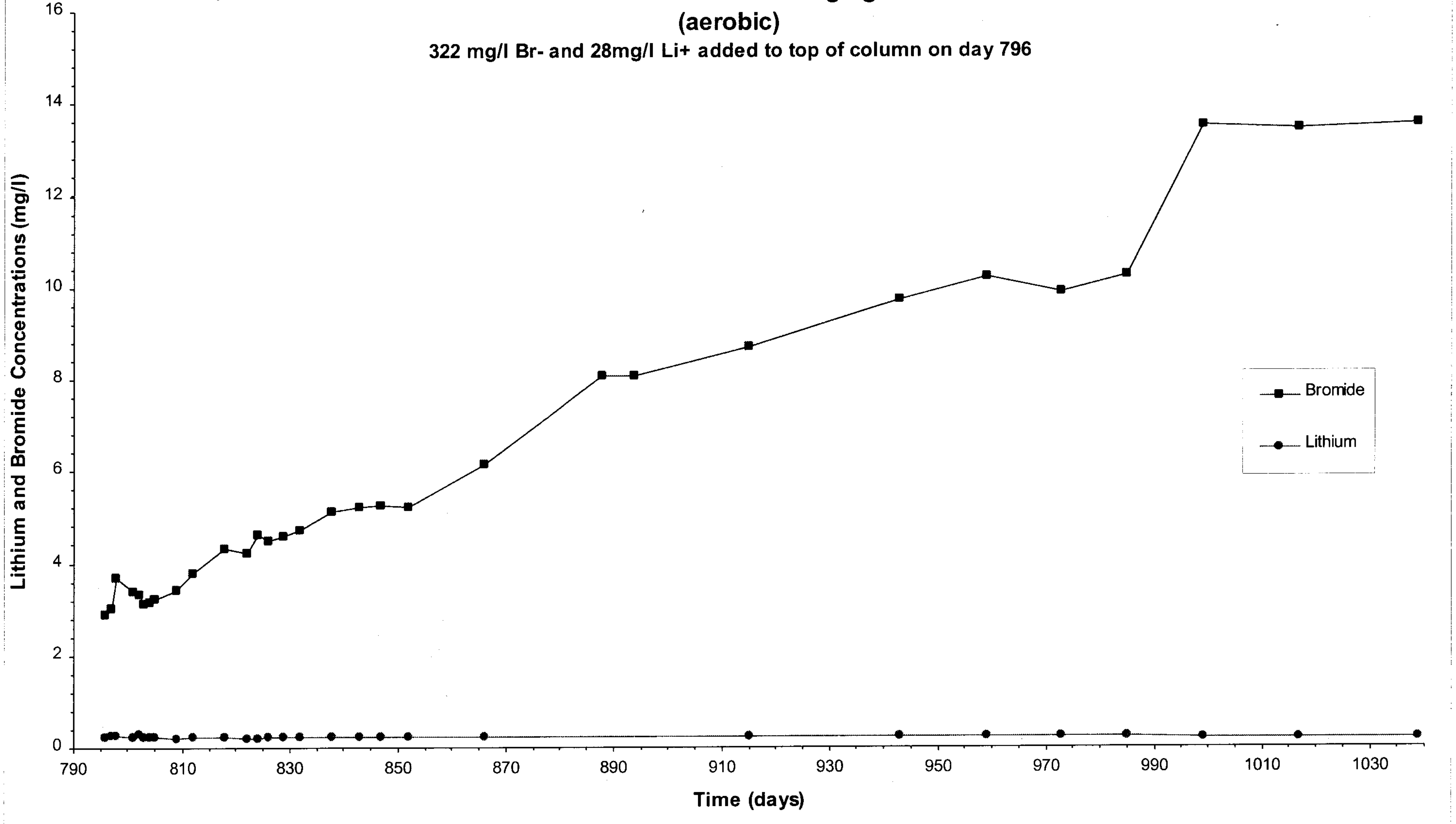


Fig. A2.5.2 Lithium Bromide Tracer Study:
Lithium and Bromide Concentrations in Leachate Emerging from the base of CAMR Column 6
(aerobic)
322 mg/l Br- and 28mg/l Li+ added to top of column on day 796



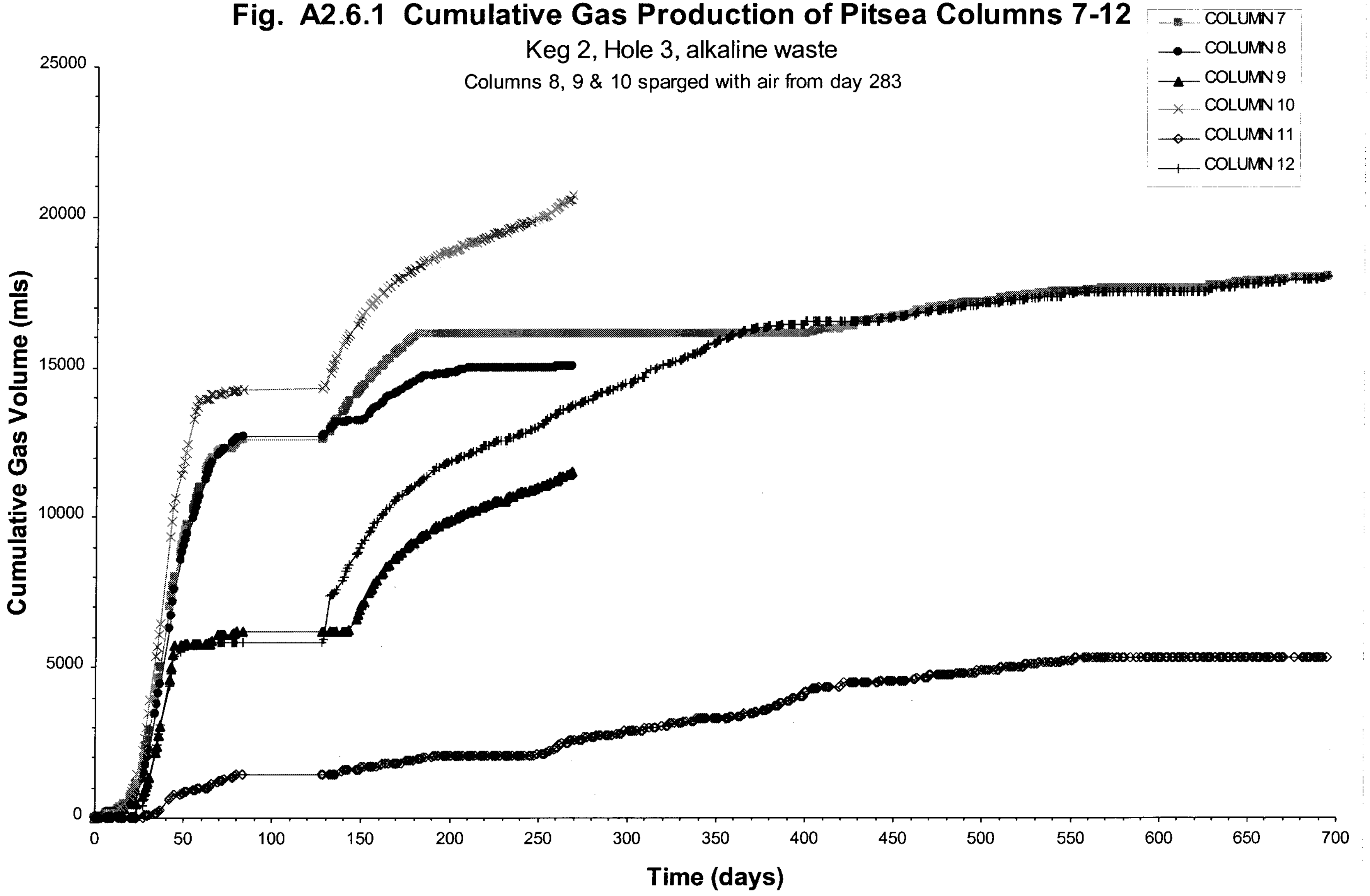


Fig. A2.6.1 Cumulative Gas Production of Pitsea Columns 7-12

Keg 2, Hole 3, alkaline waste

Columns 8, 9 & 10 sparged with air from day 283

Fig. A2.6.2 Cumulative Gas Production of Pitsea Columns 13-18

Keg 1, Hole 1, acid waste

Columns 14, 15 & 16 sparged with air from day 283

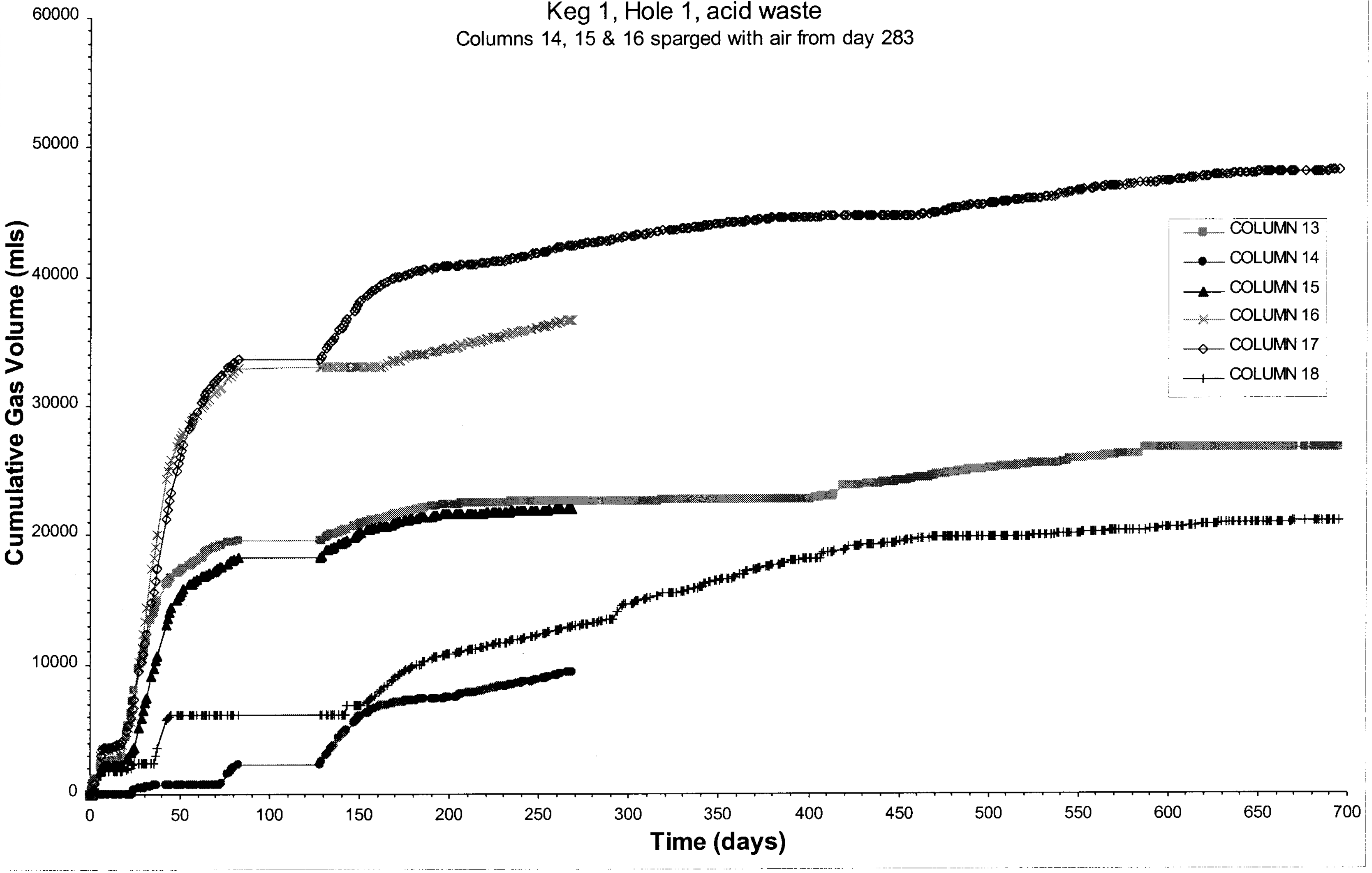


Fig. A2.7.1 'Rain' Addition and Removal from Pitsea Refuse Column 7 (Hole 3, keg 2, alkaline waste area)

Leachate drainage trap fitted from day 212

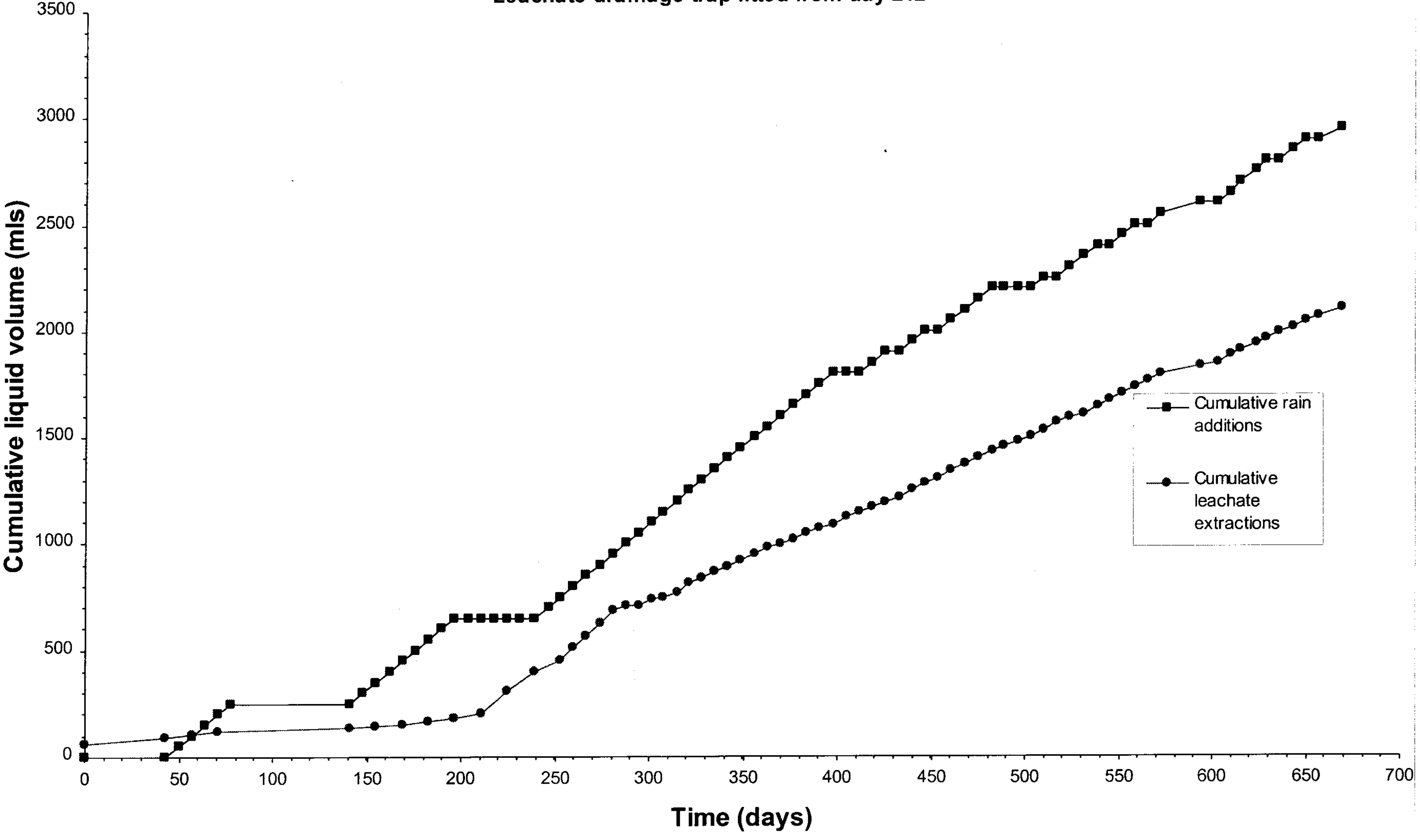
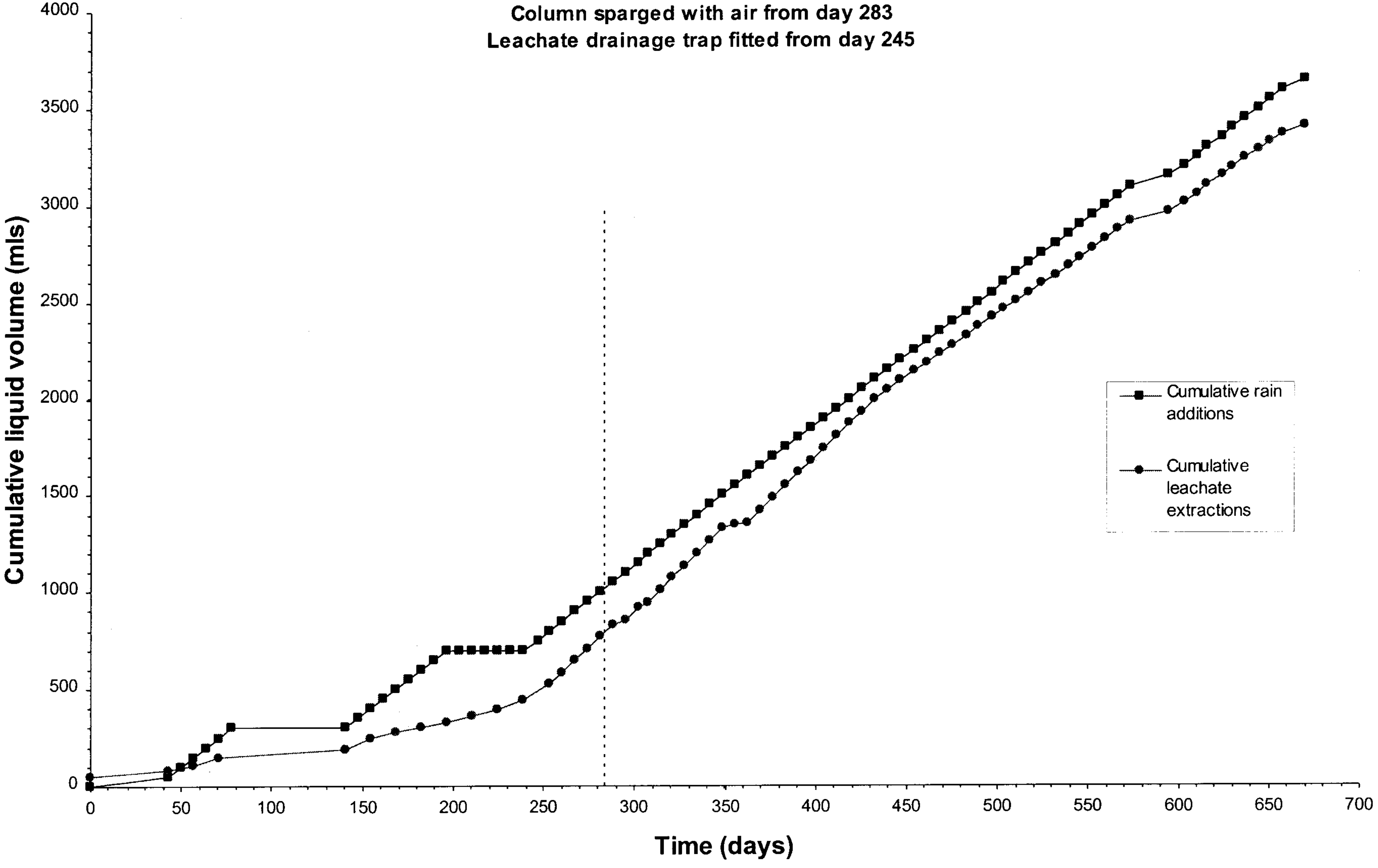


Fig. A2.7.2 'Rain' Addition and Removal from Pitsea Refuse Column 8
(Hole 3, keg 2, alkaline waste area)



Column sparged with air from day 283
Leachate drainage trap fitted from day 245

Fig. A2.7.3 'Rain' Addition and Removal from Pitsea Refuse Column 9 (Hole 3, keg 2, alkaline waste area)

Column sparged with air from day 283

Leachate drainage trap fitted from day 245

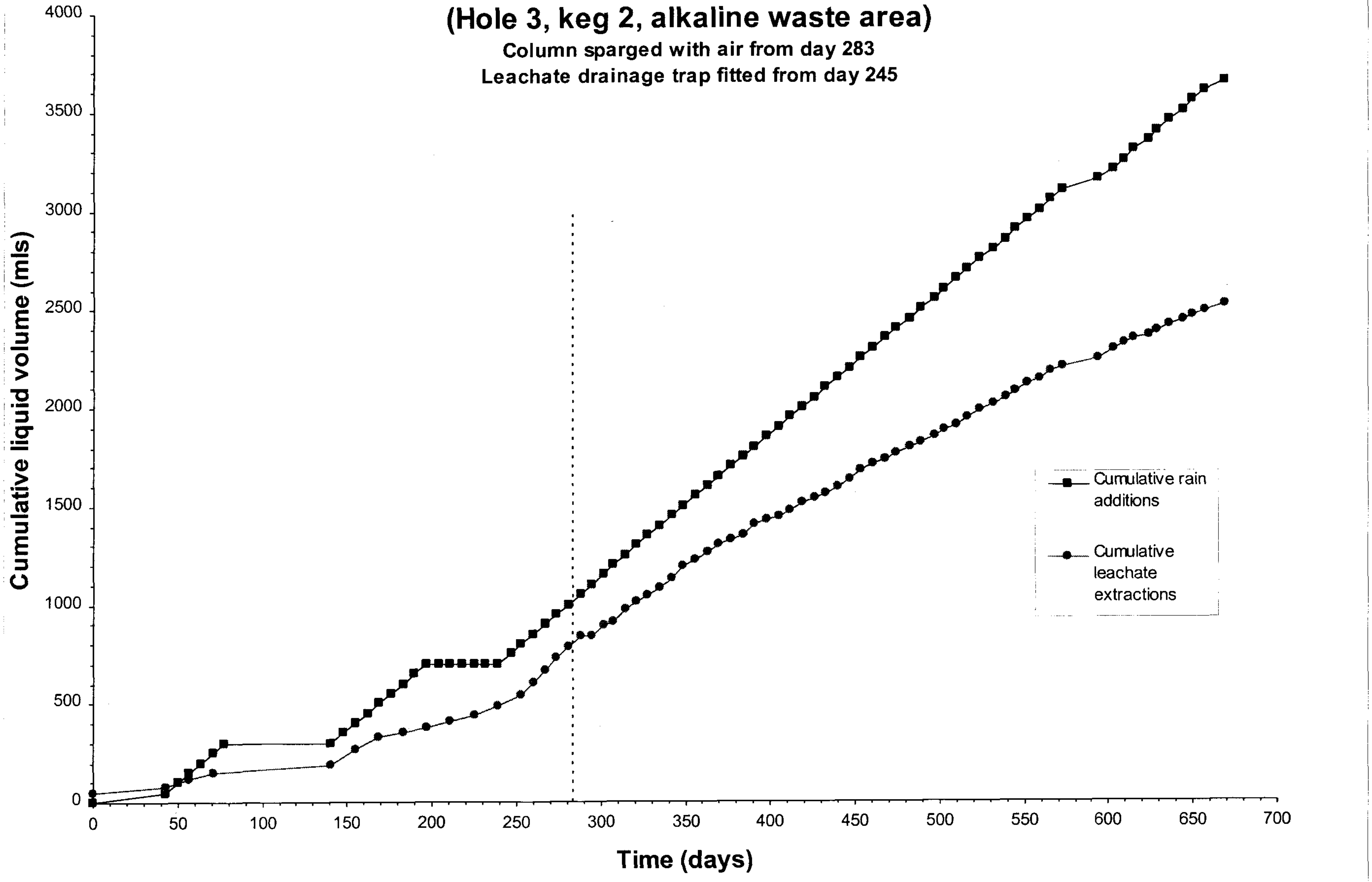
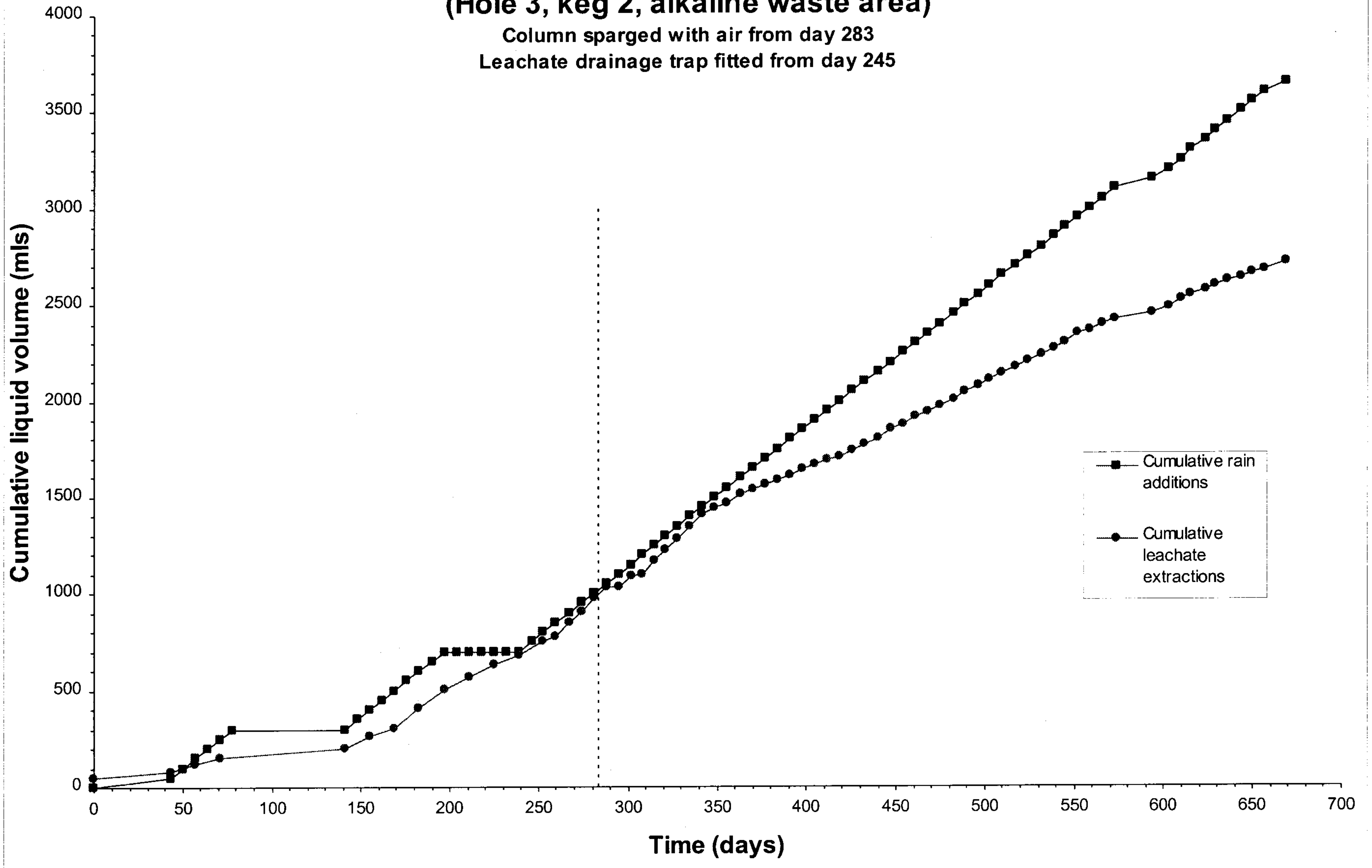


Fig. A2.7.4 'Rain' Addition and Removal from Pitsea Refuse Column 10
(Hole 3, keg 2, alkaline waste area)



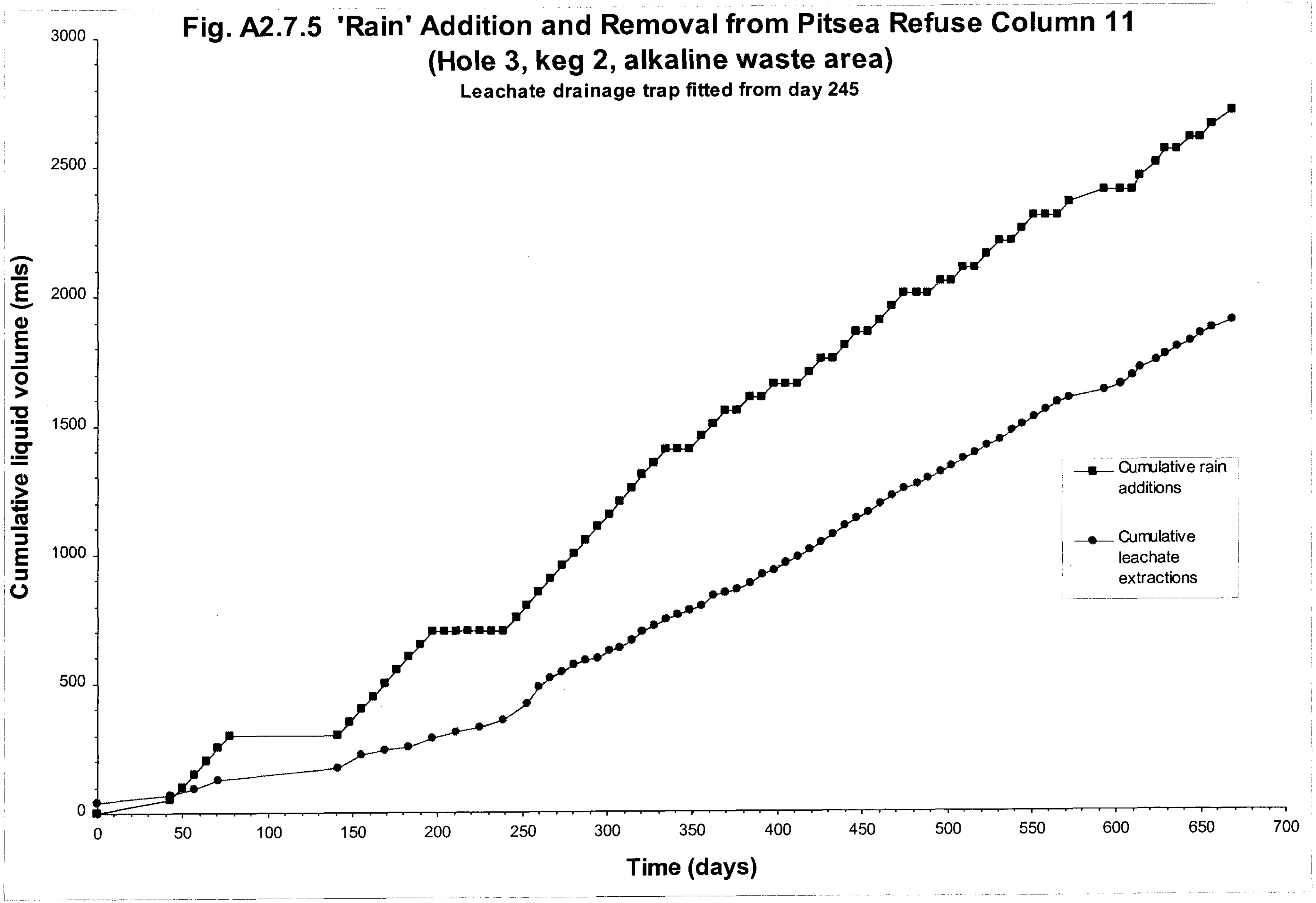
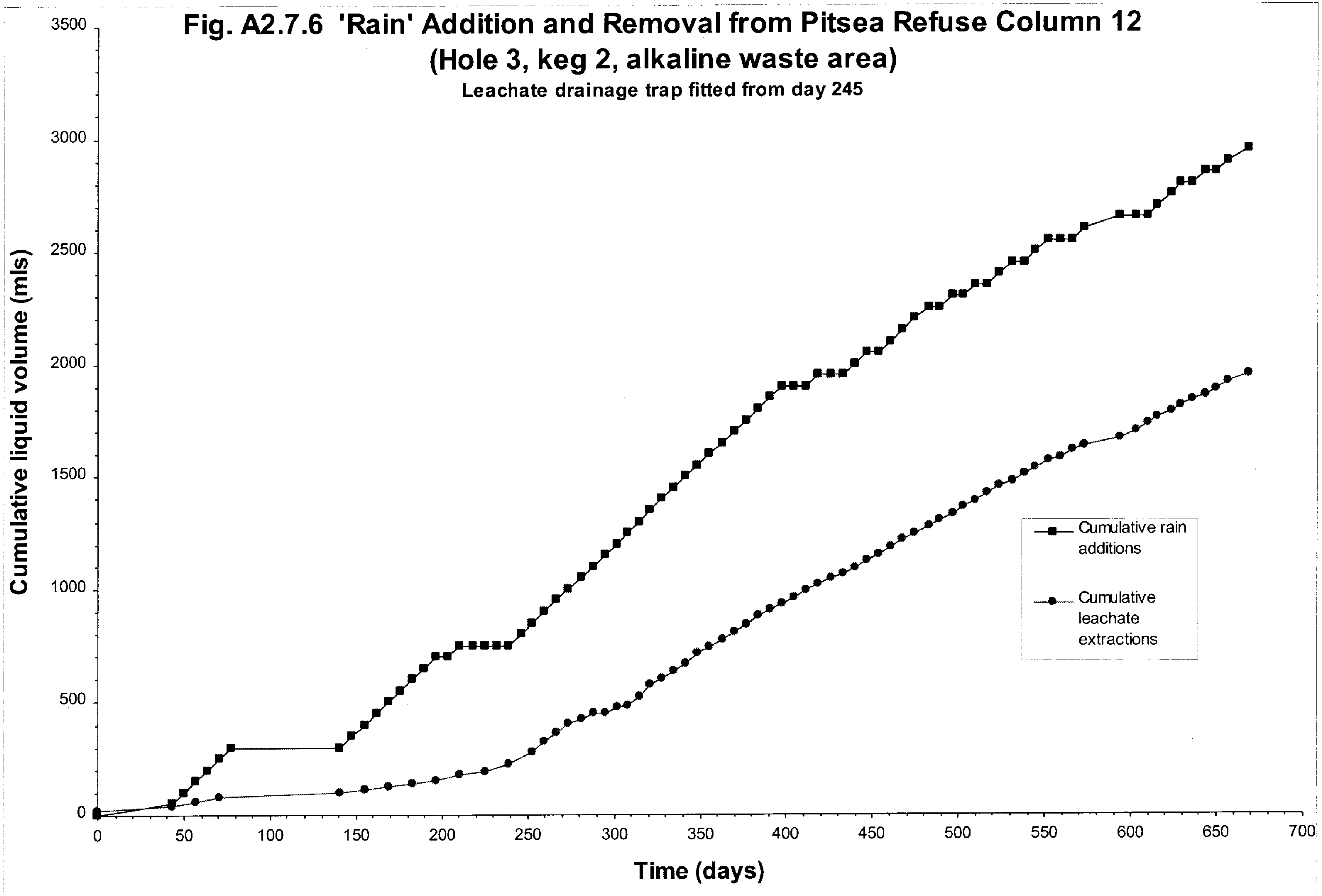


Fig. A2.7.5 'Rain' Addition and Removal from Pitsea Refuse Column 11 (Hole 3, keg 2, alkaline waste area)

Leachate drainage trap fitted from day 245

Fig. A2.7.6 'Rain' Addition and Removal from Pitsea Refuse Column 12
(Hole 3, keg 2, alkaline waste area)

Leachate drainage trap fitted from day 245



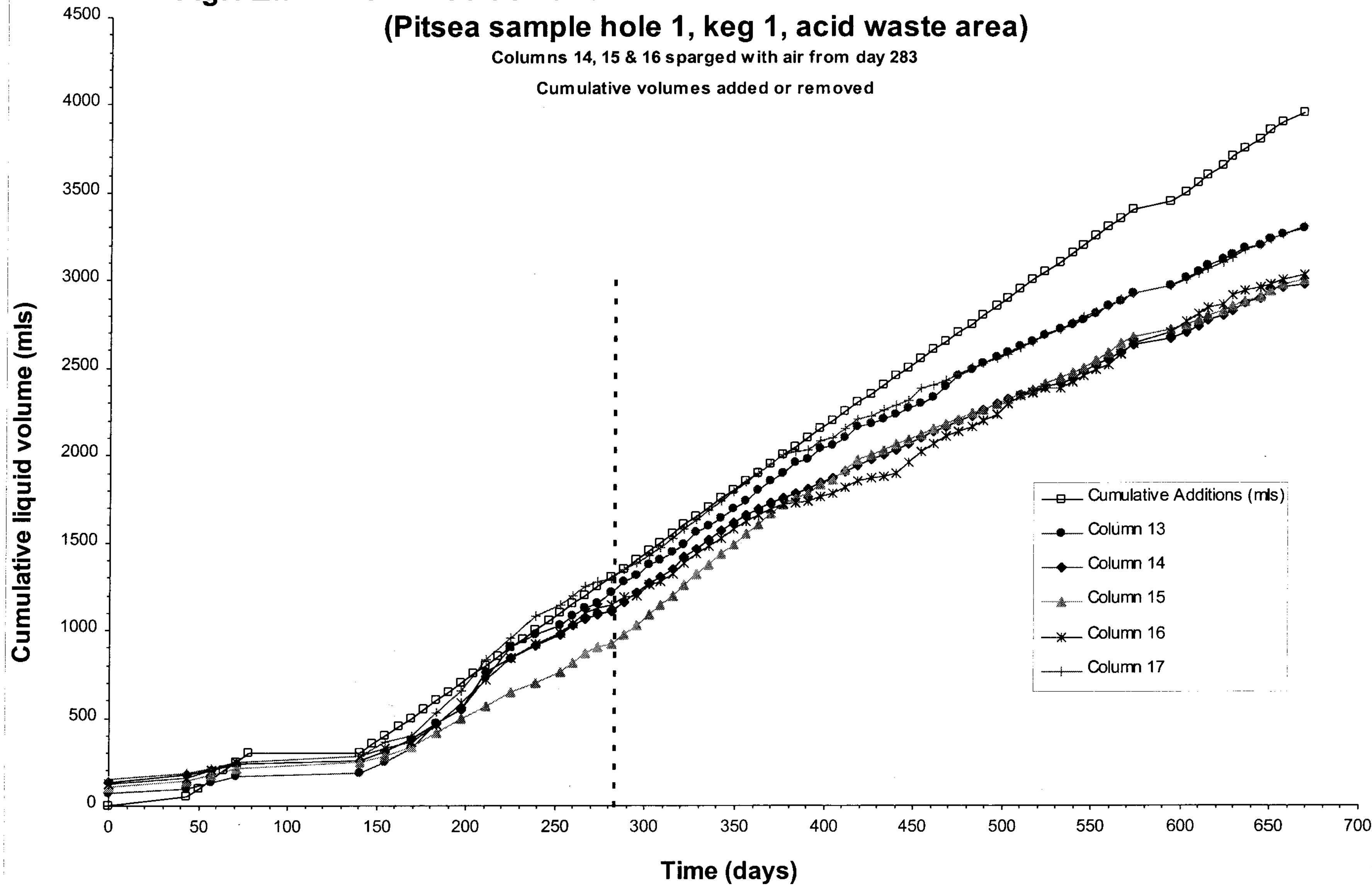


Fig. A2.7.7 'Rain' Addition and Removal from Pitsea Refuse Columns 13-17 (Pitsea sample hole 1, keg 1, acid waste area)

Columns 14, 15 & 16 sparged with air from day 283

Cumulative volumes added or removed

Fig. A2.7.8 'Rain' Addition and Removal from Pitsea Refuse Column 18
(Hole 1, keg 1, acid waste area)
Leachate drainage trap fitted from day 245

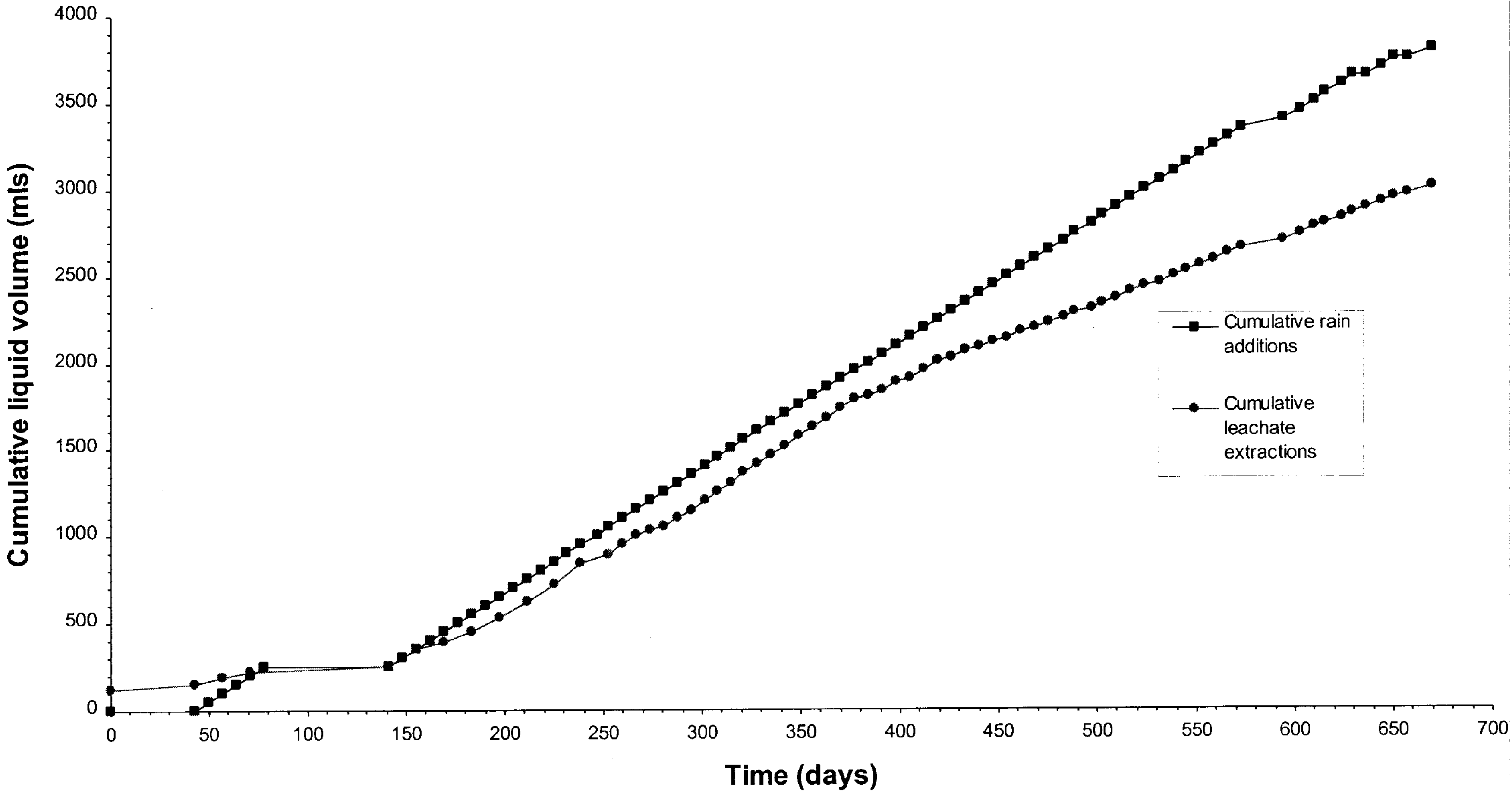


Fig. A2.8.1 Ammoniacal-Nitrogen Analysis of Pitsea Refuse Column Leachates

Columns 7-12: Hole 3, keg 2, alkaline waste area; Columns 13-18: Hole 1, keg 1, acid waste area

Columns 8, 9, 10 & 14, 15, 16 sparged with air from day 283

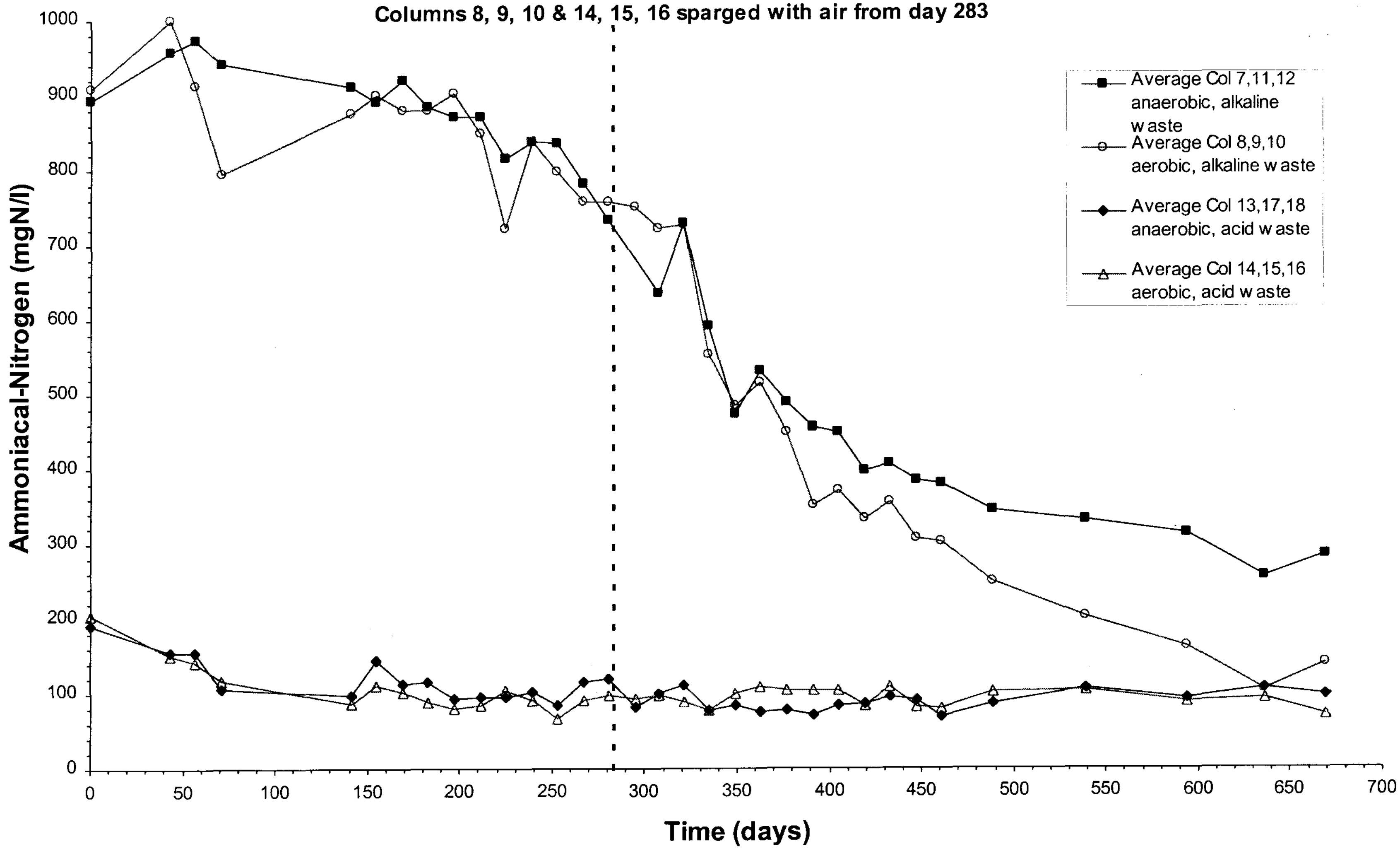


Fig. A2.8.2 pH of Leachates from Pitsea Refuse Columns

Columns 7-12: Hole 3, keg 2, alkaline waste area; Columns 13-18: Hole1, keg 1, acid waste area
Columns 8, 9, 10 & 14, 15, 16 sparged with air from day 283

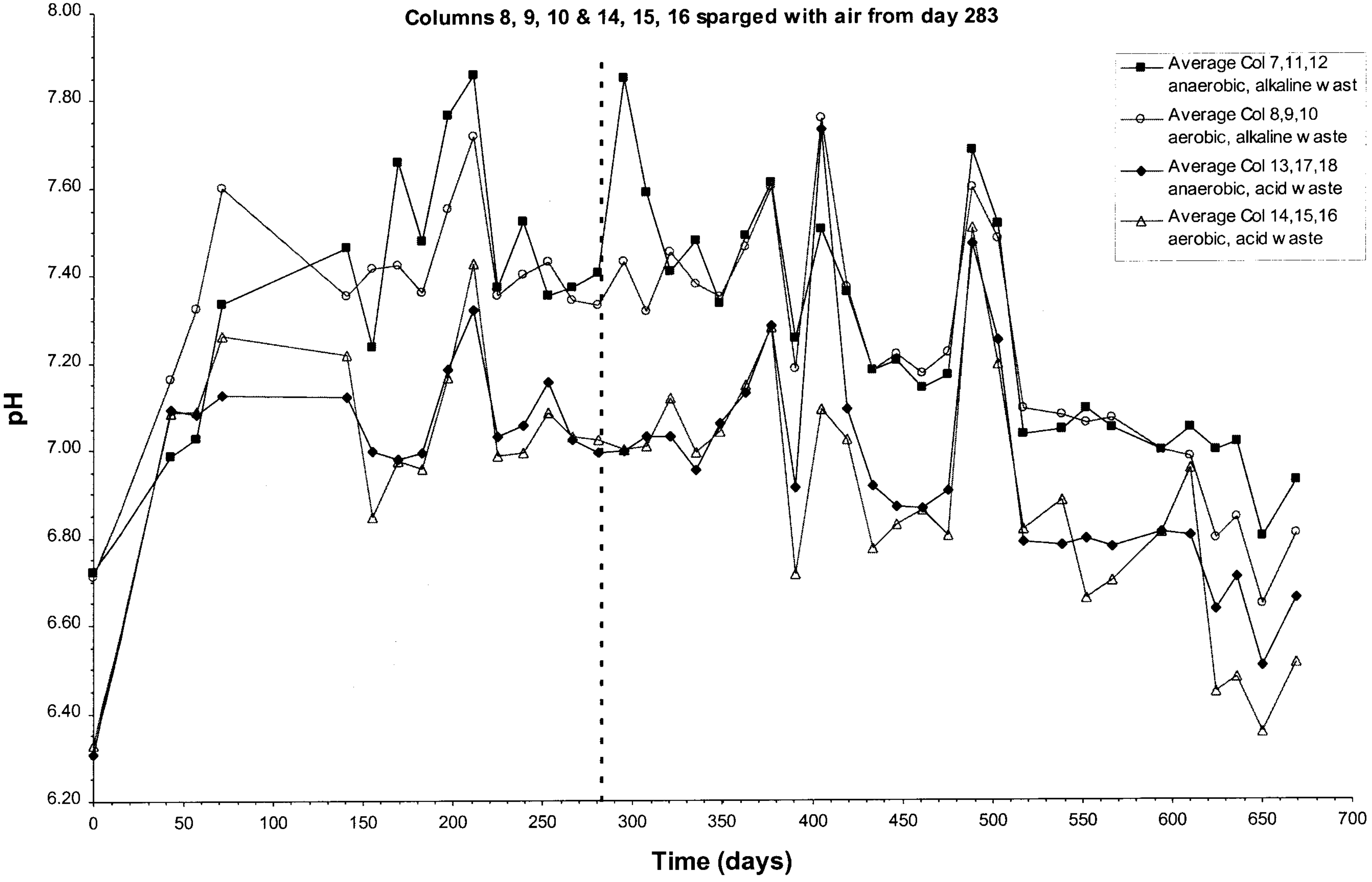


Fig. A2.8.3 Chloride Concentrations of Leachates from Pitsea Refuse Columns

Columns 7-12: Hole 3, keg 2, alkaline waste area; Columns 13-18: Hole 1, keg 1, acid waste area
Columns 8, 9, 10 & 14, 15, 16 sparged with air from day 283

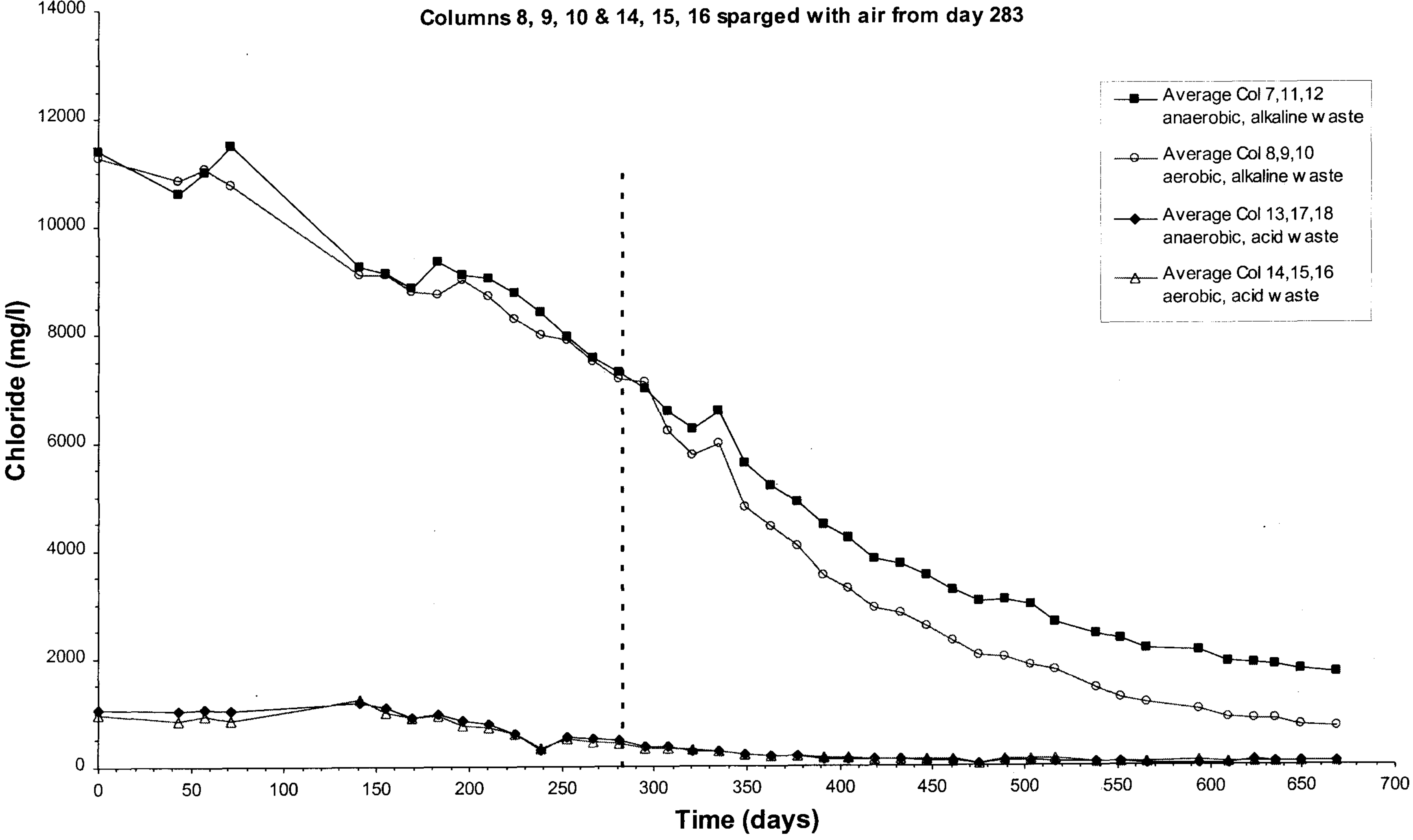


Fig. A2.8.4 Electrical Conductivity of Leachates from Pitsea Refuse Columns

Columns 7-12: Hole 3, keg 2, alkaline waste area; Columns 13-18: Hole 1, keg 1, acid waste area
Columns 8, 9, 10 & 14, 15, 16 sparged with air from day 283

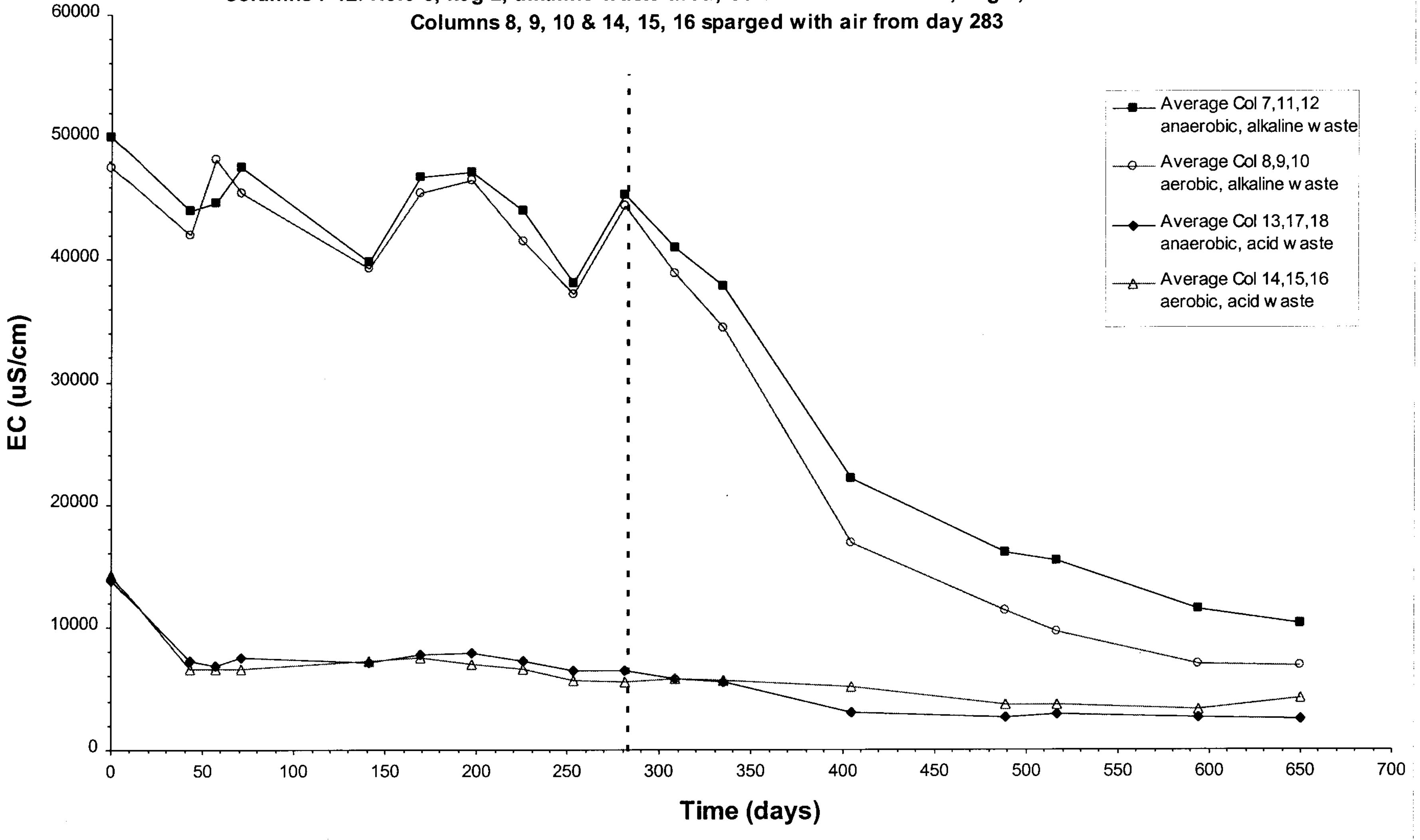
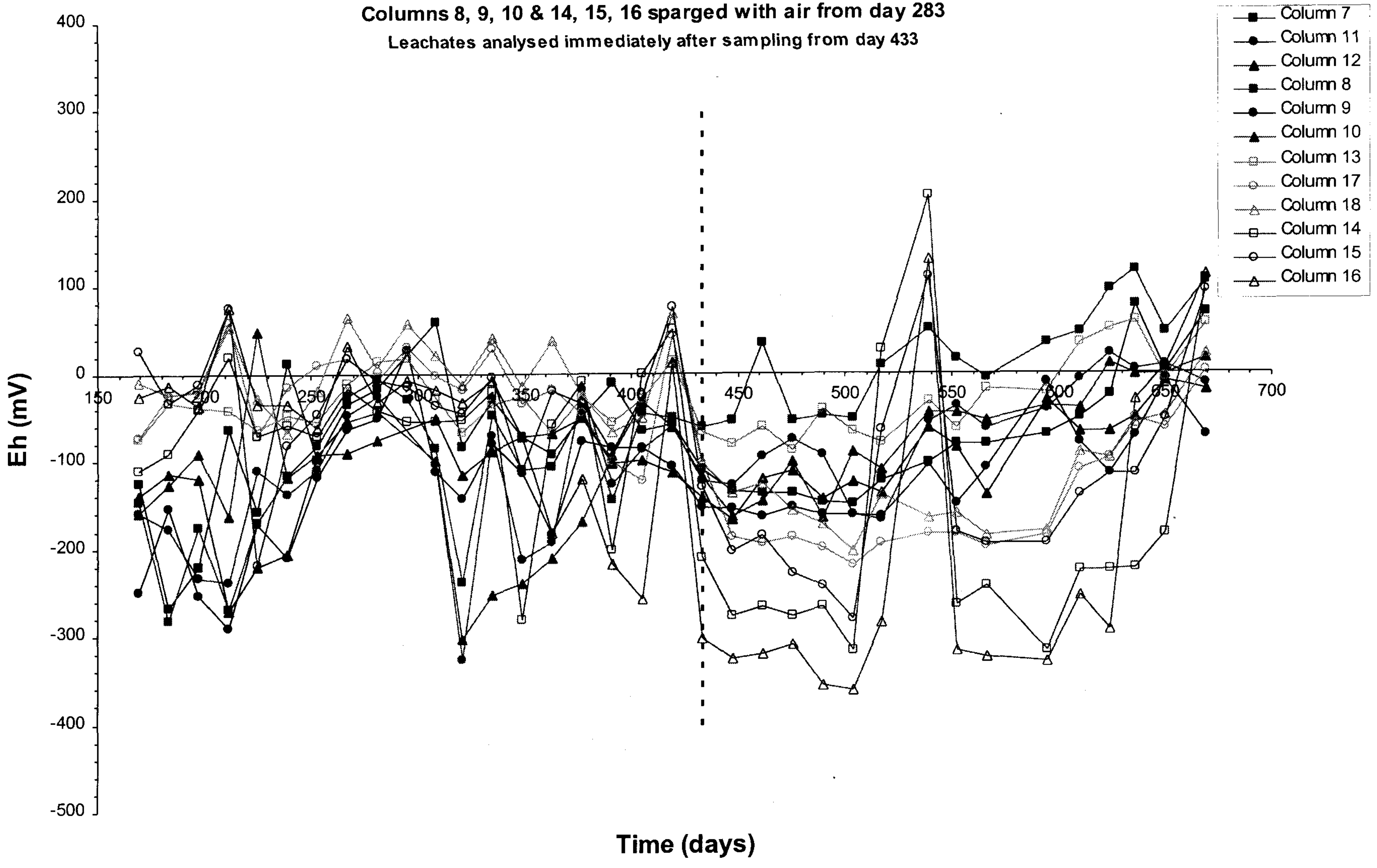


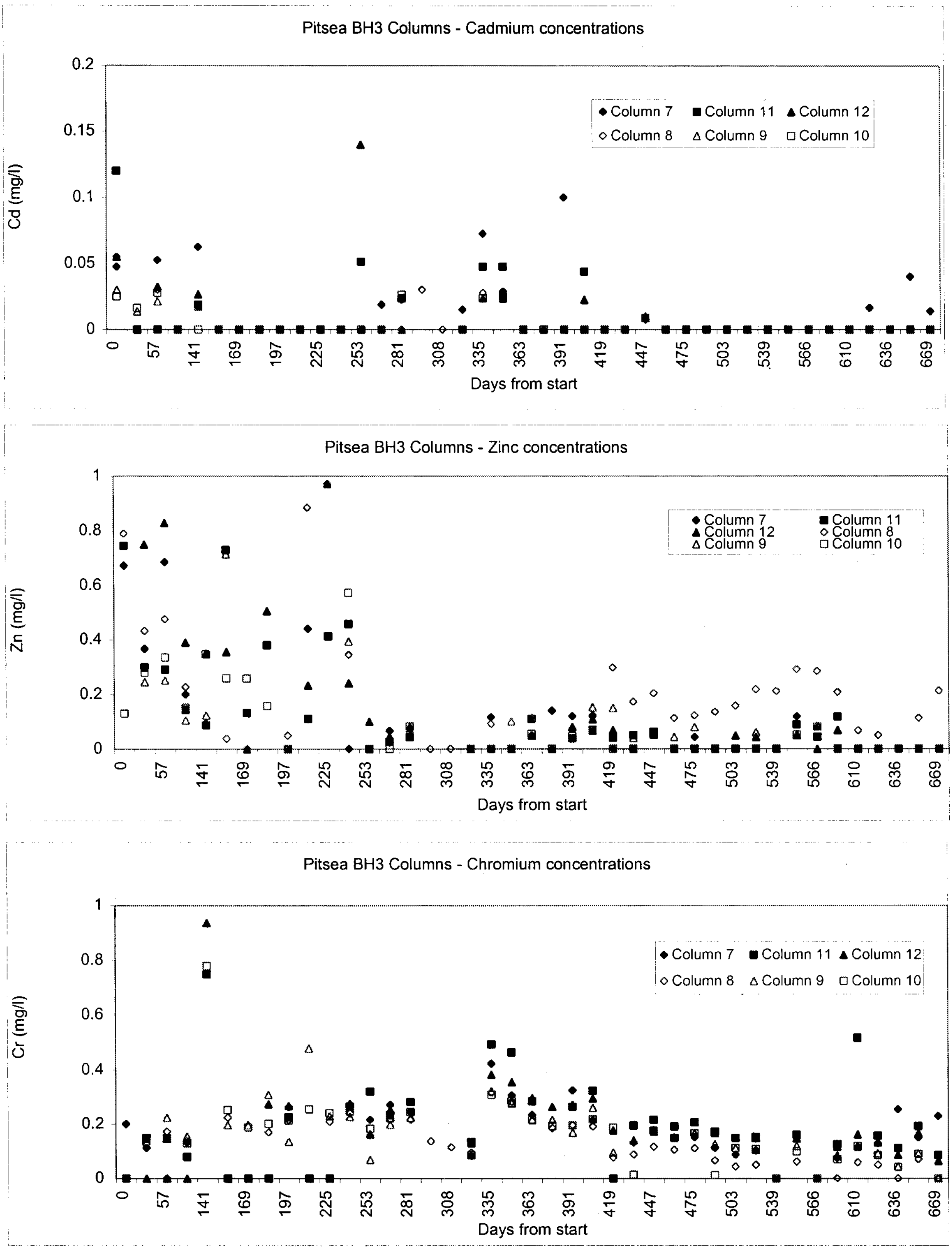
Fig. A2.8.5 Eh of Leachates from Pitsea Refuse Columns

Columns 7-12: Hole 3, keg 2, alkaline; Columns 13-18: Hole 1, keg 1, acid

Columns 8, 9, 10 & 14, 15, 16 sparged with air from day 283

Leachates analysed immediately after sampling from day 433



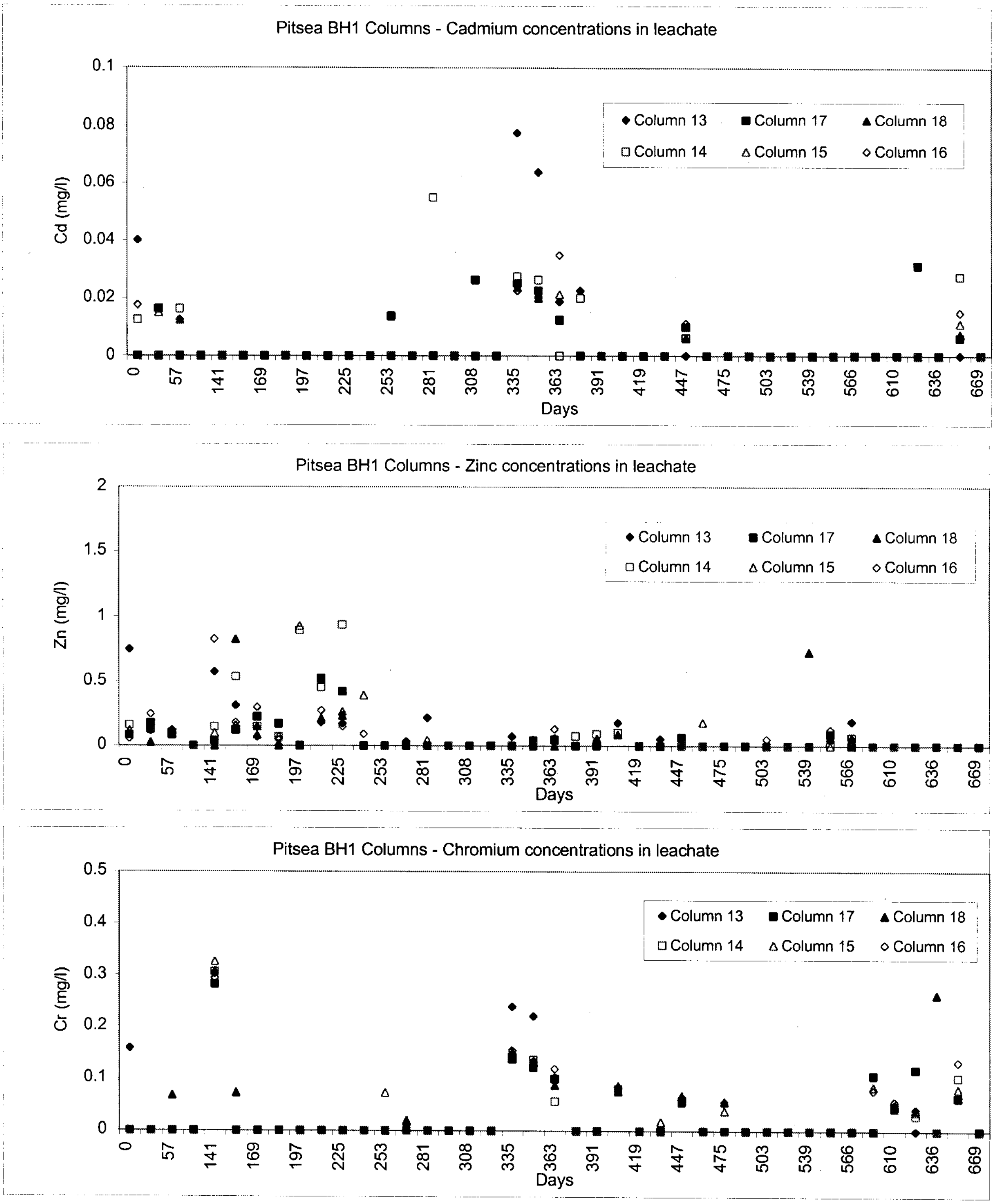


Analytical data at detection limit plotted as zero

Closed symbols are anaerobic columns, open symbols are aerobic columns

Note: anomalously high experimental data excluded

Figure A.2.8.6 Summary of dissolved metal concentrations in Pitsea BH3 column leachates


Pitsea BH1 Columns - Cadmium concentrations in leachate

Pitsea BH1 Columns - Zinc concentrations in leachate

Pitsea BH1 Columns - Chromium concentrations in leachate

Analytical data at detection limit plotted as zero
Closed symbols are anaerobic columns, open symbols are aerobic columns
Note: anomalously high experimental data excluded

Figure A.2.8.7 Summary of dissolved metal concentrations in Pitsea BH1 column leachates

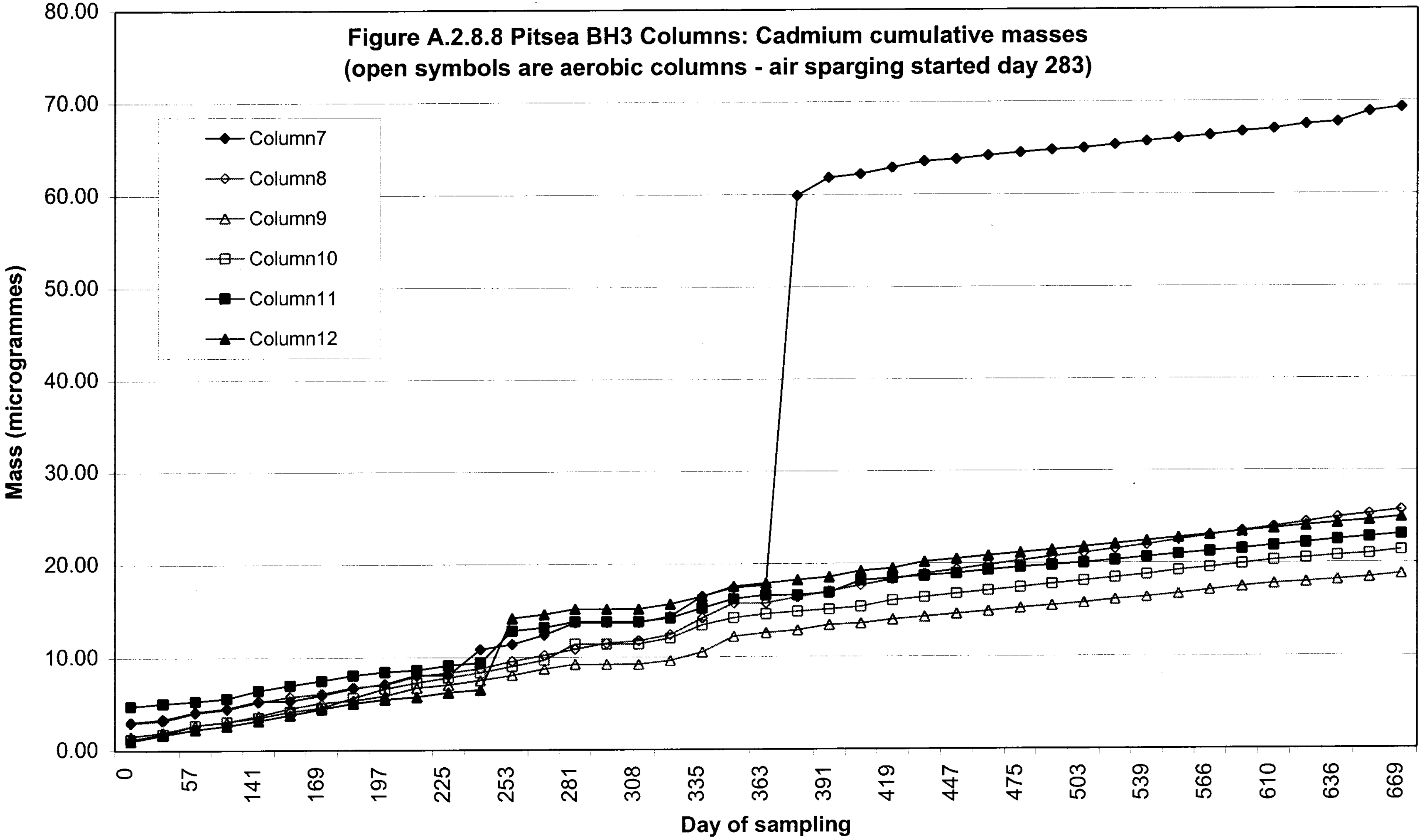


Figure A.2.8.8 Pitsea BH3 Columns: Cadmium cumulative masses (open symbols are aerobic columns - air sparging started day 283)

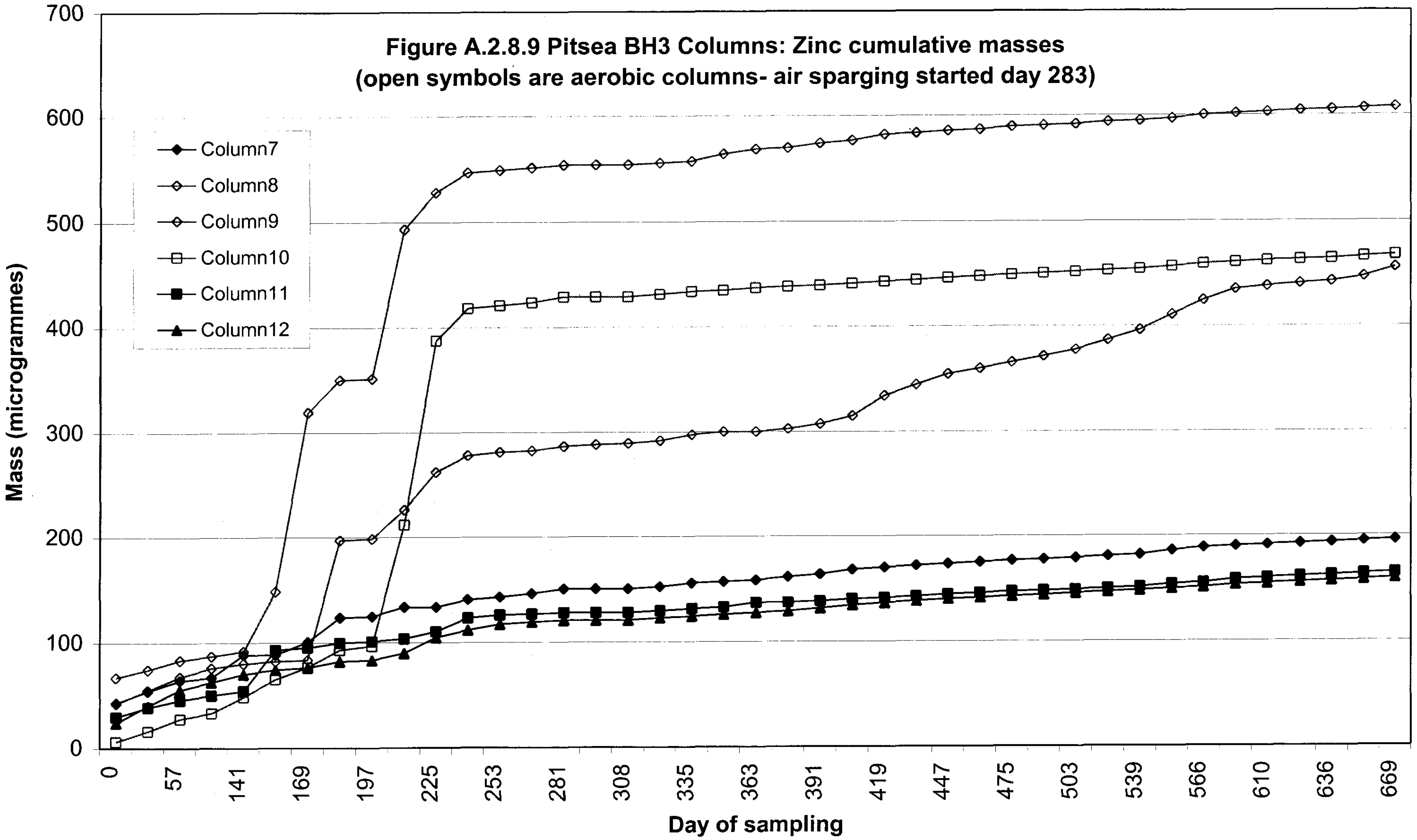


Figure A.2.8.9 Pitsea BH3 Columns: Zinc cumulative masses
(open symbols are aerobic columns- air sparging started day 283)

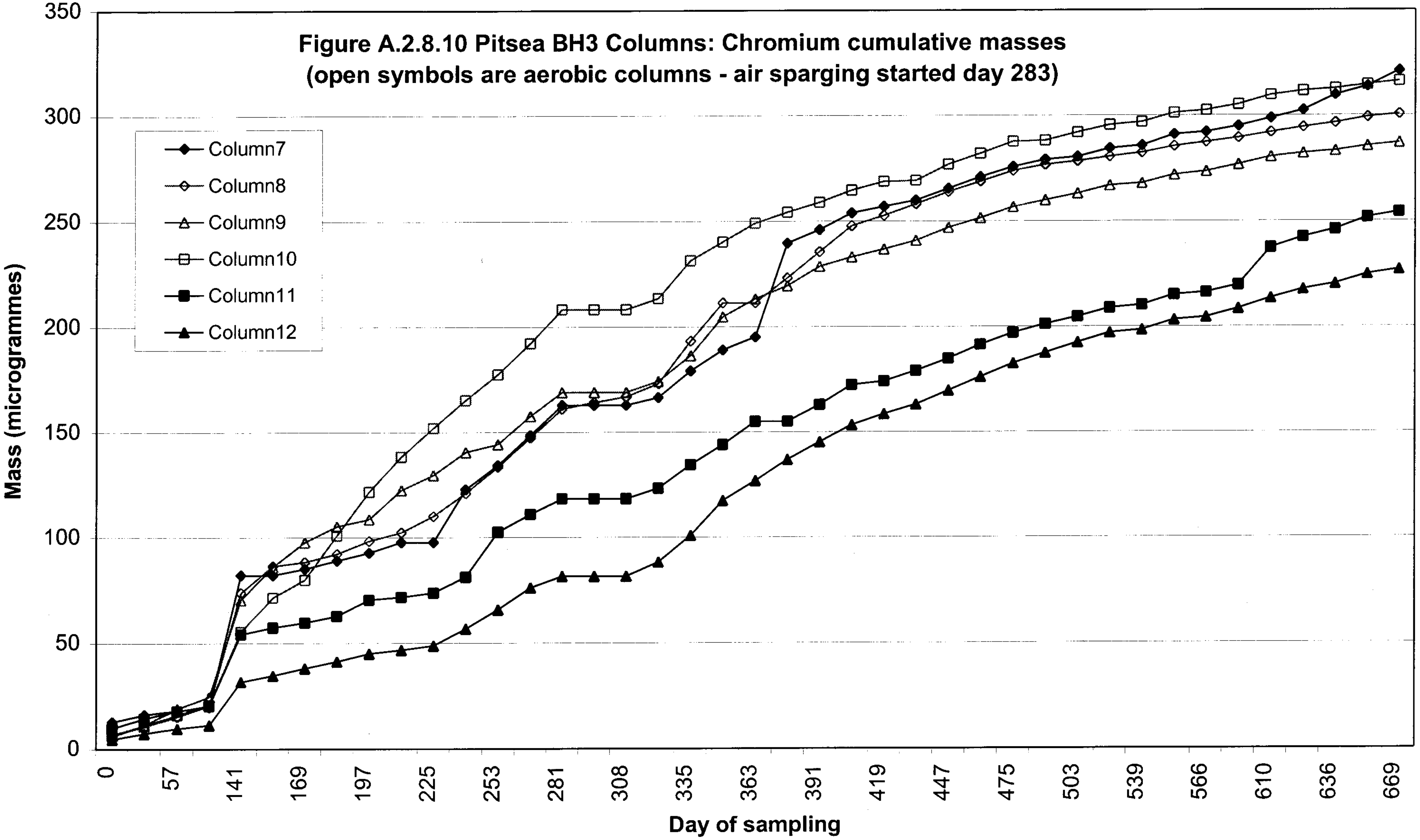


Figure A.2.8.10 Pitsea BH3 Columns: Chromium cumulative masses (open symbols are aerobic columns - air sparging started day 283)

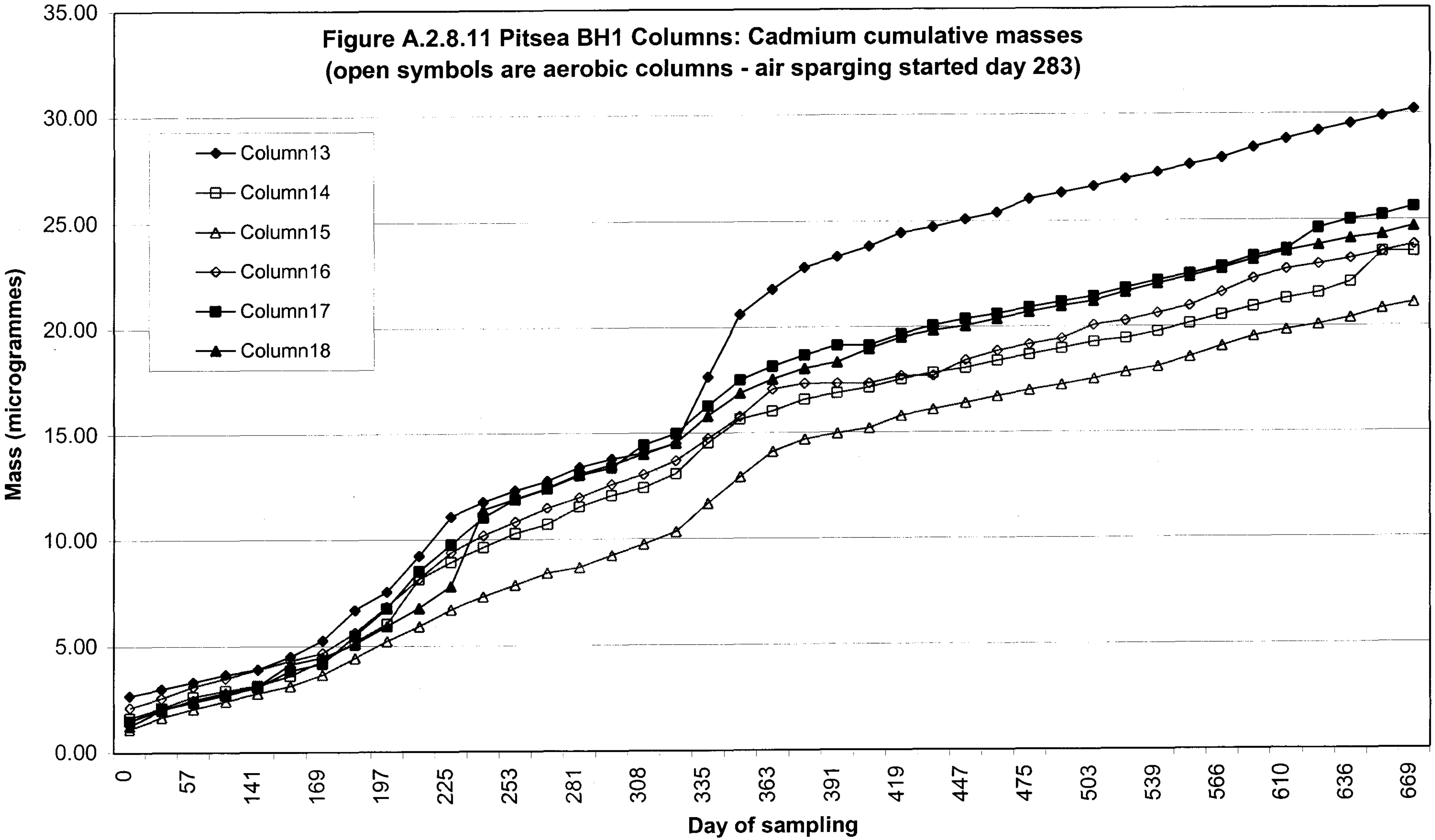


Figure A.2.8.11 Pitsea BH1 Columns: Cadmium cumulative masses (open symbols are aerobic columns - air sparging started day 283)

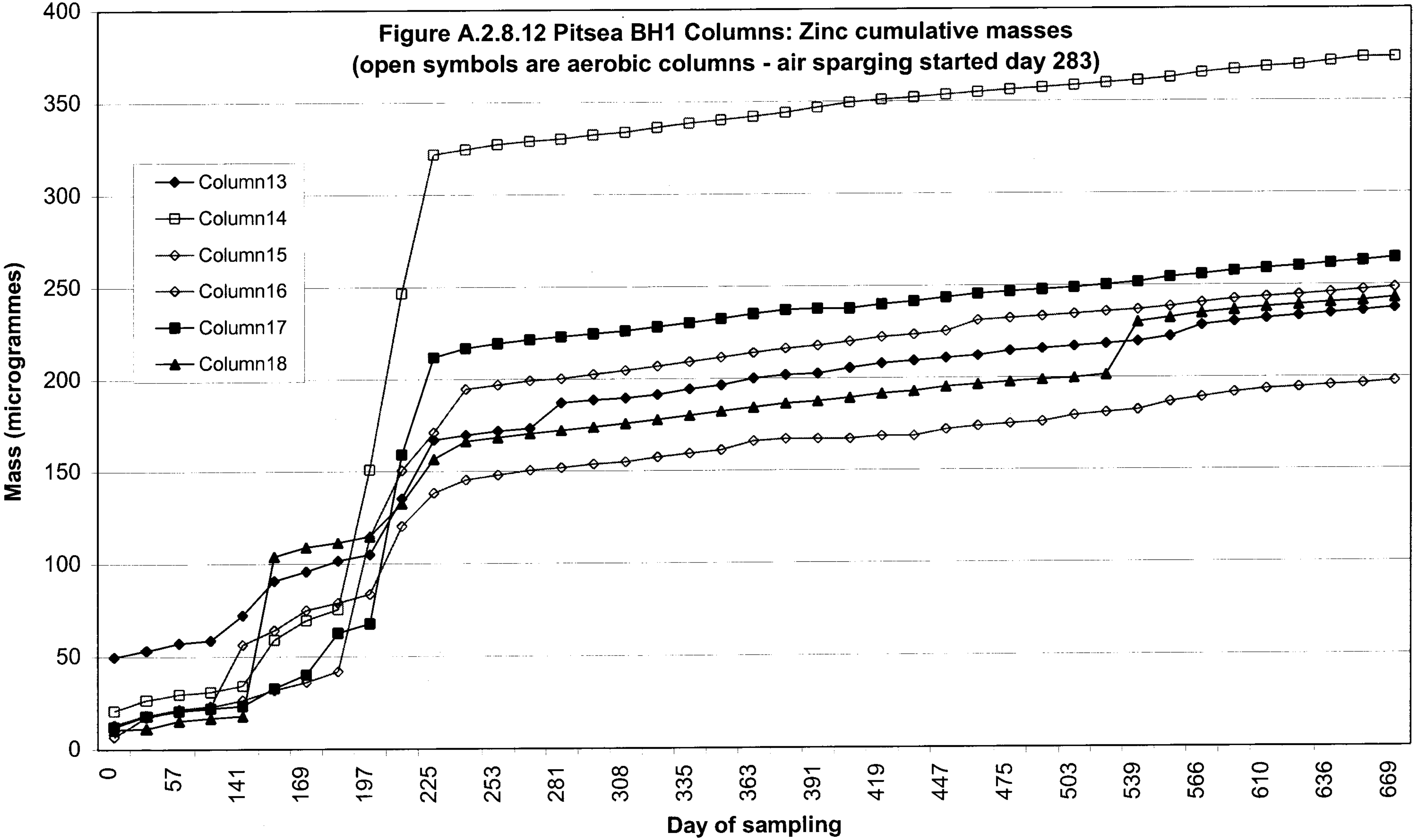


Figure A.2.8.12 Pitsea BH1 Columns: Zinc cumulative masses
(open symbols are aerobic columns - air sparging started day 283)

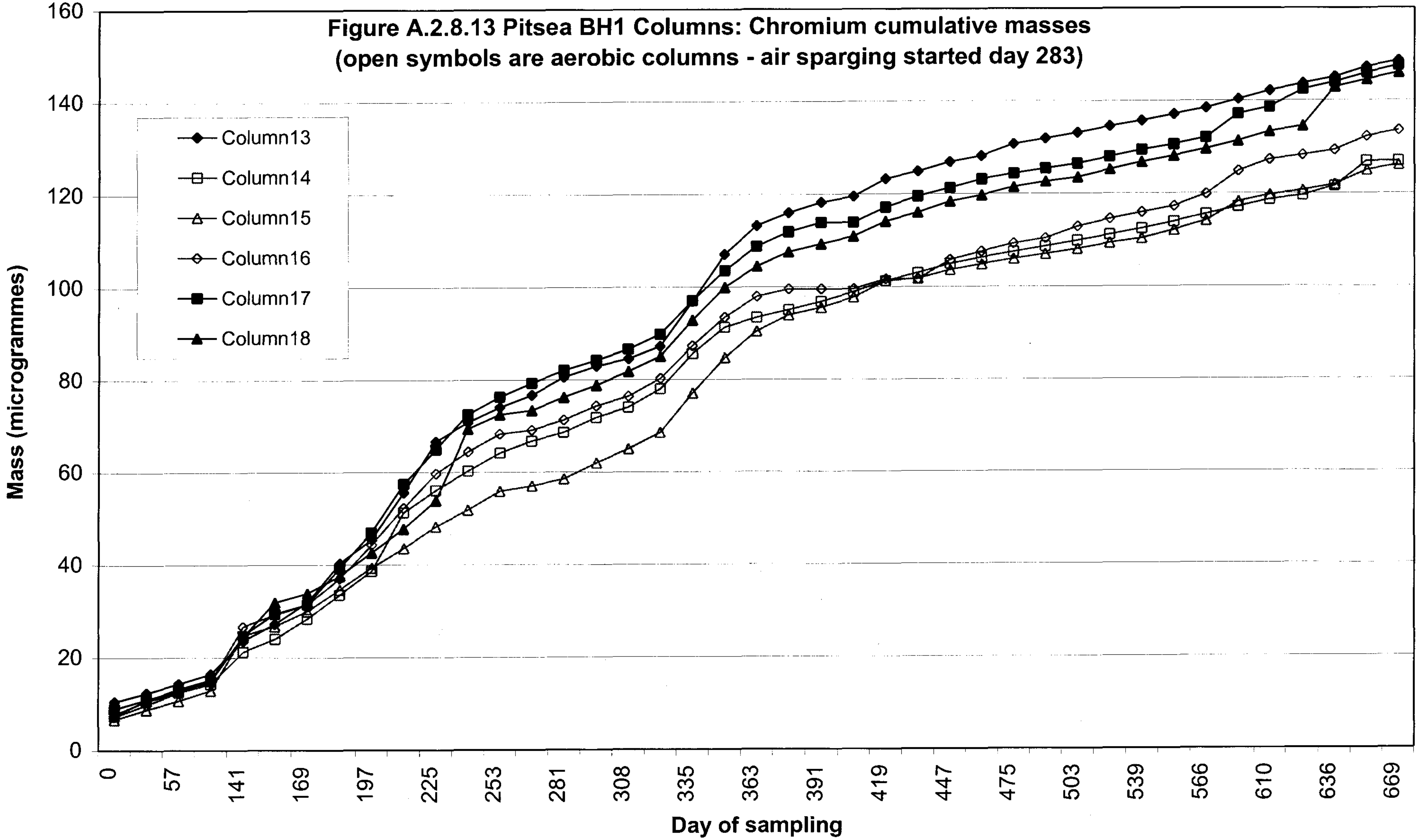


Figure A.2.8.13 Pitsea BH1 Columns: Chromium cumulative masses (open symbols are aerobic columns - air sparging started day 283)

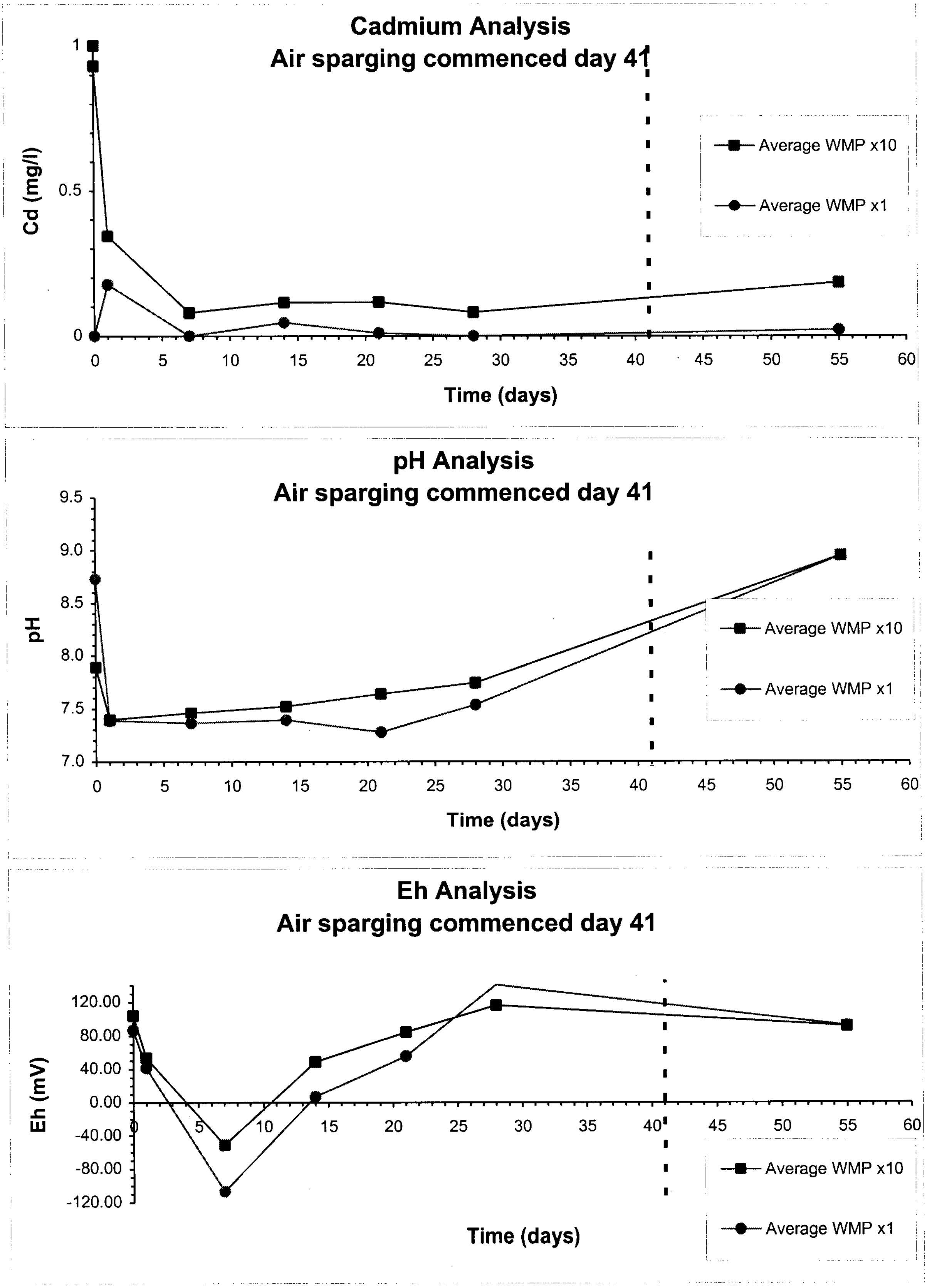


Figure A2.11.1 Cadmium amended batch experiments: Cadmium, pH and Eh analysis

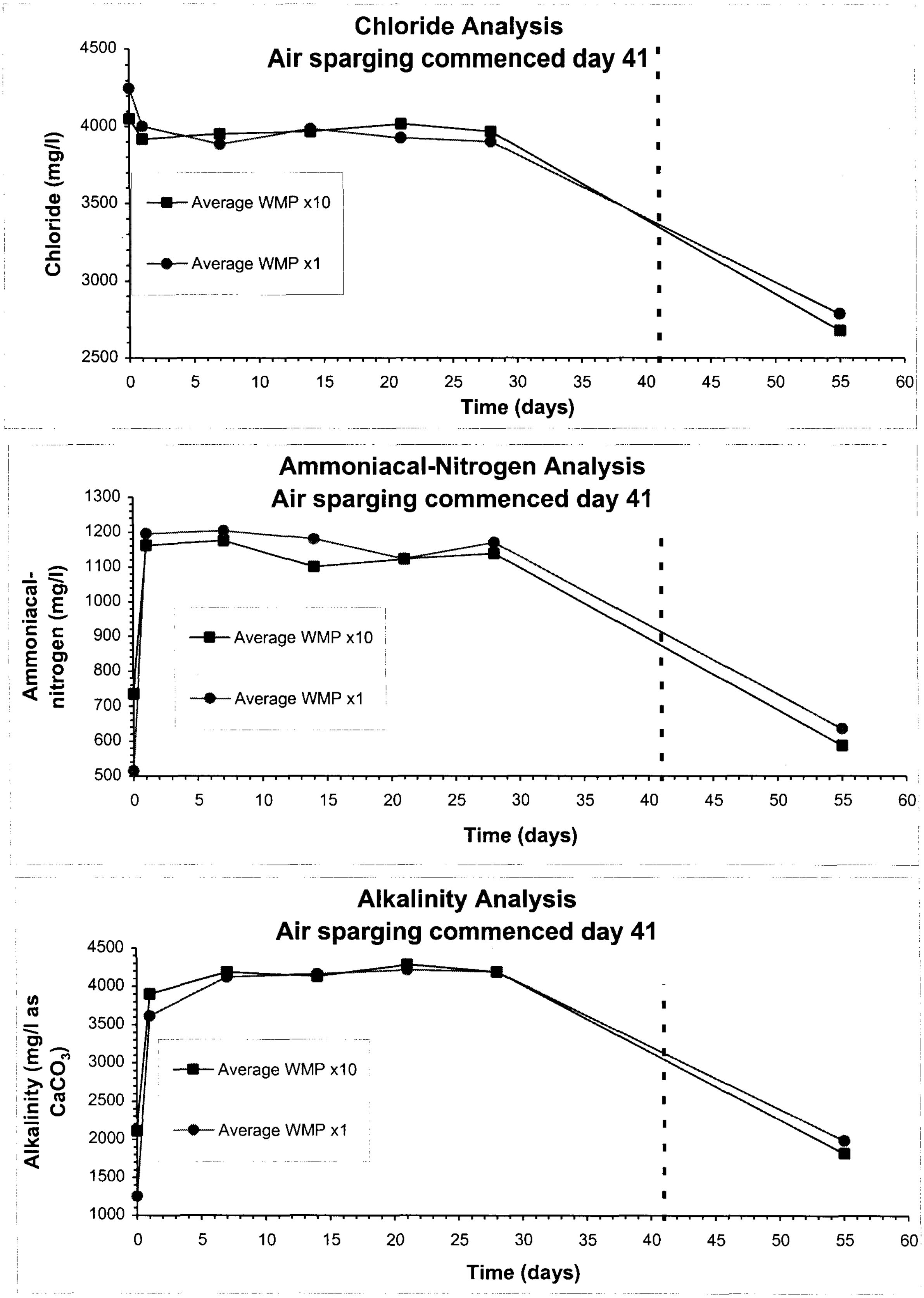


Figure A2.11.2 Cadmium amended batch experiments: Chloride, ammoniacal-N and alkalinity analysis

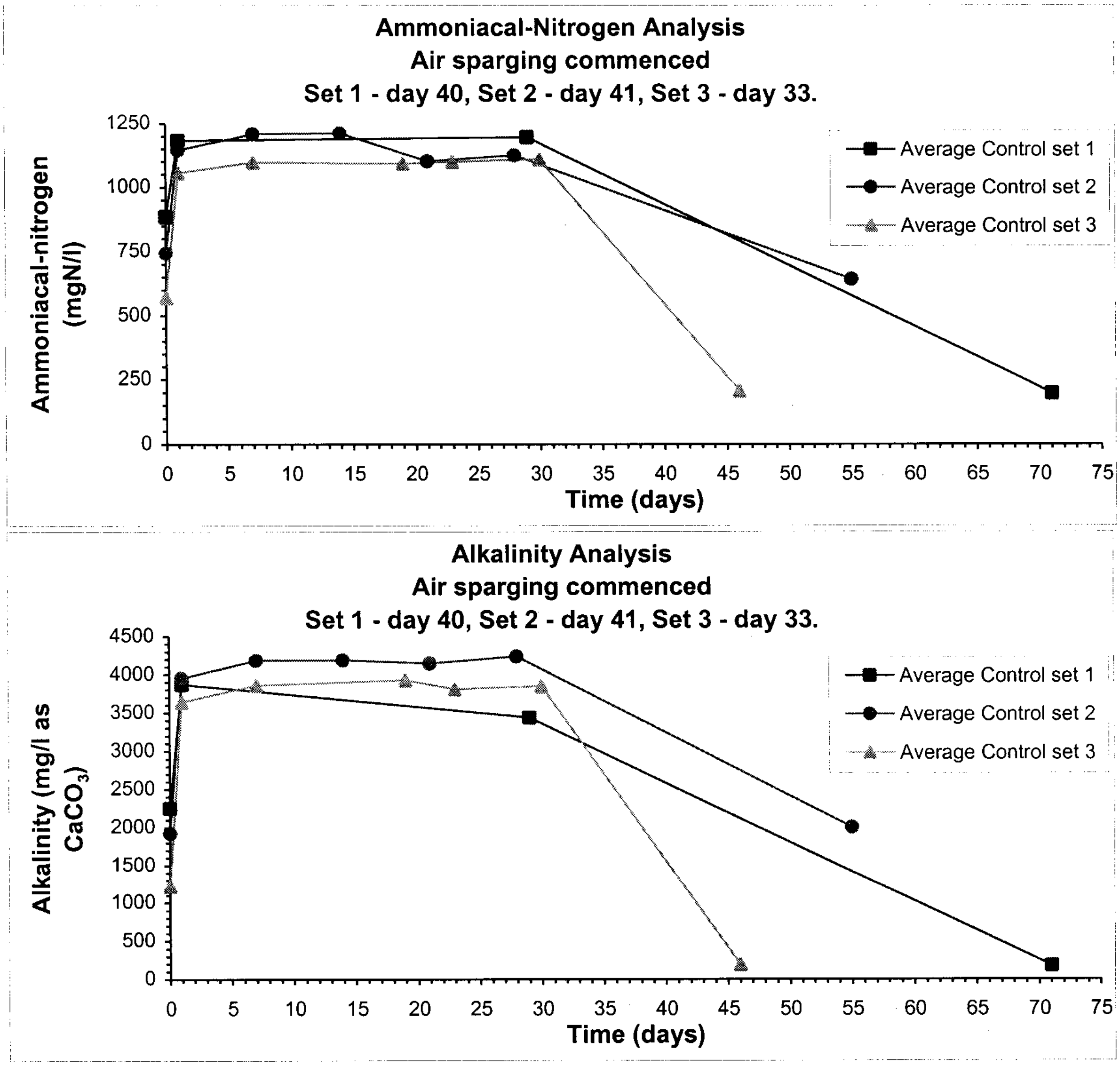


Figure A2.11.9 Batch experiments: Controls - Ammoniacal-N and alkalinity analysis

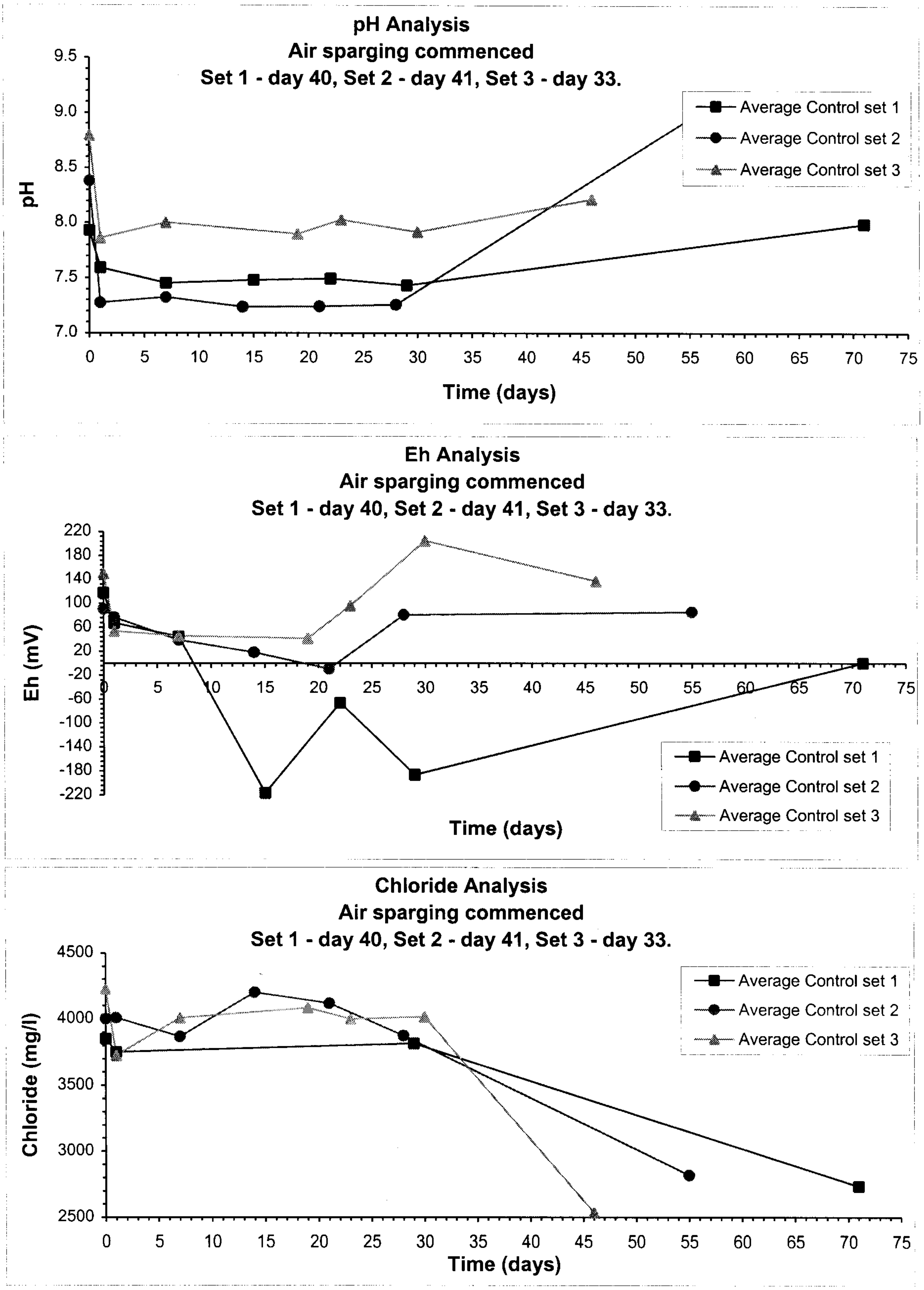


Figure A2.11.8 Batch experiments: Controls - pH, Eh and Chloride analysis

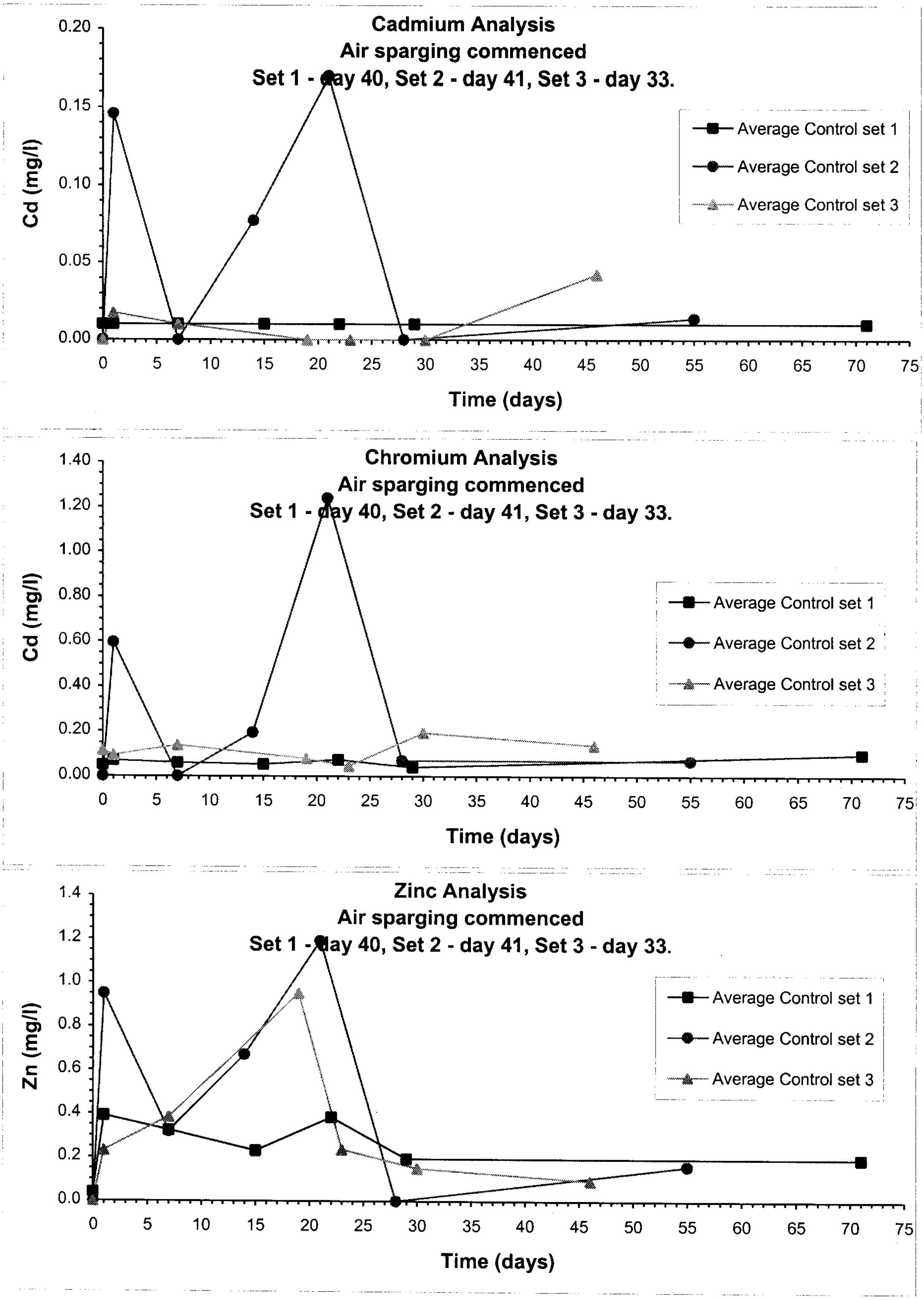


Figure A2.11.7 Batch experiments: Controls - Cadmium, chromium and zinc analysis

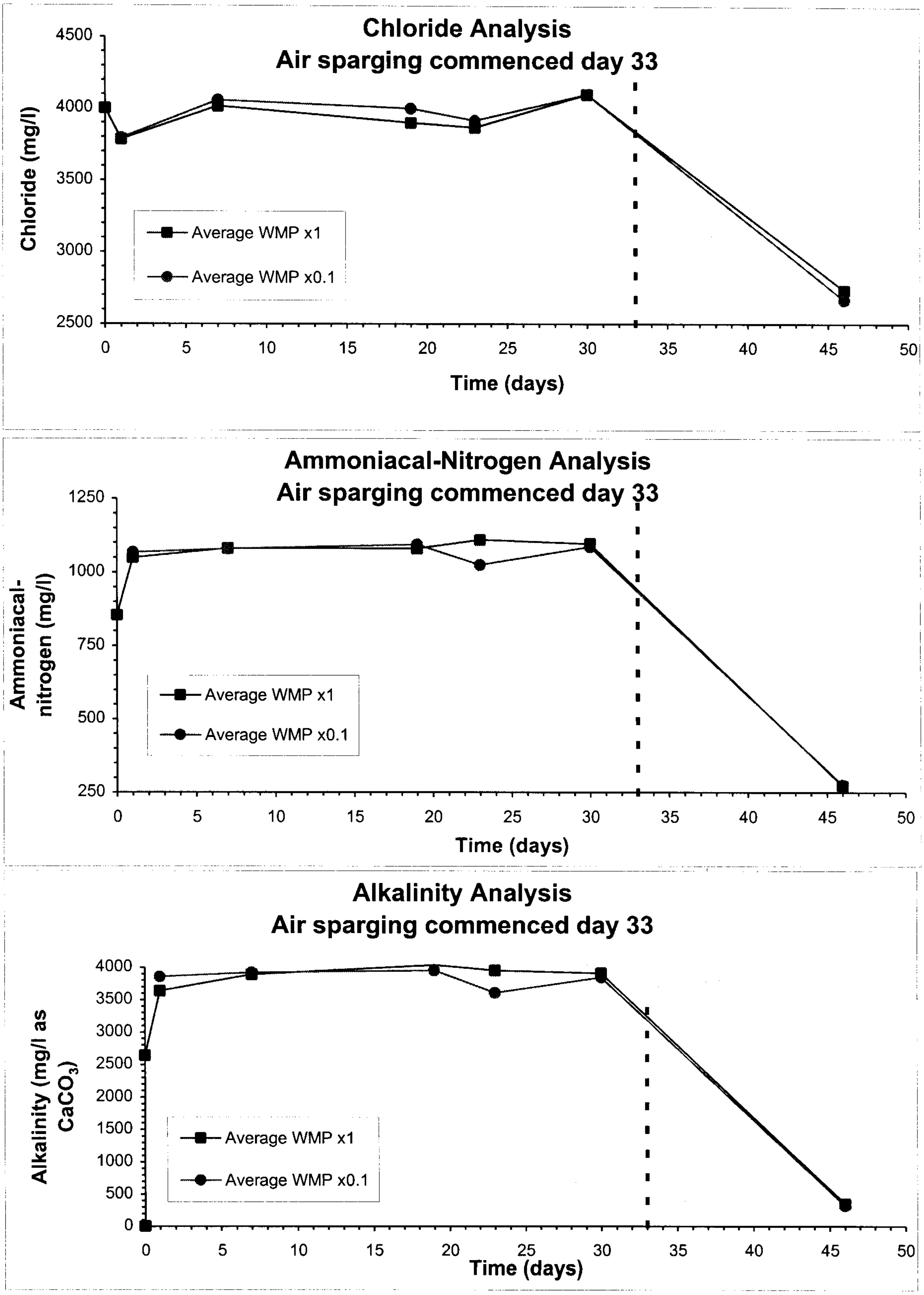


Figure A2.11.6 Zinc amended batch experiments: Chloride, ammoniacal-N and alkalinity analysis

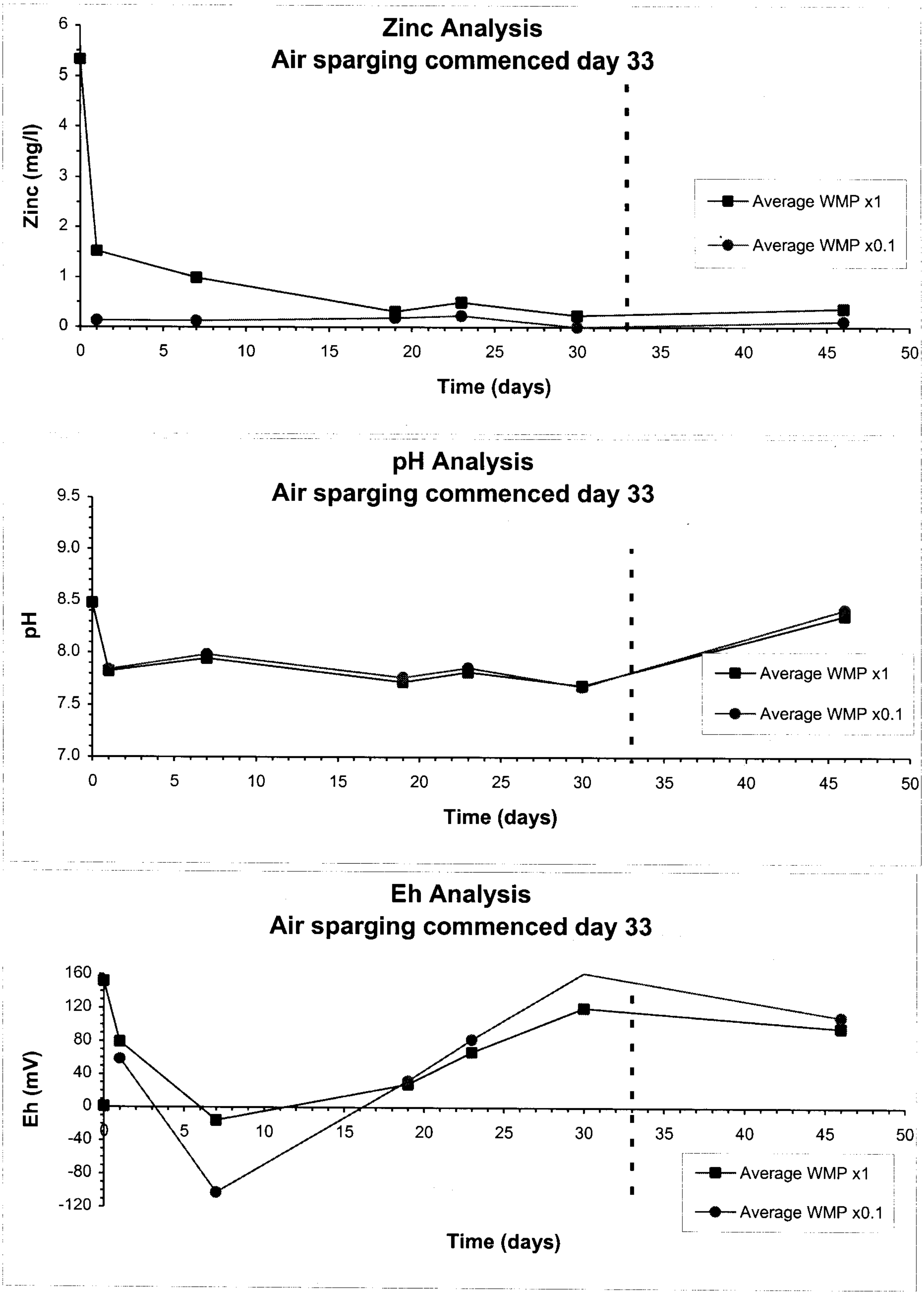


Figure A2.11.5 Zinc amended batch experiments: Cadmium, pH and Eh analysis

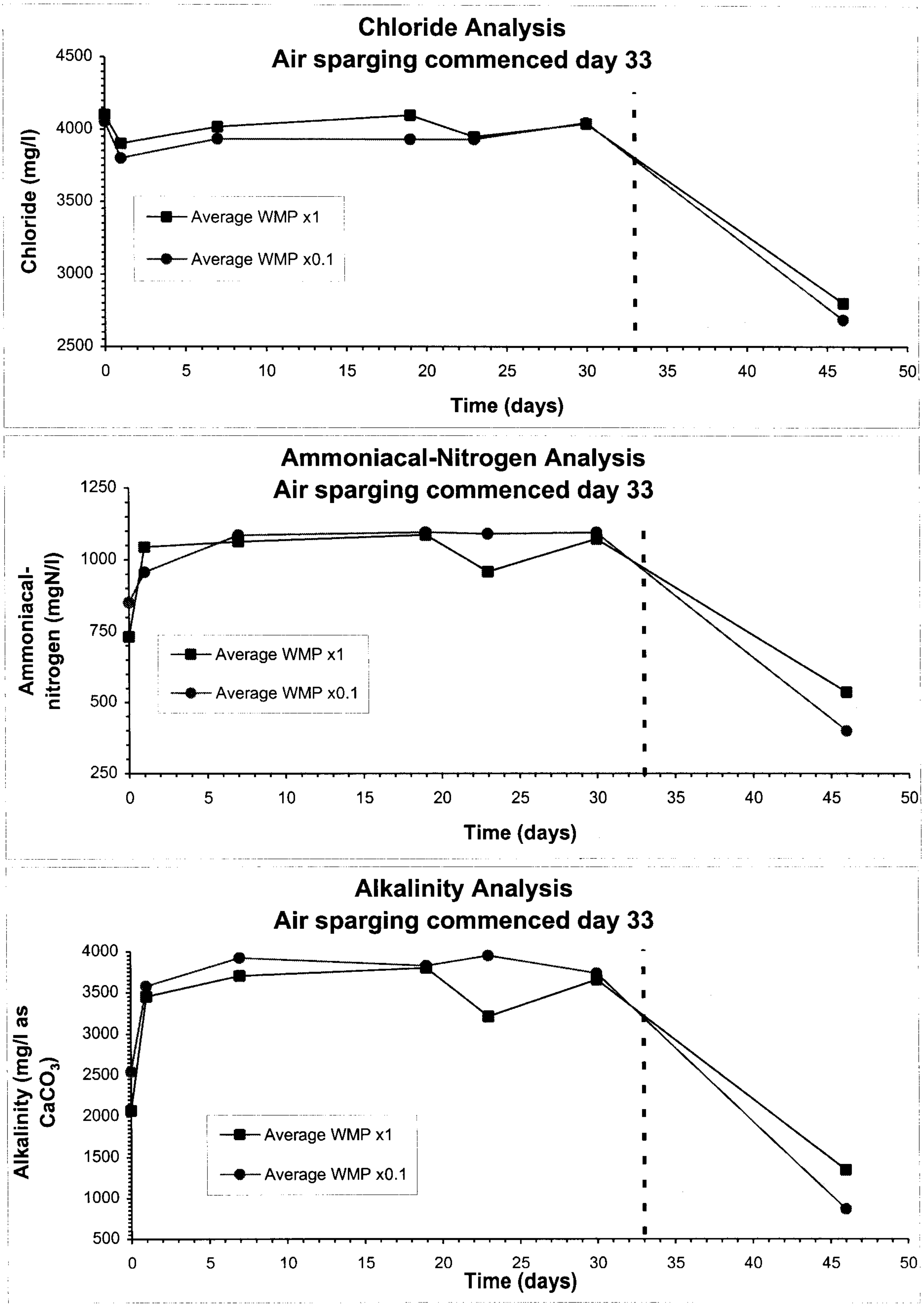


Figure A2.11.4 Chromium amended batch experiments: Chloride, ammoniacal-N and alkalinity analysis

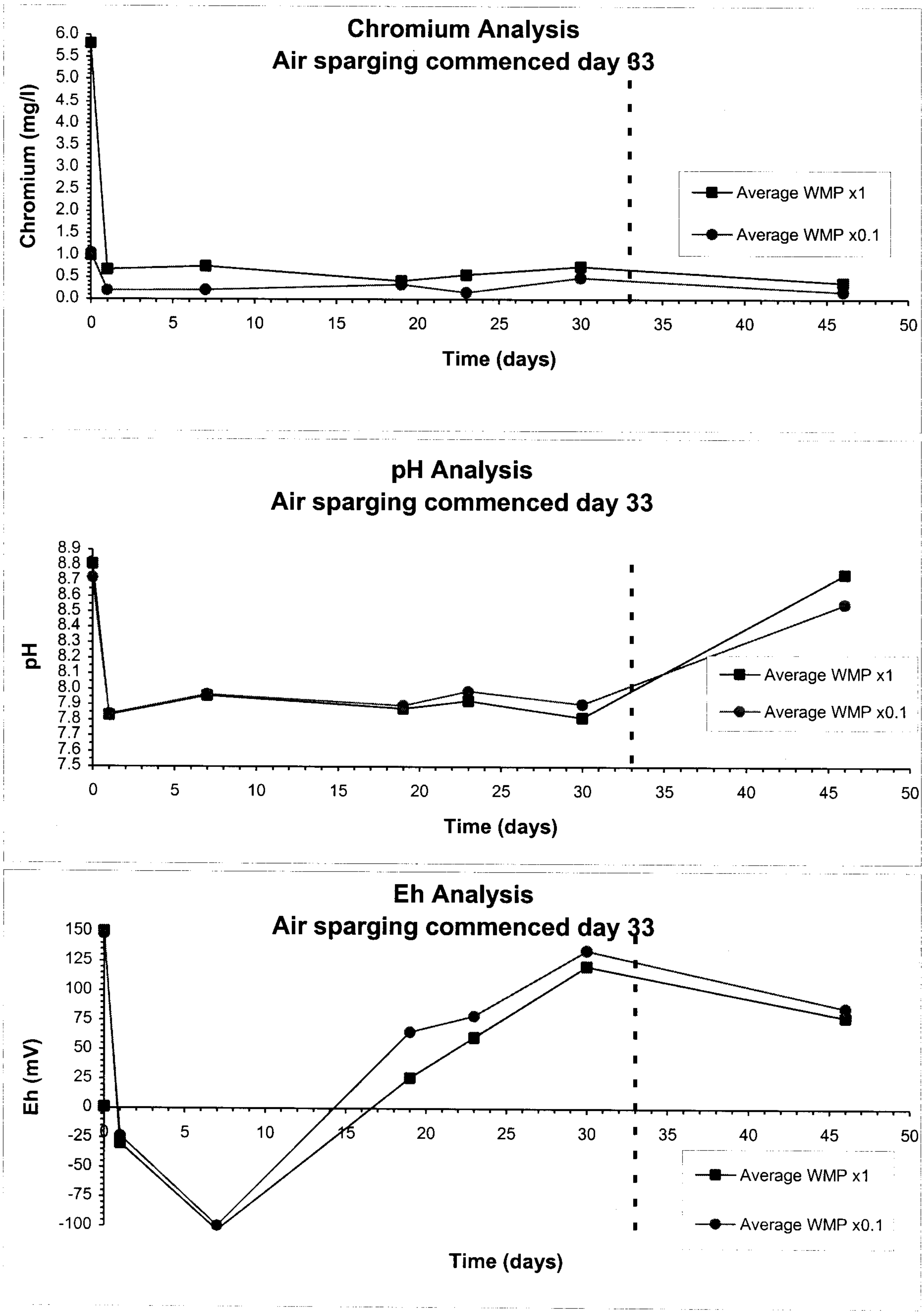


Figure A2.11.3 Chromium amended batch experiments: Cadmium, pH and Eh analysis

Table A2.3.1 Analysis of CAMR waste column leachate

Column 1 - 'aerobic', sparged with air from day 129

Week	Day	Date	mg/l						NH$_3$-N	Cl$^-$	pH	Total VFAs	EC	Eh	Total S
			Cd	Cr	Pb	Zn	Ni	Fe	(mg N/l)	mg/l		mg/l	uS/cm	(mV)	(mg/l)
1	62	08/05/96	<0.03	<0.13	<0.38	<0.08	<0.18	2.08	212.8	▨	▨	394	▨	▨	▨
2	69	15/05/96	<0.01	<0.07	<0.22	<0.04	0.26	11.90	237.9	▨	▨	77	▨	▨	▨
3	76	22/05/96	0.03	<0.07	<0.22	<0.04	0.29	11.80	214.6	2400	6.94	41	5580	▨	▨
4	83	29/05/96	<0.01	<0.07	<0.21	<0.04	0.18	6.78	218.3	1600	7.30	48	7770	▨	▨
5	90	05/06/96	<0.01	<0.07	<0.20	<0.04	0.22	16.51	234.9	1650	7.08	195	7570	▨	▨
6	97	12/06/96	0.01	<0.06	<0.19	0.05	0.30	2.16	239.9	1530	7.07	<20	7660	▨	▨
7	104	19/06/96	▨	▨	▨	▨	▨	▨	232.8	1380	7.23	▨	6810	▨	21.48
8	111	26/06/96	0.03	<0.06	▨	0.10	0.24	1.44	252.5	1490	7.09	52	6910	▨	▨
9	118	03/07/96	0.02	<0.06	▨	0.07	0.42	11.17	253.8	1550	7.20	<20	7650	▨	21.58
12	139	24/07/96	<0.01	<0.06	▨	0.51	0.29	9.23	238.1	1435	6.90	24	7870	▨	▨
13	146	31/07/96	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	19.59
14	153	07/08/96	0.09	<0.06	▨	0.52	0.33	6.82	225.8	1660	6.95	<20	6160	▨	▨
16	167	21/08/96	0.03	<0.06	▨	0.13	0.20	5.86	172.9	1340	6.98	▨	6590	▨	▨
18	181	04/09/96	0.11	<0.08	▨	1.40	0.22	5.82	220.8	1405	6.85	▨	6920	▨	▨
20	195	18/09/96	0.03	<0.25	▨	0.33	0.41	2.50	210.7	1340	7.52	▨	7340	▨	▨
22	209	02/10/96	0.20	<0.13	▨	0.62	0.37	5.85	217.6	1335	6.84	▨	7130	▨	▨
24	223	16/10/96	0.11	<0.08	▨	0.30	0.21	5.75	236.8	1325	7.04	▨	8400	▨	19.33
26	237	30/10/96	0.02	<0.06	▨	0.04	0.20	3.20	220.6	1255	7.04	27	8520	▨	▨
28	251	13/11/96	0.06	<0.06	▨	0.13	0.17	1.19	201.3	1225	7.10	▨	8650	▨	▨
29	258	20/11/96	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	22.72
30	265	27/11/96	0.05	0.06	▨	0.23	0.18	0.60	250.8	1225	7.46	▨	7020	▨	▨
34	292	24/12/96	0.12	<0.13	▨	0.27	<0.18	2.43	212.5	1155	7.02	▨	7450	▨	▨
36	306	08/01/97	0.21	0.54	▨	0.33	<0.35	0.17	195.0	1110	6.96	▨	7340	▨	▨
38	320	22/01/97	0.39	<0.25	▨	1.04	<0.35	1.12	255.2	1080	6.97	▨	7130	▨	▨
40	334	05/02/97	0.17	0.10	▨	0.21	0.43	1.02	164.3	1050	7.12	▨	6920	▨	▨
42	348	19/02/97	0.01	<0.06	▨	0.26	0.17	16.32	207.4	1095	7.11	▨	7380	▨	▨
44	362	05/03/97	0.02	<0.06	▨	0.09	0.18	5.13	228.4	1010	7.15	▨	6930	▨	▨
46	376	19/03/97	0.11	<0.06	▨	<0.04	0.14	2.42	257.5	910	7.41	▨	7010	▨	376
48	390	02/04/97	0.02	<0.06	▨	0.27	0.16	2.22	220.1	850	7.18	▨	6700	▨	▨
50	404	16/04/97	0.02	<0.06	▨	0.21	0.21	1.73	190.9	800	7.20	▨	7020	▨	▨
52	418	30/04/97	<0.01	<0.06	▨	0.11	0.12	2.32	176.0	825	7.09	▨	6270	▨	▨
54	432	14/05/97	<0.01	<0.06	▨	0.05	<0.09	3.22	192.1	613	7.03	▨	5750	▨	432
56	446	29/05/97	<0.01	<0.06	▨	0.08	0.10	2.49	193.4	650	7.14	▨	6070	▨	▨
58	460	11/06/97	<0.01	0.07	▨	<0.04	<0.09	1.72	192.2	588	7.11	▨	5840	▨	▨
60	474	25/06/97	0.05	<0.06	▨	0.22	0.09	2.51	171.0	575	7.18	▨	5750	▨	▨
62	488	09/07/97	<0.01	<0.06	▨	<0.04	<0.09	1.15	156.4	500	7.06	▨	5750	▨	▨
64	502	23/07/97	<0.01	<0.06	▨	<0.04	<0.09	1.04	157.3	450	6.98	▨	▨	▨	502
66	516	06/08/97	0.02	<0.06	▨	0.04	<0.09	1.70	135.6	450	7.25	▨	5430	28.5	▨
68	530	20/08/97	<0.01	<0.06	▨	0.10	<0.09	5.50	139.7	400	7.04	▨	▨	35	▨
70	544	03/09/97	<0.01	<0.06	▨	<0.04	<0.09	4.21	▨	350	7.41	▨	▨	64	▨
72	558	17/09/97	<0.01	<0.06	▨	<0.04	<0.09	12.53	129.2	375	7.42	▨	▨	67	558
74	572	01/10/97	<0.05	<0.06	▨	0.14	<0.09	15.74	121.5	300	7.07	▨	5000	52	▨
76	586	15/10/97	<0.01	<0.06	▨	<0.04	0.04	0.79	116.7	275	7.10	▨	▨	94	▨
78	600	29/10/97	<0.01	<0.06	▨	<0.04	<0.09	3.30	106.2	250	7.21	▨	4250	48	▨
80	614	12/11/97	0.67	0.65	▨	0.04	0.65	2.51	137.9	200	7.23	▨	4500	123	▨
82	628	26/11/97	0.03	<0.06	▨	<0.04	<0.09	4.94	95.0	225	7.13	▨	▨	136	▨
84	642	12/12/97	0.04	<0.06	▨	0.05	<0.09	1.75	113.7	175	7.14	▨	4600	133	642
86	655	23/12/97	0.03	<0.06	▨	<0.04	<0.09	2.28	105.8	200	7.14	▨	▨	127	▨
88	670	07/01/98	<0.01	<0.06	▨	<0.04	<0.09	4.37	109.7	200	7.26	▨	4400	114	▨
90	684	21/01/98	0.09	0.21	▨	0.10	0.15	4.19	90.5	250	7.26	▨	▨	154	▨
92	698	04/02/98	0.07	0.20	▨	0.10	0.14	2.43	78.5	125	7.42	▨	▨	108	▨
94	712	18/02/98	<0.01	<0.06	▨	0.07	<0.09	1.51	95.5	117	7.35	▨	3150	100	712
96	726	04/03/98	0.07	0.10	▨	0.07	0.09	1.54	72.8	100	7.59	▨	▨	120	▨
98	740	18/03/98	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
100	754	01/04/98	<0.03	<0.13	▨	0.06	<0.18	0.79	130.6	200	8.14	▨	▨	-6	▨
102	768	15/04/98	<0.01	<0.06	▨	0.08	0.12	4.60	120.2	67	6.89	▨	▨	-26	▨
104	782	29/04/98	<0.01	<0.06	▨	<0.04	0.13	0.75	124.3	117	6.71	▨	▨	-64	782
106	796	13/05/98	0.01	0.06	▨	0.04	0.14	0.44	147.5	100	6.78	▨	▨	-85	▨
108	810	27/05/98	<0.01	0.04	▨	0.04	0.10	39.83	78.2	75	6.85	▨	7200	-112	▨
110	824	10/06/98	<0.01	0.05	▨	0.05	0.06	67.19	157	75	6.93	▨	▨	-150	▨
112	838	24/06/98	<0.01	<0.04	▨	0.06	0.04	28.48	▨	83	7.02	▨	▨	-148	838
114	852	08/07/98	<0.01	<0.04	▨	0.18	0.03	51.83	101.5	100	6.87	▨	▨	-125	▨
116	866	22/07/98	0.01	<0.04	▨	0.07	0.04	20.76	▨	67	6.80	▨	5700	-109	▨
119	888	13/08/98	<0.01	<0.04	▨	<0.04	<0.02	15.69	79.2	67	6.88	▨	▨	-131	▨

Maximum	0.67	0.65	0.00	1.40	0.65	67.19	257.5	2400	8.14	394	8650	154	838
Minimum	0.01	0.04	0.00	0.04	0.03	0.17	72.8	67	6.71	24	3150	-150	19.33

▨ Not analysed

Table A2.3.2 Analysis of CAMR waste column leachate

Column 2 - 'anerobic control', no air sparging.

Week	Day	Date	mg/l						NH$_3$-N	Cl$^-$	pH	Total VFAs	EC	Eh	Total S
			Cd	Cr	Pb	Zn	Ni	Fe	(mg N/l)	mg/l		mg/l	uS/cm	(mV)	(mg/l)
1	62	08/05/96	<0.03	<0.16	<0.47	<0.09	<0.22	22.89	185.9	▨	▨	580	▨	▨	▨
2	69	15/05/96	<0.01	<0.07	<0.21	0.08	0.23	8.01	160.7	▨	▨	24	▨	▨	▨
3	76	22/05/96	<0.01	<0.07	<0.22	<0.04	0.29	9.88	213.4	1500	6.94	37	4890	▨	▨
4	83	29/05/96	<0.01	<0.07	<0.21	<0.04	0.16	13.89	208.7	1467	7.20	37	7340	▨	▨
5	90	05/06/96	<0.03	<0.13	<0.38	0.18	0.33	5.88	192.8	1400	7.39	71	7870	▨	▨
6	97	12/06/96	<0.02	<0.08	<0.24	0.06	0.27	2.08	194.4	1500	7.17	<20	7450	▨	▨
7	104	19/06/96	▨	▨	▨	▨	▨	▨	198.8	1470	7.37	▨	6600	▨	21.86
8	111	26/06/96	0.03	<0.08	▨	0.07	0.28	2.12	218.4	1520	7.29	<20	8300	▨	▨
9	118	03/07/96	<0.03	<0.13	▨	0.15	<0.18	7.19	218.7	1550	7.01	<20	6910	▨	24.32
12	139	24/07/96	<0.01	<0.06	▨	160.28	0.17	2.24	230.2	1290	6.41	1410	7970	▨	▨
13	146	31/07/96	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	22.44
14	153	07/08/96	<0.01	<0.06	▨	6.65	0.22	1.34	212.2	1340	6.78	428	7440	▨	▨
16	167	21/08/96	0.02	<0.06	▨	2.36	0.22	6.20	163.6	1480	6.89	22	6480	▨	▨
18	181	04/09/96	0.02	<0.08	▨	0.33	0.21	5.34	188.7	1468	6.84	<20	6050	▨	▨
20	195	18/09/96	<0.03	<0.13	▨	0.67	0.29	1.29	238.7	1520	7.43	▨	8080	▨	▨
22	209	02/10/96	0.01	<0.06	▨	0.43	0.20	2.78	193.3	1375	6.92	▨	7550	▨	▨
24	223	16/10/96	0.02	<0.06	▨	0.10	0.15	4.45	198.0	1450	7.02	▨	8830	▨	18.46
26	237	30/10/96	<0.01	<0.06	▨	0.14	0.18	3.82	217.4	1310	6.99	<20	8320	▨	▨
28	251	13/11/96	<0.01	<0.06	▨	<0.04	0.11	1.16	191.6	1125	7.20	▨	8200	▨	▨
29	258	20/11/98	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨		▨	15.72
30	265	27/11/96	<0.01	<0.06	▨	0.64	<0.09	0.80	226.3	1095	7.22	▨	7380	▨	▨
34	292	24/12/96	<0.03	<0.13	▨	5.43	<0.18	2.54	170.3	865	6.86	▨	6930	▨	▨
36	306	08/01/97	0.02	<0.06	▨	0.10	<0.09	0.26	200.7	940	7.07	▨	7020	▨	▨
38	320	22/01/97	<0.01	<0.06	▨	0.07	<0.09	0.52	180.4	920	7.07	▨	6660	▨	▨
40	334	05/02/97	0.04	<0.06	▨	0.12	0.10	0.58	204.7	820	6.97	▨	6060	▨	▨
42	348	19/02/97	0.04	<0.06	▨	2.71	0.11	21.45	168.8	455	7.04	▨	5220	▨	▨
44	362	05/03/97	<0.01	<0.06	▨	0.08	0.22	7.56	174.9	495	6.99	▨	4780	▨	▨
46	376	19/03/97	0.03	<0.06	▨	<0.04	<0.09	3.27	189.2	505	6.91	▨	5430	▨	8.41
48	390	02/04/97	0.02	<0.06	▨	0.16	<0.09	1.93	161.0	490	7.05	▨	4990	▨	▨
50	404	16/04/97	<0.01	<0.06	▨	0.15	0.10	1.04	167.9	500	7.1	▨	4890	▨	▨
52	418	30/04/97	<0.01	<0.06	▨	0.12	<0.09	1.73	135	438	7.31	▨	4880	▨	▨
54	432	14/05/97	<0.01	<0.06	▨	0.13	<0.09	3.50	174.1	425	6.98	▨	5420	▨	7.93
56	446	29/05/97	<0.01	<0.06	▨	<0.04	<0.09	2.33	138.5	450	7.04	▨	5000	▨	▨
58	460	11/06/97	<0.01	0.07	▨	0.04	<0.09	2.19	138.5	400	7.18	▨	5210	▨	▨
60	474	25/06/97	<0.01	<0.06	▨	0.10	<0.09	3.20	193.5	400	7.11	▨	4350	▨	▨
62	488	09/07/97	<0.01	4.80	▨	0.09	<0.09	0.55	141.2	325	7.01	▨	4680	▨	▨
64	502	23/07/97	<0.01	<0.06	▨	<0.04	<0.09	0.64	162.1	350	7.04	▨	▨	▨	5.37
66	516	06/08/97	<0.01	<0.06	▨	<0.04	<0.09	1.53	171.7	275	7.11	▨	5550	-4	▨
68	530	20/08/97	<0.01	0.09	▨	0.12	<0.09	7.26	161.4	325	7.05	▨	▨	30	▨
70	544	03/09/97	<0.01	<0.06	▨	<0.04	<0.09	3.07	165.4	350	7.23	▨	5410	63	▨
72	558	17/09/97	<0.01	<0.06	▨	0.24	<0.09	11.01	157.6	263	7.70	▨	▨	64	4.65
74	572	01/10/97	<0.01	<0.06	▨	1.19	<0.09	18.38	143.7	250	7.13	▨	4580	34	▨
76	586	15/10/97	<0.01	<0.06	▨	<0.04	<0.09	1.52	139.4	225	7.12	▨	▨	100	▨
78	600	29/10/97	<0.01	<0.06	▨	<0.04	<0.09	3.66	122.1	250	7.12	▨	4580	58	▨
80	614	12/11/97	0.19	0.04	▨	0.05	0.06	3.12	163	225	7.11	▨	5300	122	▨
82	628	26/11/97	<0.01	<0.06	▨	<0.04	<0.09	5.39	152.3	200	7.21	▨	▨	131	▨
84	642	10/12/97	<0.01	<0.06	▨	<0.04	<0.09	1.16	125.2	175	7.01	▨	4900	133	3.86
86	655	23/12/97	<0.01	<0.06	▨	<0.04	<0.09	1.42	117.1	225	7.05	▨	▨	130	▨
88	670	07/01/98	<0.01	<0.06	▨	<0.04	<0.09	7.00	188.8	250	7.18	▨	4900	102	▨
90	684	21/01/98	0.02	0.11	▨	0.04	0.11	5.43	132.5	188	7.07	▨	▨	117	▨
92	698	04/02/98	0.03	0.13	▨	<0.04	0.11	1.60	104.1	150	7.1	▨	▨	22	▨
94	712	18/02/98	<0.01	<0.06	▨	0.05	<0.09	3.13	131.5	133	7.19	▨	3600	73	2.68
96	726	04/03/98	<0.01	<0.06	▨	0.02	<0.09	4.61	99.5	167	7.24	▨	▨	115	▨
98	740	18/03/98	0.03	<0.06	▨	0.05	0.09	3.12	98.8	150	7.08	▨	▨	126	▨
100	754	01/04/98	<0.01	<0.06	▨	<0.04	<0.09	3.89	118.1	133	7.22	▨	▨	24	▨
102	768	15/04/98	<0.01	<0.06	▨	0.07	<0.09	4.36	109.4	133	7.25	▨	▨	31	▨
104	782	29/04/98	<0.01	<0.06	▨	<0.04	<0.09	1.47	125.5	117	6.99	▨	▨	-123	2.40
106	796	13/05/98	<0.01	<0.04	▨	0.04	0.05	1.53	123.7	100	7.00	▨	▨	-85	▨
108	810	27/05/98	<0.01	<0.04	▨	<0.04	0.03	3.53	96.2	108	6.98	▨	3300	-131	▨
110	824	10/06/98	<0.01	<0.04	▨	0.06	0.04	7.77	113.3	125	7.00	▨	▨	-121	▨
112	838	24/06/98	<0.01	<0.04	▨	0.06	<0.02	5.37	▨	117	7.01	▨	▨	-124	2.28
114	852	08/07/98	<0.01	<0.04	▨	0.07	<0.02	7.89	108.9	100	6.98	▨	▨	-114	▨
116	866	22/07/98	<0.01	<0.04	▨	0.07	0.02	9.43	▨	100	7.02	▨	3000	-104	▨
119	888	13/08/98	<0.01	<0.04	▨	<0.04	<0.02	6.58	143.8	83	6.91	▨	▨	-106	▨

Maximum	0.19	4.80	0.00	160.28	0.33	22.89	238.7	1550	7.70	1410	8830	133	24.32
Minimum	0.01	0.04	0.00	0.02	0.02	0.26	96.2	83	6.41	22	3000	-131	2.28

▨ Not analysed

Table A2.3.3 Analysis of CAMR waste column leachate

Column 3 - 'aerobic', sparged with air from day 129

Week	Day	Date	mg/l						NH$_3$-N	Cl$^-$	pH	Total VFAs	EC	Eh	Total S
			Cd	Cr	Pb	Zn	Ni	Fe	(mg N/l)	mg/l		mg/l	uS/cm	(mV)	(mg/l)
1	62	08/05/96	<0.01	<0.07	<0.21	<0.04	0.13	14.32	166.9	▨	▨	157	▨	▨	▨
2	69	15/05/96	<0.02	<0.08	<0.24	<0.05	0.23	20.15	102.0	▨	▨	81	▨	▨	▨
3	76	22/05/96	<0.01	<0.06	<0.19	<0.04	0.31	8.99	191.1	1533	6.91	<20	4040	▨	▨
4	83	29/05/96	<0.01	<0.07	<0.21	<0.04	0.15	16.75	209.3	1520	7.18	<20	6910	▨	▨
5	90	05/06/96	<0.01	<0.06	<0.19	<0.04	0.28	18.26	215.4	1500	6.92	<20	7440	▨	▨
6	97	12/06/96	<0.01	<0.06	<0.19	0.11	0.24	1.95	211.4	1530	6.95	93	9790	▨	▨
7	104	19/06/96	▨	▨	▨	▨	▨	▨	220.1	1520	7.02	▨	8290	▨	19.68
8	111	26/06/96	0.02	<0.06	▨	0.06	0.27	1.75	175.3	1435	6.98	<20	7130	▨	▨
9	118	03/07/96	0.01	<0.06	▨	0.05	0.24	11.01	211.6	1385	7.04	<20	7340	▨	14.80
12	139	24/07/96	<0.01	<0.06	▨	0.41	0.21	1.85	178.8	1425	6.83	27	7640	▨	▨
13	146	31/07/96	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	18.63
14	153	07/08/96	<0.01	<0.06	▨	0.30	0.28	3.40	187.3	1460	6.87	<20	7230	▨	▨
16	167	21/08/96	0.03	<0.06	▨	0.16	0.14	22.47	180.2	1200	7.12	▨	6060	▨	▨
18	181	04/09/96	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
20	195	18/09/96	<0.05	<0.25	▨	1.57	0.52	2.86	229.4	1280	7.10	▨	8620	▨	▨
22	209	02/10/96	0.01	<0.06	▨	0.17	0.30	1.06	181.1	1195	6.79	▨	7660	▨	▨
24	223	16/10/96	<0.01	<0.06	▨	0.52	0.27	<0.13	184.7	1180	6.84	▨	9360	▨	583.6
26	237	30/10/96	<0.05	<0.25	▨	0.97	<0.35	<0.50	170.9	1125	6.82	<20	8000	▨	▨
28	251	13/11/96	0.03	<0.06	▨	1.03	0.17	<0.13	158.8	1035	7.11	▨	7890	▨	▨
29	258	20/11/96	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	425.2
30	265	27/11/96	▨	▨	▨	▨	▨	▨	151.9	1020	▨	▨	▨	▨	▨
34	292	24/12/96	0.06	<0.06	▨	1.30	0.27	<0.13	134.5	895	6.62	▨	9580	▨	▨
36	306	08/01/97	0.18	<0.06	▨	1.86	<0.09	<0.13	160.0	870	6.40	▨	8940	▨	▨
38	320	22/01/97	0.14	<0.06	▨	2.06	0.28	<0.13	▨	▨	6.36	▨	8840	▨	▨
40	334	05/02/97	▨	▨	▨	▨	▨	▨	8.3	1180	-	▨	▨	▨	▨
42	348	19/02/97	▨	▨	▨	▨	▨	▨	4.5	660	-	▨	7890	▨	▨
44	362	05/03/97	0.09	<0.06	▨	2.02	0.38	<0.13	4.9	670	6.57	▨	9580	▨	▨
46	376	19/03/97	0.07	<0.06	▨	1.52	0.34	<0.13	9.0	765	6.49	▨	10400	▨	1171.2
48	390	02/04/97	0.03	<0.06	▨	1.51	0.32	0.12	23.3	685	6.78	▨	8840	▨	▨
50	404	16/04/96	0.06	<0.06	▨	1.50	0.33	0.26	37.9	725	6.80	▨	9560	▨	▨
52	418	30/04/97	0.01	<0.06	▨	1.04	0.23	0.53	<1	688	6.99	▨	9480	▨	▨
54	432	14/05/97	0.01	<0.06	▨	0.88	0.21	0.30	33.3	688	6.59	▨	8420	▨	960
56	446	29/05/97	<0.01	<0.06	▨	0.43	0.21	1.74	30.2	775	6.71	▨	8410	▨	▨
58	460	11/06/97	<0.01	<0.06	▨	0.29	0.19	<0.13	13.1	688	6.83	▨	8540	▨	▨
60	474	25/06/97	<0.01	<0.06	▨	0.11	0.19	0.41	61.7	700	6.99	▨	7550	▨	▨
62	488	09/07/97	<0.01	<0.06	▨	0.19	0.17	<0.13	<1	600	6.85	▨	6910	▨	▨
64	502	23/07/97	<0.01	<0.06	▨	0.05	<0.09	2.97	23.5	625	6.93	▨	▨	▨	623.20
66	516	06/08/97	<0.01	<0.06	▨	0.21	<0.09	1.39	<1	625	6.89	▨	8180	11	▨
68	530	20/08/97	<0.01	<0.06	▨	0.36	0.11	0.11	25.3	600	6.82	▨	▨	65.4	▨
70	544	03/09/97	<0.01	<0.06	▨	0.06	0.16	2.15	9.7	500	7.01	▨	7350	46	▨
72	558	17/09/97	<0.01	<0.06	▨	0.24	0.15	3.05	<1	513	7.44	▨	▨	72	457.60
74	572	01/10/97	<0.01	<0.06	▨	0.37	0.16	0.55	<1	450	6.79	▨	6130	55	▨
76	586	15/10/97	<0.01	<0.06	▨	0.22	0.13	0.34	<1	450	6.96	▨	▨	127	▨
78	600	29/10/97	<0.01	<0.06	▨	0.11	0.11	0.88	<1	425	6.95	▨	6380	94	▨
80	614	12/11/97	<0.01	<0.06	▨	0.03	0.10	0.57	10.7	325	6.90	▨	7100	127	▨
82	628	26/11/97	<0.01	<0.06	▨	<0.04	0.11	0.77	37.5	350	6.93	▨	▨	101	▨
84	642	10/12/97	<0.01	<0.06	▨	<0.04	<0.09	0.14	2.2	288	6.83	▨	6400	147	364.36
86	655	23/12/97	<0.01	<0.06	▨	<0.04	<0.09	0.21	<1	300	7.04	▨	▨	131	▨
88	670	07/01/98	<0.01	<0.06	▨	<0.04	<0.09	0.98	<1	325	7.11	▨	6100	110	▨
90	684	21/01/98	0.02	0.12	▨	0.11	0.17	0.28	<1	288	7.11	▨	▨	162	▨
92	698	04/02/98	0.02	0.13	▨	0.05	0.15	0.42	<1	200	7.01	▨	▨	82	▨
94	712	18/02/98	<0.01	<0.06	▨	0.07	<0.09	0.21	<1	250	7.14	▨	4250	108	254.00
96	726	04/03/98	<0.01	<0.06	▨	0.06	<0.09	<0.13	<1	208	7.29	▨	▨	125	▨
98	740	18/03/98	<0.01	<0.06	▨	0.13	0.11	<0.13	<1	267	7.02	▨	▨	138	▨
100	754	01/04/98	<0.01	<0.06	▨	0.10	0.10	<0.13	<1	183	7.22	▨	▨	54	▨
102	768	15/04/98	<0.01	<0.06	▨	<0.04	<0.09	0.21	<1	150	7.16	▨	▨	56	▨
104	782	29/04/98	<0.01	<0.06	▨	0.07	<0.09	<0.13	<1	167	7.01	▨	▨	49	254.80
106	796	13/05/98	0.01	0.05	▨	0.12	0.08	0.11	<1	167	7.09	▨	▨	13	▨
108	810	27/05/98	<0.01	<0.04	▨	0.08	0.05	0.17	<1	125	7.05	▨	3600	7	▨
110	824	10/06/98	0.02	0.04	▨	####	0.09	23.56	<1	117	6.66	▨	▨	-91	▨
112	838	24/06/98	<0.01	<0.04	▨	5.24	0.03	2.05	▨	117	7.16	▨	▨	-113	192.78
114	852	08/07/98	<0.01	<0.04	▨	4.13	0.02	0.05	<1	117	7.02	▨	▨	53	▨
116	866	22/07/98	<0.01	<0.04	▨	3.81	<0.02	1.89	▨	100	7.02	▨	3600	-70	▨
119	888	13/08/98	<0.01	<0.04	▨	3.43	<0.02	1.11	<1	83	7.00	▨	▨	-39	▨

Maximum	0.18	0.13	0.00	####	0.52	23.56	229.4	1533	7.44	157	10400	162	1171.20
Minimum	0.01	0.04	0.00	0.03	0.02	0.05	2.2	83	6.36	27	3600	-113	14.80

▨ Not analysed

Table A2.3.4 Analysis of CAMR waste column leachate

Column 4 - 'anaerobic control', no air sparging

Week	Day	Date	mg/l						NH_3-N	Cl^-	pH	TOTAL VFAs	EC	Eh	Total S
			Cd	Cr	Pb	Zn	Ni	Fe	(mg N/l)	mg/l		mg/l	uS/cm	(mV)	(mg/l)
1	62	08/05/96	<0.03	<0.14	<0.42	<0.08	0.22	24.07	177.8	▨	▨	271	▨	▨	▨
2	69	15/05/96	<0.01	<0.07	<0.21	0.08	0.23	7.13	169.9	▨	▨	40	▨	▨	▨
3	76	22/05/96	<0.01	<0.07	<0.21	<0.04	0.32	12.33	233.0	1650	6.87	<20	4990	▨	▨
4	83	29/05/96	<0.01	<0.07	<0.21	<0.04	0.25	13.45	229.7	1550	7.35	<20	5640	▨	▨
5	90	05/06/96	<0.01	<0.06	<0.19	<0.04	0.28	15.49	248.1	1600	7.07	41	7550	▨	▨
6	97	12/06/96	<0.01	<0.06	<0.19	<0.04	0.25	1.90	213.8	1520	7.06	24	6700	▨	▨
7	104	19/06/96	▨	▨	▨	▨	▨	▨	251.9	1545	7.16	▨	7340	▨	25.78
8	111	26/06/96	<0.01	<0.06	▨	0.05	0.28	2.15	228.8	1510	7.20	<20	7760	▨	▨
9	118	03/07/96	<0.03	<0.13	▨	0.20	0.24	14.08	224.2	1380	7.02	<20	6910	▨	22.70
12	139	24/07/96	<0.01	<0.06	▨	6.28	0.17	<0.13	197.4	1420	6.81	100	7640	▨	▨
13	146	31/07/96	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	20.94
14	153	07/08/96	<0.02	<0.08	▨	0.77	0.32	2.30	177.2	1440	6.89	20	6810	▨	▨
16	167	21/08/96	0.02	<0.06	▨	0.62	0.34	2.16	168.3	1620	7.06	<20	7550	▨	▨
18	181	04/09/96	<0.01	<0.06	▨	0.45	0.25	1.09	187.2	1378	6.92	▨	7870	▨	▨
20	195	18/09/96	<0.01	<0.06	▨	0.43	0.28	3.59	201.5	1480	7.18	▨	6810	▨	▨
22	209	02/10/96	<0.02	<0.08	▨	0.38	0.20	7.77	201.7	1425	6.86	▨	7680	▨	▨
24	223	16/10/96	<0.01	<0.06	▨	0.25	0.18	1.68	193.4	1335	7.06	▨	8620	▨	19.02
26	237	30/10/96	<0.01	<0.06	▨	0.14	0.22	2.66	204.0	1250	7.04	<20	8300	▨	▨
28	251	13/11/96	<0.01	<0.06	▨	0.06	0.18	0.45	181.5	1165	7.16	▨	7550	▨	▨
29	258	20/11/96	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨		▨	36.28
30	265	27/11/96	<0.01	<0.06	▨	0.07	0.11	1.16	204.3	960	7.14	▨	7020	▨	▨
34	292	24/12/96	<0.03	<0.13	▨	1.43	<0.18	2.96	175.3	805	7.00	▨	6830	▨	▨
36	306	08/01/97	0.02	<0.06	▨	0.16	<0.09	0.34	228.6	800	7.08	▨	6700	▨	▨
38	320	22/01/97	0.13	<0.06	▨	2.18	0.38	<0.13	164.8	710	6.98	▨	6380	▨	▨
40	334	05/02/97	<0.01	<0.06	▨	0.06	0.12	0.36	172.8	670	7.10	▨	6480	▨	▨
42	348	19/02/97	0.02	<0.06	▨	1.01	<0.09	14.78	158.9	530	7.08	▨	5430	▨	▨
44	362	05/03/97	<0.01	<0.06	▨	0.17	0.09	7.59	162.0	520	7.03	▨	5430	▨	▨
46	376	19/03/97	0.02	<0.06	▨	<0.04	<0.09	2.87	184.4	490	7.60	▨	5970	▨	8.96
48	390	02/04/97	<0.01	<0.06	▨	0.68	<0.09	3.38	166.4	450	7.11	▨	5010	▨	▨
50	404	16/04/97	<0.01	<0.06	▨	0.42	0.10	5.83	138.5	450	7.01	▨	4470	▨	▨
52	418	30/04/97	<0.01	<0.06	▨	0.12	<0.09	1.81	136.3	388	7.14	▨	4370	▨	▨
54	432	14/05/97	<0.01	<0.06	▨	33.15	<0.09	0.73	186.8	325	7.05	▨	4890	▨	7.43
56	446	29/05/97	<0.01	<0.06	▨	0.05	<0.09	2.23	184.0	288	7.02	▨	4680	▨	▨
58	460	11/06/97	<0.01	0.07	▨	<0.04	<0.09	0.44	175.3	288	7.06	▨	4890	▨	▨
60	474	25/06/97	<0.01	<0.06	▨	<0.04	<0.09	4.28	193.8	275	7.07	▨	3920	▨	▨
62	488	07/09/97	0.03	<0.06	▨	0.04	<0.09	1.07	124.1	225	7.00	▨	3940	▨	▨
64	502	23/07/97	<0.01	<0.06	▨	<0.04	<0.09	1.93	133.1	225	6.78	▨	▨	▨	6.24
66	516	07/08/97	<0.01	<0.06	▨	0.06	<0.09	3.11	154.8	250	7.03	▨	4580	-20.9	▨
68	530	20/08/97	<0.01	<0.06	▨	0.02	<0.09	2.71	154.1	250	6.98	▨	▨	29.2	▨
70	544	03/09/97	<0.01	<0.06	▨	<0.04	<0.09	2.71	152.4	225	7.22	▨	4890	54	▨
72	558	17/09/97	<0.01	<0.06	▨	0.33	<0.09	10.61	130.4	175	7.32	▨	▨	51	6.86
74	572	01/10/97	<0.01	<0.06	▨	1.74	<0.09	14.30	147.0	150	6.96	▨	3820	32	▨
76	586	15/10/97	<0.01	<0.06	▨	<0.04	<0.09	2.23	134.2	175	7.12	▨	▨	103	▨
78	600	29/10/97	<0.01	<0.06	▨	0.17	<0.09	8.82	119.8	150	7.02	▨	4360	-28	▨
80	614	12/11/97	<0.01	<0.06	▨	0.03	0.01	2.46	150.2	125	7.01	▨	4500	127	▨
82	628	26/11/97	<0.01	<0.06	▨	<0.04	<0.09	4.16	163.8	150	7.02	▨	▨	114	▨
84	642	10/12/97	<0.01	<0.06	▨	<0.04	<0.09	1.80	120.7	113	6.92	▨	4100	140	4.33
86	655	23/12/97	<0.01	<0.06	▨	<0.04	<0.09	1.55	131.3	150	7.02	▨	▨	128	▨
88	670	07/01/98	0.03	<0.06	▨	0.05	<0.09	7.30	152.9	150	7.08	▨	4400	102	▨
90	684	21/01/98	0.02	0.12	▨	0.13	0.11	4.11	120.6	125	7.16	▨	▨	154	▨
92	698	04/02/98	0.02	0.12	▨	<0.04	0.10	2.56	86.4	100	7.05	▨	▨	78	▨
94	712	18/02/98	<0.01	<0.06	▨	<0.04	<0.09	1.84	118.4	83	7.11	▨	3350	2	4.00
96	726	04/03/98	<0.01	<0.06	▨	<0.04	<0.09	0.82	99.1	92	7.23	▨	▨	120	▨
98	740	18/03/98	<0.01	<0.06	▨	<0.04	<0.09	3.34	109.3	25	7.04	▨	▨	133	▨
100	754	01/04/98	<0.01	<0.06	▨	0.05	<0.09	2.86	116.5	92	7.19	▨	▨	20	▨
102	768	15/04/98	▨	▨	▨	▨	▨	▨	92.2	67	7.2	▨	▨	5	▨
104	782	29/04/98	<0.01	<0.06	▨	<0.04	<0.09	1.60	123.8	83	6.97	▨	▨	-110	3.03
106	796	13/05/98	<0.01	<0.04	▨	0.07	0.05	0.70	113.6	83	6.97	▨	▨	-108	▨
108	810	27/05/98	<0.01	<0.04	▨	0.07	0.03	5.95	74.5	58	6.93	▨	3000	-119	▨
110	824	10/06/98	<0.01	<0.04	▨	0.54	0.04	8.37	108.8	67	7.02	▨	▨	-127	▨
112	838	24/06/98	<0.01	<0.04	▨	0.30	<0.02	7.67	▨	83	6.96	▨	▨	-113	2.68
114	852	08/07/98	<0.01	<0.04	▨	0.43	<0.02	10.61	118.6	67	6.94	▨	▨	-106	▨
116	866	22/07/98	<0.01	<0.04	▨	0.22	<0.02	6.41	▨	83	6.87	▨	2850	-105	▨
119	888	13/08/98	<0.01	<0.04	▨	0.06	<0.02	3.91	112.6	50	6.86	▨	▨	-84	▨

Maximum			0.13	0.12	0.00	33.15	0.38	24.07	251.9	1650	7.60	271	8620	154	36.28
Minimum			0.02	0.07	0.00	0.02	0.01	0.34	74.5	25	6.78	20	2850	-127	2.68

▨ Not analysed

Table A2.3.5 Analysis of CAMR waste column leachate

Column 5 - 'anaerobic control', no air sparging

Week	Day	Date	mg/l						NH$_3$-N	Cl$^-$	pH	Total VFAs	EC	Eh	Total S
			Cd	Cr	Pb	Zn	Ni	Fe	(mg N/l)	mg/l		mg/l	uS/cm	(mV)	(mg/l)
1	62	08/05/96	<0.01	<0.06	<0.19	<0.04	0.22	22.69	216.0	1400	▨	108	▨	▨	▨
2	69	15/05/96	<0.01	<0.06	<0.19	<0.04	0.24	8.16	216.3	▨	▨	40	▨	▨	▨
3	76	22/05/96	<0.01	<0.06	<0.19	<0.04	0.27	9.58	199.6	1633	6.89	<20	5080	▨	▨
4	83	29/05/96	<0.01	<0.07	<0.21	<0.04	0.16	20.30	251.9	1550	7.19	<20	7870	▨	▨
5	90	05/06/96	<0.01	<0.06	<0.19	<0.04	0.12	19.44	212.3	1550	7.02	<20	7760	▨	▨
6	97	12/06/96	<0.01	<0.06	<0.19	<0.04	0.24	5.85	198.8	1510	6.97	22	7230	▨	▨
7	104	19/06/96	▨	▨	▨	▨	▨	▨	194.1	1500	7.05	▨	6810	▨	18.17
8	111	26/06/96	0.01	<0.06	▨	0.04	0.27	1.75	214.3	1505	7.02	<20	7440	▨	▨
9	118	03/07/96	<0.01	<0.06	▨	<0.04	0.24	6.78	263.0	1470	7.04	<20	7660	▨	17.04
12	139	24/07/96	<0.01	<0.06	▨	0.07	0.21	7.28	203.1	1445	6.86	<20	8290	▨	▨
13	146	31/07/96	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	21.60
14	153	07/08/96	<0.01	<0.06	▨	0.24	0.19	17.78	184.5	1500	6.93	▨	7230	▨	▨
16	167	21/08/96	<0.01	<0.06	▨	0.13	0.23	3.22	202.7	1680	7.09	▨	7460	▨	▨
18	181	04/09/96	<0.01	<0.06	▨	0.16	0.21	3.25	200.2	1403	6.90	▨	7130	▨	▨
20	195	18/09/96	<0.01	<0.06	▨	0.13	0.23	2.47	205.5	1260	7.24	▨	7120	▨	▨
22	209	02/10/96	<0.01	<0.06	▨	0.14	0.17	2.40	199.3	1325	6.96	▨	7020	▨	▨
24	223	16/10/96	<0.01	<0.06	▨	2.22	0.15	1.24	202.8	1280	7.11	▨	8080	▨	21.78
26	237	30/10/96	<0.01	<0.06	▨	1.23	0.17	1.40	210.5	1200	7.11	<20	8330	▨	▨
28	251	13/11/96	<0.01	<0.06	▨	0.47	<0.09	0.84	235.4	1085	7.26	▨	7990	▨	▨
29	258	20/11/96	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	20.54
30	265	27/11/96	<0.01	<0.06	▨	0.44	<0.09	1.00	271.3	1060	7.33	▨	7240	▨	▨
34	292	24/12/96	<0.03	<0.13	▨	1.74	<0.18	3.07	235.8	870	7.02	▨	7020	▨	▨
36	306	08/01/96	0.02	0.10	▨	0.27	<0.09	0.18	208.5	800	7.08	▨	6380	▨	▨
38	320	22/01/97	<0.01	<0.06	▨	0.13	<0.09	<0.13	183.0	620	7.11	▨	5420	▨	▨
40	334	05/02/97	0.02	<0.06	▨	0.17	0.16	0.47	162.7	580	7.07	▨	5960	▨	▨
42	348	19/02/97	<0.01	<0.06	▨	1.18	0.12	12.08	178.3	545	7.12	▨	5640	▨	▨
44	362	05/03/97	0.01	<0.06	▨	0.08	0.11	4.91	167.0	480	7.24	▨	5870	▨	▨
46	376	19/03/97	0.01	<0.06	▨	<0.04	<0.09	2.32	165.0	465	7.22	▨	5740	▨	26.86
48	390	02/04/97	<0.01	<0.06	▨	0.14	<0.09	3.12	159.7	400	7.17	▨	5220	▨	▨
50	404	16/04/97	0.01	<0.06	▨	87.26	0.54	1.06	170.6	425	7.15	▨	5000	▨	▨
52	418	30/04/97	<0.01	<0.06	▨	<0.04	<0.09	0.81	136	313	7.15	▨	5230	▨	▨
54	432	14/05/97	<0.01	<0.06	▨	33.15	<0.09	0.73	297.7	325	7.05	▨	4570	▨	26.44
56	446	29/05/97	<0.01	<0.06	▨	0.83	<0.09	1.11	135.2	263	7.16	▨	4980	▨	▨
58	460	11/06/97	<0.01	0.07	▨	0.86	<0.09	1.44	174.7	238	7.17	▨	4470	▨	▨
60	474	25/06/97	<0.01	<0.06	▨	0.77	<0.09	2.53	303.8	225	7.2	▨	4380	▨	▨
62	488	09/07/97	<0.01	<0.06	▨	0.56	<0.09	0.54	131.0	175	7.08	▨	▨	▨	▨
64	502	23/07/97	<0.01	<0.06	▨	<0.04	<0.09	0.90	▨	175	7.05	▨	▨	▨	6.37
66	516	06/08/97	<0.01	<0.06	▨	0.11	<0.09	5.03	146.9	150	7.1	▨	3830	1.6	▨
68	530	20/08/97	<0.01	<0.06	▨	0.13	<0.09	5.45	174.0	175	7.1	▨	▨	28.1	▨
70	544	03/09/97	<0.01	<0.06	▨	<0.04	<0.09	1.73	153.4	75	7.35	▨	4000	61	▨
72	558	17/09/97	<0.01	<0.06	▨	0.73	<0.09	7.78	123.0	100	7.28	▨	▨	73	17.37
74	572	01/10/97	<0.01	<0.06	▨	1.98	<0.09	12.36	110.0	100	7.04	▨	3620	36	▨
76	586	15/10/97	<0.01	<0.06	▨	<0.04	<0.09	3.40	115.5	50	7.13	▨	▨	113	▨
78	600	29/10/97	<0.01	<0.06	▨	<0.04	<0.09	0.54	113.1	50	7.13	▨	3510	56	▨
80	614	12/11/97	<0.01	<0.06	▨	<0.04	<0.09	2.37	131	50	7.1	▨	3850	133	▨
82	628	26/11/97	<0.01	<0.06	▨	<0.04	<0.09	4.40	135	50	7.06	▨	▨	140	▨
84	642	10/12/97	<0.01	<0.06	▨	<0.04	<0.09	2.32	136.4	38	6.99	▨	3850	144	15.23
86	655	23/12/97	<0.01	<0.06	▨	<0.04	<0.09	3.87	107.8	75	7.03	▨	▨	133	▨
88	670	07/01/98	<0.01	<0.06	▨	<0.04	<0.09	5.27	142.4	25	7.22	▨	3600	110	▨
90	684	21/01/98	0.02	0.11	▨	<0.04	0.10	4.58	133.9	63	7.16	▨	▨	145	▨
92	698	04/02/98	0.02	0.12	▨	0.04	0.09	2.71	79.4	0	7.04	▨	▨	136	▨
94	712	18/02/98	<0.01	<0.06	▨	<0.04	<0.09	3.41	100.1	17	7.21	▨	2500	61	14.62
96	726	04/03/98	<0.01	<0.06	▨	<0.04	<0.09	4.49	94.4	8	7.32	▨	▨	117	▨
98	740	18/03/98	<0.01	<0.06	▨	<0.04	<0.09	3.63	87.1	25	7.1	▨	▨	130	▨
100	754	01/04/98	<0.01	<0.06	▨	<0.04	<0.09	3.59	86.4	8	7.96	▨	▨	40	▨
102	768	15/04/98	<0.01	<0.06	▨	0.05	<0.09	<0.13	82.2	0	7.27	▨	▨	53	▨
104	782	29/04/98	<0.01	<0.06	▨	<0.04	<0.09	1.88	78.6	33	6.97	▨	▨	-113	13.93
106	796	13/05/98	<0.01	0.04	▨	0.04	0.04	1.05	86.5	33	7.00	▨	▨	-112	▨
108	810	27/05/98	<0.01	<0.04	▨	<0.04	0.02	3.32	91.3	8	6.98	▨	2550	-114	▨
110	824	10/06/98	<0.01	<0.04	▨	0.12	0.03	7.92	101	17	7.03	▨	▨	-116	▨
112	838	24/06/98	<0.01	<0.04	▨	0.07	<0.02	4.50	▨	17	7.04	▨	▨	-113	8.70
114	852	08/07/98	<0.01	<0.04	▨	0.10	<0.02	6.96	114.7	17	7.00	▨	▨	-84	▨
116	866	22/07/98	<0.01	<0.04	▨	0.09	<0.02	6.67	▨	17	6.93	▨	2400	-72	▨
119	888	13/08/98	<0.01	<0.04	▨	<0.04	<0.02	5.13	94.7	<1	6.92	▨	▨	-92	▨

Maximum	0.02	0.12	0.00	87.26	0.54	22.69	303.8	1680	7.96	108	8330	145	26.86
Minimum	0.01	0.04	0.00	0.04	0.02	0.18	78.6	0	6.86	22	2400	-116	6.37

▨ Not analysed

Table A2.3.6 Analysis of CAMR waste column leachate

Column 6 - 'aerobic', sparged with air from day 129

Week	Day	Date	mg/l						NH$_3$-N	Cl$^-$	pH	Total VFAs	EC	Eh	Total S
			Cd	Cr	Pb	Zn	Ni	Fe	(mg N/l)	mg/l		mg/l	uS/cm	(mV)	(mg/l)
1	62	08/05/96	<0.01	<0.06	<0.19	0.07	0.12	11.38	252.8	1500	▨	78	▨	▨	▨
2	69	15/05/96	<0.01	<0.06	<0.19	<0.04	0.23	10.86	214.4	▨	▨	39	▨	▨	▨
3	76	22/05/96	<0.01	<0.06	<0.19	<0.04	0.28	5.73	200.9	1450	6.89	<20	4890	▨	▨
4	83	29/05/96	<0.01	<0.07	<0.21	<0.04	0.23	23.43	206.5	1525	7.17	<20	7660	▨	▨
5	90	05/06/96	<0.01	<0.07	<0.21	<0.04	0.25	20.03	202.7	1500	6.99	<20	7020	▨	▨
6	97	12/06/96	<0.01	<0.07	<0.21	<0.04	0.21	10.80	209.0	1500	6.93	<20	7550	▨	▨
7	104	19/06/96	▨	▨	▨	▨	▨	▨	193.5	1400	6.96	▨	6920	▨	20.46
8	111	26/06/96	<0.01	<0.07	▨	<0.04	0.27	1.61	183.4	1425	6.95	27	8300	▨	▨
9	118	03/07/96	<0.01	<0.07	▨	0.05	0.20	15.51	195.5	1390	6.93	<20	8080	▨	14.04
12	139	24/07/96	<0.01	<0.07	▨	0.15	0.23	3.46	184.0	1350	6.80	<20	7450	▨	▨
13	146	31/07/96	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	15.15
14	153	07/08/96	0.02	<0.07	▨	0.30	0.14	14.28	173.1	1420	6.89	▨	5790	▨	▨
16	167	21/08/96	0.02	<0.07	▨	0.13	0.17	3.09	173.6	1240	6.89	▨	6170	▨	▨
18	181	04/09/96	<0.01	<0.07	▨	0.24	0.19	2.54	166.2	1343	6.89	▨	6920	▨	▨
20	195	18/09/96	<0.05	<0.25	▨	1.60	<0.35	2.03	171.9	1420	7.63	▨	6590	▨	▨
22	209	02/10/96	<0.03	<0.13	▨	0.36	0.25	4.89	177.0	1235	6.67	▨	5860	▨	▨
24	223	16/10/96	<0.03	<0.13	▨	0.40	0.26	0.65	162.6	1140	6.79	▨	8740	▨	404.40
26	237	30/10/96	0.03	<0.13	▨	1.39	0.25	0.56	208.6	1050	6.68	<20	9360	▨	▨
28	251	13/11/96	▨	▨	▨	▨	▨	▨	131.7	825	7.82	▨	8520	▨	▨
29	258	20/11/96	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	702.67
30	265	27/11/96	▨	▨	▨	▨	▨	▨	229.3	1155	▨	▨	9870	▨	▨
34	292	24/12/96	0.23	<0.13	▨	1.84	0.24	<0.25	41.5	755	6.12	▨	9370	▨	▨
36	306	08/01/97	▨	▨	▨	▨	▨	▨	▨	750	6.35	▨	7870	▨	▨
38	320	22/01/97	0.05	<0.09	▨	1.62	0.20	<0.19	<1	750	6.22	▨	9150	▨	▨
40	334	05/02/97	0.06	<0.06	▨	1.10	0.28	<0.13	17.2	790	6.57	▨	9370	▨	▨
42	348	19/02/97	0.06	<0.06	▨	1.05	0.27	0.16	5.2	800	6.76	▨	9470	▨	▨
44	362	05/03/97	0.02	<0.06	▨	0.89	0.20	0.11	4.0	745	6.72	▨	9570	▨	▨
46	376	19/03/97	0.02	<0.06	▨	0.27	0.28	1.15	12.7	720	6.68	▨	8510	▨	984.00
48	390	02/04/97	0.02	<0.06	▨	0.93	0.26	1.12	7.2	685	7.27	▨	7980	▨	▨
50	404	16/04/97	0.01	<0.06	▨	87.26	0.54	1.06	14.4	700	6.62	▨	8840	▨	▨
52	418	30/04/97	<0.01	<0.06	▨	5.81	0.27	0.18	<1	663	6.84	▨	9150	▨	▨
54	432	14/05/97	<0.01	<0.06	▨	5.02	0.24	3.28	17.5	638	6.72	▨	8670	▨	847.60
56	446	29/05/97	<0.01	<0.06	▨	0.07	0.18	5.04	<1	675	6.74	▨	8520	▨	▨
58	460	11/06/97	0.01	<0.06	▨	0.40	0.14	2.51	13.6	613	6.89	▨	8000	▨	▨
60	474	25/06/97	<0.01	<0.06	▨	0.39	0.12	<0.13	25.6	625	6.87	▨	7880	▨	▨
62	488	09/07/97	<0.01	<0.06	▨	0.15	0.14	<0.13	13.4	550	6.84	▨	7870	▨	▨
64	502	23/07/97	<0.01	<0.06	▨	<0.04	<0.09	1.30	▨	575	7.05	▨	▨	▨	9.90
66	516	06/08/97	<0.01	<0.06	▨	0.25	<0.09	6.06	4.0	575	6.88	▨	8840	-6	▨
68	530	20/08/97	<0.01	<0.06	▨	<0.04	<0.09	0.45	7.7	550	6.91	▨	▨	52.1	▨
70	544	03/09/97	<0.01	<0.06	▨	<0.04	<0.09	0.11	22.7	450	7.03	▨	7980	75	▨
72	558	17/09/97	<0.01	<0.06	▨	1.00	<0.09	3.54	<1	85	7.33	▨	▨	34	742.40
74	572	01/10/97	<0.01	<0.06	▨	2.28	0.13	0.18	64.7	400	6.87	▨	4790	60	▨
76	586	15/10/97	<0.01	<0.06	▨	0.06	0.07	0.24	<1	400	6.76	▨	▨	120	▨
78	600	29/10/97	<0.01	<0.06	▨	<0.04	<0.09	1.03	<1	375	6.73	▨	7770	99	▨
80	614	12/11/97	<0.01	<0.06	▨	0.95	0.06	0.05	1.6	325	6.73	▨	8800	147	▨
82	628	26/11/97	<0.01	<0.06	▨	<0.04	<0.09	<0.13	28.2	313	6.79	▨	▨	163	▨
84	642	10/12/97	<0.01	<0.06	▨	0.61	<0.09	<0.13	<1	288	7.00	▨	8550	152	676.80
86	655	23/12/97	<0.01	<0.06	▨	0.42	<0.09	<0.13	<1	275	6.94	▨	▨	144	▨
88	670	07/001/98	<0.01	<0.06	▨	0.14	<0.09	0.36	<1	325	6.87	▨	8150	106	▨
90	684	21/01/98	0.02	0.13	▨	0.29	0.14	0.21	<1	263	6.95	▨	▨	157	▨
92	698	04/02/98	0.02	0.14	▨	0.08	0.12	0.67	<1	200	6.90	▨	▨	113	▨
94	712	18/02/98	<0.01	<0.06	▨	0.07	<0.09	0.28	<1	217	7.06	▨	6000	91	618.40
96	726	04/03/98	<0.01	<0.06	▨	0.07	<0.09	0.27	<1	192	7.18	▨	▨	124	▨
98	740	18/03/98	<0.01	<0.06	▨	0.90	0.11	<0.13	<1	192	6.90	▨	▨	137	▨
100	754	01/04/98	0.03	<0.06	▨	5.2	0.14	<0.13	<1	200	6.80	▨	▨	119	▨
102	768	15/04/98	<0.01	<0.06	▨	2.00	<0.09	<0.13	<1	167	6.96	▨	▨	111	▨
104	782	29/04/98	<0.01	<0.06	▨	1.78	<0.09	<0.13	<1	167	6.86	▨	▨	63	2.52
106	796	13/05/98	0.01	0.06	▨	1.14	0.07	0.47	<1	167	6.86	▨	▨	-20	▨
108	810	27/05/98	<0.01	<0.04	▨	0.36	0.05	0.04	<1	158	7.04	▨	5150	4	▨
110	824	10/06/98	<0.01	0.05	▨	0.34	0.05	0.05	<1	133	7.09	▨	▨	26	▨
112	838	24/06/98	<0.01	<0.04	▨	0.29	0.03	0.02	▨	113	7.21	▨	▨	19	2.06
114	852	08/07/98	<0.01	<0.04	▨	0.34	0.03	0.02	<1	142	7.02	▨	▨	24	▨
116	866	22/07/98	<0.01	<0.04	▨	0.40	0.03	0.08	▨	125	6.83	▨	5000	8	▨
119	888	13/08/98	<0.01	<0.04	▨	0.23	0.02	1.38	<1	92	6.89	▨	▨	-50	▨

Maximum	0.23	0.14	0.00	87.26	0.54	23.43	252.8	1525	7.82	78	9870	163	984.00
Minimum	0.01	0.05	0.00	0.05	0.02	0.02	1.6	85	6.12	27	4790	-50	2.06

▨ Not analysed

Table A2.4.1 Initial Analysis of CAMR Waste (results 22/7/99)

Column	Wet Weight (g)	Water Content (% wet weight)	Dry weight present (g)	Total metals present (mg)					
				Cd	Cr	Pb	Zn	Ni	Fe
1	4671.8	48.14	2422.80	247.13	575.41	1332.54	2196.26	196.25	53119.79
2	4716.7	48.14	2446.08	249.50	580.94	1345.34	2217.37	198.13	53630.32
3	4740.9	48.14	2458.63	250.78	583.92	1352.25	2228.75	199.15	53905.48
4	4603.9	48.14	2387.58	243.53	567.05	1313.17	2164.34	193.39	52347.75
5	4558.9	48.14	2364.25	241.15	561.51	1300.34	2143.19	191.50	51836.08
6	4441.6	48.14	2303.41	234.95	547.06	1266.88	2088.04	186.58	50502.35

Table A2.4.2 Final Destructive Analysis of CAMR Waste Column Fractions

Sample		mg/kg dry weight							Dry weight	Water Content	Total metals present (mg)						
Column	Fraction	Cd	Cr	Pb	Zn	Ni	Fe	Li	present (g)	(% wet weight)	Cd	Cr	Pb	Zn	Ni	Fe	Li
1	Top	142	190	980	1187	89	8386	9	735.6	37.71	104	140	721	873	65	6168	7
	Middle	106	172	498	882	73	7512	10	844.8	41.68	90	145	421	745	62	6346	8
	Bottom	33	217	306	711	59	8340	7	1109.4	31.52	37	241	339	789	65	9253	8
	Total								**2689.8**		**231**	**526**	**1481**	**2407**	**193**	**21767**	**23**
2	Top	164	195	795	1267	84	9316	10	708.1	34.26	116	138	563	897	59	6597	7
	Middle	126	185	819	838	75	8985	9	780.3	39.83	98	144	639	654	59	7011	7
	Bottom	86	201	502	588	60	8497	4	951.2	36.78	82	191	478	559	57	8082	4
	Total								**2439.6**		**296**	**474**	**1680**	**2110**	**175**	**21690**	**18**
3	Top	125	187	771	1182	78	10389	9	823.6	32.57	103	154	635	973	64	8556	7
	Middle	168	243	786	1030	91	11205	9	895.6	35.86	150	218	704	922	81	10035	8
	Bottom	101	196	460	723	73	9328	5	1000.0	34.65	101	196	460	723	73	9328	5
	Total								**2719.2**		**354**	**568**	**1799**	**2619**	**219**	**27919**	**20**
4	Top	89	189	777	1029	83	9633	9	718.2	46.71	64	136	558	739	60	6918	6
	Middle	117	159	818	961	69	8494	11	850.7	40.77	100	135	696	818	59	7226	9
	Bottom	48	231	316	1202	75	8114	4	1125.3	30.49	54	260	356	1353	84	9131	5
	Total								**2694.2**		**217**	**531**	**1610**	**2909**	**203**	**23275**	**20**
5	Top	91	159	571	902	67	7654	11	824.7	40.34	75	131	471	744	55	6312	9
	Middle	114	185	592	838	166	9259	11	835.9	39.09	95	155	495	700	139	7740	9
	Bottom	44	253	379	629	78	8108	13	983.0	31.69	43	249	373	618	77	7971	13
	Total								**2643.6**		**214**	**534**	**1338**	**2063**	**271**	**22022**	**31**
6	Top	130	204	767	1081	87	12991	11	758.4	47.79	99	155	582	820	66	9852	8
	Middle	126	177	873	1137	85	10599	12	850.1	37.60	107	150	742	967	72	9011	10
	Bottom	49	151	373	573	62	8958	5	1160.3	30.64	57	175	433	665	72	10394	6
	Total								**2768.8**		**263**	**480**	**1757**	**2451**	**210**	**29257**	**24**

Table A2.4.3 Summary of results - metal analysis of solid waste before and after column treatment

Waste	Column		Total metals present (mg)											
			Cd	% Loss	Cr	% Loss	Pb	% Loss	Zn	% Loss	Ni	% Loss	Fe	% Loss
CAMR	1	Initial	247		575		1333		2196		196		53120	
		Final	**231**	7	**526**	9	**1481**	-11	**2407**	-10	**193**	2	**21767**	59
	2	Initial	250		581		1345		2217		198		53630	
		Final	**296**	-19	**474**	18	**1680**	-25	**2110**	5	**175**	12	**21690**	60
	3	Initial	251		584		1352		2229		199		53905	
		Final	**354**	-41	**568**	3	**1799**	-33	**2619**	-18	**219**	-10	**27919**	48
	4	Initial	244		567		1313		2164		193		52348	
		Final	**217**	11	**531**	6	**1610**	-23	**2909**	-34	**203**	-5	**23275**	56
	5	Initial	241		562		1300		2143		192		51836	
		Final	**214**	11	**534**	5	**1338**	-3	**2063**	4	**271**	-41	**22022**	58
	6	Initial	235		547		1267		2088		187		50502	
		Final	**263**	-12	**480**	12	**1757**	-39	**2451**	-17	**210**	-13	**29257**	42

Table A2.8.1 Analysis of Pitsea waste column leachate

Column 7 - 'anaerobic control', no air sparging

Date	Day	mg/l						NH_3-N	Cl^-	pH	Total VFAs	EC	Eh
		Cd	Cr	Pb	Zn	Ni	Fe	(mg N/l)	mg/l		mg/l	uS/cm	(mV)
19/02/97	0	0.05	0.20	0.75	0.67	<0.18	242.1	873.0	11475	6.72	6854.43	47900	▨
02/04/97	43	<0.01	0.11	0.34	0.37	0.15	21.68	1023.7	8960	6.97	▨	39300	▨
16/04/97	57	0.05	<0.13	<0.38	0.69	<0.18	7.50	1088.5	10000	6.97	▨	45800	▨
30/04/97	71	<0.03	0.13	<0.38	0.20	<0.18	9.62	1007.1	11650	7.31	1634.26	46800	▨
09/07/97	141	0.06	4.87	<0.38	1.69	<0.18	8.99	928.8	9300	7.45	▨	38300	▨
23/07/97	155	▨	▨	▨	▨	▨	▨	845.2	8800	6.76	▨	▨	▨
06/08/97	169	<0.05	<0.25	<0.75	1.01	<0.35	3.24	920.5	8500	7.74	▨	43600	-125
20/08/97	183	<0.05	<0.25	<0.75	1.52	<0.35	15.45	789.1	9300	7.37	▨	▨	-267
03/09/97	197	<0.03	0.26	<0.38	<0.08	<0.18	8.41	845.1	8900	7.60	▨	45800	-220
17/09/97	211	<0.05	<0.25	<0.75	0.44	<0.35	8.57	865.8	8950	7.75	▨	▨	-63
01/10/97	225	▨	▨	▨	▨	▨	▨	826.3	8400	7.36	▨	40400	-157
15/10/97	239	<0.03	0.27	0.07	<0.08	0.12	13.88	825.0	8350	7.63	1659	▨	13
29/10/97	253	<0.01	0.22	0.03	<0.04	0.09	7.51	901.2	7600	7.38	▨	35100	-97
12/11/97	267	0.02	0.27	0.05	0.07	0.10	12.86	773.8	7400	7.37	▨	▨	-35
26/11/97	281	0.02	0.25	0.62	0.07	0.13	10.68	733.5	7250	7.39	▨	44000	-16
10/12/97	295	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
23/12/97	308	▨	▨	▨	▨	▨	▨	641.8	6400	7.74	▨	40000	60
07/01/98	321	0.02	0.08	<0.19	<0.04	<0.09	6.54	752.6	6050	7.40	▨	▨	-83
21/01/98	335	0.07	0.42	<0.19	0.12	0.22	9.56	624.1	6400	7.40	▨	35500	-30
04/02/97	349	0.03	0.31	<0.19	<0.04	0.15	9.46	423.5	5400	7.20	▨	▨	-73
18/02/98	363	<0.01	0.23	<0.19	0.05	0.10	10.58	437.9	5000	7.59	▨	▨	-92
04/03/98	377	1.92	2.02	<0.38	0.14	1.90	1.84	416.9	4700	7.43	▨	▨	-49
18/03/98	391	0.10	0.33	<0.38	0.12	<0.18	12.63	425.4	4250	7.27	▨	▨	-12
01/04/98	405	<0.01	0.21	0.22	0.12	0.09	11.76	410.6	4000	7.4	▨	20500	-66
15/04/98	419	<0.03	<0.13	<0.38	<0.08	<0.18	10.79	331.7	3600	7.38	▨	▨	-58
29/04/98	433	<0.03	0.13	<0.38	<0.08	<0.18	3.23	335.3	3500	7.16	▨	▨	-111
13/05/98	447	0.0075	0.18	<0.13	0.06	0.08	6.69	319.4	3300	7.17	▨	▨	-136
27/05/98	461	<0.01	0.15	<0.13	<0.04	0.06	10.17	306.7	2950	7.09	▨	▨	-137
10/06/98	475	<0.01	0.15	<0.13	0.04	0.06	9.72	▨	2900	7.13	▨	▨	-138
24/06/98	489	<0.01	0.11	<0.13	<0.04	0.03	8.89	299.7	2800	7.58	▨	13500	-148
08/07/98	503	<0.01	0.09	<0.25	<0.08	<0.04	7.19	▨	2850	7.5	▨	▨	-151
22/07/98	517	<0.01	0.1	<0.13	<0.04	0.03	8.49	▨	2450	7.01	▨	14000	-123
13/08/98	539	<0.01	<0.04	<0.13	<0.04	<0.02	7.47	285.9	2250	7.01	▨	▨	-104
26/8/98	552	<0.01	0.15	<0.13	0.12	0.05	6.74	▨	2300	7.06	▨	▨	-81
9/9/98	566	<0.01	<0.04	0.16	0.08	0.06	6.38	▨	1900	7.04	▨	▨	-81
7/10/98	594	<0.01	0.08	<0.13	<0.04	<0.02	6.07	280.2	1925	6.98	▨	9600	-71
23/10/98	610	<0.01	0.12	<0.13	<0.04	0.04	5.24	▨	1750	7.01	▨	▨	-51
6/11/98	624	0.02	0.13	<0.13	<0.04	0.06	4.59	▨	1650	6.93	▨	▨	-26
18/11/98	636	0.0	0.26	0.19	<0.04	0.06	4.18	162.6	1650	7.06	▨	▨	78
02/12/98	650	0.04	0.15	<0.13	<0.04	0.08	4.05	▨	1550	6.78	▨	9050	2
21/12/98	669	0.01	0.23	<0.13	<0.04	0.05	3.09	237.3	1525	6.91	▨	▨	69

Maximum	1.92	4.87	0.75	1.69	1.90	242.11	1088.5	11650	7.75	6854.43	47900	78
Minimum	0.01	0.08	0.03	0.04	0.03	1.84	162.6	1525	6.72	1634.26	9050	-267

▨ Not analysed

Table A2.8.2 Analysis of Pitsea waste column leachate

Column 8 - 'aerobic', sparged with air from day 283

Date	Day	mg/l						NH$_3$-N	Cl$^-$	pH	Total VFAs	EC	Eh
		Cd	Cr	Pb	Zn	Ni	Fe	(mg N/l)	mg/l		mg/l	uS/cm	(mV)
19/02/97	0	0.06	<0.13	<0.38	0.79	<0.18	193.0	953.0	11525	6.7	5979.71	46800	▨
02/04/97	43	<0.01	0.13	<0.19	0.43	<0.09	72.58	1024.3	10240	6.99	▨	39100	▨
16/04/97	57	0.03	0.17	<0.19	0.48	0.13	8.58	922.9	10500	7.26	▨	45800	▨
30/04/97	71	<0.01	0.14	<0.19	0.23	<0.09	7.67	758.9	10650	7.53	1362.94	43600	▨
09/07/97	141	0.02	1.20	0.39	0.10	<0.09	3.47	907.5	9200	7.38	▨	39200	▨
23/07/97	155	<0.01	0.22	<0.19	0.04	<0.09	7.86	924.2	9100	7.29	▨	▨	▨
06/08/97	169	<0.01	<0.06	<0.19	<0.04	<0.09	<0.13	864.5	9700	7.51	▨	46800	-146
20/08/97	183	<0.03	0.17	0.65	5.05	<0.25	53.55	895.9	8400	7.43	▨	▨	-282
03/09/97	197	<0.01	0.22	<0.19	0.05	<0.09	8.26	904.8	9200	7.55	▨	45800	-175
17/09/97	211	<0.03	<0.13	<0.38	0.89	<0.18	16.26	869.8	8950	7.76	▨	▨	-269
01/10/97	225	<0.01	0.21	<0.19	0.97	0.10	18.36	727.4	8600	7.38	▨	43800	-170
15/10/97	239	<0.01	0.24	<0.19	0.35	0.10	12.20	841.3	8050	7.39	552	▨	-115
29/10/97	253	<0.01	0.16	<0.19	<0.04	<0.09	0.55	823.8	8300	7.47	▨	39300	-81
12/11/97	267	<0.01	0.22	0.02	0.02	0.09	8.63	801.1	8050	7.37	▨	▨	-25
26/11/97	281	<0.01	0.22	0.61	0.06	0.12	10.02	782.9	7500	7.39	▨	46000	-5
10/12/97	295	0.03	0.14	<0.38	<0.08	<0.18	8.17	752.0	7100	7.43	▨	▨	-30
23/12/97	308	<0.01	0.12	<0.19	<0.04	<0.09	6.25	900.0	6600	7.33	▨	40000	-86
07/01/98	321	<0.01	0.10	<0.19	<0.04	<0.09	4.77	804.6	6100	7.52	▨	▨	-238
21/01/98	335	0.03	0.32	<0.19	0.09	0.18	4.98	605.9	6350	7.36	▨	36500	-48
04/02/98	349	0.03	0.28	<0.19	<0.04	0.14	4.66	530.0	5100	7.33	▨	▨	-111
18/02/98	363	▨	▨	▨	▨	▨	▨	633.0	4800	7.76	▨	▨	-107
04/03/98	377	<0.01	0.19	<0.19	<0.04	<0.09	5.05	459.7	4300	7.52	▨	▨	-40
18/03/98	391	<0.01	0.20	<0.19	0.07	<0.09	5.70	343.9	3800	7.20	▨	▨	-144
01/04/98	405	<0.01	0.19	0.19	0.12	<0.09	5.70	342.6	3350	7.40	▨	17000	-45
15/04/98	419	<0.01	0.08	<0.19	0.30	<0.09	4.60	356.7	3000	7.38	▨	▨	-51
29/04/98	433	<0.01	0.09	<0.19	0.17	<0.09	3.13	306.1	2800	7.30	▨	▨	-62
13/05/98	447	0.01	0.12	<0.13	0.20	0.06	1.09	228.6	2400	7.36	▨	▨	-54
27/05/98	461	<0.01	0.11	<0.13	0.11	0.05	2.19	276.0	2050	7.36	▨	▨	34
10/06/98	475	<0.01	0.11	<0.13	0.12	0.05	1.80	▨	1800	7.44	▨	▨	-55
24/06/98	489	<0.01	0.07	<0.13	0.14	0.29	1.44	225.8	1600	7.48	▨	10000	-49
08/07/98	503	<0.01	0.04	<0.13	0.16	0.02	1.19	▨	1500	7.41	▨	▨	-52
22/07/98	517	<0.01	0.05	<0.13	0.22	0.03	1.21	▨	1300	7.39	▨	8400	8
13/08/98	539	<0.01	<0.04	<0.13	0.21	<0.02	0.86	177.1	1200	7.41	▨	▨	51
26/8/98	552	<0.01	0.06	<0.13	0.29	<0.02	0.30	▨	850	7.40	▨	▨	15
9/9/98	566	<0.01	<0.04	0.14	0.29	0.03	0.72	▨	850	7.38	▨	▨	-6
7/10/98	594	<0.01	<0.04	<0.13	0.21	<0.02	0.34	164.7	625	7.35	▨	7000	34
23/10/98	610	<0.01	0.06	<0.13	0.07	0.02	0.06	▨	600	7.14	▨	▨	47
6/11/98	624	<0.01	0.05	<0.13	0.05	<0.02	0.47	▨	500	6.92	▨	▨	96
18/11/98	636	<0.01	<0.04	<0.13	<0.04	0.03	0.74	132.9	500	7.05	▨	▨	116
02/12/98	650	<0.01	0.07	<0.13	0.11	0.02	<0.01	▨	450	6.74	▨	8800	46
21/12/98	669	<0.01	<0.03	<0.13	0.21	0.02	<0.01	172.6	400	6.83	▨	▨	104

Maximum	0.06	1.20	0.65	5.05	0.29	192.98	1024.3	11525	7.76	5979.71	46800	116
Minimum	0.01	0.04	0.02	0.02	0.02	0.06	132.9	400	6.70	552.00	7000	-282

▨ Not analysed

Table A2.8.3 Analysis of Pitsea waste column leachate

Column 9 - 'aerobic', sparged with air from day 283

Date	Day	mg/l						NH_3-N	Cl^-	pH	Total VFAs	EC	Eh
		Cd	Cr	Pb	Zn	Ni	Fe	(mg N/l)	mg/l		mg/l	uS/cm	(mV)
19/02/97	0	0.03	<0.13	0.44	1.33	<0.18	215.2	901.4	11400	6.73	4939.7	50000	▨
02/04/97	43	0.01	0.15	<0.19	0.25	0.09	72.19	945.5	11360	7.05	▨	45800	▨
16/04/97	57	0.02	0.22	<0.19	0.25	0.12	17.50	876.1	11700	7.45	▨	49900	▨
30/04/97	71	<0.01	0.16	<0.19	0.11	<0.09	10.46	764.7	10500	7.80	2043.13	44700	▨
09/07/97	141	0.02	1.19	0.53	0.12	<0.09	7.42	808.2	8800	7.35	▨	39300	▨
23/07/97	155	<0.01	0.20	0.28	0.71	<0.09	16.71	867.9	8800	7.25	▨	▨	▨
07/08/97	169	<0.01	0.20	0.39	2.88	<0.09	2.34	877.0	8000	7.31	▨	42600	-159
20/08/97	183	<0.01	0.31	<0.19	1.27	<0.09	19.78	818.8	8700	7.36	▨	▨	-178
03/09/97	197	<0.02	0.14	<0.25	<0.05	<0.12	6.38	887.2	8700	7.55	▨	45800	-233
17/09/97	211	<0.03	0.48	0.52	4.87	<0.18	29.90	842.9	8500	7.68	▨	▨	-239
01/10/97	225	<0.01	0.23	<0.19	1.14	0.10	24.36	744.0	8200	7.31	▨	40400	-110
15/10/97	239	<0.01	0.23	<0.19	0.39	0.11	10.45	843.0	8200	7.42	169	▨	-137
29/10/97	253	<0.01	0.07	0.04	<0.04	0.06	4.66	781.7	7900	7.41	▨	37200	-108
12/11/97	267	<0.01	0.20	0.04	0.04	0.10	8.89	777.5	7450	7.34	▨	▨	-47
26/11/97	281	<0.01	0.22	0.61	0.05	0.12	10.37	765.6	7100	7.32	▨	44000	-26
10/12/97	295	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
23/12/97	308	▨	▨	▨	▨	▨	▨	706.3	6200	7.32	▨	38500	-104
07/01/98	321	<0.01	0.14	<0.19	<0.04	0.10	4.12	715.5	5750	7.38	▨	▨	-326
21/01/98	335	0.02	0.32	<0.19	<0.04	0.18	10.47	540.6	6250	7.28	▨	35000	-70
04/02/98	349	0.03	0.28	<0.19	0.10	0.16	4.94	464.1	4900	7.50	▨	▨	-213
18/02/98	363	<0.01	0.22	<0.19	0.12	0.10	7.62	454.9	4500	7.32	▨	▨	-194
04/03/98	377	<0.01	0.22	<0.19	<0.04	0.09	7.28	445.4	4350	7.76	▨	▨	-18
18/03/98	391	<0.01	0.17	<0.19	0.08	0.08	6.43	308.9	3600	7.19	▨	▨	-126
01/04/98	405	<0.01	0.26	<0.38	0.15	<0.18	3.71	378.1	3550	7.65	▨	17000	-87
15/04/98	419	<0.01	0.10	<0.19	0.15	<0.09	4.97	300.2	3200	7.41	▨	▨	-60
29/04/98	433	<0.01	0.14	<0.19	0.04	<0.09	4.21	414.0	3100	7.13	▨	▨	-123
13/05/98	447	0.01	0.17	<0.13	0.06	0.09	3.73	386.0	3000	7.17	▨	▨	-128
27/05/98	461	<0.01	0.15	<0.13	0.04	0.07	5.77	349.1	2800	7.08	▨	▨	-96
10/06/98	475	<0.01	0.17	<0.13	0.08	0.07	4.55	▨	2400	7.13	▨	▨	-77
24/06/98	489	<0.01	0.13	<0.13	<0.04	0.05	3.93	294.2	2450	7.77	▨	13000	-95
08/07/98	503	<0.01	0.11	<0.13	<0.04	0.04	3.63	▨	2200	7.60	▨	▨	-162
22/07/98	517	<0.01	0.11	<0.13	0.06	0.05	4.55	▨	2000	7.00	▨	11000	-168
13/08/98	539	<0.01	<0.04	<0.13	<0.04	<0.02	4.20	▨	1700	6.92	▨	▨	-56
26/8/98	552	<0.01	0.12	<0.13	0.05	0.03	4.11	▨	1650	6.94	▨	▨	-38
9/9/98	566	<0.01	<0.04	<0.13	0.09	0.05	4.20	▨	1450	6.91	▨	▨	-63
7/10/98	594	<0.01	0.09	<0.13	<0.04	<0.02	4.32	175.1	1350	6.81	▨	7100	-41
23/10/98	610	<0.01	0.12	<0.13	<0.04	0.04	2.96	▨	1150	6.92	▨	▨	-8
6/11/98	624	<0.01	0.09	<0.25	<0.08	<0.04	4.35	▨	1050	6.73	▨	▨	22
18/11/98	636	<0.01	0.05	<0.13	<0.04	0.05	4.11	65.7	1050	6.73	▨	▨	4
02/12/98	650	<0.01	0.09	<0.13	<0.04	0.03	3.15	▨	925	6.60	▨	6100	9
21/12/98	669	<0.01	<0.04	<0.13	<0.04	0.04	3.35	137.8	900	6.77	▨	▨	-13

Maximum	0.03	1.19	0.61	4.87	0.18	215.17	945.5	11700	7.80	4939.70	50000	22
Minimum	0.01	0.05	0.04	0.04	0.03	2.34	65.7	900	6.60	169.00	6100	-326

▨ Not analysed

Table A2.8.4 Analysis of Pitsea waste column leachate

Column 10 - 'aerobic', sparged with air from day 283

Date	Day	mg/l						NH_3-N	Cl^-	pH	Total VFAs	EC	Eh
		Cd	Cr	Pb	Zn	Ni	Fe	(mg N/l)	mg/l		mg/l	uS/cm	(mV)
19/02/97	0	0.03	<0.13	0.44	0.13	<0.18	12.83	875.6	10900	6.7	4171.31	45700	▨
02/04/97	43	0.02	0.14	<0.19	0.28	<0.09	69.29	1031.9	11000	7.45	▨	41300	▨
16/04/97	57	0.03	0.15	<0.19	0.34	0.12	9.42	940.9	11000	7.26	▨	48800	▨
30/04/97	71	<0.01	0.13	<0.19	0.15	<0.09	7.46	860.0	11100	7.47	1635.72	47900	▨
09/07/97	141	<0.01	0.78	<0.19	0.35	<0.09	6.78	908.6	9300	7.33	▨	39300	▨
23/07/97	155	<0.01	0.25	<0.19	0.26	<0.09	10.51	910.1	9400	7.71	▨	▨	▨
06/08/97	169	<0.01	0.19	<0.19	0.26	<0.09	8.09	898.4	8700	7.45	▨	46800	-160
20/08/97	183	<0.01	0.20	<0.19	0.16	<0.09	9.90	925.6	9100	7.29	▨	▨	-126
03/09/97	197	<0.01	0.21	<0.19	<0.04	0.10	7.46	918.0	9100	7.56	▨	47800	-91
17/09/97	211	<0.01	0.26	0.19	1.77	<0.09	17.31	836.7	8700	7.71	▨	▨	-162
01/10/97	225	<0.01	0.24	<0.19	3.07	0.13	34.80	692.8	8100	7.37	▨	40400	48
15/10/97	239	<0.01	0.25	0.04	0.57	0.11	13.76	830.8	7700	7.39	<50	▨	-117
29/10/97	253	<0.01	0.18	<0.19	<0.04	0.08	7.65	787.6	7500	7.41	▨	35100	-92
12/11/97	267	<0.01	0.22	0.04	<0.04	0.10	0.70	693.8	7000	7.32	▨	▨	-54
26/11/97	281	0.03	0.25	0.62	0.08	0.13	10.59	725.3	6900	7.28	▨	43000	-43
10/12/97	295	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
23/12/97	308	▨	▨	▨	▨	▨	▨	563.4	5800	7.30	▨	38000	-100
07/01/98	321	<0.01	0.09	<0.19	<0.04	<0.09	4.64	659.6	5350	7.46	▨	▨	-303
21/01/98	335	0.02	0.31	<0.19	<0.04	0.16	3.81	512.9	5300	7.50	▨	31500	-253
04/02/98	349	0.03	0.29	<0.19	<0.04	0.14	4.39	456.9	4300	7.22	▨	▨	-240
18/02/98	363	<0.01	0.22	<0.19	0.06	0.08	6.10	461.9	3950	7.31	▨	▨	-211
04/03/98	377	<0.01	0.19	<0.19	<0.04	<0.09	5.05	439.6	3550	7.52	▨	▨	-170
18/03/98	391	<0.01	0.20	<0.19	0.05	0.07	7.28	399.3	3150	7.16	▨	▨	-95
01/04/98	405	<0.01	0.22	<0.19	0.07	0.09	5.01	390.6	2900	8.22	▨	16500	-33
15/04/98	419	<0.03	0.19	<0.38	<0.08	<0.18	9.74	344.5	2500	7.33	▨	▨	-61
29/04/98	433	<0.01	0.01	<0.19	<0.04	<0.09	3.25	346.9	2500	7.11	▨	▨	-120
13/05/98	447	0.01	0.18	<0.13	0.05	0.08	3.16	307.5	2300	7.12	▨	▨	-164
27/05/98	461	<0.01	0.15	<0.13	<0.04	0.06	5.34	283.2	2050	7.08	▨	▨	-146
10/06/98	475	<0.01	0.17	<0.13	<0.04	0.06	4.92	▨	1900	7.09	▨	▨	-101
24/06/98	489	<0.01	0.01	<0.13	<0.04	0.04	4.14	228.0	1950	7.55	▨	11000	-166
08/07/98	503	<0.01	0.11	<0.13	<0.04	0.04	3.35	▨	1800	7.44	▨	▨	-91
22/07/98	517	<0.01	0.11	<0.13	<0.04	0.03	4.71	▨	2000	6.89	▨	9500	-110
13/08/98	539	<0.01	<0.04	<0.13	<0.04	<0.02	4.04	228.6	1400	6.90	▨	▨	-45
26/8/98	552	<0.01	0.10	<0.13	0.05	0.02	3.97	▨	1200	6.84	▨	▨	-46
9/9/98	566	<0.01	<0.04	0.14	0.08	0.04	3.58	▨	1150	6.92	▨	▨	-54
7/10/98	594	<0.01	0.07	<0.13	<0.04	<0.02	3.53	145.8	1150	6.83	▨	6750	-39
23/10/98	610	<0.01	0.12	<0.13	<0.04	0.04	3.19	▨	900	6.89	▨	▨	-40
6/11/98	624	<0.01	0.09	<0.13	<0.04	0.03	2.19	▨	950	6.73	▨	▨	11
18/11/98	636	<0.01	0.04	0.24	<0.04	0.04	3.84	114.2	950	6.75	▨	▨	-2
02/12/98	650	<0.01	0.09	<0.25	<0.08	0.03	3.69	▨	825	6.59	▨	5450	-3
21/12/98	669	<0.01	<0.04	<0.13	<0.04	0.03	3.28	107.7	750	6.82	▨	▨	15

Maximum	0.03	0.78	0.62	3.07	0.16	69.29	1031.9	11100	8.22	4171.31	48800	48
Minimum	0.01	0.01	0.04	0.05	0.02	0.70	107.7	750	6.59	1635.72	5450	-303

▨ Not analysed

Table A2.8.5 Analysis of Pitsea waste column leachate

Column 11 - 'anaerobic control', no air sparging

Date	Day	mg/l						NH_3-N	Cl^-	pH	Total VFAs	EC	Eh
		Cd	Cr	Pb	Zn	Ni	Fe	(mg N/l)	mg/l		mg/l	uS/cm	(mV)
19/02/97	0	0.12	<0.25	0.81	0.75	<0.35	151.28	895.5	11300	6.69	4535.86	50100	▨
02/04/97	43	<0.01	0.15	<0.19	0.30	<0.09	149.00	933.1	11500	7.13	▨	44700	▨
16/04/97	57	<0.01	0.15	<0.19	0.29	0.13	17.76	910.0	11600	7.06	▨	39400	▨
30/04/97	71	<0.01	0.08	<0.19	0.14	<0.09	6.04	867.5	11300	7.33	2137.07	47900	▨
09/07/97	141	0.02	0.75	<0.19	0.09	<0.09	1.76	894.0	8900	7.31	▨	39300	▨
23/07/97	155	<0.01	<0.06	0.23	0.73	<0.09	9.60	893.8	9000	7.46	▨	▨	▨
06/08/97	169	<0.03	<0.13	<0.38	0.13	<0.18	3.27	948.9	9100	7.49	▨	49900	-249
20/08/97	183	<0.05	<0.25	<0.75	0.38	<0.35	12.40	876.8	9000	7.52	▨	▨	-153
03/09/97	197	<0.01	0.23	<0.19	<0.04	<0.09	5.80	905.1	9200	7.47	▨	45800	-253
17/09/97	211	<0.01	<0.06	<0.19	0.11	<0.09	4.04	870.8	9100	7.94	▨	▨	-291
01/10/97	225	<0.03	<0.13	<0.38	0.41	<0.18	9.90	860.0	9300	7.31	▨	46900	-172
15/10/97	239	<0.01	0.27	0.03	0.46	0.12	9.35	848.7	8400	7.50	<50	▨	-210
29/10/97	253	0.05	0.32	0.08	<0.04	0.15	8.22	789.9	8100	7.33	▨	39800	-118
12/11/97	267	<0.01	0.23	0.04	0.03	0.10	8.05	780.1	7700	7.42	▨	▨	-64
26/11/97	281	0.02	0.28	0.62	0.04	0.15	7.00	779.0	7500	7.41	▨	46000	-50
10/12/97	295	▨	▨	▨	▨	▨	▨	731.5	7000	7.85	▨	▨	27
23/12/97	308	▨	▨	▨	▨	▨	▨	1151.2	6900	7.45	▨	43000	-112
07/01/98	321	<0.01	0.13	<0.19	<0.04	<0.09	7.32	831.4	6450	7.48	▨	▨	-143
21/01/98	335	0.05	0.49	<0.38	<0.08	0.27	7.41	655.5	6900	7.52	▨	40000	-79
04/02/98	349	0.05	0.46	<0.38	<0.08	0.13	4.06	477.6	5900	7.43	▨	▨	-114
18/02/98	363	<0.01	0.29	<0.19	0.11	0.12	7.09	614.4	5650	7.42	▨	▨	-185
04/03/98	377	▨	▨	▨	▨	▨	▨	573.8	5350	7.79	▨	▨	-78
18/03/98	391	<0.01	0.26	<0.19	0.04	0.11	8.69	476.5	4950	7.28	▨	▨	-85
01/04/98	405	0.04	0.32	<0.19	0.07	0.15	8.67	506.2	4750	7.51	▨	24000	-85
15/04/98	419	<0.01	<0.06	<0.19	0.04	<0.09	2.47	462.5	4400	7.4	▨	▨	-107
29/04/98	433	<0.01	0.2	<0.19	0.05	<0.09	5.56	464.8	4250	7.18	▨	▨	-153
13/05/98	447	0.01	0.22	<0.13	0.06	0.11	4.83	466.7	4100	7.21	▨	▨	-156
27/05/98	461	<0.01	0.19	<0.13	<0.04	0.09	7.16	482.1	3850	7.18	▨	▨	-164
10/06/98	475	<0.01	0.21	<0.13	<0.04	0.09	7.68	▨	3550	7.22	▨	▨	-153
24/06/98	489	<0.01	0.17	<0.13	<0.04	0.07	6.49	394.8	3700	7.68	▨	19500	-162
08/07/98	503	<0.01	0.15	<0.13	<0.04	0.06	5.57	▨	3400	7.48	▨	▨	-163
22/07/98	517	<0.01	0.15	<0.13	<0.04	0.06	6.69	▨	3250	7.08	▨	18000	-165
13/08/98	539	<0.01	<0.04	<0.13	<0.04	<0.02	1.87	405.2	2950	7.12	▨	▨	-105
26/8/98	552	<0.01	0.16	<0.13	0.09	0.05	5.87	▨	2700	7.11	▨	▨	-151
9/9/98	566	<0.01	<0.04	<0.13	0.04	0.07	4.19	▨	2750	7.06	▨	▨	-108
7/10/98	594	<0.01	0.13	<0.13	0.12	0.03	4.18	389.6	2600	7.03	▨	15000	-11
23/10/98	610	<0.01	0.52	<0.13	<0.04	0.07	3.91	▨	2350	7.11	▨	▨	-80
6/11/98	624	<0.01	0.16	<0.13	<0.04	0.05	5.69	▨	2350	7.09	▨	▨	-116
18/11/98	636	<0.01	0.11	<0.13	<0.04	0.07	5.19	327.4	2275	7.05	▨	▨	-72
02/12/98	650	<0.01	0.19	<0.13	<0.04	0.07	4.24	▨	2200	6.85	▨	13000	-9
21/12/98	669	<0.01	0.09	<0.13	<0.04	0.06	5.01	341.2	2100	6.98	▨	▨	-73

Maximum	0.12	0.75	0.81	0.75	0.27	151.28	1151.2	11600	7.94	4535.86	50100	27
Minimum	0.01	0.08	0.03	0.03	0.03	1.76	327.4	2100	6.69	2137.07	13000	-291

▨ Not analysed

Table A2.8.6 Analysis of Pitsea waste column leachate

Column 12 - 'anaerobic control', no air sparging

Date	Day	mg/l						NH_3-N	Cl^-	pH	Total VFAs	EC	Eh
		Cd	Cr	Pb	Zn	Ni	Fe	(mg N/l)	mg/l		mg/l	uS/cm	(mV)
19/02/97	0	0.06	<0.25	<0.75	1.30	<0.35	158.6	910.6	11400	6.75	4634.21	52100	▨
02/04/97	43	<0.03	<0.13	<0.38	0.75	<0.18	104.6	917.0	11400	6.86	▨	47900	▨
16/04/97	57	0.03	<0.13	<0.38	0.83	0.19	15.63	920.8	11400	7.05	▨	48900	▨
30/04/97	71	<0.02	<0.08	<0.25	0.39	<0.12	7.08	951.1	11550	7.37	4064.56	47900	▨
09/07/97	141	0.03	0.94	<0.25	0.35	<0.12	2.01	▨	9600	7.63	▨	41600	▨
23/07/97	155	<0.05	<0.25	<0.75	0.36	<0.35	29.81	931.7	9550	7.49	▨	▨	▨
06/08/97	169	<0.05	<0.25	<0.75	<0.15	<0.35	6.70	893.7	9000	7.75	▨	46800	-140
20/08/97	183	<0.05	0.28	<0.75	0.51	<0.35	18.40	988.1	9700	7.55	▨	▨	-114
03/09/97	197	<0.03	0.27	<0.38	<0.08	<0.18	6.13	861.9	9200	8.22	▨	49900	-120
17/09/97	211	<0.01	<0.06	<0.19	0.23	<0.09	7.73	878.1	9100	7.88	▨	▨	-271
01/10/97	225	<0.03	<0.13	<0.38	0.97	<0.18	11.48	762.0	8600	7.45	▨	44800	-220
15/10/97	239	<0.01	0.28	<0.19	0.24	0.13	8.52	842.7	8500	7.44	<50	▨	-206
29/10/97	253	0.14	0.16	0.04	0.10	0.17	1.12	813.6	8200	7.35	▨	39500	-93
12/11/97	267	<0.01	0.25	0.04	0.05	0.11	9.85	793.4	7600	7.33	▨	▨	-91
26/11/97	281	<0.03	0.28	1.23	0.08	<0.18	7.68	743.9	7200	7.41	▨	46000	-77
10/12/97	295	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
23/12/97	308	▨	▨	▨	▨	▨	▨	702.8	6400	7.58	▨	40000	-50
07/01/98	321	<0.01	0.13	<0.19	<0.04	<0.09	6.61	773.5	6150	7.35	▨	▨	-115
21/01/98	335	0.02	0.38	<0.19	<0.04	0.20	8.61	633.2	6400	7.52	▨	38000	-88
04/02/98	349	0.02	0.36	<0.19	<0.04	0.18	10.38	520.3	5500	7.37	▨	▨	-73
18/02/98	363	<0.01	0.30	<0.19	0.05	0.13	8.87	543.5	4900	7.46	▨	▨	-69
04/03/98	377	<0.01	0.26	<0.19	<0.04	0.11	10.25	479.1	4550	7.61	▨	▨	-50
18/03/98	391	<0.01	0.27	<0.19	0.08	0.11	10.07	464.0	4100	7.21	▨	▨	-104
01/04/98	405	0.02	0.30	<0.19	0.11	<0.09	8.29	432.9	3850	7.6	▨	21500	-99
15/04/98	419	<0.01	0.18	<0.19	0.07	<0.09	8.52	402.4	3450	7.3	▨	▨	-114
29/04/98	433	<0.03	0.20	<0.38	<0.08	<0.18	4.91	421.1	3450	7.2	▨	▨	-142
13/05/98	447	0.01	0.22	<0.13	0.06	0.09	4.26	368.4	3100	7.23	▨	▨	-169
27/05/98	461	<0.01	0.19	<0.13	<0.04	0.07	5.93	352.4	2900	7.15	▨	▨	-121
10/06/98	475	<0.01	0.21	<0.13	<0.04	0.09	7.68	▨	2650	7.16	▨	▨	-113
24/06/98	489	<0.01	0.17	<0.13	<0.04	0.05	4.05	339	2700	7.79	▨	15000	-145
08/07/98	503	<0.01	0.15	<0.13	0.05	0.04	4.02	▨	2600	7.57	▨	▨	-124
22/07/98	517	<0.01	0.15	<0.13	0.04	0.04	4.90	▨	2200	7.01	▨	14000	-137
13/08/98	539	<0.01	<0.04	<0.13	<0.04	<0.02	0.74	303.7	2050	7.01	▨	▨	-64
26/8/98	552	<0.01	0.15	<0.13	0.05	0.03	4.23	▨	2000	7.11	▨	▨	-86
9/9/98	566	<0.01	<0.04	0.14	<0.04	0.05	4.61	▨	1800	7.05	▨	▨	-140
7/10/98	594	<0.01	0.12	<0.13	0.07	0.02	3.74	270.6	1825	6.98	▨	9600	-31
23/10/98	610	<0.01	0.16	<0.13	<0.04	0.05	3.40	▨	1600	7.03	▨	▨	-68
6/11/98	624	<0.01	0.13	<0.13	<0.04	0.04	3.81	▨	1650	6.97	▨	▨	-68
18/11/98	636	<0.01	0.09	<0.13	<0.04	0.06	3.65	274.3	1575	6.94	▨	▨	-51
02/12/98	650	<0.01	0.17	<0.13	<0.04	0.06	3.12	▨	1500	6.77	▨	8850	-9
21/12/98	669	<0.01	0.07	<0.13	<0.04	0.05	3.10	274	1475	6.89	▨	▨	-20

Maximum	0.14	0.94	1.23	1.30	0.20	158.59	988.1	11550	8.22	4634.21	52100	-9
Minimum	0.01	0.07	0.04	0.04	0.02	0.74	270.6	1475	6.75	4064.56	8850	-271

▨ Not analysed

Table A2.8.7 Analysis of Pitsea waste column leachate

Column 13 - 'anaerobic control', no air sparging

Date	Day	mg/l						NH_3-N	Cl^-	pH	Total VFAs	EC	Eh
		Cd	Cr	Pb	Zn	Ni	Fe	(mg N/l)	mg/l		mg/l	uS/cm	(mV)
19/02/97	0	0.04	0.16	0.52	0.75	<0.18	217.6	130.3	975	6.28	2116	12000	▨
02/04/97	43	<0.01	<0.06	0.21	0.11	<0.09	1.67	187.9	1000	7.06	▨	8510	▨
16/04/97	57	<0.01	<0.06	<0.19	0.12	0.11	2.08	162.1	1000	7.10	▨	5940	▨
30/04/97	71	<0.01	<0.06	<0.19	<0.04	0.10	1.55	132.6	1025	7.18	<20	7680	▨
09/07/97	141	<0.01	0.30	<0.19	0.57	0.09	2.40	128.8	1250	7.25	▨	7880	▨
23/07/97	155	<0.01	<0.06	0.34	0.31	<0.09	7.45	189.5	1125	6.94	▨	▨	▨
06/08/97	169	<0.01	<0.06	<0.19	0.07	<0.09	3.46	133.6	900	6.98	▨	7770	-75
20/08/97	183	<0.01	<0.06	<0.19	<0.04	<0.09	5.00	135.5	1050	6.91	▨	▨	-32
03/09/97	197	<0.01	<0.06	<0.19	<0.04	0.11	5.16	100.7	750	7.11	▨	8930	-38
17/09/97	211	<0.01	<0.06	<0.19	0.18	<0.09	4.64	114.5	750	7.25	▨	▨	-42
01/10/97	225	<0.01	<0.06	<0.19	0.17	<0.09	8.80	104.5	500	6.89	▨	8620	-63
15/10/97	239	<0.01	<0.06	<0.19	<0.04	0.07	5.70	117.6	250	6.97	<50	▨	-48
29/10/97	253	<0.01	<0.06	0.04	<0.04	0.07	5.70	74.2	500	7.06	▨	7970	-54
12/11/97	267	<0.01	<0.06	0.06	0.03	0.05	4.79	91.1	425	6.98	▨	▨	-11
26/11/97	281	<0.01	<0.06	0.65	0.22	<0.09	4.41	117.9	450	7.05	▨	6700	14
10/12/97	295	<0.01	<0.06	<0.19	<0.04	<0.09	3.31	89.8	300	6.99	▨	▨	18
23/12/97	308	<0.01	<0.06	<0.19	<0.04	<0.09	7.37	102.0	300	7.01	▨	5050	-27
07/01/98	321	<0.01	<0.06	<0.19	<0.04	<0.09	3.11	121.3	225	7.04	▨	▨	-67
21/01/98	335	0.08	0.24	<0.19	0.07	0.17	3.01	73.2	225	7.05	▨	5150	-34
04/02/98	349	0.06	0.22	<0.19	0.04	0.14	2.98	62.1	200	7.09	▨	▨	-27
18/02/98	363	0.02	0.10	<0.19	0.06	<0.09	2.99	79.3	150	7.08	▨	▨	-69
04/03/98	377	0.02	<0.06	<0.19	<0.04	<0.09	2.99	69.4	125	7.21	▨	▨	-28
18/03/98	391	<0.03	<0.13	<0.38	<0.04	<0.18	1.42	65.3	113	6.90	▨	▨	-57
01/04/98	405	<0.03	0.08	<0.38	0.18	<0.18	2.02	86.3	88	8.18	▨	2700	-29
15/04/98	419	<0.01	<0.06	<0.19	<0.04	<0.09	2.79	99.3	75	7.09	▨	▨	14.8
29/04/98	433	<0.01	<0.06	<0.19	0.05	<0.09	1.26	94.2	75	6.90	▨	▨	-68
13/05/98	447	<0.01	0.06	<0.13	<0.04	0.05	1.56	106.1	50	6.87	▨	▨	-81
27/05/98	461	<0.01	<0.04	<0.13	<0.04	<0.02	2.25	77.9	50	6.88	▨	▨	-62
10/06/98	475	<0.01	<0.04	<0.13	<0.04	<0.02	2.29	▨	13	6.96	▨	▨	-88
24/06/98	489	<0.01	<0.04	<0.13	<0.04	<0.02	1.13	91.7	50	7.42	▨	2350	-42
08/07/98	503	<0.01	<0.04	<0.13	<0.04	<0.02	0.72	▨	50	7.21	▨	▨	-67
22/07/98	517	<0.01	<0.04	<0.13	<0.04	<0.02	2.03	▨	63	6.79	▨	2650	-80
13/08/98	539	<0.01	<0.04	<0.13	<0.04	<0.02	1.93	132.3	<1	6.79	▨	▨	-33
26/8/98	552	<0.01	<0.04	<0.13	0.08	0.03	1.77	▨	38	6.82	▨	▨	-63
9/9/98	566	<0.01	<0.04	0.13	0.19	0.06	1.94	▨	13	6.78	▨	▨	-19
7/10/98	594	<0.01	<0.04	<0.13	<0.04	<0.02	1.70	89.4	25	6.81	▨	2550	-22
23/10/98	610	<0.01	0.05	<0.13	<0.04	0.05	1.66	▨	50	6.84	▨	▨	33
6/11/98	624	<0.01	<0.04	<0.13	<0.04	0.03	1.79	▨	▨	6.62	▨	▨	51
18/11/98	636	<0.01	<0.04	<0.13	<0.04	0.05	1.75	110.7	50	6.72	▨	▨	60
02/12/98	650	<0.01	0.07	<0.13	<0.04	0.05	1.60	▨	25	6.56	▨	2650	-6
21/12/98	669	<0.01	<0.04	<0.13	<0.04	0.05	1.62	114.3	50	6.68	▨	▨	55

Maximum	0.08	0.30	0.65	0.75	0.17	217.63	189.5	1250	8.18	2116.00	12000	60
Minimum	0.02	0.05	0.04	0.03	0.03	0.72	62.1	13	6.28	2116.00	2350	-88

▨ Not analysed

Table A2.8.8 Analysis of Pitsea waste column leachate

Column 14 - 'aerobic', sparged with air from day 283

Date	Day	mg/l						NH_3-N	Cl$^-$	pH	Total VFAs	EC	Eh
		Cd	Cr	Pb	Zn	Ni	Fe	(mg N/l)	mg/l		mg/l	uS/cm	(mV)
19/02/97	0	0.01	<0.06	<0.19	0.16	0.17	121.0	182.3	875	6.38	3248	13200	▨
02/04/97	43	<0.01	<0.06	<0.19	0.12	0.12	2.15	145.2	750	7.07	▨	▨	▨
16/04/97	57	0.02	<0.06	<0.19	0.10	0.17	1.80	135.6	800	7.05	▨	5760	▨
30/04/97	71	<0.01	<0.06	<0.19	<0.04	0.15	0.97	111.2	750	7.52	<20	6060	▨
19/07/97	141	<0.01	0.31	<0.19	0.15	0.11	3.92	79.8	1100	7.29	▨	6280	▨
23/07/97	155	<0.01	<0.06	0.30	0.54	<0.09	15.66	122.1	900	6.91	▨	▨	▨
06/08/97	169	<0.01	<0.06	<0.19	0.15	<0.09	7.90	130.9	950	6.99	▨	7340	-110
20/08/97	183	<0.01	<0.06	<0.19	0.07	<0.09	9.10	82.9	850	6.99	▨	▨	-90
03/09/97	197	<0.01	<0.06	<0.19	0.89	0.12	8.27	86.1	750	7.16	▨	6590	-40
17/09/97	211	<0.01	<0.06	<0.19	0.45	<0.09	7.88	76.7	700	7.86	▨	▨	20
01/10/97	225	<0.01	<0.06	<0.19	0.94	0.09	17.49	105.0	550	6.97	▨	5970	-71
15/10/97	239	<0.01	<0.06	<0.19	<0.04	0.09	9.43	89.6	325	6.93	<50	▨	-58
29/10/97	253	<0.01	<0.06	0.02	<0.04	0.07	8.94	60.2	425	7.08	▨	5220	-70
12/11/97	267	<0.01	<0.06	0.03	<0.04	0.06	8.56	86.8	400	6.97	▨	▨	-17
26/11/97	281	0.06	<0.13	1.24	<0.08	<0.18	8.25	84.8	375	6.99	▨	4900	-42
10/12/97	295	<0.01	<0.06	<0.19	<0.04	<0.09	5.87	90.4	275	6.86	▨	▨	-55
23/12/97	308	<0.01	<0.06	<0.19	<0.04	<0.09	2.43	80.9	275	6.92	▨	5050	-55
07/01/98	321	<0.01	<0.06	<0.19	<0.04	<0.09	7.56	74.4	250	7.02	▨	▨	-52
21/01/98	335	0.03	0.14	<0.19	<0.04	0.14	0.62	71.4	238	6.95	▨	5450	-21
04/02/98	349	0.03	0.14	<0.19	<0.04	0.12	0.42	94.8	200	6.90	▨	▨	-282
18/02/98	363	<0.01	0.06	<0.19	0.05	<0.09	2.75	104.7	150	7.01	▨	▨	-58
04/03/98	377	0.02	<0.06	<0.19	0.08	<0.09	0.21	113.3	150	6.87	▨	▨	-10
18/03/98	391	<0.01	<0.06	<0.19	0.09	<0.09	2.41	102.7	138	6.31	▨	▨	-202
01/04/98	405	<0.01	0.08	<0.19	0.10	<0.09	1.07	74.6	125	6.76	▨	6600	-1.1
15/04/98	419	<0.01	<0.06	<0.19	<0.04	<0.09	0.34	62.2	100	6.80	▨	▨	51
29/04/98	433	<0.01	<0.06	<0.19	<0.04	<0.09	0.22	92.2	113	6.41	▨	▨	-211
13/05/98	447	0.01	0.06	<0.13	<0.04	0.04	0.33	68.1	100	6.54	▨	▨	-278
27/05/98	461	<0.01	<0.04	<0.13	<0.04	<0.02	0.49	83.1	125	6.52	▨	▨	-267
10/06/98	475	<0.01	<0.04	<0.13	<0.04	<0.02	2.29	▨	38	6.50	▨	▨	-278
24/06/98	489	<0.01	<0.04	<0.13	<0.04	<0.02	0.13	93.2	100	7.32	▨	4750	-267
08/07/98	503	<0.01	<0.04	<0.13	<0.04	<0.02	0.11	▨	125	7.02	▨	▨	-317
22/07/98	517	<0.01	<0.08	<0.25	<0.08	<0.04	<0.02	▨	125	6.84	▨	▨	26
13/08/98	539	<0.01	<0.04	<0.13	<0.04	<0.02	1.62	86.4	50	7.03	▨	▨	202
26/8/98	552	<0.01	<0.04	<0.13	<0.04	<0.02	1.81	▨	75	6.24	▨	▨	-266
9/9/98	566	<0.01	<0.04	<0.13	0.07	0.02	1.22	▨	63	6.35	▨	▨	-244
7/10/98	594	<0.01	<0.04	<0.13	<0.04	<0.02	0.30	92.5	100	6.40	▨	3900	-317
23/10/98	610	<0.01	0.04	<0.13	<0.04	0.02	0.69	▨	50	6.32	▨	▨	-225
6/11/98	624	<0.01	0.03	<0.13	<0.04	<0.02	0.67	▨	75	6.07	▨	▨	-225
18/11/98	636	<0.01	<0.04	<0.13	<0.04	0.03	0.71	99.8	75	6.29	▨	▨	-224
02/12/98	650	0.03	0.10	<0.13	<0.04	0.06	0.62	▨	63	6.18	▨	4775	-184
21/12/98	669	▨	▨	▨	▨	▨	▨	44.2	63	6.48	▨	▨	106

Maximum	0.06	0.31	1.24	0.94	0.17	120.97	182.3	1100	7.86	3248.00	13200	202
Minimum	0.01	0.03	0.02	0.05	0.02	0.11	44.2	38	6.07	3248.00	3900	-317

▨ Not analysed

Table A2.8.9 Analysis of Pitsea waste column leachate

Column 15 - 'aerobic', sparged with air from day 283

Date	Day	mg/l						NH_3-N (mg N/l)	Cl^- mg/l	pH	Total VFAs mg/l	EC uS/cm	Eh (mV)
		Cd	Cr	Pb	Zn	Ni	Fe						
19/02/97	0	<0.01	<0.06	<0.19	0.12	0.26	54.08	204.1	1075	6.28	3700	14800	▨
02/04/97	43	0.02	<0.06	<0.19	0.14	0.10	2.09	151.5	800	7.05	▨	6280	▨
16/04/97	57	0.01	<0.06	<0.19	0.10	0.13	1.66	132.5	950	7.02	▨	6700	▨
30/04/97	71	<0.01	<0.06	<0.19	<0.04	0.16	1.54	114.0	850	7.09	<20	6280	▨
19/07/97	141	<0.01	0.33	<0.19	0.10	0.13	2.42	108.7	1400	7.10	▨	8000	▨
23/07/97	155	<0.01	<0.06	<0.19	0.16	<0.09	4.83	125.1	1050	6.84	▨	▨	▨
06/08/97	169	<0.01	<0.06	<0.19	0.08	0.10	3.98	97.5	900	7.04	▨	7550	26
20/08/97	183	<0.01	<0.06	<0.19	0.07	1.10	5.86	92.3	1000	6.94	▨	▨	-32
03/09/97	197	<0.01	<0.06	<0.19	0.93	0.12	8.44	80.1	800	7.16	▨	7440	-12
17/09/97	211	<0.01	<0.06	<0.19	0.52	<0.09	7.59	99.0	800	7.27	▨	▨	75
01/10/97	225	<0.01	<0.06	<0.19	0.26	0.14	6.35	140.6	650	6.98	▨	7130	-218
15/10/97	239	<0.01	<0.06	0.11	0.39	0.15	10.68	96.0	350	6.98	<50	▨	-82
29/10/97	253	<0.01	0.07	0.04	<0.04	0.15	5.48	72.6	625	7.09	▨	5950	-46
12/11/97	267	<0.01	0.02	0.04	<0.04	0.13	3.81	92.7	525	7.08	▨	▨	18
26/11/97	281	<0.01	<0.06	0.62	0.04	0.14	3.21	105.7	500	7.05	▨	6400	-7
10/12/97	295	<0.01	<0.06	<0.19	<0.04	<0.09	0.89	89.0	450	7.04	▨	▨	-15
23/12/97	308	<0.01	<0.06	<0.19	<0.04	<0.09	3.15	93.1	400	7.05	▨	6700	-37
07/01/98	321	<0.01	<0.06	<0.19	<0.04	<0.09	2.60	102.0	350	7.13	▨	▨	-45
21/01/98	335	0.02	0.15	<0.19	<0.04	0.16	2.55	74.5	313	7.01	▨	5900	-4
04/02/98	349	0.02	0.13	<0.19	<0.04	0.14	2.39	81.6	250	7.03	▨	▨	-112
18/02/98	363	0.02	0.10	<0.19	0.04	<0.09	0.27	73.0	250	7.04	▨	▨	-21
04/03/98	377	<0.01	<0.06	<0.19	<0.04	<0.09	2.04	83.0	225	7.13	▨	▨	-34
18/03/98	391	<0.01	<0.06	<0.19	0.06	<0.09	1.85	80.9	200	6.85	▨	▨	-90
01/04/98	405	<0.01	0.09	<0.19	0.09	<0.09	1.50	97.3	225	7.11	▨	3200	-26
15/04/98	419	<0.01	<0.06	<0.19	<0.04	<0.09	0.45	85.2	163	7.13	▨	▨	75
29/04/98	433	<0.01	0.02	<0.19	<0.04	<0.09	0.23	95.3	163	6.89	▨	▨	-130
13/05/98	447	0.01	0.06	<0.13	0.07	0.08	0.29	77.6	125	6.92	▨	▨	-205
27/05/98	461	<0.01	<0.04	<0.13	0.18	0.05	0.30	73.1	125	6.92	▨	▨	-187
10/06/98	475	<0.01	0.04	<0.13	<0.04	0.05	0.18	▨	25	6.93	▨	▨	-229
24/06/98	489	<0.01	<0.04	<0.13	<0.04	0.04	0.15	114.8	125	7.61	▨	3000	-243
08/07/98	503	<0.01	<0.04	<0.13	<0.04	0.03	0.12	▨	125	7.32	▨	▨	-282
22/07/98	517	<0.01	<0.04	<0.13	<0.04	<0.02	0.19	▨	113	6.86	▨	2650	-66
13/08/98	539	<0.01	<0.04	<0.13	<0.04	<0.02	5.16	133.1	50	7.39	▨	▨	110
26/8/98	552	<0.01	<0.04	<0.13	<0.04	0.04	0.31	▨	63	6.85	▨	▨	-182
9/9/98	566	<0.01	<0.04	0.13	<0.04	0.07	1.23	▨	75	6.89	▨	▨	-196
7/10/98	594	<0.01	0.09	<0.13	<0.04	0.04	0.70	85.3	100	7.03	▨	2900	-196
23/10/98	610	<0.01	0.05	<0.13	<0.04	0.06	0.38	▨	75	7.32	▨	▨	-140
6/11/98	624	<0.01	0.04	<0.13	<0.04	0.05	0.12	▨	75	6.59	▨	▨	-115
18/11/98	636	<0.01	<0.04	<0.13	<0.04	0.07	0.64	80.0	50	6.67	▨	▨	-115
02/12/98	650	0.01	0.08	<0.13	<0.04	0.09	0.48	▨	50	6.59	▨	2875	-53
21/12/98	669	<0.01	<0.04	<0.13	<0.04	0.06	0.43	47.7	50	6.59	▨	▨	93

Maximum	0.02	0.33	0.62	0.93	1.10	54.08	204.1	1400	7.61	3700.00	14800	110
Minimum	0.01	0.02	0.04	0.04	0.03	0.12	47.7	25	6.28	3700.00	2650	-282

▨ Not analysed

Table A2.8.10 Analysis of Pitsea waste column leachate

Column 16 - 'aerobic', sparged with air from day 283

Date	Day	mg/l						NH_3-N	Cl^-	pH	Total VFAs	EC	Eh
		Cd	Cr	Pb	Zn	Ni	Fe	(mg N/l)	mg/l		mg/l	uS/cm	(mV)
19/02/97	0	0.02	<0.06	<0.19	0.06	0.37	91.61	229.8	975	6.33	3617	14530	▨
02/04/97	43	<0.01	<0.06	<0.19	0.24	0.10	6.81	155.2	1000	7.14	▨	6800	▨
16/04/97	57	0.01	<0.06	<0.19	0.10	0.30	7.60	160.8	1050	7.20	▨	7240	▨
30/04/97	71	<0.01	<0.06	<0.19	<0.04	0.15	6.36	127.9	950	7.17	<20	7220	▨
09/07/97	141	<0.01	0.29	<0.19	0.83	0.13	6.75	71.5	1200	7.26	▨	7340	▨
23/07/97	155	<0.01	<0.06	<0.19	0.18	<0.09	8.96	87.7	1050	6.79	▨	▨	▨
06/08/97	169	<0.01	<0.06	<0.19	0.30	<0.09	6.73	78.6	850	6.89	▨	7660	-25
20/08/97	183	<0.01	<0.06	<0.19	0.04	1.10	6.61	91.6	950	6.94	▨	▨	-13
03/09/97	197	<0.01	<0.06	<0.19	<0.04	0.14	5.66	73.0	750	7.18	▨	7000	-36
17/09/97	211	<0.01	<0.06	<0.19	0.27	0.18	4.06	74.6	700	7.15	▨	▨	76
01/10/97	225	<0.01	<0.06	<0.19	0.15	0.09	7.26	69.7	600	7.01	▨	6480	-34
15/10/97	239	<0.01	<0.06	<0.19	0.09	0.10	5.57	85.7	300	7.07	<50	▨	-35
29/10/97	253	<0.01	<0.06	<0.19	<0.04	0.08	5.96	66.8	475	7.09	▨	5860	-62
12/11/97	267	<0.01	0.01	0.04	<0.04	0.08	4.75	94.0	400	7.04	▨	▨	32
26/11/97	281	<0.03	<0.13	1.23	<0.08	<0.18	2.13	100.5	375	7.03	▨	5250	-32
10/12/97	295	<0.05	<0.25	<0.75	<0.15	<0.35	14.37	103.8	300	7.10	▨	▨	-8
23/12/97	308	<0.03	<0.13	<0.38	<0.08	<0.18	1.61	120.4	300	7.06	▨	5400	-18
07/01/98	321	<0.01	<0.06	<0.19	<0.04	<0.09	2.62	93.1	263	7.21	▨	▨	-33
21/01/98	335	0.02	0.15	<0.19	<0.04	0.15	2.44	84.7	263	7.02	▨	5650	-7
04/02/98	349	0.02	0.13	<0.19	<0.04	0.13	1.23	123.6	175	7.19	▨	▨	-73
18/02/98	363	0.03	0.12	<0.19	0.13	<0.09	0.42	151.7	150	7.39	▨	▨	-183
04/03/98	377	<0.01	<0.06	<0.19	<0.04	<0.09	1.36	114.4	150	7.84	▨	▨	-121
18/03/98	391	▨	▨	▨	▨	▨	▨	126.6	150	6.98	▨	▨	-218
01/04/98	405	▨	▨	▨	▨	▨	▨	140.2	113	7.41	▨	5500	-258
15/04/98	419	<0.01	<0.06	<0.19	<0.04	<0.09	1.15	109.0	75	7.14	▨	▨	13
29/04/98	433	▨	▨	▨	▨	▨	▨	135.9	125	7.02	▨	▨	-303
13/05/98	447	0.01	0.07	<0.13	0.06	0.07	0.20	99.5	125	7.02	▨	▨	-326
27/05/98	461	<0.01	<0.04	<0.13	<0.04	0.03	0.53	87.1	100	7.14	▨	▨	-322
10/06/98	475	<0.01	0.06	<0.13	<0.04	0.04	0.69	▨	25	6.98	▨	▨	-310
24/06/98	489	<0.01	<0.04	<0.13	<0.04	0.03	0.38	99.0	100	7.59	▨	3150	-357
08/07/98	503	<0.01	<0.04	<0.13	0.05	0.02	0.32	▨	100	7.25	▨	▨	-363
22/07/98	517	<0.01	<0.08	<0.25	<0.08	<0.04	0.46	▨	100	6.75	▨	4600	-286
13/08/98	539	<0.01	<0.04	<0.13	<0.04	<0.02	3.68	95.6	<1	6.23	▨	▨	130
26/8/98	552	<0.01	<0.04	<0.13	0.13	0.04	0.23	▨	50	6.89	▨	▨	-318
9/9/98	566	<0.01	<0.04	0.14	<0.04	0.06	0.26	▨	25	6.86	▨	▨	-325
7/10/98	594	<0.01	0.08	0.15	<0.04	0.04	0.02	89.8	50	7.00	▨	2900	-330
23/10/98	610	<0.01	0.06	<0.13	<0.04	0.06	0.27	▨	50	7.23	▨	▨	-255
6/11/98	624	<0.01	0.04	<0.13	<0.04	0.05	0.57	▨	25	6.68	▨	▨	-295
18/11/98	636	<0.01	<0.04	<0.13	<0.04	0.06	2.34	97.2	50	6.48	▨	▨	-31
02/12/98	650	0.02	0.13	<0.25	<0.04	0.08	2.09	▨	50	6.29	▨	5000	6
21/12/98	669	<0.01	<0.04	<0.13	<0.04	0.04	0.40	123.7	50	6.47	▨	▨	111

Maximum	0.03	0.29	1.23	0.83	1.10	91.61	229.8	1200	7.84	3617	14530	130
Minimum	0.01	0.01	0.04	0.04	0.02	0.02	66.8	25	6.23	3617	2900	-363

▨ Not analysed

Table A2.8.11 Analysis of Pitsea waste column leachate

Column 17 - 'anaerobic control', no air sparging

Date	Day	mg/l						NH_3-N	Cl^-	pH	Total VFAs	EC	Eh
		Cd	Cr	Pb	Zn	Ni	Fe	(mg N/l)	mg/l		mg/l	uS/cm	(mV)
19/02/97	0	<0.01	<0.06	<0.19	0.08	0.21	120.6	216.4	1075	6.34	3457	14780	▨
02/04/97	43	0.02	<0.06	<0.19	0.17	<0.09	5.03	114.9	960	7.21	▨	5950	▨
16/04/97	57	<0.01	<0.06	<0.19	0.08	0.13	5.78	118.4	1050	7.09	▨	6810	▨
30/04/97	71	<0.01	<0.06	<0.19	<0.04	0.14	5.76	67.0	925	7.05	<20	7140	▨
09/07/97	141	<0.01	0.28	<0.19	0.04	<0.09	9.04	15.2	850	7.00	▨	4990	▨
23/07/97	155	<0.01	<0.06	<0.19	0.12	<0.09	13.09	64.4	950	7.04	▨	▨	▨
06/08/97	169	<0.01	<0.06	<0.19	0.22	<0.09	6.65	56.0	950	6.90	▨	6690	-72
20/08/97	183	<0.01	<0.06	<0.19	0.17	<0.09	29.60	77.3	850	7.06	▨	▨	-24
03/09/97	197	<0.01	<0.06	<0.19	<0.04	<0.09	4.06	66.2	700	7.22	▨	6240	-18
17/09/97	211	<0.01	<0.06	<0.19	0.52	<0.09	3.68	69.2	700	7.39	▨	▨	60
01/10/97	225	<0.01	<0.06	<0.19	0.42	<0.09	6.88	88.8	500	7.17	▨	5740	-71
15/10/97	239	<0.01	<0.06	<0.19	<0.04	0.06	2.78	89.1	275	7.11	<50	▨	-15
29/10/97	253	0.01	<0.06	<0.19	<0.04	0.05	3.38	72.2	500	7.22	▨	4890	10
12/11/97	267	<0.01	<0.06	0.03	<0.04	0.05	2.51	129.5	400	7.06	▨	▨	17
26/11/97	281	<0.03	<0.13	0.61	<0.08	<0.18	2.60	114.5	400	6.91	▨	5200	-8
10/12/97	295	<0.01	<0.06	<0.19	<0.04	<0.09	2.26	72.3	275	6.91	▨	▨	31
23/12/97	308	0.03	<0.06	<0.19	<0.04	<0.09	2.22	78.2	325	7.01	▨	5000	-2
07/01/98	321	<0.01	<0.06	<0.19	<0.04	<0.09	2.44	104.9	238	6.98	▨	▨	-18
21/01/98	335	0.03	0.14	<0.19	<0.04	0.14	2.36	65.3	213	6.89	▨	4700	28
04/02/98	349	0.02	0.12	<0.19	0.04	0.11	2.19	86.8	150	7.05	▨	▨	-34
18/02/98	363	0.01	0.10	<0.19	0.05	<0.09	0.14	55.4	150	7.13	▨	▨	-18
04/03/98	377	<0.01	<0.06	<0.19	<0.04	<0.09	2.27	79.4	125	7.25	▨	▨	-45
18/03/98	391	<0.03	<0.13	<0.38	<0.04	<0.18	2.45	78.3	125	6.96	▨	▨	-101
01/04/98	405	▨	▨	▨	▨	▨	▨	63.6	100	7.48	▨	2750	-123
15/04/98	419	<0.01	<0.06	<0.19	<0.04	<0.09	2.28	67.1	100	7.05	▨	▨	42
29/04/98	433	<0.01	<0.06	<0.19	<0.04	<0.09	2.42	79.2	100	6.93	▨	▨	-103
13/05/98	447	0.01	0.06	<0.13	0.07	0.05	1.419	64.0	50	6.84	▨	▨	-188
27/05/98	461	<0.01	<0.08	<0.25	<0.08	<0.04	0.998	53.0	75	6.82	▨	▨	-195
10/06/98	475	<0.01	<0.04	<0.13	<0.04	0.02	2.188	▨	<1	6.85	▨	▨	-188
24/06/98	489	<0.01	<0.04	<0.13	<0.04	<0.02	1.06	68.6	75	7.44	▨	2300	-200
08/07/98	503	<0.01	<0.04	<0.13	<0.04	<0.02	0.903	▨	63	7.18	▨	▨	-221
22/07/98	517	<0.01	<0.04	<0.13	<0.04	<0.02	2.615	▨	50	6.77	▨	2450	-196
13/08/98	539	<0.01	<0.04	<0.13	<0.04	<0.02	0.283	78.7	<1	6.76	▨	▨	-184
26/8/98	552	<0.01	<0.04	<0.13	0.09	<0.02	0.124	▨	50	6.78	▨	▨	-184
9/9/98	566	<0.01	<0.04	0.14	<0.04	0.04	2.243	▨	25	6.78	▨	▨	-198
7/10/98	594	<0.01	0.11	0.31	<0.04	0.03	<0.01	76.1	50	6.82	▨	2500	-187
23/10/98	610	<0.01	0.05	<0.13	<0.04	0.03	2.488	▨	25	6.77	▨	▨	-111
6/11/98	624	0.03	0.12	<0.13	<0.04	0.06	1.813	▨	50	6.63	▨	▨	-97
18/11/98	636	<0.01	<0.04	<0.13	<0.04	0.04	3.15	107	38	6.72	▨	▨	-53
02/12/98	650	0.01	0.06	<0.13	<0.04	0.04	2.324	▨	38	6.48	▨	2250	-64
21/12/98	669	<0.01	<0.04	<0.13	<0.04	0.06	1.153	60	25	6.65	▨	▨	1

Maximum	0.03	0.28	0.61	0.52	0.21	120.59	216.4	1075	7.48	3457	14780	60
Minimum	0.01	0.05	0.03	0.04	0.02	0.12	15.2	25	6.34	3457	2250	-221

▨ Not analysed

Table A2.8.12 Analysis of Pitsea waste column leachate

Column 18 - 'anaerobic control', no air sparging

Date	Day	mg/l						NH_3-N	Cl^-	pH	Total VFAs	EC	Eh
		Cd	Cr	Pb	Zn	Ni	Fe	(mg N/l)	mg/l		mg/l	uS/cm	(mV)
19/02/97	0	<0.01	<0.06	<0.19	0.09	0.20	126.5	226.9	1125	6.3	3640	14590	▨
02/04/97	43	<0.03	<0.13	<0.38	0.03	<0.18	2.64	162.3	1090	7.01	▨	7240	▨
16/04/97	57	0.01	0.07	<0.19	0.11	0.18	1.77	183.7	1150	7.06	▨	7780	▨
30/04/97	71	<0.01	<0.06	<0.19	<0.04	<0.09	<0.13	121.8	1100	7.15	<20	7560	▨
09/07/97	141	<0.01	0.31	<0.19	<0.04	0.13	2.12	149.3	1400	7.12	▨	8420	▨
23/07/97	155	<0.01	0.07	0.28	0.83	0.14	5.96	180.9	1150	7.01	▨	▨	▨
06/08/97	169	<0.01	<0.06	<0.19	0.15	0.10	3.25	153.7	900	7.06	▨	8940	-10
20/08/97	183	<0.01	<0.06	<0.19	<0.04	0.10	5.56	134.8	1000	7.01	▨	▨	-23
03/09/97	197	<0.01	<0.06	<0.19	<0.04	0.14	4.07	111.1	1050	7.22	▨	8390	-20
17/09/97	211	<0.01	<0.06	<0.19	0.21	0.15	4.40	103.6	950	▨	▨	▨	53
01/10/97	225	<0.01	<0.06	<0.19	0.23	0.11	8.13	96.7	800	7.03	▨	7230	-28
15/10/97	239	<0.03	<0.13	<0.38	<0.08	0.11	9.32	99.6	400	7.09	<50	▨	-68
29/10/97	253	<0.01	<0.06	0.02	<0.04	0.11	8.15	106.9	675	7.18	▨	6280	-19
12/11/97	267	<0.01	0.02	0.05	<0.04	0.10	6.12	129.0	675	7.03	▨	▨	64
26/11/97	281	<0.03	<0.13	1.23	<0.08	<0.18	4.01	126.3	613	7.02	▨	7400	7
10/12/97	295	<0.01	<0.06	<0.19	<0.04	<0.09	5.56	84.6	525	7.09	▨	▨	58
23/12/97	308	<0.01	<0.06	<0.19	<0.04	<0.09	5.46	122.0	475	7.07	▨	7300	22
07/01/98	321	<0.01	<0.06	<0.19	<0.04	<0.09	4.58	109.1	375	7.07	▨	▨	-13
21/01/98	335	0.02	0.15	<0.19	<0.04	0.14	3.81	93.3	350	6.92	▨	6550	41
04/02/98	349	0.02	0.13	<0.19	<0.04	0.13	4.35	104.4	300	7.04	▨	▨	-15
18/02/98	363	0.01	0.09	<0.19	<0.04	<0.09	<0.13	91.8	275	7.18	▨	▨	38
04/03/98	377	<0.01	<0.06	<0.19	<0.04	<0.09	4.14	86.4	250	7.39	▨	▨	-26
18/03/98	391	<0.01	<0.06	<0.19	0.04	<0.09	3.32	▨	▨	6.88	▨	▨	-68
01/04/98	405	<0.03	0.076	<0.38	0.09	<0.18	1.40	102.4	188	7.54	▨	3600	-50
15/04/98	419	<0.01	<0.06	<0.19	<0.04	<0.09	3.26	92.8	175	7.14	▨	▨	69
29/04/98	433	<0.01	<0.06	<0.19	<0.04	<0.09	1.63	115.6	150	6.92	▨	▨	-103
13/05/98	447	0.01	0.07	<0.13	0.07	0.07	1.6163	106.5	138	6.90	▨	▨	-137
27/05/98	461	<0.01	<0.04	<0.13	<0.04	0.04	2.2213	76.8	125	6.89	▨	▨	-126
10/06/98	475	<0.01	0.06	<0.13	<0.04	0.05	2.4713	▨	25	6.91	▨	▨	-157
24/06/98	489	<0.01	<0.04	<0.13	<0.04	0.03	1.2138	100.8	125	7.55	▨	3100	-174
08/07/98	503	<0.01	<0.04	<0.13	<0.04	0.03	0.70	▨	138	7.36	▨	▨	-204
22/07/98	517	<0.01	<0.04	<0.13	<0.04	0.02	1.79	▨	113	6.80	▨	3500	-140
13/08/98	539	<0.01	<0.04	<0.13	0.73	<0.02	0.19	106.2	50	6.79	▨	▨	-166
26/8/98	552	<0.01	<0.04	<0.13	0.07	0.16	1.69	▨	88	6.79	▨	▨	-161
9/9/98	566	<0.01	<0.04	<0.13	0.07	0.07	1.57	▨	63	6.77	▨	▨	-187
7/10/98	594	<0.01	<0.04	<0.13	<0.04	0.04	1.41	112.9	50	6.80	▨	2950	-180
23/10/98	610	<0.01	0.05	<0.13	<0.04	0.63	1.35	▨	50	6.80	▨	▨	-90
6/11/98	624	<0.01	0.04	<0.13	<0.04	0.06	1.28	▨	125	6.65	▨	▨	-97
18/11/98	636	<0.01	0.26	<0.13	<0.04	0.08	1.40	102	88	6.68	▨	▨	-59
02/12/98	650	0.01	0.07	<0.13	<0.04	0.08	1.35	▨	75	6.47	▨	2450	-49
21/12/98	669	<0.01	<0.04	<0.13	<0.04	0.06	1.15	120.6	75	6.65	▨	▨	22

Maximum	0.02	0.31	1.23	0.83	0.63	126.53	226.9	1400	7.55	3640	14590	69
Minimum	0.01	0.02	0.02	0.03	0.02	0.19	76.8	25	6.30	3640	2450	-204

▨ Not analysed

Table A2.9.1 Initial Analysis of Pitsea Waste (results 22/7/99)

Column	Wet	Water Content	Dry weight	Total metals present (mg)					
	Weight (g)	(% wet weight)	present (g)	Cd	Cr	Pb	Zn	Ni	Fe
13	2251.0	59.8	904.9	2.71	147.50	589.09	412.64	40.72	17668.21
14	2250.3	59.8	904.6	2.71	147.45	588.91	412.51	40.71	17662.72
15	2249.3	59.8	904.2	2.71	147.39	588.65	412.32	40.69	17654.87
16	2249.9	59.8	904.5	2.71	147.43	588.80	412.43	40.70	17659.58
17	2248.6	59.8	903.9	2.71	147.34	588.46	412.20	40.68	17649.37
18	2117.6	59.8	851.3	2.55	138.76	554.18	388.18	38.31	16621.15

Column	Wet	Water Content	Dry weight	Total metals present (mg)					
	Weight (g)	(% wet weight)	present (g)	Cd	Cr	Pb	Zn	Ni	Fe
7	2251.3	62.76	838.4	4.19	115.70	227.20	1670.06	31.02	22971.72
8	2250.1	62.76	837.9	4.19	115.64	227.08	1669.17	31.00	22959.48
9	2250.9	62.76	838.2	4.19	115.68	227.16	1669.76	31.01	22967.64
10	2250.0	62.76	837.9	4.19	115.63	227.07	1669.10	31.00	22958.46
11	2251.3	62.76	838.4	4.19	115.70	227.20	1670.06	31.02	22971.72
12	2250.0	62.76	837.9	4.19	115.63	227.07	1669.10	31.00	22958.46

Table A2.9.2 Final Destructive Analysis of Pitsea Waste Column Fractions

Keg 2, Hole 3, alkaline waste

Sample		mg/kg dry weight						Dry weight	Water Content	Total metals present (mg)					
Column	Fraction	Cd	Cr	Pb	Zn	Ni	Fe	present (g)	(% wet weight)	Cd	Cr	Pb	Zn	Ni	Fe
7	Top	**3**	**201**	**428**	**2957**	**41**	18509	189.6	66.27	0.6	38	81	561	8	3509
	Middle	**3**	**135**	**553**	**2968**	**33**	17663	271.0	59.96	0.8	37	150	804	9	4787
	Bottom	**3**	**124**	**409**	**3314**	**28**	17611	315.1	53.94	0.9	39	129	1044	9	5549
	Total							**775.7**		**2.3**	**114**	**360**	**2409**	**26**	**13845**
8	Top	**4**	**154**	**445**	**3304**	**40**	17470	295.8	56.28	1.2	46	132	977	12	5168
	Middle	**3**	**130**	**385**	**2902**	**32**	17527	237.1	58.03	0.7	31	91	688	8	4156
	Bottom	**3**	**134**	**372**	**2910**	**36**	17133	241.0	56.67	0.7	32	90	701	9	4129
	Total							**773.9**		**2.6**	**109**	**313**	**2367**	**28**	**13452**
9	Top	**3**	**170**	**406**	**3648**	**39**	18136	243.4	63.89	0.7	41	99	888	9	4414
	Middle	**4**	**170**	**428**	**3142**	**44**	18762	270.6	59.30	1.1	46	116	850	12	5077
	Bottom	**3**	**155**	**413**	**2985**	**35**	18458	266.0	55.03	0.8	41	110	794	9	4910
	Total							**780.0**		**2.6**	**129**	**324**	**2532**	**31**	**14401**
10	Top	**4**	**166**	**368**	**3311**	**39**	18440	312.0	63.55	1.2	52	115	1033	12	5753
	Middle	**6**	**150**	**409**	**3301**	**37**	17816	219.3	58.72	1.3	33	90	724	8	3907
	Bottom	**3**	**131**	**392**	**3102**	**33**	17235	222.1	54.52	0.7	29	87	689	7	3828
	Total							**753.4**		**3.2**	**114**	**292**	**2446**	**28**	**13488**
11	Top	**3**	**175**	**375**	**2953**	**43**	16620	274.8	64.97	0.8	48	103	811	12	4567
	Middle	**3**	**138**	**385**	**3215**	**31**	17681	253.6	57.79	0.8	35	98	815	8	4484
	Bottom	**4**	**131**	**339**	**3276**	**35**	17846	255.4	53.98	1.0	33	87	837	9	4558
	Total							**783.8**		**2.6**	**117**	**287**	**2463**	**29**	**13609**
12	Top	**4**	**237**	**382**	**3047**	**39**	19199	283.0	62.49	1.1	67	108	862	11	5433
	Middle	**3**	**140**	**375**	**3232**	**33**	18096	255.0	53.84	0.8	36	96	824	8	4615
	Bottom	**6**	**194**	**385**	**3298**	**38**	16729	252.5	51.14	1.5	49	97	833	10	4224
	Total							**790.5**		**3.4**	**152**	**301**	**2519**	**29**	**14272**

Table A2.9.3 Final Destructive Analysis of Pitsea Waste Column Fractions

Keg 1, Hole 1, Acid Waste

Sample		mg/kg dry weight						Dry weight	Water Content	Total metals present (mg)					
Column	Fraction	Cd	Cr	Pb	Zn	Ni	Fe	present (g)	(% wet weight)	Cd	Cr	Pb	Zn	Ni	Fe
13	Top	3	217	487	741	72	11593	302.3	55.05	0.9	66	147	224	22	3505
	Middle	6	150	637	763	46	13789	252.2	50.06	1.5	38	161	192	12	3478
	Bottom	8	101	545	557	101	17660	288.5	53.85	2.3	29	157	161	29	5095
	Total							**843.0**		**4.7**	**133**	**465**	**577**	**63**	**12077**
14	Top	3	171	676	665	51	14232	280.4	49.98	0.8	48	190	186	14	3991
	Middle	5	186	639	783	43	17223	247.3	51.90	1.2	46	158	194	11	4259
	Bottom	8	246	11651	392	46	18229	271.4	52.62	2.2	67	3162	106	12	4947
	Total							**799.1**		**4.2**	**161**	**3510**	**486**	**37**	**13197**
15	Top	3	184	1737	849	57	14292	288.2	61.19	0.9	53	501	245	16	4119
	Middle	4	102	713	832	15	8702	250.8	53.16	1.0	26	179	209	4	2182
	Bottom	3	154	653	799	32	6000	256.9	51.30	0.8	40	168	205	8	1541
	Total							**795.9**		**2.6**	**118**	**847**	**659**	**28**	**7843**
16	Top	4	237	674	766	83	19500	292.0	33.44	1.2	69	197	224	24	5694
	Middle	4	113	754	620	10	10235	226.5	39.28	0.9	26	171	140	2	2318
	Bottom	5	147	539	674	18	9964	261.8	37.64	1.3	38	141	176	5	2609
	Total							**780.3**		**3.4**	**133**	**509**	**541**	**31**	**10621**
17	Top	3	140	551	110	45	14880	291.0	56.92	0.9	41	160	32	13	4330
	Middle	4	222	715	718	45	15012	331.8	52.45	1.3	74	237	238	15	4981
	Bottom	4	139	543	672	28	11928	196.1	64.18	0.8	27	106	132	5	2339
	Total							**818.9**		**3.0**	**142**	**504**	**402**	**34**	**11650**
18	Top	214	195	557	780	254	16343	190.8	65.55	40.8	37	106	149	48	3118
	Middle	15	148	663	1379	64	18675	335.6	51.11	5.0	50	223	463	21	6267
	Bottom	4	208	2560	628	91	11160	306.7	48.26	1.2	64	785	193	28	3423
	Total							**833.1**		**47.1**	**151**	**1114**	**804**	**98**	**12808**

Table A2.9.4 Summary of results - metal analysis of solid waste before and after column treatment

Waste	Column		Total metals present (mg)											
			Cd	% Loss	Cr	% Loss	Pb	% Loss	Zn	% Loss	Ni	% Loss	Fe	% Loss
Pitsea W009	7	Initial	4		116		227		1670		31		22972	
		Final	**2**	44	**114**	2	**360**	-58	**2409**	-44	**26**	18	**13845**	40
	8	Initial	4		116		227		1669		31		22959	
		Final	**3**	38	**109**	6	**313**	-38	**2367**	-42	**28**	9	**13452**	41
	9	Initial	4		116		227		1670		31		22968	
		Final	**3**	38	**129**	-11	**324**	-43	**2532**	-52	**31**	1	**14401**	37
	10	Initial	4		116		227		1669		31		22958	
		Final	**3**	23	**114**	2	**292**	-28	**2446**	-47	**28**	11	**13488**	41
	11	Initial	4		116		227		1670		31		22972	
		Final	**3**	38	**117**	-1	**287**	-26	**2463**	-48	**29**	8	**13609**	41
	12	Initial	4		116		227		1669		31		22958	
		Final	**3**	19	**152**	-31	**301**	-33	**2519**	-51	**29**	6	**14272**	38
Pitsea W001	13	Initial	3		147		589		413		41		17668	
		Final	**5**	-74	**133**	10	**465**	21	**577**	-40	**63**	-53	**12077**	32
	14	Initial	3		147		589		413		41		17663	
		Final	**4**	-57	**161**	-9	**3510**	-496	**486**	-18	**37**	8	**13197**	25
	15	Initial	3		147		589		412		41		17655	
		Final	**3**	3	**118**	20	**847**	-44	**659**	-60	**28**	30	**7843**	56
	16	Initial	3		147		589		412		41		17660	
		Final	**3**	-25	**133**	10	**509**	14	**541**	-31	**31**	23	**10621**	40
	17	Initial	3		147		588		412		41		17649	
		Final	**3**	-10	**142**	4	**504**	14	**402**	2	**34**	18	**11650**	34
	18	Initial	3		139		554		388		38		16621	
		Final	**47**	-1744	**151**	-9	**1114**	-101	**804**	-107	**98**	-155	**12808**	23

Table A2.10.1 pH Analysis of Batch Experiment Leachate

Batch Set	Metal	WMP Guideline Multiple	Rep.	Day														
				0*	1	7	14	15	19	21	22	23	28	29	30	46	55	71
1	Cocktail	x100	A	7.23	5.18	6.06		6.37			6.55			6.56				6.91
			B	7.23	6.46	5.94		6.21			6.42			6.49				7.09
			C	7.23	6.53	6.16		6.18			6.26			6.30				7.01
2	Cocktail	x1	A	7.85	7.43	7.28	7.20			7.28			7.22				8.89	
			B	7.85	7.47	7.24	7.22			7.18			7.13				8.83	
			C	7.85	7.22	7.42	7.62			7.74			7.79				8.88	
2	Cocktail	x0.1	A	7.83	7.43	7.51	7.74			7.91			8.02				8.94	
			B	7.83	7.41	7.27	7.22			7.22			7.20				8.97	
			C	7.83	7.34	7.32	7.25			7.24			7.23				8.75	
2	Cadmium	x10	A	7.89	7.48	7.49	7.57			7.80			7.82				8.95	
			B	7.89	7.39	7.37	7.36			7.35			7.55				8.95	
			C	7.89	7.31	7.52	7.63			7.76			7.85				8.94	
2	Cadmium	x1	A	8.73	7.33	7.35	7.23			7.28			░				8.94	
			B	8.73	7.51	7.41	7.64			░			7.79				8.96	
			C	8.73	7.31	7.32	7.30			7.27			7.28				8.94	
3	Zinc	x1	A	8.48	7.81	7.95			7.73			7.83			7.68	8.49		
			B	8.48	7.83	7.94			7.69			7.79			7.64	8.17		
			C	8.48	7.83	7.95			7.74			7.83			7.74	8.42		
3	Zinc	x0.1	A	░	7.85	7.99			7.78			7.83			7.68	8.43		
			B	░	7.88	8.00			7.77			7.90			7.68	8.43		
			C	░	7.79	7.96			7.74			7.84			7.67	8.39		
3	Chromium	x1	A	8.81	7.81	7.93			7.92			7.98			7.90	8.80		
			B	8.81	7.83	7.95			7.75			7.79			7.65	8.63		
			C	8.81	7.85	7.99			7.95			8.00			7.90	8.80		
3	Chromium	x0.1	A	8.72	7.83	7.95			7.95			8.04			7.96	8.77		
			B	8.72	7.83	7.99			7.93			8.03			7.97	8.22		
			C	8.72	7.85	7.95			7.80			7.89			7.78	8.66		
1	Control	-	A	7.93	7.60	7.42		7.45			7.47			7.41				7.94
			B	7.93	7.62	7.46		7.50			7.50			7.43				8.19
			C	7.93	7.56	7.48		7.49			7.51			7.46				7.83
2	Control	-	A	8.83	7.32	7.26	7.25			7.23			7.26				8.94	
			B	8.83	7.25	7.31	7.22			░			░				8.96	
			C	8.83	7.25	7.40	7.24			7.25			7.25				8.93	
3	Control	-	A	8.79	7.89	7.99			7.81			7.88			7.75	8.12		
			B	8.79	7.84	8.01			7.98			8.16			8.03	8.15		
			C	8.79	7.85	8.00			7.90			8.04			7.97	8.38		

*Day 0 is leachate and metals before addition to the waste.

░ Limited sample volume

Table A2.10.2 Eh Analysis of Batch Experiment Leachate

Batch Set	Metal	WMP Guideline Multiple	Rep.	Day														
				0*	1	7	14	15	19	21	22	23	28	29	30	46	55	71
1	Cocktail	x100	A	178	67	33		-51			36			14				125
			B	178	-22	25		-28			31			51				121
			C	178	-10	20		-4			22			25				125
2	Cocktail	x1	A	107	78	-120	-196			-142			-42				92	
			B	107	68	-131	-159			-136			189				78	
			C	107	81	-12	38			3			52				76	
2	Cocktail	x0.1	A	110	9	7	65			93			164				80	
			B	110	69	-36	-144			-10			77				177	
			C	110	38	-135	-145			-123			97				90	
2	Cadmium	x10	A	104	76	-104	48			81			117				107	
			B	104	52	-86	42			77			115				78	
			C	104	33	36	56			95			116				89	
2	Cadmium	x1	A	87	25	-71	-18			60			░				97	
			B	87	52	-125	78			░			156				91	
			C	87	48	-124	-39			51			125				88	
3	Zinc	x1	A	152	77	21			95			117			153	97		
			B	152	73	11			-47			-2			79	97		
			C	152	88	-79			37			86			129	94		
3	Zinc	x0.1	A	░	76	-115			48			55			161	107		
			B	░	47	-109			24			103			169	107		
			C	░	53	-83			24			89			155	114		
3	Chromium	x1	A	150	-82	-158			66			96			140	78		
			B	150	-40	-97			-30			15			88	79		
			C	150	32	-55			42			70			134	76		
3	Chromium	x0.1	A	148	-28	-161			62			80			120	84		
			B	148	-10	-30			77			82			141	88		
			C	148	-33	-108			56			74			141	85		
1	Control	-	A	118	97	91		-51			8			-177				103
			B	118	66	50		-28			-18			-179				89
			C	118	38	-8		-4			-188			-203				107
2	Control	-	A	90	94	73	110			-59			93				72	
			B	90	65	-21	-15			░			░				74	
			C	90	71	64	-7			40			68				109	
3	Control	-	A	150	57	88			62			104			223	149		
			B	150	9	9			0			86			201	135		
			C	150	94	40			62			98			191	128		

*Day 0 is leachate and metals before addition to the waste.

All results in mV

░ Limited sample volume

Table A2.10.3 Chloride Analysis of Batch Experiment Leachate

Batch Set	Metal	WMP Guideline Multiple	Rep.	Day														
				0*	1	7	14	15	19	21	22	23	28	29	30	46	55	71
1	Cocktail	x100	A	7500	7250	7125		7275			7150			7250				5200
			B	7500	7350	7150		7275			7250			7250				5300
			C	7500	7250	7200		7225			7200			7125				5150
2	Cocktail	x1	A	4000	3900	4000	4000			3800			3850				2500	
			B	4000	3875	4000	3950			3950			3950				2700	
			C	4000	3925	3950	4050			3850			3800				2550	
2	Cocktail	x0.1	A	3925	3900	4050	3950			3800			4000				2575	
			B	3925	3900	4050	4100			3850			3800				2700	
			C	3925	3900	3950	3850			3750			3800				2400	
2	Cadmium	x10	A	4050	3950	3900	3900			4050			3850				2750	
			B	4050	4800	3900	4000			3950			4100				2900	
			C	4050	3000	4050	4000			4050			3950				2375	
2	Cadmium	x1	A	4250	3900	3850	4050			4000			░				2800	
			B	4250	4050	3850	3950			░			3850				2775	
			C	4250	4050	3950	3950			3850			3950				2775	
3	Zinc	x1	A	4000	3800	4025			3900			3850			4000	2850		
			B	4000	3800	3925			4000			3800			4200	2650		
			C	4000	3750	4100			3800			3950			4100	2700		
3	Zinc	x0.1	A	░	3875	4000			3950			3950			4075	2650		
			B	░	3750	4025			4075			3950			4175	2650		
			C	░	3750	4150			3975			3850			4050	2700		
3	Chromium	x1	A	4100	3900	3950			4150			3900			4150	2800		
			B	4100	3900	4000			4150			4050			4125	2800		
			C	4100	3900	4100			4000			3900			3850	2800		
3	Chromium	x0.1	A	4050	3700	4000			3900			4000			4025	2800		
			B	4050	3800	3900			4000			3850			4075	2600		
			C	4050	3900	3900			3900			3950			4050	2650		
1	Control	-	A	3850	3850	3825		3825			3850			3800				2800
			B	3850	3700	4025		3750			4050			3750				2750
			C	3850	3700	3825		3900			3850			3900				2650
2	Control	-	A	4000	4000	3800	4200			3900			3800				2700	
			B	4000	4025	3900	4150			4550			░				3000	
			C	4000	4000	3900	4250			3900			3950				2750	
3	Control	-	A	4225	3650	4025			4150			3950			3950	2450		
			B	4225	3750	4025			4100			4000			3950	3050		
			C	4225	3775	3975			4000			4050			4150	2100		

*Day 0 is leachate and metals before addition to the waste.

All results in mg/l

░ Limited sample volume

Table A2.10.4 Ammoniacal-Nitrogen Analysis of Batch Experiment Leachate

Batch Set	Metal	WMP Guideline Multiple	Rep.	Day 0*	1	7	14	15	19	21	22	23	28	29	30	46	55	71
1	Cocktail	x100	A	908	1141	1251		1243			1251			1299				747
			B	908	1075	1211		1235			1253			1223				894
			C	908	1101	1230		1257			1271			1226				766
2	Cocktail	x1	A	779	1130	1243	1169			1148			1160				526	
			B	779	1107	1192	942			░			░				484	
			C	779	1062	1162	1181			1150			1132				588	
2	Cocktail	x0.1	A	851	1103	1195	1187			1112			1128				590	
			B	851	1066	1133	1124			1095			░				521	
			C	851	1040	1186	1185			1133			1144				350	
2	Cadmium	x10	A	736	1135	1175	897			1100			1117				595	
			B	736	1160	1180	1183			1146			1139				662	
			C	736	1190	1171	1222			░			1158				504	
2	Cadmium	x1	A	515	1122	1201	1184			1135			1249				681	
			B	515	1351	1228	1163			░			1136				642	
			C	515	1115	1182	1193			1111			1125				580	
3	Zinc	x1	A	854	1046	1066			1069			1091			1079	292		
			B	854	1011	1083			1083			1125			1105	235		
			C	854	1091	1093			1084			1111			1102	287		
3	Zinc	x0.1	A	░	1043	1098			1088			931			1095	282		
			B	░	1071	1085			1099			1074			1110	275		
			C	░	1085	1051			1093			1068			1050	270		
3	Chromium	x1	A	731	1041	1057			1101			1007			1074	618		
			B	731	1065	1092			1094			1150			1103	417		
			C	731	1027	1042			1067			717			1044	576		
3	Chromium	x0.1	A	851	775	1093			1089			░			1114	551		
			B	851	1062	1080			1107			1069			1052	254		
			C	851	1032	1085			1091			1113			1120	391		
1	Control	-	A	886	1174	1213		1216			1201			1214				232
			B	886	1192	1175		1211			1243			1195				197
			C	886	1182	1205		1217			1198			1184				161
2	Control	-	A	743	973	998	1196			1102			1128				654	
			B	743	1190	1428	1232			░			1074				704	
			C	743	1274	1202	1211			░			1175				568	
3	Control	-	A	571	1049	1077			1105			1082			1094	173		
			B	571	1094	1098			1102			1122			1131	210		
			C	571	1026	1117			1072			1095			1104	236		

*Day 0 is leachate and metals before addition to the waste.

All results in mgN/l

░ Limited sample volume

Table A2.10.5 Alkalinity Analysis of Batch Experiment Leachate

Batch Set	Metal	WMP Guideline Multiple	Rep.	Day														
				0*	1	7	14	15	19	21	22	23	28	29	30	46	55	71
1	Cocktail	x100	A	░	░	░		░			░			400				55
			B	░	375	░		░			░			150				70
			C	░	<50	░		░			░			501				60
2	Cocktail	x1	A	779	1130	1243	1169			1148			1160				526	
			B	779	1107	1192	942			░			░				484	
			C	779	1062	1162	1181			1150			1132				588	
2	Cocktail	x0.1	A	851	1103	1195	1187			1112			1128				590	
			B	851	1066	1133	1124			1095			░				521	
			C	851	1040	1186	1185			1133			1144				350	
2	Cadmium	x10	A	736	1135	1175	897			1100			1117				595	
			B	736	1160	1180	1183			1146			1139				662	
			C	736	1190	1171	1222			░			1158				504	
2	Cadmium	x1	A	515	1122	1201	1184			1135			1249				681	
			B	515	1351	1228	1163			░			1136				642	
			C	515	1115	1182	1193			1111			1125				580	
3	Zinc	x1	A	854	1046	1066			1069			1091			1079	292		
			B	854	1011	1083			1083			1125			1105	235		
			C	854	1091	1093			1084			1111			1102	287		
3	Zinc	x0.1	A	░	1043	1098			1088			931			1095	282		
			B	░	1071	1085			1099			1074			1110	275		
			C	░	1085	1051			1093			1068			1050	270		
3	Chromium	x1	A	731	1041	1057			1101			1007			1074	618		
			B	731	1065	1092			1094			1150			1103	417		
			C	731	1027	1042			1067			717			1044	576		
3	Chromium	x0.1	A	851	775	1093			1089			░			1114	551		
			B	851	1062	1080			1107			1069			1052	254		
			C	851	1032	1085			1091			1113			1120	391		
1	Control	-	A	2252	3804	░		░			░			2202				167
			B	2252	3904	░		░			░			4004				233
			C	2252	3904	░		░			░			4104				133
2	Control	-	A	1922	░	4137	4144			4144			4236				2052	
			B	1922	4137	4232	4236			░			░				2252	
			C	1922	3756	4184	░			░			░				1701	
3	Control	-	A	1223	3481	3576			4046			3607			3940	192		
			B	1223	3670	4140			3950			3854			3748	96		
			C	1223	3764	3585			3780			3952			3844	288		

*Day 0 is leachate and metals before addition to the waste.

All results in mg/l as $CaCO_3$

░ Limited sample volume

Table A2.10.6 Cadmium Analysis of Batch Experiment Leachate

Batch Set	Metal	WMP Guideline Multiple	Rep.	Day														
				0*	1	7	14	15	19	21	22	23	28	29	30	46	55	71
1	Cocktail	x100	A	130.88	70.01	15.29		5.72			2.49			1.30				0.15
			B	130.88	72.39	17.46		6.17			3.12			1.47				0.16
			C	130.88	78.55	13.25		5.17			2.74			1.34				0.11
2	Cocktail	x1	A	0.53	0.14	<0.01	0.02			<0.01			<0.01				0.03	
			B	0.53	0.13	<0.01	<0.01			<0.01			<0.01				0.02	
			C	0.53	0.13	<0.01	<0.01			<0.01			<0.01				0.03	
2	Cocktail	x0.1	A	<0.01	0.11	<0.01	<0.01			<0.01			<0.01				0.01	
			B	<0.01	0.13	<0.01	0.15			<0.01			<0.01				<0.01	
			C	<0.01	0.11	<0.01	0.04			<0.01			<0.01				<0.01	
2	Cadmium	x10	A	0.93	0.40	<0.01	0.12			0.13			0.06				0.16	
			B	0.93	0.43	0.08	0.17			0.17			0.10				0.24	
			C	0.93	0.20	<0.01	0.05			0.04			<0.01				0.15	
2	Cadmium	x1	A	<0.01	0.13	<0.01	0.01			0.01			░				0.02	
			B	<0.01	0.20	<0.01	0.01			░			<0.01				0.03	
			C	<0.01	0.19	<0.01	0.12			<0.01			<0.01				0.02	
3	Zinc	x1	A	<0.01	<0.01	<0.01			<0.01			<0.01			<0.01	<0.01		
			B	<0.01	<0.01	<0.01			<0.01			<0.01			<0.01	<0.01		
			C	<0.01	<0.01	<0.01			<0.01			<0.01			<0.01	<0.01		
3	Zinc	x0.1	A	░	<0.01	<0.01			<0.01			<0.01			<0.01	0.01		
			B	░	<0.01	<0.01			<0.01			<0.01			<0.01	<0.01		
			C	░	<0.01	<0.01			<0.01			<0.01			<0.01	<0.01		
3	Chromium	x1	A	<0.01	<0.01	<0.01			<0.01			<0.01			<0.01	0.03		
			B	<0.01	<0.01	<0.01			<0.01			<0.01			<0.01	0.02		
			C	<0.01	<0.01	<0.01			<0.01			<0.01			<0.01	0.01		
3	Chromium	x0.1	A	<0.01	<0.01	<0.01			<0.01			<0.01			<0.01	<0.01		
			B	<0.01	<0.01	<0.01			<0.01			<0.01			<0.01	<0.01		
			C	<0.01	<0.01	<0.01			<0.01			<0.01			<0.01	0.07		
1	Control	-	A	0.01	0.01	0.01		<0.01			0.01			<0.01				0.01
			B	0.01	0.01	<0.01		<0.01			<0.01			<0.01				0.01
			C	0.01	0.01	<0.01		0.01			<0.01			<0.01				<0.01
2	Control	-	A	<0.01	0.18	<0.01	0.20			0.30			<0.01				0.02	
			B	<0.01	0.11	<0.01	0.03			░			░				0.01	
			C	<0.01	0.15	<0.01	0.01			0.04			<0.01				<0.01	
3	Control	-	A	<0.01	0.02	0.01			<0.01			<0.01			<0.01	0.08		
			B	<0.01	<0.01	<0.01			<0.01			<0.01			<0.01	0.04		
			C	<0.01	<0.01	<0.01			<0.01			<0.01			<0.01	0.01		

*Day 0 is leachate and metals before addition to the waste.

All results in mg/l

░ Limited sample volume

Table A2.10.7 Chromium Analysis of Batch Experiment Leachate

Batch Set	Metal	WMP Guideline Multiple	Rep.	Day														
				0*	1	7	14	15	19	21	22	23	28	29	30	46	55	71
1	Cocktail	x100	A	1226.90	46.51	0.44		0.13			0.82			0.20				0.15
			B	1226.90	49.35	0.44		0.46			0.18			0.09				0.13
			C	1226.90	76.35	0.63		0.16			0.16			0.05				0.29
2	Cocktail	x1	A	11.55	0.78	0.12	0.33			0.34			0.33				0.16	
			B	11.55	0.68	0.05	0.27			0.30			0.31				0.14	
			C	11.55	0.77	0.12	0.35			0.32			0.28				0.16	
2	Cocktail	x0.1	A	0.97	0.56	<0.04	0.10			0.09			0.08				0.07	
			B	0.97	0.56	<0.04	0.37			0.13			0.12				0.08	
			C	0.97	0.56	<0.04	0.16			0.12			0.11				0.06	
2	Cadmium	x10	A	<0.08	0.54	<0.04	0.12			0.07			0.05				0.06	
			B	<0.08	0.54	<0.04	0.08			0.09			<0.08				0.06	
			C	<0.08	0.54	<0.04	0.07			0.08			0.05				0.06	
2	Cadmium	x1	A	<0.08	0.51	<0.04	0.10			0.10			░				0.06	
			B	<0.08	0.52	<0.04	0.08			░			0.06				0.06	
			C	<0.08	0.64	<0.04	0.27			0.08			0.06				0.06	
3	Zinc	x1	A	0.11	0.08	0.07			0.08			0.04			0.13	0.05		
			B	0.11	0.09	0.06			0.08			0.05			0.13	0.04		
			C	0.11	0.08	0.07			0.16			0.05			0.22	<0.04		
3	Zinc	x0.1	A	░	0.08	0.06			0.08			0.04			0.14	0.07		
			B	░	0.07	0.07			0.08			0.05			0.13	0.06		
			C	░	0.08	0.07			0.07			0.05			0.13	0.05		
3	Chromium	x1	A	5.81	0.75	0.81			0.61			0.56			0.85	0.37		
			B	5.81	0.65	0.74			0.55			0.60			0.68	0.37		
			C	5.81	0.62	0.72			0.10			0.52			0.71	0.39		
3	Chromium	x0.1	A	1.06	0.19	0.18			0.20			0.13			0.25	0.08		
			B	1.06	0.19	0.21			0.20			0.16			0.44	0.09		
			C	1.06	0.20	0.22			0.60			0.17			0.78	0.33		
1	Control	-	A	0.05	0.08	0.08		<0.04			0.07			0.04				0.11
			B	0.05	0.06	0.05		<0.04			0.07			0.04				0.10
			C	0.05	0.07	0.05		0.08			0.08			0.04				0.09
2	Control	-	A	<0.08	0.64	<0.04	0.38			2.28			0.05				0.08	
			B	<0.08	0.53	<0.04	0.11			░			░				0.06	
			C	<0.08	0.62	<0.04	0.09			0.20			0.09				0.06	
3	Control	-	A	0.12	0.10	0.27			0.08			0.06			0.33	0.26		
			B	0.12	0.08	0.07			0.07			0.04			0.13	0.10		
			C	0.12	0.09	0.07			0.08			0.04			0.12	0.06		

*Day 0 is leachate and metals before addition to the waste

All results in mg/l

░ Limited sample volume

Table A2.10.8 Zinc Analysis of Batch Experiment Leachate

Batch Set	Metal	WMP Guideline Multiple	Rep.	Day														
				0*	1	7	14	15	19	21	22	23	28	29	30	46	55	71
1	Cocktail	x100	A	1187.80	572.75	224.88		94.16			55.66			43.06				4.79
			B	1187.80	593.38	246.13		112.80			78.81			68.36				4.19
			C	1187.80	643.63	215.63		3116.99			98.19			84.59				4.91
2	Cocktail	x1	A	11.26	0.83	0.26	0.24			░			<0.04				0.05	
			B	11.26	0.98	0.35	0.32			0.11			0.08				0.05	
			C	11.26	0.66	0.51	0.35			0.51			0.29				0.11	
2	Cocktail	x0.1	A	0.92	0.33	<0.04	0.09			<0.04			<0.04				<0.04	
			B	0.92	0.88	0.42	0.46			<0.04			<0.04				<0.04	
			C	0.92	0.38	0.31	0.20			0.09			<0.04				<0.04	
2	Cadmium	x10	A	<0.08	0.33	0.08	0.32			<0.08			<0.04				<0.04	
			B	<0.08	0.81	<0.04	0.23			<0.04			<0.08				<0.04	
			C	<0.08	0.38	0.97	0.34			0.13			<0.04				<0.04	
2	Cadmium	x1	A	<0.08	0.38	0.13	0.32			0.04			░				<0.04	
			B	<0.08	1.42	0.20	0.24			░			<0.04				<0.04	
			C	<0.08	0.33	0.16	0.66			0.25			0.22				<0.04	
3	Zinc	x1	A	5.32	1.84	1.01			0.30			0.66			0.26	0.53		
			B	5.32	1.48	0.83			0.33			0.46			0.21	0.37		
			C	5.32	1.24	1.13			<0.04			0.37			<0.04	0.22		
3	Zinc	x0.1	A	░	0.11	<0.04			<0.04			<0.04			<0.04	0.10		
			B	░	<0.04	0.09			0.07			0.23			<0.04	0.12		
			C	░	0.16	0.16			0.29			<0.04			<0.04	0.13		
3	Chromium	x1	A	<0.04	0.28	0.09			0.12			<0.04			<0.04	0.13		
			B	<0.04	<0.04	<0.04			0.27			0.08			<0.04	0.15		
			C	<0.04	0.11	0.24			0.05			0.08			<0.04	0.10		
3	Chromium	x0.1	A	<0.04	0.13	<0.04			0.06			<0.04			<0.04	0.15		
			B	<0.04	<0.04	<0.04			0.48			0.04			<0.04	0.10		
			C	<0.04	0.12	0.38			<0.04			0.06			<0.04	0.34		
1	Control	-	A	<0.04	0.19	0.27		0.25			0.30			0.10				0.18
			B	<0.04	0.50	0.41		0.22			0.36			0.38				0.27
			C	<0.04	0.48	0.29		0.22			0.49			0.10				0.13
2	Control	-	A	<0.08	0.41	0.19	1.30			1.98			<0.04				0.16	
			B	<0.08	0.36	0.36	0.56			░			░				<0.04	
			C	<0.08	2.09	0.41	0.15			0.41			<0.04				<0.04	
3	Control	-	A	<0.04	<0.04	<0.04			<0.04			<0.04			<0.04	0.13		
			B	<0.04	<0.04	0.27			<0.04			<0.04			<0.04	0.08		
			C	<0.04	0.23	0.50			0.95			0.24			0.15	0.07		

*Day 0 is leachate and metals before addition to the waste.

All results in mg/l

░ Limited sample volume

Table A2.10.9 Iron Analysis of Batch Experiment Leachate

Batch Set	Metal	WMP Guideline Multiple	Rep.	Day														
				0*	1	7	14	15	19	21	22	23	28	29	30	46	55	71
1	Cocktail	x100	A	0.04	13.76	10.41		6.27			1.41			0.45				0.02
			B	0.04	13.80	12.53		3.98			2.30			0.34				<0.1
			C	0.04	12.31	30.03		6.86			6.56			4.17				0.06
2	Cocktail	x1	A	<0.02	1.65	3.15	2.65			2.66			2.79				1.59	
			B	<0.02	1.47	2.73	2.62			3.05			3.65				1.24	
			C	<0.02	1.27	2.58	3.32			2.76			3.10				1.49	
2	Cocktail	x0.1	A	<0.02	1.46	3.73	3.96			3.95			3.50				1.68	
			B	<0.02	1.36	2.51	2.69			2.78			3.40				1.46	
			C	<0.02	1.87	3.02	3.20			4.65			4.56				1.58	
2	Cadmium	x10	A	<0.02	1.52	3.28	3.74			4.45			3.34				1.67	
			B	<0.02	2.25	3.37	3.81			4.28			4.85				1.93	
			C	<0.02	2.05	3.33	3.58			3.00			2.74				1.67	
2	Cadmium	x1	A	<0.02	2.25	3.10	3.40			3.98			░				2.50	
			B	<0.02	2.38	3.44	3.44			░			4.20				1.70	
			C	<0.02	1.33	2.15	2.44			2.79			2.85				2.35	
3	Zinc	x1	A	<0.01	0.91	2.22			1.93			2.63			2.95	0.84		
			B	<0.01	0.82	2.00			2.30			2.65			2.25	1.94		
			C	<0.01	1.68	2.63			2.95			3.15			3.30	1.10		
3	Zinc	x0.1	A	░	1.49	1.79			1.88			2.25			2.70	1.62		
			B	░	1.62	2.16			1.80			1.95			2.35	1.53		
			C	░	1.67	2.06			2.32			2.46			3.23	1.35		
3	Chromium	x1	A	<0.01	4.30	3.28			2.10			2.99			2.93	1.55		
			B	<0.01	2.12	2.50			2.19			2.18			2.43	2.73		
			C	<0.01	1.61	2.36			1.82			2.62			3.00	1.88		
3	Chromium	x0.1	A	<0.01	3.79	3.14			2.37			3.54			3.60	1.67		
			B	<0.01	2.41	2.12			2.16			2.86			3.41	2.29		
			C	<0.01	1.69	2.19			2.38			2.31			3.14	2.36		
1	Control	-	A	<0.01	2.01	1.73		3.22			2.87			2.56				1.40
			B	<0.01	2.45	2.96		4.15			3.21			2.77				1.39
			C	<0.01	2.24	2.07		2.62			5.07			3.30				1.12
2	Control	-	A	<0.02	1.17	2.73	2.93			3.15			2.89				1.96	
			B	<0.02	2.24	2.84	2.77			░			░				2.21	
			C	<0.02	2.00	3.02	2.79			4.09			3.20				2.49	
3	Control	-	A	<0.01	1.66	2.23			2.36			3.52			2.84	1.17		
			B	<0.01	2.39	2.53			1.62			1.84			2.16	1.35		
			C	<0.01	2.00	1.95			1.45			2.14			2.25	1.24		

*Day 0 is leachate and metals before addition to the waste.

All results in mg/l

░ Limited sample volume

Table A2.10.10 Total Sulphur Analysis of Batch Experiment Leachate

Batch Set	Metal	WMP Guideline Multiple	Rep.	Day														
				0*	1	7	14	15	19	21	22	23	28	29	30	46	55	71
1	Cocktail	x100	A	6.61	4.16	6.11		9.59			8.95			5.47				3.74
			B	6.61	4.25	6.06		9.99			10.07			6.26				4.71
			C	6.61	3.55	5.94		9.54			9.83			5.70				3.94
2	Cocktail	x1	A	8.64	26.21	3.15	16.41			10.31			7.78				18.10	
			B	8.64	17.38	2.73	11.55			8.19			6.66				22.23	
			C	8.64	14.65	2.58	13.70			10.03			8.19				17.61	
2	Cocktail	x0.1	A	8.82	17.49	3.73	17.16			13.69			11.81				19.48	
			B	8.82	18.31	2.51	17.01			11.76			9.53				19.25	
			C	8.82	21.03	3.02	12.63			8.93			8.53				23.39	
2	Cadmium	x10	A	8.79	19.68	3.28	18.79			7.26			9.48				18.80	
			B	8.79	22.29	3.37	17.58			12.18			5.33				20.24	
			C	8.79	19.95	3.33	16.24			11.35			9.23				21.30	
2	Cadmium	x1	A	9.09	17.25	3.10	18.44			12.81			░				20.66	
			B	9.09	19.24	3.44	16.30			░			9.78				20.29	
			C	9.09	16.33	2.15	19.26			12.04			9.13				17.08	
3	Zinc	x1	A	8.69	11.74	12.33			7.56			7.38			6.06	28.44		
			B	8.69	12.08	13.03			9.23			6.67			8.86	31.55		
			C	8.69	21.96	17.13			10.94			8.80			11.30	26.13		
3	Zinc	x0.1	A	░	15.51	14.30			9.37			8.12			8.45	27.46		
			B	░	16.15	15.20			9.33			8.74			9.29	30.10		
			C	░	15.13	14.71			8.03			9.13			8.95	30.11		
3	Chromium	x1	A	8.66	30.60	22.48			13.05			11.38			11.59	23.98		
			B	8.66	26.41	23.09			15.51			10.64			10.91	29.70		
			C	8.66	23.84	23.44			10.16			11.69			11.60	21.44		
3	Chromium	x0.1	A	8.66	26.50	19.29			12.66			10.63			11.30	26.13		
			B	8.66	21.49	19.23			11.02			11.39			13.55	25.58		
			C	8.66	18.44	17.46			13.01			9.76			11.08	25.60		
1	Control	-	A	6.74	13.53	9.35		9.38			7.98			7.58				22.68
			B	6.74	10.83	9.12		9.68			8.60			5.34				23.43
			C	6.74	10.41	8.98		9.55			10.39			6.57				22.74
2	Control	-	A	8.80	15.08	2.73	15.64			10.26			7.70				17.28	
			B	8.80	15.99	2.84	7.40			░			░				17.71	
			C	8.80	11.36	3.02	16.84			14.80			8.65				20.55	
3	Control	-	A	8.91	17.09	16.46			9.32			9.76			9.88	25.91		
			B	8.91	15.74	16.28			9.07			9.07			9.28	41.83		
			C	8.91	16.41	14.85			9.83			9.00			9.58	30.84		

*Day 0 is leachate and metals before addition to the waste

All results in mg/l

░ Limited sample volume

Table A2.10.11 Sulphate Analysis of Batch Experiment Leachate

Batch Set	Metal	WMP Guideline Multiple	Rep.	Day														
				0*	1	7	14	15	19	21	22	23	28	29	30	46	55	71
1	Cocktail	x100	A	░	░	19.88		19.00			22.63			11.39				6.42
			B	░	9.85	16.27		26.84			23.13			18.88				10.68
			C	░	7.39	50.69		10.75			16.22			12.14				7.37
2	Cocktail	x1	A	32.50	95.09	75.17	47.78			16.04			░				39.20	
			B	32.50	74.22	68.60	28.34			11.64			░				52.40	
			C	32.50	61.71	47.97	32.28			10.67			6.69				39.40	
2	Cocktail	x0.1	A	31.50	67.04	66.93	43.76			23.69			19.90				44.10	
			B	31.50	72.85	64.78	49.07			17.18			7.76				43.60	
			C	31.50	80.54	71.07	34.12			6.05			░				52.40	
2	Cadmium	x10	A	34.50	77.54	68.08	45.96			28.45			7.82				40.90	
			B	34.50	90.94	64.35	40.89			19.52			15.26				44.10	
			C	34.50	72.84	57.28	38.53			11.96			7.70				48.60	
2	Cadmium	x1	A	32.20	66.01	60.38	57.89			22.82			░				65.60	
			B	32.20	66.73	48.90	38.74			░			11.92				49.30	
			C	32.20	59.75	76.31	47.72			18.90			░				38.70	
3	Zinc	x1	A	37.63	57.50	28.20			24.79			19.54			░	65.93		
			B	37.63	55.35	33.25			16.68			17.24			░	68.56		
			C	37.63	106.81	40.96			27.89			10.84			░	79.19		
3	Zinc	x0.1	A	░	65.11	44.12			14.26			25.68			░	78.82		
			B	░	129.70	27.13			16.88			12.69			░	79.81		
			C	░	68.35	11.25			21.28			26.00			10.29	76.54		
3	Chromium	x1	A	33.82	178.73	126.61			23.79			28.96			░	60.76		
			B	33.82	124.59	104.44			18.04			13.20			░	72.66		
			C	33.82	103.81	85.35			22.19			18.11			0.87	44.68		
3	Chromium	x0.1	A	35.91	214.67	176.76			31.28			66.43			14.58	66.69		
			B	35.91	175.51	30.67			22.25			27.41			11.83	61.21		
			C	35.91	85.93	84.35			14.49			12.62			░	55.78		
1	Control	-	A	28.51	38.90	24.04		34.71			52.90			21.06				64.05
			B	28.51	36.51	71.95		130.67			34.80			18.59				62.57
			C	28.51	33.39	25.67		22.28			38.62			25.69				65.61
2	Control	-	A	35.50	64.61	59.65	36.67			16.66			░				69.80	
			B	35.50	59.80	47.77	35.27			░			░				57.00	
			C	35.50	68.31	73.99	42.37			░			8.15				60.20	
3	Control	-	A	34.35	123.83	74.37			26.52			102.47			8.60	65.40		
			B	34.35	183.51	88.62			27.12			22.43			11.91	123.91		
			C	34.35	63.76	37.35			14.89			16.04			5.14	89.16		

*Day 0 is leachate and metals before addition to the waste.

All results in mg/l

░ Limited sample volume

APPENDIX B THE MODELLING PROGRAMME

CONTENTS

LIST OF FIGURES

LIST OF TABLES

GLOSSARY

CAMR	Centre for Applied Microbiology Research
Ferrihydrite	Amorphous iron hydroxide mineral FeO.OH
Franklinite	Zinc iron oxide mineral $ZnFe_2O_4$
Goethite	Crystalline iron hydroxide mineral FeO.OH
Jarrosite	Iron hydroxy sulphate minerals Na/K/H $Fe_3^{3+}(SO_4)_2(H_2O)_6$
K_d	Distribution coefficient: the ratio of adsorbed to soluble metal
Lepidocrocite	Crystalline iron hydroxide mineral FeO.OH
MTD	Minton Treharne & Davies Ltd
Otavite	Cadmium carbonate mineral $CdCO_3$
Saturation Index	A measure of the potential for a mineral to precipitate
Smithsonite	Zinc carbonate mineral $ZnCO_3$
Sorption	Processes, controlling the partition of ions between solid and aqueous phases (excluding precipitation).
Speciation	The distribution of an element/ion between aqueous complexes
VFA	Volatile Fatty Acid
Willemite	Zinc silicate mineral, $ZnSiO_4$

B.1 INTRODUCTION

Landfill sites containing domestic and/or commercial wastes may contain elevated levels of heavy metals. In order to assess the sustainability of the landfill option, it is important to investigate whether metals continue to be immobilised within landfill in the long term. In particular, as the nature of the waste evolves, more aerobic conditions may become established and it has been argued by some that this may lead to the release of heavy metals.

The processes by which metals are retained in landfill are poorly understood. However, extensive research on soils and groundwater has provided considerable insights into the processes that control the metal mobility porous media. Precipitation/dissolution reactions and the interaction of metals with matrix via adsorption have been identified as important processes in soils and groundwaters. However, as yet relatively few such modelling studies have been carried out on landfill.

In this project, techniques developed in research on metal mobility in soils and aquifers and have been integrated with research on landfill and applied to aid in the interpretation of the experimental studies and to address the broader objectives of the project. The geochemical models and databases utilised in this project are all well established, are in the public domain, and have been widely used in studies of metals in groundwater and soil.

B.2 OBJECTIVES AND SCOPE

In recognition of the need for close integration of the modelling and experimental studies, the programme for the two aspects were closely linked. The modelling studies therefore focus on the same metals (zinc, cadmium and chromium) and were used to investigate metal behaviour in the mature landfill wastes from the Centre for Applied Microbiology Research CAMR, and the two field sampled wastes from Pitsea Landfill.

Modelling studies addressed a number of fundamental questions.

1. What are the dominant aqueous metal complexes (eg organic complexes, chlorides, carbonates, hydroxides) likely to be present in landfill leachates?
2. What are the most insoluble metal precipitates likely to be present in landfill over a range of conditions and are these precipitates likely to limit metal concentrations in leachate?
3. Is sorption important in immobilising metals in landfill, and if so, can this process be understood and predicted?
4. What are the likely metal concentrations in leachate for different metal loading ratios?
5. How is the potential for metal release likely to change as a landfill matures?

In order to address these questions, it was important to build understanding from the simple to the complex. The techniques used in this study are described in Section B.3. Following this, the types of aqueous complexes likely to be present in landfill are investigated using speciation models in Section B.4. A more detailed investigation of the importance of precipitation in controlling metal concentrations in leachate follows in Section B.5. In Section B.6, the role of sorption in retaining metals in landfill, based on techniques developed in soil and groundwater studies is investigated using the results of batch tests and validated against the column experiments. The results are summarised in Section B.7.

B.3 MODELLING TECHNIQUES

Modelling has been undertaken predominantly with the speciation-solubility model PHREEQE (pH-redox-equilibrium-equations) (Parkhurst *et al.*, 1980). Initial feasibility modelling used an updated UNIX version of this model with enhanced sorption capabilities (PHREEQ96, Arthur & Read, 1996). All of the results reported here, however, were generated from the PHREEQC model (Parkurst, 1995) which is available on the internet and can be run on a PC. The PHREEQE suite is one of the most widely used geochemical models and can be used to assess both the solubility and sorption of metals in groundwaters and leachates.

Geochemical modelling relies on the availability of high quality and comprehensive thermodynamic data to describe the range of reactions that may occur in the system being studied. For the purposes of this study, thermodynamic data are based on the MINTEQA2 (Allison *et al.,* 1991) database. This data base is contains one of the most comprehensive sets of data for geochemical modelling of metals in the environment. Supplementary data have been derived from the CHEMVAL database Version 6.0 (Falck and Read, 1996), which was developed over 8 years in a multi-country EC R&D programme.

In most groundwater contaminant transport models, the concept of a distribution coefficient (Kd) is used to represent sorption, where the Kd is defined as the ratio of adsorbed metal to metal in solution.

However, Kds for individual metals vary over many orders of magnitude, depending on a range of factors including the concentrations of metals and ligands, pH and the nature of the matrix material. For example in a regional study of cadmium sorption in soils in Denmark it was found that Kds generally double for each increase in pH of 0.5 units or in organic matter corresponding to 2% weight percent (Christensen, 1989). The use of inappropriate distribution coefficients in contaminant transport modelling and groundwater risk assessment therefore has the potential to lead to grossly misleading predictions of contaminant migration.

In this study, a more rigorous approach to sorption has been adopted, based on the concepts of surface complexation modelling. In this approach, the sorption of metals is sensitive to the leachate concentrations, pH and the nature of the matrix material. The approach is compatible with the thermodynamic equilibrium assumptions that are also applicable to the speciation and solubility modelling and has been widely applied and tested in studies of soils and groundwater (Sposito, 1994; Dzombak & Morel, 1990; Read, 1997). The thermodynamic data for modelling surface complexation in this study were derived largely from a literature search and from previous published by the authors.

B.4 METAL SPECIATION IN LEACHATES

B.4.1 Basis for speciation modelling

In the natural water environment, metals occur as a wide range of aqueous complexes. The types of complexes vary depending on the metal being considered and the types and concentrations of ligands in the solution. In landfill leachates that have near neutral pH, quite high alkalinities and high chloride and organic contents; aqueous complexes are likely to include hydroxides, carbonates, chlorides and organic complexes.

In order to understand the behaviour of metals, in any aqueous environment, it is important to understand aqueous speciation. The principal reasons why metal speciation needs to be understood are:

- the toxicity and uptake of some metals is dependent on speciation;
- the mobility, solubility and sorption of metals are controlled by interactions with aqueous complexes.

In standard water analyses e.g., for leachate, surface and groundwaters, metals are reported as dissolved and/or total concentrations. Metal speciation can be analysed in the laboratory but this is time consuming and expensive. It is therefore far more common to assess speciation using geochemical models. These models take analytical data for dissolved concentrations and, by referencing databases of equilibrium constants, calculate the distribution of aqueous species by iterating between multiple equilibria of the form:

$$Cd^{+2}(aq) + Cl^{-}(aq) = CdCl^{+}(aq)$$

Where the equilibrium constant K for the forward association reaction is defined as:

$$\log K = \log\frac{[CdCl^{+}]}{[Cd^{2+}][Cl^{-}]}$$

And square brackets denote activities, rather than concentrations.

Speciation modelling in this study was carried out on a range of leachate types using analytical results from the experimental programme. In the experiments, only relatively small volumes of leachate were recovered from the experimental columns and these were required primarily for the close monitoring of metal concentrations. Modelling studies, however, require a broader suite of analyses and therefore, where necessary, data have been supplemented by generic parameters for UK leachates (Robinson, 1995).

In order to investigate metal speciation over a range of landfill maturities, the four following leachate analyses have been modelled.

1. Leachate from Pitsea Borehole 3 which had high concentrations of fatty acids and chlorides and is representative of a high concentration acetogenic leachate.
2. Leachate from Pitsea Borehole 1 which had moderate to high concentrations of fatty acids and chlorides and is representative of a late acetogenic phase leachate.
3. Leachate from CAMR waste at the beginning of the column experiments which had moderate fatty acid and chloride concentrations and is representative of methanogenic phase leachate.
4. Leachate from CAMR waste at the end of the column experiments which had low fatty acid and chloride concentrations and is representative of post-methanogenic phase leachate.

The input parameters used for the modelling of the CAMR and Pitsea wastes are summarised, and compared with generic UK leachates in Table B.4.1

Table B.4.1 Summary of input parameters for metal speciation modelling and comparison with generic UK leachates

	PitBH3F	PitBH1F	CAMRE	CAMRL	UK Mean Acetogenic	UK Mean Methanogenic
pH	6.73	6.3	7.1	7	6.7	7.52
Ammoniacal-N	2040	889	207	76	922	889
Chloride	11525	1125	1564	83	1805	2074
Fatty acids as (C)	3427	1058	103	20	8197	18
Alkalinity as CaCO3	(3191)	3191	*5376*	1013	7251	5376
Nitrate-N	*0.86*	*0.86*	*0.86*	*0.86*	1.8	0.86
Sulphate-SO4	(6299)	6299	*67*	*67*	676	67
Sodium	(3153)	3153	*1480*	*1480*	1371	1480
Magnesium	(321)	321	*250*	*250*	384	250
Potassium	(1088)	1088	*854*	*854*	1143	854
Calcium	(1858)	1858	*151*	*151*	2241	151
Cadmium	0.12	0.04	0.01	0.01	0.02	0.015
Zinc	1.3	0.75	0.1	1.78	17.4	1.14
Chromium	0.2	0.16	0.05	0.05	0.13	0.09
Iron	242	218	25	67	654	27.4

CAMRE leachate based on early concentrations from column experiments (first 3 months)
CAMRL leachate based on late concentrations from column experiments (last 3 months)
PitBH1F and PitBH3F based on mean analysis of waste porewaters from field sampling from boreholes 1 and 3 respectively
Where no analyses available from Pitsea BH3 (du to small sample volume), data transposed from BH1 – denoted by ()
Analyses in italics retained from generic UK data based on Robinson (1995)

Comparison of parameters such as chloride and fatty acids (shaded in grey) with generic UK leachates indicates that the four analyses selected for modelling are representative of a range of landfill maturities. With regard to the CAMR columns, an exponential decline of gas production and of chloride concentrations in leachate was observed during the experiments. Volume balance considerations confirms that at least three bed volumes had passed through the columns. The late CAMR leachate analysis can therefore be considered as being representative of a very mature landfill.

B.4.2 Results of speciation modelling

The results of the speciation modelling indicate that a wide range of metal complexes occur in landfill leachates and that the types of complexes evolve as a landfill matures. Modelling results for metals investigated in this study, cadmium, zinc and chromium, are detailed below.

B.4.2.1 Predicted Speciation of Cadmium in Leachates

Considering cadmium first, the modelling results show that particularly for the mature leachates, speciation is dominated by carbonate complexes and the divalent metal ion Cd^{2+} (Table B.4.2). In the high chloride, high VFA leachates from Pitsea, chloride and acetate complexes are significant. Additional multiple sulphates and chlorides are present in very low amounts and account for the small deficit in total percentage in the two Pitsea wastes. Hydroxides are insignificant.

The strong complexation of cadmium by chloride has been noted previously (Alloway, 1990; Ross, 1994). In immature landfill leachates, formation of chloride and organic complexes will tend to compete against immobilising processes such as precipitation and sorption. Based on speciation considerations alone, this could potentially lead to higher metal concentrations in immature landfill leachate compared with mature leachates. This issue is discussed further, in the context of other potential controls on metal mobility, in the main report.

Table B.4.2 Predicted speciation of cadmium in leachates (components >20% shaded)

Cd	PitBH3F	PitBH1F	CAMR Early	CAMR Late
Cd+2_m	4	18	11	42
CdHCO3+_m	7	28	37	30
CdCO3_m	2	4	34	23
CdCl+_m	34	14	15	4
CdCl2_m	19	1	2	0
CdSO4_m	2	11	0	1
CdAcetate+_m	18	18	1	1
CdAcetate2_m	8	3	0	0
Total	95	96	100	100

B.4.2.2 Predicted Speciation of Zinc in Leachates

The results for zinc show some similarities to those for cadmium. Speciation in all of the leachates is dominated by carbonate complexes and the divalent metal ion Zn^{2+} (Table B.4.3) In the leachate from Pitsea BH3, with very high VFAs, organic complexation is also significant. As for cadmium, the small deficit in total percentage for the two Pitsea wastes is accounted for by multiple sulphate and chloride complexes. Hydroxides are insignificant. The overall similarity in complexes in immature and mature leachates indicates that, with the exception of very organic-rich leachates, zinc speciation does not change greatly during landfill maturation.

These results are in good agreement with speciation studies of metals in soils that predict zinc speciation to be dominated by Zn^{2+}, carbonates, and sulphates (Sposito, 1994; Alloway, 1990).

Table B.4.3 Predicted speciation of zinc in leachates (components >20% shaded)

Zn	PitBH3F	PitBH1F	CAMR Early	CAMR Late
Zn+2_m	22	27	7	41
ZnHCO3+_m	28	42	26	32
ZnCO3_m	8	4	19	20
Zn(CO3)2-2_m	6	1	47	6
ZnCl+_m	5	1	0	0
ZnSO4_m	7	13	0	1
ZnAcetate+_m	20	8	0	0
ZnAcetate2_m	2	0	0	0
ZnAcetate3-_m	0	0	0	0
Total	97	97	100	100

B.4.2.3 Predicted Speciation of Chromium in Leachates

Chromium in the natural environment occurs primarily in two oxidation states, Cr(VI) and Cr(III). Cr(VI) is relatively mobile and acutely toxic whereas Cr(III) has relatively low toxicity and is immobile under moderately alkaline to slightly acidic conditions (Palmer & Puls 1994). Fortunately Cr(VI), the more toxic form, only occurs under highly oxidising conditions, with the critical Eh for transformation being around +8000 mV at pH 8 (Sposito 1994). In landfill, where Eh values are typically between –500 to 0 mV, chromium will be entirely present as Cr(III).

Chromium (III) is a trivalent ion and has a different speciation to zinc and cadmium. In immature leachates, although some hydroxides occur, speciation is strongly dominated by organic complexes (represented here as acetates). The formation of these organic complexes in could contribute to chromium mobility in immature landfill. In mature leachates where VFAs concentrations are lower, organic complexes are insignificant and only hydroxides, which are also dominant in soil systems (Ross, 1994) remain.

Table B.4.4 Predicted speciation of chromium in leachates (components >20% shaded)

Cr	PitBH3F	PitBH1F	CAMR Early	CAMR Late
Cr+3_m	0	0	0	0
Cr(OH)2+_m	1	3	56	60
Cr(OH)3_m	0	0	39	35
Cr(OH)+2_m	0	1	4	5
CrOHSO4_m	0	1	0	0
CrO2-_m	0	0	0	0
CrAcetate3_m	92	72	0	0
CrAcetate2+_m	6	15	0	0
CrAcetate+2_m	1	7	0	0
Total	100	100	100	100

B.4.2.4 Summary of Metal Speciation in Leachates

Modelling of the speciation of cadmium, zinc and chromium in landfill leachates representative of a range of maturities demonstrates that speciation is likely to evolve as leachates mature. The main results of the speciation modelling are as follows.

1. In immature leachates cadmium complexes strongly with the high concentrations of chlorides and organics. As the concentrations of these components decline cadmium complexation becomes dominated $Cd^{2+}$and carbonates.
2. Zinc complexation for all leachate types is dominated by $Zn^{2+}$and carbonates. In immature leachates organic complexes may be significant.
3. Chromium complexation is dominated by organics in immature leachates and hydroxides in mature leachates.
4. Overall, reducing concentrations of organics and chloride as leachates mature will tend to lead to weaker aqueous complexation and this may favour immobilising processes such as precipitation and sorption.

B.5 METAL SOLUBILITY IN LEACHATES

B.5.1 Basis for metal solubility modelling

Heavy metals in the natural environment may exist as solid precipitates. The solubility and stability of these preciptates, which may include sulphides, carbonates, hydroxides etc., depends upon, among other factors, the concentration of the metal and associated ligands and the prevailing pH and redox conditions.

Under the anaerobic, strongly reducing, conditions present in landfill, it is likley that most heavy metals are immobilised as insoluble sulphides. However, if conditions become more aerobic, the potential exists for sulphides to become soluble and for metals to be released. An initial aim of the modelling was therefore to investigate the stability of metal precipitates in a typical landfill leachate over a range of redox conditions.

Methanogenic bacteria generally require a redox potential of lower than –200 mV. When methanogenesis ceases, redox potential could rise above this value, particularly if the landfill becomes partially aerobic. As a representative range for mature landfills, modelling trials were based on varying the Eh potential from -300 mV to +200 mV. The role of precipitation in immobilising metals in landfill was investigated in two ways using the geochemical model PHREEQC.

In the first stage, mineral saturation indices (*SI*) were calculated for a range of leachates. Saturation indices provide a measure of the tendency of a mineral to precipitate. *SI* is defined for the equilibrium dissociation reaction having a solubility product K_{sp}:

$$CdS(s) = Cd^{2+}(aq) + S^{2-}(aq)$$

and having a solubility product K_{sp}:

$$\log K_{sp} = \log\frac{[\mathrm{Cd}^{2+}][S^{2-}]}{[CdS\ ]}$$

as:

$$SI = \log\frac{[\mathrm{Cd}^{2+}][\mathrm{S}^{2-}]}{K_{sp}}$$

where [ ] indicates activity rather than concentration. The tendency of a mineral to precipitate is indicated by the saturation index as follows:

- below zero means that the solution is undersaturated and the mineral phase is unlikely to be present;
- close to zero - the mineral is approximately in equilibrium with the soution and is likely to be present as a precipitate; and
- above zero means that the solution is supersaturated, i.e the mineral will tend to precipitate.

In the second stage of the solubility modelling, having identified the most insoluble mineral phase likely to be present in aerobic landfill, the model was used to calculate metal solubility limits for a range of leachate types. These results are then compared with typical metal concentrations in landfill leachates and conclusions have been drawn on the likely role of precipitation in immobilising metals in landfill.

In order to investigate metal solubility over a range of landfill maturities, three leachate analyses have been simulated, each over an Eh range of –300 mV to +200 mV. However, it is important to note that there is no universal scale of Eh (Parkurst, 1980). In other words each redox system has its own Eh scale. In addition, Eh is difficult to measure accurately in the laboratory. In the discussion of the modelling results, care has therefore been taken in interpreting redox controls and relating these to laboratory measurements.

In order to assess whether solubility constraints can explain the leachate concentrations both early and late in the three sets of column experiments, and to represent a range of leachate maturities, modelling has been carried out for the three waste types based on both early and late leachate concentrations. In the case of the Pitsea wastes, analysis of field sampled leachates are used as representative of the early leachates. Details of input parameters for the solubility modelling are given in Table B.5.2.

Table B.5.1 Summary of input parameters for metal solubility modelling and comparison with generic UK leachates

	PitBH3F	PitBH3L	PitBH1F	PitBH3L	CAMRE	CAMRL
pH	6.73	6.9	6.3	6.7	7.1	7
Ammoniacal-N	2040	210	889	109	207	76
Chloride	11525	1349	1125	241	1564	83
Fatty acids as (C)	3427	400est	1058	<50	103	20
Alkalinity as CaCO3	(3191)	(3191)	3191	3191	*5376*	1013
Nitrate-N	*0.86*	*0.86*	*0.86*	*0.86*	*0.86*	*0.86*
Sulphate-SO4	(6299)	(6299)	6299	6299	*67*	*67*
Sodium	(3153)	(3153)	3153	3153	*1480*	*1480*
Magnesium	(321)	(321)	321	321	*250*	*250*
Potassium	(1088)	(1088)	1088	1088	*854*	*854*
Calcium	(1858)	(1858)	1858	1858	*151*	*151*
Cadmium	0.12	0.04	0.04	0.02	0.01	0.01
Zinc	1.3	0.1	0.75	<0.04	0.1	1.78
Chromium	0.2	0.2	0.16	0.14	0.05	0.05
Iron	242	4	218	2	25	67

CAMRE leachate based on early concentrations from column experiments (first 3 months)
CAMRL leachate based on late concentrations from column experiments (last 3 months)
PitBH1F and PitBH3F based on mean analysis of waste porewaters from field sampling from boreholes 1 and 3 respectively
PitBH1L and PitBH3L based on late concentrations from column experiments (last 3 months)
Where no analyses available from Pitsea BH3 (du to small sample volume), data transposed from BH1 – denoted by ()
Analyses in italics retained from generic UK data based on DoE (1995)

The main focus of solubility modelling was to determine whether solubility could limit metal concentrations in leachate and to investigate the effect of aerobic conditions on cadmium, zinc and chromium solubilities. Prior to reporting the results for heavy metals, the likely ranges of Eh in the columns are established with reference to experimental measurements of Eh and visual observations of precipitation in the columns.

B.5.2 Results of solubility modelling

B.5.2.1 Eh Ranges in the Experimental Columns

On of the main focuses of this project was to compare metal release from anaerobic and aerobic waste. As described in Section 2 of the main report, despite the precautions taken, Eh monitoring showed quite strong fluctuations within individual columns (See Appendix A) and showed little contrast between the anaerobic and aerobic columns for any of the wastes.

Although Eh monitoring showed little contrast between the aerobic and anaerobic clumns, visual inspection of the columns indicated that in the air sparged columns, an ochreous oxidation front progressed down the columns. The rate of progress of the aerobic front varied between individual columns, however the front had progressed to the base of all of the CAMR columns and half of the Pitsea air-sparged columns by the end of the experimental programme.

The ochreous colour change observed in the columns represents a chageover in iron minerals from sulphide dominated to oxy-hydroxide dominated. Modelling of the CAMR leachates over a range of Ehs indicates that iron sulphide (pyrite) would be expected to become soluble above Ehs of around –200 mV. Above this Eh the iron oxyhydroxide minerals goethite and lepidocrocite have the potential to precipitate. However, it is not until Eh rises to above +20 to +40 mV that ochre minerals ferrihydrite and jarrosite have the potential to precipitate. These latter minerals have been widely reported in natural ochreous deposits, for example associated with mine drainage and are likely to be cause of the red colouration in the waste columns.

The modelling results in Figure B.5.1 demonstrate that as aerobic conditions become established, the solubility limiting phase for iron changes from sulphide to oxyhydroxide. Confidence in the modelling is provided by comparison with the colour changes observed in the experimental columns. In the following sections, similar principles are used to investigate the role of precipitation in limiting the concentration of heavy metals in landfill leachates.

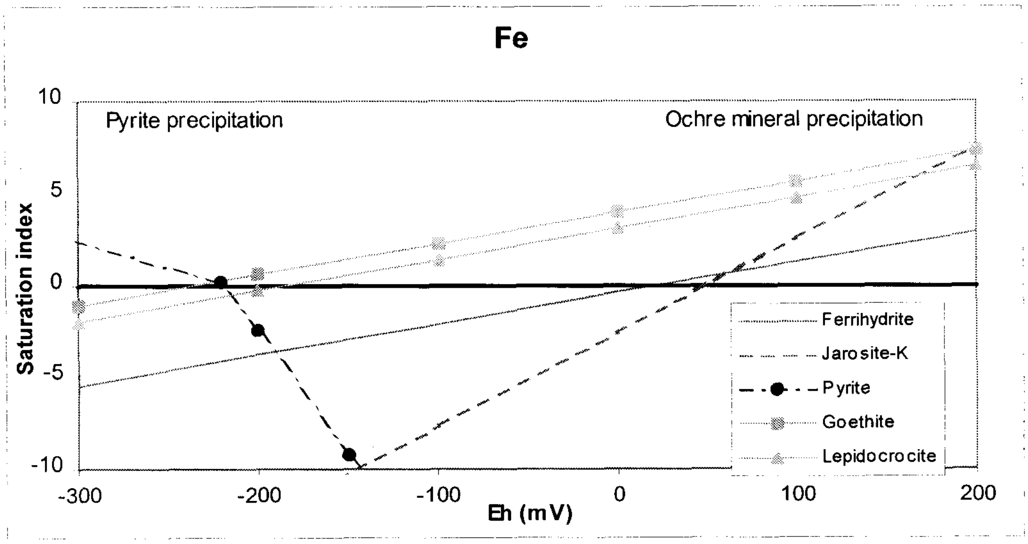


Figure B.5.1 Saturation indices for iron minerals in CAMR column leachates

B.5.2.2 Solubility of Cadmium in Leachates

Modelling results for cadmium indicate that cadmium sulphide is oversaturated under reducing conditions (Figure B.5.2). The Eh at which cadmium sulphide is predicted to become undersaturated varies between the different leachates, but is around –80 to –150 mV. In methanogenic landfill where Eh is likely to be lower than –200 mV it is likely that sulphide precipitation is important in reducing cadmium mobility.

Under more aerobic conditions, cadmium sulphide will become undersaturated. Overall, the laboratory measurements supported by modelling & interpretation of iron mineralisatin, suggest that positive Ehs were established in the majority of the air-sparged columns. Under these conditions, cadmium sulphide is likely to become soluble and cadium carbonate (otavite) will become the solubility limiting phase. Lindsay (1979) shows that otavite is also likely to be the main mineral to control cadmium concentrations in soil solutions.

Having identified cadium carbonate as the likely solubility limiting phase for cadmium in aerobic landfill leachate, the second stage of modelling has been carried out, in which equilibrium is imposed between the cadmium carbonate and the three leachates under investigation. The model has been used to predict the solubility limits for cadmium in each leachate. Cadmium concentrations in leachate below the predicted limits will be soluble, and therefore precipitation is unlikely to contribute to metal retention.

The results of this solubility modelling indicate that in immature leachates with high chloride and VFAs, cadmium solubility limits are between 170 and 840 μg/l whereas in mature post methanogenic leachates such as the mature CAMR waste, carbonate precipitation is likely to prevent cadmium concentrations rising above 60 to 90 μg/l (Table B.5.3). Laboratory results indicate that even for the aerobic columns, cadmium concentrations generally remain below 10 μg/l. Overall, the results of the experimental and modelling studies in combination suggest that cadmium is retained in landfill under aerobic conditions, but that the retention mechanism is probably not precipitation alone.

Table B.5.2 Predicted solubility limits for cadium carbonate in a range of landfill leachates

	Cd solubility limit in Initial column leachates	Cd solubility limit in Final column leachates
Pitsea BH3 (high chloride and VFAs)	0.84	0.14
Pitsea BH1 (moderate chloride and VFAs)	0.55	0.17
CAMR (mature waste)	0.06	0.09

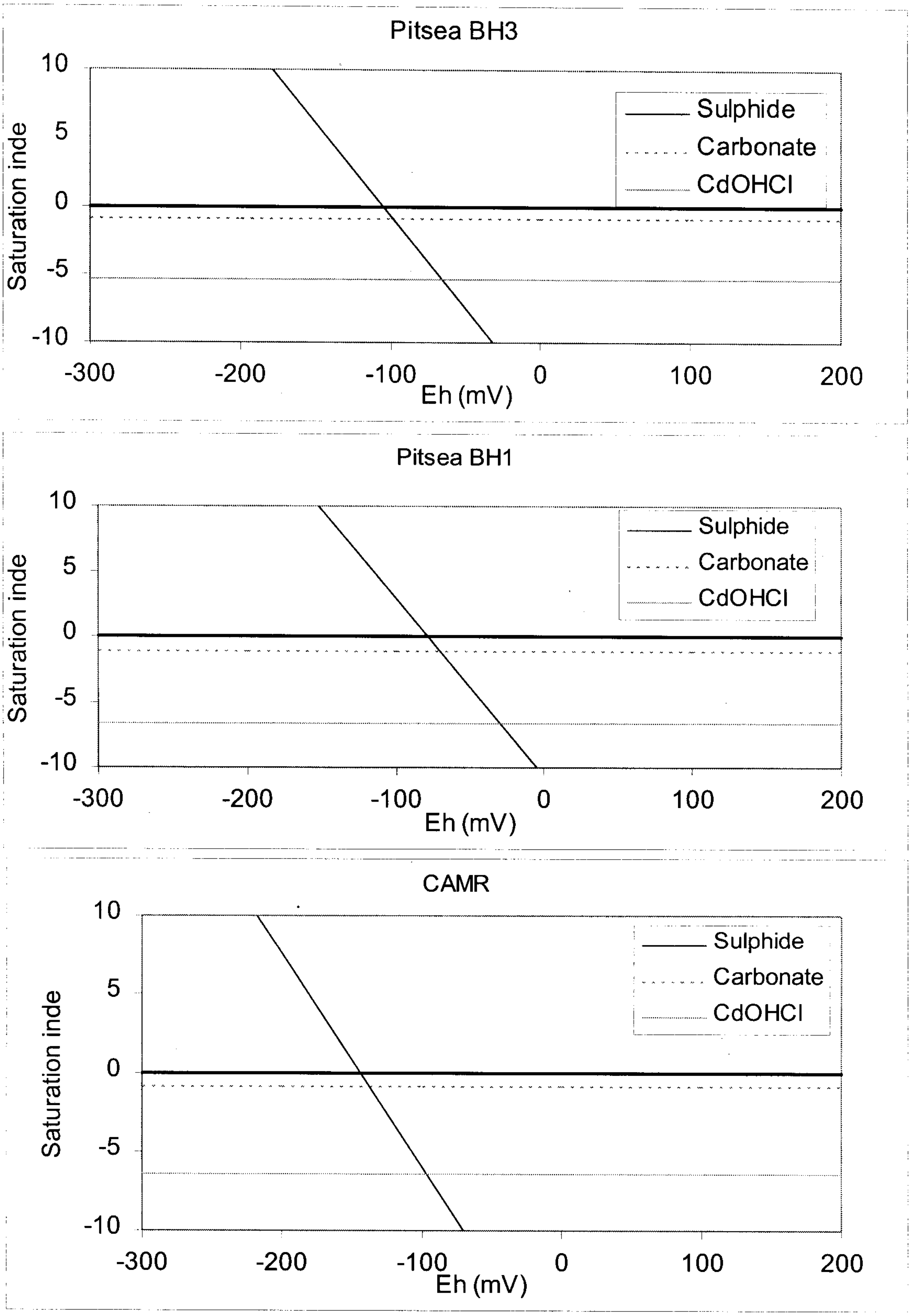


Figure B.5.2 Saturation indices for cadmium minerals in column leachates, showing the changeover from sulphide to carbonate as the solubility limiting phase

B.5.2.3 Solubility of Zinc in Leachates

Modelling results for zinc indicate that solubility trends are similar to those for cadmium. Zinc sulphide is oversaturated under reducing conditions at Ehs lower than –100 to –180 mV. As for cadmium it is likely that in methanogenic landfill, zinc sulphide precipitation is important in reducing zinc mobility.

Under more aerobic conditions, the two most likely precipitates are $ZnCO_3$ (smithsonite) and its hydrated equivalent $ZnCO_3.H_2O$, with the latter having a slightly higher saturation index. Investigations into zinc solubility in soil suggest that willemite (Zn silicate) and franklinite (Zn-ferric oxide) may also be important in limiting solubility (Lindsay, 1979). However, solubility products for the formation of these minerals were not available in the thermodynamic databases used in this study, therefore, they have not been included. Such limitations need to be borne in mind when evaluating modelling results and it is likely that the solubility modelling for zinc may be pessimistic in terms of the predicted solubility limits in leachates (ie predict unduly high equilibrium zinc concentrations).

For the positive Eh values impilied for the majority of the air sparged columns, zinc sulphide is likely to become soluble and, based on the available thermodynamic data, the two zinc carbonate phases will become solubility limiting phases. Having selected zinc carbonates as the likely solubility limiting phases in aerobic landfill leachate, the model has been used to predict the solubility limits for zinc in each leachate. The results of solubility modelling indicate that in immature leachates with high chloride and VFAs, zinc solubility limits are between 14.7 and 4.7 mg/l whereas in mature post methanogenic leachates such as the mature CAMR waste, the solubility limits are around 3.6 mg/l (Table B.5.4).

Laboratory results indicate that even for the aerobic columns, zinc concentrations remain below 1 to 2 mg/l. Measured zinc concentrations in the mature leachates are therefore quite close to the predicted zinc solubility limits, even for carbonate phases. Overall, the results of the experimental and modelling studies in combination suggest that zinc is retained in landfill under aerobic conditions and that precipitation of carbonates, or potentially less soluble silicate and iron oxide phases, may be a contributing process.

Table B.5.3 Predicted solubility limits for $ZnCO_3.H_2O$ in a range of landfill leachates

	Zn solubility limit in Initial column leachates (mg/l Zinc)	Zn solubility limit in Final column leachates (mg/l Zinc)
Pitsea BH3 (high chloride and VFAs)	8.11	4.73
Pitsea BH1 (moderate chloride and VFAs)	14.77	6.22
CAMR (mature waste)	3.66	3.59

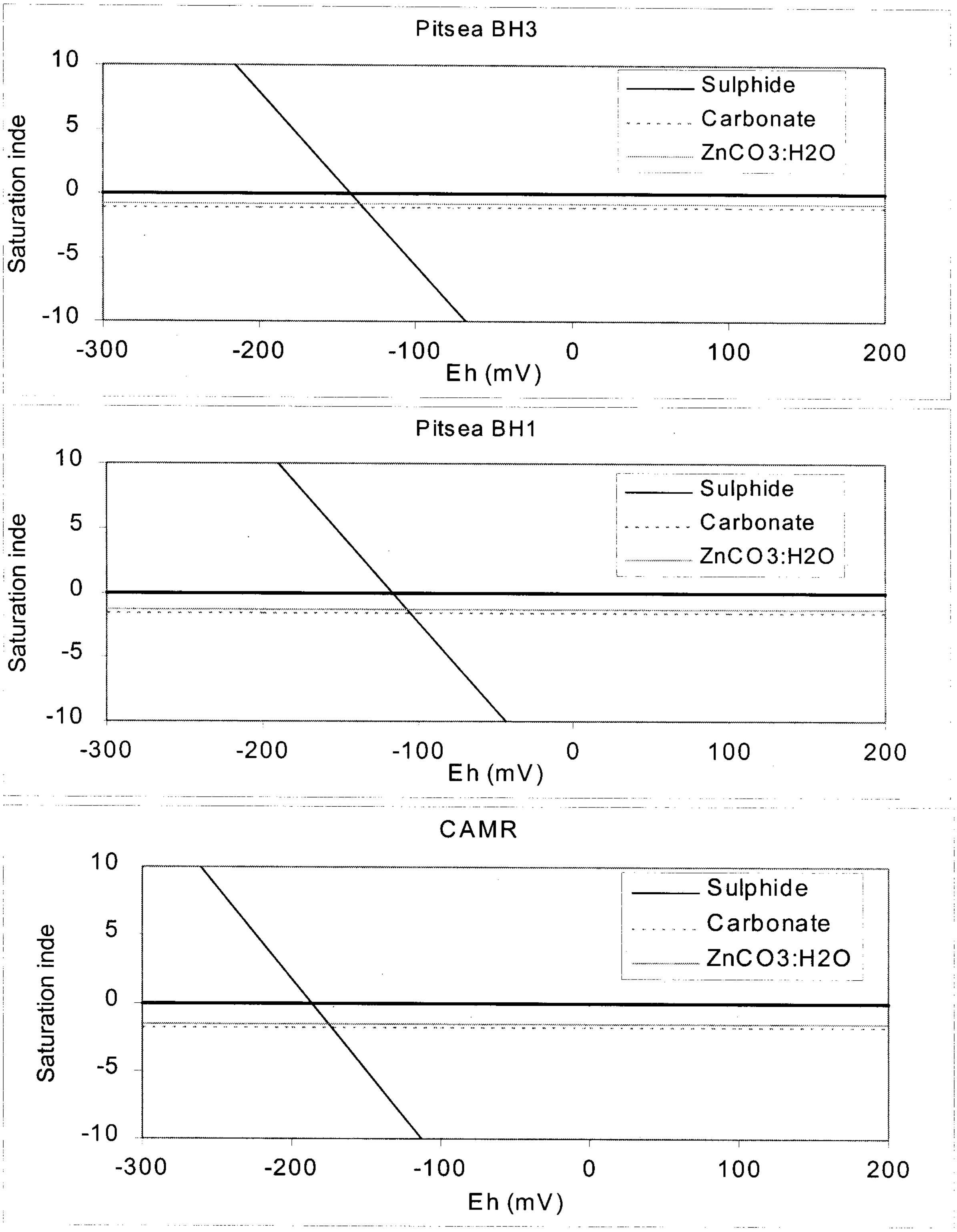


Figure B.5.3. Saturation indices for zinc minerals in column leachates, showing the changeover from sulphide to carbonate as the solubility limiting phase

B.5.2.4 Solubility of Chromium in Leachates

As discussed in Section B.4, chromium in landfill leachates will be present as Cr(III) which is relatively immobile. Solubility modelling results for chromium indicate the most likely precipitates are Cr_2O_3 and $Cr(OH)_3$ (Figure B.5.4). Particularly for the CAMR waste columns, the measured chromium concentrations imply that Cr_2O_3 and amorphous $Cr(OH)_3(A)$ would be supersaturated in the leachates.

Studies of chromium at contaminated sites indicate that chromium typically precipitates as amorphous $Cr(OH)_3(A)$ and that, under different conditions, this amorphous form can crystallise as $Cr(OH)_3$ (C) or Cr_2O_3 (Palmer and Puls, 1994). Particularly as Cr_2O_3 is grossly supersaturated in the Pitsea leachates, it seems more likely that $Cr(OH)_3(A)$ is the solubility limiting phase in landfill leachates. If $Cr(OH)_3(A)$ is taken as the most likely solubility limiting phase, a further problem remains; the apparent supersaturation of chromium in the CAMR leachates. The most likely explanation for this is that the geochemical representation for chromium is over-simplified. In particular, it may be that the use of acetate as a generic organic ligand is too simple, especially for mature leachates where longer-lived humic and fulvic acids will dominate the organic fraction.

Geochemical modelling studies carried out by the US Environmental Protection Agency investigating $Cr(OH)_3(A)$, concluded that chromium concentrations in groundwater contaminant plumes should be less than 0.05 mg/l, based on $Cr(OH)_3(A)$ solubility considerations in an entirely inorganic model (Palmer and Puls, 1994). In our study, organic complexation is included, with acetate being used as a generic organic ligand. Based on this slightly more sophisticated model, chromium solubility in leachate is predicted to be in the order of 0.23 to 0.37 mg/l for the Pitsea leachates compared with measured values of around 0.1 to 0.5 mg/l. For the CAMR leachates the model predicts very low solubilities of 0.002 mg/l compared with measured concentrations in leachates generally below 0.1 mg/l.

The combined experimental and modelling results of this study suggest that in landfill leachates, organic complexation of chromium is important and may cause chromium solubility to be significantly elevated above values predicted by geochemical models based on inorganic complexation. In mature leachates with low organic contents, chromium hydroxide solubility is predicted to be very low and is likely to contribute to the immobilisation of chromium in landfill.

Table B.5.4 Predicted solubility limits for chromium in a range of landfill leachates

	Cr solubility limit in initial column leachates (mg/l Cr)	Cr solubility limit in final column leachates (mg/l Cr)
Pitsea BH3 (high chloride and VFAs)	0.37	0.003
Pitsea BH1 (moderate chloride and VFAs)	0.23	0.004
CAMR (mature waste)	0.002	0.002

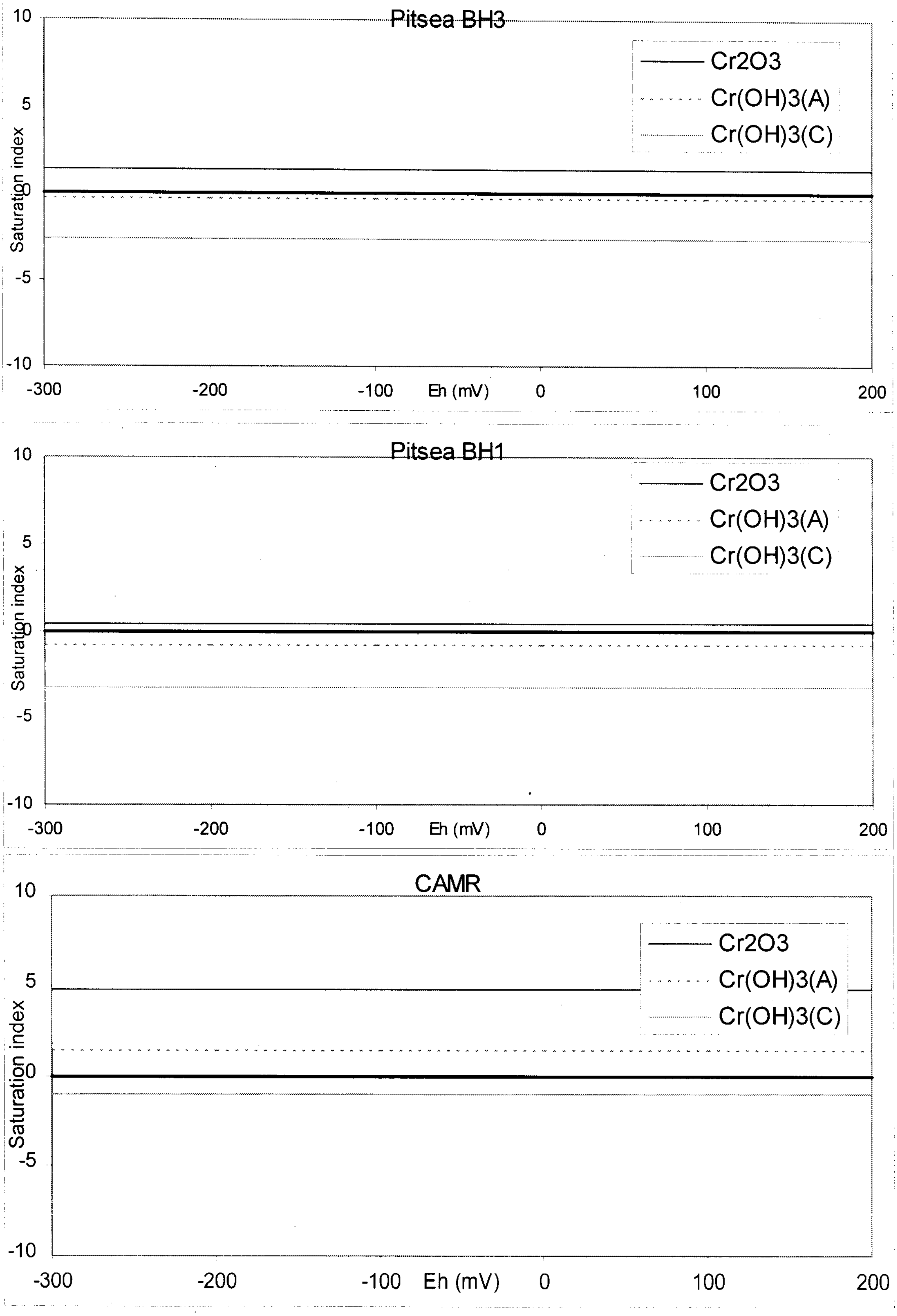


Figure B.5.4. Saturation indices for chromium minerals in column leachates.

B.5.2.5 Summary of solubility modelling results

By comparing the modelling results with measurements from the experiments and with research on metals in soils and at contaminated sites, a number of conclusions can be drawn from the solubility studies studies.

- Metals such as iron, cadmium and zinc (and other metals such as lead and nickel) are likely to be present as insoluble sulphides in landfill under reducing conditions below about -150 mV to -200 mV. If aerobic conditions become established in landfill, sulphides will tend to be oxidised to soluble sulphates.

- Under more aerobic conditions solubility limiting phases vary for different metals, but include carbonates and hydroxides.

- For cadmium, the modelling studies suggest that under aerobic conditions, the measured leachate concentrations (generally below 0.01 mg/l) are around an order of magnitude below predicted solubility limits for cadmium carbonate, and therefore that other mechnisms are limiting cadmium release.

- For zinc, the modelling studies studies suggest that under aerobic conditions, the measured leachate concentrations (generally below 1 to 2 mg/l) are close to predicted solubility limits, and therefore that precipitation of carbonates or less soluble silicate or iron oxide phases may be a controlling factor limiting zinc release.

- Modelling results for chromium indicate that organic complexation is important and may cause chromium solubility to be significantly elevated above values predicted by geochemical models based on inorganic complexation - in mature leachates with low organic contents, chromium hydroxide solubility is predicted to be very low and is likely to contribute to the immobilisation of chromium in landfill.

B.6 MODELLING METAL SORPTION IN LANDFILL

B.6.1 Basis for sorption modelling

The adsorption of metal ions to solid phases exerts a strong control on the concentrations of metal ions in solution and their movement through a solid matrix. Adsorption is recognised as being a major component of natural attenuation in aquifers, particularly those rich in organic material, and is the main cause of the long term retention of metals in soils (Alloway, 1990).

Mechanisms for removing ions from solution include ion exchange and specific adsorption. Ion exchange relates to the removal of ions from solution by permanent charge sites on silicate minerals and organic material. However, since heavy metal ions such as Cd^{2+}, Zn^{2+} must compete for exchange sites with much more abundant ions such as Ca^{2+} and Mg^{2+}, strong electrostatic sorption of heavy metals on to these sites is rarely expected (Ross, 1994). Instead, more specific mechanisms are needed to explain the retention of trace metals in soils, aquifers and waste.

In PHREEQC, sorption is simulated as an equilibrium reaction, based on user specified sorption surface parameters and equilibrium constants for the reaction:

$Cd^{2+} + SOH^0 = SOCd^+ + H^+$

Where SOH^0 is a surface site where a proton can be replaced by a metal ion.

For a detailed discussion of the theoretical basis for sorption modelling the see Dzombak and Morel (1990).

Although sorption is a key process in controlling metal mobility in natural waters, it is complex and cannot generally be predicted in natural systems with the same degree of confidence as more simple chemical processes such as aqueous complexation and solubility. In landfill where the matrix material is highly heterogeneous and alters in composition as the landfill matures, sorption processes are likely to be particularly complex and this may explain why very few attempts have been made to model sorption processes in landfill. The modelling study reported here makes some significant steps in translating and applying existing models to landfill systems but should be considered as a pilot study.

Parameters for the sorption of trace metals to surfaces such as iron hydroxide, silica and soils can be found in the literature. However, due to the variability of sorption processes between different media, it is common practice to carry out flask or batch tests to study metal uptake on the matrix being studied and to use the results to calibrate sorption models. This approach has been adopted in this study and the calibrated models have then been tested against the column experiments.

B.6.2 Sorption modelling of batch experiments

Triplicate batch experiments were carried for out over a range of concentrations equating to 1, 10 and 100 g/tonne loadings for Cd, Zn and Cr on their own and for a combined case (Appendix A). Experiments at the higher loadings were prone to precipitation, which masked the effect of sorption, whereas experiments at lower loadings resulted in metal concentrations below the standard detection limits of the analytical techniques. Therefore, following a review of the results, data from the 10 g/tonne individual metal experiments were selected for modelling.

In order to model sorption processes based on the surface complexation approach it is necessary: to know the ratio of solid to liquid; to estimate surface parameters of solid phase; and to estimate the metal to surface complexation constant. Sorption models for the batch experiments were initially set up using the generic literature values and experimental parameters summarised in Table B.6.1.

Table B.6.1. Initial parameters for modelling batch sorption experiments

Parameter	**Value**	**Reference**
Mass of waste / litre of solution (g/l)	140	Experimental data
Specific surface area of waste m^2/g	500 to 5000	Tipping & Woof (1990) for organic rich soils
Site density of sorption sites eq/m^2	$1x10^{-6}$ to $1x10^{-5}$	Based on Tipping & Woof (1990) for organic rich soils
LogK $Cd^{2+} + SOH^0 = SOCd^+ + H^+$	-6.0	Ross et al 1997 for sorption to silica/sandstone
LogK $Zn^{2+} + SOH^0 = SOZn^+ + H^+$	-3.0	Ivanovich et al 1996 for sorption to silica/sandstone
LogK $Cr(OH)_2^+ + SOH^0 = SOCr(OH)_2 + H^+$	-4.0	Ivanovich et al 1996 for sorption to silica/sandstone

For a particular solution, the positions of sorption equilibria are determined primarily by the concentration of sorption sites and the surface complexation logK. Each of these parameters needs to be scoped in the optimisation procedure. As can be seen from Table B.6.1, surface parameters vary over quite a wide range. Therefore, initial bounding cases to derive equilibrium constants runs carried using the maximum and minimum literature values for site densities and specific surface areas. In addition, there was some analytical variability in the measured final aqueous concentrations in the batch experiments and sorption calibration was carried out against both extreme high and low values.

As would be expected, the bounding runs using extreme literature values and experimental results produce a wide range of logK values (Tables B.6.2 to B.6.4).

Table B.6.2. Sorption model calibration results based on low surface parameters

Surface area m2/g	**500**		
Site dentisy Eq/m2	**1.00E-06**		
Mass matrix g/dm3	140		
Total sites Eq/dm3	0.07		
Maximum experimental sorption	Cd	Zn	Cr
Starting Concentration mg/l	0.93	5.32	5.81
Final Concentration mg/l	0.01	0.04	0.1
Modelled concentration mg/l	0.01	0.04	0.10
Equilibrium coefficient	**-3**	**-2.25**	**-4.05**
Minimum experimental sorption	Cd	Zn	Cr
Starting Concentration mg/l	0.93	5.32	5.81
Final Concentration mg/l	0.1	0.15	0.85
Modelled concentration mg/l	0.10	0.15	0.09
Equilibrium coefficient	**-4.05**	**-2.85**	**-5.05**

Table B.6.3. Sorption model calibration results based on medium surface parameters

Surface area m2/g	**500**		
Site dentisy Eq/m2	**1.00E-05**		
Mass matrix g/dm3	140		
Total sites Eq/dm3	0.7		
Maximum experimental sorption	Cd	Zn	Cr
Starting Concentration mg/l	0.93	5.32	5.81
Final Concentration mg/l	0.01	0.04	0.1
Modelled concentration mg/l	0.01	0.04	0.09
Equilibrium coefficient	**-4.45**	**-3.75**	**-5.05**
Minimum experimental sorption	Cd	Zn	Cr
Starting Concentration mg/l	0.93	5.32	5.81
Final Concentration mg/l	0.1	0.15	0.85
Modelled concentration mg/l	0.10	0.15	0.83
Equilibrium coefficient	**-5.5**	**-4.3**	**-6.05**

Table B.6.4. Sorption model calibration results based on high surface parameters

Surface area m2/g	**5000**		
Site dentisy Eq/m2	**1.00E-05**		
Mass matrix g/dm3	140		
Total sites Eq/dm3	7		
Maximum experimental sorption	Cd	Zn	Cr
Starting Concentration mg/l	0.93	5.32	5.81
Final Concentration mg/l	0.01	0.04	0.1
Modelled concentration mg/l	0.01	0.04	0.10
Equilibrium coefficient	**-5.45**	**-4.7**	**-6.1**
Minimum experimental sorption	Cd	Zn	Cr
Starting Concentration mg/l	0.93	5.32	5.81
Final Concentration mg/l	0.1	0.15	0.85
Modelled concentration mg/l	0.10	0.15	0.82
Equilibrium coefficient	**-6.5**	**-5.3**	**-7.05**

In order to impose some constraints on the selection of appropriate sorption parameters, an assumption was imposed: that the surface complexation constants for cadmium, zinc and chromium to household waste should be close to, or stronger than the literature values for sorprtion to silica/sandstone. Taking this assumption into account, the preferred surface parameters are at the low end of literature values for site densities and specific surface area. The parameters selected are detailed in the following section.

B.6.3 Sorption modelling of column experiments

The sorption model calibrated against the batch experiments has been applied to the column experiments. Experimentally determined metal loadings for the Pitsea and CAMR wastes have been entered into the model and predictions made of leachate concentrations. The metal loadings that were used in the modelling studies were based on preliminary analyses of the wastes; these differ slightly from the final analyses reported in Appendix A. The predictions are then compared with experimental measurements of leachate concentrations.

Table B.6.5. Summary of input parameters and validation results for modelling column experiments

Sorption model parameters			
Surface area m2/g	500	Cd eqm coef.	-3
Site dentisy Eq/m2	1.00E-06	Zn eqm coef.	-2.25
Mass matrix g/dm3	2300	Cr eqm coef.	-4.05
Total sites Eq/dm3	1.2		
Validation Results			
CAMR	Cd	Zn	Cr
Loading mg/kg wet waste	70	735	113
Measured leachate concentration mg/l	0.01 to ~ 0.25	0.18 to ~3.0	0.05 to ~ 0.2
Modelled concentration mg/l	0.11	0.19	0.81
Pitsea BH1			
Loading mg/kg wet waste	1.1	311	84
Measured leachate concentration mg/l	0.02 to ~ 0.08	0.04 to ~1.0	0.14 to ~ 0.3
Modelled concentration mg/l	0.01	0.40	1.22
Pitsea BH3			
Loading mg/kg wet waste	1.8	1353	52
Measured leachate concentration mg/l	0.01 to ~ 0.15	0.1 to ~1.0	0.2 to ~ 0.5
Modelled concentration mg/l	0.01	1.28	0.61

The validation results in Table B.6.5 demonstrate that the sorption model developed from the batch experiments provides a reasonable representation of measured metal concentrations in the column leachates. In the experimental data, for a specific metal in a particular waste type, there was a considerable range of leachate metal concentrations. It should be noted that very high concentrations, that are considered likely to be anomalous, have been excluded from the ranges quoted in Table B.6.5.

The pilot sorption model approach represents an improvement on the use of dissociation constants (Kds), in particular where predictions are required across a range of loadings. For example, for cadmium, loadings are around 60 to 70 times higher in the CAMR columns than in the Pitsea BH1 columns, but measured leachate concentrations were only slightly higher in the CAMR columns. A simple Kd approach assumes a constant ratio between loading and leachate concentrations and would predict leachate concentrations to be 60 to 70 times higher for the high loading case. By contrast, the pilot sorption model predicted concentrations to be around 11 times higher in the CAMR leachates.

Because of the ranges in experimental data, it is difficult to rigorously test the sorption model. However, for cadmium and zinc, the model predictions are within, or very close to, the range of experimental data. For chromium, the sorption model tends to over-predict leachate concentrations. This may be a result of poor calibration against the batch experiments, where VFA concentrations (which are an important control on chromium speciation) were poorly constrained.

In translating the sorption model from the batch experiments to predict leachate concentrations from metal loaded waste in the columns, there are four main factors that need to be taken into account.

1. In batch tests, metal sorption is generally investigated under conditions in which the ratio of waste to liquid was relatively low. In the MTD experiments, 200g wet waste was added to 1 litre of metal loaded leachate. By contrast, in column experiments, which are more representative of real landfill conditions the ratio of waste to liquid is much higher with solid waste forming 60 to 70 % of the bulk volume. Therefore, the concentration of sorption sites per unit volume of leachate is far higher in the columns and higher Kds would be expected.
2. In batch tests it is rarely possible to investigate metal soprtion under high metal concentrations because the low solubilities of trace metals causes precipitation to occur. In the MTD experiments, extensive precipitation occurred for loadings greater than 10 mg/Kg. By contrast, analysis of the column waste demonstrates loadings in excess of 1000 mg/kg for zinc in some columns. The validity of the low concentration sorption models at higher loadings/concentrations therefore needs to be assessed.
3. In batch tests, the regular agitation, and slurry consistency of the waste will encourage reasonable mixing and, therefore, relatively homogenous conditions. By contrast, waste-leachate equilibria in the columns will be highly heterogeneous, with leachate being distributed between isolated impermeable areas and interconnected preferential flow paths.
4. Differences in leachate chemistry (eg. pH, alkalinity, VFA concentrations) between the batch and column experiments.

The factors above may well be very important in controlling metal concentrations in leachate. Although this pilot study shows some cause for encouragement, it is therefore considered unwise to attempt to use this relatively simple sorption model to predict metal leachate concentrations in landfill based on different metal loadings.

B.7 SUMMARY

In order to assess the long term stability of heavy metals in landfills, it is essential that the full range of processes controlling metal retention and mobility are understood. The primary pupose of the modelling studies was to improve understanding of the controlling processes and to predict whether landfill maturation, and in particular the potential return of aerobic conditions, might lead to a significant release of metals from landfill. The main results of the modelling studies are summarised below. A more detailed discussion of the implications of the modelling and experimental programmes is included in the main report.

- This study represents one of the first attempts to apply the well-established modelling techniques developed through research into metal behaviour in soils and groundwaters to the landfill context.
- Modelling has been carried out on a range of leachates from the experimental programme. The leachates included: immature acetogenic leachates, rich in chloride and VFAs, from Pitsea landfill; mature methanogenic leachates from the initial CAMR columns and "supermature" post-methanogenic, low chloride leachates from the late stages of the CAMR experiments. Comparison of parameters such as chloride and fatty acids (shaded in grey) with generic UK leachates indicates that the analyses selected for modelling are representative of a range of landfill maturities.
- Aqueous speciation controls the toxicity of some metals and, by influencing processes such as precipitation and sorption, also controls metal mobility. For zinc and cadmium, speciation was found to be dominated by carbonates and the divalent metal ion for all leachate types, with chloride complexation being important for cadmium in immature leachates. Chromium was found to be strongly complexed with organics in immature leachates, potentially leading to enhanced mobility compared with hydroxide dominated speciation in mature leachates.
- Solubility modelling studies for cadmium indicate that sulphide precipitation is likely to be important in immobilising cadmium in anaerobic landfill. Under aerobic conditions, predicted solubility limits are around an order of magnitude higher than measured leachate concentrations (generally below 0.01 mg/l), suggesting that other mechnisms are limiting cadmium release.
- Solubility results for zinc also suggest that sulphide precipitation is likely to be an important retention mechanism in anaerobic landfill. Under aerobic conditions, the predicted solubility limits for zinc carbonate are close to measured leachate concentrations (generally below 1 to 2 mg/l) suggesting that precipitation of carbonates or less soluble silicate or iron oxide phases may be limit zinc release.
- Chromium does not form a simple sulphide. Modelling results for chromium indicate that irrespective of redox conditions, in immature leachates solubility is enhanced due to organic complexation whereas in mature leachates with low organic contents, chromium hydroxide

solubility is predicted to be very low and is likely to contribute to the immobilisation of chromium in landfill.

- It is likely that adsorption is a major component of metal retention in landfill and prevents the release of metals at concentrations below their solubility limits. Perhaps due to the highly heterogeneous nature of landfill material, very few attempts have been made to model sorption processes in landfill. The pilot study reported here makes some significant steps in translating and applying existing models to landfill systems. Although the models represent an improvement on the use of Kds, they cannot currently be used to predict "safe" operational metal loading ratios.

B.8 REFERENCES

Allison, J. D., Brown, D.S. and Novo-Gradac, K. J., (1991) MINTEQA2/PRODEFA2 A geochemical assessment model for environmental systems. Version 3.0 User's Manual, US Environmental Protection Agency Report EPA/600/3-91/021

Alloway, B. J. (1990) Heavy Metals in Soils, Blackie and Son, Glasgow.

Arthur, D.J. and Read, D. (1996) PHREEQE 96 Theoretical Overview. UK DoE HMIP Draft Report.

Christensen, T.H. (1989) Cadmium soil sorption at low concentrations: VIII. Correlation with soil parameters. *Water, Air and Soil Pollution* **44,** 71-82.

Dzombak, A. and Morel, MM. (1990) Surface complexation modelling: Hydrous Ferric Oxide, Wiley, New York.

Falck, W.E. and Read, D. (1996) CHEMVAL II: A co-ordinated research initiative for evaluating and enhancing chemical models used in radiological risk assessment. Final report on the thermodynamic database. CEC EUR Report 16897.

Ivanovich, M., Gardiner, M.P., Baumann, T., Delakowitz, B., Fruhstrofer, P., Klein, T., Niessner, R., Kim, J., Tellam, J.H., Lloyd, J.W., Kleinert, U., Read, D., Wilcox, D., Ross, D. and Thomas J.T. (1996) The role of colloids in the transport of pollutants in shallow groundwaters: development of monitoring and assessment procedures. CEC Contract EV5V-CT-92-0228 Draft Report.

Lindsay, W. L. (1979) Chemical equilibria in soils. Wiley, New York.

Palmer, C.D. and Puls, R.W. (1994) Natural attenuation of hexavalent chromium in groundwater. US Environmental Protection Agency Ground Water Issue EPA/540/s-94/505

Parkhurst, D.L., Thorstenson, D.C. and Plummer, L.N. (1980) PHREEQE - a computer programme for geochemical calculations. US Geological Survey Report No. PB81 167801.

Parkhurst, D.L. (1995) User guide to PHREEQC – A computer program for speciation, reaction-path, advective transport, and inverse geochemical calculations. US Geological Survey, Water Resources Investigations Report 95-4227

Read, D ed. (1997) CHEMVAL II: A co-ordinated research initiative for evaluating and enhancing chemical models used in radiological risk assessment. Final report. CEC EUR Report 16648.

Robinson, H.D., (1995) A review of the compostion of leachates from domestic wastes in landfill sites. Report No CWM/072/95 UK Department of the Environment Waste Technical Division, London.

Ross, S. M. (1994) Toxic metals in soil-plant systems. John Wiley & Sons, Chichester, UK.

Sposito, G. (1994) Chemical Equilibria and Kinetics in Soils, Oxford University Press, New York.

Tipping, E. and Hurley, M.A. (1992) Modelling the binding of cations by humic substances, UK Department of the Environment Report No. DoE/HMIP/RR/089.

Tipping, E and Woof, C (1990) Humic substances in acid soils: modelling their release to the soil solution in terms of humic charge. Journal of Soil Science, 41, 573-586.