Modern landfill leachates – quality and treatment

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by

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Abstract

Waste management in Europe has changed, mainly as a result of stricter regulations, most notably the European Landfill Directive 1999/31/EC. In Sweden, landfill tax and a ban on the landfilling of waste with total organic carbon content over 10 % have diverted large amounts of waste from landfills. The biogeochemistry of landfills has changed due to their reduced organic content. The research presented in this thesis aimed at improving understanding of leachate quality in modern landfills. Biodegradation and leaching tests were employed on wastes typical of a waste management system shifting away from landfilling. Multivariate data analysis using principal component analysis and canonical correlation analysis was employed to identify processes governing leachate quality and relations between leachate parameters. As heavy metals are expected to be relatively more pronounced in modern landfills, sorption to granular activated carbon, bone meal and iron fines was evaluated as a means of removing heavy metals from leachate.

The main difference in two leachates from landfills with less than 10 % organic carbon in the waste in relation to leachates from older landfills containing municipal solid waste was the extremely low ammonium content. Very low dissolved organic carbon content was also observed. Leaching of heavy metals in the same order of magnitude as in MSW landfills was observed in modern landfills. The results further indicate that a certain degradation potential must be expected, even in the carbon poor wastes deposited in modern landfills. Therefore reducing conditions will be likely to occur in the landfills. Although landfill gas formation will be low, degradation is likely to significantly affect the biogeochemical conditions, thus affecting metal leaching and rendering it relatively similar to that in municipal solid waste landfills. However, since the amounts of biodegradable organic matter are smaller they will be depleted sooner than in municipal solid waste landfills. As a result, the long term differences may be greater.

The multivariate data analysis identified variation in the concentration of salts as the most important process governing leachate quality. This variation had various causes, including dilution, depletion and varying input materials. Redox potential was also identified as an important process. In the cases where samples were taken before and after treatment, the effect of the treatment strongly influenced the results. All the sorption materials studied had the potential to remove heavy metals, but none was effective against all the metals in the leachate. They also all had the drawback of releasing unwanted substances into the leachate. This illustrates the importance of site-specifically evaluating all treatments and analysing a large number of substances in the leachates, not just those targeted by the treatment.

The main pollutants to be expected in modern landfills with only small amounts of organic matter will probably be inorganic, e.g. heavy metals. While the organic matter emitted by older landfills can be changed into more or less inert forms, metals can never be destroyed, just concentrated, diluted or moved to another medium. Enhancing biodegradation and flushing pollutants by allowing water to infiltrate into landfills is advocated as a sustainable management option for municipal solid waste landfills. However, in the case of mainly inorganic landfills, containment aimed at keeping the metals in the landfills for as long as possible rather than dispersing them into the environment might be a better option.

Key words: Biodegradation; European Landfill Directive; Heavy metals; Landfill leachate; Leaching tests; Multivariate data analysis; Organic matter; Sorption filters

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Cover: Landfill leachate pond at the Högbytorp waste management site (run by Ragn-Sells Avfallsbehandling AB) outside Bro, Sweden

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POPULÄRVETENSKAPLIG SAMMANFATTNING

Deponier (soptippar) har förändrats kraftigt de senaste decennierna. Detta beror främst på ändrad lagstiftning vilken i sin tur till stor del bygger på en önskan att skydda miljön. Dock har lagstiftningen implementerats utan riktig kännedom om dess konsekvenser för utsläppen från deponier på lång sikt. För att öka förståelsen för konsekvenserna genomfördes det forskningsprojekt som beskrivs här. Resultaten visar att även om utsläppen av organiskt material och näringsämnen är mycket mindre ur moderna deponier så är skillnaderna mellan äldre och nyare deponiers inre inte så stora som kunde förväntas, i alla fall inte på kort sikt. Detta gör att utsläppen av tungmetaller blir i ungefär samma storleksordning.

Deponier orsakar utsläpp till luft och vatten. Fram till för inte så länge sedan slängdes vad som helst på en deponi, till exempel stora mängder hushållsavfall. Som de flesta vet så innehöll en vanlig soppåse en stor andel nedbrytbart material, bland annat matrester. När detta bryts ned i deponin förbrukas syre och därför är de flesta deponier syrefria. När organiskt material bryts ned i den syrefria miljön bildas så kallad deponigas som är en växthusgas. Vatten som kommer i kontakt med avfallet i deponin kallas för lakvatten och innehåller en mängd olika föroreningar. De största miljöproblemen med lakvatten har hittills varit orsakade av organiskt material och salter, inklusive näringsämnen. För att komma tillrätta med miljöproblemen har lagstiftarna förbjudit deponering av organiskt avfall. Eftersom det är biologiska nedbrytningsprocesser som styr lakvattnets sammansättning i gamla deponier så kan moderna deponier med små mängder organiskt material förväntas vara väldigt annorlunda. På vad sätt de är annorlunda var huvudfrågan för det aktuella forskningsprojektet.

Resultaten visar att det trots allt går att uppmäta en liten nedbrytningspotential i sådant avfall som hamnar på moderna deponier. Därför kan syrefria förhållanden uppstå även där. Utsläppen av deponigas kommer troligen inte att bli särskilt stora, men syrebristen verkar leda till att lakvattnets kemi inte blir så annorlunda som förväntat. Läckaget av tungmetaller påverkas kraftigt av syretillgången, och det har funnits farhågor om att utsläppen av metaller skulle vara mycket större i moderna deponier. Så verkar dock inte vara fallet; de verkar bli ungefär lika stora eller något större. Forskningen visar att vissa metaller kan komma att ha förhöjda halter i lakvattnet även efter lång tids urlakning, så i likhet med äldre deponier kan de moderna förväntas vara en belastning under lång tid vilket i deponisammanhang kan betyda decennier, århundraden eller ännu längre.

Den största skillnaden mellan lakvatten från moderna och gamla deponier är de låga halterna av organiskt kol och ammonium i de moderna. Ammonium betraktas som den allvarligaste föroreningen från gamla deponier på lång sikt, men i vissa moderna deponier är dess halter extremt låga. Det betyder att i framtiden behöver reningen av lakvatten inte längre fokusera på organiskt material och näringsämnen vilket varit vanligast hittills. I stället kan den fokusera på att ta hand om till exempel tungmetaller. En del av studien handlade om att rena lakvatten från tungmetaller med olika filter. Aktivt kol, benmjöl och järnfilspån visade sig kunna avskilja många metaller, men inget material kunde ensamt ta bort alla. En kombination av filtermaterial skulle kunna vara ett relativt billigt sätt att rena framtidens lakvatten, men det är viktigt att tänka på att det material som fungerar för ett vatten kanske inte fungerar för ett annat.

ABSTRACT

Waste management in Europe has changed, mainly as a result of stricter regulations, most notably the European Landfill Directive 1999/31/EC. In Sweden, landfill tax and a ban on the landfilling of waste with total organic carbon content over 10 % have diverted large amounts of waste from landfills. The biogeochemistry of landfills has changed due to their reduced organic content. The research presented in this thesis aimed at improving understanding of leachate quality in modern landfills. Biodegradation and leaching tests were employed on wastes typical of a waste management system shifting away from landfilling. Multivariate data analysis using principal component analysis and canonical correlation analysis was employed to identify processes governing leachate quality and relations between leachate parameters. As heavy metals are expected to be relatively more pronounced in modern landfills, sorption to granular activated carbon, bone meal and iron fines was evaluated as a means of removing heavy metals from leachate.

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PAPERS

Appended papers

This thesis is based on the following papers, which will be referred to in the text by their Roman numerals. The papers are appended at the end of the thesis.

I. **H. Modin**, M. van Praagh and K. M. Persson. Multivariate data analysis of regular landfill leachate monitoring data. Waste Management (submitted).

II. M. van Praagh, J. Heerenklage, E. Smidt, **H. Modin**, R. Stegmann and K. M. Persson, 2009. Potential emissions from two mechanically-biologically pretreated (MBT) wastes. Waste Management 29 (2), 859-868.

III. **H. Modin**, V. Pallier, G. Feuillade-Catahlifaud, E. Redon and K. M. Persson. Principal component analysis to correlate waste degradation to specific analytical parameters in landfill leachate: Application to landfills in France and Sweden. Journal of Hazardous Materials (submitted).

IV. **H. Modin**, M. van Praagh, K. M. Persson and H. Palm. Heavy metal mobility in waste from a landfill with low organic carbon content. Journal of Hazardous Materials (submitted).

V. **H. Modin**, L. Gustavsson and K. M. Persson. Toxicity in landfill leachate during treatment studied with multivariate data analysis. Journal of Environmental Management (submitted).

VI. **H. Modin**, K. M. Persson, A. Andersson and M. van Praagh, 2011. Removal of metals from real landfill leachate by sorption to activated carbon, bone meal and iron fines. Journal of Hazardous Materials 189, 745-754.

Author's contributions to the appended papers

I. The author planned the work together with the co-authors, performed the statistical analysis and speciation modelling together with the co-authors, analysed the results together with the co-authors and wrote the paper together with the co-authors.

II. The author assisted the co-authors in planning the study, performed the experimental work that was done in Hamburg with assistance from the co-authors and assisted in analysing the results and writing the paper.

III. The author performed the experimental work related to the Swedish landfills with assistance from the co-authors, planned the statistical modelling together with the co-authors, performed the statistical analyses, analysed the results together with the co-authors and wrote the paper together with the co-authors.

IV. The author planned the study together with the co-authors, assisted in the experimental work, analysed the data together with the co-authors and wrote the paper assisted by the co-authors.

V. The author planned the statistical analysis together with the co-authors, performed the statistical analysis, analysed the results together with the co-authors and wrote the paper together with the co-authors.

VI. The author planned the study together with the co-authors, performed the experimental work, interpreted the results together with the co-authors, and wrote the paper assisted by the co-authors.

Related publications not included in this thesis

Journals and Magazines

H. Modin, M. van Praagh and K. M. Persson, 2008. Kvalitet i nya deponiers lakvatten – resultat från Renovas deponi Fläskebo (Quality in leachate from new landfills – results from Renova's landfill Fläskebo). Vatten 64(4), 283-290. (In Swedish)

Conference papers

J. Heerenklage, E. Smidt, E. Redon, M. van Praagh, **H. Modin**, and R. Stegmann, 2008. Huminstoffbildung während der mechanisch-biologischen Vorbehandlung von Restabfällen (Formation of humic substances during mechanical and biological pre-treatment of waste). Abfallforschungstage 2008, Hannover, Germany. (In German)

H. Modin and K. M. Persson, 2008. Sorption filters for removal of heavy metals from landfill leachate. Waste 2008, Waste & Resource Management - A Shared Responsibility, Stratford-upon-Avon, UK.

H. Modin, M. van Praagh, and K. M. Persson, 2009. A modern landfill - experiences from Fläskebo landfill, Sweden. Sardinia 2009, Twelfth International Waste Management and Landfill Symposium, CISA, Cagliari, Italy.

K. M. Persson, **H. Modin**, A. Andersson and M. van Praagh, 2009. Removing metals form leachate: When is sorption the solution? Sardinia 2009 Twelfth International Waste Management and Landfill Symposium, CISA, Cagliari, Italy.

H. Modin, H. Palm, M. van Praagh and K. M. Persson, 2010. Lab Scale Simulation of a Leak in a Landfill Cover. Linnaeus ECO-TECH '10, Kalmar, Sweden.

A. Ilyas, **H. Modin**, K. M. Persson and M. Persson, 2011. Quality and biodegradation of residual organic matter in MSWI bottom ash. Sardinia 2011, Thirteenth International Waste Management and Landfill Symposium, CISA, Cagliari, Italy.

H. Modin, H. Palm, M. van Praagh and K. M. Persson, 2011. Leaching test using samples from a modern, carbon-poor landfill. Sardinia 2011, Thirteenth International Waste Management and Landfill Symposium, CISA, Cagliari, Italy.

Abstracts

H. Modin, K. M. Persson, A. Ilyas, and M. van Praagh, 2010. Organic matter in carbon poor landfills. Sixth Intercontinental Landfill Research Symposium, Kiroro Resort, Hokkaido, Japan.

Reports

H. Modin, 2008. Sorption filters for removal of heavy metals from landfill leachate – Laboratory experiments with leachate from Sysav's landfill Spillepeng. Kildesamarbetet (The Source Partnership). Water Resources Engineering, Lund University, Lund, Sweden.

Avfall Sverige, (Swedish Waste Management), 2009. Kvalitet i nya deponiers lakvatten - exemplet Fläskebo (Quality in leachate from new landfills - the example of Fläskebo). Deponeringssatsningen (The landfilling undertaking): D2009:03. Avfall Sverige, Malmö, Sweden. (In Swedish).

Avfall Sverige, (Swedish Waste Management), 2009. Kontroll av lakvattenrening genom toxicitetstester statistiskt korrelerat med kemisk-fysikaliska mätningar (Control of leachate treatment through toxicity tests correlated with physico-chemical measurements). Deponeringssatsningen (The landfilling undertaking): D20011:04. Avfall Sverige, Malmö, Sweden. (In Swedish).

Master theses supervised by the author

H. Palm, 2010. The future of landfills. Leaching and degradation tests on waste from Fläskebo landfill. Water Resources Engineering. Lund University, Lund, Sweden.

C. Mårtensson, 2010. Geokemisk modellering av genomförda nedbrytnings- och urlakningstester av deponerat avfall från en modern deponi (Geochemical modelling of degradation and leaching tests on waste landfilled in a modern landfill). Centre for Environmental and Climate Research, Lund University, Lund, Sweden. (In Swedish)

ABBREVIATIONS AND SYMBOLS

BM	Bone meal
BOD_5, BOD_7	Biological oxygen demand measured over 5 or 7 days, respectively
CCA	Canonical correlation analysis
COD	Chemical oxygen demand
C&D waste	Construction and demolition waste
DAX-8 resin	DAX-8 resin, a non-ionic, slightly polar polymeric absorbent
DOC	Dissolved organic carbon
DSC	Differential scanning calorimetry
DTG	Differential thermogravimetry
EC	Electrical conductivity
EC_{50}	Effective concentration in per cent that causes 50 % effect in a toxicity test
EU	European Union
FA	Fulvic acids, humic substances soluble at any pH
FT-IR	Fourier transform infrared spectroscopy
GAC	Granular activated carbon
GP_{21}	Anaerobic gas formation potential measured over 21 days
HA	Humic acids, humic substances soluble in pH above 2
HPO	Hydrophobic substances, absorbed in a DAX-8 resin
HPI	Hydrophilic substances, neither absorbed in DAX-8 nor XAD-4 resin
HS	Humic substances
IC	CO_2 ion current mass spectrometry
IF	Iron fines
K	Permeability
L/S	Liquid to solid ratio
LoI	Loss on ignition, a measure of the organic content in waste
MBT	Mechanical and biological treatment
MBT waste	Mechanically and biologically treated waste
MSW	Municipal solid waste
MSWIBA	Municipal solid waste incineration bottom ash
MVDA	Multivariate data analysis

MWWTP	Municipal waste water treatment plant
N_{tot}	Total concentration of nitrogen
PCA	Principal component analysis
PC	Principal component
RA_4	Aerobic respiration activity measured as oxygen consumption over 4 days
SUVA	Specific ultraviolet absorption, ratio of the absorbance at 254 nm to the dissolved organic carbon concentration
TOC	Total organic carbon
TPH	Transphilic substances, absorbed in XAD-4 resin
TU	Toxic unit. A high number implies high toxicity. 1 TU = $1/EC_{50}$
XAD-4 resin	XAD-4 resin, a non-ionic, non-polar polymeric absorbent

CONTENTS

1 INTRODUCTION

1.1 Background

For a long time, landfilling was the most common waste management option. In many European countries, not to mention the rest of the world, this is still the case (EEA 2009; Laner et al. 2012). In several respects landfilling is the opposite of sustainability. Not only is it a waste of resources but landfills as such constitute a health hazard and an environmental burden (Ettler et al. 2008; Öman and Junestedt 2008; Kalčíková et al. 2011). Organic waste biodegradation in landfills creates a greenhouse gas called landfill gas. Water that enters the landfill forms leachate which can carry pollutants to the surroundings. Environmental problems related to leachate include groundwater pollution and oxygen depletion and ecotoxicity in surface waters (Kjeldsen et al. 2002; Pablos et al. 2011).

In order to decrease the environmental impact of landfills, most countries regulate their management. During recent decades, the European Union (EU) has issued several pieces of legislation on waste management and landfilling (EEA 2009). Of most importance for landfills is the Waste Framework Directive (75/442/EEC amended, later replaced by 2008/98/EC) with its hierarchy of waste management options stating that recycling and reuse are to be prioritised. The EU Landfill Directive (1999/31/EC) requires, among other things, all waste to be pre-treated prior to landfilling and restricts the landfilling of organic waste. It also sets requirements on the construction of landfills, e.g. all landfills must have a natural or constructed geological barrier to prevent exchange of water with the surroundings.

Together with an increasing interest in utilising the resources found in waste, such as energy and recyclable materials, the new regulation has led to a transformation of waste management in general and landfill management in particular. In Sweden, for example, the percentage of municipal solid waste (MSW) that goes to landfill has decreased from 35 % in 1995 to 1 % in 2010. (EEA 2009; Avfall Sverige 2011)

The diversion of waste from landfills has led to the closure of many landfill sites in Sweden and elsewhere (EEA 2009; Avfall Sverige 2010). The types of waste that go to landfill have also changed. The concentration of organic matter has decreased and its degradability is reduced due to pre-treatment (EEA 2009). The water content has also changed towards drier waste (van Praagh 2007).

The changes in waste management have potential environmental impacts (van Praagh 2007; Manfredi et al. 2010). Gas formation may become negligible in landfills complying with the new legislation, making leachate the major emission pathway. The decrease in organic content means that inorganic pollutants, e.g. heavy metals, may become relatively more pronounced in the leachate. Although some advances have been made, see e.g. van Praagh (2007), Parker et al. (2007), Kumpiene et al. (2011) and Scharff et al. (2011), knowledge of the emission potential of altered landfills is still incomplete.

Landfill leachate is a very complex mixture containing many types of pollutant with different and varying concentrations. Mixing of leachates from different parts of the landfill before sampling and large variations further complicate the picture (Kängsepp and Mathiasson 2009; Kalčíková et al. 2011). Traditional, uni- and bivariate statistics are therefore often insufficient for studying leachate data and multivariate tools are necessary (Ecke et al. 1996; Ludvigsen et al. 1996; van Praagh 2007).

In Sweden, the most common options for landfill leachate treatment are various biological processes, either in a municipal waste water treatment plant (MWWTP) or on the landfill site (Avfall Sverige 2007). The main targets of biological processes are organic matter and nutrients, as opposed to heavy metals, although some immobilisation of the latter may occur (Avfall Sverige 2007). As the organic character of leachates will become less pronounced, the focus of treatment will probably have to be shifted towards inorganic parameters, such as metals.

1.2 Objective and scope

The objective of the research described in this thesis was to investigate the future environmental impact of landfills with respect to heavy metals and organic matter. This focus was chosen since (i) changes in the quantity and quality of organic matter are among the major changes expected in landfills due to the differences in waste management and (ii) heavy metals are likely to be among the pollutant groups of most concern in future landfill leachates.

Physical, chemical and biological characterisation methods and multivariate data analysis were employed and the following main questions were addressed:

- How will the emission potential from modern landfills differ compared to that from conventional landfills with regard to heavy metals and the emissions stemming from organic matter?
- What parameters govern leachate quality in conventional and modern landfills and which ones are important for the leaching of heavy metals?
- What type of information and insights can be gained by studying landfill leachate data with multivariate data analysis?
- Can sorption filters be an option for removing heavy metals from landfill leachate?

The research focused on landfills within the legal framework of the European Union but is to a large extent also relevant for landfills in other parts of the world. Sweden is in focus, but German and French landfills were included for comparison purposes. Although relevant for emissions from landfills, neither liner and capping systems nor the geological barrier are within the scope of this thesis, nor are recipient-related issues. Although one part of the research concerns treatment methods, presenting an exhaustive assessment of treatment alternatives is beyond the scope of this thesis. The research mainly focused on heavy metals and bulk organic matter. Specific organic pollutants were not addressed but should be included in future research.

1.3 Thesis structure and appended papers

This thesis is based on the research presented in the six appended papers. After the introduction in Chapter 1, the theoretical background of the appended papers is presented in Chapter 2 together with references to recent research. Thereafter, an overview of the methods and data sets used as well as the studied landfills is presented in Chapter 3. In Chapter 4 the main results from the appended papers together with a few findings not presented in the papers are summarised, discussed, evaluated and related to current landfill management and regulation. Finally, in Chapter 5, conclusions, implications, unresolved questions and suggestions for future research are presented.

The main methods used and results arrived at are included in this thesis but a more detailed account can be found in the appended papers, referred to by bold Roman numerals. Here follows a short description of the papers.

Landfill operators are legally required to monitor leachate quality, which generates large amounts of data. In **Paper I**, the use of multivariate data analysis (principal component analysis and canonical correlation analysis) for evaluation of data from regular leachate monitoring is described. Data from seven landfill cells were analysed in order to find important processes for leachate quality and parameters that can be related to heavy metal concentrations. Multivariate data analysis (MVDA) was further used to compare the different cells. One of the landfills studied was the first to be entirely constructed in accordance with the Swedish implementation of the EU Landfill Directive.

Paper II describes a study of the emission potential of two types of waste typical of the waste management system after national implementation of the EU Landfill Directive. One type of waste was from Sweden and the other from Germany. Potential emissions caused by leaching and degradation were studied. MVDA was employed to compare the different parameters used to assess the biological stability of the waste and to identify relations between the concentrations of heavy metals and organic matter.

Fractionation of leachate organic matter based on hydrophobicity has been developed as a tool for assessing the state of biological stability in municipal solid waste landfills. The study described in **Paper III** employed this method on mixed waste landfills from Sweden and France, including two modern landfills with low total organic carbon content. MVDA, as developed in **Paper I**, was used to study how the method could be applied to modern compared to MSW landfills.

Refining the emission potential investigations from **Paper II**, results of leaching tests on waste material in a modern landfill that only accepts waste with less than 10 % total organic carbon are presented in **Paper IV**. The aim of the study was to increase understanding of how a residual waste landfill with low organic content can differ from an MSW landfill in terms of heavy metal leaching. Batch and continuous leaching and biodegradation tests were employed.

In the study presented in **Paper V,** pre and post pilot scale leachate treatment quality data were evaluated by means of MVDA using the experiences from **Papers I** and **III**. The aim was both to

relate chemical parameters, such as heavy metals, to bioassays, and to find a suitable battery of tests to evaluate the treatment.

Paper VI describes a study of removal of metals from landfill leachate, in which three different materials: granular activated carbon, bone meal and iron fines were evaluated for their capacities to sorb heavy metals.

2 THEORETICAL BACKGROUND

This chapter provides the background and a literature review as a basis for the discussions about landfilling in the following chapters. It is not intended to present a full account of the state of the art, but rather the necessary facts to familiarise the reader with the context in which the investigations were performed.

2.1 Environmental issues pertaining to landfills

Conventional landfills contain a mixture of different types of waste, including municipal, industrial, and construction and demolition waste (C&D waste), with various organic and inorganic materials and a wide range of physical and chemical properties (Christensen et al. 2001; Öman and Junestedt 2008). MSW typically contains a substantial fraction of organically degradable material, and therefore most conventional landfills hold significant amounts of organic matter (Andreas et al. 1999; Berthe et al. 2008; Valencia et al. 2009).

The two main emission pathways for pollutants from landfills are gas and leachate. Landfill gas is formed by the degradation of organic matter. Its main constituents are carbon dioxide and methane, both of which are greenhouse gases, with methane being over 20 times more potent than CO_2 on a one hundred year time scale (Ramaswamy et al. 2001). Degradation of organic matter can also cause landfill settlement, which, if uneven, can damage the landfill cover and cause increased infiltration and leachate generation (Machado et al. 2008). According to the Landfill Directive (1999/31/EC), leachate is defined as any liquid percolating through the deposited waste and emitted from or contained within a landfill. A combination of physical, chemical and microbial processes transfers pollutants from the waste material to the leachate making it a complex solution containing the following main groups of pollutant: dissolved organic matter, inorganic macro components, heavy metals, xenobiotic organic compounds and pathogens (Kjeldsen et al. 2002; Schiopu and Gavrilescu 2010).

For many years waste was disposed of in dumps with no liner or pollution control (Lyngkilde and Christensen 1992; Bjerg et al. 1995). Pollution of surface and groundwater is considered the most severe environmental impact of landfills (Kjeldsen et al. 2002; Scharff et al. 2011). Organic matter may cause oxygen depletion in the recipient (Barlaz et al. 2002; Kjeldsen et al. 2002). Many heavy metals and xenobiotic compounds are toxic (Jurkonienė et al. 2004; Pivato and Gaspari 2006; Avfall Sverige 2007). Inorganic macro components include nutrients that can cause eutrophication, and a range of inorganic compounds common in landfill leachate, e.g. chloride and ammonia, are toxic to many fresh water species (Barlaz et al. 2002; Waara et al. 2008; Pablos et al. 2011).

2.2 Phases of degradation

The environment within a landfill depends on various physical, chemical and biological processes. In spite of large differences in water content, waste composition and management, it is possible to

make generalisations and identify a set of typical landfill processes (Kjeldsen et al. 2002; Robinson et al. 2005). In a landfill with significant amounts of organic waste, biodegradation of organic matter is the dominant process that governs the landfill biogeochemistry. The transformation of organic matter proceeds through a number of different phases that are relatively similar between MSW landfills, although heterogeneities exist. For example landfill cells are sometimes filled with different types of waste over the course of several years. Furthermore, the availability of water can vary a great deal within a landfill. These heterogeneities mean that different parts of the landfill can be in different phases of degradation at the same time. The delimitation between and naming of the phases is not always consistent between publications. In this thesis the following names will be used:

I. Aerobic phase
II. Acid phase
III. Initial methanogenic phase
IV. Stable methanogenic phase
V. Second aerobic phase

In the following, the phases and their typical leachate and gas composition will be described. The description is for the most part based on publications by Åkesson (1997), Bozkurt et al. (2000), Kjeldsen et al. (2002), Barlaz et al. (2002) and Valencia et al. (2009).

When deposited, the waste contains oxygen and the landfill is in phase I. Microorganisms that thrive in oxygen-rich conditions start to degrade the organic matter. The oxygen is depleted relatively quickly, and when new waste is placed on top or the landfill is covered, no additional oxygen can reach the waste. The aerobic phase typically lasts for only a few hours or days and aerobic degradation of organic matter leads to a high rate of CO_2 formation.

When the oxygen is depleted anaerobic microorganisms take over. Initially hydrolytic microorganisms are the most active, degrading large organic molecules into monosaccharides, alcohols, carboxylic acids, etc. This leads to a build-up of volatile fatty acids causing the pH to decrease, sometimes down towards pH 5, and the landfill enters phase II, the acid phase. The chemical oxygen demand (COD) and biological oxygen demand (BOD) in the leachate are high, and at between 0.7 and close to 1, the BOD/COD ratio is also high. The acid leachate enhances dissolution and leads to high concentrations of pollutants, such as heavy metals. Release of ammonium can be elevated due to ion exchange with H^+ (Pivato and Gaspari 2006). H_2 appears in the gas.

Phase II typically lasts for months to years and ends when microorganisms degrading the intermediate products into CO_2, H_2 and acetate become more active and the pH increases. Methanogenic bacteria that are sensitive to low pH thrive and produce methane from these molecules. During phase III, the initial methanogenic phase, most leachate concentrations decrease. Methane production increases until it reaches a relatively stable value.

During phase IV the landfill enters a stable state of methanogenesis with only gradual changes in gas and leachate composition. Landfill gas typically consists of 50–70 % methane and 30–50 % carbon dioxide. The pH during this phase is neutral or slightly alkaline. Ammonium is formed due to degradation of organic matter and typically accumulates in the leachate, as it has no biodegradation mechanism under methanogenic conditions. The rate of ammonium release is relatively low (Pivato and Gaspari 2006), and thus ammonium is expected to be the most significant long-term pollutant at landfills (Kjeldsen et al. 2002). The BOD/COD ratio is also low, approaching 0.1, because most degradable dissolved organic matter is consumed by the microbial population. However, concentrations of more stable organic molecules, such as humic and fulvic acids, increase.

After years, or even decades or centuries, when the organic matter that is degradable by anaerobic microorganisms has been depleted, the formation of landfill gas will decrease and eventually the gas pressure within the landfill will equal the atmospheric pressure. At that point oxygen begins to enter the landfill by diffusion and advection, marking the start of phase V, the second aerobic phase. This phase has rarely been observed, but predicted. It probably consists of several different phases, but due to uncertainty in the data they are not separated here. Initially, the oxygen is consumed by microbes that oxidise the remaining organic matter and produce stable molecules such as humic substances (HS). At this stage, CO_2 is formed by the oxidation, but as degradation ceases, the gas composition approaches that of the atmosphere. Depending on various factors such as the quality of the cover and the water content of the landfill, the time it takes for a landfill to become completely oxidised varies between hundreds and tens of thousands of years.

2.3 Inorganic landfill processes

In landfills with mainly inorganic waste, the degradation of organic matter will be less significant than physical and chemical processes. A Dutch pilot study of landfills with mainly inorganic waste by van Zomeren et al. (2005) revealed that, in spite of a relatively heterogeneous waste mixture, it was possible to define the leaching mechanisms relatively accurately. In the case of constituents that are easily dissolved, such as Cl and K, leaching was controlled by availability, while for elements such as Cu and Pb, it was governed by solubility. A dissolved organic carbon (DOC) leaching curve similar to Cl was observed (Scharff and Jacobs 2005).

It has been suggested that, at the end of the methanogenic phase, when most of the organic carbon has been degraded, organic waste landfills behave in much the same way as inorganic ones (Mathlener et al. 2006). This could also apply to certain hazardous waste landfills (Scharff et al. 2011).

2.4 Water in landfills

Among the most important factors for the environmental impact of a landfill is the availability of water. The water content affect the degradation of organic matter, and water is crucial for leachate formation. (Bengtsson et al. 1994; Reinhart and Al-Yousfi 1996; Bendz 1998) The chief sources of water in a landfill are precipitation and fluid present in the waste when it was landfilled

(Bengtsson et al. 1994). Water can also be added as part of landfill management, e.g. by leachate recirculation (Reinhart and Al-Yousfi 1996; Berthe et al. 2008). Surface and groundwater intrusion also occur but are typically of less significance (Bendz and Bengtsson 1996; Yuen et al. 2001). In an active landfill, or one with a simple cover that is a few years old, water infiltration is generally higher than in natural fields (Bendz and Bengtsson 1996). On the other hand, in landfills with modern covers, infiltration can be as small as a few per cent of precipitation, even after 20 years (Yuen et al. 2001; Berger et al. 2009).

Percolation of leachate through a landfill is very heterogeneous due to channels or macro pores with much higher hydraulic conductivity than the surrounding matrix (Bengtsson et al. 1994; Bendz 1998; Capelo and de Castro 2007). Horizontal barriers, e.g. plastic sheets and low permeability zones, make horizontal flow important (Rosqvist and Destouni 2000; Fellner and Brunner 2010). The very uneven distribution of the flow can cause large parts of the landfill to be bypassed and left dry, thus only part of the landfill contributes to the leaching (Yuen et al. 2001; Huber et al. 2004; Scharff et al. 2011).

2.5 Landfill management strategies

Various strategies have been proposed to minimise environmental problems caused by landfills and to optimise landfill management. Landfilling of different wastes in separate cells was introduced in Sweden in the 1980s. At that time the main purpose was to optimise landfill gas production by creating co called biocells (see section 2.7). The waste with smaller gas generation potential would then be directed to other cells. However, at the end of the 1990s this type of separate landfilling was still only practiced in a few places in Sweden. (Åkesson 1997; Andersson et al. 2007) The major changes over recent decades were driven by political goals rather than technical developments or market demands. Therefore, landfilling has to be studied in a legislative context as much as in a technical one.

The overall goal of landfill strategies and legislation is *sustainability*. However, landfilling can be regarded as the opposite of sustainability and there has been some debate on the concept of "sustainable landfilling". It may thus be more appropriate to discuss the concept of *acceptable risk* (Scharff et al. 2011). Waste management strategies are different ways of achieving *final storage quality*, or *functional stability*: "(…) when the waste mass, post-closure, does not pose a threat to human health and the environment (…)" and the landfill no longer needs extensive management or monitoring (Lefebvre et al. 2007; Scharff et al. 2011). In most countries, the exact final storage quality has not been explicitly defined (Laner et al. 2012) but one suggestion is that the acceptance criteria for inert waste could be used as the leaching limit value since inert waste landfills do not need any containment measures (section 2.7) (Valencia et al. 2009; Scharff et al. 2011).

The European Landfill Directive (1999/31/EC) from 1999 has as its main goal to limit the environmental impact of landfills, e.g. by avoiding landfilling whenever possible, especially organic waste. Although several European countries including Sweden had already implemented national legislation with similar goals the Directive significantly impacted landfill management throughout Europe. Important regulations in the directive include:

- Targets for progressively reducing the amount of biodegradable municipal waste in landfills are implemented.
- Only pre-treated waste can be landfilled.
- Higher technical standards for landfills are required.
- Landfills are to be divided into categories for inert, non-hazardous and hazardous waste.

In 2002, the European Council also agreed landfill acceptance criteria (Council Decision 2003/33/EC). The directive is relatively flexible and allows the member states a certain degree of freedom. Therefore, although subject to the same legal framework, national implementation differs (van Praagh and Persson 2006; EEA 2009).

In Sweden a ban on the landfilling of organic waste was implemented through the Ordinance on the landfilling of waste (SFS 2001:512). However, in the Swedish Environmental Protection Agency's regulations and general guidelines on the management of combustible and organic waste (NFS 2004:4) there are exemptions, e.g. residue from incineration with less than 18 % total organic carbon (TOC) and heterogeneous waste with less than 10 % TOC may be landfilled. Due to the allocation criteria for landfills for hazardous and inert waste contained in the Swedish Environmental Protection Agency's regulations on landfilling, criteria and procedures for acceptance of waste at facilities for landfilling of waste (NFS 2004:10), the exemptions only applies to landfills for non-hazardous waste. Thus, in practice in Sweden there is a limit of 10 % TOC for the landfilling of non-hazardous waste that does not consist of incineration residues. If waste is classified as non-hazardous, leaching tests are not required before landfilling in Sweden (NFS 2004:10). Furthermore, an inorganic waste landfill does not need gas collection or monitoring (SFS 2001:512).

In Sweden, only 1 % of MSW was landfilled in 2010, while 49 % was incinerated, 36 % recycled, 14 % treated biologically and 1 % was hazardous waste (Avfall Sverige 2011). The most common types of landfilled waste include MSW incineration bottom ash (MSWIBA), residues from the sorting and separation of waste, unsorted waste and chemical waste (Naturvårdsverket 2010). The number of landfills has decreased dramatically. From approximately 300 active landfills accepting MSW in 1994, the number decreased to 76 in 2010 (Avfall Sverige 2010; Avfall Sverige 2011).

2.6 Pre-treatment

Pre-treatment is required prior to landfilling unless it is unnecessary. Many different methods can be employed, depending on the characteristics of the waste (Naturvårdsverket 2004). One method employed in many countries for pre-treatment of MSW is mechanical and biological treatment

(MBT). However, due to the 10 % limit on TOC in Swedish landfills MBT is not a viable pre-treatment option in Sweden.

MBT has several aims: to save landfill space, recover useful materials and stabilise biodegradable waste prior to landfilling in order to improve leachate quality and reduce the risk of settlement, landfill gas production and the need for aftercare. (Read et al. 2001; Binner 2002; Robinson et al. 2005)

The first step in MBT is the mechanical and generally consists of separation or sorting, shredding and sieving to recover metals and the high heating value fraction. The remaining material is treated biologically, typically for a period of two to eight months. Although composting is most common, anaerobic treatment is sometimes used. (Binner 2003; Robinson et al. 2005; Heerenklage et al. 2007; Bayard et al. 2008; Berthe et al. 2008)

Landfills containing mechanically and biologically treated waste (MBT waste) have improved leachate quality, most importantly because of the elimination of the acid phase. Leachate concentrations of organic matter and ammonium are lower than from MSW landfills, especially when the landfills are young. Perhaps most importantly, landfill gas generation is significantly reduced. However, some degradation potential still remains in the MBT waste and methane production which, although small, has been observed in pilot as well as full scale MBT landfills, demonstrate reducing conditions. The small gas volumes are can be difficult to recover. (Binner 2002; Robinson et al. 2005; Bayard et al. 2008; Berthe et al. 2008)

A common pre-treatment method for hazardous waste is to stabilise it prior to landfilling in order to decrease leaching. For example contaminants in certain types of hazardous waste can be immobilised by mixing them with a binding agent. This results in a monolithic material that can be formed into blocks or layers to build a monolith landfill. (Scharff et al. 2011)

2.7 Landfill types

Based on the type of waste to be disposed and the management strategy adopted different ways to construct and operate landfills are suitable. The EU Landfill Directive defines three landfill classes:

- Landfills for inert waste
- Landfills for non-hazardous waste
- Landfills for hazardous waste

The landfill classes differ in the technical standards required. The technical requirements pertaining to leachate formation and management are compared in Table 1. Furthermore the member states may prescribe top covers on landfills. In Sweden, for example, landfills for non-hazardous and hazardous waste must be supplied with a top cover as soon as possible after the completion of landfilling in order to limit the amounts of leachate formed and pollutant mobilised (Naturvårdsverket 2004).

Table 1. Technical requirements pertaining to formation and management of landfill leachate according to Annex 1 of the EU Landfill Directive (1999/31/EC). K = permeability

	Landfill for inert waste	Landfill for non-hazardous waste	Landfill for hazardous waste
Measures to prevent infiltration	Not required	Required	Required
Leachate collection and treatment	Not required	Required	Required
Geological barrier	$K \leq 1.0 \times 10^{-7}$ m·s-1; thickness ≥ 1 m	$K \leq 1.0 \times 10^{-9}$ m·s^{-1}; thickness ≥ 1 m	$K \leq 1.0 \times 10^{-9}$ m·s^{-1}; thickness ≥ 5 m
Artificial sealing layer	Not required	Required	Required
Drainage layer	Not required	Required	Required

The landfill classes also differ in the type of waste they may accept. The Council Decision (2003/33/EC) lay down acceptance criteria for the three classes although the criteria for non-hazardous waste only apply for non-hazardous waste which is landfilled in the same cell as stable, non-reactive hazardous waste. The acceptance criteria are most strict for inert waste landfills while landfills for hazardous waste can accept waste with a higher emission potential. MSW and MBT waste is normally landfilled in landfills for non-hazardous waste.

The strategy for environmental protection adopted through the landfilling directive is based on *containment* of the pollutants in landfills. However, the containment approach to landfilling has been much criticised. Preventing water from entering the landfill inhibits microbial stabilisation of organic matter and mobilisation of contaminants, thus keeping contaminants inside the landfill. However, the lining and capping systems cannot be expected to last indefinitely and at some point leakage must be expected. It has been argued that in a contained landfill a large part of the emission potential still remains at that point. Therefore this practice has been described as leaving waste problems for future generations (Reinhart and Al-Yousfi 1996; Allen 2001; Valencia et al. 2009) For certain hazardous waste, however, containment landfilling of stabilised waste is proposed as a sustainable option (Scharff et al. 2011).

In order to optimise gas generation, speed up stabilisation and avoid preservation of the waste the concept of *bioreactor landfilling* was introduced (Reinhart and Al-Yousfi 1996; Åkesson and Nilsson 1998; Barlaz et al. 2002). In bioreactor landfills or *biocells* the degradation conditions are improved by supplying sufficient water to degradable waste, often by recirculating the collected leachate (Reinhart and Al-Yousfi 1996; Berthe et al. 2008; Valencia et al. 2009). The increased through-flow of water also makes sure that the microorganisms responsible for degradation are distributed to different parts of the landfill and that a build-up of degradation products is avoided. As the methane production is stimulated the capture rates can be optimised, resulting in reduced methane emissions and improved energy recovery (Scharff et al. 2011).

Bioreactor landfilling has been proposed as a sustainable option for biodegradable waste (Scharff et al. 2011). Drawbacks of this approach include geotechnical stability, lack of process control as well as field-scale operation and monitoring difficulties (Valencia et al. 2009). Although biological stabilisation was achieved in pilot scale bioreactors, Valencia et al. (2009) found that chemical stabilisation was not, i.e. the leaching of salts and metals remained high. Moreover, the waste could be better utilised if digested in a properly operated and monitored anaerobic digestion reactor. In that case the nutrient rich solid residues could also be reused, not just the gas (Hartmann and Ahring 2006).

The typical biocell is anaerobic, but sometimes landfills are operated *aerobically* in order to enhance stabilisation. Japan has a semi-aerobic type of landfill, where air is allowed to passively move through the leachate collection system (Read et al. 2001). Budka et al. (2009) proposed that for landfills with relatively low organic content, such as MBT waste, aerobic conditions are most suitable for achieving rapid stabilisation. Forced aeration can also be applied to old anaerobic landfills to achieve stability within a short period (Ritzkowski et al. 2006). Cossu et al. (2003) proposed semi-aerobic landfilling of MBT waste in combination with intensive flushing as a means of achieving rapid stabilisation.

As an increasing proportion of landfill waste is inorganic, many landfills will, in the future, contain predominantly inorganic waste (Parker et al. 2007; van Praagh 2007). Furthermore, different landfill management is considered suitable for different wastes, and for that reason inorganic waste is sometimes separated and landfilled in designated cells (Scharff et al. 2011).

One concept for *inorganic landfills* is exemplified by a Dutch pilot study described in several publications (Scharff and Jacobs 2005; van Zomeren et al. 2005; Manfredi et al. 2010; Scharff et al. 2011). With a pH close to neutral, slightly reducing conditions, low organic content (DOC acceptance criterion 1500 $mg \cdot kg^{-1}$) and relatively low salt loads (Cl acceptance criterion 4000 $mg \cdot kg^{-1}$) the landfill was designed to minimise leaching. Mainly waste from soil separation and cleaning, dredging, sludge treatment, construction and demolition as well as from sorting and recycling were landfilled there. The purpose of the landfill concept is to create a biogeochemical equilibrium between the landfill and its environment within a limited time, in order to reduce the long-term risk and need for aftercare, thus providing permanent storage inside the landfill body with low emission levels. Specific types of inorganic waste can neutralise each other's negative effects. Processes such as adsorption and precipitation can be stimulated based on better knowledge of the waste materials.

Biocells and (semi-)aerobic landfills usually contain MSW and can be seen as types of MSW landfills. Older municipal landfills in Sweden usually contain a variety of wastes including MSW, industrial waste, construction and demolition waste, ash, sludge and excavation material (Öman and Junestedt 2008). All these landfills will be included in the term *MSW landfill* in this thesis. Landfills for mainly inorganic waste that comply with the national implementation of the Landfilling Directive will be called *modern landfills*. Landfills for only MBT waste will also be included in this term.

2.8 Leachate treatment

Landfill leachate can either be treated locally at the landfill site, or transferred off site for treatment, most commonly to a MWWTP, where it will be mixed with other waste water and typically treated by means of biological processes. Local treatment can be physico–chemical, biological or a combination of both. Using the leachate for irrigation or recirculating it into the landfill are other treatment options. (Reinhart and Al-Yousfi 1996; Avfall Sverige 2007; Cheng and Chu 2007; Schiopu and Gavrilescu 2010)

Biological treatment can roughly be divided into low tech and high tech systems. Low tech systems include wetlands, reed beds, aerated ponds, infiltration areas and various soil-plant methods as well as leachate irrigation. Examples of high tech biological treatment systems are SBR (sequencing batch reactor), activated sludge reactors and trickling filters. Biological treatments mainly target degradable organic matter and nutrients, especially nitrogen. Physico–chemical treatments are often required to remove other pollutants such as xenobiotics, heavy metals and refractory organic matter. Physico–chemical treatments are also used to enhance biological degradability as a pre-treatment before biological treatment. Physico–chemical treatments applied to landfill leachate include coagulation/flocculation, precipitation, sand filtration, sorption, nano filtration, reverse osmosis, evaporation/thermal treatment, air stripping and oxidation. (Marttinen et al. 2002; Avfall Sverige 2007; Schiopu and Gavrilescu 2010)

Although high tech biological and physico-chemical treatment options are common in some European countries, for a long time many Swedish landfills mostly relied on MWWTPs to treat their leachates. In recent years, however, more and more landfills are installing local treatment. This shift is mainly due to MWWTPs becoming more reluctant to accept leachates. (Andersson et al. 2007; Avfall Sverige 2007).

2.9 Organic matter in landfills

Due to its potential environmental impact (see sections 2.1 and 2.2), there are several waste acceptance criteria related to bulk organic matter in waste to landfill. In the German Ordinance on Environmentally Compatible Storage of Waste from Human Settlements (AbfAblV) for example, loss on ignition (LoI) and TOC in solid waste and DOC in eluate are restricted for non-hazardous waste landfills. Germany has implemented special acceptance criteria for MBT waste, for which higher TOC and DOC limits apply, although the waste has to comply with a limit regarding the biological degradability measured as either respiration activity (RA_4) or gas formation potential (GP_{21}). In Sweden, no acceptance criteria apply for landfills for non-hazardous waste as long as all waste landfilled there can be classified as non-hazardous. However, in practice there is a limit of 10 % TOC as explained in section 2.5. Like in Sweden, the French regulation (adopted on 9 September 1997 and strengthened in 2006) does not set acceptance criteria for landfilled wastes. Instead the French regulation imposes recovery and treatment of the leachate and gas produced during the landfill operation and the aftercare period of 30 years. (Berthe et al. 2008)

Other methods attempt to assess the biological stability of waste rather than just the bulk organic matter content. Examples include the ratio between BOD and COD (Barlaz et al. 2002), the HS content in the waste (Smidt and Lechner 2005), thermal methods (Smidt and Lechner 2005), fractionation of leachate organic matter based on hydrophobicity (Berthe et al. 2008), specific UV absorbance (SUVA) index (Croué et al. 1993) and Fourier transform infrared spectroscopy (FT-IR) (Smidt et al. 2008). Some of these methods, such as BOD/COD, can be considered standard while others are mainly used in research.

Humic substances are products of the degradation of organic matter in the environment. They are highly complex molecules with numerous different functional groups and highly aromatic structures (Christensen et al. 1998). HS are usually divided into humic acids (HA) that are soluble in pH above 2, fulvic acids (FA) that are soluble in any pH and insoluble humins. (Fourti et al. 2010) Similar substances are formed during degradation in landfills. Although not necessarily identical to natural humic substances, for simplicity they will be referred to in this thesis as humic substances. In environmental terms, HS are highly relevant in landfill leachate. Since HS are refractory against biological degradation (Rodriguez et al. 2004) they are unlikely to cause problems related to rapid degradation. They also act as ligands for heavy metals (Ingelmo et al. 2012). Non-humic organic matter consists of molecules such as polysaccharides, sugars, proteins, amino acids, lipids, fatty acids, waxes, pigments and other substances of low molecular weight (Fourti et al. 2010).

Fractionation of organic matter based on hydrophobicity[1] divides it into HA, hydrophobic substances (HPO), transphilic substances (TPH) and hydrophilic substances (HPI). HA are the most hydrophobic and HPI are the most hydrophilic. A higher fraction of hydrophobic substances are characteristic of leachate from more stabilised waste. Therefore this type of fractionation has been employed as a means to use leachate organic matter quality as an indicator of the state of degradation of the waste inside a landfill. (Berthe et al. 2008)

As will be described in section 2.10, organic matter plays an important role in both short and long term metal mobility (Bozkurt et al. 2000). It has been suggested that the amount of organic matter in modern landfills is not sufficient to sustain reducing conditions (Avfall Sverige 2009b). A shift to oxidising conditions would thus have significant consequences for metal mobility.

[1] Hydrophobic molecules have a tendency not to dissolve in water while hydrophilic molecules readily dissolve in water.

2.10 Heavy metals in landfills

The environmentally relevant amount of heavy metals in a landfill is that which can be mobilised, leach and cause harm. This is not the same as the total content. According to Pettersen and Hertwich (2008), three levels of leaching potential can be identified:

- the total mass in the landfill
- the potentially leachable fraction
- the fraction actually released under given conditions

For environmental relevance a fourth level can be added:

- the fraction of the released metals that reach a point where they can cause harm.

Research compiled by Claret (2011) shows that metal mobility in the soil below landfills is generally very low: elevated metal concentrations were rarely detected except for in the very vicinity of the landfill. However, elevated metal concentrations have been observed downgradient of landfills (Baumann et al. 2006; Ettler et al. 2008) and Pastor and Hernández (2012) found elevated metal concentrations in landfill cover soils in older landfills.

The mobility of metals inside landfills is dependent on a number of factors related to both the solid material with which they were first landfilled and the surrounding liquid. In an anaerobic landfill with a pH near to or above neutral, most metals have low solubility; usually less than 1 % of the total content of toxic metals are released during the active phase of a MSW landfill (Baccini et al. 1987; Flyhammar et al. 1998; Huber et al. 2004).

The form in which metals are present in the waste, e.g. water soluble, cation exchangeable or bound to carbonates, (hydr)oxides, organic matter or sulfides, influences their mobility (Flyhammar et al. 1998; Esakku et al. 2008; Zhang et al. 2011). At the time of landfilling almost 70 % of the heavy metals in MSW have been estimated to be in lattice structures such as metal and polymer items (Flyhammar et al. 1998).

Important metal scavengers include organic matter, sulfides and to a certain extent carbonates (Belevi and Baccini 1989; Bozkurt et al. 2000; Erses and Onay 2003). Calculations by several authors (Bozkurt et al. 2000; van Praagh et al. 2007; Östman et al. 2008) have shown that organic matter and sulfides are more than enough to bind all the heavy metals in an MSW landfill given that it is completely homogeneous and that competition with other elements is insignificant.

When the methanogenic phase ends, oxidation of organic matter may cause the release of the metals bound to it and the concomitant CO_2 release can lower the pH, increasing the solubility of most heavy metals (Bozkurt et al. 2000). Although oxidation of methanogenic landfill leachate can cause metals to precipitate (Sletten et al. 1995), many minerals containing metals, e.g. sulfides, are more soluble under conditions of a high redox potential (Flyhammar and Håkansson 1999). Therefore, it was previously feared that a great increase in metal mobility can occur during the second aerobic phase of a landfill, and landfills were labelled “chemical time bombs” (Stigliani 1991). However, although a small (up to twofold) increase in metal concentrations have been

observed upon oxidation (Flyhammar and Håkansson 1999; Mårtensson et al. 1999; Barlaz et al. 2002), recent research has predicted that metal mobility is also low during the second aerobic phase of MSW landfills.

As the landfill becomes oxidised, solid iron oxides are formed with a large surface area capable of binding great amounts of heavy metals (Bozkurt et al. 2000). According to van Praagh et al. (2007), a combination of iron oxides and organic matter has the potential to sorb most metals in an oxidised landfill, while Bozkurt et al. (2000) found the iron itself is sufficient to bind all metals, although in the very long term sorbed metals can be released during crystallisation of ferric iron hydroxides. Furthermore, the capacity of the landfill to buffer changes in pH has been found sufficient for maintaining a neutral pH over very long periods, thus limiting the risk of metal solubilisation due to pH changes (Flyhammar and Håkansson 1999; Bozkurt et al. 2000; Östman et al. 2008). In summary, a low heavy metal leaching is expected in MSW landfills, even in the long term.

Until recently, most studies focused on landfills with high organic content. Those concerning landfills with low organic carbon content also predicted relatively low metal mobility, although the long term potential to sorb mobilised metals might not be as high. The buffering capacity, and in the case of MSWIBA, the formation of secondary minerals, is important. In the absence of organic matter metal leaching is expected to be controlled mainly by the solubility of minerals. Oxygen and CO_2 entering the landfill could reduce the buffering capacity, creating a reaction front that moves downwards. (Bozkurt et al. 2000; van Zomeren et al. 2005; Øygard et al. 2005; van Praagh et al. 2007)

Leachate concentrations of possible ligands further affect metal leaching, bioavailability and toxicity (Bozkurt et al. 2000; Christensen et al. 2001; Baun and Christensen 2004). Complexing agents such as chlorides or organic molecules, e.g. humic substances, can lower the activity of the dissolved metals, thus increasing their solubility (Belevi and Baccini 1989). In leachate, heavy metals are often associated with colloids of varying size and composition which is something that also can affect their mobility (Claret et al. 2011) although Baumann et al. (2006) found no evidence that colloids increase heavy metal mobility.

Baun and Christensen (2004) found that metals (Cd, Cr, Cu, Ni, Pb and Zn) in colloids in landfill leachate were mostly associated to organic matter. In the dissolved fraction Cd, Cu and Pb mainly took the form of organic complexes while Ni and Zn were partly associated to organic matter although other forms dominated. As was only related to inorganic species, in colloids as well as the dissolved fraction (Baun and Christensen 2004). Organic metal complexes have also been found to dominate in leachate pollutant groundwater samples. Christensen et al. (1999) found more than 90 % of Pb and 95 % of Cu to be bound to organic matter and Christensen and Christensen (1999) found organic complexes to account for 60–80 % of the concentrations of Ni, Zn and Cd in leachate polluted groundwater.

3 MATERIALS AND METHODS

3.1 Waste materials, leachates and data sets

The research presented in this thesis was based mainly on data and waste and leachate samples from full scale Swedish landfill cells. These landfills are presented in Table 2. Among them there are three landfills that were commissioned and are operated entirely according to the Swedish implementation of the EU landfilling directive and can be classified as modern landfills for mainly inorganic waste: Fläskebo, the soil cell at Högbytorp and the residual waste cell at Högbytorp. Filborna, the old landfill at Högbytorp and Mosserud are examples of old and big landfills containing mixed waste. Tagene is mainly a landfill for ashes but as most older landfills it has received a mixture of waste types including waste rich in organic matter. Spillepeng and Löt are examples of landfill sites where different types of waste are landfilled in separate cells but while the leachate collection system at Spillepeng allows leachate to be collected separately from each cell this is not the case at Löt.

In the study described in **Paper II** two waste materials undergoing mechanical and biological treatment were studied. Material M1consisted of residues form sieving of MSW that was tunnel composted for nine weeks in Germany. Samples were taken from the input to the composting, after two and six weeks and after the full nine week process. Material M2 consisted of residues from sieving of C&D waste that were mixed with green compost and sludge and subsequently stockpile composted for 24 weeks in Sweden. Samples were taken from the input and output materials from the process. The treated M2 was intended for landfilling while M1 was intended mainly for construction purposes at landfill sites.

In **Paper III** leachate samples from several Swedish landfill cells are compared to leachates from a number of French landfills. The French landfills were of different types, including biocells with only MSW and cells with no MSW at all. These data were compiled from several research projects performed at the University of Limoges, France. More details about them can be found in **Paper III**.

3.2 Multivariate data analysis

Multivariate data analysis provides tools for handling complex data, such as landfill leachate data, since it is a field in statistics that deals with several related variables. In the research described in this thesis two multivariate techniques, principal component analysis (PCA) and canonical correlation analysis (CCA), were used. Some background information about these techniques is presented in the Appendix. The Appendix also explains how to interpret the results from the MVDA.

Table 2. Swedish landfills studied in the research presented in this thesis

Landfill	Period of operation	Type of waste landfilled	Included in papers
Fläskebo	2003–present	Mixed industrial waste and C&D waste, <10 % TOC	**Paper I** (regular leachate monitoring data), **Paper III** as F (leachate sample), **Paper IV** (waste sample)
Tagene	1974–present	Mainly ash from waste incineration, some organic waste such as MWWTP sludge and industrial sludge	**Paper I** (regular leachate monitoring data)
Högbytorp, old landfill	1964–2008	Mixed MSW, industrial waste, soil, C&D waste, etc.	**Paper I** (regular leachate monitoring data); **Paper III** as H1 (leachate sample)
Högbytorp, soil cell	2003–present	Mainly soil	**Paper III** as H2 (leachate sample)
Högbytorp, residual waste cell	2009–present	Mainly residues from recycling centres	Only in thesis
Filborna	1951–present	Mixed municipal and industrial waste	**Paper I** (regular leachate monitoring data)
Spillepeng, special waste cell	1990–1993	Mainly fly ash, bottom ash, blasting sand, asbestos wastes and contaminated soil	**Paper I** (regular leachate monitoring data)
Spillepeng, older MSW cell	1990-1994	Mainly MSW	**Paper III** as S1 (leachate sample)
Spillepeng, younger MSW cell	1994–2001	Mainly MSW	**Paper I** (regular leachate monitoring data), **Paper III** as S2 (leachate sample); **Paper VI** (leachate sample)
Löt	1995–present	Mainly non-hazardous waste, including some organic waste. Small amounts of hazardous waste	**Paper I** (regular leachate monitoring data)
Mosserud	Approx. 1950–present	MSW, other non-hazardous wastes and ashes	**Paper V** (leachate data from before and after pilot scale treatment)

PCA is a multivariate technique that is widely used in various fields of research for noise reduction, data simplification and for multivariate visualisation and prediction. It is a powerful tool to simplify large and complex data sets and obtain an overview of the relations among different parameters. PCA transforms the data set in order to concentrate the *variance* in as few variables as possible. These new variables are termed principal components (PCs). If the PCA is successful the resulting data set is of reduced dimensionality but still includes the majority of the information contained in the original data and it is often possible to identify the processes underlying the PCs. (Jackson 1991)

Previous applications of PCA of landfill leachate data include finding differences in leachate quality among landfills in the same area (Gómez Martín et al. 1995), classifying landfill cells or leachate samples (Ludvigsen et al. 1996; Andreas et al. 1999; Lou et al. 2009; Rodriguez Ruiz et al. 2009), finding relations among leachate parameters or identifying parameters that are particularly important for leachate quality (Kylefors 2003; Durmusoglu and Yilmaz 2006; Galvez et al. 2010) and evaluating toxicological tests for studying leachates (Clément et al. 1997; Olivero-Verbel et al. 2008; Pablos et al. 2011).

CCA is a multivariate method for discovering and quantifying the patterns of correlation between two complex data sets (Barnett and Preisendorfer 1987). It can be seen as an extension of linear regression, but instead of using two variables, one fully multidimensional data set, the *predictor*, is used to model another, the *predictand*. CCA transforms the two data sets into two new sets in a way that maximises the *correlation* between a limited number of new variables termed canonical components. van Praagh and Persson (2004) carried out the only CCA of landfill leachate data known to the author of this thesis. They successfully modelled conductivity in a landfill leachate through measurements of water levels in the landfill.

In this thesis the results from PCA are presented in plots where two PCs are plotted against each other. The *loading plot* displays the co-variance between the *variables*; in this thesis mainly leachate parameters (see e.g. Figure 1 in section 4.1.1). The variables that contribute most to the respective PC are located far from the origin. Variables located close to the origin are thus not well represented by these PCs. Variables located close to each other have a strong co-variance while those opposite each other have a negative co-variance. A *score plot* displays the co-variance of the *samples* (see Figure 2 in section 4.1.1 for an example of a score plot). A more detailed explanation of the plots can be found in the Appendix.

The results from CCA are in this thesis presented as a so called *homogeneous correlation map* (see Table 5 in section 4.1.1). The homogeneous correlation map is presented as a table that displays the correlations between the original variables and the canonical components. Predictor and predictand variables that are strongly correlated to the first component of the respective data set can be assumed to be related to the same process. A more detailed explanation of the correlation map can be found in the Appendix.

In the study described in **Paper I** PCA and CCA were applied on regular landfill leachate monitoring data from six Swedish landfills. The data sets employed are summarised in Table 3 and information about the landfills can be found in Table 2. One aim of the study was to check

for redundancies and interdependencies in order to improve understanding of the factors that govern leachate quality with a special focus on heavy metals and organic matter. Another aim was to test the susceptibility of PCA and CCA to variable landfill leachate data input in addition to the impact on the reproducibility and reliability of the results. Previous studies comparing leachates using PCA (e.g. Gómez Martín et al. 1995; Andreas et al. 1999; Rodriguez Ruiz et al. 2009) included all studied leachate data sets in a joint analysis. In the study described in **Paper I,** data sets were analysed separately in order to focus on the individual properties of each landfill and compare the landfills to each other.

In the study described in **Paper II**, PCA was employed on a data set containing total solid and eluate content from M1 waste at different stages of MBT. The purpose was to identify parameters describing similar information pertaining to organic matter in the waste as well as those affecting metal mobility.

The aim of the PCA described in **Paper III** was twofold. The main objective was to investigate whether fractionation of organic matter can be used as an indicator of the state of degradation of landfills where other types of waste in addition to MSW have been deposited. In order to do so, the correlation between degradation and organic matter fractionation was first modelled with PCA using leachate data landfills containing only MSW. The leachate data used to build the PCA model originated from ten French landfills described in Table 4. From site A one sample from each of the four cells, taken directly at the end of the operation, was employed in the analysis. From the cells at sites B and C samples taken continuously during the operation were employed. From the full scale landfill D two samples taken five years after the end of operation were employed. In total 37 samples were used to build the model. Thereafter a number of Swedish and French landfills containing other waste types than only MSW were fitted to the model in order to see to what degree the model based on MSW landfill leachate data was adapted for them (see Table 2 for a description of the Swedish landfills and **Paper III** for the French landfills).

*Table 3. Regular landfill leachate monitoring data employed in **Paper I***

Landfill	Period of data used	Sampling point	Data set size
Fläskebo	2004–2008	Pond	15×39
Tagene	2000–2008	Pipe	36×34
Högbytorp	1997–2006 resp. 1997–2000	Aerated pond	98×12 resp. 42×15
Filborna	2006–2009	Pipe	45×21
Spillepeng younger MSW cell	2000–2010 resp. 2005–2010	Pumping station	41×17 resp. 21×20
Spillepeng special waste cell	2005–2010 resp. 2007–2010	Pumping station	21×10 resp. 13×19
Löt	2005–2008	Aerated pond	15×23

*Table 4. French landfills and pilot scale landfills containing only MSW. * = Wastes were mechanically and biologically pre-treated before landfilling. ** = Leachate was recirculated in the wastes mass. 1 and 2 signify duplicates. Data from these landfills were employed in* ***Paper III***

Landfill	Input waste	Reference
Pilot scale landfill A	Untreated MSW	Berthe et al. (2008)
Pilot scale landfill A**	Untreated MSW	
Pilot scale landfill A1*	MBT waste (12 weeks)	
Pilot scale landfill A2*	MBT waste (25 weeks)	
Pilot scale landfill B	Untreated MSW	Unpublished data
Pilot scale landfill B1*	MBT waste	
Pilot scale landfill B2*	MBT waste	
Pilot scale landfill C	Untreated MSW	Mansour et al. (2011)
Pilot scale landfill C*	MBT waste	
Full scale landfill D	Untreated MSW	Labanowski and Feuillade (2009)

Paper IV includes a PCA performed to compare landfill leachate data to lab scale eluates and to compare batch and column eluates to each other. Five annual averages of leachate data were included in addition to six data sets from columns (two replicates of L/S 0.1, 2 and 10 respectively) and three batch eluate replicates.

In the study described in **Paper V,** a data set from treatment of the leachate from Mosserud (see Table 2) using reed beds was analysed with PCA in order to identify correlations between bioassays and chemical parameters. The PCA results were also used to identify a suitable battery of toxicity tests for assessment of the treatment.

Prior to PCA, all data sets were pre-treated. In the study described in **Paper I,** samples and parameters were removed to create a data set with acceptable amounts (< 10 %) of missing data. In all cases the $\log_{10}$ of the input data was used in order to normalise data and reduce the impact of extreme values. Each parameter was standardised by extracting the mean and dividing by the standard deviation. Parameters with more than 10 % missing data were excluded with the exception of two in the study described in **Paper V,** where 12.5 % missing data were accepted. Missing values were replaced by the parameter mean.

Before performing CCA, the data sets were transformed individually using PCA. The purpose of this pre-treatment was to reduce the influence of noise and create more stable models. The number of PCs required to include at least 80 % of the original variance was subsequently used in the CCA.

3.3 Leaching tests

Leaching tests are often used to estimate the emission potential of waste materials. Although a great deal of work has been done to standardise such tests, many different types remain in use. One form of categorisation is batch and column tests. The former are faster and easier to perform, while the latter are generally considered closer to reality (Kylefors et al. 2003; Kalbe et al. 2008; Grathwohl and Susset 2009).

The research presented in this thesis employed both batch and column leaching. In the study described in **Paper II,** batch leaching in accordance with DIN 12457-4 was applied to M1 and M2 waste. In the case of M1 waste, four samples at different stages of MBT were leached, while for M2, the MBT input and output materials were investigated. The study described in **Paper IV** employed both batch leaching in accordance with DIN 12457-4 and column leaching as set out in CEN/TS 14405.

The waste studied in **Paper IV** originated from the Fläskebo landfill. It was collected from a cell with a relatively homogeneous composition of mainly C&D waste sorting residues. This waste will be referred to as Fläskebo residual waste. The biggest volume part of the waste samples consisted of insulation material and a fragmented material including plaster board residues. There were also fragments of wood, chipboard and similar organic materials. Bigger pieces of concrete, stone, brick etc. were removed.

According to DIN 12457-4, the waste is leached for 24 h in a head-over-end tumbler at a liquid to solid ratio (L/S) of 10. The size of the flasks used was between 250 and 2000 ml. CEN/TS 14405 is a continuous, saturated, up-flow column leaching test with a maximum L/S ratio of 10. The columns had a height of 50 cm and an inner diameter of 105 mm. To create an oxygen-free atmosphere, the filled columns and the container with leaching fluid (deionised water) were flushed with nitrogen. The contact time between waste and leachant averaged 48 hours. Modifications of the standards were made as described in **Paper IV**.

The effluent from the columns as well as the fluid from the batch tests will be referred to as *eluate* to differentiate it from the *leachate* from a landfill. The column eluate was sampled at L/S 0.1, 0.2, 0.5, 1, 2, 5 and 10. The samples from L/S 0.2, 0.5, 1 and 2 were mixed into a flow proportional sample labelled L/S 2 and the samples from L/S 5 and 10 into a flow proportional sample labelled L/S 10.

3.4 Organic matter characterisation and degradability

As described in chapter 2.1, 2.2 and 0 above, organic matter in solid waste and leachate is important for the environmental impact of landfills. Therefore all papers in this thesis describe research that employed methods for measuring the organic content in waste.

In the study described in **Paper II,** various methods for characterising organic matter were applied to solid samples and eluates of M1 and M2 waste. For the solids, LoI, TOC, humic acids (HA) and HS were measured, in addition to spectral analysis using FT-IR, and the thermal methods

differential thermogravimetry (DTG), differential scanning calorimetry (DSC) and CO_2 ion current mass spectrometry (IC). BOD, COD, DOC and HA were analysed in the eluates.

Degradation tests were employed in the studies described in **Papers II** and **IV**. In **Paper II,** two German standards, aerobic respiration activity in accordance with RA_4 and anaerobic gas formation potential as set out in GP_{21}, were applied to M1 and M2 waste. **Paper IV** describes a study of residual waste from Fläskebo landfill that also employed RA_4 but in which anaerobic tests were conducted using a non-standard approach aimed at more closely resembling real landfill conditions by maintaining a relatively low temperature (20 °C).

In the study described in **Paper III,** fractionation of leachate organic matter according to hydrophobicity was applied on several leachates including five from Sweden (see Table 2). Initially HA were precipitated through acidification to pH 2. The HPO fraction that corresponds to FA was absorbed in a DAX-8 resin (non-ionic and slightly polar). The TPH fraction was absorbed in a XAD-4 resin (non-ionic and non-polar). The HPI is that which passed through both resins. Determining the DOC before and after each step allowed calculating the percentage of each extracted fraction as the ratio of its DOC to the total DOC content. The study described in **Paper III** also applied the SUVA index.

3.5 Toxicity tests

In the study described in **Paper V,** data from toxicity testing of leachate were employed. The leachate from the Mosserud landfill (Table 2) was treated in a pilot scale reed bed system and samples from before and after the treatment were analysed using bioassays including inhibition of growth of the macrophyte *Lemna minor* (Swedish standard SS-EN ISO 20079:2006) and the green algae *Pseudokirchneriella subcapitata* (Swedish standard SS-EN ISO 8692:2005), inhibition of luminescence in the marine bacteria *Vibrio fischeri* after 30 minutes (Microtox test ISO 11348) and embryo development of the freshwater fish *Danio rerio* over 48 hours (protocol by Braunbeck and Zeilke (2010)).

The results of toxicity tests are often given as EC_{50}, the concentration or (in the case of e.g. landfill leachate) dilution that causes 50 % effect, e.g. 50 % dead organisms or 50 % decrease in growth or luminescence. The more toxic a substance, the lower its EC_{50}. Due to this inverse relationship, EC_{50} was converted into toxic units, TUs (1 TU = $1/EC_{50}$).

3.6 Sorption filtration experiments

Sorption filtration is a promising technique for removing metals from contaminated waters, as it has shown potential to achieve good removal at relatively low cost and energy demand (Oh et al. 2007; Kalderis et al. 2008). *Sorption* is here used as a collective term for adsorption to the surface and absorption into the structure of a material. Strictly speaking, precipitation is not sorption. In practice, however, it is often difficult to distinguish between the two and therefore, in this thesis, precipitation is included in the term "sorption".

In order to evaluate the usefulness of sorption filters as a means of removing metals from landfill leachate, a study was performed as described in **Paper VI**. The aim was to mimic real conditions as closely as possible while restricting the size of the experimental setup to lab scale. Therefore real landfill leachate was used. The leachate was collected from the Spillepeng landfill from a cell with mainly MSW.

Based on a literature study (Hoyer and Persson 2007) and screening tests (Modin and Persson 2008), granular activated carbon (GAC), bone meal (BM) and iron fines (IF) were selected for study. Over the course of 29 days the leachate was pumped through columns filled with the respective filter materials. The filtration was performed in a continuous up-flow mode. The columns had a height of approximately 50 cm and an inner diameter of 10.5 cm. The flow rate was initially set to 1 $m \cdot day^{-1}$ in the GAC columns and to 0.2 $m \cdot day^{-1}$ in the BM and IF columns. The smaller flow rate was chosen for materials expected to have lower permeability. After 18 days the flow rate was increased to approximately 4.4 and 1.2 $m \cdot day^{-1}$, respectively. The metal concentrations in the influent and the effluent were measured on three occasions, allowing the removal efficiencies of the different filter materials to be inferred.

4 RESULTS AND DISCUSSION

4.1 Methods

4.1.1 Multivariate data analyses in landfill research

In the research presented in this thesis the choice of parameters to include in the MVDA was always restricted by the availability and quality of data. The data was not collected with the purpose of MVDA; rather the statistical techniques were applied to extract more value from existing data. In most, if not all cases certain parameters could not be included in the MVDA although they would have been relevant. This includes possible toxicants and nutrients in the study presented in **Paper V**, salts, metals and organic parameters in some of the data sets in the study presented in **Paper I** and parameters related to the redox state in the study presented in **Paper IV**. The reason was either that the parameter had not been measured at all, or that the data were not of sufficient quality, e.g. too many missing values or too many values below the detection limit. In some cases, mainly in **Paper I** it was also necessary to remove outlying data points since they would otherwise strongly influence the results. When all relevant parameters cannot be included in the analysis the results will not give the whole picture of the leachate studied. This must be taken into account when interpreting the results.

Physical processes captured by MVDA

Both PCA and CCA, but especially PCA, proved useful for statistically elucidating possible relationships between parameters in regular landfill leachate monitoring data. This made it possible to interpret the patterns underlying the co-variations between single parameters and physical processes such as dilution, redox potential and organic matter–metal complexation.

The concentration of salts was an important factor in the PCAs described in **Paper I**. It dominated in the first principal component of the leachate data from the Fläskebo (Figure 1) and Tagene landfills and in the first canonical components of the data from Högbytorp and Filborna. All data sets described in **Paper I** except for those from the special waste cell at Spillepeng and Löt produced a cluster of salinity related parameters in the loading plot. The electrical conductivity (EC) and Cl were always present in the cluster as was total nitrogen (N_{tot}) or NH_4. Na was present in the two cases where it was analysed. Ba, Cr and SO_4 were present on one occasion each. In the case of Fläskebo, the importance of this cluster for PC1 was clearly related to temporal trends; many of the concentrations decreased rapidly at the beginning, probably due to leaching of bottom ash that was used as a construction material inside the landfill cells.

Other authors (Gómez Martín et al. 1995; Clément et al. 1997; Galvez et al. 2010) also found that salts dominated PC1. Rodriguez Ruiz et al. (2009) identified a very clear salinity cluster in a PC1 and PC2 loading plot based on data from hundreds of landfills. Ettler et al. (2008) studied variations in leachate data during precipitation events using uni- and bivariate techniques and found that EC decreased in response to a decrease in the concentration of major components such

as Na, K, Ca, HCO_3 and Cl due to rainwater dilution. In some of the data sets described in **Paper I** (Högbytorp and Filborna), leachate dilution seemed to be the main process captured by the first PC, since all parameters were located on the same side. This phenomenon was also observed by Waara et al. (2008). However, dilution was not the only process responsible for the concentration differences. For example in the Fläskebo landfill, they were caused by variation in input materials and depletion. Ettler et al. (2008) found that although most metal concentrations decreased due to dilution during rainfall events, some did not something they attributed to geochemical reactions such as desorption and dissolution. Furthermore, in the PCA described in **Paper IV,** the differences in concentration caused by factors other than dilution clearly separated the leachate and eluate samples.

Redox processes seem to be another reason for variations in leachate quality captured by PCA and CCA. Variations caused by redox conditions were among the processes behind PC2 in Fläskebo and Tagene and PC1 in the Löt landfill. (**Paper I**)

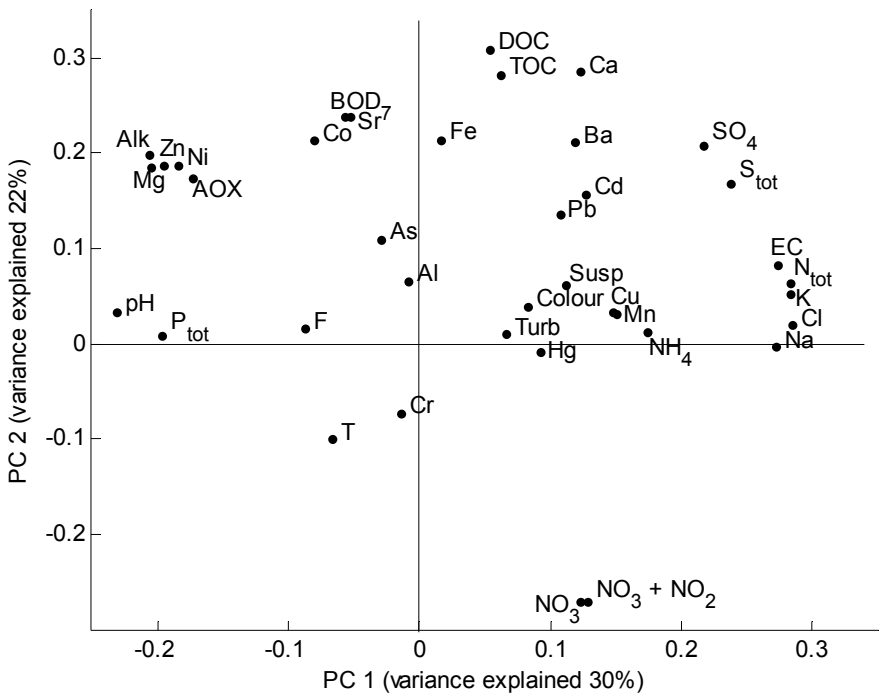

*Figure 1. Loading plot from principal component analysis of leachate from Fläskebo landfill displaying re relation between leachate parameters (from **Paper I**)*

In the studies described in **Papers II** and **V** where samples were taken at different stages of a treatment process, the effect of the treatment was the main source of variation behind PC1. This was most obvious in the study of the reed bed system (**Paper V**), where the score plot very clearly separated treated from untreated leachates (Figure 2). In **Paper III**, which describes a PCA of leachate parameters used to assess the biological stability of waste, stability was the main factor separating the different samples.

The CCA frequently indicated patterns similar to those identified using PCA. For example, in the data from Fläskebo, trends were most important for the first canonical component and the redox state for the second, i.e. the same patterns as for PC1 and PC2. The homogeneous correlation maps from the CCA of the data from Fläskebo are presented in Table 5.

One of the main objectives of the study described in **Paper I** was to investigate the relations between heavy metals and other parameters. Such relations were found in several cases using PCA and CCA and will be discussed in section 4.2 below.

The type of information described by the PCs is affected by at least two factors:

- Reality: The main part of the leachate variation is caused by physical processes. When they differ between landfills different processes dominate the PCs.
- The data included: If many parameters related to a certain process are included in the data set, it is more likely that this process will be statistically correlated with one of the higher PCs.

As an example, the salinity clusters observed in **Paper I** are probably due to both these factors. Salinity is an important aspect of leachate quality, but in the PCA the pattern is enhanced by the fact that many, partly redundant, parameters related to it are included: EC, Cl, NH_4, Na, etc. The fact that treatment efficiency was dominant in the data sets described in **Papers II** and **V** is mainly related to the first factor. The finding that both PCs in **Paper III** were related to the stabilisation of organic matter is due to the second factor; only parameters that could somehow be related to stabilisation were included in that analysis. Understanding this is very important when comparing the results from separate PCAs, as described in **Paper I**.

*Table 5. Homogeneous correlation maps from canonical correlation analysis of leachate data from Fläskebo landfill. The numbers presented are coefficients of correlation between the canonical components and the original variables. Correlation coefficients > 0.6 are in bold, while statistically significant correlations ($p < 0.05$) are underlined. The correlations between the predictor and the predictand are 0.98, 0.77 and 0.65 for the first three components (from **Paper I**)*

Predictor (left field)				Predictand (right field)			
Param.	**Comp. 1**	**Comp. 2**	**Comp. 3**	**Param.**	**Comp. 1**	**Comp. 2**	**Comp. 3**
EC	**-0.85**	0.40	-0.07	Al	-0.01	0.42	**0.85**
Cl	**-0.94**	0.27	0.05	As	0.15	-0.06	-0.03
pH	**0.77**	0.06	0.22	Ba	-0.32	**0.71**	0.22
N_{tot}	**-0.87**	0.40	-0.22	Ca	-0.18	**0.77**	-0.42
NH_4	-0.52	0.40	-0.28	Cd	-0.25	0.39	**-0.67**
NO_3	-0.57	**-0.72**	-0.31	Co	0.41	0.18	-0.33
NO_3+NO_2	-0.55	**-0.72**	-0.30	Cu	-0.48	0.43	-0.07
P_{tot}	**0.61**	-0.09	0.42	Cr	0.01	-0.57	0.22
TOC	0.01	**0.64**	-0.47	Fe	0.05	**0.78**	0.20
BOD_7	0.38	**0.64**	-0.25	Hg	-0.31	-0.11	**-0.61**
DOC	0.05	**0.77**	-0.30	K	**-0.89**	0.24	-0.26
F	0.27	0.34	0.45	Mg	**0.82**	0.44	-0.26
Susp	-0.43	0.30	**0.77**	Mn	-0.40	0.13	**-0.72**
Turb	-0.32	0.25	**0.84**	Na	**-0.92**	0.27	0.18
Colour	-0.28	0.49	**0.56**	Ni	**0.75**	0.19	-0.13
T	0.16	-0.02	0.01	Pb	-0.33	0.36	0.56
Alk	**0.84**	0.36	-0.21	Sr	0.34	**0.80**	-0.08
S_{tot}	**-0.67**	0.55	-0.22	Zn	**0.75**	0.54	0.20
SO_4	-0.58	**0.70**	-0.17				
AOX	**0.65**	0.15	0.35				

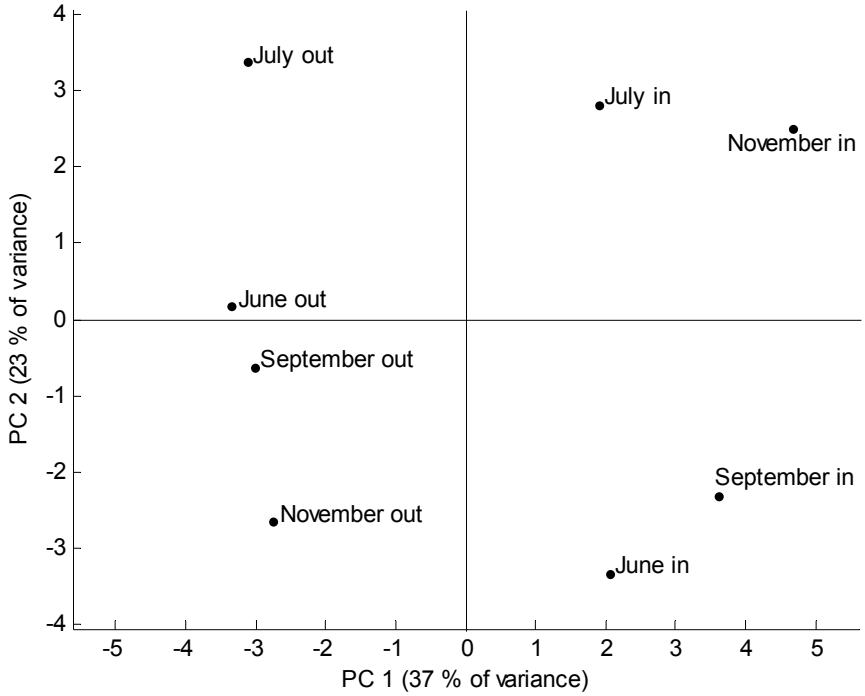

*Figure 2. Principal component analysis score plot of data on landfill leachate quality before (in) and after (out) treatment of the leachate from Mosserud landfill (from **Paper V**)*

Potential uses of PCA in landfill management

The knowledge produced by MVDA of parameters related to, and thus possibly governing, target substances can be valuable in landfill leachate management. As will be discussed in section 4.2 below, Cr was often found to be related to inorganic parameters, while Al was related to suspended matter. This indicates that a treatment like sedimentation would target Al but not Cr in these leachates. As is discussed in **Paper I**, PCA was efficient in identifying parameters providing redundant information and also those with a major impact on leachate quality. This method could therefore be useful when evaluating leachate monitoring programmes.

Paper V provides an example of how the evaluation of a leachate treatment system can be enhanced by PCA. The biggest benefit of using PCA was the possibility of identifying toxicity tests that reacted in similar ways to the treatment and thus provide redundant information. This enables identification of a suitable battery of bioassays for monitoring the process.

MVDA methodology recommendations

The results presented in **Paper I** demonstrate that stronger correlations and more detailed information can be obtained by including more leachate parameters. Since leachate data series

often contain gaps, it is tempting to exclude parameters with missing data (thus reducing the number of parameters) in order to increase the length of the time series. However, in two data sets described in **Paper I,** this diminished the chances of finding strong correlations. When leachate parameters are removed, important information about leachate quality is excluded, leaving some variation unexplained. This cannot be compensated for by including more samples as they will lack important predicting variables.

The importance of including as many relevant parameters as possible was also demonstrated in **Paper V,** where the relation between toxicity and other leachate parameters was assessed. Toxicity tests usually measure growth inhibition. Apart from direct toxicity, growth inhibition can be caused by lack of or imbalance in nutrients (Cheng and Chu 2007). Furthermore, alkalinity is suspected to increases ammonia toxicity (Clément and Merlin 1995; Clément et al. 1997). However, the data set utilised in the study described in **Paper V** lacked several nutrients (e.g. K, Ca, and Mg) in addition to alkalinity. Although these substances are not considered to be directly related to toxicity, their inclusion in the PCA would probably contribute to a fuller understanding of the causes of growth inhibition.

4.1.2 Leaching tests

In the study described in **Paper IV,** batch and column leaching tests were performed on residual waste from the modern Fläskebo landfill. Lab scale eluates were compared with actual landfill leachate. The biggest concentration differences between the eluates and the landfill leachates were due to the fact that the leachate originated from a mixture of different wastes. It was not possible to obtain data on full scale landfill leachate originating exclusively from the residual waste that was used in the leaching tests. In the PCA score plot seen in Figure 3 the difference between the leachate and eluate samples is also clearly visible since they are located at opposite sides of the figure.

Repeatability was higher in batch than in column tests in the study described in **Paper IV**. This can be seen from Figure 3 since the three batch replicate samples are located closer together than the two column duplicates at each L/S. As the waste material leached is relatively heterogeneous and the sample volumes are much larger in the columns, the opposite was expected and would have been in line with previous findings (Kalbe et al. 2008; Grathwohl and Susset 2009). The explanation could be that variations were increased by the irregular flow rate in the columns due to problems with the operation of the pumps. Contamination may also have played a role, as washing with acid to remove metals is more complicated in the four-litre columns compared to the smaller flasks used in the batch tests.

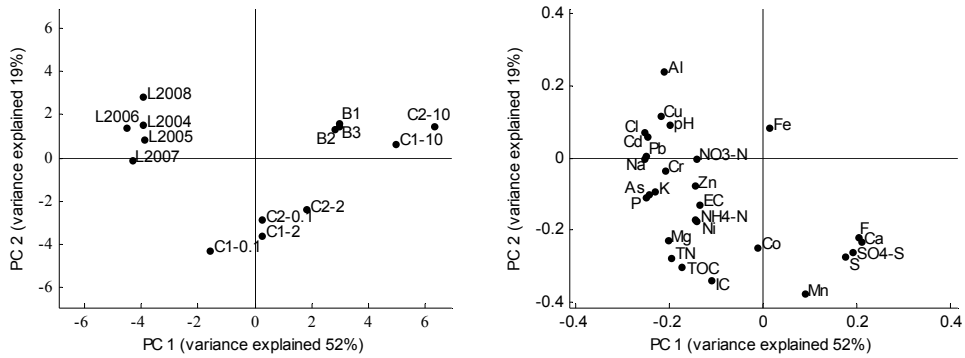

*Figure 3. PCA score plot (left) and loading plot (right) of leachate data (five yearly averages) from a full scale landfill (L) and eluate data from three replicate batch tests at L/S 10 (B1, B2 and B3) and from two replicate column tests (C1 and C2) at L/S 0.1, 2 and 10 (from **Paper IV**)*

Batch tests are often claimed to over-predict the release from column tests (López Meza et al. 2008; Grathwohl and Susset 2009) although the opposite has also been observed (Kalbe et al. 2008). In the study described in **Paper IV,** the release in the columns was higher than that from the batch in the case of approximately half of the elements analysed and vice versa for the other half. It may be that the waste particles leached (approx. 10 mm) were too big for equilibrium to be reached in the relatively short batch test, but the discrepancy is more likely due to the much higher redox potential in the batch. Mn and Fe that form insoluble oxides have a much higher release in the columns. van Zomeren et al. (2005) also found a higher release of Mn and Fe associated with low redox potential.

4.1.3 Organic matter and degradability

In the research described in **Paper II,** two wastes (M1 and M2) were treated mechanically and biologically. Several methods related to the content and stability of organic matter were used to evaluate the effect of the treatment (see section 3.4). As anticipated, all tests indicated increased biological stability. Samples from four different stages of M1waste treatment were compared using PCA. In the resulting loading plot (shown in **Paper II**), RA_4 and GP_{21} were found in the same quarter as and close to COD, DOC, BOD_5, as well as close to a DTG peak caused by combustion of organic matter. TOC and LoI were very close to each other and formed a cluster together with peaks from DTG, DSC and IC, representing combustion of organic matter. All these parameters decreased during treatment, indicating increased stabilisation, and were located to the left in the loading plot. The amount of humic and fulvic acids increased as expected and were found to the right in the loading plot. The results from the PCA indicated that these methods provide very similar information about the degree of stabilisation of M1 waste and can be used more or less interchangeably. However, as these results are based on four samples from the same waste, they should therefore be considered a strategy for more detailed investigation of the waste material and not as a means of evaluating the methods. Analysing data from more than one waste would be an interesting topic for future research and allow a better comparison of the methods.

The research described in **Paper III** used fractionation of leachate organic matter based on hydrophobicity to assess the stability of waste materials. A PCA model was built using data from MSW landfills in different stages of degradation. The resulting score plot is displayed in Figure 4 and the loading plot in Figure 5. Parameters representing a low degree of stabilisation, e.g. high fractions of TPH and HPI, are located to the left in Figure 5 while parameters representing a more stabilised leachate, i.e. HA, and HPO, SUVA, and HA/HPO are located to the right. Thus PC1 seems related to the degree of stabilisation. In Figure 4 the first PC differentiate between more and less stabilised landfills. The samples from landfills B and C containing untreated waste are located to the left. The initial samples from landfills B1* and B2* containing MBT waste are located to the bottom left while during the course of landfilling the samples are moving up and to the right signifying an increased stabilisation. In the topmost part of the score plot the two oldest leachates can be found. Thus PC2 also seem to be related to an aspect of stabilisations. According to the loading plot PC2 is mainly related to HPO, a parameter that signifies a high degree of stabilisation.

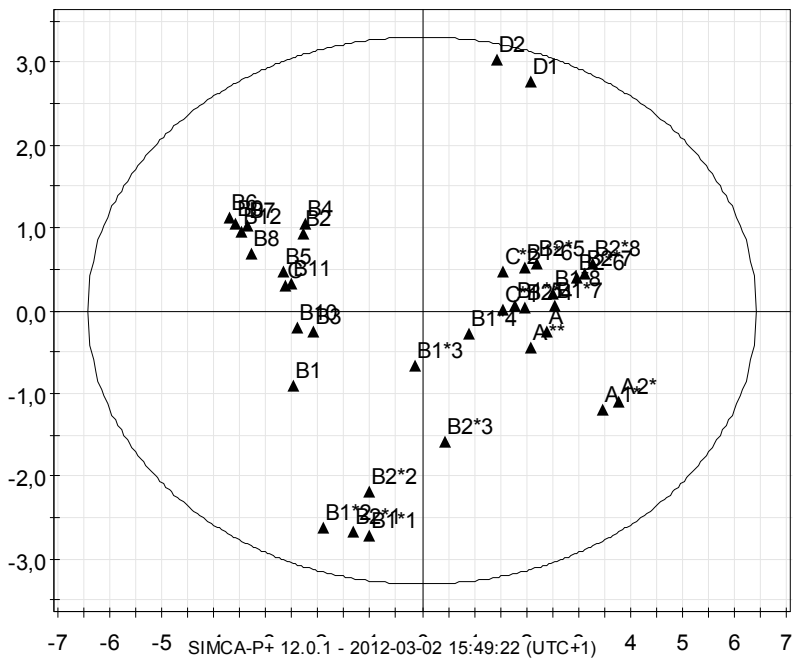

*Figure 4. PCA score plot displaying MSW and MBT waste landfill leachate samples. A: Pilot scale MSW landfill, A**: Pilot scale MSW landfill with leachate recirculation, A1* and A*2: Pilot scale landfills for MBT waste treated during 12 and 25 weeks respectively, B: Pilot scale MSW landfill, B1* and B2*: Pilot scale landfill for MBT waste, C: Pilot scale MSW landfill, C*: Pilot scale landfill for MBT waste, D: Full scale MSW landfill. Samples from landfills B, B1* and B2* are numbered from the youngest to the oldest landfill (from **Paper III**)*

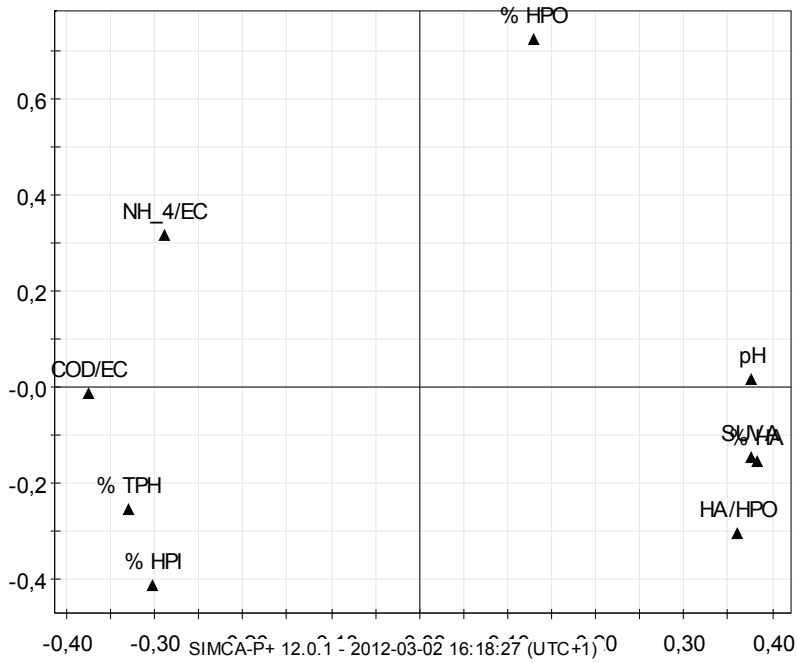

*Figure 5. Principal component analysis loading plot displaying leachate parameters related to the biostabilisation of waste (from **Paper III**)*

Based on the grouping of parameters in the loading plot (Figure 5), fractionation of the organic matter based on hydrophobicity seems to describe three different characteristics of the leachate organic matter. One is represented by HA, the second by HPO and the third by TPH and HPI combined. SUVA and HA are very closely related and can probably be used interchangeably. However, HPO and TPH/HPI contribute additional information as shown by the PCA and therefore the fractionation scheme adds additional value compared to the SUVA index.

Although it was possible to apply the PCA model to mixed waste landfills, it was clearly less suited to them (see **Paper III**). NH_4 and COD were the parameters that caused most of the deviation. The extremely low NH_4-concentration in the leachates from the modern landfills Fläskebo and the soil cell from Högbytorp made the model unsuitable for them. PC2 seemed to better capture the degree of stabilisation than PC1 for some of the mixed waste landfills.

4.2 The relation of heavy metals to other parameters

This section presents the results concerning the co-variance and correlations of heavy metals with other leachate parameters. These relations were investigated using MVDA, and although they are purely statistical they can be an indication of complex formation or other types of association that affect metal leaching and solubility.

In the study described in **Paper I**, co-variations and/or correlations between *inorganic parameters* such as EC, Cl and N_{tot} and metals were found using PCA and CCA in all seven leachate data sets. The metal most often related to the inorganic parameters was Cr, for which relations were found in the leachates from Tagene, Högbytorp and Filborna. However, clear correlations between *organic matter* and heavy metals were only found in the leachate data sets from Högbytorp and Fläskebo, although in data from Tagene and Löt, heavy metal relations with organic matter were also indicated. The metals most strongly related to organic matter varied between leachates. In the leachate from Fläskebo, Ba, Ca, Fe and Sr had the strongest correlations, while in Högbytorp it was Co and Hg. Al was included in the data from two landfills studied in **Paper I** (Fläskebo and Tagene) and in both cases was found to co-vary with parameters describing suspended matter.

A PCA of the eluate from M1 waste at four different stages of MBT was performed. Co-variance between organic matter and several metals was found from the loading plot (presented in **Paper II**). Pb and Zn, and to a lesser extent Cr, co-varied with parameters describing dissolved organic matter, which could indicate that these metals form complexes with dissolved organic matter. However, since all concentrations decrease during treatment, this common trend could also explain the co-variance. This explanation is even more plausible since other parameters that decreased, but are not directly related to metals, e.g. RA_4, have an equally strong co-variance.

The HA concentration in M1 solid material co-varied with Zn, Cr and Ni loadings for solids and, to a lesser extent, with Pb and Cd according to the score plot presented in **Paper II**. This suggests a possible affinity of these heavy metals to solid humic acids, although in line with the reasoning in the above paragraph, it could also be due to similarities in trends.

In the PCA of the data set from a reed bed leachate treatment system described in **Paper V,** TOC co-varied with Ti, Cr, Mo and Ni. This indicates that their removal patterns are similar.

4.3 Leachate quality in modern landfills

4.3.1 Organic matter, ammonium and sulfate

The modern landfills Fläskebo and the soil cell at Högbytop had very low DOC concentrations compared to Swedish landfills as presented by Öman and Junestedt (2008), see Table 6. The COD of the leachate from the soil cell at Högbytorp and was also low. However, another compliant cell at the Högbytorp landfill, mainly containing residues from recycling centres, had approximately five times higher COD values (Table 6). The BOD_7/COD ratio of approximately 0.2 in the residual cell was however relatively low, lower than the soil cell, the old landfill at Högbytorp and the Swedish landfills described by Öman and Junestedt (2008) (Table 6). MBT wastes such as M1 and M2 described in **Paper II** are also typical of the modern waste management system, although not in Sweden as mentioned in section 2.5. After treatment their eluate DOC concentrations were higher than the leachate concentrations from the studied modern landfill cells but lower than the concentrations form the older landfills (Table 6).

A low NH_4 concentration is another similarity between the modern cells at the Fläskebo and Högbytorp landfills (Table 6). The cell at Högbytorp containing recycling centre residues had higher values, although is slightly lower than all the older cells described in **Paper I**. The NH_4 concentration in the eluate from composted M1 was 10 $mg \cdot l^{-1}$, while in M2 it was 20 $mg \cdot l^{-1}$ while the median for Swedish landfills is 180 mg $NH_4 \cdot l^{-1}$ (Table 6).

In summary, compared to the DOC and NH_4 concentrations found in MSW landfills, those in modern landfills can be expected to be low, but vary depending on the type of waste landfilled in the cell. MBT waste should be expected to give rise to slightly higher concentrations than source separated mainly inorganic waste.

Table 6. Data related to organic matter and ions in leachate from three modern landfills, two MBT waste eluates, one old landfill and median values for Swedish landfills. n.a. = not analysed

Landfill	DOC [$mg \cdot l^{-1}$]	COD [$mg \cdot l^{-1}$]	BOD_7/ COD	NH_4 [$mg \cdot l^{-1}$]	SO_4 [$mg \cdot l^{-1}$]	Source
Fläskebo	21	n.a.	n.a.	0.4	900	**Paper I**
Högbytorp, soil cell	35	130	0.03	0.6	1350	**Paper III** and leachate monitoring data[2]
Högbytorp, residual waste cell	n.a.	650	0.02	42	1500	Leachate monitoring data[3]
Eluate from M1	180	n.a.	n.a.	10	n.a.	**Paper II**
Eluate from M2	41	n.a.	n.a.	20	n.a.	**Paper II**
Högbytorp, old landfill	530	440	0.07	n.a.	n.a.	**Paper I** and leachate monitoring data[4]
Swedish landfills	165	560	0.03	180	130	Öman and Junestedt (2008)

[2] The data from Högbytorp were provided by Ragn-Sells Avfallsbehandling AB, Bro, Sweden

[3] Ibid.

[4] Ibid.

High sulfate concentrations are also something that the modern landfills described here have in common. The two modern cells at Högbytorp have median SO_4 concentrations which are approximately one order of magnitude higher than the old landfill at the same site and the median concentrations in Swedish leachates presented by Öman and Junestedt (2008) (see Table 6). The average SO_4 concentration in the Fläskebo landfill was also high something that is likely caused by relatively large amounts of non-combustible plaster board residues landfilled there.

The study on fractionation of organic matter based on hydrophobicity described in **Paper III** demonstrated that the leachates from the modern cells at the Fläskebo and Högbytorp landfills contained relatively large amounts of humic substances. Thus these landfills can be considered relatively stable although they are young. The evaluation of the PCA results revealed that one major difference between the above-mentioned landfills and landfills receiving some amount of MSW or MBT waste is the extremely low NH_4 concentration in their leachates. Although this may be partly explained by the low level of degradable organic matter that can act as a source of NH_4, it could also indicate that the landfills are somewhat oxidised. Similar findings are presented in **Paper I**.

The degradation potential of the residual waste from the Fläskebo landfill described in **Paper IV** as well as that of MBT wastes exemplified in P**aper II** is low, but clearly detectable with aerobic degradation tests. Some degree of gas production in landfills for mainly inorganic waste has been previously observed (Parker et al. 2007), and van Zomeren et al. (2005) found negative redox potential, a sign of degradation, in a predominantly inorganic landfill.

Due to the remaining degradation potential, even modern landfills with a low organic content may become anaerobic, at least partially and for a certain period of time. Reducing conditions will affect the mobility of pollutants, most likely rendering it more similar to old MSW landfills than would be expected in the case of completely inorganic, oxidised landfills. Reducing conditions were found by van Zomeren et al. (2005) to cause decreased leaching of Cu and increased leaching of Fe and Mn.

In the study described in **Paper I** co-variances and/or correlations between metal concentrations and organic matter were only found in a few cases, one of which was the Fläskebo landfill with its low carbon content (section 4.2). Thus there is no evidence that the impact of organic matter on metal concentrations is smaller in landfills with low organic content, which could be due to the biochemical environment being similar to MSW landfills as a consequence of degradation.

4.3.2 Heavy metals

In **Paper IV** heavy metal release from the residual waste from the Fläskebo landfill (see section 3.1) is discussed. Only a small part of the heavy metal content of the residual waste was mobile; the accumulated amount leached at L/S 10 was several orders of magnitude lower than the total content for all heavy metals except Mn. The emission potential was relatively low; compared to other C&D residues a smaller total release was observed, but mobility was within the same range. Compared to MSW and MBT waste, the metal mobility of the residual waste from Fläskebo was lower, or in the lower part of the wide range found in the literature reviewed in **Paper IV**.

The availability of ligands such as organic matter and ions, e.g. chlorides was low in the residual waste eluates (**Paper IV**), which might be one explanation for the low metal mobility observed. It could also be due to the material itself, i.e. the form in which the metals are present. However, this aspect was not included in the study described in **Paper IV**. The design of the study, e.g. particle size, L/S ratio and contact time can also affect the release of metals (Fällman 1997; Kylefors et al. 2003; Kalbe et al. 2008; van Praagh et al. 2009). This is not considered the main cause of the differences observed, since the study used parameters within the same range as the studies used for comparison.

Table 7. Concentrations of selected heavy metals in leachate from three modern landfills, two MBT waste eluates (L/S 10), one residual waste eluate (L/S 10), one old landfill and median values for Swedish landfills. n.a. = not analysed, n.d. = not detected

Landfill	Cd [µg·l^{-1}]	Cr [µg·l^{-1}]	Cu [µg·l^{-1}]	Ni [µg·l^{-1}]	Pb [µg·l^{-1}]	Zn [µg·l^{-1}]	Source
Fläskebo	0.45	6.9	76	47	1.5	229	**Paper I**
Högbytorp, soil cell	1.7	3.2	93	38	0.88	500	Leachate monitoring data[5]
Högbytorp, residual waste cell	1.4	47	350	150	3.3	1200	Leachate monitoring data[6]
Eluate from M1	6.9	26	806	191	16	690	**Paper II**
Eluate from M2	<0.5	<10	62	56	<5	270	**Paper II**
Eluate from residual waste from Fläskebo	0.01 – 0.03	2 – 6	0.1 – 4.9	6 – 48	0.003 – 0.13	9 – 119	**Paper IV**
Högbytorp, old landfill	0.86	53	39	262	16	346	**Paper I**
Swedish landfills	0.20	8.2	13	26	3.7	46	Öman and Junestedt (2008)

[5] Ibid.

[6] Ibid.

Since residual waste is not "diluted" with organic matter it could be expected to give rise to leachate with higher metal concentrations. The low mobility found in the study presented in **Paper IV** suggests the opposite. The eluate concentrations at L/S 10 resented in Table 7 are also very low. However, the study described in **Paper IV** only included one type of residual waste, and although it is considered typical of a waste management system moving away from landfilling, it is not entirely representative. The results presented in **Paper IV** clearly show that the actual leachate from Fläskebo landfill was also affected by other types of waste with a higher emission potential.

Data from the actual Fläskebo landfill presented in **Papers I** and **IV** revealed salt and metal concentrations within the same range as MSW landfills (see some examples in Table 7). A comparison with another landfill (Avfall Sverige 2009a) and unpublished water balance calculations show that the leachate from Fläskebo landfill is relatively diluted and that the release per kg of waste is no less than from older landfills. Two modern landfill cells at the Högbytorp landfill site had much elevated concentrations of Al, Cd, Cu and Zn compared to the old landfill at the same site while the other metal concentrations were in the same order of magnitude or even lower (some metal concentrations are exemplified in Table 7).

The leachates sampled at L/S 10 can be used as a predictor of the future leachate quality of the waste after many years of leaching. In **Paper IV,** the Fläskebo landfill is estimated to reach L/S 10 after approximately 400 years. Assuming that the eluate quality at L/S 10 resembles the leachate quality when post-closure care is ended and that that leachate is released without treatment, the concentrations measured at L/S 10 will be released to the environment. Cr, Ni, Mn and Zn seem most likely to cause a long-term environmental burden, as the concentrations in the eluate are in the same order of magnitude as the proposed guidelines and/or elevated compared to surface water concentrations (see Figure 6). Compared to the eluates, the actual leachate has many elevated concentrations, exemplified by Zn in Figure 6. But even when only considering the relatively unpolluted residual waste used to produce the eluates, it seems that elevated metal concentrations can be expected for a very long time.

In the PCA loading plot described in **Paper II,** the solid and liquid heavy metal concentrations were clearly separate, which demonstrates that they evolve differently during MBT. In fact, the mobility of almost all metals decreased, explanations for which include

- the solid organic matter changing into forms (HA and FA) with a higher affinity to heavy metals,
- the heavy metal leaching being highly dependent on complexation with dissolved organic matter and therefore the reduction in organic matter leaching led to decreased metal leaching and
- the increased oxidation of the material favouring the formation of less soluble inorganic metal species, e.g. iron (hydr)oxides.

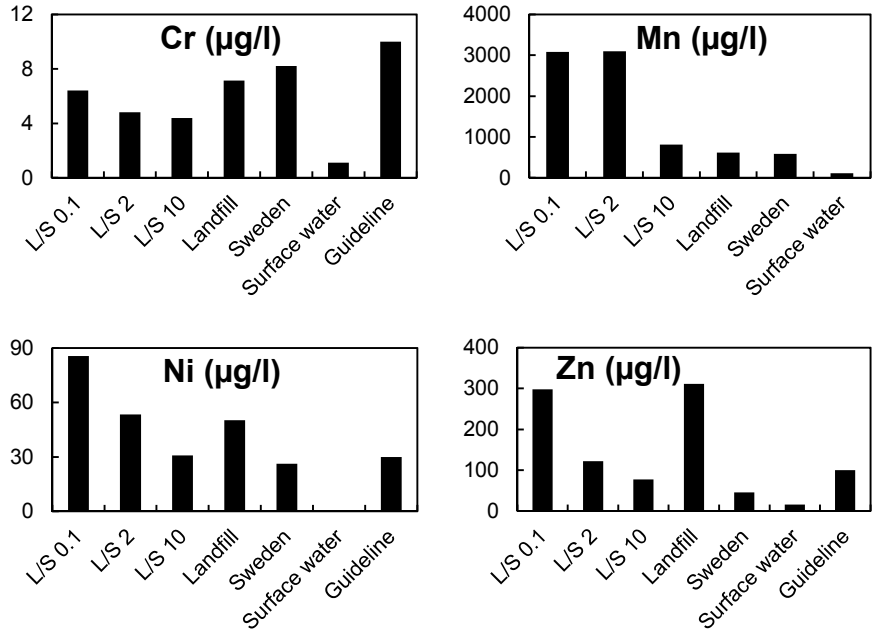

*Figure 6. Eluate concentrations at liquid to solid ratios (L/S) 0.1, 2 and 10 compared to Swedish leachate concentrations (Öman and Junestedt 2008), flow weighted average leachate concentrations for the Fläskebo landfill for the period 2004-2008, ambient surface water data at the landfill site prior to the start of landfilling (Renova AB 2004) and preliminary release guidelines (Renova AB 2010) (except for Mn, for which no guideline has been set) (adapted from **Paper IV**)*

As described in **Paper II** Cu leaching increased in both M1 and M2 which might be explained by an affinity of Cu to dissolved humic acids. In M2, HA was the only concentration apart from Cu that was higher in the output than the input eluate. Despite of the decreased metal mobility the eluate concentrations at L/S 10 were relatively high from M1 (Table 7). The eluate metal concentrations from M2 were however much lower (Table 7).

During the MBT and leaching tests described in **Paper II**, the waste was subject to anaerobic conditions. Due to the remaining degradation potential (see section 4.3.1) the landfill cell where MBT waste will eventually be landfilled can become anaerobic. The impact of anaerobia on metal leaching from aerobically stabilised waste should therefore be assessed in future research.

As described in section 2.10 the heavy metals in methanogenic landfills are immobilised by organic matter and sulfides. Long term immobilisation is dependent on organic matter and iron oxides. The situation in modern landfills is, however, not as well studied. Assessing the long-term sorptive capacity of organic matter, sulfur and iron in various types of landfill for mainly inorganic waste is an interesting topic for future studies.

4.3.3 Toxicity

Paper V describes a study that employed chemical characterisation and toxicity tests to evaluate treatment of leachate from a landfill containing both MSW and MSWIBA. PCA indicated that heavy metals contributed to the toxicity to the test organisms *Pseudokirchneriella subcapitata* and *Lemna minor*. The toxicity to *Danio rerio* and *Vibrio fischeri* seemed to have been caused by TOC, NH_4 and heavy metals, most notably vanadium. Landfill leachate toxicity is often attributed to NH_4 and DOC (Svensson et al. 2005; Pivato and Gaspari 2006) but all the substances suspected to contribute to toxicity in the study described in **Paper V** have been found to be toxic in some previous studies (Cook et al. 2000; Jurkonienė et al. 2004; Pivato and Gaspari 2006; Amezcua-Allieri and Salazar-Coria 2008). Since the concentrations of both NH_4 and DOC are much lower in modern landfills, the contribution from these parameters to leachate toxicity should decrease substantially in the future. Thus, from a toxicity perspective, metals may become increasingly important in modern landfills.

4.4 Sorption filters for heavy metal removal

A study of sorption filters for heavy metal removal is described in **Paper VI**. Granular activated carbon, bone meal and iron fines were tested for their capacity to remove metals from MSW landfill leachate from the Spillepeng landfill.

Granular activated carbon effectively removed many metals, i.e. more than 90 % of Co, Cr, Fe, Mn and Ni. Ca, Cu, Pb, Sr and Zn were also removed but not to the same extent, while As, Cd, Hg, Mg and Mo were released in one or more samples. More than 90 % of the organic carbon and some of the P were removed, while the GAC had no effect on N. Since no pH decrease was observed and the carbon seemed to have a basic character, sorption to basic sites appears to have been the main removal mechanism. Sorption probably also occurred with organic matter. To optimise a GAC process for the sorption of heavy metals from landfill leachate, the maximum sorption capacity of the carbon is the most important parameter.

Bone meal was less effective than GAC but released fewer metals. It removed more than 90% of Sr and Mn, 80% or more of Cr, Fe and Hg and between 20 and 80% of Al, Ca, Cu, Mo, Ni, Pb and Zn. Cd and Mg were released initially. The greatest drawback was a very large release of TOC, N and P. Microbial activity is likely to have occurred in the columns. Ion exchange with Ca^{2+} and precipitation of new, heavy metals containing phosphate minerals have been proposed as important mechanisms of metal sorption to hydroxyapatite, the main mineral component of BM (Deydier et al. 2003; Dybowska et al. 2009). In the study described in **Paper VI** there was a net removal of Ca but a release of P, suggesting that Ca re-precipitated with other counter ions. It is also possible that complexation with organic matter in the BM contributed to the sorption.

Iron fines were the least effective sorbent. Although most metals (As, Co, Cr, Cu, Fe, Mg, Mn, Pb, Sr and Zn) were removed to some extent in almost all samples, Ca was the only one to be removed by more than 90%. Cd, Mo, Al, Hg and Ni were released, some of which are common in stainless steel alloys. The IF released some TOC, probably from cutting fluid residues. This had no effect on N but removed some P. Metal removal by zero-valent iron is usually attributed to

adsorption to or co-precipitation with iron corrosion products on the surface of the sorbent (Benjamin et al. 1996; Wu and Zhou 2009). In the study described in **Paper VI,** all Fe seemed to precipitate. The pH appeared to be controlled by OH^- release due to anion exchange, although as the metals were assumed to mainly exist in positively charged species in the leachate, this mechanism was not important for sorption. Co-precipitation was probably the main mechanism. Aeration is paramount for an optimal process due to the importance of iron oxidation.

One important lesson from the study is the risk of release. Even the GAC that was marketed as suitable for drinking water purification released some undesirable substances. Therefore, when evaluating potential filter materials it is important to study a large number of pollutants, not just the substances targeted for removal.

The filtration study described in **Paper VI** employed landfill leachate from a MSW cell. Due to its higher DOC content, this leachate differs from what is expected in modern landfills. Nevertheless, the sorption mechanisms suggested above should be even more efficient in a leachate with less DOC, with the possible exception of sorption with organic matter to GAC.

5 DISCUSSION: LANDFILL MANAGEMENT FOR THE FUTURE

5.1 Differences between MSW landfills and modern landfills

Organic matter and nutrients that to date have been the main foci of leachate treatment will constitute a far smaller problem in leachates from modern Swedish landfills because of the very small amounts of organic matter landfilled there (see section 4.3.1). Thus treatment of leachates such as those from Fläskebo and the soil cell at Högbytorp (**Papers I** and **III**) does not need to target bulk organic matter and nutrients. However, the quality of the leachate depends on the waste and somewhat higher concentrations of these contaminants were observed in the leachate from a modern cell for recycling centre residues at the Högbytorp waste management site (see section 4.3.1). Since modern landfill cells tend to be more specialised, the variation in the leachate quality between cells will increase. One single landfill site may have several different leachates in need of various types of treatment. It cannot be ruled out that biological treatment can be necessary in some cases, even in landfills that comply with the Swedish implementation of the EU Landfill Directive, since the waste may theoretically contain up to 10 % of easily degradable carbon.

The leaching tests described in **Paper IV** indicated that metal concentrations could be a smaller problem in the future. However, data from the actual Fläskebo landfill presented in **Papers I** and **IV** revealed salt and metal concentrations within the same range as MSW landfills. The modern landfill cells at the Högbytorp landfill site had much elevated concentrations of certain metals compared to the old landfill at the same site, while the other metal concentrations were in the same order of magnitude or even lower. Since the research presented in this thesis has illustrated that some degradation potential exists in modern Swedish landfills the conditions will most likely be reducing, at least in parts of the landfill. This would make metal leaching from modern landfills relatively similar to landfills rich in organic matter.

The changes over time in landfills for mainly inorganic waste will probably be smaller than those in MSW landfills, as the main mechanisms that lead to changes are depletion of easily soluble substances and solubility control as opposed to biological processes. The absence of an initial acid phase may decrease emissions, or at least the maximum leachate concentrations.

Although modern landfills have similar emissions of inorganic pollutants, the total number of landfills has decreased dramatically in Sweden as well as in many other countries and thus the total environmental burden of landfilling is smaller. However, as pointed out by van Praagh and Persson (2006), the new legislation has also led to the closure of many old landfills which are not subject to the same strict emission control and thus constitute a significant burden on the environment.

Since according to Swedish legislation the gas emissions from inorganic landfills do not need to be monitored, knowledge of the actual gas emissions from modern landfills is very limited. However, the amounts of landfill gas generated are often assumed to be negligible. This study found a measurable degradation potential in one waste from a modern Swedish landfill although it is not clear to what extent this degradation potential will actually lead to landfill gas emissions. Future research should study gas emissions and also try to investigate the on-site redox potential, since it is difficult to infer the redox conditions inside the landfill by means of leachate samples.

5.2 Fate of metals in leachate

Metals in landfill leachate can be managed in at least three different ways:

- Removal
- Recycling
- Release

Removal of metal pollution from leachate can be successful. Sorption filters can be a viable option for the treatment of landfill leachates when the focus is to remove heavy metals (**Paper VI**). However, metals can never be eliminated, only concentrated in another liquid or solid material, i.e. filtration retentate, sorption material, ion exchange resin, regenerating fluid, etc. This material will then need management, for example by incineration and/or landfilling. Through incineration much of the metals will be concentrated in fly ash and air pollution control residues, which will in turn need management. It seems likely that the metals not released into water and air will eventually be returned to a landfill. Unless they are in a more stable state than when first landfilled, they may again end up in leachate.

Recycling of metals, e.g. from incineration residues, is the topic of on-going research and an interesting option for the future (see e.g. Karlfeldt Fedje 2010). However, this technology is still being developed.

The metal concentration in MSW landfill leachate is often low and considered relatively un-problematic (Barlaz et al. 2002). In practice, therefore, the third option, release, is not un-common. Most landfills, whether or not they have treatment for metals, have release limits that allow a certain amount of metals to be released into the environment. When the metals reach the environment they are expected to be either sufficiently diluted to prevent harm or to become bound in inert forms to sediments etc. However, when released the metals are no longer under our control and they will contribute to diffuse ubiquitous pollution.

5.3 Containment or not?

The containment approach implemented in many parts of the world has been questioned, mainly because it may prevent stabilisation of the waste, thus preserving the emission potential until possible break down of the liner (Allen 2001). In some countries, e.g. Sweden, a tight top cover should be added to landfills as soon as possible after completion and thus the containment

approach is in practice prescribed. Therefore the discussion of this approach is relevant. In the case of MSW, bioreactors are among the most important alternatives (section 2.5). Flushing of contaminants during the active phase has also been suggested (Cossu et al. 2003).

Landfill gas and leachate organic matter and nutrients are among the main pollutants from landfills with a significant amount of degradable waste. These pollutants can be treated and eliminated, or at least turned into other, less harmful molecules. However, containment can slow down gas production and render the gas more difficult to utilise or treat, and it may delay the leaching of treatable contaminants until after treatment has ended. In many modern Swedish landfills, inorganic pollutants represent the main emission potential. Flushing these landfills or allowing water to infiltrate in order to enhance leaching would move inorganic pollutants such as heavy metals from the waste material to the leachate. Although they can be removed from the leachate that is not a final solution as discussed in section 5.2 above.

In the case of landfills for hazardous waste, the containment approach is still accepted. For example, Scharff et al. (2011) pointed out the beneficial effect of a tight cover over a landfill for stabilised hazardous waste, as it slowed down the leaching of contaminants. However, this means that in the case of landfills for hazardous waste, leaving the contaminants concentrated is considered acceptable. In order to protect the environment this seems a reasonable solution, as the main pollutants cannot be effectively treated but merely relocated, concentrated or dispersed.

Since the pollutants in inorganic, non-hazardous waste landfills are similar to, although less concentrated than, those in certain hazardous waste, the containment approach could be considered for them also. Some degree of leaching is probably inevitable, but that is not a reason for trying to slow it down. Slower leaching means that the flux into the environment is smaller, allowing the ecosystem a better chance to adapt and probably leading to lower concentrations. Furthermore, although future developments are impossible to predict, many trace metals are becoming increasingly valuable and landfills could become important mines for these elements (Krook et al. 2012).. In order to minimise leaching, infiltration of water should be avoided, e.g. by means of a tight cap. Although the cap is likely to deteriorate, as long as it is not completely destroyed it will restrict infiltration and pollutant mobilisation to some degree.

Some have argued that the lifetime of a landfill is not over until the concentration gradient between its interior and the surroundings has been eliminated. However, it will take an extremely long time to achieve this, even without containment measures, something that is obvious due to the uneven spatial concentration of elements in the crust of the earth. Furthermore, in a northern country such as Sweden, it is only relevant to aim at containing the waste until the next ice age which can be expected in some tens of thousands of years or sooner (Berger and Loutre 2002; EPICA community members 2004). If the concentration of metals in the landfill is still higher than in the surroundings at the start of the next ice age, the containment approach will in some respects have been successful. Bozkurt et al. (2000) suggested that it is possible to design a landfill where the duration of complete oxidation is of the same order of magnitude or even longer. On the one hand, this is not particularly long on a geological time scale, but on the other, it is of the same order of magnitude as the age of human civilisation. This means that if the containment approach is adopted, containment measures must be passive.

6 CONCLUSIONS AND OUTLOOK

The most striking difference between modern landfills for mainly inorganic waste and municipal solid waste landfills is the extremely low concentrations of dissolved organic carbon and NH_4 in some of the modern leachates. In addition, based on leachate organic matter fractionation, two modern landfills were classified as relatively stable in spite of their young age. The mechanically and biologically treated wastes that were included in the study leached slightly higher concentrations of dissolved organic carbon and NH_4.

A comparison between modern landfills and municipal solid waste landfills revealed similar metal concentrations. However, even a relatively unpolluted residual waste leached elevated metal concentrations at a liquid to solid ration of 10. Thus metal leaching at an environmentally relevant degree must be expected for a very long time.

Landfilling of different types of waste in specialised cells is becoming increasingly common and greater variations in leachate quality between cells should be expected in the future. On the other hand, the changes over time in landfills for mainly inorganic waste will probably be smaller due to the more moderate effect of biological processes.

As a result of the remaining (small) biodegradation potential modern landfills may be at least partly anaerobic. This is mainly expected to affect leachate quality, rendering it more similar to that of MSW landfills than expected from completely inorganic materials. However, the low degradation potential is likely to be depleted sooner and the oxidation of the modern landfills thus brought forward. The effect of degradation and subsequent oxidation on the long term leachate quality should be assessed in future studies. The abundance of metal scavengers such as organic matter, sulfur and iron relative to the heavy metal content and their long term sorptive capacity in modern, mainly inorganic, landfills should also be estimated in future studies. Identification of other potential scavengers would also be an interesting topic for further research.

Inorganic parameters were dominant in the multivariate data analyses, probably due to the fact that they are related to much of the variation caused by dilution, depletion and input materials, and because many salinity related parameters are included in most monitoring programmes. Co-variations and/or correlations between inorganic parameters and metals were found in all relevant leachate data sets. Cr was the metal most often related to the inorganic parameters. In landfill research, discussions about heavy metal solubility tend to focus on organic matter complexes, but the present findings suggest that attention should also be paid to inorganic complexes and their role in heavy metal leaching.

Clear correlations between organic matter and heavy metals were only found in a few of the data sets, one of which came from a modern landfill with low organic content. Thus there is no evidence that the impact of organic matter on metal concentrations is smaller in such landfills. This could be due to the biochemical environment being similar to MSW landfills as a consequence of degradation.

The multivariate tools employed in the research presented in this thesis proved useful for statistically elucidating possible relationships between parameters in regular landfill leachate monitoring data. They facilitated identification of the causes of the variation in the leachate data such as dilution, redox potential, treatment effect and biostabilisation. Principal component analysis could be used to optimise leachate monitoring programmes due to its ability to identify important or redundant parameters. It can also be employed in finding a suitable battery of bioassays.

Future work using statistical tools to study landfill leachate data should focus on deepening the understanding of and, if possible, quantifying the physical processes underlying the statistical parameters. This might be achieved by including parameters describing environmental and operational conditions in the model. As time series grow longer every year, the possibilities of creating strong models are improving.

Treatment of leachate from modern landfills probably needs to focus on inorganic parameters such as salts and heavy metals. Sorption filtration could be one option for heavy metal removal, as the research described in this thesis demonstrated that granular activated carbon, bone meal and iron fines can sorb heavy metals from real landfill leachate. It is, however, essential to case-specifically evaluate the proposed sorption technique. One important lesson from the research is the risk of release of unwanted substances. Therefore, when evaluating potential filter materials studying a large number of pollutants, not just the substances targeted for removal, is necessary.

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APPENDIX: MULTIVARIATE DATA ANALYSIS

This appendix explains two multivariate data analysis tools; principal component analysis (PCA) and canonical correlation analysis (CCA). First, PCA is illustrated by a simple example with fictional data, which demonstrates how to interpret the results presented in the main text of this thesis. Thereafter follows a brief explanation of CCA.

Principal component analysis

The purpose of PCA is to take a large and complex data set where the variables are related to each other, and thus present redundant information, and transform it into a smaller data set with only a few variables that are not related.

In Figure 1, six fictional variables, a to f, are presented. They could represent, for example, six leachate parameters sampled on five different occasions, in which case the x axis would indicate time and the y axis concentration. A PCA was performed in order to investigate these variables more efficiently. The variables were compiled into a data matrix X, where variable a represents the first column, variable b the second, etc. PCA transforms the original matrix X into a new matrix Z, where $Z = X \cdot U$. The transformation matrix U is selected so that as much of the variance as possible is concentrated in the first Z column. The second Z column is orthogonal to the first and contains as much of the remaining variance as possible. The columns of the new matrix Z are called *principal components* (PCs). In this example, after performing the PCA the first PC explains 59 % of the original variance and the second 40 %. Thus it is possible to study two variables instead of six and only 1 % of the variance is overlooked.

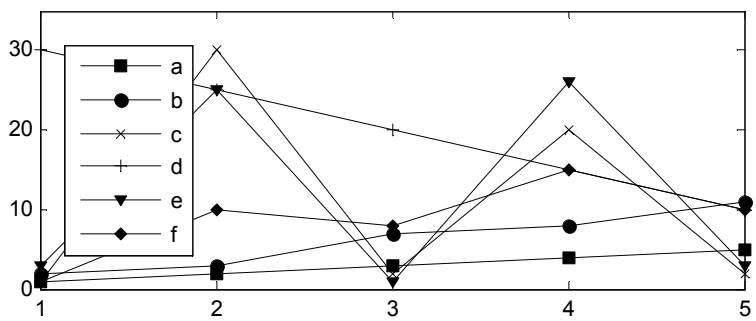

Figure 1. A fictional data set with six variables (a – f) sampled on five occasions.

The transformation matrix U contains the *loadings* to be applied to each variable in X when transforming it. Plotting two columns of U against each other produces a *loading plot*; see the example in Figure 2 where the first two columns in U, corresponding to PC1 and PC2, are plotted. The loading plot illustrates the co-variance of the *variables* (a – f). The variables that contribute most to the respective PC are located far from the origin. Those located close to the origin are thus not well represented in these two PCs. Variables located close to each other have a strong co-variance with each other, while those opposite each other have a negative co-variance.

Figure 2 is a loading plot of variables a – f. As variables a and b are located close to each other, they have a strong co-variance as would be expected, since they both exhibit increasing trends (see Figure 1). Variable d has a decreasing trend (see Figure 1) and is located opposite a and b, thus having a strong negative co-variance with them. The first principal component, PC1, is related to variables a, b, d and f, since these are all located far from the origin with respect to the x axis. The pattern that variables a, b, d and f have in common is a trend, and thus in this example, the underlying process behind PC1 is also a trend. The second principal component, PC2, is most strongly related to variables c and e, as they are located far from the origin with respect to the y-axis. Variable f is also related to PC2, but not as strongly as c and e, since it is closer to the origin. Variables c, e and f exhibit oscillating behaviour, which is most likely the pattern underlying PC2 in this example.

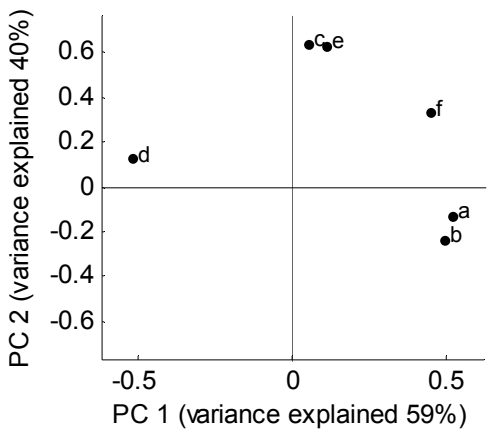

Figure 2. PCA loading plot of a fictional data set.

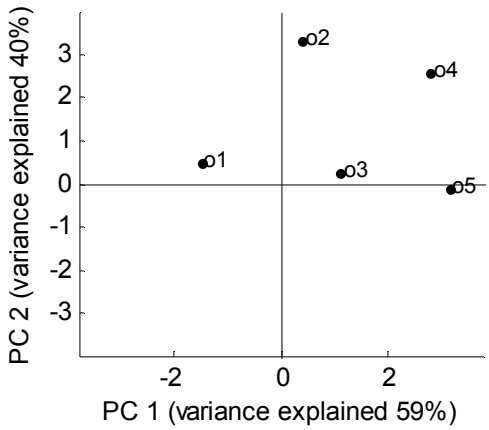

Figure 3. PCA score plot of a fictional data set.

In the matrix Z that resulted from the transformation, the rows are the transformed objects (e.g. leachate samples or time steps) and the columns are the PCs. Plotting two PCs against each other produces a *score plot*, which describes the co-variances between *objects* (see e.g. Figure 3). The relative position of the objects (o1 – o5) in the score plot (lined up from left to right) confirms that PC1 is related to trends. The loading plot showed that PC2 is related to the variables c, e and, to a lesser extent, f. That it captures their oscillation is quite clear from the score plot, as the objects reproduce this behaviour in Figure 3.

Canonical correlation analysis

CCA is a method for studying two related data sets. It identifies the linear combinations of the variables in the two data sets that have a maximum correlation and, as a result, it identifies the patterns that occur together in the two data sets. The aim of a CCA is to enable the study of a small number of variables that capture the most important correlations between the two data sets.

Assume, for example, that there are two data sets, Y and Z. The columns in each data set are variables (e.g. leachate parameters) and the rows are objects (e.g. time steps or samples). Y is called the *predictor* (the explaining variables), while Z is the *predictand* (the explained variables). Using two separate transformation matrices, R and Q, the CCA transforms the data sets into two new data sets, U and V. $U = Y \cdot R$ and $V = Z \cdot Q$. The columns of the new matrices U and V are termed canonical components and the rows are the transformed objects. The transformation matrices R and Q are chosen so that the correlation between the first column in U and the first column in V is maximised. The correlation between the second pair of canonical components is maximised with the constraint that they are orthogonal to the first.

In this thesis, the results from the CCA are presented as so-called *homogeneous correlation maps*. These are tables that display the correlation between the original variables (columns of Y and Z) and the canonical components (columns of U and V). The correlations between each column of Y and those of U form the *left homogeneous correlation map*. The correlations between each column

V and those of Z form the *right homogeneous correlation map*. If the CCA is successful, the canonical components that form the first pair, i.e. the first column of U and the first column of V, are strongly correlated. Therefore, the original variables that are strongly correlated with these components are likely to be related to the same process, i.e. the process causing the correlation. For an example of a correlation map, the reader is referred to the main text of this thesis.

Appended paper

I

H. Modin, M. van Praagh and K. M. Persson. Multivariate data analysis of regular landfill leachate monitoring data. Waste Management (submitted).

Multivariate data analysis of regular landfill leachate monitoring data

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Abstract

Regular landfill leachate monitoring generates large amounts of data that could provide valuable information about the parameters and processes governing leachate quality. In this work two multivariate data analysis (MVDA) tools have been used to extract information from these complex data; principle component analysis (PCA) and canonical correlation analysis (CCA). With PCA it was possible to find co-varying leachate parameters and CCA was used to find correlations between two fully multidimensional data sets, in this case between physico-chemical leachate data and metal concentrations. Correlation between organic matter and heavy metals was a recurring pattern but inorganic parameters seem to be at least as important for metal concentrations. When comparing a modern landfill with little organic matter to older landfills no indications were found that the organic parameters are less correlated to metal concentrations in the "carbon-poor" landfill. Combining PCA and CCA provided more detailed understanding and stronger support for the conclusions. Geochemical modelling further improved the analysis. The findings further indicate that PCA and CCA could be used to optimise leachate management and sampling as they can identify parameters that describe redundant information. However, for two of seven data sets it seemed that MVDA did not contribute valuable additional information.

Keywords: Landfill leachate monitoring; Multivariate data analysis; Principal component analysis; Canonical correlation analysis; Heavy metals; Organic matter

1 Introduction

The main potential long-term environmental risk from waste landfilling is posed by its liquid emission - the leachate (Galvez et al., 2010; Kjeldsen et al., 2002). Consequently, leachate monitoring is usually required by legislation or authorities as for example in the EU (Council of

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the European Union, 1999), British Columbia (Ministry of Environment, 1996) and the USA (CFR, 1991). This type of monitoring generates large amounts of data on leachate composition and could provide valuable information about the parameters and processes governing leachate quality. Due to time and resource limitations collection and analysis of leachate becomes a compromise between information density and applicability; leading to a restricted number of sampling occasions per year. Non-regular leachate sampling campaigns with higher sampling frequencies, replicate sampling and an increased number of parameters render improved information density but suffer from short time series (Kjeldsen et al., 2002). Parameters and sampling frequencies at landfills in Sweden are determined by the competent authorities, although the Swedish implementation (NFS, 2004; SFS, 2001) of the EU landfilling directive (Council of the European Union, 1999) sets minimum requirements. As a consequence, different landfills in Sweden are monitored according to partly different programs.

Sampling errors, mixing of leachates from different parts of the landfill before sampling, and the complex chemical nature of landfill leachates restrict the interpretation to identify trends and dependencies such as between total organic carbon (TOC) and biological oxygen demand (BOD). Many of the parameters measured are interrelated and some may provide redundant information, such as electrical conductivity (EC) and Cl. Variations are usually large, not only from site to site but even within a site (Kängsepp and Mathiasson, 2009). Large variations and noise complicate interpretability with univariate techniques (Nixon et al., 1997).

Multivariate data analysis (MVDA) provides tools for dealing with complex data, since it is a field in statistics that deals with more than two related variables. Principle component analysis (PCA) is a multivariate technique that is widely used in various fields of research for noise reduction, data simplification and for multivariate visualisation and prediction (Jackson, 1991). It is a powerful tool to simplify large and complex data sets and obtain an overview of the relations among different parameters, and it is becoming popular within landfill research. Regarding leachate, PCA has previously been used to find differences in leachate quality among landfills in the same area (Gómez Martín et al., 1995) and to classify landfill cells or leachate samples (Andreas et al., 1999; Lou et al., 2009; Ludvigsen et al., 1996; Rodriguez Ruiz et al., 2009). It has also been used to find relations among leachate parameters, or to identify parameters that are particularly important for leachate quality (Durmusoglu and Yilmaz, 2006; Galvez et al., 2010; Kylefors, 2003).

Canonical correlation analysis (CCA) is a multivariate method for discovering and quantifying the correlation between two complex data sets (Barnett and Preisendorfer, 1987). van Praagh and Persson (2004) carried out the only CCA in waste research known to the authors. They successfully used it to model conductivity in a landfill leachate through measurements of water levels in the landfill, thus revealing a strong influence from the water table on leachate quality. A similar method, canonical correspondence analysis, which assumes a Gaussian instead of a linear relationship, has been used to study species communities affected by landfills (Chang et al., 2010; Williams et al., 1997).

This work aims at analysing regular landfill leachate monitoring data using PCA and CCA and check for redundancies and interdependencies in order to improve the understanding of factors governing leachate quality. A special focus is given to heavy metals and organic matter. Another

aim is to test PCA's and CCA's susceptibility for variable landfill leachate data input and the impact on reproducibility and reliability of the results.

The study is undertaken with regular leachate monitoring data from six Swedish landfills. Previous studies comparing leachates using PCA (e.g. Andreas et al., 1999; Gómez Martín et al., 1995; Rodriguez Ruiz et al., 2009) include all studied leachate data sets in one joint analysis. In this study each leachate monitoring data set was analysed separately to focus on the individual properties of each of the landfills and compare them to each other.

In the EU landfilling of organic waste has become restricted. As a result, new landfills have much lower organic content compared to traditional municipal solid waste (MSW) landfills (van Praagh and Persson, 2006). Although there is a relatively good understanding of the processes governing the leachate quality from MSW landfills (Kjeldsen et al., 2002), the knowledge of what to expect from new and future landfills is incomplete. Therefore one landfill constructed and managed entirely according to the new legislation is included in this study in order to compare it to older landfills.

2 Materials and methods

Principle component analysis (PCA) was used to create an overview of relationships between the leachate parameters. Canonical correlation analysis (CCA) was applied to quantify correlations between metals and other parameters. All statistical analyses were performed using Matlab® 7 (The MathWorks Inc., 2009) with its statistics toolbox.

2.1 Landfills

Regular landfill monitoring data were obtained from six Swedish landfills of different age and size and containing different types of waste. The data used in this study were created by landfill owners as a part of monitoring and reporting on leachate quality, but have not been statistically analysed extensively until now. Some parameters have been measured in all leachates, but the number of parameters and the sampling frequencies vary. The parameters included from each landfill can be found in Table 1. Efforts were made to include a wide variety of landfills. For each landfill the sampling point was used that was believed to best represent untreated leachate.

2.1.1 Fläskebo

The Fläskebo[1] landfill site southeast of Gothenburg in the southwest of Sweden was, as it opened in 2003, the first landfill in Sweden commissioned entirely according to the Swedish implementation of the EU landfill directive. It is a landfill for non-hazardous waste and receives mainly sorting residues, non-combustible industrial waste and contaminated soils. Only waste with <10 % TOC has been landfilled here. Leachate from the entire landfill is jointly collected and stored in ponds. Samples for analyses were collected from a pipe that leads the leachate from the ponds to a treatment facility. A maximum of one leachate sample per quarter was used.

[1] The data from Fläskebo was provided by Renova AB, Göteborg, Sweden

However, in some years the ponds were dry in the summer and, therefore, there were only three samples collected these years. The concentrations of many parameters (e.g. EC, Cl, NH_4, Na, K, Ba and Cu) were decreasing rapidly during the first months. The high initial concentrations were possibly due to MSW incineration bottom ash used inside the landfill during its construction. A preliminary PCA (not included in this paper) showed that the first three quarterly samples were quite different from the others, as they were separated from them in the score plot. They were thought to represent the construction material of the landfill rather than the waste and therefore they were excluded. That left 15 samples from August 2004 to November 2008. The dataset included 38 parameters.

2.1.2 Tagene

Tagene[2] landfill has been operated since 1974 just north of Gothenburg. It has mainly received ash from waste incineration but during its first years waste rich in organic material such as waste water treatment sludge was also disposed of. In 2008, ash, non-combustible waste, asbestos and industrial sludge were the main waste types landfilled at Tagene. Parts of the landfill have been supplied with final capping while others remained active in 2008. The data used in this study were derived from analyses of leachate collected from a pipe that drains the middle part of the landfill as the leachate is almost undiluted by surface water at this point. Data collected quarterly was available from the time period 2000 to 2008 and all 36 samples were included in the analysis that comprised 34 parameters.

2.1.3 Högbytorp

The Högbytorp[3] waste facility is situated northwest of Stockholm in eastern Sweden and received a mixture of MSW and different kinds of industrial waste between the mid 1960's and 2008 when the main part of the landfill was closed. A final cap was constructed continuously from 2003 and onwards, and in 2006 approximately one third of the landfill was capped. Before 2007 the leachates from the landfill and from waste treatment areas were jointly collected and lead to two sedimentation ponds with forced aeration. Leachate samples for analysis were collected monthly or quarterly, from the inlet to the ponds. The data used for this study ranges from 1997 to 2006. However, not all parameters were measured during the whole period. For inter-comparison, one dataset was created containing data from the whole period (98 samples) with 12 parameters, and one dataset comprised the years 1997 to 2000 containing 15 parameters in 42 samples.

2.1.4 Filborna

The Filborna[4] landfill just outside Helsingborg in southern Sweden has been receiving mixed municipal and industrial waste since 1951. The landfill was closed in the end of 2008 with the exception of a small part. The landfill had been capped continuously. Leachate used for the analyses was collected monthly from a pipe that drains both a major part of the landfill and areas

[2] The data from Tagene was provided by Renova AB, Göteborg, Sweden
[3] The data from Högbytorp was provided by Ragn-Sells Avfallsbehandling AB, Bro, Sweden
[4] The data from Filborna was provided by NSR AB, Helsingborg, Sweden

for waste sorting and treatment, including composting of garden waste. Samples were taken several times a month, but the sampling frequency was not the same for all parameters and not all parameters were sampled at the same day. Therefore, monthly means were used. This resulted in 45 data points with a monthly interval comprising 21 parameters from the time period 2006 to 2009.

2.1.5 Spillepeng

At Spillepeng[5], just north of Malmö in southernmost Sweden, landfilling has been going on since the 1940's. In this work leachate data from two landfill cells are studied. One cell received mainly MSW between 1994 and 1999. The other is a so called "special waste cell" where mainly fly ash, bottom ash, blasting sand, asbestos wastes and contaminated soil were landfilled between 1990 and 1993. Within a year after closing the cells were supplied with temporary soil covers. The leachate from each cell is collected separately and sampled from pumping stations before treatment. Data was available from 2000 to 2010. The sampling frequency varied during the period from monthly to yearly sampling. For each cell two datasets with quarterly data were prepared. For the special waste cell one set includes the period 2005 to 2010 (21 samples and 10 parameters) and the other one includes the years 2007 to 2010 (13 samples and 19 parameters). The leachate from the MSW cell was sampled more often and the first data set represent the whole period (2000 to 2010, 41 samples and 17 parameters) while the other represent 2005 to 2010 (21 samples and 20 parameters).

2.1.6 Löt

The Löt[6] landfill, situated north of Stockholm in eastern Sweden, has been in operation since 1995. Mainly non-hazardous waste, including some organic waste is landfilled at Löt. In addition to that, small amounts of asbestos and ash are landfilled separately. Previously the landfill also received electronic waste and spent fluorescent lamps. Leachate from all landfill cells is collected jointly in an aerated pond, together with water from waste treatment areas, before being sent to further treatment. Samples from the pond were used in this study. The sampling intervals varied from less than a month to every three months, but in general the sampling occasions in April, May, August and October comprised the largest number of parameters. Therefore, data from these months were used except for 2008 when April was replaced with February since that year the complete set of parameters was not analysed in April but in February. Data from April 2005 to August 2008 were used, in total 15 samples with 23 parameters.

2.2 Data preparation and processing

Leachate data were collected according to the respective monitoring programs of the landfills. All analyses except field measurements such as pH and EC were performed at accredited, commercial labs. No samples were filtered prior to analysis.

[5] The data from Spillepeng was provided by Sysav, Malmö, Sweden
[6] The data from Löt was provided by Söderhalls Renhållnings AB, Vallentuna, Sweden

All data sets required individual management, as described above, but the procedures common for all data sets are presented in this section. The number of parameters and the time period length for each landfill were chosen as a compromise between maximizing time series length and including as many parameters as possible. Outlying values have shown to strongly affect the result of the PCA (Stanimirova et al., 2007). Therefore, outliers (defined as values more than five inter-quartile ranges from the mean) were considered as missing data. Data below the detection limit was replaced with half of the detection limit. Parameters with more than 10 % missing data (as recommended by Lau and Sheu (1988)) or more than 50 % of the data below detection limit were discarded. Remaining missing data were replaced with the parameter mean. All data were normalized by taking the $\log_{10}$ and standardized by extracting the mean and dividing by the standard deviation as recommended by Wold et al. (1987). Consequently all parameters had the mean zero and large nominal differences between the parameters were prevented from artificially affecting the variance of the data.

Seasonal variations were evident in some of the data sets. Seasonal variations can be expected to come from external influences such as temperature, precipitation and wind mixing at the sampling site, rather than from the landfill itself. Therefore, seasonality was extracted from all parameters by dividing data from a certain season by the mean of that season in the particular landfill. Trends were also present in certain data sets and were not considered to be within the scope of this study. However, finding an unbiased way of removing trends proved difficult since different parameters showed trends of different type and strength. Therefore trends were left in the data but will be discussed in the following.

2.3 Principle component analysis

PCA is an operation that transforms a data matrix in a way that concentrates as much as possible of the original variance into the first columns of the new matrix. The columns of the transformed matrix are called principle components (PCs). The goal is to describe most of the original variance with only a few PCs. This results in a great simplification, since just a handful of components can be used to describe information originally distributed over a large number of parameters.

2.4 Canonical correlation analysis

CCA is a regression technique used for its ability to find correlations between two fully multidimensional data sets (Barnett and Preisendorfer, 1987). In this study CCA was used to find correlations between metal concentrations and physico-chemical data such as pH, EC, element concentrations, suspended solids, etc. The purpose was to find whether the variance in metal concentrations could be explained statistically by the physico-chemical parameters' variance.

To apply CCA, the leachate monitoring data from each landfill was first divided into two data sets representing the predictor (physico-chemical parameters) and the predictand (metal concentrations). In order to reduce the influence of noise, each data set was pre-filtered with PCA. The resulting principal components needed to explain minimum 80 % of the variance were input into the CCA.

The predictand (the data to be explained), and the predictor (the data doing the explaining) are transformed in a way that maximises the correlation between the components in the transformed matrices. The CCA computations in this study are based on the theory outlined in detail by Barnett and Preisendorfer (1987).

2.5 Geochemical modelling

To find possible solubility controlling minerals and dissolved species that are likely to be present in the leachates, equilibrium speciation modelling was performed using PHREEQC Interactive 2.15 with the "minteq" database (USGS, 2007). The data sets from Fläskebo and Tagene were the only ones that included the parameters needed for modelling in PHREEQC. All complete samples from these landfills were used. pH, temperature, alkalinity and all reported concentrations available in the PHREEQC database were included. No solids were allowed to precipitate. The redox potential was set to be controlled by the couple N(-3)/N(5). PHREEQC does not allow for including organic matter in the simulation, and metals are known to form organic complexes (Baun and Christensen, 2004). As both Fläskebo and Tagene have considerable amounts of organic matter in the leachate (Table 1) the amount of metal ions and inorganic metal complexes might be overestimated as well as the metals' saturation indices.

3 Results and discussion

The average of all leachate parameters as included in the principal component analysis (PCA) and canonical component analysis (CCA) are presented in Table 1. For Högbytorp the data set with 15 parameters was used to calculate the means, for Spillepeng's special waste cell the data set with 19 parameters was used and for Spillepeng's MSW cell the data set with 20 parameters was used. As could be expected, the landfills that have received MSW (Högbytorp, Filborna and Spillepeng's bio cell) have the highest TOC concentrations in the leachate while the modern landfill Fläskebo has the lowest.

3.1 Fläskebo landfill

The PCA on the Fläskebo dataset resulted in the first three principal components (PCs) explaining 30, 22 and 15 % of the original variance, respectively. A total of just above 50 % of the original variance explained by the first two PCs is in agreement with other studies of physico-chemical data from full scale landfill leachate (Durmusoglu and Yilmaz, 2006; Gómez Martín et al., 1995).

Table 1. Parameter averages for leachate data sets used for statistical analyses. (n.a. = parameter was not included in the statistical analysis since the data was not available or not of sufficient quality)

Parameter	Unit	Fläskebo	Tagene	Högbytorp	Filborna	Spillepeng special	Spillepeng bio	Löt
EC	mS/m	294	906	609	613	2712	1057	341
Cl	mg/l	393	1605	736	657	12308	2440	449
pH	-	7.9	8.0	n.a.	7.4	6.9	7.3	7.5
N_{tot}	mg/l	3.2	235	249	333	160	395	68
NH_4-N	mg/l	0.36	202	n.a.	176	122	301	55
NO_3-N	mg/l	0.79	1.4	n.a.	n.a.	n.a.	n.a.	2.6
NO_2-N	mg/l	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.39
NO_3+ NO_2-N	mg/l	0.84	n.a.	n.a.	n.a.	n.a.	n.a.	3.5
P_{tot}	mg/l	0.044	4.6	n.a.	9.3	0.2	1.7	0.66
PO_4-P	mg/l	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.20
TOC	mg/l	24	163	531	611	28	304	94
BOD_7	mg/l	6.6	n.a.	n.a.	827	3.6	34	28
DOC	mg/l	21	n.a.	444	n.a.	n.a.	n.a.	n.a.
COD_{cr}	mg/l	n.a.	503	1725	n.a.	468	692	n.a.
Susp	mg/l	8.7	7.2	n.a.	380	252	11	28
Turb	FNU	6.5	5.0	n.a.	n.a.	n.a.	n.a.	n.a.
Colour	-	36	912	n.a.	n.a.	n.a.	n.a.	n.a.
T	°C	9.0	25	n.a.	12	n.a.	n.a.	n.a.
Alk	mEq/l	2.7	53	n.a.	n.a.	n.a.	n.a.	n.a.
O_2	mg/l	n.a.	1.2	n.a.	n.a.	n.a.	n.a.	n.a.
S_{tot}	mg/l	305	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
SO_4-S	mg/l	895	n.a.	n.a.	103	n.a.	n.a.	n.a.
F	mg/l	0.16	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
AOX	µg/l	53	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Phenol	mg/l	n.a.	0.0087	n.a.	n.a.	n.a.	n.a.	n.a.
TEX_{alif}	mg/l	n.a.	1.3	n.a.	n.a.	n.a.	n.a.	n.a.
Al	µg/l	269	177	n.a.	n.a.	n.a.	n.a.	n.a.
As	µg/l	5.1	13	16	22	10	7.6	10
Ba	µg/l	49	437	n.a.	n.a.	n.a.	n.a.	n.a.
Ca	mg/l	317	78	n.a.	n.a.	n.a.	n.a.	n.a.
Cd	µg/l	0.45	0.38	0.86	0.7	25	n.a.	0.15
Co	µg/l	2.3	6.8	40	16	10	11	n.a.
Cr	µg/l	6.9	75	53	71	7	55	23
Cu	µg/l	76	85	39	49	23	12	16
Fe	mg/l	0.56	1.6	n.a.	11	n.a.	3.8	1.1
K	mg/l	76	331	n.a.	n.a.	n.a.	n.a.	n.a.

Hg	µg/l	0.011	n.a.	0.047	n.a.	n.a.	n.a.	0.043
Mg	mg/l	29	30	n.a.	n.a.	n.a.	n.a.	n.a.
Mn	µg/l	253	464	n.a.	2077	1619	378	711
Na	mg/l	333	1684	n.a.	n.a.	n.a.	n.a.	n.a.
Ni	µg/l	47	59	262	67	n.a.	55	13
Pb	µg/l	1.5	5.5	16	30	178	2.3	9.6
Sr	µg/l	921	339	n.a.	n.a.	n.a.	n.a.	n.a.
Zn	µg/l	229	63	346	1.5	1368	57	69

A loading plot of PC1 versus PC2 (representing a total of 52 % of the original variance in the data set) is presented in Figure 1. Each parameter is represented by a dot in the figure; parameters located close to each other have a strong co-variance. Parameters far from the origin are contributing more to the PC while parameters close to the origin are not explained well by that PC. In Figure 1, like in the majority of the other loading plots presented below, the third quadrant contains relatively few parameters. The Matlab function used to create the plots (*biplot* from Statistics Toolbox) forces the element with largest magnitude in each column of coefficients to be positive. This means that the parameters most highly correlated to the first principal component will always be to the right in the figure. The parameters most highly correlated to the second component will always be in the top of the figure. If many correlations between the parameters are strong and positive, as in Fläskebo's leachate, most parameters will be found in the top right part of the figure.

As described above, the first three data points in the Fläskebo data set were considered outliers and discarded. Excluding fewer or more (up to six) of the initial samples mainly affected the distribution of the variance among the PC's, something that manifested itself as a rotation of the loading plot. The relative positions of the parameters largely remained.

In the rightmost part of Figure 1 a cluster with EC, Cl, K, Na and total nitrogen (N_{tot}) is clearly visible demonstrating a strong covariance between these parameters, as well as a strong contribution to PC1. A co-variance between these parameters may be expected since they are all related to the salinity of the leachate. All these parameters have values decreasing with time (not shown), although the trends are not statistically significant. In the opposite upper half of Figure 1 we find a cluster containing alkalinity (Alk), Mg, Zn, Ni and AOX (absorbable organohalogens). The values of these parameters are all increasing with time. Also pH that is located far to the left has an increasing trend. Therefore the main process behind PC1 seems to be changes with time, e.g. depletion of easily soluble salts, or changes in the composition of the waste landfilled. Trends are not the main interest here and the focus will be moved to PC2.

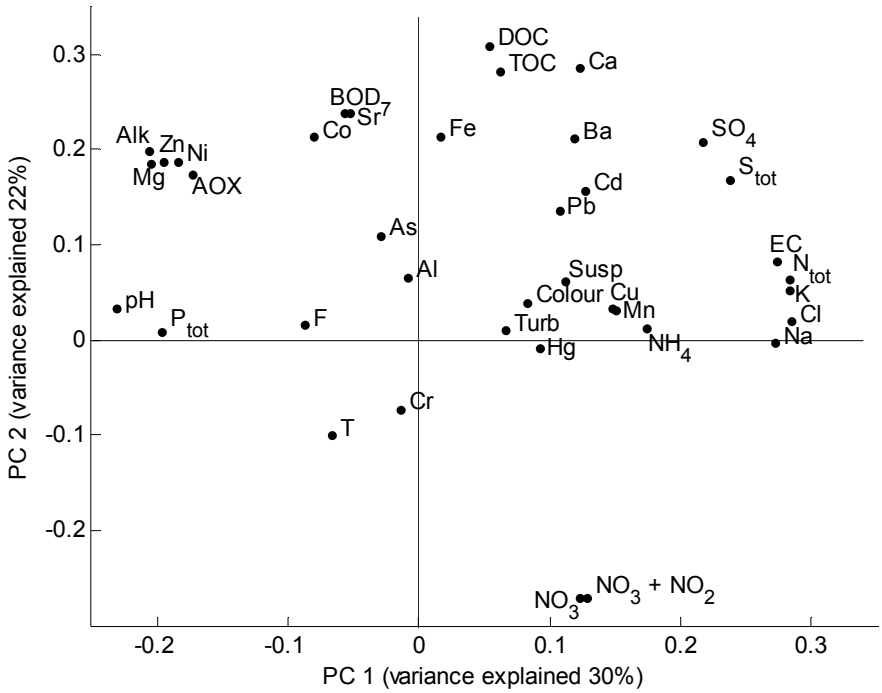

Figure 1. Loading plot of the first two principal components from principle component analysis of leachate data from Fläskebo landfill

The most important contributors to PC2 are the oxidized N species and, on the opposite side, the organic sum parameters DOC (dissolved organic carbon) and TOC. This indicates that PC2 is related to the redox state of the leachate since organic matter consumes oxygen as it degrades and acts as a reducing agent. The reduced species NH_4 is on the same side as the organic parameters. So is also the oxidized species SO_4, which complicates the picture, and suggests that the redox couple SO_4^{2-}/HS^- is not in equilibrium. The concentration of SO_4^{2-} is most likely controlled by the relatively large amounts of plaster board fragments present in the construction and demolition waste landfilled at Fläskebo.

When performing the CCA, four PCs each from the predictor (physico-chemical parameters) and predictand (metals) were used in order to include 80 % of the original variance. The resulting correlations between the first three pairs of canonical components were 0.98, 0.77, and 0.65. The correlations between the original parameters and the canonical components, the so called homogeneous correlation maps, are presented in Table 2. Parameters that have a high (>0.6) and significant ($p<0.05$) correlation with the first canonical component of the predictor (left part of table) are said to explain parameters that are highly correlated with the first component of the predictand (right part). The same is true for the second and third pair of components.

Table 2. Homogeneous correlation maps from canonical correlation analysis of leachate data from Fläskebo landfill. Correlation coefficients >0.6 are bold and statistically significant correlations (p<0.05) are underlined

Predictor (left field)				Predictand (right field)			
Param.	Comp. 1	Comp. 2	Comp. 3	Param.	Comp. 1	Comp. 2	Comp. 3
EC	**-0.85**	0.40	-0.07	Al	-0.01	0.42	**0.85**
Cl	**-0.94**	0.27	0.05	As	0.15	-0.06	-0.03
pH	**0.77**	0.06	0.22	Ba	-0.32	**0.71**	0.22
N_{tot}	**-0.87**	0.40	-0.22	Ca	-0.18	**0.77**	-0.42
NH_4	-0.52	0.40	-0.28	Cd	-0.25	0.39	**-0.67**
NO_3	-0.57	**-0.72**	-0.31	Co	0.41	0.18	-0.33
NO_3+NO_2	-0.55	**-0.72**	-0.30	Cu	-0.48	0.43	-0.07
P_{tot}	**0.61**	-0.09	0.42	Cr	0.01	-0.57	0.22
TOC	0.01	**0.64**	-0.47	Fe	0.05	**0.78**	0.20
BOD_7	0.38	**0.64**	-0.25	Hg	-0.31	-0.11	**-0.61**
DOC	0.05	**0.77**	-0.30	K	**-0.89**	0.24	-0.26
F	0.27	0.34	0.45	Mg	**0.82**	0.44	-0.26
Susp	-0.43	0.30	**0.77**	Mn	-0.40	0.13	**-0.72**
Turb	-0.32	0.25	**0.84**	Na	**-0.92**	0.27	0.18
Colour	-0.28	0.49	**0.56**	Ni	**0.75**	0.19	-0.13
T	0.16	-0.02	0.01	Pb	-0.33	0.36	0.56
Alk	**0.84**	0.36	-0.21	Sr	0.34	**0.80**	-0.08
S_{tot}	**-0.67**	0.55	-0.22	Zn	**0.75**	0.54	0.20
SO_4	-0.58	**0.70**	-0.17				
AOX	**0.65**	0.15	0.35				

CCA transforms the data in order to achieve the strongest possible *correlation* between components from *two data sets* while PCA finds the components that maximises the *variance* in *one dataset*. Therefore the canonical components resulting from the CCA do not necessarily represent the same patterns as the PCs from the PCA. Still, from Table 2 we can see that the parameters strongly related to the first canonical component are the same that were strongly related to the first PC. Therefore the most important pattern underlying the first component from the CCA is also trends, and more focus will be given to the later components.

Equilibrium speciation modelling with PHREEQC was used to further elucidate the mechanisms behind leachate quality. The ionic strength varied between 0.029 moles/l and 0.11 moles/l. The per cent error (difference between cations and anions divided by the total number of ions) varied between ±0.18 and ±12.34. The total number of samples with an error of more than 10 % was five of 22. According to PHREEQC the water from Fläskebo is oxidised (pe around five), which is in agreement with the properties of the sampling location, a pipe draining an open pond.

Strongly positively correlated to the second canonical components of the predictor are TOC, BOD_7 (biological oxygen demand during seven days), COD (chemical oxygen demand) and SO_4 while NO_3 and NO_3+NO_2 are negatively correlated (Table 2). Thus, the second canonical component seems to be influenced by the redox state, like the second PC. Ba, Ca, Fe and Sr are positively correlated to the second predictand component. Possibly organic matter - metal complexation is one underlying mechanism for the correlations captured by the second pair of canonical components. Some support for this can be found in Figure 1 since these metals are located rather close to the organic parameters. Organic matter – metal correlations will be discussed further in the general discussion below.

The third pair of canonical correlations relates Susp (suspended solids) and Turb (turbidity) to Al, and, with a negative correlation, to Cd, Hg and Mn. These results suggest that part of the Al is associated with suspended material in the leachate, but the negative correlations between metals and Turb and Susp are not straightforward to explain.

Although pH has a great influence on the solubility of heavy metals in theory, it does not correlate strongly with any metal concentrations in Fläskebo's leachate, except for the cases where there are similar or opposite trends. The pH range in the leachate is probably too high and too narrow (7.3 to 8.3) for variations in pH to have any significant effect on the metal solubility. Rodriguez Ruiz et al. (2009) pointed out that pH has a Gaussian (normal) distribution while most other leachate parameters have a lognormal distribution. However, in this study all data were normalized using $\log_{10}$ so the data distribution is not likely to have caused the weak relationship between pH and other parameters.

3.2 Tagene landfill

The first three principal components from the PCA of Tagene's leachate explain 46, 11 and 7 %, respectively. PHREEQC calculated the ionic strength to between 0.050 moles/l and 0.15 moles/l. The per cent error varied between ±0.28 and ±23.08 and the total number of samples with an error of more than 10 % six of 34.

A loading plot can be seen in Figure 2. A cluster including salinity related parameters is dominating the first PC like in the PCA from Fläskebo (Figure 1). Like for Fläskebo, EC, Cl and Na belong to this cluster, bur for Tagene K is not included and Ba, N_{tot}, NH_4 and Cr are additional. P_{tot} (total phosphorous) is also close to this cluster but varying the data set by excluding some samples caused this correlation to weaken slightly (results not shown). In Tagene the effect from trends is less obvious than in Fläskebo and extracting trends from the data before performing the PCA has little effect (results not shown). The effect from removing up to six of the initial samples was also quite small.

With O_2 and NO_3 to the left of Figure 2 and NH_4 and the organic parameters TOD and COD to the right, the redox state of the leachate is most likely one of the processes behind PC1. However, it is not possible to know whether the variations in oxidation are due to conditions within the landfill or effects from sample handling. According to PHREEQC, all leachate samples are oxidised (pe between 3.7 and 6.3).

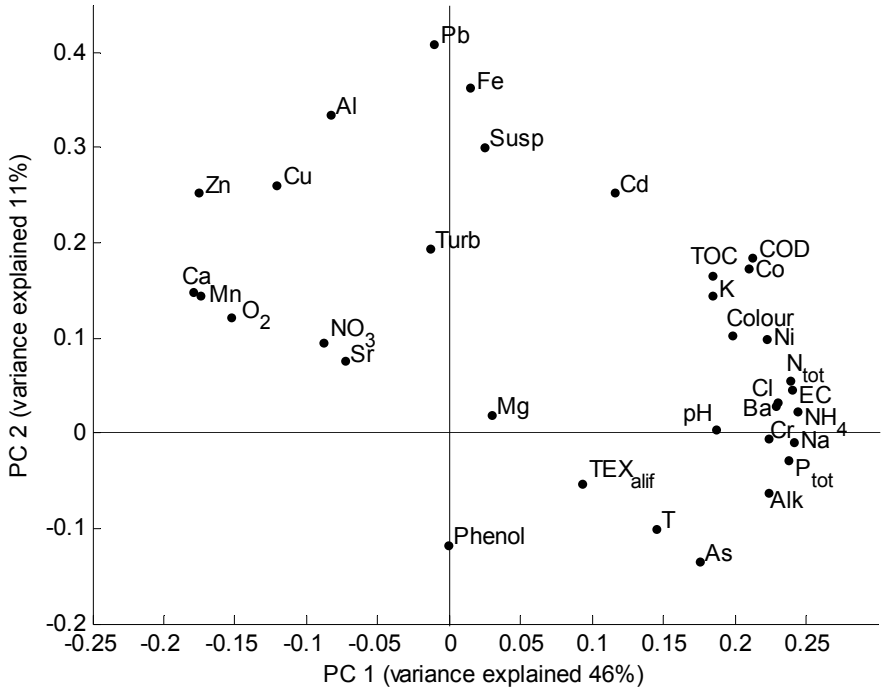

Figure 2. Loading plot of the first two principal components from principle component analysis of leachate data from Tagene landfill

In order to include 80 % of the variance five PCs from the predictand and predictor datasets were included in the CCA. The correlations between the first three pairs of canonical components are 0.95, 0.84 and 0.56 respectively. Many leachate parameters, including organic parameters, nutrients, salts and several metals are strongly and significantly correlated to the first pair of canonical components (Table 3). This makes it difficult to identify relations between individual parameters. The data from Tagene was collected during a relatively long time period (eight years). Although the effect from trends was not evident in the PCA it is still likely that changes in the landfill over time have a significant impact on the variance and may thus mask more interesting relations between leachate parameters.

Table 3. Homogeneous correlation maps from canonical correlation analysis of leachate data from Tagene landfill. Correlation coefficients >0.6 are bold and statistically significant correlations (p<0.05) are underlined

	Predictor (left field)				Predictand (right field)		
Param.	Comp. 1	Comp. 2	Comp. 3	Param.	Comp. 1	Comp. 2	Comp. 3
EC	**0.96**	-0.01	-0.09	Al	-0.24	**-0.65**	0.03
Cl	**0.92**	0.05	0.10	As	**0.65**	0.35	-0.40
pH	**0.72**	-0.10	-0.40	Ba	**0.88**	0.13	0.18
N_{tot}	**0.95**	-0.05	-0.03	Ca	**-0.68**	0.00	0.42
NH_4	**0.96**	0.01	-0.08	Cd	0.56	-0.24	0.34
NO_3	-0.24	-0.23	0.07	Co	**0.88**	-0.10	0.20
P_{tot}	**0.94**	0.03	-0.19	Cu	-0.42	-0.22	0.23
TOC	**0.78**	-0.21	-0.01	Cr	**0.90**	0.16	-0.12
COD	**0.89**	-0.25	0.01	Fe	0.10	**-0.74**	0.36
Susp	0.15	**-0.67**	0.37	K	**0.78**	-0.02	0.38
Turb	-0.07	**-0.69**	-0.25	Mg	0.12	0.50	0.51
Colour	**0.81**	0.06	0.30	Mn	**-0.68**	-0.26	0.14
T	0.55	0.38	-0.02	Na	**0.95**	0.15	0.00
Alk	**0.87**	0.11	-0.32	Ni	**0.94**	0.02	0.05
O_2	-0.56	-0.49	-0.11	Pb	0.05	-0.59	0.52
Phenol	-0.02	0.11	**-0.68**	Sr	-0.30	0.25	0.45
TEX_{alif}	0.29	-0.03	-0.24	Zn	**-0.61**	-0.40	0.12

O_2 has a significant, although not strong, negative correlation to the first canonical component. Like in PC1 the redox state seems to be among the underlying processes. Significant and strong negative correlations to the first canonical component in the predictor can be seen for Ca, Mn and Zn. A similar pattern can be seen in Figure 2 suggesting that these metals are more soluble when the leachate is more oxidized. However, that close relationship between O_2, Mn and Ca weakens somewhat when a few of the initial samples are removed from the data set. It might be surprising to find the Mn concentration positively correlated to the oxygen concentration since this element is known to form insoluble oxides. At the pe and pH conditions prevailing in Tagene's leachate the stable form of Mn should be the solid phase Rhodochrosite ($MnCO_3$) (Stumm and Morgan, 1996). The PHREEQC model also found this mineral to be close to saturation (saturation index, SI, between 1 and 0) or slightly oversaturated (SI between 1 and 2) in all samples from Tagene. Changing the pe within the interval found in Tagene's leachate should not affect this, while relatively small variations in pH could affect the solubility. It is therefore possible that the correlations found in the PCA and the CCA are due to pH rather than the redox state.

The second pair of canonical components relates suspended solids and turbidity to Fe and Al. The relationship between suspended matter and Al can be recognized from Fläskebo. Fe, like Mn, is famous for forming insoluble oxides and hydroxides. In Tagene's leachate it lacks covariance with O_2 entirely. According to the PHREEQC model many Fe oxides and hydroxides are strongly

oversaturated. This suggests that the concentrations of dissolved Fe are overestimated when assuming that the total concentration represents dissolved species, something that supports the finding that Fe is related to the suspended solids.

Only Phenol has a strong and significant correlation to the third canonical component so no relationship with metals can be identified from there.

3.3 Högbytorp

Initially a CCA was performed on the dataset with long time series (1997 – 2006, 98 samples) and only 12 parameters (see Table 4). To include 80 % of the variance two and four PCs were included from the predictor and the predictand, respectively. The correlations between the canonical vectors were relatively week: 0.68 and 0.51. Homogeneous correlation maps are presented in Table 4. The first canonical component relates EC and N_{tot} to Cr. The second canonical component relates COD and pH (inversely) to Co.

Next a CCA was performed on the dataset with shorter time series (1997 – 2000, 42 samples) and a total of 15 parameters (see Table 1 and Table 5). Again two and four PCs were included, respectively. The correlations were stronger: 0.78 and 0.58. The first canonical component now relates EC, Cl and N_{tot} to As and Cr. The second canonical component seems to describe organic matter - metal correlations as is suspected for Fläskebo. However, the only metal that is strongly and significantly correlated to this component is now Hg, although the Co and Ni correlations are just below 0.6. Hg has previously been shown to form complexes with natural DOC (Wu et al., 2004) and it is likely that that could occur also in landfills.

Table 4. Homogeneous correlation maps from canonical correlation analysis of leachate data from Högbytorp landfill representing the years 1997 to 2006. Correlation coefficients >0.6 are bold and statistically significant correlations (p<0.05) are underlined

Predictor (left field)			Predictand (right field)		
Parameter	Component 1	Component 2	Parameter	Component 1	Component 2
EC	**0.85**	0.45	Cd	-0.05	0.06
pH	-0.05	**0.86**	Co	0.40	**-0.78**
N_{tot}	**0.82**	0.50	Cr	**0.86**	0.26
COD	0.44	**-0.79**	Cu	0.09	0.24
			Hg	-0.06	-0.20
			Ni	0.43	-0.58
			Pb	-0.14	0.14
			Zn	0.49	-0.32

Table 5. Homogeneous correlation maps from canonical correlation analysis of leachate data from Högbytorp landfill representing the years 1997 to 2000. Correlation coefficients >0.6 are bold and statistically significant correlations (p<0.05) are underlined

Predictor (left field)			Predictand (right field)		
Parameter	Component 1	Component 2	Parameter	Component 1	Component 2
EC	**-0.95**	0.15	As	**-0.64**	0.13
Cl	**-0.76**	0.19	Cd	0.29	-0.36
N_{tot}	**-0.91**	0.12	Co	-0.34	-0.57
TOC	-0.36	**-0.90**	Cr	**-0.86**	0.29
DOC	-0.33	**-0.90**	Cu	-0.03	0.33
COD	-0.21	**-0.87**	Hg	-0.15	**0.76**
			Ni	-0.30	-0.58
			Pb	0.47	0.11
			Zn	-0.22	-0.17

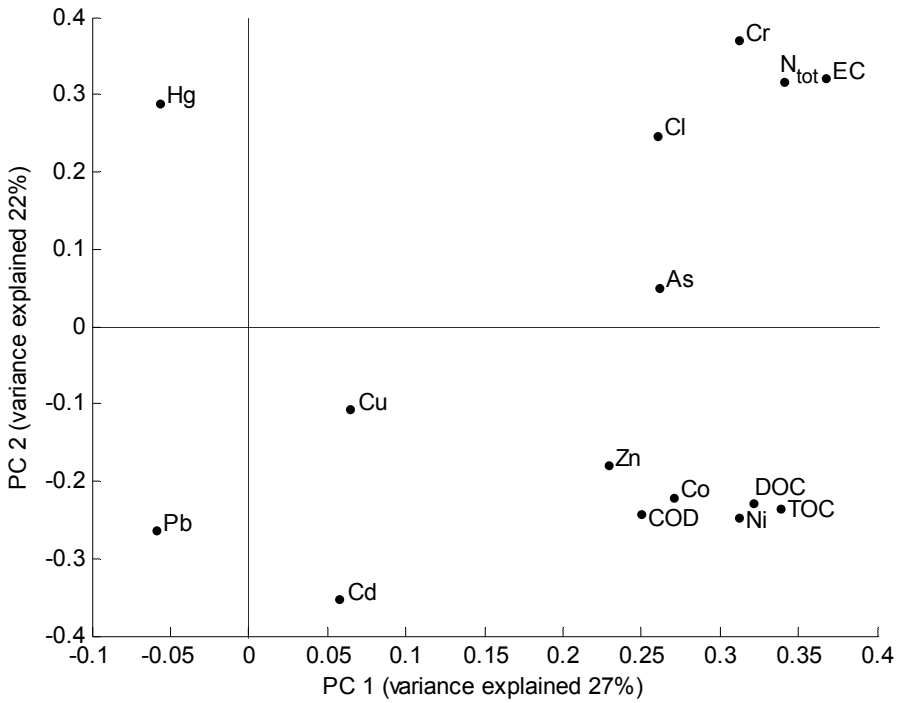

Figure 3. Loading plot of the first two principal components from principle component analysis of leachate data from Högbytorp landfill representing the years 1997 to 2000

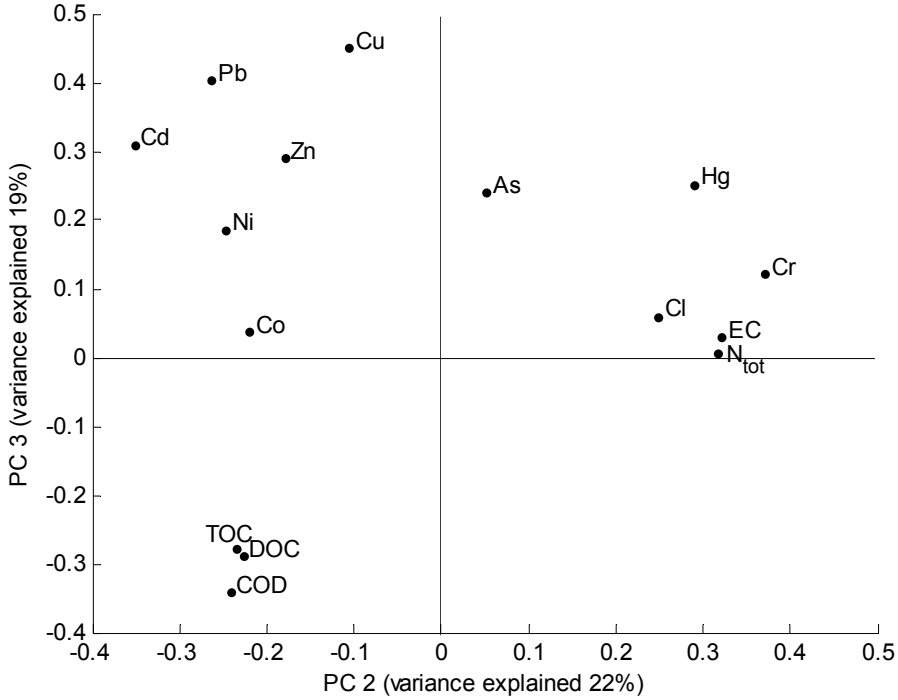

Figure 4. Loading plot of principal components 2 and 3 from principle component analysis of leachate data from Högbytorp landfill representing the years 1997 to 2000

Based on the CCA results the data set from 1997 – 2000 was chosen for the PCA of Högbytorp's leachate. The variance was relatively evenly distributed among the first three components that represented 27, 22 and 19 %, respectively. The loading plot of PC1 and PC2 is presented in Figure 3. In this case extracting the seasonality had a relatively large impact on these results as can be expected since the leachate was sampled from a pond where external influence should be important. In Figure 3 most parameters are to the right suggesting that PC1 is mainly related to the strength, or dilution, of the leachate. This has been previously observed by Waara et al. (2008). In an attempt to depict other, perhaps more interesting, patterns a loading plot of PC2 and PC3 was created (Figure 4). This plot contains 41 % of the original variance.

In Figure 3 as well as Figure 4 we find a salinity related cluster with EC, Cl and N_{tot}. Like for Tagene, Cr co-varies with the salinity cluster, confirming its relation to the inorganic parameters found from the CCA. Both plots show a close relationship between TOC, DOC and COD, also confirming the results from the CCA. The co-variations within the salinity cluster and within the organic cluster are stable towards varying the dataset by removing up to six initial samples. However, the separation between the two clusters is not as stable.

Figure 3 shows Co, Ni and Zn to co-vary with the organic parameters thus confirming results found from the CCA. However, since this cluster does not exist in Figure 4 the metal concentrations must be partly affected by other parameters or processes also. Also, in Figure 3 this cluster did not remain when the initial five or more samples were discarded.

3.4 Filborna

The first three PCs from the PCA of Filborna's leachate explain 37, 15 and 9 % of the original variance, respectively. A salinity related cluster including EC, Cl, N_{tot}, NH_4 and SO_4 is visible in the lower right corner of the loading plot (Figure 5). As NH_4 concentrations are relatively high (Table 1) they can be expected to contribute to salinity. pH is also close to this cluster, but that co-variance is not entirely stable. In general, however, the results are stable towards varying the data set. All parameters are in the right half of the figure. As for Högbytorp this indicates that the first PC is related to the dilution of the leachate. However, the third PC only explains 10 % of the variance, so no more loading plots were considered relevant for interpretation.

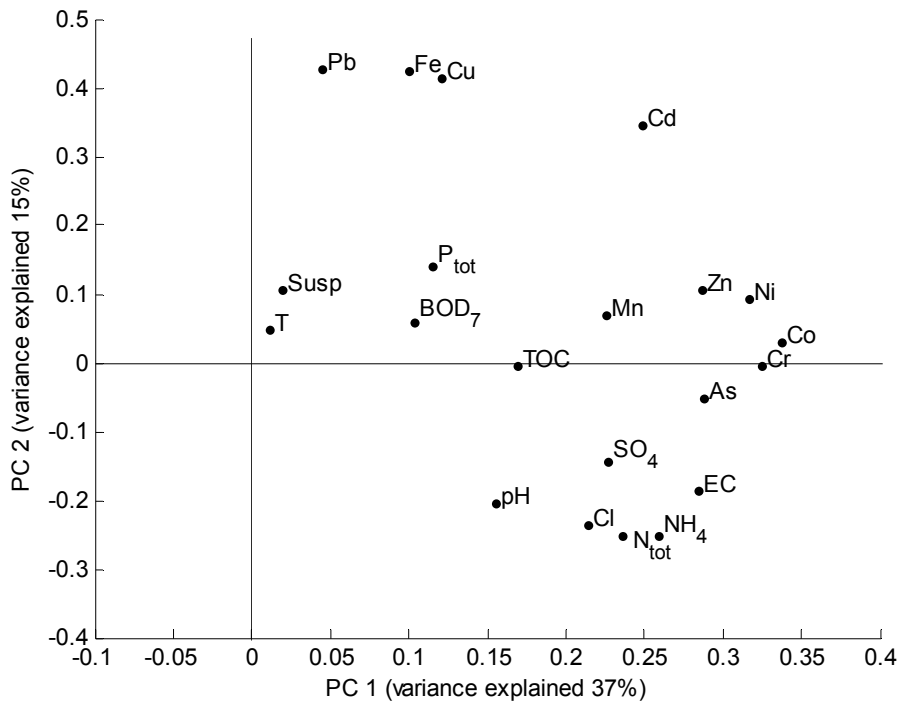

Figure 5. Loading plot of the first two principal components from principle component analysis of leachate data from Filborna landfill

Table 6. Homogeneous correlation maps from canonical correlation analysis of leachate data from Filborna landfill. Correlation coefficients >0.6 are bold and statistically significant correlations (p<0.05) are underlined

Predictor (left field)			Predictand (right field)		
Parameter	Component 1	Component 2	Parameter	Component 1	Component 2
EC	**-0.84**	-0.10	As	**-0.82**	0.08
Cl	**-0.70**	0.59	Cd	-0.41	-0.15
pH	**-0.61**	-0.28	Co	**-0.86**	-0.07
N_{tot}	**-0.84**	0.03	Cr	**-0.86**	0.08
NH_4	**-0.87**	0.39	Cu	0.00	0.23
P_{tot}	-0.25	-0.09	Fe	0.08	0.25
TOC	-0.47	0.04	Mn	-0.54	0.48
BOD_7	-0.25	-0.10	Ni	**-0.81**	-0.23
Susp	0.02	0.51	Pb	0.28	0.24
T	-0.10	-0.54	Zn	**-0.72**	-0.38
SO_4	**-0.60**	0.55			

In order to include 80 % of the variance in the CCA five and three PCs were needed from predictor and predictand data set, respectively. The number of predictand components must not be smaller than the number from the predictor so 5 PCs from each dataset were included. The correlations between the first three pairs of canonical components were relatively weak; 0.83, 0.73 and 0.42 respectively. Homogeneous correlation maps are presented in Table 6. The parameters from the salinity cluster in the PCA are all strongly and significantly related to the first component. In the predictand several metals (As, Co, Cr, Ni and Zn) are related to the first component. Again, Cr is among the metals correlated to inorganic parameters. No strong correlations between metals and organic parameters can be found.

3.5 Spillepeng

Initially a CCA was performed on the two datasets from the special waste cell. For the dataset with longer time series and fewer parameters three PCs were included from the predictor as well as the predictand dataset. The correlations were 0.41, 0.37 and 0.32. For the dataset with more parameters but shorter time series four PCs were included and the correlations were stronger: 0.93, 0.73 and 0.37. The shorter time series were chosen for further study.

A PCA was performed on the dataset with 13 samples and 19 parameters. The first principal component represents 26 % of the original variance and the second 22 %. A loading plot can be seen in Figure 6. The leachate from Spillepeng's special waste cell seems very different from the other landfills studied here. There is no salinity cluster and there is no co-variance between Cl and EC. Since Cl is the most abundant ion, with extremely high concentrations (see Table 1), this is hard to explain. This landfill is situated close to the sea, on reclaimed sea bottom, and there might

be other significant sources of Cl than just the waste. However, the main part of the Cl must stem from the waste since the nearby MSW cell has much lower, although still high, Cl concentrations (Table 1). A weak relationship between Cl and EC has been observed before, e.g. in an dataset including a mixed waste landfill and degradation test cells (Andreas et al., 1999) and in a landfill leachate polluted aquifer (Ludvigsen et al., 1996).

Not many strong relationships can be found from Figure 6, and plotting PC2 towards PC3 (results not shown) provides little additional information. It seems that PCA does not offer much additional understanding about this particular leachate. Varying the dataset (results not shown) weakens some co-variances, most notably the one between N_{tot} and NH_4, and strengthens others, e.g. between N_{tot} and Cl. The correlation maps resulting from the CCA changed significantly when the data pre-treatment was changed, e.g. by removing trends. Therefore they are not presented here.

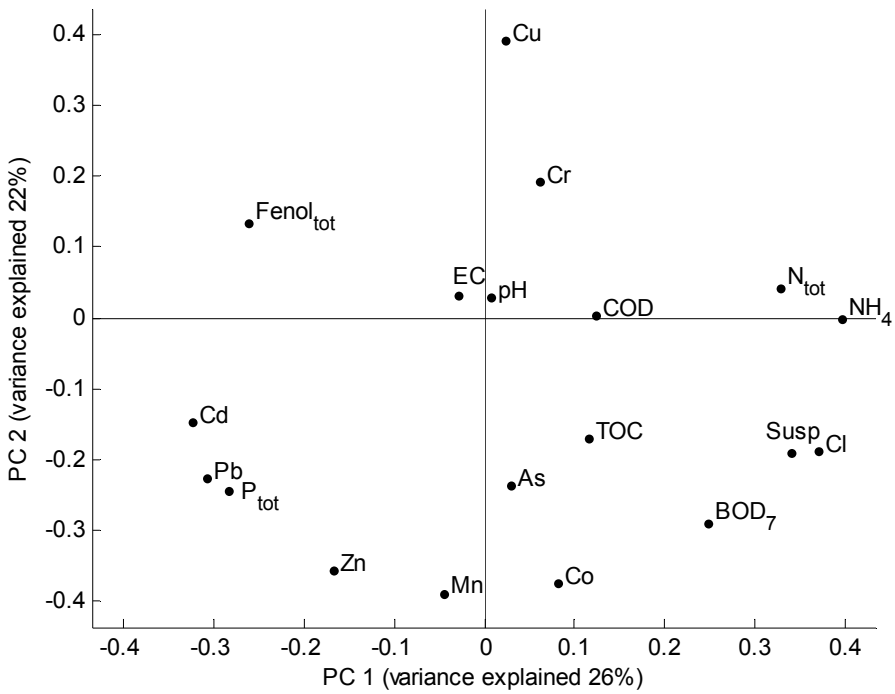

Figure 6. Loading plot of the first two principal components from principle component analysis of leachate data from Spillepeng's special waste cell

For the MSW cell at Spillepeng two data sets were also compared using CCA. For the data set with 41 samples and 17 parameters the correlations were 0.83, 0.78 and 0.53. For the dataset with 21 samples and 20 parameters the correlations were somewhat stronger: 0.89, 0.79 and 0.65. The latter was chosen for further analysis. Five PCs from each dataset were included in the analysis in order to retain 80 % of the original variance. Like for the data from the special waste cell, changing the data treatment significantly changed the correlation maps from the CCA and therefore they are not included here.

A PCA was performed on the data set from the MSW cell that contained 21 samples and 20 parameters and the first PCs represented 30, 19 and 12 % of the original variance. A loading plot is presented in Figure 7. Here the co-variance between Cl and EC is strong, and together with NH_4 they can be said to form a salinity related cluster. Varying the data set leads to small changes in the plot that suggest that N_{tot} also belongs to this cluster (not shown). The reason that BOD_7 and COD does not co-vary with TOC seem to be difference in trends in the original data (not shown); BOD_7 and COD have slight decreasing trends while there is no trend in TOC. This indicates that although constant in concentration, the organic matter gets less oxidisable with time, in agreement with findings by He et al. (2011).

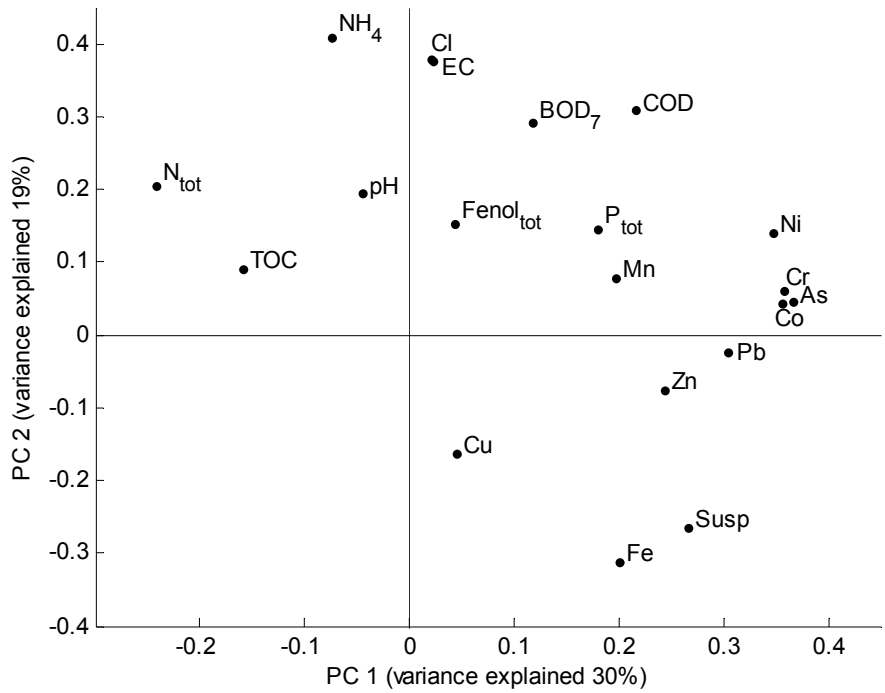

Figure 7. Loading plot of the first two principal components from principle component analysis of leachate data from Spillepeng's MSW cell

3.6 Löt

The first three PCs from the PCA of Löt's leachate explain 36, 16 and 12 %, respectively. A loading plot can be seen in Figure 8. There is no clear salinity related cluster although EC, Cl, N_{tot} and NH_4 are among the strong contributors to PC1 as they are all located far to the right in Figure 8.

All parameters related to oxidizing conditions (NO_3, NO_3+NO_2, NO_2, PO_4) are located on the left side of Figure 8, and those that are related to reducing conditions (BOD_7, TOC, NH_4) are located to the right. Thus redox conditions may be one of the processes behind PC1 like for Fläskebo and Tagene. The location of PO_4 is, however, not entirely stable towards varying the data set. Trends might be another factor affecting PC1.

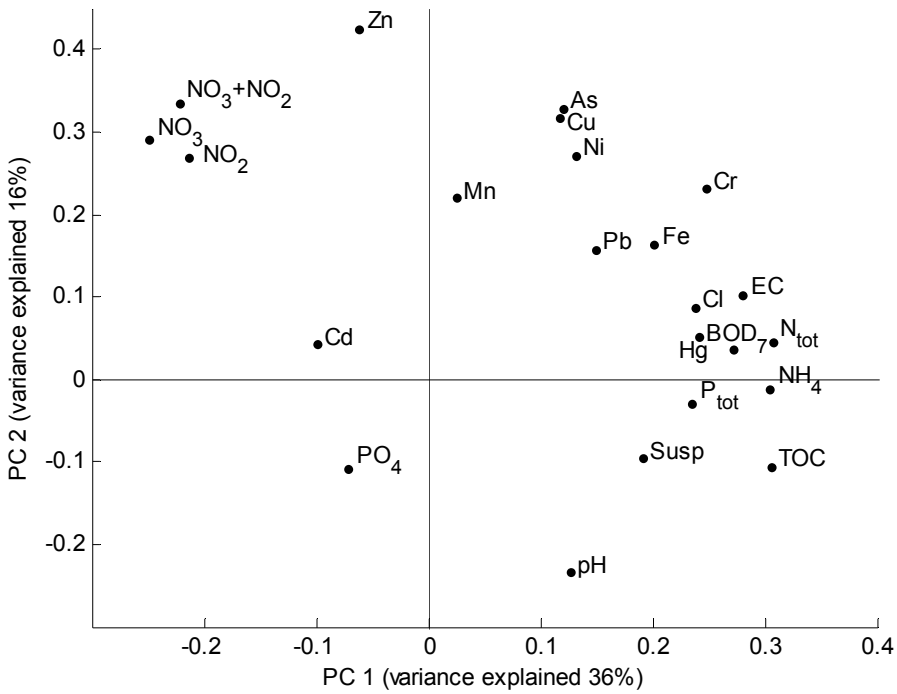

Figure 8. Loading plot of the first two principal components from principle component analysis of data from Löt landfill

Table 7. Homogeneous correlation maps from canonical correlation analysis of leachate data from Löt landfill. Correlation coefficients >0.6 are bold and statistically significant correlations (p<0.05) are underlined

Predictor (left field)				Predictand (right field)			
Param.	Comp. 1	Comp. 2	Comp. 3	Param.	Comp. 1	Comp. 2	Comp. 3
EC	**-0.89**	-0.06	-0.20	As	-0.40	0.30	-0.48
Cl	**-0.66**	0.24	-0.04	Cd	0.41	0.49	-0.37
pH	-0.45	0.22	-0.02	Cr	**-0.74**	0.23	-0.35
N_{tot}	-0.88	0.05	-0.02	Cu	-0.49	-0.35	**-0.66**
NO_3	0.55	-0.17	**-0.76**	Fe	**-0.61**	0.12	-0.35
NH_4	**-0.84**	-0.03	0.13	Hg	**-0.62**	-0.30	0.22
NO_2	0.42	-0.43	**-0.75**	Mn	-0.03	**-0.76**	-0.26
NO_3+NO_2	0.47	-0.16	**-0.85**	Ni	-0.32	-0.13	0.05
P_{tot}	**-0.65**	**-0.62**	0.40	Pb	-0.46	-0.29	-0.11
PO_4	0.26	**-0.78**	0.39	Zn	0.14	-0.34	-0.45
TOC	**-0.88**	0.26	0.23				
BOD_7	**-0.81**	-0.15	0.15				
Susp	-0.47	0.17	0.38				

In order to include 80 % of the original variance in the CCA four PCs from the predictor and five from the predictand were included. The correlations between the first three pairs of components were 0.93, 0.79 and 0.70. Several physico-chemical parameters are strongly and significantly correlated to the predictor's first component (Table 7). Cr, Fe and Hg are strongly and significantly related to the predictand's first component. As both organic and inorganic parameters are related in the predictor the cause behind this correlation is not clear. The PCA (Figure 8) does not enhance the interpretability. The second canonical correlation relates P_{tot} and PO_4 to Mn. This could be due to redox conditions. The third component relates NO_3, NO_3+NO_2, NO_2 to Cu.

3.7 General discussion

3.7.1 Methodological considerations

The results from Högbytorp and from Spillepeng's both cells demonstrate that stronger correlations and more detailed information can be gained by including more leachate parameters. Decreasing the number of parameters to increase the time series length is in disfavour of finding strong correlations, given that the time series are sufficiently long to give significant results. A likely explanation is that when removing leachate parameters important information about the leachate quality is excluded and that leaves some variation unexplained. This cannot be mended by including more samples as they will lack important predicting variables.

Varying the datasets by excluding some samples can affect the distribution of parameters among the principal and canonical components. Therefore it is important to control that the conclusions drawn are based on correlations and co-variances that are stable towards these variations. This has been done in this work by excluding up to six samples from each data set. The loading plots remained largely similar with the exception of Högbytorp, but some specific correlations were affected, e.g. for P_{tot} in Tagene, pH in Filborna and N_{tot} in Spillepeng's MSW cell. In future work procedures like cross-validation are recommended for this purpose.

In the case of Fläskebo and Tagene, using speciation modelling provided additional understanding of processes in the leachate. However, the speciation model used, PHREEQC Interactive 2.15, is created for groundwater which is very different from leachate, not least because of the high concentrations of organic matter and ions such as NH_4^+ in leachate. As the model used does not account for organic matter – metal interactions (with the exception of some small organic molecules) it cannot be expected to capture all processes in leachates. However, a previous attempt of using a humic model to explain the metal – organic matter interactions in these leachates lacked agreement with the statistical data (Modin et al., 2009).

The age and operation of the landfills of the landfills differ, as well as the waste deposited. Major changes in operation, such as the start of a new landfill cell, are likely to change the correlations of leachate parameters in the long term. Operational changes have not been taken into regard in this work, instead maximum time series length was a prerequisite in order to gain significant correlations. However, including operational changes with suspected effects on leachate quality in multivariate analysis is a promising topic for further research when time series become long enough to allow validation of the models.

3.7.2 Leachate composition

In most landfills studied here, a cluster of salinity related parameters was dominating the first or second principal component. In some cases, most clearly for Fläskebo, the importance of this cluster for PC1 was due to temporal trends. Other authors have also found salts to dominate PC1 (Clément et al., 1997; Galvez et al., 2010; Gómez Martín et al., 1995). Rodriguez Ruiz et al. (2009) found a very clear salinity cluster in a loading plot of PC1 and PC2 that was based on data from hundreds of landfills. Kylefors (2003) found a similar cluster although Cl did not belong to it.

Co-variations between inorganic parameters and metals were found in all data sets, most often in the first canonical component. Cr was the metal most often correlated to inorganic parameters (in Tagene, Högbytorp and Filborna). It is not obvious which inorganic parameters are responsible for these correlations but Cl, EC and nitrogen in various forms seem to be involved. A review by Baun and Christensen (2004) found that carbonates, chlorides and hydroxides were the most important inorganic metal complexes. Cl has previously been found to enhance solubilisation of Cd and Zn in soil due to formation of soluble complexes (Norrström, 2005). Olsson et al. (2009) found Cl to enhance As leaching from bottom ash. Ammonia concentrations are high in Tagene's and Filborna's leachate, and ammonia-metal complexes could also be present.

Correlation between organic matter and heavy metals was found in the leachate data from Högbytorp and Fläskebo. Also in Tagene and Löt organic matter - heavy metal correlations can be suspected to be behind part of the canonical correlations. The metals that were most strongly correlated varied between leachates. In Fläskebo it was Ba, Ca, Fe and Sr and in Högbytorp it was Co and Hg. Baun and Christensen (2004) found metals (Cd, Cu, Ni and Pb) in landfill leachate to mostly exist in the form of organic complexes. Organic complexes of Pb, Cu, Ni, Zn and Cd have previously been found to explain metal concentrations in leachate polluted groundwater (Christensen et al., 1999; Christensen and Christensen, 1999). In this study none of these metals have been identified as strongly correlated to organic matter, although Ni had a correlation of 0.58 with the canonical component related to organic matter in Högbytorp. Correlations with inorganic parameters were at least as important. Interestingly, there is no evidence that the correlations between organic parameters and metals in the modern and carbon-poor landfill Fläskebo are weaker than in the other landfills, in spite of the low concentrations of organics in Fläskebo's leachate (Table 1).

3.7.3 Landfill operation and management

The findings indicate that MVDA of regular leachate monitoring data could be used to optimize leachate management, e.g. choice of treatment options. With the aid of PCA and CCA, the governing factors for target substances can be discerned. E.g. in the case of the covariance of salt release and leaching of Cr, improved sedimentation is unlikely to reduce metal concentrations in the leachate. However, Fe and Al have been found to co-vary with suspended matter and improved sedimentation could be useful in those cases.

Leachate monitoring programs could also be optimised using MVDA. For example, when two parameters that describe similar processes co-vary, as in the case of TOC and COD, they most likely capture very similar information. Analysing both may be unnecessary and the sampling effort can be concentrated on only those parameters that contribute with additional information. Alternatively, a different filter cut-off for determining DOC from TOC could be chosen or further fractionation of the leachate might be useful to reveal weather smaller particles are behind the covariance of DOC and metals. BOD_7 seems to contribute with more additional information and should be prioritized over analysing both DOC and TOC. The redox state appears to be an important process behind the variance in the leachate data. Therefore at least one redox couple should always be included as a part of a regular landfill leachate monitoring program.

Kylefors (2003) suggested that parameters co-varying strongly with others could be modeled rather than measured except for some verifying occasions. The present study gives some support to this suggestion. However; a large number of parameters are needed to correctly describe the processes determining the leachate quality, as shown in this study. The time series should be relatively long as the data will be needed both for model building and validation. Therefore an extensive sampling campaign is needed to provide the input to the model. Which parameters that could be modelled in this way have to be determined site-specifically.

4 Conclusions

Two multivariate data analysis (MVDA) methods, principle component analysis (PCA) and canonical component analysis (CCA), proved useful for statistically elucidating possible relationships between parameters in regular landfill leachate monitoring data. These techniques make it possible to interpret the patterns underlying the co-variations between single parameters such as dilution, redox potential, organic matter – metal complexation etc. They also allow presenting the results in a more compact way than univariate techniques (e.g. correlation matrices). Since only the parameters' variance and not their absolute concentrations are studied the difference in leachate strength between landfills should not affect the interpretation and the comparison between landfills is simplified. However, MVDA did not enhance interpretation of the leachate data from Spillepeng landfill.

In landfill research organic matter complexes tend to be in focus when heavy metal solubility is discussed but the findings from this study suggest that attention must also be paid to inorganic complexes and their role in heavy metal leaching.

PCA and CCA of regular leachate monitoring data can be used to evaluate monitoring programs, as both expected and unexpected correlations and the lack of correlations can be used to optimise the choice of parameters, sampling occasion or sampling frequency. The results further indicate that PCA and CCA could be used to optimise leachate management, e.g. choice of treatment options.

In order to find strong correlations and detailed information using MVDA it should be favoured to include as many parameters as possible rather than maximising the time series length, given that the time series are long enough to produce significant correlations. Otherwise important predicting variables may be overlooked.

Future work should focus on trying to further understand and, if possible, quantify the physical processes underlying the statistical parameters. This might be achieved by including parameters describing environmental and operational conditions in the model. As time series grow longer every year, the possibilities of creating strong models are improving. It would also be valuable to find simple methods to optimise leachate monitoring programs to improve their usefulness and reduce the cost.

Acknowledgements

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Appended paper

II

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Potential emissions from two mechanically–biologically pretreated (MBT) wastes

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ABSTRACT

The interaction of parameters determining the potential emissions of two different mechanically–biologically pretreated municipal solid wastes (MBT wastes) is elucidated in this work. The origins of the wastes are Germany and Sweden. By means of lab-scale experiments, increased stabilisation through composting is preferably determined by a decrease in respiration activity. Concurrently, the stabilisation is verified for the leachates by a decrease in COD, DOC, and BOD_5. Total organic carbon content reflects stabilisation less accurately. FT-IR and thermal analytical methods add valuable information about the state of degradation, especially when several distinct thermal parameters are taken into account. Mobility of Cr, Ni, Pb, and Zn produced by a batch leaching test with deionized water is reduced by the pretreatment of both materials. Mobility of copper unambiguously increased. A principle component analysis (PCA) of membrane fractionated leachates indicates an affinity of Cu to mobile humic acids or dissolved organic carbon. High Cr, Zn, and Ni contents in the solid co-occur with high contents of solid humic acids. To a lesser extent, this is also true for solid Cd, Cu, and Pb contents. Due to differences in required landfilling conditions, actual emissions and after-care phase length will depend on whether each waste is landfilled in Germany or Sweden.

1. Introduction

Besides crushing, sorting and/or sieving, mechanical–biological treatment (MBT) of municipal solid wastes comprises composting of sewage sludge, garden wastes, or sorted municipal solid waste (MSW), or the fermentation and anaerobic digestion of these (Christensen, 2001). Mechanical–biological treatments of wastes are employed either to enable reuse, such as an amendment for soils through composting of yard waste or sewage sludge (Sanchez-Monedero et al., 2004), or to reduce the risk for settlement and landfill gas production when the material is landfilled (Komilis et al., 1999). With the easily degradable organic matter removed by pretreatment, liquid emissions can be regarded as the main long-term threat to the environment. The landfill gas production will have ceased long before the leachate contents have dropped to background values (Leikam and Stegmann, 1999; Kjeldsen et al., 2002). Although reduced compared to untreated wastes, leachate constituents of concern are residual biologically degradable material, measured as dissolved organic carbon (DOC) or biological oxygen demand (BOD), nitrogen compounds, and heavy metals (Von Felde and Doedens, 1999; Zach et al., 2000; Kjeldsen et al., 2002). Composting has been shown to increase the content of humic substances in biologically degradable waste (Smidt et al., 2004). The DOC of leachates from composted waste consists of varying parts of non-easily degradable organic matter (Christensen and Nielsen, 1983). Depending on the age, waste leachates show different allocations of high and low organic molecular weight fractions (Calace et al., 2001). Heavy metals can be associated with both dissolved and solid organic materials. Complexes with DOC have been found to explain observed concentrations of lead (Pb) and copper (Cu) in leachate polluted groundwater (Christensen et al., 1999). Christensen and Christensen (1999) made comparable observations for nickel (Ni) and zinc (Zn), alongside cadmium (Cd). Lair et al. (2007) detected that organic material in soil showed a 6 to 13 times greater sorption capacity for Cd, Cu and Zn than its mineral content.

Pretreatment of waste containing organic matter has been shown to affect heavy metal mobility. Paré et al. (1999) detected that residual fractions of Cr, Cu, Pb, and Zn increased during co-composting of sewage sludge and MSW. Liu et al. (2007), however, observed an increase in mobile fractions of Zn and Pb. The question remains, whether the controlled pretreatment of MSW containing organic matter alters the mobility of heavy metals and the remaining emission potential, and in what way.

This work aims to elucidate the changes in emission potential and stated environmental risk of two wastes containing organic matter with regard to biological stability and leaching of Cd, Cr, Cu, Ni, Pb, and Zn. Both wastes are treated by composting in order to be stabilized against degradation. Their origins and final

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treatments differ: One is originating from Sweden and is intended to serve either as a construction material onsite or offsite a landfill, or is to be landfilled according to the acceptance criteria of the Swedish landfill ordinance (Swedish EPA, 2001); the other is produced in Germany and to be landfilled as an MBT-waste in Germany according to the national landfill ordinance (German EPA, 2001). The analytical work was planned and to a major extent carried out at the Institute of Waste Resource Management, Hamburg University of Technology in Germany.

Focus is laid on the co-variance of measured characterization parameters, both in the solid material and in the leachate, with a special emphasis on the possible role of humic substances for the mobilisation of heavy metals.

Legislative regulation often comprises specific requirements for either the reuse of by-products or for waste to landfill. Within the European Union, the landfill directive 1999/31/EC provides a legal framework based on the general requirement for design and operation of landfills, as well as for the reduction of biologically degradable waste and the pretreatment of wastes to landfills (European Council, 1999).

Germany and Sweden are two EU countries comparable in GNP per capita, and both have well developed MSW management systems based on kerbside collection, separation of recyclables and centralised waste facilities (SCB, 2007; European Communities, 2003). Based on the diversity of waste management systems within the EU, national implementations of this legal framework have, however, led to a diversity of specific regulations (van Praagh and Persson, 2006). An amendment of the waste framework directive aims to reduce legal heterogeneity within the EU in the nearby future (European Parliament and Council, 2006). Regarding the reuse of waste derived materials for soil amendment, construction or other uses, the legal framework is in the offing within the EU. Legal regulation is fully enforced only for sludge from wastewater treatment (European Council, 1989).

MBT wastes form a special subcategory of non-hazardous waste in Germany (German EPA, 2001). Besides other limit values, the compliance with "biological degradability of dry residue in original substance" determined as respiration activity or gas formation potential in a fermentation test has to be proven (German EPA, 2001). In Sweden, landfilling of any waste that contains organic carbon is by definition prohibited, with three exceptions: the total organic carbon content does not exceed 10% by weight, the waste in question is digested and composted sludge from wastewater treatment or the material is ash from combustion with a TOC below 18% by weight (Swedish EPA, 2004). Both TOC measurements, and respiration and gas formation tests have shown to vary substantially between different laboratories, although tested on the same mother sample (Bockreis, 2006). Regardless of management options, the short-term and long-term emission potential and the actual impacts of materials distributed into the technosphere or allocated at landfills have to be investigated in order to prevent or restrict possible adverse effects.

2. Materials and methods

The waste materials studied were chosen to represent waste types with properties typical of their treatment and final purpose: low content of combustible waste, relatively low content of organic carbon (<20%) for landfilling or reuse as construction material (Table 1).

The eluates from cross-filtration were stored at below 4 °C if filtration or frozen if they could not be analysed within 4 days. Analytical errors were less than 5% according to the respective laboratories. The methods and methodological details of solid and eluate analyses are listed in Tables 2 and 3. As a reference, material M2 was eluted by means of an upward flow column set up to an L/S ratio of 10, according to CEN/TS 14405 (CEN, 2003), described in van Praagh et al. (submitted for publication). The metals analysed in this work (Cd, Cr, Cu, Ni, Pb, and Zn) were selected due to two facts: (1) leaching limit values exist according to EU landfill acceptance criteria; (2) these metals and their interaction with organic material have been investigated previously (see Baun and Christensen (2004) and Kjeldsen et al. (2002) for reviews).

The aerobic and anaerobic methods employed in this work for testing the stability of solid waste materials against biological degradation have been intensively tested on MBT wastes (Heerenklage and Stegmann, 1997, 2005; Adani et al., 2004).

Humic substances (HS) are synthesis products of mixtures of naturally occurring materials found or extracted from soils, sediments, and natural waters, which result from the decomposition of plant and animal residues (MacCarthy, 2001; Hayes and Clapp, 2001). As a consequence, analysis of humic-like substances and their contribution to organic carbon has been used to study the state of degradation of biologically degradable wastes (Ciavatta et al., 1993a; Castaldi et al., 2005). HS can be categorized as a subgroup of naturally occurring, heterogeneous organic substances of yellow to black colour (MacCarthy, 2001; Schwarzenbach et al., 2003). HS consist of humic acids (HA) and fulvic acids (FA). Humic acids are precipitated at either pH 2 (accepted by water scientist) or at pH 1 (accepted by soil scientist), according to Hayes and Clapp (2001). Fulvic acids remain in solution at all pH values. As degradation of organic matter in wastes normally differs in chemical prerequisites and time for degradation, the humic substances in composts appear to be different from humic substances derived from peat bogs and forest soils (Senesi et al., 2007). For the sake of simplicity, however, the humic-like substances analysed from the waste materials in this work are called 'humic substances' in the following discussion.

Depending on the microcosms from which they originate, humic substances vary in size, and exhibit various amounts of carboxylic and phenolic functional groups (Hayes and Clapp, 2001). A measurement of both solid humic and fulvic acid content in the solids was received as the difference between original extract and extracted fulvic acids measured with a modified Dannenberg

Table 1
Sample origin and preparation

	M1	M2
Treatment	Sorting, sieving, tunnel composting	Sorting, mixing, stock- pile composting
Origin	Germany	Sweden
Final contents	Residual MSW fraction	Residual MSW fraction, garden compost, dewatered sewage sludge
Final use	Landfilling	Landfill cover material or landfilling
Sampling at week	0, 2, 6, 9	0, 24
Sampling procedure	German EPA, 2001	Nordtest 1996
Sample handling	Grinding (<25 mm), drying, stored in freezer	Grinding (<25 mm), drying, stored in freezer
Eluation	100 g, L/S 10 deionised water, rotating for 24 h	
Filtration 1	Centrifugation 4–6 k rpm, pressure filtration 0.45 μm, 50 mm, cellulose mixed ester, and Spartan 30/0.45 RC, 30 mm, Whatmann plc, UK	
Filtration 2	Cross-filtration, 6 bar, cut-offs 100 kDa, 30 kDa and 5 kDa, 0.1 m^2 ULTRAN Slice, Schleicher & Schuell, Dassel, Germany	

Table 2
Analytical methods for solid materials

Parameter	Method and/or apparatus
Dry matter, DS	DIN 38 414-S2[a]
Loss of ignition., LOI	DIN 38 414-S3[b]
pH	DIN 38 404-C5[a]
Total organic carbon, TOC	Removal of inorganic carbon and IR measurement, CNS analyser (Leco)[a]
Respiration activity, AT_4	O_2 consumption over 4 days, Sapromat D12, data collection unit DDES 12-48, (VOIT GmbH, Germany)[a,d]
Gas formation potential, GB_{21}	Gas formation over 21 days with inoculum, Eudiometer[a,d]
Cd, Cr, Cu, Pb, Ni, Zn	Homogenised and boiled with aqua regia, PE-Elan 6000 ICP-MS or PE-Optima 2000 DV ICP-OES[b]
Total nitrogen, N_{tot}	N-analyser (Büchi)[b]
Ammonia, NH_4-N	Water vapour distillation, back filtration, then same as metals
Humic acids, HA1	Mixed with NaOH/Na oxalate solution, UV–Vis Spectral photometer at 530 nm (Shimadzu, Japan)[b]
Humic substances, HS2	Sodium pyrophosphate extraction at pH 10.5 for 15 h, centrifug., precipitation with HCl, Centrifuge, photometer 400 nm[c,e]
Spectral analysis, FT-IR	Grind into pellets with KBr (FT-IR grad at 1:100), gas flow 150 ml m^{-1} m, He/O_2 ratio 8/2 heating rate 10 K min^{-1}, linear increase from 30 to 950 °C, Equinox 55 FT-IR-Spectrometer (Bruker), 32 scans per spectrum[c]
Differntial thermogravimetry, DTG_x	
Differential scanning calorimetry, DSC_x	Thermal weighing machine, Calorimeter, MS STA 409 CD Skimmer, (Netzsch GmbH, Germany)[c]
CO_2-ion current Mass spectrometry, IC_x	

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[d] German Landfill Ordinance (2002).
[e] Modified danneberg method.

Table 3
Analytical methods for eluates

Parameter	Method and/or apparatus
pH	DIN 38 404-C5[a]
Electrical Conductivity, EC	DIN 38 404-C8[a]
Biological Oxygen Demand, BOD_5	DIN 38 409-H51[a]
Chemical Oxygen Demand, COD	DIN 38 409 - H41[a]
Dissolved Organic Carbon, DOC	DIN 38 409-H3[a]
Humic Acids, HA	Same as solids HA1
Cd, Cr, Cu, Pb, Ni, Zn	Boiled with HNO_3, measured spectrometrically, PE-Elan 6000 ICP-MS or PE-Optima 2000 DV ICP-OES[b]
Ammonia nitrogen, NH_4–N	Shaken with $CaCl_2$, filtered, measured spectrometrically[b]

[a] Institute for Waste Resource Management, Hamburg University of Technology.
[b] Central Laboratory of Analytical Chemistry, Hamburg University of Technology.

method (Table 2). Additionally, solid samples were subjected to Fourier-transformed infrared (FT-IR) spectroscopy in order to test the degree of degradation of the waste materials during pretreatment (Smidt and Meissl, 2007). Additionally, material M1 was analysed by differential thermogravimetry (DTG) and differential scanning calorimetry (DSC) in order to analyse loss of mass, heat flow, and ion current during controlled combustion (Smidt and Lechner, 2005; Smidt and Tintner, 2007). Analytical techniques are described in more detail in Tables 2 and 3.

Parameter values resulting from the total content analyses of M1 and the eluate characterizations of M1 and M2 were analysed statistically with principle component analyses (PCA). PCA is a multivariate statistical method which allows finding structures to reduce noise and to decrease redundancies in data sets by PCA (Jackson, 1991). Co-variation of parameters can be depicted through transformation of the data. This new data set is preferably of reduced dimensions without having lost the majority of the original information contained in the input data. The transformation chosen for the statistical analyses in this work delivered linearly independent transformation. The reader is referred to Ecke et al. (1998) and van Praagh and Persson (2004) for a more detailed description of PCA on waste and leachate analyses. Computations were carried out with commercially available software (Matlab 6.5, MathWorks Inc., MA, US).

In the following, analytical results are referred to as totals if not otherwise stated.

3. Results and discussion

3.1. Chemical and thermal characterization

Reductions in total organic carbon (TOC), and respiration activity (AT_4) revealed an increased degradation and stability through pretreatment of both materials (Table 4). In the case of material M1, the same is true for the gas formation potential (GB_{21}). The gas formation potential of M2 was too low to be verified. Total organic carbon is reduced by 38% and 50% compared to the input materials M1 and M2, respectively. The respiration activity is reduced by 95% and 90%, respectively. In the case of M1, the gas formation potential is reduced by 97%. These observations are in line with results from a study on samples of organic MSW samples, after having been composted for 16 weeks (Leikam and Stegmann, 1999).

Increased degradation of organic material is indicated by higher solid humic acids contents being associated with long pretreatment times for both M1 and M2 (Table 4). Due to its content of previously digested sewage sludge and compost, the lower degree of degradation was expected for M2. Composting of MSW containing organic material has shown to render higher contents of humic substances (Smidt et al., 2004).

The degradation of organic matter into carbon dioxide results in a loss of material, which is indicated by the reduction of loss on ignition (LoI) before and after the aerobic treatments of the materials (Table 4). Consequently, an increase of heavy metal content can be expected, as the studied metals are not volatilized at the temperatures reigning during pretreatment (50–70 °C). An increase of heavy metal content in composted wastes has been observed previously (Ciavatta et al., 1993b; Paré et al., 1999; Amir et al., 2005). Heavy metal contents of the solid materials in this study are corrected for this loss according to the following approach, used by Amir et al. (2005):

Table 4
Solid contents of untreated and treated waste materials (referred to dry matter)

	Unit	M1				M2		
		0 weeks	2 weeks	6 weeks	9 weeks	Input	Output	In L[d]
pH	–	5.5	6.9	7.9	7.5	n.d.	7.3	n.d.
AT4	mg O2 g^{-1}	79.4	39.0	6.3	4.1	4.6	0.5	3.3
GB21	Nl kg^{-1}	248.4	187.6	17.8	6.5	<limit	<limit	<limit
TOC	g kg^{-1}	185.5	196.1	126.5	115.1	143.5	71.9	n.d.
LoI	%	42.6	44.4	28.0	25.6	30.1	22.7	n.d.
HA[a]	g kg^{-1}	14.0	7.0	19.0	15.0	22.0	25.0	25.0
HA[b]	g kg^{-1}	10.0	15.0	17.0	20.0	23.0	27.0	28.0
FA[b]	OD[c] g^{-1} org	145	142	247	275	362	424	325
N	g kg^{-1}	9.9	10.0	8.4	7.8	8.6	6.8	n.d.
C/N	–	18.7	19.6	15.1	14.8	16.7	10.6	–
Cd	mg kg^{-1}	1.4	11.7	13.2	11.7	0.8	0.9	0.8
Cr	mg kg^{-1}	708.8	823.7	842.3	847.1	843.2	1007.3	1042.3
Cu	mg kg^{-1}	472.2	1848.2	1232.3	697.9	158.6	342.0	292.9
Ni	mg kg^{-1}	330.6	441.9	458.2	467.0	347.3	413.5	549.7
Pb	mg kg^{-1}	288.5	401.5	281.2	336.3	193.0	197.4	496.1
Zn	mg kg^{-1}	586.9	915.7	1055.3	1560.9	1006.7	595.4	797.8

[a] By method HA1.
[b] By method HS2.
[c] Optical density.
[d] Input leached to L/S 10 (van Praagh et al., submitted for publication).

$$C_{\text{corr}} = C_i \times \left(\frac{1 - \text{LoI}_{\text{ini}}}{1 - \text{LoI}_i}\right), \quad (1)$$

with C_i representing the measured heavy metal solid content at stage i of the pretreatment process, and LoI_{ini} and LoI_i the values for loss on ignition for the untreated material and for the material at stage i, respectively. Still, the heavy metal content in the solids increases, except for Zn in case of M2. TOC, total nitrogen, and heavy metal values for M2, with the exception of Cr and Ni, are within the range of previous results from characterization (average of three replicate samples, van Praagh et al., submitted for publication). Consequently, the surplus increase in heavy metal content after having been corrected by Eq. (1) might be due to the heterogeneities of the input materials due to enrichment through the pretreatment process, or due to the transportation of heavy metals to sampled fractions. This deviation might be avoided by sampling the same input material along the process of pretreatment, rather than sampling at the same time at different stages. This was, however, not possible in this investigation.

The development of the C/N ratio of organic waste can be also used as an indicator of degradation and stabilisation. A C/N-ratio of 20–25 has been suggested as suitable for composting (Norbu et al., 2005). It should drop to below 15 for stabilised compost (Jiménez and Garcia, 1992). Ratios decrease in this study from 19 to 15 and from 17 to 11 for M1 and M2, respectively. During biological treatment, total nitrogen is expected to increase initially, and decrease again as the material becomes degraded (Körner et al., 2003; Said-Pullicino et al., 2007). As nitrogen can be lost as NH_3 through the gas phase, indicated changes in total nitrogen content during pretreatment measured with dried samples have to be interpreted with care. In particular, the pH values of M1 at 7.9 and 7.6 for six and nine weeks of pretreatment, respectively, are in favour of nitrogen loss through the gas phase: The NH_3—NH_4^+ equilibrium is shifted towards NH_3. A wet sub-sample of M1 was analysed for NH_4–N, resulting in 1.6, 2.2, 1.8 and 0.8 g kg^{-1} NH_4–N at 0, 2, 6, and 9 weeks, respectively. Based on the N_{tot}-concentrations of the dried materials, a maximum of between 9% and 18% of the total nitrogen could have been lost through drying (if all the NH_4–N was lost as NH_3). Consequently, the differences in total nitrogen between the samples are too low to be interpreted in terms of indicating increased degradation.

The results from the Fourier-transformed infrared (FT-IR) spectroscopy on the M1 and M2 samples show distinct decreasing and increasing band heights at certain wave numbers (Figs. 1 and 2, respectively). The first major band height at 3400 cm^{-1} is attributed to non-bonded hydroxyl groups and water (Smidt and Meissl, 2007). The decreasing band heights at 2920 and 2850 cm^{-1} indicate a relative decrease of aliphatic methylene groups in the organic matter, and the reduction of the band height at 1720–1740 cm^{-1} for M1 in Fig. 1 indicates the decrease of aldehyde, ketone, carboxylic acids and esters (Smidt and Meissl, 2007). Increasing band heights at 875 and 1420 cm^{-1} indicate an increase in carbonate. This is apparent for M1, but not for M2. Still, the results of FT-IR spectroscopy suggest a degradation of organic matter and an increased mineralization.

Band heights at 2920 and 2859 cm^{-1} are higher for the fraction of M1 that was treated for two weeks than for the untreated material (Fig. 1). This corresponds to the TOC measurements (Table 4), and is probably a result of the input material's heterogeneity.

Band heights in the range of 1200 and 600–700 cm^{-1} for M2 in Fig. 2 might be attributed to phosphate and sulphate, respectively. Gypsum carton has a fitting band height around 1200 cm^{-1}, and due to the content of sorted construction waste, it can be expected to be found in M2. The band height at 1384 cm^{-1} indicates an increase in nitrate and, thus, nitrification of the material. For comparison, the FT-IR spectrum of an untreated but leached sample of M2 is given (Fig. 2). Band heights at 2920 and 2850 cm^{-1} are lower compared to the untreated samples' band heights, but band heights attributed to phosphate and sulphate are not. These results indicate that either biological degradation might take place in a percolation experiment with material with low organic content (<15% by weight), or that the band heights at 2920 and 2850 cm^{-1} cannot necessarily be accounted for by microbially induced degradation of organic matter only.

The results from the first thermal analyses of the material M1, the loss of mass per minute versus increasing temperature, show distinct local maxima at 100, 290 and 470, and 660 °C, which indicate the evaporation of water, the combustion of organic material and the disintegration of carbonates, respectively (Fig. 3a). Relative change in percentage of mass loss at the same temperature is a measure of change in amount of material present. The peaks at 290 and 470 °C are typical of organic wastes (Smidt and Lechner, 2005). They decrease parallel to the pretreatment time, except for the two week sample, and indicate progressed degradation. This is in line with the decrease of TOC, AT_4 and GB_{21} (Table 4).

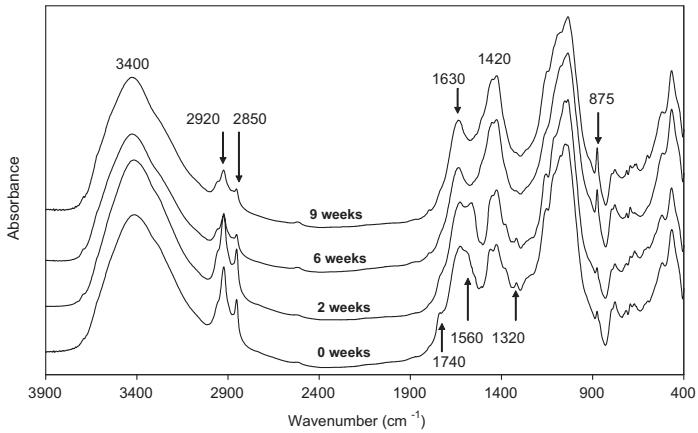

Fig. 1. FT-IR spectrum of M1.

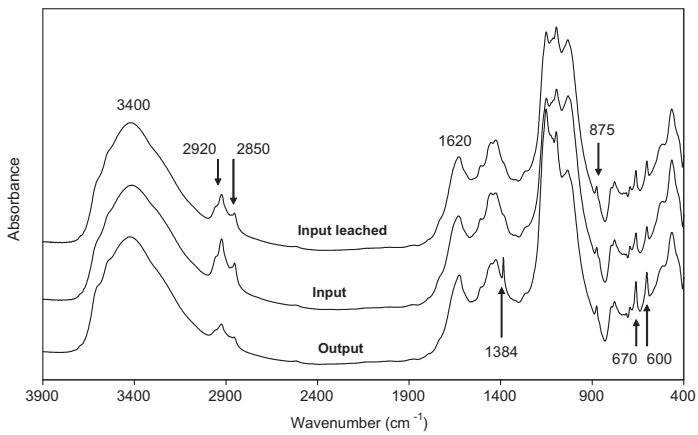

Fig. 2. FT-IR spectrum of M2.

The largest differences between local maxima occur between the second and the sixth weeks, indicating that the largest part of degradation takes place within this timeframe. No distinct local maximum can be discerned for carbonates in the two week sample. The peak for the six week sample is lower than for the sample that has been pretreated the longest, which is in accordance with increased mineralization in the course of the pretreatment process.

Local maxima of the CO_2-ion current (Fig. 3b), and, accordingly, of the heat flux (Fig. 3c), substantiate the interpretation of local maxima at 290 and 470 °C in Fig. 3a: the different heights indicate the change in combustible material through pretreatment.

Calculated with the analytical results described in Table 5, the BOD_5/COD ratio found in the eluates of M1 and 2 decreased from 0.52 and 0.11 to 0.08 and 0.04, respectively. This can be regarded as an indication of increased degradation of organic matter, which is in concurrence with findings by Zach et al. (2000). All eluate values are reduced when compared between input and output materials. The only exceptions are copper in the case of M1, and humic acids and copper in the case of M2. Cr, Pb and Cd input and output values were below detection limits in case of M2. Paré et al. (1999) observed a constant concentration of Cu extracted with water during 41 days of composting sewage sludge and residual MSW, but an increase in residual Cr, Cu, Pb, and Zn (residual fractions were defined as the ones extracted with HNO_3, $HCLO_4$, and HF). Ciavatta et al. (1993b) observed a statistically significant increase of water extractable Zn, Pb, Cr, Ni, and Cd during winter composting of MSW with increased stabilisation, but in the case of copper this was observed only for the extraction with a much more potential extract (ethylene diamine tetraacetic acid, EDTA). Leita and De Nobili (1991) found a strong correlation between concentrations of humic substances and copper in eluates from compost. In this study, an indication of the mobility of copper through leaching is given by the reduction of copper concentration by three orders of magnitude in the eluate of the input sample of M2 at L/S 10, produced with a percolation setup (Table 5; for more details see van Praagh et al., submitted for publication).

3.2. Principle component analysis of waste characterization data

Analyses of total contents in solid and eluate were simultaneously treated in principle component analyses for M1. All input data were standardised and normalised by taking the $\log_{10}$,

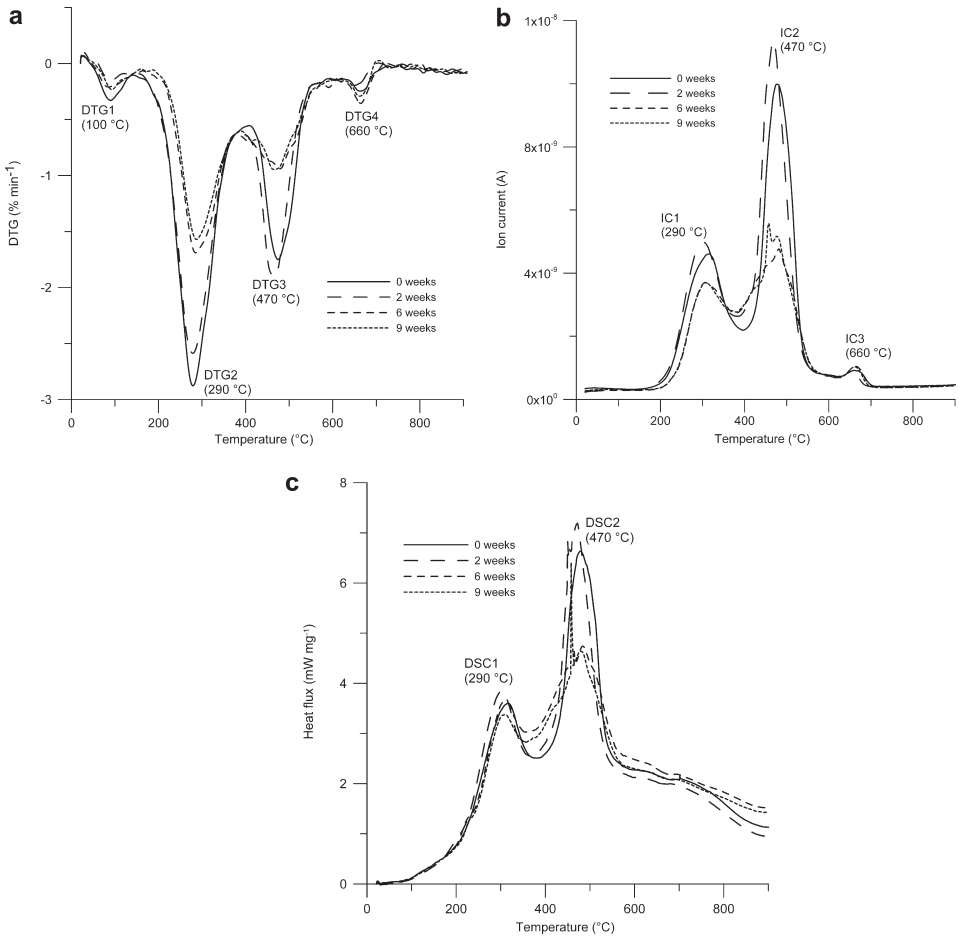

Fig. 3. (a) Thermogram of M1. (b) CO_2 ion current of M1. (c) Heat flux of M1.

extracting the mean and dividing by the standard deviation per column (that means per parameter). Consequently, all values vary around zero, and large nominal differences between parameters are prevented from affecting the variance of the data artificially. Missing values were substituted by means, as this does not affect the variance of the parameter. Missing values did not exceed 10% of the input data in any case. In order to be able to include results from the thermal analyses of M1, these were parameterised as follows: percentage mass loss in the DTG at 100, 290 and 470, and 660 °C as DTG1 to DTG4, respectively; heat flow at 290 and 470 °C as DSC1 and DSC2; and ion current at 290 and 470, and 660 °C as IC1 to IC3.

The PCA for M1 resulted in three principle components explaining 72%, 18%, and 9% of the original data variance, respectively. In the so-called loading plot, the co-variance of variables is displayed (Fig. 4a and b as zoomed in on the right centre part of Fig. 4a). The stabilisation parameters AT_4 and GB_{21} are found in the same quarter as and close to COD, DOC, BOD_5, and DTG2 (Fig. 4b). DOC, BOD_5, and GB_{21} overlap, and thus, show nearly the same variance. Pb and Zn, and to a lesser extent Cr in the eluate loadings are positioned closely to the DOC score, indicating co-variance of these parameters. Cd and Cu in the eluate have different loadings, especially within the second principle component (PC), and they are found in the lower left hand quarter.

TOC and LoI overlap and build a cluster together with DTG3, DSC2 and IC1. All heavy metal solid loadings differ substantially from their respective eluates (opposite signs within the first, or first and second principle component).

The humic acid concentration analysed according to method HS2 has a loading plot position in the vicinity of the Zn, Cr, and Ni loadings for the solids, and, to a lesser extent even to Pb, Cd and Cu. This suggests a possible affinity of these heavy metals to solid humic acids. Ciavatta et al. (1993b) found that increased heavy metal contents co-occur with high degrees of decomposition of MSW composts. This is in line with a study by Paré et al. (1999), in which the extractable fractions of Cu, Cr, Pb, Ni, and Zn decreased during co-composting of sewage sludge and MSW.

In the so-called score plot, the relationship between samples is presented (Fig. 4c). The untreated and lesser treated samples, 0 and 2 weeks, respectively, are positioned in the left half of the plot. As their AT_4, GB_{21}, BOD_5, and DOC are at least one order of magnitude higher than of the longer treated samples, they are likely to explain

Table 5
Characterization of leachates at L/S 10 of M1 (empty cells = no analyses carried out)

Sample	Fraction	pH	EC (mS cm^{-1})	NH_4 (g l^{-1})	DOC (mg l^{-1})	HA (mg l^{-1})	Cd (μg l^{-1})	Cr (μg l^{-1})	Cu (μg l^{-1})	Ni (μg l^{-1})	Pb (μg l^{-1})	Zn (mg l^{-1})
M1												
0 w.	<0.45 μm	5.90	6.57	0.14	3620	12.3	9.7	118	401	444	43	13.50
	<100 kDa	5.92	6.72	0.15	3320	21.0	12	98	448	403	53	11.70
	<30 kDa	5.98	6.55	0.14	3130	53.0	12	103	413	395	42	11.40
	<5 kDa	6.05	6.36	0.14	3000	16.0	11	103	389	382	15	11.20
2 w.	<0.45 μm	7.25	6.83	0.22	2780	16.4	34	72	1340	1270	35	6.39
	<100 kDa	7.09	6.54	0.20	2370	13.4	34	67	1060	1215	37	6.19
	<30 kDa	6.82	6.61	0.21	2590	12.6	30	58	815	952	19	5.05
	<5 kDa	6.78	6.63	0.20	2240	9.4	35	68	969	1125	17	5.88
6 w.	<0.45 μm	8.19	4.18	0.10	298	36.3	6.6	40	498	377	21	0.67
	<100 kDa	7.93	4.05	0.11	398	31.8	3.7	34	173	355	15	0.61
	<30 kDa	8.05	4.00	0.10	195	13.8	2.2	24	98	261	5	0.33
	<5 kDa	7.80	3.86	0.10	92	11.2	2.0	20	62	213	5	0.29
9 w.	<0.45 μm	8.11	5.19	0.02	181	9.7	6.9	26	806	191	16	0.69
	<100 kDa	7.59	4.95	0.02	152	9.2	7.4	25	769	181	10	0.70
	<30 kDa	7.68	5.08	0.02	124	7.6	6.4	23	588	164	5	0.62
	<5 kDa	7.52	4.97	0.02	74	7.1	5.8	26	488	164	5	0.58
M2												
Input	<0.45 μm	7.57	3.55	0.14	46	0.7	[a]	[b]	18	72	[c]	0.27
	<100 kDa	7.50	3.36		35	0.7	[a]	[b]	32	75	[c]	0.34
	<30 kDa	7.54	3.47		30	2.0	[a]	[b]	29	69	[c]	0.25
	<5 kDa	7.79	3.38	0.13	26	0.4	[a]	[b]	27	58	[c]	0.38
output	<0.45 μm	7.58	3.09	0.01	41	6.0	[a]	[b]	62	56	[c]	0.27
	<100 kDa	7.52	2.96		38	15.0	[a]	[b]	58	56	[c]	0.17
	<30 kDa	7.62	2.98		31	18.0	[a]	[b]	57	59	[c]	0.20
	<5 kDa	7.76	3.02	0.01	30	33.0	[a]	[b]	64	69	[c]	0.26
Input[e]	<0.45 μm	7.4	2.45	0.03	43	n.d.	0.001[d]	3.4	0.3	17.8	0.7	0.01

[a–d] Below limit of detection of 0.5, 10, 5 and 0.001 μg l^{-1}, respectively.
[e] Concentration at L/S 10 column test leachate (van Praagh et al., submitted for publication).

the position of the loadings. Differences in scores for six weeks and nine weeks of treatment appear to be small. The changes in emission potential seem to be largest for the preceding period, which is visualised by the comparatively large differences in variances for both the first and the second principle component scores of the second and sixth weeks of treatment.

Smidt and Tintner (2007) found that the heat flow profiles between 394 and 589 °C of DSC performed on composts best explained the variance in their data. In this study, the peaks at 290 and 470 °C (DSC1 and DSC2) are rather associated with the two week sample, whereas IC3 and DTG4 (CO_2-ion current and percentage mass loss at 660 °C) are rather explained by the final product (nine week sample). This suggests that monitoring the pretreatment process might require different parameters than measuring the quality of the final product. Meissl et al. (2007) used the FT-IR spectroscopy bands around 2900, 1700 to 1500, and around 1300 cm^{-1} in a partial least square regression model in order to describe the respiration activity of composted waste rich in organic material (coefficient of determination R^2 = 0.94).

In future work, FT-IR and thermal analytical data should both be included in a statistical analysis for an increased number of samples and prolonged treatment time of M1, accompanied by an increased number of samples (for example a sample from every week of treatment), in order to verify the most suitable parameter for monitoring the applied pretreatment process.

3.3. Eluate fractionation and principle component analysis

The COD leachate concentrations of material M1 were 11.7, 7.9, 0.88 and 0.59 g l^{-1} for the samples for weeks 0, 2, 6, and 9, respectively (after filtration with 0.45 μm). The BOD_5 concentrations were 6105, 4216, 47, and 48 mg O_2 l^{-1}, respectively. Values for leachate concentrations of M2 were 0.12 and 0.11 g l^{-1} of COD, and 13 and 4 mg O_2 l^{-1}, for the input and output material, respectively. The pH changed during filtration, and heavy metal concentrations increased in some cases in the filtrate. Electrical conductivity showed only minor variations (standard deviation between 0.06 and 0.13 at a 95% confidence level). A material recovery of more than 100% has been observed in fractionation experiments elsewhere (pressure applied 1.2 bar). Elongated or compressed loosely structured molecules were suspected to pass membranes, although they should have been cut off (Wang et al., 2006). Lower pressure or a different technical approach might have been more accurate. Nevertheless, results indicate that humic acids in the leachates of the longer treated M1 samples exhibit a larger proportion of the DOC (Fig. 5).

3.4. Emission potential of pretreated wastes at final use

With respect to the measured parameters in the solid and eluate samples in this work, nine weeks pretreated M1, and both untreated and pretreated M2 can be disposed of at a non-hazardous waste landfill in Germany (class II), classified as MBT waste. Except for the loss on ignition and solid TOC, pretreated M2 fulfils acceptance criteria for class I landfills, and with a further exception for Ni in the eluate, even for inert waste landfills in Germany (class 0).

Pretreated M2 can be landfilled at a non-hazardous waste landfill in Sweden. Due to the TOC, M1 cannot be landfilled in Sweden after nine weeks of pretreatment. A longer pretreatment time might enable this, though. Regarding the respiration index, M1 would fulfil the limits set by the EU already after six weeks, if the 10 mg O_2 g^{-1} DS stated in the working paper gained force (European Commission, 2001).

Untreated M2 shows a respiration index already below the German limit value of 5 mg O_2 g^{-1} DS, and a DOC and heavy metal concentrations below the Swedish leaching limit to be accepted at landfills for inert waste. Consequently, with regard to gaseous and leachate emissions derived from organic matter, a

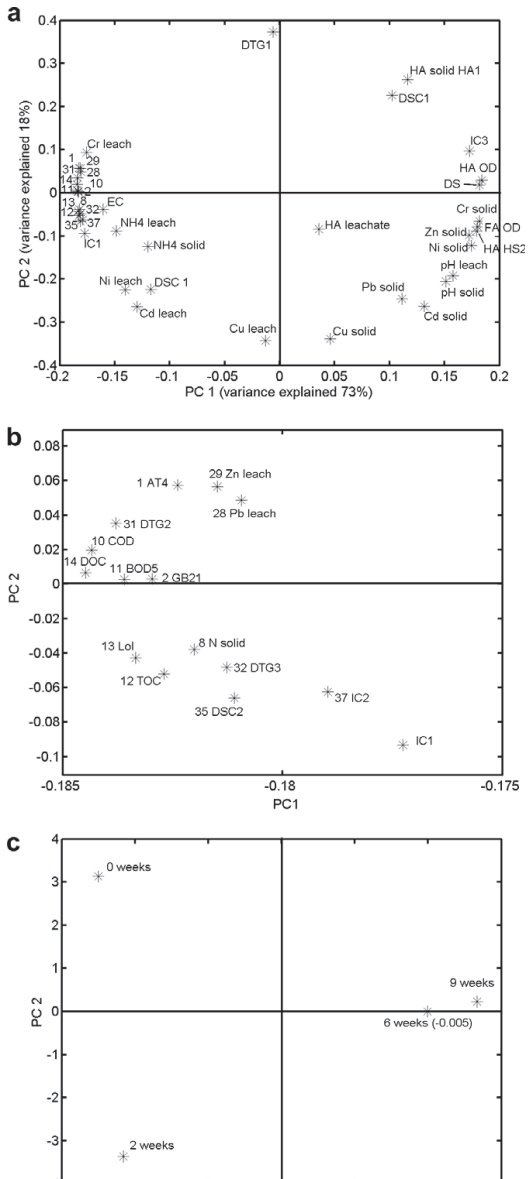

Fig. 4. Loading plot of the PCA on material M1 (a), indicated details (b) and score plot of the PCA on material M1 (c).

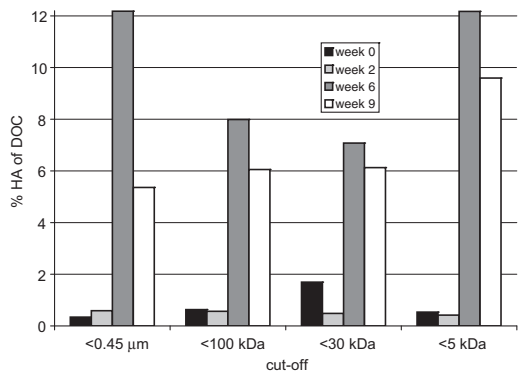

Fig. 5. Percentage humic acids concentration of TOC in leachate fractions.

limit value of 3% for inert waste and 10% by weight as an exception rule for organic waste to non-hazardous landfills in Sweden lacks substance in the case of M2 (for the sake of discussion, M2 is thought to be either landfilled or used as a smoothing construction layer on top of a non-hazardous landfill, below the drainage layer in a final cap, in which case the leachate would be collected together with the leachate from the waste it is covering). M2 could even with restrictions be used for construction in Denmark, a neighbouring country with enforced criteria for the reuse of refuse and contaminated soils for construction purposes (Danish EPA, 2000).

The emissions of landfilled wastes depend on waste constituency, pretreatment processes and technical landfill criteria. Dry, highly compacted waste exhibits lower gas formation potential than in lab-scale digestion tests (Leikam et al., 1999). Fully pretreated M1 (and, of course, M2) has a gas formation potential so low that the extraction of landfill gas produced would neither be technically nor economically feasible. Still, MBT waste complying with the German limit value for AT_4 might produce a total of 0–25 Nl kg^{-1} DS (Scheelhase, 2002; Doedens, 2002), with the higher values at a water content above 36% by weight.

The resulting landfill gas flux is estimated to 2–3 m^3 mg^{-1} DS a^{-1}, and within range which can be oxidised by a methane-oxidising covers (Scheelhase, 2002). A landfill simulation reactor study conducted on pretreated M1 (manuscript) resulted in an accumulated landfill gas volume of 2.3 l kg^{-1} DS over 116 days, with a remaining respiration activity (AT_4 value) of 1.1 mg O_2 g^{-1} DS (5 l reactor volume under anaerobic conditions, at 35 °C and water saturated).

A drier sample (66% DS instead of 48%) showed a respiration activity of 0.7 mg O_2 g^{-1} DS, with a remaining AT_4 value of 2.2 mg O_2 g^{-1} DS. Consequently, the actual environmental impact of landfilling this MBT waste through the gas phase is on the lower end of the range mentioned above. The actual emissions of M1 and M2 depend mainly on the bulk density as stored, on the time until capping with a methane-oxidising layer, and on the water content. Storage bulk density is unlikely to deviate between countries. In Sweden, legislation encourages the application of a methane-oxidising layer until final capping (Swedish EPA, 2001). In Germany, gas collection for landfilled wastes exhibiting emission potential such as M2 is not required (German EPA, 2002). Additionally, the water content might be very different between countries, as the potential infiltration (precipitation minus potential evaporation) into an uncapped landfill is usually larger in Sweden than in Germany, with extreme local variation in both countries (van Praagh and Persson, 2006). Even after capping, the respective landfills containing M1 and M2 will produce different leachate emissions: The allowed infiltration into the respective landfill is three times higher in Germany (158–50 l m^{-2} a^{-1}). With higher infiltration rates, leachate constituents might reach a background concentration earlier, and the necessary after-care phase for leachate emissions might be significantly shorter.

4. Conclusions

Increased stabilisation through composting of MSW containing both high (18.5%) and low (14.3%) amounts of organic matter can preferably be determined by the concurring decrease of AT_4, COD, DOC, and BOD_5, and in the case of high organic matter content, of GB_{21}. It coincides with an increasing content of humic acids and fulvic acids in the solids. FT-IR and thermal analytical methods add valuable information about the state of degradation, when several distinct thermal parameters are taken into account. For one sample, principle component analysis revealed that DOC, BOD_5, GB_{21}, and mass loss at 290 °C could be used interchangeably.

TOC and values for LoI co-vary with mass loss and heat production at 470 °C, as well as CO_2-ion current at 290 °C. Total Cr, Ni, Pb, and Zn mobility with deionized water was reduced by pretreatment for both materials. Leachability of copper unambiguously increased after pretreatment, and this co-occurred with higher concentrations of mobile humic substances and dissolved organic carbon. An affinity of Cr, Zn, and Ni to solid humic acids is suggested, and to a lesser extent, this is true even for solid Cd, Cu, and Pb. The indicated differences in interactions of immobile and mobile humic substances with heavy metals need further attention, in order to allow tailor made monitoring schemes for MBT wastes and to optimize pretreatment processes toward a more distinct desired quality. Due to differences in legal requirements for infiltration and emission reduction, actual gas and leachate emissions of the materials differ dependent on whether they are landfilled in Germany or Sweden.

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Appended paper

III

H. Modin, V. Pallier, G. Feuillade-Catahlifaud, E. Redon and K. M. Persson. Principal component analysis to correlate waste degradation to specific analytical parameters in landfill leachate: Application to landfills in France and Sweden. Journal of Hazardous Materials (submitted).

Principal component analysis to correlate waste degradation to specific analytical parameters in landfill leachate: Application to landfills in France and Sweden

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Abstract

Despite the increasingly sustainable waste management according to political decisions, landfilling is still among the most important waste management options in Europe. In France, 31 % of municipal solid waste (MSW) was landfilled in 2010 whereas Sweden has limited the landfilling to less biodegradable wastes. The monitoring of chemical parameters in MSW leachate is required during 30 years after the end of the exploitation. However, these parameters are not as relevant indicators of MSW degradation as the fractionation of leachate organic matter. However, the applicability of organic matter fractionation to landfills with not only MSW has not yet been discussed. Therefore this study compares landfill leachate data related to the stabilisation of waste from many full and pilot scale landfills containing either only MSW, MSW mixed with other wastes or only other types of wastes. A first overview of the data indicated that mixed waste degradation cannot be as easily defined as MSW degradation. Principal component analysis was successfully used to create a model of waste degradation using specific data from the MSW landfills. The applicability of this model to mixed waste landfills was restricted by the low chemical oxygen demand and NH_4 concentration in the mixed waste leachates.

Keywords: Landfilling, Municipal Solid Waste, Mixed Waste, Waste degradation, Principal Component Analysis

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1 Introduction

The municipal solid waste (MSW) management in Europe depends highly on the urbanisation, the consumption, the income levels and the lifestyle of the households, but also on political decisions. Countries like Belgium, Denmark, Germany, the Netherlands, and Sweden have changed towards more sustainable ways of management like recycling and biological treatment whereas other countries still use landfilling as the preponderant way of waste management (e.g. Romania, Greece, Spain, United Kingdom, Finland and Italy). Sweden and France are medium waste producers with between 300 and 600 kg MSW generated per capita and year in 2007 [1]. However, MSW management differs greatly between these two countries: landfilling (31 %) and energy recovery by incineration (29 %) are the predominant ways of MSW treatment in France [2], whereas Sweden has minimised the landfilling to industrial waste and construction waste and soils and promotes MSW incineration (49 %) and recycling (37 %) [3]. However, despite the increasingly sustainable waste treatment in many European countries and the decrease of MSW landfilled (from 41 to 31 % in France between 2002 and 2007 and from 35 to 1 % in Sweden between 1995 and 2010), 37 % of the MSW landfilled in Europe in 2010 [3,4].

Landfilling in the European Union has undergone major changes since the EU Landfill Directive [5] came into force. This Directive aims at reducing the environmental impact of landfilling, e.g. by reducing the amount of biodegradable MSW to landfill to 35 % of the amounts in 1995 before 2016 and by requiring all waste to be pre-treated before landfilling. During the last decade different strategies have therefore been developed and tested to improve and accelerate MSW degradation and decrease the amount of organic matter (OM) being landfilled by considering the main methods for accelerating MSW degradation (shredding, buffering, composting, leachate recirculation etc.) [6-13]. As a consequence the waste landfilled today can be suspected to be relatively well stabilised. However, some quantities of OM may still be present even in pre-treated or residual waste and therefore some degradation may occur also in modern landfills [12,14,15]. Thus landfills still represent a potential source of environmental pollution by the emissions of biogas and leachate.

Degradation of OM is among the most important process determining the biogeochemical environment inside landfills containing organic waste [16]. Humic substances (HS) are products of OM degradation. They are highly complex organic molecules with numerous functional groups and highly aromatic structures [17]. HS are usually divided into humic acids (HA) that are soluble in pH above 2, fulvic acids (FA) that are soluble in any pH, and insoluble humins. These compounds differ by their aromatic character. Specific parameters, such as specific UV absorbance (SUVA) index and distribution of OM according to hydrophobicity, are known to be related to the aromatic characters of molecules contained in a given sample [18,19]. They have previously been demonstrated as relevant indicators of MSW degradation [20]. Organic molecules in leachate from MSW landfills thus represent an important tool to evaluate MSW degradation inside the landfill: the more hydrophobic and aromatic the organic molecules are, the more degraded the MSW is. However, such correlation between OM in leachate and waste degradation has so far only been proven for MSW landfills as most studies on OM fractionation according to hydrophobicity has been performed on leachate from relatively homogeneous batches of MSW.

However, in Sweden most older municipal landfills contain a mixture of MSW and other types of waste, e.g. industrial and construction waste, ash, slag, sludge, lime, sediment and excavation material [21]. Most often these landfills contain significant amounts of OM and therefore the biological stabilisation processes determines the evolution of these landfills. It is, however, not obvious that the OM fractionation in leachates from mixed waste landfills will undergo the same evolution as in MSW landfill leachates.

The objectives of the study described in this article were twofold. The main objective was to investigate if the same indicators of the state of degradation can be used for landfills where other types of waste, and not only MSW, have been landfilled, for example older mixed landfills and modern landfills with low organic carbon content. In order to do that, the second objective of the study was to create a model of the parameters indicating the state of degradation. This was performed by modelling data from a number of leachate samples from full and pilot scale landfills containing only MSW using the multivariate data analysis tool principal component analysis (PCA). Finally a number of landfills containing other waste types, here referred to as mixed waste landfills, were fitted to the model in order to see if it was relevant for them also.

Previous applications of PCA of landfill leachate data include classifying landfill cells and leachate samples [22-24], finding relations among leachate parameters or identifying parameters that are particularly important for leachate quality [25-28] and evaluating toxicological tests for studying waste leachates [29-31].

2 Materiel and methods

2.1 Characteristics of the MSW landfill and MSW pilot scale landfills

Nine MSW pilot scale landfill cells and one old fill scale MSW landfill were studied. They differ by the treatment of the input waste, the mode of landfilling (conventional or leachate recirculation) and the time of operation. The MSW leachate data were previously published by the authors listed in Table 1. The operating conditions of the MSW landfill and the MSW pilot scale landfill cells are presented in Table 1. From site A one sample from each of the four cells, taken directly at the end of the operation, was employed in the analysis. From the cells at sites B and C samples taken continuously during the operation were employed. From the full scale landfill D two samples taken five years after the end of operation were employed.

2.2 Characteristics of the mixed waste landfills

Seven landfill sites with a total of 19 cells containing not only MSW were investigated: three from Sweden (sites S, H and F) and four from France (sites E, P, L and V). Table 2 gives the composition of the waste, the mode of landfilling, the time of operation and the age at sampling.

Table 1. Operating conditions of landfill and pilot scale landfills containing only MSW

Landfill	Input waste	Mode of landfilling	Time of operation	Reference
Pilot scale landfill A	Untreated MSW	Conventional	5.5 years	[20]
Pilot scale landfill A**	Untreated MSW	Bioreactor, leachate recirculation	5.5 years	
Pilot scale landfill A1*	MBT waste (12 weeks)	Conventional	5.5 years	
Pilot scale landfill A2*	MBT waste (25 weeks)	Conventional	5.5 years	
Pilot scale landfill B	Untreated MSW	Conventional	434 days	Unpublished data
Pilot scale landfill B1*	MBT waste	Conventional	294 days	
Pilot scale landfill B2*	MBT waste	Conventional	259 days	
Pilot scale landfill C	Untreated MSW	Conventional	424 days	[32]
Pilot scale landfill C*	MBT waste	Conventional	195 days	
Full scale landfill D	Untreated MSW	Conventional	24 years	[33]

*Wastes were mechanically and biologically pre-treated before landfilling

**Leachate was recirculated in the wastes mass

The number 1 and 2 allow differentiating the duplicates

2.3 Chemical and physico-chemical characterisation of leachate

The leachate samples were stored at 4°C in polyethylene bottles to limit biological activity, and the analyses were performed as soon as possible. All chemical and physico-chemical analyses were performed according to Table 3 with the exception of NH_4 in the leachates from landfill sites S, H and F. For these landfills, NH_4 data were taken from the regular leachate monitoring data collected by the landfill owners. The median for the two years preceding the study was used.

Table 2: Operating conditions and waste composition of landfills containing mixed waste

Landfill	Waste composition (%)						Mode of landfilling	Time of operation [years]	Age at sampling [years]
	Industr. and constr.	MSW	Sludge	Green	Soil	Other			
S1	0	85	5	0	0	10	Addition of leachate from a hazardous waste cell	4	19
S2	10	75	5	0	0	10	Conventional	7	15
H1	30	15	15	0	30	10	Various irrigation and recirculation schemes	44	45
H2	0	0	0	0	100	0	Conventional	6	6
F	29	0	0	0	52	18	Conventional	6	6
E1								2	8
E2	35	55	10	0	0	0	Conventional	2	14
E3								16	20
P1								1	1
P2								3	6
P3	74	2	21	3	0	0	Conventional	2	8
P4								1	9
P5								1	10
L1								1	2
L2	34	41	0	0	0	25	Conventional	1	4
L3								1	8
L4								1	10
V1	35	45	0	1	0	19	Conventional	1	5
V2							Bioreactor	1	3

Table 3: Global parameters analyses performed on leachate samples

Analytical parameter	Unit		Pre-treatment	Analytical method and apparatus	Precision and Quantification Limit
pH	-		None	pH-meter: Eutech Instrument; model CyberScan pH 510 Combined glass electrode Ag/AgCl	±0.1 pH unit
Electrical conductivity	EC	mS/cm	None	Conductimeter WTW, LF 538 Probe tetracon 325	10<T (°C)<55 Maximal error: ±5%
Dissolved organic carbon	DOC	g C/L	Filtered on 0.45µm	TOC-meter Dohrmann, Phoenix 8000 Chemical oxidation by sodium persulfate	0.1–20 mg C/L ±0.2 mg C/L
Chemical oxygen demand	COD	g O_2/L	Filtered on 0.45µm	Chemical oxidation by potassium dichromate by using rapid test kit	0–1500 mg O_2/L ±6 mg O_2/L
Ammonium	NH_4^+	mg/L	Filtered on 0.2µm	Ion chromatography DIONEX DX-120	0–15 mg/L Maximal error: ±5 %

2.4 Leachate organic matter as an indicator of wastes degradation

2.4.1 SUVA index

The SUVA index is defined as the ratio of the absorbance at 254 nm to the dissolved organic carbon (DOC) concentration. Absorbance was measured at 254 nm using a spectrophotometer Shimadzu, model PharmaSpec 1700, with 1 cm-long quartz cells.

2.4.2 Fractionation of OM according to hydrophobicity

The fractionation of OM according to hydrophobicity was performed according to a combination of the protocols of Schnitzer and Khan [34] and Aiken et al. [35] to divide dissolved OM into four fractions grouping together molecules with similar properties: humic like acids (HA*), hydrophobic like substances (HPO*), transphilic like substances (TPH*) and hydrophilic like substances (HPI*). After removal of insoluble humins by filtration on 0.45 µm membrane, the samples were acidified to pH 2 using 37 % HCl to precipitate the HA* fraction subsequently removed by filtration on 0.45 µm membrane. The remaining OM was then separated into the HPO*, TPH* and HPI* fractions by successively passing the leachate through DAX-8 resin (non-ionic and slightly polar) to adsorb the HPO* fraction and XAD-4 resin (non-ionic and non-polar) to adsorb the TPH* fraction. The HPI* fraction was not adsorbed on the resins. The percentage of each extracted fraction was determined by calculating the ratio of the DOC in each fraction to

the total DOC in the sample. The experiments were conducted using laboratory columns (length of 4.5 cm and diameter of 1.4 cm) with volumes of resin and sample of 5 and 156 mL respectively at a filtration flow of 50 mL/h in order to achieve a capacity factor k' of 25. The capacity factor defines the ratio between sample volume and resin volume and allows adapting the sample volume to its DOC content. Choosing a low k' is in line with the findings from Labanowski and Feuillade [36].

2.5 Principal Component Analysis

PCA is a multivariate data analysis tool that offers a way to present complex data in a simplified way and to identify relations between different parameters [28,37]. PCA transforms a data matrix in a way that concentrates as much as possible of the original variance into the first columns (principle components, PCs) of the new matrix. Ideally, the first few PCs can then be used to describe the important variations within the data set, rather than studying all the original leachate parameters.

PCA was applied to the following data:

- Data from the ten MSW landfill cells described in Table 1, in total 37 leachate samples. Nine parameters (pH, SUVA, NH4/EC, COD/EC, % HA, % HPO, % TPH, % HPI and HA/HPO) were included.
- Data from the 19 mixed waste landfill cells described in Table 2, one sample from each landfill. The same nine parameters were included as for the MSW waste landfills.

The leachate parameters were chosen because they are relevant for the state of degradation and they had been analysed in most of the leachates. Since the SUVA index and the parameters originating from the fractionation are ratios it is more relevant to also include NH_4 and COD (chemical oxygen demand) as ratios also. They were therefore related to the electrical conductivity, EC. Furthermore, dilution of leachates can strongly affect the outcome of the PCA [28,38] and dividing NH_4 and COD with EC can limit the effect from different degree of dilution in different leachates.

Prior to performing the PCA the data were normalised by taking the $\log_{10}$. To give all parameters equal weight in the model each parameter was centred by extracting its mean and scaled to unit variance by dividing with the standard deviation. The vectors used for centring and scaling the MSW data set were saved and the same vectors were later applied to the mixed waste data set. The PCA was performed using Simca-P+ (Umetrics AB, Umeå, Sweden). Initially a PCA model was created using the data from the MSW landfill leachates. Thereafter the data from the mixed waste landfills were projected on this model.

3 Results and discussion

3.1 Analytical results

The SUVA index and the fractionation of OM according to hydrophobicity have previously been identified as good indicators of MSW degradation [20]. The repartition of organic molecules

continues to evolve even when the DOC, COD and BOD_5 concentrations are stable in the leachates, underlining a continued MSW degradation within the landfill that cannot be detected using these simple chemical parameters. According to previous studies, when the time of operation increased, the OM repartition evolved towards more aromatic and hydrophobic compounds [20,39,40].

Since the OM evolution in mixed waste landfills is less well studied the aim of this section is to discuss if simple chemical parameters such as COD and/or specific parameters such as OM fractionation are suited to describe their degradation? Table 4 presents the results from the analyses of the mixed waste landfills.

Leachates from landfills S1 and S2, where 85 and 75 % of MSW were landfilled respectively, were sampled 15 and 19 years after the beginning of the operation respectively. The repartition of organic compounds showed a large fraction of HS* (HA*+HPO*), 65 and 58 % for S1 and S2 respectively, and SUVA index of 15 L/cm/g C. These levels correspond well to what can be found in MSW landfills, certainly owing to the large part of MSW in S1 and S2. The addition of leachate to S1 did not accelerate the waste degradation and seemed rather to have a negative influence on waste humification as already shown by Feuillade-Cathalifaud et al. [41].

Table 4. Results from analyses of leachate from mixed waste landfills. n.a. = not analysed

Leachate landfill	COD (mg/l)	NH_4 (mg/l)	% HA	% HPO	% TPH	% HPI	pH	SUVA (L/cm/g C)	EC (mS/cm)
S1	500	390	27	38	18	17	6.9	16	30
S2	600	360	15	43	12	30	7.0	15	11
H1	630	720	9.4	33	38	20	7.5	18	11
H2	110	0.71	20	44	28	9.2	7.3	18	3.3
F	n.a.	0.46	1.2	64	5.7	29	7.7	14	2
E1	6100	1400	15	29	5.9	50	8.6	44	22
E2	650	1600	4.4	48	28	19	7.9	25	7.8
E3	440	380	15	41	31	13	7.8	21	3.9
P1	7300	220	3.4	18	17	62	6.6	1.6	18
P2	3200	360	3.3	48	22	26	7	4.4	5.6
P3	8800	1210	4.5	52	13	31	8	5.9	14
P4	3600	680	4.8	42	32	21	7.8	4	8.9
P5	3800	790	6	43	24	27	7.4	3.8	8.8
L1	6100	490	1.9	7.9	21	69	6.1	7	8.9
L2	4300	420	69	8.1	9.6	14	7.5	21	19
L3	2400	1100	28	21	14	37	7.5	16	13
L4	1400	200	17	48	17	18	7.3	17	6.7
V1	4900	1700	19	29	17	35	7.7	27	14
V2	3800	1000	14	31	18	38	7.8	27	10

The only landfills containing soils, H1, H2 and F ha soil contents varying from 30 to 100 % and MSW proportions of less than 15 %. The leachate samples were collected 45 years after the beginning of operation of H1 and 6 years for H2 and F. The % HS* were lower in the leachate from H1 compared to H2 and F and the SUVA index in this leachate was not characteristics of such an old landfill. However, the youngest parts of this very large landfill were filled only one year prior to the sampling and the leachate can represent a mixture of all parts of the landfill, something that seem to complicate the interpretation of the specific OM parameters as indicators of wastes degradation. In landfill H2 and F no easily degradable waste was landfilled and therefore a relatively high HS* percentage in the landfills could be expected. Since soils are hardly degradable materials studying their leachate OM characteristics could mainly be seen as a way of confirming their stability against degradation rather than studying an evolution of the waste characteristics within the landfill.

Wastes landfilled in landfills site E, L and V mainly consisted of industrial and demolition (approximately 30 %) waste and MSW (approximately 50 %) and thus these landfills hold relatively large amounts of OM. The amount of COD in their leachates decreased with age, as expected. However, the repartition of OM, especially the HA* content, seems to be almost independent of the type of treatment and the age of the waste unlike for MSW. This suggests that the usefulness of the specific OM parameters as indicators of the degradation in these landfills is restricted which could be due to the presence of industrial and construction waste. This conclusion was affirmed by the results from the characterisation of leachate from site P that contains approximately three fourths of industrial and construction waste and one fourth of sludge. From site P the COD value did not decrease, but varied, with age. However, the SUVA index and the HS* percentage were approximately constant in the leachate from the landfills P2 to P6 for which samples were collected between 5 and 10 years after the end of the exploitation. Such results were not expected for a mixture of MSW and construction waste.

In summary, none of the parameters usually used to describe the degradation of MSW gave obviously relevant information on degradation of soil, industrial or construction waste. However, studying the evolution of many dependant parameters using univariate techniques is difficult and possibly others parameters may be relevant to describe the wastes degradation in the mixed waste landfills. The use of multivariate techniques can help identifying the most relevant parameters taking into account the complexity of the leachate data. The use of PCA will be discussed in the two following sections.

3.2 A PCA model of degradation based on MSW leachate data

In this section the results from the PCA of the MSW landfill leachate data is presented. This PCA generated a two component model. The first principal component represents 69 % of the original leachate data, and the second PC represents 18 %. Using cross-validation it was estimated that the model can explain and predict each variable to 60 % or more, with the exception of NH_4/EC that was only predicted to 42 %. The results from the PCA are presented graphically in Figure 1 and Figure 2.

Figure 1 is a score plot presenting the co-variance between the leachate samples. Each leachate sample is represented by a dot in the model plane. Samples located close to each other resemble each other while samples located far from each other are different. Twelve samples from landfill B and eight from each of B1* and B2* were included. These samples were numbered from 1 to 12 and from 1 to 8 respectively with 1 being the first sample taken. Figure 1 displays a 95 % confidence ellipse based on the Hotellings T^2 distribution. Extreme values are located outside of the ellipse and are termed strong outliers. In the MSW leachate data set there were no strong outliers.

Figure 2 is a loading plot that displays the co-variance between the leachate parameters. Co-varying parameters are located close to each other. Parameters located on opposite sides of the plot have a negative co-variance. Parameters that are located far from the origin are contributing more to the model than parameters close to the origin. The directions in the score and loading plots correspond to each other. For example a sample located to the left in the score plot should have high values of the parameters located to the left in the loading plot.

The x-axis in Figure 1 and Figure 2 is related to the first PC. As seen from the loading plot (Figure 2) this PC is mainly related to pH, SUVA, % HA, HA/HPO and COD/EC since these are located furthest from the origin with respect to the x-axis. Parameters representing a low degree of stabilisation, e.g. high fractions of TPH and HPI, are located to the left in Figure 2 while parameters representing a more stabilised leachate, i.e. % HA, and % HPO, SUVA, and HA/HPO are located to the right. Thus PC1 seems related to the degree of stabilisation. % HPO is not related to the first component, but instead strongly related to the second. Thus % HPO is not co-varying with the other parameters and it seems to be related to a different aspect of MSW stabilisation. Thus the fractionation of the OM based on hydrophobicity seems to describe three different characteristics of the leachate OM. One is represented by HA*, one by HPO* and the third one by TPH* and HPI* together. The co-variance between TPH* and HPI* shows that they describe relatively similar information about the MSW leachates.

The conventional landfills B and C, where untreated MSW was landfilled, are located furthest to the left, indicating a low degree of stabilisation. There is no clear direction of the evolution of the leachate from landfill B, indicating that negligible stabilisation occurred during one year of landfilling. The conventional landfill A, however, is located in the right part of the plot, suggesting that it is more stabilised. The reason for this difference could be that landfill A was 5.5 years old at the sampling while B and C were maximum one year.

The initial leachate samples from the cells B1* and B2* containing pre-treated waste, are located to the bottom left in Figure 1, close to the location of TPH and HPI in Figure 2, indicating a low degree of stabilisation. These leachates show a clear evolution as the samples are moving up and to the right with time. The landfills A1* and A2* containing pre-treated waste landfilled for 5.5 years are located far to the right in Figure 1, close to the location of % HA and SUVA in Figure 2 suggesting a high degree of stabilisation. Landfill D is a full scale landfill where untreated MSW was landfilled since 24 years at the time of sampling. The leachate quality from landfill D is different to that from the pilot scale landfills due to the very high fraction of HPO.

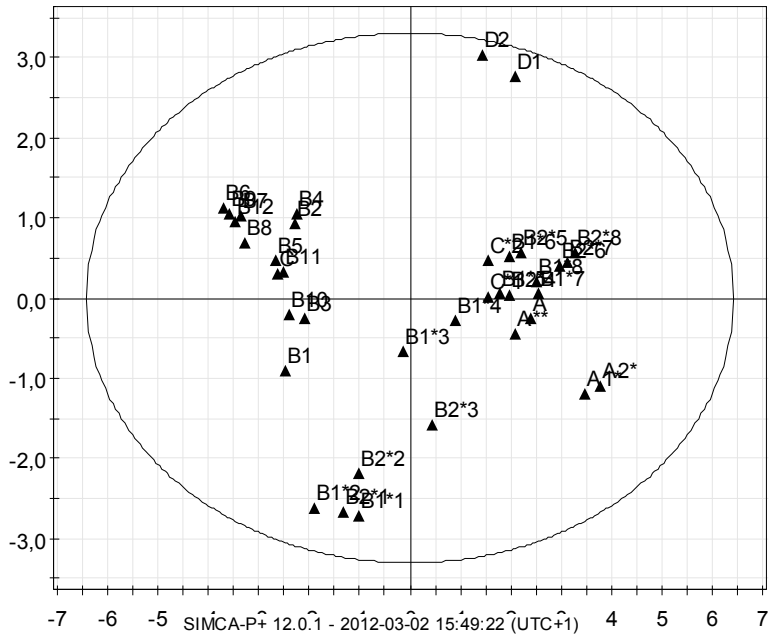

*Figure 1. PCA score plot displaying leachate samples from landfill cells A, A**, A1*, A2*, B, C, C* and D. Samples from landfills B, B1* and B2* are numbered from the youngest to the oldest landfill*

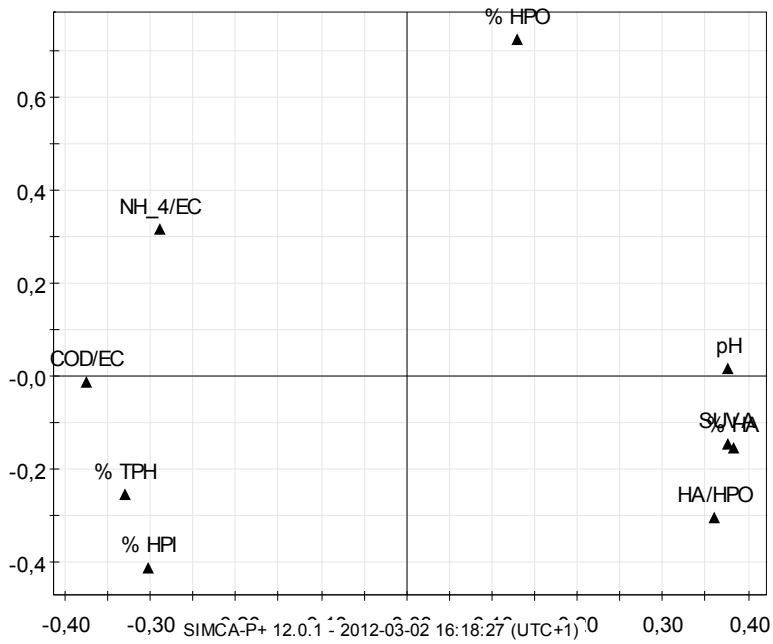

Figure 2. PCA loading plot of MSW landfill leachate data

The loading plot shows that the % HA and SUVA co-vary very strongly. Probably these two parameters can be used interchangeably if only the amount of humic acids is of interest. However, since the fraction of HPO* clearly describe another pattern of variation than the HA* the fractionation according to hydrophobicity describe more information of the leachate compared to the SUVA index.

To summarise, it was possible to create a two component PCA model incorporating 87 % of the variance in nine leachate parameters related to the biodegradation of MSW. Older landfills and landfills with pre-treated waste were located to the upper right (landfills B1*, B2* and D) or to the right (landfills A1* and A2*) of the score plot. The least stabilised landfills were located to the left (B and C). Overall the attempt to create a model was considered successful.

3.3 Application of the PCA model to leachate data from mixed waste landfills

This section describes the results from the projection of the leachate data from the mixed waste landfills (Table 2) onto the PCs generated using the MSW leachate data. Figure 3 shows the resulting score plot. The mixed waste landfill leachate data are shown in black while the MSW data used to create the model are shown in grey. Figure 3 indicates a relatively high degree of stabilisation in most of the mixed waste data sets since many are located to the right in the score plot. The score plot also show a number of strong outliers: L1, L2, P1, H2 and F. These samples are extreme in relation to the processes described by the model, and will be further discussed below.

A so called contribution plot is used to displays to what degree each parameter contributes to a certain pattern. The contribution plot in Figure 4 displays which leachate parameters contribute to the difference between the MSW landfills and the mixed waste landfills. The plot shows that although the mixed waste landfills have e.g. higher SUVA indices, higher fractions of HA* and lower fractions of TPH* and HPI*, the main differences between the two groups are the low values for NH_4/EC and COD/EC in the mixed waste landfills. The NH_4 concentration in the MSW leachates is between 400 and 4800 mg/l (data not shown) while in the mixed waste leachates it ranges from 0.5 to 1700 mg/l (Table 4). The COD was between 2900 and 125 300 in the MSW leachates (data not shown) and between 100 and 8800 mg/l in the mixed waste leachates (Table 4). Since both NH_4/EC and COD/EC are located to the left in Figure 2 these big differences are probably one reason that most of the mixed waste samples are located to the right in Figure 3.

L2 and H2 are located in the bottom right extreme of Figure 3, suggesting a high degree of stabilisation but a low fraction of HPO. L2 is a young leachate; this cell was two years old at sampling. A contribution plot for L2 (not shown) suggests that an extremely low fraction of HPO* is the main difference compared to the model. H2 is also a relatively young leachate, but contain mainly soils as discussed in section 3.1. The main difference between this leachate and the model is an extremely low NH_4/EC value in H2 (contribution plot not shown).

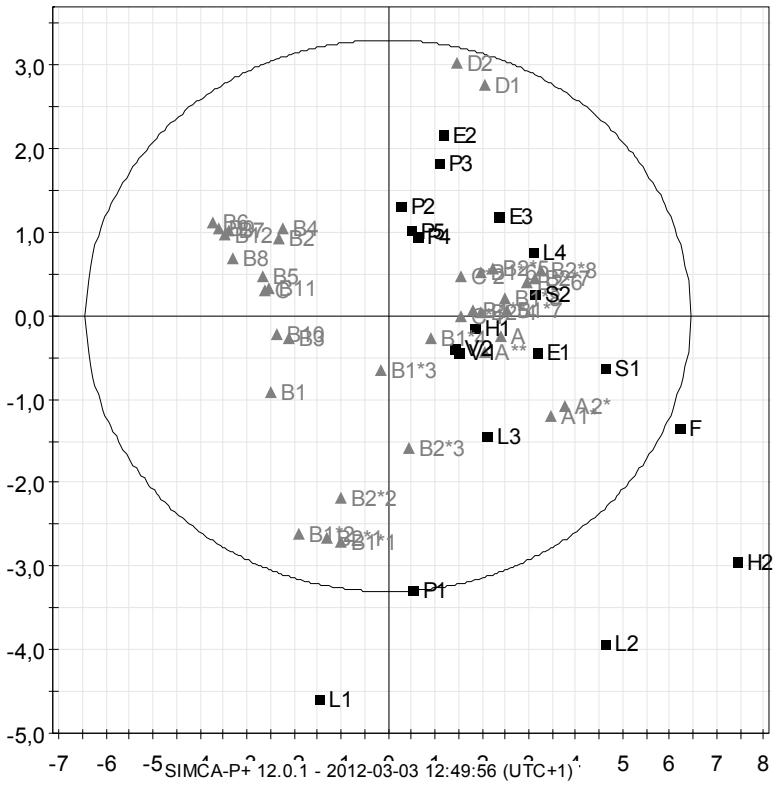

Figure 3. Score plot of the PCA model with MSW landfill leachate samples (grey) and the projected mixed waste landfill leachate data (black)

L1, the youngest cell from landfill L is located in the bottom left of Figure 3, a position that signifies a very low degree of stabilisation in the case of MSW landfills. The older cells from landfill L are located more and more to the upper right, most likely affected by an increasing fraction of HPO. Except for the location of L2 this is relatively similar to the evolution of the MSW landfill leachates B1* and B2*.

Samples 2–5 from site P are located in a cluster in the upper part of the score plot. These cells are between 6 and 10 years old. Leachate 1 from site P is much younger, only one year, and it is located alone in the bottom of the score plot. Assuming that P1 is less stabilised, this seems to show mostly in the HPO* fraction. For sites L and P increasing stabilisation thus seems more related to increasing HPO* fraction than an increasing HA* fraction since % HPO is mainly related to the second PC (the y-axis). However this could also be due to NH_4/EC and COD/EC overshadowing all other parameters relating to PC1.

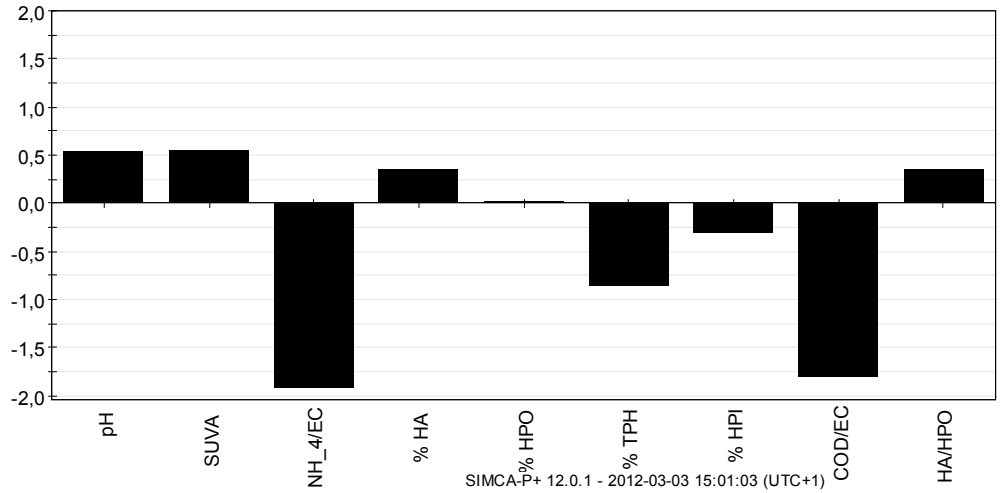

Figure 4. Contribution plot showing to what degree the parameters contribute to the difference between the MSW landfill leachate data and the mixed waste landfill leachate data

V1 and V2 are located very close to each other in Figure 3 in spite of V1 having leachate recirculation and V2 not. A similar result can be observed regarding the MSW landfills A and A** (Figure 1). Thus the leachate recirculation appears not to have enhanced the stabilisation, confirming the findings by Feuillade-Cathalifaud et al. [41].

The landfill site S contains mainly untreated MSW. The younger cell S2 is located among the more stable samples from B1* and B2* while older cell S1 is located further to the right. Since there are only two cells from this site it is difficult to discuss whether any development of the leachate quality can be observed.

For landfill E no trend can be observed since the oldest leachate, E3 is located between the other two in Figure 3. While the time of operation for E1 and E2 was two years site E3 was filled during 16 years. Thus E3 contains wastes of varying age and parts of this landfill cell are actually younger than E1 and E2 which could explain their locations in the score plot. The same problem can be observed when interpreting the results from the very big and old landfill H1 as was discussed in section 3.1 above. In Figure 3 H1 is located together with samples from the much younger landfills B1* and B2*.

In order to see to what degree the model captures the variance in the mixed landfill data set Figure 5 was created. This figure plots the distance from all the data points (landfill leachate samples) to the two-component model plane. The bars represent the amount of the variance that is left unexplained by the model. If the amount of unexplained variance for a sample exceeds the critical limit (represented as a dashed line in the figure) that sample is termed a moderate outlier. Figure 5 shows that most of the mixed waste landfills are actually moderate outliers but only A and A** among the MSW landfills. The two most extreme outliers, H2 and F, were commissioned and are operated in accordance with the Swedish implementation of the Landfilling Directive [5], and thus they have a TOC content in the waste of less than 10 %. The

variable mainly causing the deviation for H2 and F is NH_4/EC and thus the extremely low NH_4 concentrations in their leachates makes them badly are explained by the model created using MSW landfill data. For the other mixed waste landfills most of the deviation from the MSW model is caused by COD/EC. However this deviation is not as great as for the landfills F and H2.

In summary, the PCA model generated using data from MSW landfill leachates could not explain all of the variance in the leachate data from mixed waste landfills. For most of the landfills the main reason was that the low COD/EC ratios observed for the mixed waste landfills could not be captured by the model. For two landfills complying with the Swedish implementation of the EU landfilling directive [5] the main reason for the deviation was instead their extremely low NH_4/EC value.

The difference between the mixed waste landfills and the MSW landfills that were captured by the model were mainly due to lower NH_4 concentration and COD in the mixed waste landfill leachates. In the cases where an evolution of the leachate characteristics could be observed this was mainly captured by PC2, a component that is most strongly related to HPO*.

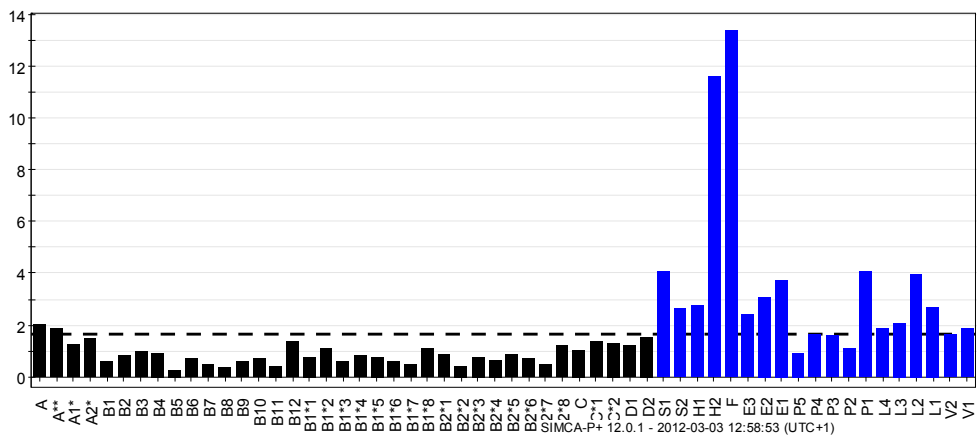

Figure 5. Distance to the PCA model for landfill leachate samples. Bars reaching above the dashed line (critical limit) signify moderate outliers

4 Conclusions

The principal component analysis of MSW landfill leachate data showed that it was possible to create a model that summarised nine parameters relevant for waste degradation into two components. This confirms the usefulness of PCA to create overviews of the complex relation between landfill leachate parameters.

The results from the PCA showed that SUVA and % HA co-vary very strongly and thus seems to describe the same properties of the MSW leachate. These two parameters can most likely be used interchangeably, but the PCA also show that HPO* and TPH* or HPI* add additional information about the variance in the data and therefore, fractionation according to hydrophobicity is more valuable than SUVA analysis when studying stabilisation of MSW.

Applying the PCA model created using data from MSW landfill leachate on leachate from mixed waste data was not entirely successful. The main difference between the mixed waste landfills and the MSW landfills was the low COD in the leachate from the cells with mixed waste, except for two cells commissioned and operated in accordance with the Swedish implementation of the landfilling directive where it was their extremely low NH_4 concentration that caused the largest deviation. In some cases the fact that large landfills contained waste of very varying age restricted the interpretation.

In some cases the model generated using MSW leachate data could depict an evolution towards more stable waste even for the mixed waste landfills. In those cases the development seemed to be mainly related to the HPO fraction of the organic matter.

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Appended paper

IV

H. Modin, M. van Praagh, K. M. Persson and H. Palm. Heavy metal mobility in waste from a landfill with low organic carbon content. Journal of Hazardous Materials (submitted).

Heavy metal mobility in waste from a landfill with low organic carbon content

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Abstract

Landfills with low organic carbon content may exhibit very different leachate quality compared to municipal solid waste landfills. The objective of this study is to increase the understanding of how a residual waste landfill can be different from an MSW landfill with focus on heavy metal leaching. One type of residual waste from a modern landfill was studied and it was found that the metal mobility, defined as the amount of leached metal relative to the total amount, was low. The small availability of possible ligands such as dissolved organic matter and ions may have contributed to this. The waste contained small amounts of degradable organic matter that can affect the redox environment and thus the solubility of metals. At L/S 10 some metal concentrations are still elevated compared to ambient surface water concentrations. A not negligible emission potential may remain in the residual waste landfill for a long time.

Keywords: Landfill leachate; Heavy metals; Leaching tests; Construction and demolition waste; Biodegradation

1 Introduction

Solid waste management in the EU has undergone major changes since the landfilling directive [1] came into force, due to the more stringent regulations, and an increasing interest in recycling and reuse [2,3]. All over the EU, measures are taken to decrease the amount of organic matter being landfilled, and in Sweden a ban on landfilling of waste with more than 10 % total organic carbon (TOC) came into force in 2005 [4,5]. Organic matter degradation is among the most important processes determining the leachate chemistry in municipal solid waste (MSW) landfills [6,7]. Thus modern landfills with little organic matter can be expected to display significantly

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different biogeochemical properties, and consequently give rise to leachate of different composition.

As an increasing part of MSW is recycled (in Sweden 98 % in 2010, including incineration [2]) almost only residual fractions will be landfilled. In 2008 MSW constituted as little as 3 % of the waste (mining waste excluded) landfilled in Sweden. The major fractions are instead residual waste, left over from sorting and recycling, mainly mineral waste, incineration residues and residues from sorting and separation of various wastes, including MSW, industrial waste and construction and demolition waste (C&DW). [3] Therefore, for modern landfills, future leachate monitoring and treatment will probably need to focus more on inorganic contaminants such as salts and heavy metals and less on organic matter and nutrients.

Studies of landfills with a significant amount of MSW have shown that only a minute part (usually below one per cent) of the heavy metals present in the waste will be mobilised and leach out [8,9]. Theoretical and experimental studies have also suggested that even in very old, oxidised, MSW landfills the mobility of the heavy metals will remain low [6,10,11]. The speciation and mobility of heavy metals in landfills is affected by pH, redox potential, complexation with organic matter and complexation with inorganic ligands such as Cl [6,12,13]. The first three of these factors are connected to the degradable organic content of the landfill and can be expected to be different in landfills with low organic content. This leads to uncertainties regarding metal mobility in modern landfills and motivates studies on that topic.

The objective of this study is to increase the understanding of how a residual waste landfill with low organic content can be different from an MSW landfill in terms of heavy metal leaching. Is the mobility of the metals different? Can the leachate need different (more or less extensive) management with regard to the inorganic contaminants? To answer these questions leaching tests will be employed, and the results will also be used to evaluate some aspects of these methods.

The landfill chosen as the study object was the Fläskebo landfill, located outside of Gothenburg, in the southwest of Sweden. This landfill is highly interesting since it is one of very few Swedish landfills that have only received waste with low organic content complying with the new legislation. Samples were taken from within a landfill cell that mainly contained residues from sorting of C&DW. This residual waste was then subjected to leaching tests and biodegradation tests. The results have been compared to literature data on both C&DW and MSW leaching as well as to regular leachate monitoring data from the Fläskebo landfill.

Residues from sorting of C&DW can be considered typical of a waste management system changing from landfilling to separation, incineration or pre-treatment, with restrictions on landfilling of biologically degradable waste [14]. C&DW is a major waste stream in many countries [15] and constitutes a large part of the deposited waste in Sweden [3]. Therefore the residue from sorting of C&DW that had been landfilled in a modern landfill was considered relevant for this study. Studies of metal release from C&DW generally show a low metal mobility [14-17]. However the number of studies and the number of metals included is still limited.

If a waste is classified as non-hazardous, like the residual waste in this study, leaching tests are not mandated before landfilling in Sweden [5]. Furthermore, a landfill for inorganic waste does not

need gas collection or monitoring [4]. Neither the leaching behaviour nor the gas formation potential from the waste used in this study has been previously measured.

2 Materials and methods

2.1 Materials

The residual waste used for this study originated from the Fläskebo landfill, operated by Renova, a modern landfill that since its opening in 2003, has only received waste complying with the 10 % limit on TOC. The landfill was described by Modin et al. [18]. Initially the dominating waste type in this landfill was incombustible residues from sorting of C&DW but this changed with time. In 2004 C&DW sorting residues constituted 65 % of the landfill mass, while in 2008 it constituted only 22 %. The other waste types were mainly contaminated soils, stone and concrete and non-combustible industrial wastes.

The samples were taken in 2009, by the staff at the landfill, from a cell with a relatively homogeneous composition of mainly C&DW sorting residues. The biggest volume part of the waste samples consisted of insulation material and a fragmented material including plaster board residues. There were also fragments of wood, chipboard and similar organic materials. Pieces of inert material (concrete, stone and brick) bigger than approximately 10 mm were removed (20 weight %). The remaining material was manually cut into pieces < 10 mm, mixed and frozen in portions that were later thawed and used for total content analyses, batch and column leaching tests, and aerobic and anaerobic degradation tests.

2.2 Landfill leachate data

Regular leachate monitoring data from the Fläskebo landfill for the years 2003 to 2008 were supplied by the landfill operator for a previous study (see to Modin et al. [19] for a detailed description of the data). Data from 2004 - 2008 were used here since the first year was not considered representative.

For comparisons, literature data on leaching tests of C&DW (Table 1) and MSW and mechanically and biologically pre-treated (MBT) waste (Table 2) were compiled. Data was considered relevant if it originated from lab scale leaching studies using water as the leachant and included at least two of the metals investigated in this study.

2.3 Column leaching test

Continuous saturated up-flow column leaching was performed until a liquid to solid ratio (L/S) of 10 according to CEN/TS 14405 [20] with modifications regarding the column size, packing weight and pump speed as described below. The modifications were due to practical reasons such as the equipment available.

Two replicate acid washed PVC columns were used. The columns had a height of 50 cm and an inner diameter of 105 mm. 90 µm HDPE filters were installed at the bottom and top of the columns, which were sealed with silicone. PVC tubing and HDPE connections were employed.

The waste was packed in layers using a 600 g weight. To create an oxygen-free atmosphere the filled columns and the container with leaching fluid (deionized water) were flushed with nitrogen.

The pump speed was set to 1 $ml \cdot min^{-1}$, although, due to practical difficulties, the average pump speed during the experiment was 1.5 $ml \cdot min^{-1}$. This corresponds to a speed of 25 cm/day in the empty columns and a contact time of 48 hours in the waste filled columns.

The effluent from the columns as well as the fluid from the batch tests will be referred to as *eluate* to separate it from the *leachate* coming from a landfill. The column eluate was sampled at L/S 0.1, 0.2, 0.5, 1, 2, 5 and 10. The samples from L/S 0.2, 0.5, 1 and 2 were mixed into a flow proportional sample that will be called L/S 2. The samples from L/S 5 and 10 were mixed into a flow proportional sample called L/S 10.

After the leaching the waste from each column was mixed and samples were taken using coning and quartering and subjected to aerobic degradation tests.

2.4 Batch leaching test

Single step batch leaching was performed at an L/S ration of 10 according to DIN EN 12457-4:2003 with the modifications that, for practical reasons, particles < 10 mm were used rather than < 4 mm, and that instead of a head-over-end tumbler a shaking table (100 rpm) was used. Three replicate samples were leached in acid washed flasks.

2.5 Biodegradation tests

The aerobic biodegradability was studied using the German standard RA_4 [21]. The waste before leaching was tested in two runs of three replicates. The leached waste from each of the two columns was tested in two replicates.

Anaerobic degradation was studied in the waste before leaching, in two replicates. The test was not performed according to a standard, but instead a method was chosen that was more similar to real landfill conditions. 300 - 400 g of waste was put in 1.6 litre gas tight bottles and fully saturated with water. The headspace was flushed with nitrogen to remove air. The bottles were kept in a constant temperature of 20 °C and the pressure increase was registered during 150 days. Gas samples were analysed on several occasions using gas chromatography with a program that detects N_2, O_2, H_2, CO_2 and CH_4.

2.6 Analyses

pH, electrical conductivity (EC) and redox potential in the eluates were measured using handheld meters Buch & Holm WTW Multi 350i and 340i. All eluate samples were filtrated (0.45 µm) and stored at < 8 °C until further analysis by the laboratory of the Section of Plant Ecology and Systematics, Department of Ecology, Lund University. Ag, Al, As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Si, V and Zn were analysed using ICP MS (Elan 6000, PerkinElmer) or ICP AES (OPTIMA 3000 DV, PerkinElmer). F, Cl and SO_4-S were analysed using ion chromatography (861 Advanced Compact IC, column Metrosep A Supp 5, Metrohm). TOC and N were analysed using TOC-VCPH with N-module TNM-1 (Shimadzu).

For analysis of the solid samples two replicate samples from the waste before leaching were collected randomly and dried. For analysis of elements the samples were dissolved and analysed by ICP MS (Elan 6000, PerkinElmer) or ICP AES (OPTIMA 3000 DV, PerkinElmer) at the section of Plant Ecology and Systematics. TOC in the solid samples was analysed by a commercial lab according to the standard SS-EN 13137.

2.7 Statistics

To compare the eluate to the landfill leachate data a principal component analysis (PCA) was performed on the concentrations. PCA is a multivariate data analysis tool that offers a way to present data in a simplified way [19,22]. It transforms a data matrix in a way that concentrates as much as possible of the original variance into the first columns (principle components) of the new matrix. Ideally, the first few principal components can then be used to describe variations within the data set in a compact way.

Prior to performing the PCA, leachate parameters with missing data or a majority of data below the detection limit were discarded. Yearly average of leachate data were included as well as all six data sets from the columns (two replicates of L/S 0.1, 2 and 10 respectively) and all three batch eluate replicates. The data were normalised by taking the $\log_{10}$ and standardised by parameter-wise extraction of the mean and dividing by the standard deviation as recommended by Wold et al. [22]. Consequently all parameters had the mean zero and large nominal differences between the parameters were prevented from artificially affecting the variance of the data. After this data treatment the PCA was performed using Matlab® 7 (The MathWorks Inc., 2009) with its statistics toolbox.

All other statistical comparisons were performed using a t-test with a 95 % confidence interval.

3 Results and discussion

3.1 pH, conductivity and redox potential

Figure 1 shows the electrical conductivity, pH and redox potential in the effluent from the two columns and in the eluate from the batch tests. Differences between batch and column tests are small with regards to EC and pH. The redox potential is much higher in the batch, showing that the measures taken to create an oxygen free environment in the columns had effect.

3.2 Metal leaching

Leachate concentrations and total content in the solid samples are appended as supplemental material. In Figure 2 accumulated release and total content are presented for selected substances.

Although only three L/S ratios were studied, Figure 2 shows that the amounts released in the column experiment (filled circles) approach asymptotically to a value several orders of magnitude below the total content. Thus, only a small part of the heavy metal content in the residual waste is mobile. The Mn release was the highest among all the heavy metals, but still about two orders of magnitude below the total content.

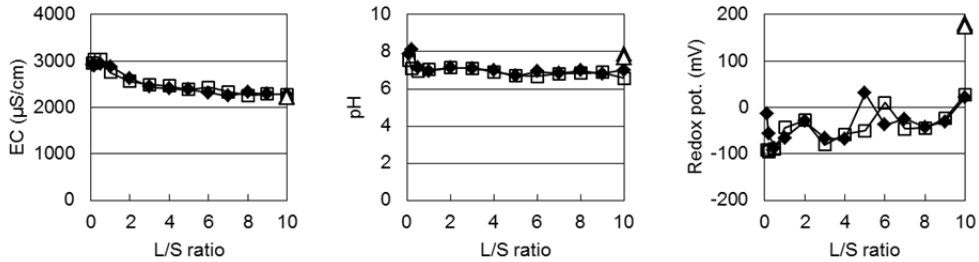

Figure 1. Electrical conductivity (EC), pH and redox potential as a function of liquid to solid ratio (L/S) in two leaching columns (squares and diamonds) and three batch tests (triangles) with residual waste

Figure 2 also compares the residual waste examined in this study to literature data on C&DW leaching in batch and column (Table 1). The release observed here follows the same pattern as from the other C&DW. Relative to the other studies a smaller release was observed here with the exceptions of SO_4, Ca, Fe, Ni and Zn, where the release was in the same order of magnitude, and Mn that was released to a higher extent. When comparing also the total contents, the mobility observed in this study is within the range of the other C&DW except for Mn that is more mobile here than in the study by van Praagh et al. [14].

Table 1. Leaching tests on C&D waste from the literature used for comparison

Reference	Material	Method	Contact time
Kalbe et al. [15]	C&DW <4 mm	Up-flow columns	14–18 h
Kalbe et al. [15]	Same as previous	Batch, head-over-end tumbler	24 h
López Meza et al. [16]	C&DW <2 mm	Columns, modified NEN 7343	110 h
López Meza et al. [23]	Demolition waste <4 mm	Columns, modified DIN 19528	16 h
van Praagh et al. [14]	C&DW <20 mm, composted with 50 vol.% compost and sludge	Columns, modified CEN/TS 14405	Not given
van Praagh et al., unpublished results (cited as van Praagh et al. [14] in Figure 2)	Same as previous	Batch, modified NT ENVIR 005 [24]	24 h
Galvín et al. [25]	Recycled C&DW aggregates	Two step batch, EN 12457-3	6±0.5 and 18±0.5 h

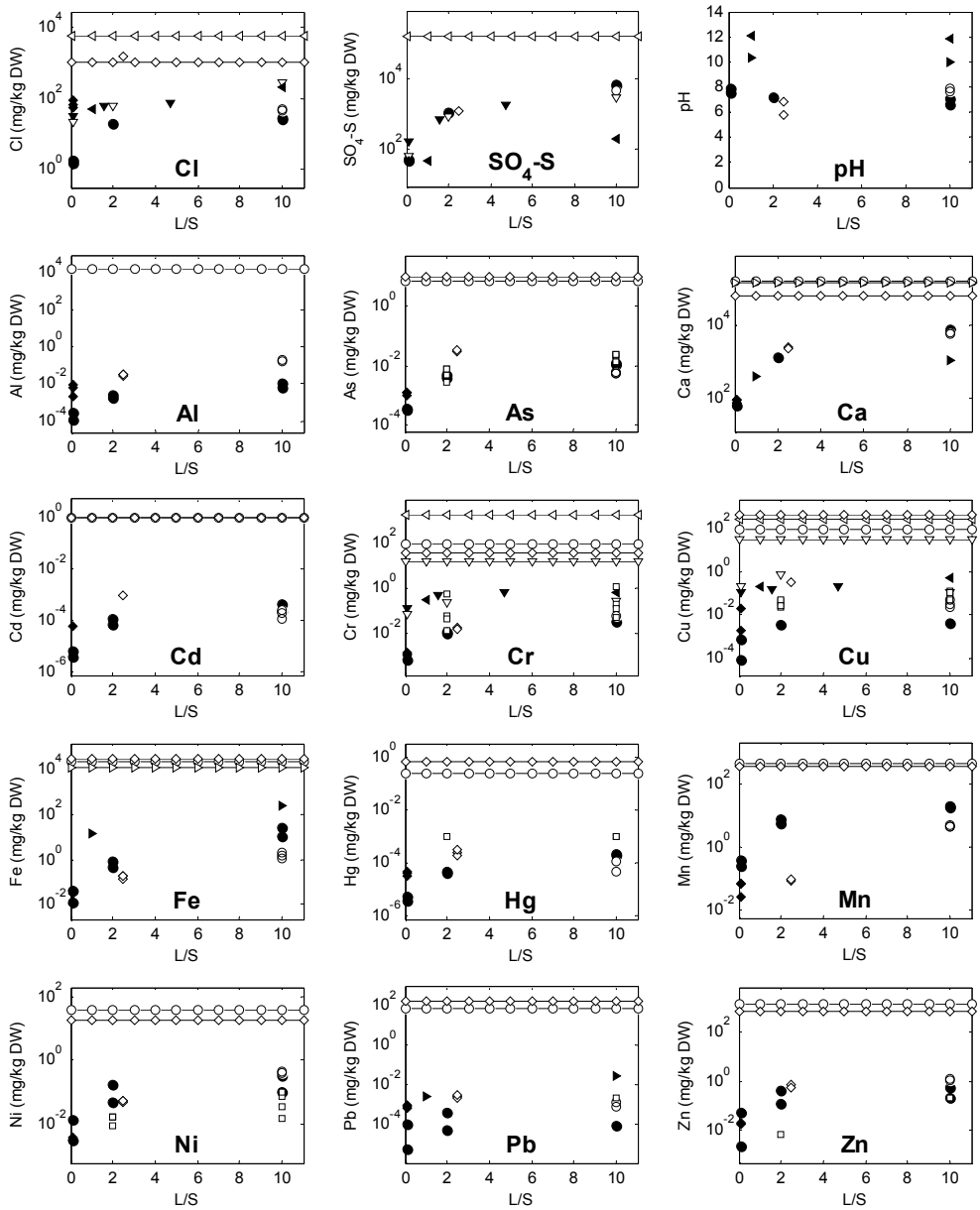

Figure 2. Accumulated metal release and pH as a function of liquid to solid ratio (L/S). Symbols connected with lines: total content. Filled symbols: continuous test. Open symbols: batch test. ●: This study, ▼: Kalbe et al. [15], ►: López Meza et al. [16], ◄: López Meza et al. [23], ♦: van Praagh et al. [14], ■: Galvín et al. [25]

The landfilling of C&DW residues at the Fläskebo landfill went on from 2003 to 2007 and the samples used in this study were taken in the beginning of 2009. Approximate water balance calculations have previously shown that the average L/S ratio of the landfill as a whole varied around L/S 1 during the first years when new waste was continuously added [26]. Thus, the material used in the leaching tests had already been leached to the certain extent within the landfill. In spite of this, it exhibits rather typical leaching curves (Figure 2). This indicates that the exchange between water and waste in the landfill has been of limited importance for the quality of the landfill material during the first six years of landfilling. Channelling or preferential flow is common in landfills [8] and thus one possible explanation is that large parts of the waste mass have not been in contact with flowing water.

Table 2. Comparison between metal leaching in the current study and in the literature. Data given in % of total metal content leached. n.r. = not reported

	This study	**Belevi and Baccini [27]**	**Esakku et al. [28]**	**van Praagh et al. [17]**	**Liu and Sang [29]**	**Zhang et al. [30]**
Material	Excavated, landfilled C&DW residues <10 mm	Excavated, landfilled MSW, pulverised. Release given in relation to fresh MSW	Fresh and excavated, landfilled MSW <150 µm	MSW before, during and after MBT, <10 mm	MSW, <20 mm	MSW
Method	Batch and column	Batch, in steps	Batch	Batch	Down flow column. Eluant pH 4.5, 6.5 and 8.8	Batch
L/S	10	40	4	10	15.84	10
Contact time	24 - 48 h	Total 288 h	168 h	24 h	Not given	24 h
As	0.08-0.2	n.r.	n.r.	n.r.	2.8–7.3	n.r.
Cd	0.01-0.05	0.06–0.22	2–5	0.5–6.9	0.25–0.5	4.4
Cr	0.03-0.07	n.r.	n.r.	0.03–0.2	1.1–1.4	4.5–8.1
Cu	0.0001-0.06	0.3–1.7	0.3–0.4	0.01–1.2	0.5–0.7	9.6
Fe	0.004-0.1	0.04–0.08	n.r.	n.r.	0.2–1.2	n.r.
Hg	0.02-0.1	n.r.	n.r.	n.r.	0.3–0.6	n.r.
Mn	1.0-4.8	n.r.	n.r.	n.r.	6.0–67	n.r.
Pb	0.0001-0.002	0.03–0.06	1.5–3.9	0.02–0.1	0.08–0.2	3.8
Zn	0.02-0.1	1.0–8	0.3–0.6	0.3–23	0.2–0.5	6.8

Compared to MSW and MBT waste, the metal mobility of the waste in this study was lower, or in the lower part of the wide range found in the literature (Table 2). Leachate concentrations of possible ligands such as organic matter and ions, e.g. chloride, can affect the metal leaching [6,12,13]. As these concentrations were low in the eluates (Figure 3) this might be one explanation to the low metal mobility observed. It could also due to the material itself. The forms in which the metals are present, e.g. water soluble, cation exchangeable or bound to carbonates, (hydr)oxides, organic matter or sulfides influence the mobility [9,28,30,31] but have not been investigated in the current study.

The design of the study, e.g. particle size, L/S ratio and contact time, can also affect the release of metals [7,14,15,32]. This is, however, not thought to be the main cause of the differences since this study is within the same range as the others with regard to these parameters (Table 2). However, the range of design parameters is wide; not one of the references found used the same method as another.

3.3 Degradation

The respiration in the waste material before the leaching tests was 0.8 mg O_2/g of dry waste. After leaching it had decreased significantly to 0.4 mg O_2/g dry waste. There was no statistically significant difference between the two columns and therefore these samples have been regarded as coming from the same population.

The accumulated anaerobic gas formation in the samples before the leaching test was on average 0.3 normal l/kg of dry waste. The degradation seemed to stop after approximately 130 days as no pressure increase could be detected after that. A steadily increasing CO_2 content in the gas was detected, but neither methane nor H_2 could be detected at any time. The fact that CO_2 was formed, but neither H_2 nor methane could be detected, suggest that there is a H_2 sink other than methanogenesis. One such could be sulfate reducing bacteria that are known to compete with methanogens [33]. Most likely due to the gypsum rich plaster board residues, the residual waste contained large amounts of sulfate (90 g/kg total S in the solids and 500 mg/l SO_4-S in the eluate) providing plenty of substrate for such bacteria.

The degradation potential in the residual waste is very low, e.g. far below the German limit values for landfilling of MBT waste; 5 mg O_2/g and 20 normal l/kg respectively [21]. However, since there is a potential for O_2 consumption, reducing conditions may well occur in the part of the landfill where this waste is located. This is supported by observations made at the landfill site during excavation. The visual appearance, e.g. dark coating on particles, that turned lighter when exposed to air, and the smell of the excavated material, suggested that microbial degradation was taking place. It has previously been observed that so called inorganic landfills may have sufficient degradation potential to create oxygen free conditions [34].

It has been feared that low carbon landfills will remain oxidized and that metals therefore will be more mobile than in methanogenic landfills where they tend to be immobilised [6,35]. This study indicates that this will not necessarily be the case since reducing conditions can occur also in low carbon landfills. Due to the low organic content, the degradable matter can, however, become

depleted more rapidly than in an MSW landfill. Therefore the long-term effect from degradation might be limited.

3.4 Implications for leachate management

Selected eluate concentrations are presented in Figure 3. For comparison, concentrations in typical Swedish municipal landfills containing a mixture of wastes including MSW, industrial waste and C&DW from Öman and Junestedt [36] are presented. From the Fläskebo landfill site, flow weighted average leachate concentration, average ambient surface water concentrations measured before the start of landfilling [37], and preliminary release guidelines, specific to this landfill [38], are presented.

Based on the eluate concentrations (Figure 3) a treatment plant designed for a leachate from the residual waste studied here does not need to focus on organic matter and nutrients. As the leaching tests also suggest that the heavy metal release will be considerably lower than from MSW (Table 2 and Figure 3), the leachate may become more easily treated also regarding metals. However, the concentrations of several metals in the actual landfill leachate are much higher compared to the lab scale eluates (Figure 3). As will be discussed in section 3.6 below, this is most likely due to other wastes in the landfill contributing significantly to the metal concentrations. Although, in some cases, the landfill leachate concentrations exceed the guideline, it should be noted that the untreated leachate is presented, and that these guidelines are applicable for the treated leachate that has considerably lower concentrations [38].

The temporary guidelines in Figure 3 are under evaluation for application to the treated leachate during the operation of the landfill. Eventually the active treatment will stop, and the untreated leachate will be released to the environment. If this leachate corresponds to the eluate at L/S 10, the concentrations of Ni and Cr could be problematic. The actual concentrations at L/S 10 are most likely lower since the eluate presented here is a mixture of all eluates above L/S 2. Since L/S 10 for this landfill has been estimated to be reached after 400 years [26], the treatment is likely to have stopped earlier which means that the concentrations presented here can be relevant.

Compared to the ambient surface water concentrations the concentrations at L/S 10 are elevated also for Cr and Cu (Figure 3). It is not certain that a landfill leachate has to reach ambient concentrations in order to be considered safe, but possibly some safety measures will be needed, and even at L/S 10 a certain emission potential remain in the leachate. Thus, this landfill can potentially impact the environment for a very long time.

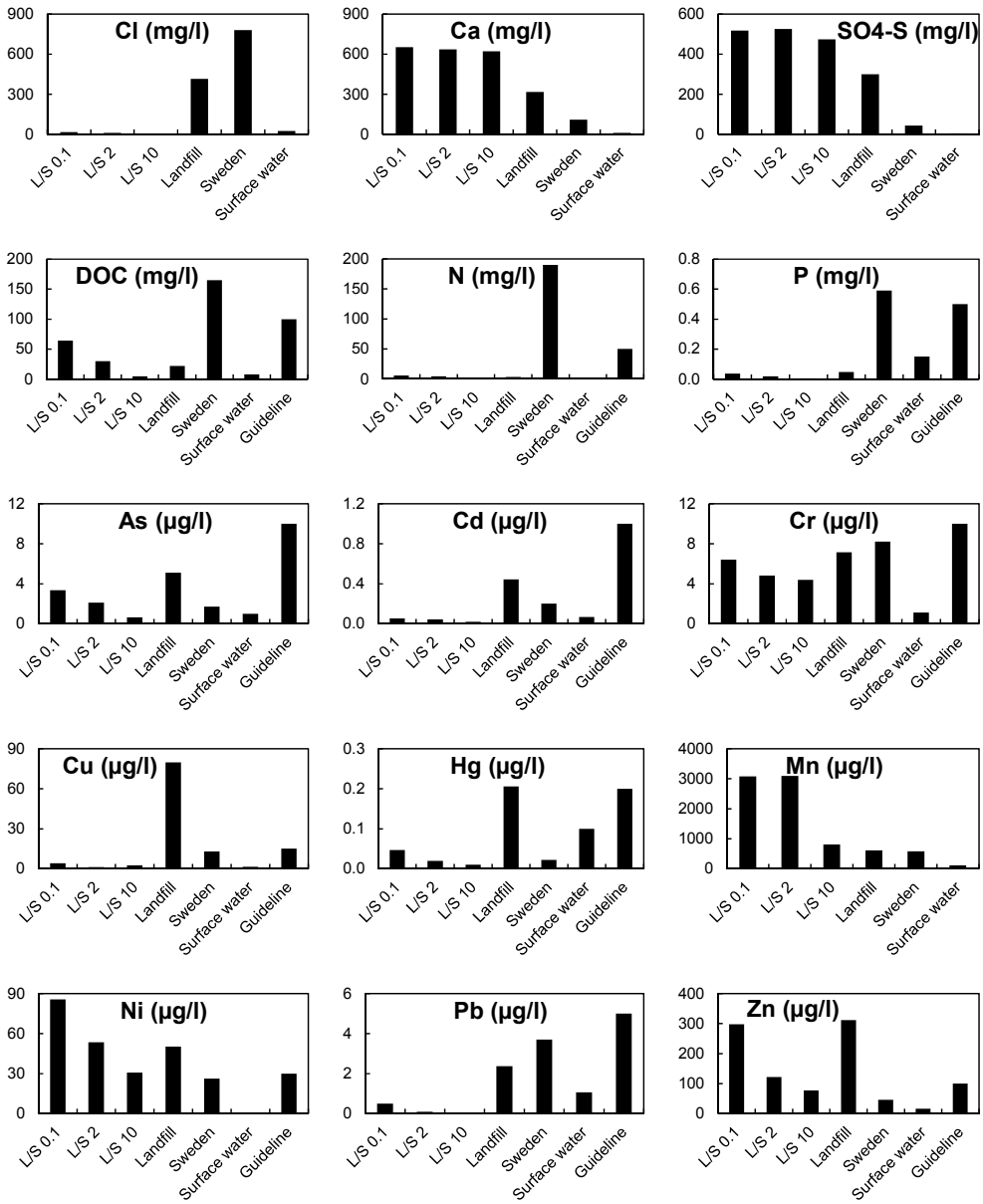

Figure 3. Eluate concentrations at liquid to solid ratio (L/S) 0.1, 2 and 10 compared to Swedish leachate concentrations [36], flow weighted average leachate concentrations for the Fläskebo landfill for the period 2004-2008, ambient surface water data at the landfill site prior to the start of landfilling [37], and preliminary release guidelines [38] (except for Cl, Ca, SO_4-S and Mn for which no guideline is set).

3.5 Predictability of landfill leachate composition using lab scale eluates

The results from the PCA of concentration data are shown in Figure 4 in the form of a score plot presenting the leachate samples, and a loading plot presenting the leachate parameters. Samples or parameters located close to each other co-vary. Parameters with high loadings on one axis (principle component) are related to samples with high scores on the corresponding axis.

The landfill leachate samples form a separate group in Figure 4 and are thus different from the eluates. According to the loading plot the landfill samples are associated with low concentrations of Ca, F, S and SO_4-S and high concentrations of the large group of substances located close to or above the x-axis to the left in the figure. Figure 3 confirms that the concentrations in Cl, Cd, Cu, Pb are higher in the landfill leachate compared to the eluates.

Higher concentrations in landfill leachate compared to lab scale eluates could be due to longer contact times which can lead to more efficient leaching [14,15]. In this study however, the substances assumed to derive mainly from the C&DW, SO_4 and Ca, had lower concentrations in the leachate, same as Mn, an element shown to be very mobile in the residual waste (Figure 2 and Figure 3). This suggests that the main reason for the differences was that the landfill does not only contain the residual waste studied here but also other wastes that seem to have a higher emission potential. Many of the parameters most closely related to the landfill leachate samples in Figure 4, e.g. high concentrations of Cl and Cu and high pH, are characteristic for MSW incineration bottom ash leachate [39], a material that has been used as a construction material in the landfill and that seems to have affected the landfill leachate.

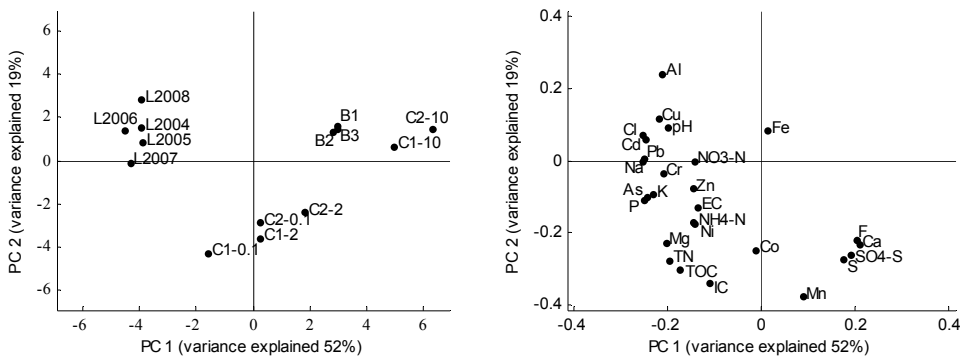

Figure 4. Score plot (left) and loading plot (right) from a principal component analysis of leachate concentrations (L) representing yearly averages, batch eluate concentrations (B) at liquid to solid ratio (L/S) 10 and column eluate concentrations (C) at L/S 0.1, 2 and 10.

3.6 Comparisons between batch and column tests

In Figure 4 there is a clear drift in the eluates from L/S 0.1 at the left to L/S 10 at the right, similarly to results found by van Praagh et al. [17]. Partly this difference is related to higher concentrations of most substances at L/S 0.1. The batch samples are not exactly in line with the column samples suggesting some other difference between the two setups than just dilution.

Although not included in the PCA, the redox potential will affect many other parameters and has previously been seen to affect the outcome of PCA [19]. Here, the redox potential (Figure 1) is much higher in the batch. In the columns it is slightly higher at L/S 10 compared to lower L/S. The redox active element Mn is strongly related to the samples from L/S 0.1 and 2 in Figure 4 as it has high concentrations in these samples, and low concentrations at L/S 10 in batch as well as column (not shown separately in Figure 3).

The batch test samples are located very close to each other in Figure 4, suggesting that repeatability is higher in batch than in column tests. This is surprising, since the sample volumes are much bigger in the columns, and contradicts previous findings [15,40]. The explanation could be the irregular flow rate experienced due to problems with the operation of the pumps, or possibly contamination, since the columns are much more difficult to acid wash compared to the flasks used for the batch tests.

Batch test are most often said to over-predict the release from column tests [31,40,41] although the opposite has also been observed [15]. In this study the release in the columns was higher than the release from the batch for approximately half of the elements presented in Figure 2 and vice versa for the other half. Possibly, the particles were too big for equilibrium to be formed in the relatively short batch test, but more likely the discrepancy is due to the much higher redox potential in the batch. Mn and Fe that form insoluble oxides both have a much higher release in the columns.

3.7 Further research

The results from this study have pointed to that the point of depletion of degradable material can be an important milestone also in residual waste landfills as the onset of oxidising conditions can affect metal mobility. The effect of degradation and subsequent oxidation on the long term leachate quality from landfills should be assessed in future studies.

Although the type of residual waste studied here is expected to be important in landfills in the future, it is only one of many types, and in future studies the scope should be widened to include other wastes. To account for a wider range of possible scenarios, the pH and redox potential should be varied in the tests. In long-term leaching studies, inhibition of degradation might be appropriate for this type of waste if the purpose is not to account for its effects. In order to better understand and predict the heavy metal leaching, sequential extraction might also be of use.

4 Conclusions

Heavy metal mobility, in terms of released amount relative to total amount, in the residual waste studied here, was low compared to MSW and MBT waste. Thus a leachate stemming from this waste only, would contribute with a smaller heavy metal load to the treatment or the environment.

The low availability of possible ligands such as organic matter and ions probably plays a role in the low mobility. The residual waste did contain small amounts of degradable organic matter that can

cause a reducing redox environment in the landfill, something that can make many metals less soluble.

In spite of having been subjected to leaching in the landfill for a few years prior to the experiment, the studied waste exhibited typical leaching curves for all studied heavy metals. Thus the exchange between water and waste in the landfill during the first years of landfilling seems to have been of limited importance for the leaching.

At L/S 10 some metal concentrations are still elevated compared to ambient surface water concentrations. A certain emission potential will remain in the residual waste landfill for a long time. Due to the slow leaching, the emission potential may even last longer than in MSW landfills. This should be taken into account when designing landfill closure systems.

The quality of the landfill leachate studied here could not have been predicted using the lab scale eluates of one residual waste. The most important reason for the differences between the two was that many different waste types have been landfilled in the actual landfill. This is the case for many landfills and thus mixing of leachates from different wastes appears to be among the big hurdles for using lab scale tests to predict landfill leachate quality. In addition, leachates in the field may also be mixed with other waters such as rain, surface and groundwater.

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Appended paper

V

H. Modin, L. Gustavsson and K. M. Persson. Toxicity in landfill leachate during treatment studied with multivariate data analysis. Journal of Environmental Management (submitted).

Toxicity in landfill leachate during treatment studied with multivariate data analysis

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Abstract

A reed bed system for treatment of landfill leachate was evaluated using physico-chemical and toxicity assays. The resulting leachate quality data were evaluated using the multivariate data analysis tool principal component analysis (PCA) to link the toxicities to physico-chemical leachate parameters, to assess if a limited amount of toxicity tests could replace a larger amount of physic-chemical leachate parameters, and to find an optimal test battery for this application. A very clear treatment effect was demonstrated using PCA. The PCA divided the toxicity assays into three groups that responded differently to the treatment. One included *Pseudokirchneriella subcapitata* and *Lemna minor*, the second included *Danio rerio* and *Vibrio fischeri,* and EROD was alone in the third group. Heavy metals most likely contributed to the toxicity to *P. subcapitata* and *L. minor*. The toxicity to *D. rerio* and *V. fischeri* seemed to have been caused by TOC, NH_4 and heavy metals, most notably Vanadium. A suitable battery of toxicity tests for evaluation of this treatment process would consist of *V. fischeri* and either *L. minor* and *P. subcapitata*. Toxicity and physico-chemical assays cannot replace each other; they complement each other and are both needed when characterising leachates.

Keywords: Chemical analysis, Toxicity; Landfill leachate treatment; Principal component analysis; Reed beds

1 Introduction

Landfill leachate contains many groups of pollutants and potential environmental impacts caused by leachate emissions include oxygen depletion and toxicity (Barlaz et al., 2002; Mackenzie et al., 2003; Marttinen et al., 2002; Pivato and Gaspari, 2006; Waara et al., 2008). In Sweden, Europe and other parts of the world, management and treatment of landfill leachate is a long-term commitment, even after closing of the landfill, and can last through decades (Jones et al., 2006;

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Noaksson et al., 2005; Osaki et al., 2006; SFS, 2001). The goal is to achieve a quality of the treated leachate that allows for it to be released into the environment.

Treatment of leachate locally, at the landfill site, is becoming increasingly common in Sweden (Avfall Sverige, 2009; Waara et al., 2008). Biological treatment systems such as aerated ponds, activated sludge and wetlands are the most common treatment options there (Avfall Sverige, 2007; Waara et al., 2008). Constructed wetlands and reed bed systems for water pollution control are becoming an accepted technology worldwide due to their low cost of energy and technology (Bialowiec and Randerson, 2010; Mackenzie et al., 2003; Senzia et al., 2003). The usefulness of reed beds for the treatment of landfill leachate has been demonstrated in several studies (Saeed and Sun, 2011; Waara et al., 2008; Van de Moortel et al., 2009; Wang et al., 2010; Wu et al., 2011).

Leachate quality data is crucial when evaluating new treatment processes. Chemical parameters such as concentrations of specific parameters are usually evaluated, but are not sufficient to estimate the potential toxic effect of the leachate (Pablos et al., 2011; Schiopu and Gavrilescu, 2010). In contrast to chemical parameters, toxicity bioassays integrate the biological effects of all compounds and degradation products present and reveal complex interaction phenomena such as bioavailability, synergism and antagonism (Marttinen et al., 2002; Pandard et al., 2006; Pivato and Gaspari, 2006). Numerous studies have employed bioassays to evaluate landfill leachate toxicity (Clément et al., 1997; Clément et al., 1996; Noaksson et al., 2005; Osaki et al., 2006; Pablos et al., 2011; Pivato and Gaspari, 2006; Svensson et al., 2005; Waara et al., 2008).

In order to correctly assess the environmental risks of leachates, and to effectively design their treatment, it is valuable to be able to relate the results from toxicity tests to specific chemical parameters. However, leachate data is characterised by many, partly co-varying, parameters and a high degree of noise, making it difficult to see the links between parameters using uni- or bivariate techniques. Therefore multivariate data analysis tools, such as principal component analysis, are useful to study leachate data. (Modin et al., submitted for publication; Pablos et al., 2011; Pandard et al., 2006; Waara et al., 2008) Principal component analysis (PCA) is a powerful tool to simplify large and complex data sets and obtain an overview of the relations among different parameters. With it, the highly complex leachate data can be described with only a few variables without excluding much of the information since it transforms the matrix in a way that concentrates as much as possible of the variance in only a few variables, called principal components (PCs). Furthermore, the PCs are orthogonal and thus PCA can handle co-linearity between leachate parameters. Previous studies have successfully used PCA to evaluate toxicological tests for studying waste leachates (Clément et al., 1996; Pablos et al., 2009; Pandard et al., 2006). Multivariate data analysis has also been shown useful to identify relationships between physico-chemical parameters and toxicity tests (Clément et al., 1997; Olivero-Verbel et al., 2008; Pablos et al., 2011; Ribé et al., 2012; Waara et al., 2008). Since PCA focuses on the co-variance between parameters rather than their nominal values, toxicants that affect the organisms even at low concentrations can potentially be identified.

The study described in this paper was initiated to study the relations between toxicity tests and chemical data in a landfill leachate data set originating from a pilot scale reed bed system treating

landfill leachate. The aim of the study was to use multivariate data analysis (MVDA) to evaluate the treatment results, to investigate if the toxicity responses could be linked to specific leachate parameters using PCA, and to assess if a limited amount of toxicity tests could replace a larger amount of physico-chemical leachate parameters. The results from PCA were also used to compare the different toxicity tests with the goal of finding an optimal test battery for this application.

2 Materials and Methods

2.1 Leachate samples

The leachate samples were taken from a pilot scale leachate treatment system using reed beds with combined vertical and horizontal flow and a surface area of 0.8 m^2 and 4.2 m^2, respectively. The beds were installed in series and had an average loading rate of 12 $l \cdot m^{-2}$ day^{-1} and a hydraulic retention time of 22 days. All beds were constructed in triplicates. The leachate to be treated originated from a leachate pond that collected effluents from a municipal landfill. Cells containing municipal solid waste (MSW) and bottom ash were drained into the pond as well as leachate from treatment processes, e.g. composting. The leachate and the treated outflow from the reed bed system were collected every second day, stored frozen and pooled into monthly samples representing June, July, September and November.

2.2 Chemical analyses

Analysis of total nitrogen (N_{tot}), total phosphorous (P_{tot}), ammonium nitrogen (NH_4-N), nitrate nitrogen (NO_3-N), nitrite nitrogen (NO_2-N), total organic carbon (TOC) and chloride (Cl^-) were performed using spectrophotometer (Hach-Lange, DR 3200). The results from September and November were also verified by analyses at Eurofins laboratory, Lidköping, Sweden. Metals were analysed by the division of Plant Ecology and Systematics, Lund University, Sweden, using ICP-MS and ICP-AES. Phenolic index was analysed at Alcontrol Laboratories, Linköping, Sweden.

2.3 Toxicity analyses

Toxicity tests were performed in collaboration with Mälardalen University in Västerås, Sweden and Aachen University, Germany. The following toxicity tests were performed: Inhibition of growth of the macrophyte *Lemna minor* (Swedish standard SS-EN ISO 20079:2006) and the green algae *Pseudokirchneriella subcapitata* (Swedish standard SS-EN ISO 8692:2005), genotoxicity using the Umu-C assay (International standard ISO 13829), inhibition of luminescence (30 min Microtox®) in the marine bacteria *Vibrio fischeri* (Microtox® ISO 11348-3 test), embryo development of the freshwater fish *Danio rerio* during 48 hours (German DIN 38415-6, 2005 with some minor modifications described by Braunbeck et al. (2005)) and, detection of dioxin like activity assessed by using the EROD assay (RTL W1 (Rainbow trout, *Oncorhynchus mykiss*) according to Lee et al. (1993) as described by Behrens et al. (2001), Brack et al. (2002) and Klee et al. (2004)).

2.4 PCA

In this study, physico-chemical data including salt and metal concentrations were analysed together with toxicity data in one joint principal component analysis. Toxicity was input as toxic units, TU (TU = $1/EC_{50}$). For EROD bio-TEQ values were used. A high TU or bio-TEQ value means a high toxicity. The Umu-C induction factor has to be 1.5 for the sample to be considered toxic, but in the study described here it never reached above 1.45. Thus all samples were considered not toxic according to the Umu-C assay and thus the variance for this parameter was zero and it was not meaningful to include it in the PCA.

The result "not toxic", including EC_{50} values above 1000 and samples where the leachate stimulated growth, was replaces with an EC_{50} of 1000 which corresponds to a toxic unit of 0.001. Missing data were replaced with the parameter mean. Toxicity tests yielding a reversed dose response (decreasing toxicity with increasing dose) were considered as missing data. A rule of thumb is that no more than 10 % missing data should be allowed in any parameter when performing a PCA (Lau and Sheu, 1988). However parameters with one missing datum (P_{tot}, pH and *P. subcapitata*) were included in spite of having 12.5 % missing data. The data set used in the PCA contained eight samples (untreated and treated leachate from four months) and 31 leachate parameters (see Figure 2).

Prior to the analysis the data were normalised by taking the $\log_{10}$ to minimise the influence from extreme values, centred by extracting the mean, and scaled to unit variance by dividing by the standard deviation as recommended by Wold et al. (1987). This means that all parameters vary around zero and the analysis will not be affected by the parameters having large nominal differences, different units etc. The PCA was performed using Matlab® 7 (The MathWorks Inc., 2011) with its statistics toolbox.

3 Results and discussion

The PCA resulted in a new set of parameters (PCs) where the first one, PC1, represents 37 % of the original variance and the second, PC2, represents 23 %. With only two principal components 60 % of the variance in the data can be captured. The results are graphically presented using a score plot (Figure 1) and a loading plot (Figure 2). The score plot represents all samples in the plane of the first two PC's while the loading plot represents all original leachate parameters. Co-varying samples or parameters are located close to each other. If they are located on opposite sides of the plot, they have a negative co-variance, i.e. high values of one are connected to low values of the other.

The fact that the samples from the ingoing and outgoing leachates are clearly separated in Figure 1 shows that the main process described by PC1 is the difference between treated and untreated leachate; the treatment has made a difference. Figure 2 shows which parameters are changed by the treatment. High concentrations of the parameters to the right are more strongly related to the untreated leachate while high concentrations of the parameters to the left are more strongly related to the treated leachate. For example TOC and NH_4 are to the right and NO_3 and NO_2 are to the left. Removing organic matter and oxidising NH_4 are two of the main purposes with a

treatment system like the one under study. We can also see that Cl, that is generally considered conservative, is not affected by the treatment.

From Figure 2 we can also see that the bioassays *D. rerio* (DR), *V. fischeri* (VF), *L. minor* (LM) and *P. subcapitata* (PS) are all located to the right indicating that high toxicities are related to the ingoing leachate. The results presented in Table 1 confirm that the toxicity to these organisms decreased with the treatment, and the PCA was able to capture this decrease correctly. The EROD toxicity was affected differently and increased with the treatment in some cases (Table 1). This is consistent with the deviating behaviour that EROD shows in Figure 2.

The five toxicity tests are separated into three different clusters. *D. rerio* and *V. fischeri* form one cluster together with NH_4, N_{tot} and V. *L. minor* and *P. subcapitata* are located in a large cluster containing TOC, P_{tot} and a group of metals. EROD is located close to a cluster with a group of metals, NO_2 and possibly phenol index.

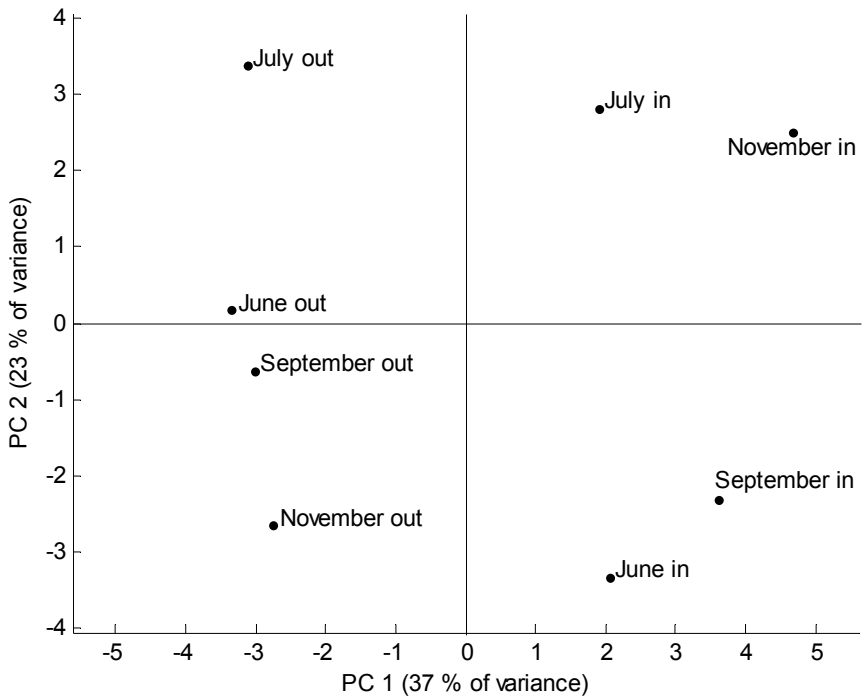

Figure 1. Score plot showing the relationship between landfill leachate samples before (in) and after (out) treatment in reed beds.

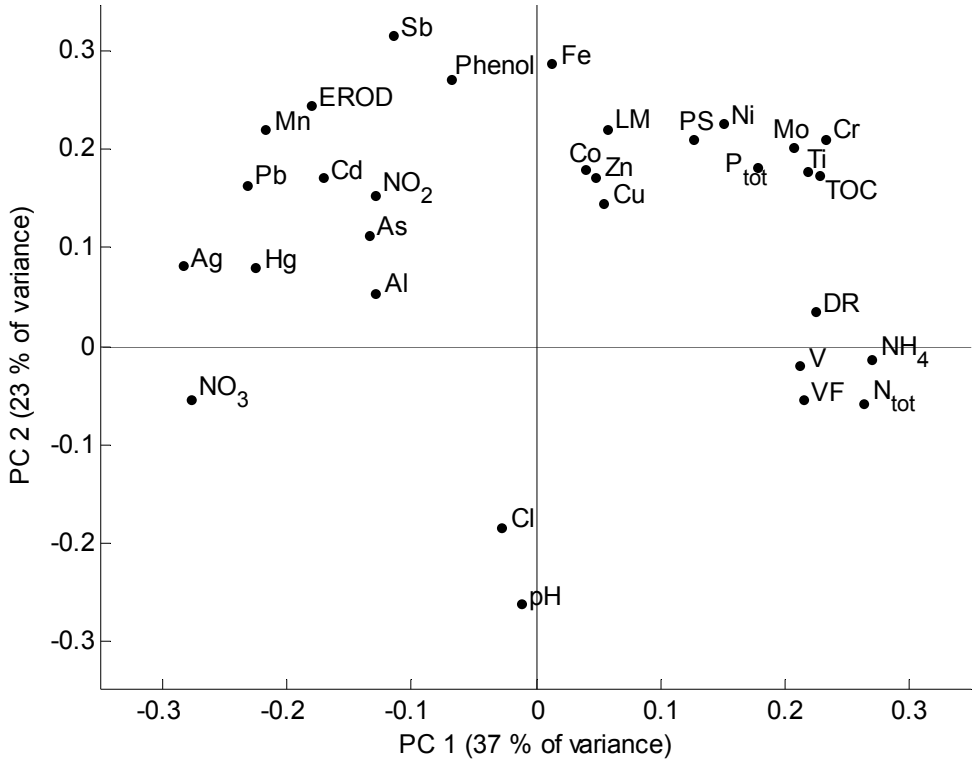

Figure 2. Loading plot showing the relationship between landfill leachate parameters

3.1 L. minor and P. subcapitata

Finding *L. minor* and *P. subcapitata* in the same cluster in the loading plot from the PCA (Figure 2) might be expected as they belong to the same phyla and naturally have many common traits. However, their similar behaviour cannot be taken for granted since the sensitivity among species, and even between individuals within a species, can vary significantly (Bialowiec and Randerson, 2010), and Clement et al. (1996) found *L. Minor* and the microalgae *Scenedesmus subcapitatus* to be related to different PCs.

L. minor and *P. subcapitata* co-vary with TOC, P_{tot} and several heavy metals (Co, Cr, Cu, Mo, Ni, Ti and Zn) since they are located in the same cluster. Since they are all to the right in the loading plot they are affected similarly by the treatment, something that suggests that these physico-chemical parameters are affecting the toxicity to these species. Toxic effect of algae can be caused by metals interfering with the energy enzymes. A study by Jurkonienė et al. (2004) found Co, Cr and Cu to inhibit ATPase from the macrophytic algae *Nitellopsis obtuse*, although the EC_{50} values found by those authors are higher than any concentrations found in the study described here.

Table 1. Toxicity detected through bioassays of landfill leachate going in to (IN) or out from (OUT) a reed bed treatment system. TU = toxic unit, $1/EC_{50}$

	June		July		September		November	
Bioassay	IN	OUT	IN	OUT	IN	OUT	IN	OUT
V. fischeri (TU)	0.014	0.001	0.02	0.001	0.125	0.001	0.012	0.001
L. minor (TU)	0.024	0.022	1.43	0.029	0.001	stim[1]	0.009	stim[1]
P. subcapitata (TU)	0.001	0.001	0.029	n.a[2]	0.001	stim[1]	0.063	0.0125
D. rerio (TU)	0.001	0.001	0.001	0.001	0.0065	0.001	0.011	0.001
EROD (bio-TEQ, $pg \cdot ml^{-1}$)	4.18	8.82	15.74	32.68	5.52	16.02	6.22	9.44

[1]Stimulation of growth rather than inhibition
[2]Toxicity could not be detected

Waara et al. (2008) suggest that ammonium could partly explain the toxic of *P. subcapitata* and *L. minor* in a study of landfill leachate treated in a wetland. Clément and Merlin (1995) pointed out that un-ionised ammonia (pKa=9.24) is the most toxic form of ammonia and this compound appears to be the major toxicant for most MSW landfill leachates. In the leachate described here the dominating form was however ammonium ions since the pH was between 7.4 and 8.7. In the study described here, the PCA shows a very week relation between *L. minor*, *P. subcapitata* and ammonium. There are plenty of parameters that seem to contribute more to these toxicities.

According to Waara et al. (2008) *P. subcapitata* could be affected by salts. Higher plants can also be sensitive to high concentrations of chlorides (Dimitriou et al., 2006; Kalčíková et al., 2011) and Bialowiec and Randerson (2010) saw a negative relationship between plant growth and electrical conductivity. In this study, however, the conductivity could not be included in the PCA and Cl very clearly had no relation to the variation in toxicity to *P. subcapitata* or *L. minor*.

According to Cheng and Chu (2007) toxicity to higher plants could be due to an imbalance between metal ions needed by the cells since cell membrane structure can be disrupted if there is a depletion of Ca when Na is present. In the study described here, neither Ca nor Na was analysed.

When weighing all these facts together heavy metals seem to be the most probable cause for the toxicity to *L. minor* and *P. subcapitata*.

3.2 D. rerio and V. fischeri

The loading plot from the PCA (Figure 2) places the toxicities to *D. Rerio* (DR) and *V. Fischeri* (VF) in the same cluster to the right in the figure. The *D. rerio* assay only had toxic response in two cases which limits the interpretability using PCA.

N_{tot}, NH_4 and vanadium (V) can be found in the same cluster as *D. rerio* and *V. fischeri*. Therefore NH_4 and V are the main suspects for the toxicities to those organisms. However, several parameters in the cluster in the first quadrant, e.g. TOC, Ti, Mo and Cr, have similar loadings on PC1 and could therefore also have contributed.

V. Fischeri is relatively insensitive to ammonium at the concentrations in the leachate described here (Calza et al., 2008; Lalonde et al., 2009; Łukawska-Matuszewska et al., 2009; Thomas et al., 2009; Waara et al., 2003) although toxic effects are observed with high ammonium strength waters (Žgajnar Gotvajn et al., 2009; Öman et al., 2000). Pivato and Gaspari (2006) found ammonium and COD to contribute to toxicity to *V. fischeri*.

TOC has almost exactly the same loading on PC1 as both *D. rerio* and *V. fischeri* and since organic matter has previously been found to cause toxicity to *V. fischeri* (Clément et al., 1997; Pivato and Gaspari, 2006; Waara et al., 2003) it is likely that it has contributed in this study also.

Vanadin has previously shown toxicity to both *D. rerio* (Beusen and Neven, 1987) and *V. fischeri* (Amezcua-Allieri and Salazar-Coria, 2008). The LC_{50} values of V to *D. rerio* found by Beusen and Neven are however about three orders of magnitude higher than the concentrations in this study. Several other metals (Cr, Mo, Ti and possibly Ni) have similar loadings on PC1 although they do not co-vary as strongly as V with *D. rerio* and *V. fischeri*. Many metals have been found to contribute to toxicity to these organisms. Pivato and Gaspari (2006) found *V. fischeri* to be affected by Hg, Co, Fe, Cu, Zn and Mn and Cook et al. (Cook et al., 2000) found it to be sensitive to Cr. Toxic effects from especially Cu, Co and Hg have been found to cause toxicity to fish embryos and Cu, Pb and Ni (Dave and Xiu, 1991) and Cd (Cheng et al., 2000) to affect hatched larvae.

The parameters that were found to most likely contribute to the toxicity to *V. fischeri* and *D. rerio* were TOC, NH_4 and several heavy metals, especially V.

3.3 EROD

In this study, the EROD bio-TEQ levels were higher after the reed bed treatment than before in several months. Treatment using plant systems is known to increase the EROD activity. A previous study demonstrated that the difference in bio-TEQ level between bed material from planted and unplanted reed beds were 8.9 and 6.7 $pg \cdot g^{-1}$ dry weight, respectively (Gustavsson et al., 2006). The observed induction could be due to contribution of AhR agonists from the reed plants. For instance, production from conversion of tryptophan, e.g. indole acetic acid, showed higher AhR binding affinity than the parent compound (Chen et al., 1996; Naur et al., 2003). Additionally, several phytochemicals including caffeic acid, chlorogenic acid, diosmin, ferulic acid and resveratrol caused both inhibition and induction of EROD (Teel and Huynh, 1998).

In the loading plot in Figure 2 EROD is located relatively close to several parameters such as a group of heavy metals and phenol. The EROD assay cover a broad goup of compounds besides dioxines and PCB:s (Gustavsson et al., 2006; Gustavsson et al., 2004; Klee et al., 2004). However, such compounds were not included in the study described here and therefore it is not relevant to look for co-variances in the PCA loading plot.

3.4 Finding a battery of tests to evaluate the treatment

As can be seen from Table 1 the relative sensitivity of the organisms varied between months, similar to what have been observed by Manusdzianas et al. (2003). *L. minor* was the most sensitive

organism to the waters samples in June and July. However in September and December it was the least sensitive. *P. subcapitata* was relatively insensitive except in the sample from November. The Microtox assay with *V. fischeri* seems to have given the most reproducible results. *D. rerio* embryos were clearly the least sensitive which is accordance with previous studies (Plotkin and Ram, 1984; Silva et al., 2004). EROD was not included in these comparisons.

In order to capture as much of the variation as possible with a limited battery of toxicity tests one test from each cluster observed in the loading plot (Figure 2) should be selected, *L. minor* or *P. subcapitata*, *D. rerio* or *V. fischeri* and EROD. However, since EROD can respond to natural compounds released from plants that assay is not considered suitable to evaluate leachate treatment using reed beds. *V. fischeri* should be chosen above *D. rerio* since it shows the most reproducible results and *D. rerio* is the least sensitive test and also relatively laborious. *L. minor* and *P. subcapitata* showed similar performance and therefore the choice between them could be made based on practicalities.

3.5 PCA as a tool to study leachate toxicity

PCA was highly useful in this study thanks to its ability to group the toxicity tests and identify tests that describe similar information. This was instrumental in the selection of a suitable test battery. Other authors have used PCA in similar ways (Clément et al., 1996; Pablos et al., 2009; Pandard et al., 2006).

PCA could also identify leachate parameters possibly contributing to the toxicities. Since there are many co-varying parameters in each case it is not possible to identify exactly which parameter is responsible for which toxicity, as observed also by other authors (Clément et al., 1997). Some authors (Matejczyk et al., 2011; Olivero-Verbel et al., 2008) have suggested the use of linear regression as a technique to find more specific correlations between toxicities and other parameters. However, in a complex matrix such as landfill leachate, it is not likely that the toxicity is caused by one parameter alone, and multivariate techniques should be more suitable. Further, the main problem with identifying the parameters causing toxicity is of another nature: Only because a statistical relationship is found between two (or more) parameters that does not mean that one is the cause of the other(s). The relation might be due to other, unknown, processes or simply to chance. Related to this is the fact that there are most likely many other potentially toxic substances in the leachate than those that were analysed. The data set will never describe the complete leachate chemistry and thus we cannot be sure that all important factors are captured by the PCA. These facts clearly show that toxicity measurements cannot replace physico-chemical measurements. Likewise, physico-chemical measurements cannot replace toxicity assays.

Several of the tests measure the toxicity as growth inhibition. Other than direct toxicity this can be caused by lack of, or imbalance in, nutrients. When elucidating the cause of a toxic response it would therefore be interesting to include nutrients (e.g. K, Ca, and Mg) in the analysis. Including this data in the PCA would contribute to a fuller understanding of the causes of the growth inhibition. Alkalinity has previously been suspected to increase ammonia toxicity (Clément et al., 1997; Clément and Merlin, 1995) and including that parameter in the analysis program could

also improve correlations. Since salinity can both stimulate and inhibit growth, a salinity measurement, e.g. electrical conductivity, should also be included.

4 Conclusions

When applying PCA to a data set from treatment of landfill leachate using reed beds a very clear treatment effect was demonstrated.

The PCA divided the toxicity assays into three groups that responded differently to the treatment. One included *P. subcapitata* and *L. minor*, one included *D. rerio* and *V. fischeri,* and EROD was alone in one group.

Heavy metals most likely contributed to the toxicity to *P. subcapitata* and *L. minor*. The toxicity to *D. rerio* and *V. fischeri* seems to have been caused by TOC, NH_4 and heavy metals, most notably V. It was not possible in this study to identify what caused the EROD toxicity.

A suitable battery of toxicity tests for evaluation of this treatment process would consist of *V. fischeri* and either *L. minor* and *P. subcapitata*.

The biggest benefit from using PCA was the possibility to identify toxicity tests that reacted in similar ways to the treatment evaluated in the study described here, information that was used when selecting the test battery.

Toxicity and physico-chemical assays cannot replace each other. They complement each other and are both needed when characterising leachates.

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Appended paper

VI

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Removal of metals from landfill leachate by sorption to activated carbon, bone meal and iron fines

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ABSTRACT

Sorption filters based on granular activated carbon, bone meal and iron fines were tested for their efficiency of removing metals from landfill leachate. Removal of Al, As, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Mo, Ni, Pb, Sr and Zn were studied in a laboratory scale setup. Activated carbon removed more than 90% of Co, Cr, Cu, Fe, Mn and Ni. Ca, Pb, Sr and Zn were removed but less efficiently. Bone meal removed over 80% of Cr, Fe, Hg, Mn and Sr and 20–80% of Al, Ca, Cu, Mo, Ni, Pb and Zn. Iron fines removed most metals (As, Ca, Co, Cr, Cu, Fe, Mg, Mn, Pb, Sr and Zn) to some extent but less efficiently. All materials released unwanted substances (metals, TOC or nutrients), highlighting the need to study the uptake and release of a large number of compounds, not only the target metals. To remove a wide range of metals using these materials two or more filter materials may need to be combined. Sorption mechanisms for all materials include ion exchange, sorption and precipitation. For iron fines oxidation of Fe(0) seems to be important for metal immobilisation.

1. Introduction

Landfill is still the most common waste disposal option in the European Union [1], in spite of efforts to find alternatives. Landfills affect the environment, for example via leachate, which is water that becomes contaminated due to passing through waste. Its main groups of pollutants are dissolved organic matter, inorganic macro components (including nutrients), heavy metals and xenobiotic organic compounds [2].

Various forms of biological treatment, at the landfill site or in a municipal waste water treatment plant, are the most common methods for dealing with leachates in Sweden. Although biological processes are efficient for organic matter and nutrients, heavy metals are not their main targets [3]. The implementation of new European legislation has dramatically decreased the landfilling of organic waste in Sweden. This is expected to reduce the amount of organic matter and nutrients in the leachate and thus increase the relative importance of heavy metals [4,5]. Therefore, there is a growing interest in finding cost-effective methods to remove heavy metals from landfill leachate.

Sorption filtration has been proposed as a promising technique for removing metals from contaminated waters, since it has shown potential to achieve good removal at relatively low cost and with low energy demands [6,7]. Sorption is here defined as a collective term for adsorption to the surface and absorption into the structure of a material. Strictly speaking, precipitation is not sorption. It is, however, often difficult to distinguish between sorption and precipitation and therefore, in this paper, precipitation is included in the term "sorption".

The aim of this study was to evaluate the usefulness of sorption filters as a means of removing metals from landfill leachate. Although there is a great deal of research demonstrating that metals can be removed from solution by means of sorption, most of these studies concern idealised conditions and solutions containing only one or a few metals [6–14]. Leachate however is a complex mixture where the interactions between the different pollutants will affect their sorption behaviour. Therefore, there is a need to study sorption of a large number of metals under more realistic conditions using real landfill leachate. For this reason this study was designed to mimic real conditions as closely as possible while restricting the size of the experimental setup to lab scale.

To identify suitable filter materials a literature review and a batch screening test using real landfill leachates [15] were performed. Granular activated carbon (GAC), bone meal (BM) and iron fines (IF) were selected based on their availability, prize and ability to remove metals.

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The efficiency of activated carbon for the removal of organic matter from landfill leachate has been demonstrated by a large number of studies [16]. Metal removal from solution has also been thoroughly demonstrated [8,13,14,17]. However, relatively few studies have described heavy metal removal from real landfill leachate using activated carbon. Removal of Cr, Fe, Ni and Pb from real landfill leachate using only activated carbon has been demonstrated [18–20] and Kocasoy [21] achieved the removal of Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, and Zn with coagulation and flocculation followed by activated carbon filtration. The present study attempts to demonstrate the removal of a large number of metals using GAC. Although GAC can originate from various sources, including many by-products and types of waste [7,8,16,22], it is a relatively expensive material.

BM is a by-product from the meat industry. It is currently difficult to find a use for the whole production, which makes it relatively cheap [9]. The usefulness of bone material for removing metals from solution has been demonstrated in several studies [9–11,23,24]. However, no published studies using landfill leachate were found.

Iron fines are by-product from many industries. Its cost depends on the price of scrap metal but it is relatively inexpensive. Zero-valent iron and iron oxide containing materials have been thoroughly demonstrated to remove arsenic from contaminated waters [25,26]. Heavy metals can also be removed [6,12,27–29]. Dong et al. [30] evaluated metal removal from landfill leachate with promising results motivating further study.

2. Experimental

2.1. Filter materials

The activated carbon used in this study was a commercially available, peat derived, steam activated granular activated carbon (GAC) with a particle size of 0.25–1 mm. According to the supplier (Brenntag Nordic AB, Malmö, Sweden), it is suitable for various uses including improvement of drinking water quality.

A commercially available bone meal (BM) from Ellco Food AB (Klippan, Sweden) was used. This product is derived from cow and pig bones and contains 73% ash, 19% protein, 7% fat and 2% moisture. The product is sterilised and the particle size specified as less than 2 mm with most particles being a very fine powder.

Iron fines (IF) were collected from two cutting tools at a local metal workshop. Due to the mode of operation at the workshop, the fines were mixed with cutting fluids consisting of organic oils (CAS numbers 8002-13-9, 112-80-1, 2717-15-9, 143-19-1 and 34590-94-0). Most of the particles in this material could pass through a 2 mm sieve but there was considerable variation.

To ensure acceptable flow properties, BM and IF were mixed with filter sand (Rådasand AB, Göteborg, Sweden) with a particle size of 0.8–1.2 mm (60 vol% and 50 vol%, respectively). GAC, IF and filter sand were rinsed 4 times in deionised water and oven-dried at 105 °C. BM was not rinsed since that was not practical due to its fine, powdery particles.

2.2. Landfill leachate

Leachate was collected from a landfill cell containing 7–14 years old mixed industrial and municipal solid waste. The cell is in the methanogenic phase. Methanogenic leachate is characterised by near-neutral pH and strongly reducing conditions [2]. This leachate's composition is stable over time and some metal concentrations (especially Ni and Cr) are high enough to be considered a problem. Therefore it was chosen for the study.

One batch of leachate (1 m^3) was collected and employed throughout the study. The leachate was stored in an insulated container in a sheltered outdoor area. Outdoor temperatures remained below 10 °C throughout the study. Smaller portions of leachate needed for the experiment were stored at ambient room temperature for a maximum of three days. The composition of the leachate was analysed initially, and on three additional occasions during the experiment.

2.3. Filtration study

Ten acid washed PVC columns with a height of approximately 50 cm and an inner diameter of 10.5 cm were used. 90 μm HDPE filters were installed at the bottom and top of the columns, which were sealed with silicone. PVC tubing and HDPE connections were employed. The filter materials were filled into the columns and compacted using a 500 g weight. Three replicate columns were used for each filter material and one control was filled with filter sand.

The leachate was pumped through the columns in an up flow mode to avoid channelling. The flow rate was initially set to 1 m/day in the GAC and sand columns and to 0.2 m/day in the BM and IF columns. The smaller flow rate was chosen for materials expected to have lower hydraulic conductivity. After 18 days the flow rate was increased to approximately 4.4 and 1.2 m/day, respectively.

The experiments continued for 29 days. The pH was measured most working days in the effluent from each column. Leachate for further analysis was collected and mixed to approximately flow proportional samples representing days 1–10, days 11–20 and days 21–29, respectively. Samples from the untreated leachate were taken on days 2, 10, 20 and 29.

2.4. Analyses

All analyses were performed on unfiltered samples, as when landfill leachate is analysed for compliance control, since the aim of the study was to imitate real conditions. The pH was analysed with a handheld pH meter (Buch & Holm WTW Multi 340i). All other analyses were performed by the Plant Ecology and Systematics section of the Department of Ecology at Lund University. Element analyses were conducted using ICP MS (Elan 6000, PerkinElmer) or ICP AES (OPTIMA 3000 DV, PerkinElmer) depending on the concentration. Total organic carbon (TOC) and total nitrogen (TN) were analysed using a TOC analyser (TOV-VCPH with N-module TNM-1, Shimazdu) and Cl by means of ion chromatography (861 Advanced Compact IC, column Metrosep A Supp 5, Metrohm, Herisau, Switzerland).

3. Results

3.1. Influent leachate composition

The results from the analyses of the untreated leachate are presented in Table 1 which also includes the median values in samples taken from this leachate on site during the two years preceding the study and median values from 12 Swedish leachates from Öman and Junestedt [31]. The leachate used in this study is very similar to the median leachate on site. Also, most metal concentrations are in the same order of magnitude as those found in other Swedish leachates. Most metal concentrations remained constant throughout the study, the important exceptions being Cu and Hg. Chloride concentrations are high in this leachate.

3.2. Metal removal and leaching

The removal efficiencies in the columns are presented in Table 2 as effluent concentration/influent concentration (C/C_0). Effluent samples from each column were mixed using aliquots from several days during a time period. The sample from each column was

Table 1
Concentrations in mg/l in one batch of landfill leachate used for sorption experiments measured at four occasions, results from samples collected on site (median values from the two years preceding the collection of leachate for the experiment), and median values from 12 Swedish landfills presented by Öman and Junestedt [31]. –, not reported.

Sample	Day 2	Day 10	Day 20	Day 29	On site	Sweden
pH	7.5	7.1	7.1	7.4	7.2	7.6
BOD_7	–	–	–	–	33	12
COD	–	–	–	–	700	560
TOC	240	240	240	230	250	150
Alkalinity[a]	670	660	630	650	–	300
Cl	2200	2600	2600	2200	2400	780
N	350	380	370	360	390	190
P	2.6	1.3	0.48	2.3	1.6	0.59
Al	0.049	0.077	0.078	0.10	–	0.10
As	0.022	0.027	0.025	0.020	0.0080	0.0017
Ca	200	210	200	200	–	0.11
Cd	0.000027	0.000012	0.000016	0.000019	<0.0001	0.00020
Co	0.012	0.013	0.013	0.010	0.011	0.0066
Cr	0.039	0.037	0.037	0.041	0.054	0.0082
Cu	0.034	0.0079	0.0025	0.027	0.0098	0.013
Fe	2.3	1.2	1.5	3.3	3.1	2.9
Hg	0.00019	<0.00001	<0.00001	0.00072	<0.0001	0.000022
Mg	110	100	100	100	–	39
Mn	0.26	0.27	0.27	0.27	0.41	0.58
Mo	0.0023	0.0032	0.0023	0.0020	–	0.22
Ni	0.061	0.072	0.073	0.059	0.057	0.026
Pb	0.00082	0.00024	0.00025	0.0015	0.0021	0.0037
Sr	5.3	5.3	5.3	5.3	–	1.0
Zn	0.084	0.054	0.020	0.045	0.061	0.046

[a] Carbonate alkalinity given as mg C/l. Data for Sweden [31] calculated from bicarbonate concentrations.

Table 2
Removal efficiencies by filtration in columns filled with granular activated carbon (GAC), bone meal (BM) and iron fines (IF). Numbers represent effluent concentration/influent concentration (C/C_0). Averages for three columns are presented with the exception of the final BM sample where data were only available for two columns. Statistically significant differences ($p < 0.1$) between C and C_0 are underlined. n.d., not detected in the influent.

Material Day	GAC 1–10	GAC 11–20	GAC 21–29	BM 1–10	BM 11–20	BM 21–29	IF 1–10	IF 11–20	IF 21–29
TOC	0.032	0.011	0.054	78	19	13	2.6	1.4	1.1
Cl	0.98	0.96	0.96	1.1	0.85	1.0	0.93	0.89	0.96
Alkalinity	0.96	0.99	0.98	0.59	1.1	0.82	0.35	0.60	0.81
N	0.89	0.91	1.1	17	5.2	3.9	0.81	0.85	1.0
P	0.31	0.28	0.27	8.1	16	5.5	0.16	0.21	0.10
Al	1.0	0.73	0.72	1.0	0.27	0.66	4.4	0.33	0.70
As	2.1	1.2	1.4	0.99	1.3	1.3	0.80	0.75	0.69
Ca	0.04	0.16	0.45	0.94	0.46	0.36	0.09	0.03	0.06
Cd	2.2	0.74	0.36	2.8	0.98	0.57	31	19	4.4
Co	0.013	0.017	0.023	1.1	1.1	0.95	0.55	0.91	0.69
Cr	0.031	0.038	0.045	0.13	0.16	0.19	0.18	0.39	0.48
Cu	0.11	0.23	0.060	0.40	0.75	0.13	0.89	0.38	0.054
Fe	0.0067	0.0080	0.0058	0.089	0.12	0.12	0.37	0.20	0.32
Hg	3.9	n.d.	3.3	0.21	n.d.	1.0	1.6	n.d.	0.98
Mg	1.6	1.4	0.96	3.5	1.9	1.5	0.19	0.44	0.85
Mn	0.027	0.080	0.078	0.095	0.056	0.047	0.78	0.67	0.43
Mo	5.6	1.4	0.48	0.39	0.15	0.24	99	47	18
Ni	0.0010	0.016	0.043	0.65	0.76	0.71	1.8	1.3	0.83
Pb	0.42	0.10	0.073	0.44	0.42	0.12	1.0	0.36	0.04
Sr	0.23	0.73	0.77	0.054	0.030	0.023	0.039	0.073	0.39
Zn	0.27	0.21	0.28	0.88	1.2	0.66	0.47	0.49	0.39

analysed separately and the average of the three columns with each material was used in the calculations. Influent concentrations were taken as the average in the two influent samples collected at the beginning and the end of each period. Numbers below one indicate removal and above indicate release. The effluent concentrations were compared to the influent concentrations using two-sided heteroscedastic t-tests. The statistically significant ($p < 0.1$) differences are underlined in Table 2.

3.2.1. Granular activated carbon

The granular activated carbon (GAC) columns removed many metals very efficiently (Table 2). More than 90% of Co, Cr, Fe, Mn and Ni were removed. Ca, Cu, Pb, Sr and Zn were removed in all samples but not to the same extent. As, Cd, Hg, Mg and Mo were released from the filters in one or more samples.

3.2.2. Bone meal

Bone meal (BM) removed more than 90% of Sr and Mn and approximately 80% or more of Cr, Fe and Hg (Table 2). Between 20 and 80% of Al, Ca, Cu, Mo, Ni, Pb and Zn were removed in most samples. Cd and Mg were released initially.

3.2.3. Iron fines

In the columns with iron fines (IF) only Ca was removed by over 90% throughout the filtration, but most metals (As, Co, Cr, Cu, Fe, Mg, Mn, Pb, Sr and Zn) were removed to some extent in most samples

Table 3
Filtration removal efficiencies in one column filled with filter sand. Numbers represent influent concentration/effluent concentration (C/C_0).

Day	1–10	11–20	21–29
P	0.72	1.9	1.0
Al	1.6	1.2	1.1
Cd	9.6	1.1	0.86
Co	4.2	1.6	0.92
Cu	2.2	1.1	0.21
Fe	0.17	2.6	0.97
Mn	4.8	3.2	1.2
Mo	3.5	1.6	1.0
Pb	2.5	1.4	0.32
Zn	0.34	0.44	0.50

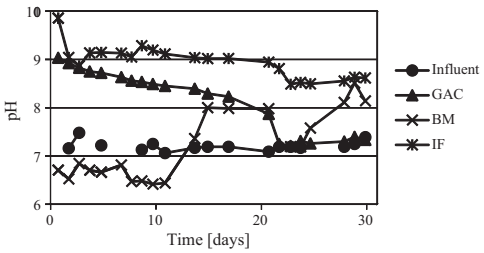

Fig. 1. pH in influent and effluent from filter columns. Data for granular activated carbon (GAC), iron fines (IF) and bone meal (BM) are the average of three columns, with the exception of BM after day 15, where the average of one to three columns is presented. Influent data are single values.

(Table 2). Concentrations of Cd and Mo increased greatly. Al, Hg and Ni were released initially.

3.2.4. Filter sand

Since BM and IF were mixed with sand, the leachate was filtered through a sand filled column for comparison. Most concentrations were unaffected by sand filtration but those affected are presented in Table 3. Since there was only one sand column it was not possible to treat this data statistically.

3.3. Other changes in leachate quality

The untreated leachate had a grey/brown colour. The effluent from the GAC columns was clear and colourless. The effluent from BM columns was cloudy and yellow, initially very strongly coloured, and smelled strongly. The IF effluent was clear and had a light yellow colour.

Changes in pH during filtration are presented in Fig. 1.

Although nutrients and organic carbon were not the main targets of this study, they are of interest because of the problems, such as eutrophication, that they can cause in the environment. In the GAC filters more than 90% of the organic carbon (measured as TOC) was removed, while the other filter materials released this material (Table 2). GAC and IF did not affect the N concentration but removed some P (Table 2). BM released large quantities of N and P (Table 2).

3.4. Flow rate

The desired flow rate was maintained in the GAC, IF and sand columns except for some startup problems in one IF column. However the BM columns had frequent leaksand after day 15 the flow rate varied between 0 and 0.2 m/day with the exception for one column that reaced the target of 1.2 m/day during approximately four days. Most likely the problems were due to clogging in the very fine BM.

4. Discussion

As clogging was observed in some of the columns part of the metal removal might be attributed to the removal of particulate matter. However, the only metal that was consistently removed by the sand filter was Zn (Table 3). Therefore it is not likely that particulate matter removal was an important removal mechanism for the other metals.

Oxidation of methanogenic landfill leachate can cause metals to precipitate [32]. In the batch tests preceding this study [15] removal of some metals was observed without the addition of filter material. However, all filter materials used in this study significantly improved the metal removal during the batch test, compared to the samples without filter material. Some oxygen was most likely available in the columns, although not to the same extent as in the batch test. Therefore part of the metal removal in the column study could be attributed to oxidation but the filter materials played a crucial role. The mechanisms for metal sorption to the filter materials are discussed in the following.

4.1. Granular activated carbon

The sorption of metals to activated carbon is affected by factors including solution pH [13,14,33] and the acidic/basic character of the carbon surface [13,17]. In this study the pH in the leachate increased from 7.2 to 9 (Fig. 1) during the initial equilibration in the columns, suggesting that the GAC was basic.

Sorption of heavy metals to activated carbon is often attributed to acidic (most notably carboxylic) sites [17,22]. The mechanism of sorption in that case is via ion exchange with H^+ (Reaction (1)) [14,17,34] or complex formation with negatively charged sites (Reaction (2)) [8,13]. In the reactions Me stands for any metal removed.

$$x\mathrm{COH} + \mathrm{Me}^{2+} \rightarrow (\mathrm{CO})_x\mathrm{Me}^{2-x} + x\mathrm{H}^+ \quad (1)$$

$$x\mathrm{CO}^- + \mathrm{Me}^{2+} \rightarrow (\mathrm{CO})_x\mathrm{Me}^{2-x} \quad (2)$$

Reaction (1) causes pH to decrease. When the exchangeable H^+ is depleted the pH reaches that of the influent and sorption ceases [14]. However, in this study, the metal removal was not affected when the solution pH stabilised at the influent level after 22 days (Fig. 1 and Table 2). Thus ion exchange cannot have been the dominating mechanism.

Sorption to basic sites, such as graphene layers, proceeds without pH decrease [17,34] which makes this mechanism more likely and, unlike Reaction (2), it is consistent with the suggested basic character of the carbonused in this study. Another mechanism that is most likely to have occurred is sorption together with organic matter since more than 90% of the organic matter was removed in the columns (Table 2) and heavy metals in landfill leachate are thought to form complexes with organic matter [35].

Precipitation of new metal containing phases can contribute to sorption [14,22] when pH is elevated. This can have occurred initially but if this was a dominating mechanism sorption should have decreased when pH was back to the influent level. Therefore this mechanism is not thought to have been important in this study.

Among the metals that were released from the GAC As, Cd, Mg and Mo were only released in the first effluent sample (Table 2), indicating that easily leachable impurities on the carbon were behind the release. In the long term, the filter might be effective also against these contaminants. After release, Cd and Mo concentrations were still not high compared to what has been found

in an earlier study of Swedish leachates [31] but As, Hg and Mg concentrations were above the highest found there.

Release of As from activated carbon has been observed previously [36]. There are, however, studies (e.g. [7]) that report successful As removal with activated carbon, while others have found the opposite [26]. In a screening test [15] preceding this study the sorption from two different leachates was studied using the same GAC as in this study. In one leachate the As concentration increased by 70% and in the other it decreased by 30%. This shows that the nature of the leachate treated is important for the treatment result.

For no metal that was sorbed the maximum sorption capacity seems to have been reached after 29 days of filtration since complete breakthrough was not reached. Within the pH range in this study (approximately 7–9) the pH does not seem to have a significant effect on metal sorption. In order to optimise a granular activated carbon process for the sorption of heavy metals from landfill leachate the maximum sorption capacity of the carbon will be the most important parameter to assess.

4.2. Bone meal

The high amount of non-degraded organic matter in the BM and the long retention time could have favoured microbial activity in these columns. The strong smell of the effluent supports this. Microbial activity would affect the conditions in the columns, including pH and redox potential. Variations in metal removal and pH were largest in these columns (Table 2 and Fig. 1) which can depend partly on microbial activity and partly on the variations in flow rate caused by the low hydraulic conductivity.

Poorly crystalline hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, the major inorganic constituent of bones, is believed to be mainly responsible for the ability of BM to remove metals. Ion exchange with Ca^{2+} has been proposed as an important mechanism of metal sorption to this mineral. This can occur as the substitution of Ca^{2+} ions in the original matrix or dissolution of hydroxyapatite followed by precipitation of other apatites, where some or all Ca are replaced by other metals. Precipitation of new, heavy metal containing phosphate minerals has also been shown to occur. It is also possible that the complexation to organic matter in the bone meal contributes to the sorption. [9,10]

Ion exchange causes Ca release [24]. Dybowska et al. [10] found that meat and bone meal dissolving in water released balanced amounts of Ca and P. In this study, however, there was an uptake of Ca and a release of P. This suggests that ion exchange with Ca was not the major metal removal mechanism. But even so, Ca must have been released at some stage since large amount of P was released. The Ca that thus must have been released on the dissolution of apatite could either have precipitated with other counter ions such as CO_3^{2-} (although variations in alkalinity does not support this as seen in Table 2) or metal anions or been sorbed to other parts of the BM, e.g. organic matter.

In the BM effluent Cd concentrations were elevated in the first sample and Mg concentrations in the first two samples. Compared to other Swedish leachates [31] Cd concentrations were close to the median even after this release but Mg concentrations were many times higher than the maximum observed. Cd was also released by the sand columns (Table 3), thus the Cd release could have originated from the sand mixed with the BM.

4.3. Iron fines

Metal removal by zero-valent iron is usually attributed to adsorption to or co-precipitation with iron corrosion products on the surface of the sorbent [25,27,28]. Iron corrosion is thus a crucial process. It can proceed aerobically (Reaction (3)) or anaerobically (Reaction (4)). Although the leachate used in this study was reduced some oxygen has undoubtedly been introduced during handling. Reaction (4) releases H_2 but no significant gas formation was observed in the columns. Therefore Reaction (3) is thought to have been dominating.

$$Fe(s) + (1/2)O_2 + H_2O \rightarrow Fe^{2+} + 2OH^- \quad (3)$$

$$Fe(s) + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^- \quad (4)$$

The Fe^{2+} can be further oxidised, e.g. through hydrolysis (Reaction (5)). If the oxidation proceeds to this step it is a pH neutral process. Since there was a net removal of Fe in the IF columns (Table 2) all Fe seem to have precipitated either through this or other mechanisms. Examples of other Fe minerals that cause H^+ release upon precipitation are summarised by Su and Puls [25].

$$4Fe^{2+} + O_2 + 10H_2O \rightarrow 4Fe(OH)_3(s) + 8H^+ \quad (5)$$

The pH was elevated compared to the influent (Fig. 1). Other authors have seen an elevated and/or fluctuating pH in water in contact with iron sorbents and attributed that to dissolution of surface minerals and ion exchange between OH^- and metal anions [27,29]. Cl^- could also take part in ion exchange. OH^- release due to anion exchange is likely to have been an important pH controlling process in this study due to the high chloride concentration (Table 1) and its apparent decrease (Table 2).

Most metals are assumed to be in the form of positive ions in the leachate. Therefore ion exchange with OH^- cannot have been the dominating removal mechanism although it is likely to have controlled pH. Another possible mechanism is ion exchange with H^+, e.g. as in Reaction (6) where Me^{2+} is a metal cation.

$$Fe(OH)_x^{3-x} + Me^{2+} \rightarrow Fe(OH)_{x-1}OMe^{3-x+2} + H^+ \quad (6)$$

However, if this mechanism would occur on a large scale it should significantly have contributed to lowering the pH and this does not seem to have been the case. Therefore co-precipitation with Fe minerals is more likely to have been the dominating mechanism. Due to the elevated pH, precipitation of other metal containing minerals, such as hydroxides, is also possible [12,27,29,30].

Although the concentrations of Cd and Mo increased drastically in the IF columns (Table 2), the Cd concentrations were still well below the highest concentrations found in Swedish leachates [31] and the Mo concentrations had the same order of magnitude. Among the elements that were released only initially (Al, Hg and Ni) only Ni showed a net release throughout the experiment. Ni had high concentrations compared to other landfills only in the first effluent sample [31]. Mo and Ni are common in stainless steel alloys that could have been present in the fines. There could also be unwanted impurities in the scrap metal. The filter sand that was mixed with the fines released Cd and Mo (Table 3) but not to an extent that explains the release from the IF columns.

The removal of some metals in the iron columns was better at the end of filtration. This could be due to initial release of these metals, but as oxidation of the iron in the columns proceeds that would create more sorption sites. To optimise metal removal the leachate should be well aerated to ensure oxidation of the IF.

5. Conclusions

This study has demonstrated that granular activated carbon (GAC), bone meal (BM) and iron fines (IF) can sorb heavy metals from real landfill leachate. It is encouraging to note that the cheaper by-products BM and IF can be used to sorb metals, and that BM showed high sorption efficiencies (>80%) for several metals. No material was efficient for removing all the studied metals. In order to remove a wide range of metals with these materials two or more filter materials need to be combined.

All materials released unwanted substances which highlights the need to study the uptake and release of a large number of compounds, not only the target metals, when assessing the usefulness of a potential filter material.

Granular activated carbon (GAC) was by far the most effective of the tested materials with regard to removal of metals. The main drawbacks of this material are its high price and the risk of As release. The dominating metal removal mechanisms by GAC seem to have been cation interaction with basic surface sites and immobilisation of metals together with organic matter being sorbed to the GAC. Ion exchange does not seem to have been among the important mechanisms of sorption in this study. Neither precipitation was among the dominating mechanisms in spite of an elevated pH.

BM released less metal than GAC, but its removal was in less effective for most metals. The main drawback of BM is the release of large amounts of organic carbon and nutrients, probably from proteins. BM could however be useful whenever these substances cannot cause a problem, e.g. where further treatment is applied or there is a need of nutrient addition. Microbial activity in the columns most likely affected sorption in the BM columns. Although ion exchange with Ca^{2+} is usually thought to be an important mechanism, there was an uptake of Ca in the columns.

Iron fines (IF) were the least effective for removing metals. The possibility of reducing As concentrations, however, is an advantage. Before using scrap iron, its leaching characteristics need to be assessed to avoid release of metals. Since the sorption improved considerably during the course of this study, IF is thought to be a promising filter material, but the source of the material must be carefully chosen and oxidation of the leachate must be ensured. Co-precipitation with iron corrosion products was likely the dominating removal mechanism. Ion exchange seems to have been less important for metal removal but can have had indirect effects as it is likely to have controlled the pH.

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