Ageing Landfills –

Development and Processes

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Cover: The landfill at Högbytorp
      (photo: M. Östman)

Ageing Landfills – Development and Processes

Abstract

In Sweden, a large number of closed landfills containing a mixture of household waste and waste from industries and other sources exist. These landfills originate from a time when regulations were less strict and contain large amounts of organic material derived from household waste, plus large amounts of metals. This partly decomposed organic material can contribute to the stability of the landfill by retaining metals. When landfills are closed they are covered to create strictly anaerobic conditions. Over time, oxygen can be expected to penetrate the landfill mass as oxygenated rainwater and atmospheric air. This will affect the deposited organic material and the leaching pattern.

The present study examined the ageing processes in landfills and the environmental impacts of these by characterising the content of metals, organic material and water. Artificially aged and original landfill material were analysed to determine changes in metal binding forms, cation exchange capacity and Cu^{2+} ion-binding ability. Changes in the concentration of dissolved organic matter in the aqueous phase due to aeration were analysed. The proton-binding and Cu^{2+}-binding capacity of dissolved organic material was investigated by titration analysis. Metal retention ability was determined in column experiments.

Ageing of the landfill material increased the cation exchange capacity and the ability to bind Cu^{2+}. The column experiment revealed that the metal-binding ability of both original and aged material was good. Ageing of the landfill material caused a decrease in the dissolved organic carbon content and thus a lack of metal-transporting ligands. Metal stability in the landfill was controlled by the pH and redox potential and by the organic matter content. Stabilisation of organic material to humic-like substances and formation of charged oxide surfaces with good metal-binding ability will be important for future landfill oxidation, whether natural or forced.

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Contents

List of Publications

This thesis is based on the work contained in the following papers, referred to by Roman numerals in the text:

I M. Östman, O. Wahlberg, S. Ågren & A. Mårtensson. 2006. Metal and organic contents in a combined household and industrial landfill. *Waste Management* 26/2006, pp. 29-40.

II M. Östman, O. Wahlberg & A. Mårtensson. 2008. Leaching and metal–binding capacity in ageing landfill material. *Waste Management* 28/2008, pp. 142-150.

III M. Östman, A. Mårtensson & O. Wahlberg. Dissolved organic carbon affects the metal mobility in ageing landfills. (manuscript).

IV M. Östman, A. Mårtensson & O. Wahlberg. Fate of metals in ageing landfills. (manuscript).

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Abbreviations

CEC	Cation exchange capacity
COD	Chemical oxygen demand
DIC	Dissolved inorganic carbon
DOC	Dissolved organic carbon
LOI	Loss on ignition
MSW	Municipal solid waste
OM	Organic matter

1 Introduction

1.1 Landfilling – social and legal concerns

Humans have always produced waste, and what has not been possible to take care of in other ways has been dumped on various types of landfills. Many traces have been found of ancient human waste collection systems intended to maintain public health. In about 3500 B.C., brick drains were built in Indian cities. In 1900 B.C., a sewage disposal system including water closets was installed in the ancient city of Knossos. In the Roman Empire sewers were built in cities and there were also regulations against littering. The Law of Moses regulated how waste should be taken care of, while outside the city of Jerusalem in the valley of Gehenna, waste was thrown on the constantly burning fires (White-Hunt, 1980). This knowledge seemed to have been lost by societies in the Middle Ages, as waste was dumped on streets and pigs and dogs scavenged on the heaps (Hogland, 1996). From the middle of the 14th century to the middle of the 19th century, rubbish was transported out of the cities and used as a fertiliser in agriculture. Waste management was the responsibility of the local landlord and farmers collected the fertiliser material. During this time, the growth of archaeological layers decreased in cities (Wetterberg, 2004). From the 17th century onwards, regulations on waste management existed in the Scandinavian capital cities (Nygård, 2004). In Sweden, dealing with human waste, even latrine waste, was considered an aesthetic issue as late as during the 19th century. Pits were dug and waste was dumped and when the pit was filled it was covered and a new one was dug (Andréasson, 1998).

As industrialisation progressed and the population in cities increased, the amount of waste also increased and had to be disposed of elsewhere. Because

of the increasing population in the cities, for instance in England, infections became an increasing problem (Nygård, 2004). The attitude towards waste management changed when cholera invaded Sweden, as household wastes and latrines were blamed for the spread of the disease. In the 19th century, regulations were introduced requiring waste disposal systems to be built in cities (Flygth, 1995; Hogland, 1996). The aim of building these waste systems was almost always to prevent the spread of diseases and improve public health. In consequence, in 1868 statutes were introduced for Swedish cities prohibiting the disposal of waste in the streets or in water courses. These statutes gradually motivated the cities to directly manage their waste and by the early 20th century most Swedish municipalities had organised waste management systems. Manure, latrine waste, household waste suitable as pig food and remaining refuse were collected separately. The latrine waste and manure were dried, pulverised and sold as a fertiliser to farmers (Flygth, 1995). In several cities the edible waste was used for feeding pigs, which were then sold back to people in the city. At that time the wastes consisted mainly of organic material and there was little remaining refuse. Wastes such as glass or metal were mostly sold directly to rag–and–bone merchants. Thus, municipal waste management at the end of the 19th century was almost entirely a closed circulation system. The remaining refuse was dumped on landfills and often burned on the site.

In the 1930s the pig food fraction began to be more homogeneous. As a consequence, most of the waste was landfilled or burned. Over the years the composition of municipal waste has developed from being dominated by organic household waste that was handled locally to more complex wastes (Hogland, 1996). It lost its value as a fertiliser due to the increased use of metals within society, and thus the closed recirculation system was discontinued. Instead, landfilling and burning became more frequent as a method of waste disposal. In the 1920s the first household waste collection system was built in an apartment house in Stockholm and this method spread rapidly throughout the country. Vehicles equipped especially for waste transport were developed. The Second World War caused a change in the pattern of waste management as people reverted to reclaiming as much as possible from the waste, but after the war waste management returned to the pre-war habits of burning and landfilling (Andréasson, 1998).

Until the 1950s, Swedish society produced relatively small amounts of waste. For example, newspapers were used as packing material and glass jars were reused (Johansson, 1997). The increased standard of living and changes

in consumer habits in the 1960s and 1970s increased the amounts and volumes of waste and also changed the content of household wastes. The use of packing materials and plastic gave rise to increasing volumes of waste, as did the use of more equipment containing metals. The political goal of creating one million new dwellings for the people led to large construction programmes for housing in the 1960s and increased the amount of construction wastes. During the same period many older buildings were demolished to make way for modern ones and the wastes thus generated were landfilled. Industrialisation and the manufacture of products containing chemicals used in households and in businesses has also created wastes that have escalated in hazardousness. In the 1970s, as the amounts of waste produced increased to become a problem, attempts to recycle material started in Sweden. In 1972 new legislation was imposed that gave Swedish municipalities a monopoly on collection of household wastes and enormous combustion facilities were constructed. The heat from the combustion facilities was used to heat water for central heating systems in the area. Wastes that were not incinerated in this way, for instance glass, scrap metals, paper and compost, were landfilled, as they were considered to be of too low quality for reuse in industries or as fertiliser in parks. The environmental problems with incineration of wastes and with methane emission and leachate water in landfills gradually became a subject of attention.

During the 1990s, the concepts of waste reduction, recycling and reuse were introduced as regards waste disposal in order to decrease the amount being incinerated or landfilled. A new law was introduced in 1994 based on the 'producer pays principle'. This law covered responsibilities for car tyres, paper and packaging, but since then it has been extended to include cars and electrical and electronic equipment (Naturvårdsverket, 2008).

The producer pays principle is meant to promote the achievement of the Swedish environmental goals. The existing law obliges producers to collect and dispose of their products at the end of their useful life. Another aim is to promote products that are more resource-efficient, easier to recycle and free from hazardous components. Landfills are at the bottom of the waste management hierarchy and since 1990, increased source separation has resulted in decreasing amounts of landfilled waste in Sweden (Naturvårdsverket, 2008).

The current waste management hierarchy is based on an EU directive and is recognised by all member states. Its aim is to reduce the

environmental burden by reducing the amount of waste. The hierarchy has five steps (Fredriksson, 2004): Minimise – Reuse – Recycle – Recycle energy – Landfill.

Landfilling of combustible waste was prohibited in 2002, while at the same time the charge for landfilling was raised. In 2005, landfilling of all organic matter was prohibited, the aim being that the organic materials should be subject to a shorter recirculation process, e.g. composting or biogas production. Thus the hazards of gaseous emissions from landfills should not exist in the future.

1.2 Landfilling – current situation

Estimates based on the number of municipalities in Sweden result in a total of 8000 landfills, most of them being closed (K.M. Persson, pers. comm. 2008). A survey made within the county of Uppsala reported 200 closed and six ongoing landfills in 2008 (G. Robinson, pers. comm. 2008). Before the mergers of municipalities carried out in 1952 and 1974, there were 2498 municipalities in Sweden (Kommunförbundet in Finland, 2008). It is reasonable to assume that there were several landfills for household waste or latrine pits of varying size in each municipality, and thus the total of 8000 is not an overestimation. To this total must be added the large number of landfills for industries and mining, which are managed by the respective enterprise. In 1994, there were ~300 landfills in operation in Sweden, and 192 of these were still operating in 2003 (RVF, 2004). Most of the landfills that are in operation today were started in the 1960s and 1970s and have permits based on maximum allowed volume. The Swedish waste management authority has estimated that after 2008 there will only be 90 landfills for household waste in Sweden, although there will still be a number of landfills operated by industries and mining companies. These closed landfills will be an environmental concern for a long period.

According to the Swedish EPA report to the European Union, ~120 million tonnes of waste (including mining wastes) were produced in Sweden in 2004 (Naturvårdsverket, 2008). Approximately 114 million tonnes of those were classified as non-hazardous waste. Landfilling accounted for 66.4 million tonnes of non-hazardous waste and 0.5 million tonnes of hazardous waste. The average amount of household waste produced per person in

Sweden is 463 kg, which gives 4.2 million tonnes for the year 2004, but the amount is increasing.

Since the ban on landfilling of organic material was introduced, the proportion of household waste produced that is landfilled is decreasing, from 20% in 2002 to 5% in 2006. This is a desirable development which means that Swedish waste management can focus on recycling material. The Swedish data compare favourably with the EU mean for 2005, where more than 40% was landfilled. The Netherlands landfills the lowest proportion of household waste in Europe (~2%), while Greece landfills the highest proportion (85-90%) (Eurostat, 2008). In the USA, 55% of household waste is landfilled (EPA, 2007). Urban areas of China, the fastest growing economy in the world, now exceed the USA in waste generation per capita (World Bank, 2005). According to Xiaoli *et al.* (2008), 90% of the waste generated in urban areas of China is landfilled.

Waste disposal sites can be constructed according to two different principles, landfilling and landraising. Landfilling is when natural or constructed cavities are filled with waste and these are constructed according to one of three different methods: 1) dilution and attenuation, 2) containment and 3) entombment (Westlake, 1995; Allen, 2001). Dilution and attenuation involves allowing the groundwater to infiltrate the landfill and dilute the leachate, so the method is environmentally risky. The waste is percolated with rainwater and degrades relatively rapidly. Dilution and attenuation requires little engineering and is a low-cost way of landfilling. Before 1980, this was the most common landfill technique. In 1980 the EU Groundwater Directive forced a change in technique to more engineered landfills (Westlake, 1995). Containment is a more engineered method involving the use of a liner, and the principle is that the leachate should not leave the landfill area. The waste is slowly degraded. This method requires effective management and is expensive to build and manage. Entombment is also an engineered method of landfill construction but with the difference that no liquids are allowed to infiltrate the waste. This technique is intended to store the waste more or less unchanged. Such dry storage of waste is expensive to build and manage.

Landraising is based on the principle that the waste is placed on ground level, with liners, and the landfill mass is allowed to rise above that. These types of landfills are visible in the landscape but are easier to control

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environmentally. In societies where space is scarce, landraised landfills are common by necessity. Large landfills in Sweden have an approximate volume of 4-6 million m^3 (RVF, 2004) but this is a small figure compared with mega-sized landfills outside the biggest cities in the world, which can range from 5-10 million m^3 up to 130 million m^3, and have waste depths of up to 200 m (Robinson, 2007).

In most cases, Swedish landfills constructed in the 1960s, when landfilling increased, have liners of clay or natural clay layers or, when the clay is not thick enough or lacking, are based on the landraising principle. When a landfill site is filled to the permitted limit the landfill mass is capped to prevent oxygen intrusion. When waste is dumped on the landfill it is mechanically compacted to prevent cavities being formed. Cavities in landfill can create problems with landfill gas accumulation, leading to explosions and fires. Accidental fires on landfill are very difficult to combat and of great environmental concern, since the smoke produced contains toxic compounds deriving from the composition of the waste.

New legislation in 2001 increased the restrictions on landfilling, with stricter demands on liners and geological barriers and with new upper limit values on leaching (Naturvårdsverket, 2008). According to EU legislation only landfills constructed on the containment principle are permitted (Allen, 2001). Natural liners are accepted if they have low permeability ($<10^{-9}$ m s^{-1}).

As a consequence, active deposition has been restricted to a smaller number of landfills with higher standards regarding control and treatment of materials. The conditions that landfill constructions now have to meet are that the material be treated before deposition on the landfill to avoid leakage of hazardous substances; and that the material be capped to avoid rainwater percolation into the landfill and thereby prevent leakage from the landfill. Drainage water should be collected and purified when necessary.

As a result of the new conditions for landfilling, landfills of the future will differ in composition from those of today. However, quite a number of landfills that are already closed or that are soon to be closed still contain organic material. Since these landfills will have to be dealt with for a considerable time, it is important to gain knowledge about how organic material influences the stability of the landfill. It is possible that the waste management practices used today with liners, final cover and anaerobic conditions are sufficient, but that has not yet been fully confirmed.

Old landfills contain large amounts of components that can pose a future threat to the environment. These components include large amounts of metals, non-metals and, since household waste was landfilled, and they contain organic material.

1.3 Landfill processes

Climatic and geological processes affect the man-made landscape formation of landfills. Precipitation occurs as surface run-off, penetrates the landfill body, or evaporates. Landfill gases are lost to the air. There is a risk of groundwater infiltrating the landfill and of leachate water coming into contact with groundwater.

Depending on the origin of the material landfilled, landfills change over time. These changes occur under the influence of the prevailing climatic conditions and affect the deposited material differently depending on the quality of the deposits. The deposited waste undergoes biological, chemical and physical transformations. The processes involved in these transformations have been described in several reports (Farquhar & Rovers, 1973; Barlaz *et al.*, 1991; Öhman, 1991; Persson, 1996; Bozkurt *et al.*, 2000). Given that a landfill contains organic wastes, the processes within the landfill can be defined as: initial phase, oxygen- and nitrate-consuming phase, acid anaerobic phase, methane-producing phase and humus-forming phase.

1.3.1 Initial phase

The initial phase starts when the refuse is dumped on the landfill, and is a short period depending on the climate. The waste has normally started to degrade before arrival at the landfill. During this phase the organic material undergoes hydrolysis. Since the biological activity is low, no landfill gas is produced. The phase ends with increased microbial activity that results in increased temperature.

1.3.2 Oxygen- and nitrate-consuming phase

In the oxygen- and nitrate-consuming phase, the degradation of dissolved organic material starts using oxygen (aerobic respiration) and later nitrate (denitrification) as an electron acceptor. The microbiological activity is high, and the temperature can reach 70 °C. The landfill gas consists of carbon

dioxide (CO_2) and nitrogen gas (N_2). The risk of metal leaching is low. This phase is limited by the availability of oxygen and nitrate and lasts up to one month.

$$CH_2O + O_2 \rightarrow CO_2 \text{ (g)} + H_2O \qquad \text{(aerobic respiration)}$$
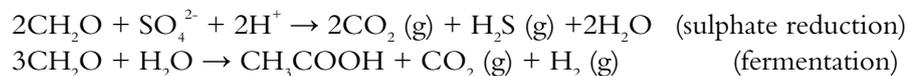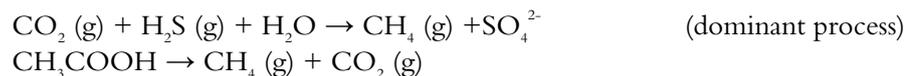$$2.5CH_2O + 2NO_3^- \rightarrow 2.5CO_2 \text{ (g)} + 2N_2 \text{ (g)} + 3.5H_2O \qquad \text{(denitrification)}$$
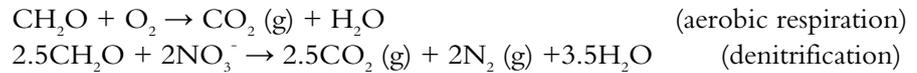
1.3.3 Acid anaerobic phase

During the acid anaerobic phase, sulphate (SO_4^{2-}) is reduced and carbon dioxide (CO_2) and hydrogen sulphide (H_2S) are produced. Short-chain aliphatic acids are produced through fermentation, which eventually results in the formation of carbon dioxide and hydrogen. The pH in the leachate is around 5 and at this stage the metal leaching is at its peak.

$$2CH_2O + SO_4^{2-} + 2H^+ \rightarrow 2CO_2 \text{ (g)} + H_2S \text{ (g)} + 2H_2O \quad \text{(sulphate reduction)}$$
$$3CH_2O + H_2O \rightarrow CH_3COOH + CO_2 \text{ (g)} + H_2 \text{ (g)} \qquad \text{(fermentation)}$$

1.3.4 Methane-producing phase

In the methane-producing phase, acetic acid, carbon dioxide and hydrogen are transformed to methane by bacteria that are strictly anaerobic. The concentration of dissolved metals decreases due to formation of metal sulphides. The pH increases to around 8 since the carboxylic acids are consumed and the carbonate system is buffering. During methanogenesis the gas pressure is generally higher than the atmospheric pressure due to the microbial activity (Fannin & Roberts, 2006). This stage of the landfill can be expected to last for 100 years.

$$CO_2 \text{ (g)} + H_2S \text{ (g)} + H_2O \rightarrow CH_4 \text{ (g)} + SO_4^{2-} \qquad \text{(dominant process)}$$
$$CH_3COOH \rightarrow CH_4 \text{ (g)} + CO_2 \text{ (g)}$$

1.3.5 Humus-forming phase

The more readily degradable organic compounds gradually break down and the remaining organic material is more resistant to decomposition. The humic phase then begins, during which more complex and stable organic compounds are formed. This phase is estimated to last for 1000 years.

The microbial activity is high during the early stages of landfill development, leading to high gas production. Later on, the microbial activity declines, causing methane production to cease. As the gas pressure decreases, there is no longer a positive pressure in the landfill and air can begin to enter through diffusion (Fannin & Roberts, 2006). The landfill then slowly begins to oxidise, which carries the risk of metal ions becoming more mobile in the landfill and then leaching out to a greater extent than under anaerobic conditions.

The processes in the landfill start with organic material that is a mixture of easily degradable compounds, more complex structures and more resilient organic material. During transformation the easily degradable material is consumed and more stable compounds are formed. Calace *et al.* (2001) found more high molecular weight organic material in leachate from older landfills than from younger. Prantl *et al.* (2006) describe the transformation to more stable compounds thus: Degradable organic material → low molecular weight fulvic acids → more stable compounds → high molecular weight humic substances.

1.3.6 Redox conditions

The low molecular weight carbon compounds function as a powerful redox buffer, with pe values ranging from –5 to –8. These compounds become a substrate for the methanogenic process. The redox conditions are strictly anaerobic (Stumm & Morgan, 1995; Bozkurt *et al.*, 2000). In the oxidised landfill, the low molecular weight compounds are depleted and higher molecular weight compounds (humic substances) are formed (Prantl *et al.*, 2006). These humic substances constitute a new redox buffer at pe ≈3 and pH ≈8 (Österberg *et al.*, 1997). When this occurs sulphides oxidise to sulphate and Fe(II) oxidises and forms Fe(III) compounds.

During landfill ageing, the possibility for oxygen intrusion increases as oxygen-rich rainwater begins to penetrate the landfill mass. This intrusion changes both the solid material and the composition of the aqueous phase of the landfill, and therefore also the composition of the leachate.

1.3.7 Leachate

As discussed above, the degradation of organic material produces gas and water. The water produced drains out of the landfill as leachate water containing traces of the contaminants that have been deposited and thus poses an environmental risk. Leachate can contain dissolved organic matter, inorganic macrocomponents, metal ions and xenobiotic organic compounds, and the concentrations of all components are higher in the acid phase than in the methanogenic phase. As landfill leachate is potentially hazardous, it has been extensively researched (Jensen & Christensen, 1999; Christensen *et al.*, 2001; Kjeldsen *et al.*, 2002; Baun & Christensen, 2004; Robinson, 2007). The leachate can be regarded as an electrolyte (approximately 0.1 M) with NH_4^+, Na^+ and K^+ as main cations and HCO_3^-, and Cl^- as main anions (Baccini *et al.*, 1987). Studies of 20 landfills in the former West Germany showed differences between leachate from landfills in the acid phase and those in the methanogenic phase (Ehrig, 1983). In the acid phase the average pH was found to be 6.1 and the chemical oxygen demand (COD) 22000 mg L^{-1}, while in the methanogenic phase the average pH was 8.0 and the COD 3000 mg L^{-1}. The COD can be used as a measure of the oxygen needed to degrade the organic compounds present in the leachate. In the German study cited above, variables that did not change were the NH_4^+, Na^+ and K^+ and Cl^- concentrations. The metals Ca, Fe, Mg, and Zn decreased in concentration when landfills were in the methanogenic phase, while the metals Cd, Cr, Co, Cu, Ni, and Pb remained unaffected (Ehrig, 1983).

1.3.8 Landfill gas emission

In addition to CO_2 and N_2, landfill gas contains different toxic compounds, among them organo-metal compounds (Michalzik *et al.*, 2007). Landfills containing organic material produce CH_4 and CO_2, both of which are potent greenhouse gases (Farquhar & Rovers, 1973; Themelis & Ulloa, 2007). Even with the best technology, there are losses of methane to the atmosphere (Huber-Humer *et al.*, 2008) and therefore landfilling of organic wastes has been banned since 2005 under EU and Swedish legislation. Organic material must be recycled or incinerated. Landfilling of source-separated combustible organic material was terminated in Sweden in 2002.

1.3.9 Odours from landfills

Landfills and waste cause environmental problems with odours. Most of the odour compounds are emitted with the landfill gas but can also be noticed in the leachate (Bowly, 2003; Senante *et al.*, 2003). The odour compounds can be divided into groups according to their chemical composition as: sulphurous, nitrogenous, aldehydes, carboxylic acids, ketones, alcohols, aromatics, chlorinated, esters, and terpenes. Each group contains a number of compounds. Hydrogen sulphide and methylmercaptan are examples from the sulphurous group, while acetic and butyric acid are examples from the carboxylic acid group.

2 Objectives

The starting point for this work was that many closed landfills contain organic material that will require consideration for many years to come. Therefore, it is important to understand the role of the organic material in those landfills and to assess the possibility to compare it with mature humified matter in soils. Organic material has the capacity to complex-bind metals, and can thereby contribute to the stability of landfills.

The overall objective of this thesis was to improve knowledge of the environmental consequences of landfills containing organic material and assess how this organic material can bind and stabilise metals. When the landfill ages, the risk of oxygen-rich rainwater intrusion increases. This could change the binding forms and the capacity to bind metals in the landfill. To predict the fate of the landfill and to evaluate the environmental risks in the future, landfill material was artificially aged and metal status was monitored. The hypothesis was that metal stability in old landfills is largely regulated by organic matter.

The specific objectives were to:

- Examine the current status of a landfill, *i.e.* its content of metals and organic material, in order to determine the extent to which the solid material is stabilised (Paper I).
- Investigate the effects of ageing of landfill material by aeration and evaluate the changes in cation exchange capacity and binding form of metals through sequential leaching (Paper II).

- Investigate the effect of ageing on dissolved organic material in the aqueous phase of the landfill in order to identify possible changes in metal–transporting ligands (Paper III).
- Determine the metal retention capacity in original and aerated landfill material and establish whether the landfill material has sufficient capacity to bind additional metal ions and whether ageing alters this capacity (Paper IV).

3   Materials and methods

3.1   The landfill site

Material from the landfill in Högbytorp was used in this work. The Högbytorp landfill is among the largest in Sweden, with a volume of 4.8 10^6 cubic metres, and contains both household and industrial waste. This landfill is currently in the methanogenic stage. Since it contains large amounts of metals and organic material from household waste, it provides the possibility to study the importance and environmental consequences of organic material in landfill.

Högbytorp is situated 40 km north-west of Stockholm (60°32'N, 17°37'E). The prevailing climate is cold temperate, with a mean annual precipitation of 600 mm. Mean annual temperature is 7 °C, with a maximum in July (18 °C) and a minimum in January (-5 °C). The landfill was established in 1964 and is now closed and sealed (2008). It occupies an area of around 30 hectares, and is built as a landraised landfill. The soil under the landfill consists of clay, glacial till and rock outcrop. Where the clay layer was not sufficiently thick to provide a sealed base, clay was added (Aulin, 1998). In 1994 a methane recovery system was installed to decrease methane emissions. Data on the annual leaching of metals and the pH in leachate from the landfill are given in Table 1. The COD is a measure of the oxygen demand when organic compounds are completely degraded and the mean COD values for leachate from the Högbytorp landfill in its methanogenic stage are also given in Table 1. The leachate water is transported to a municipal purification plant.

Table 1. *Annual leaching of metals (kg year^{-1}) and pH in leachate from the Högbytorp landfill. Chemical oxygen demand (COD) in g L^{-1} mean value over the year (Miljörapport, 1997-2006)*

Year	Amount of leachate	pH	COD	Cd	Co	Cr	Cu	Ni	Pb	Zn
	(10^3 m^3)		g L^{-1}	(kg year^{-1})						
1997	81	8.2	1.50	<0.037	2.7	5.9	2.3	17	0.9	46
1998	100	8.1	1.66	<0.093	3.2	6.1	4.3	31	1.3	34
1999	163	8.1	1.87	<0.32	7.2	9.4	7.6	56	4.2	79
2000	61	7.4	2.50	0.057	2.7	3.8	2.3	18	1.9	21
2001	57	8.0	1.56	0.043	2.0	6.5	19.0	16	2.5	35
2002	62	8.0	1.23	0.02	2.1	4.4	2.6	37	0.5	24
2003	47	7.8	1.95	0.06	12.0	9.3	3.4	39	2.0	20
2004	91	7.5	8.00	<0.22	4.7	47.0	3.8	51	0.7	11
2005	120	7.5	2.40	0.032	7.0	11.2	4.2	34	1.6	34
2006	78	7.6	2.60	0.02	6.3	18.5	39.2	25	3.4	68
mean				0.07	5.0	12.2	8.9	32	1.9	37

3.2   Characterisation of the landfill

Landfill material from three randomly chosen points was sampled with the help of drilling equipment normally used for drilling wells for gas recovery (Figure 1). The drill holes were 10-18 m deep depending on the depth of the landfill at the sampling points and the position of the clay liner. Samples were collected systematically with increasing depth as near to every 0.5 metres as possible. During sampling the landfill material was visually observed. It was mostly a greasy mass, but scrap metals such as lead pieces, copper wire and other metal items were visible. Immediately after sampling, the material was placed in 5 L gas-tight bags. The samples were first stored at 5 °C and later deep-frozen at -20 °C.

Figure 1. Sampling at Högbytorp in April 2002.

The contents of total carbon and total nitrogen were determined by dry combustion with a LECO CSN 2000 analyser. The water content was analysed by drying samples overnight at 105 °C. The pH was analysed in a water extract, one part fresh sample and two parts water (volume/volume), with a glass electrode. Organic matter was estimated as loss on ignition at (550 °C). The concentrations of metals (Al, Ca, Cd, Co, Cr, Cu, Fe, K, Mn, Mo, Ni, Pb, Zn and V) and non-metals (B, P and S) were analysed in nitric acid extracts and with inductively coupled plasma emission (Perkin Elmer Optima 3000) ICP-technique (Paper I).

3.3   Artificial ageing of landfill material

To simulate the ageing processes when air slowly penetrates the landfill mass, samples weighing approximately 2 kg each of landfill material contained in cylinders (Ø 24 cm) were diffused with humified air (flow: 9 mL min^{-1}). The aeration was continued for 14 months at 20 °C. After aeration, the samples were stored at -20 °C prior to analysis. As a reference, landfill material was diffused with humified nitrogen gas.

Peat soil is developed from organic material, (mostly from decayed Sphagnum species) and is transformed from anaerobic to aerobic conditions. This makes it interesting as an analogue to a completely oxidised landfill

(Bozkurt et al., 2001). Peat soil also has the capacity to bind metals due to its high content of organic material (Ringqvist & Öborn, 2002; Ringqvist et al., 2002). Peat soil was therefore used and treated in the same way in the experiment. The design of the aeration experiment is described in Mårtensson et al. (1999). The aerated landfill material and the nitrogen-treated landfill material were analysed for loss on ignition and pH. The cation exchange capacity (CEC), i.e. the capacity to bind sodium and the capacity to bind metals (as divalent copper), was determined. The methods used are modified standard laboratory methods and are described in Paper II. Sequential analysis is a tool to estimate how metal ions are bound in materials (Tessier et al., 1979; Ecke & Lagerkvist, 1993; Flyhammar, 1997; Hjort, 2003; Øygard et al., 2008). In this work a four-step sequential analysis of metals in the materials was also performed. The four steps used were water soluble, exchangeable, oxidisable and residual, and the methods are described in Paper II.

3.4 Dissolved carbon in the aqueous phase

When air penetrates landfill material, dissolved carbon in the aqueous phase is changed. Aerated and original anaerobic landfill material were extracted with water to achieve sufficient amounts of aqueous phase under controlled conditions, and analysed for content of organic and inorganic carbon. To determine the distribution between low and high molecular weight compounds, dialysis with a cut-off value of 8000 Dalton against distilled water was used. The water extracts and the dialysed water extracts were analysed for the capacity to bind protons and divalent copper ions by titration in a 0.1 M KNO_3 medium. Titration with copper is used to determine the capacity to form metal complexes (Stevenson & Chen, 1991; Österberg et al., 1999; Amery et al., 2007). The concentration of KNO_3 was chosen to correspond to the ionic strength in the leachate (Paper III). Calculations were based on the following two equations, where E_{jpH} and E_{jpCu} stand for liquid junction potential for H and Cu respectively:

$$E_H \ = \ E^\circ_H + 58.55 \lg [H^+] + E_{jpH} \qquad (Eq.\ 1)$$
$$E_{Cu} \ = \ E^\circ_{Cu} + 29.28 \lg [Cu^{2+}] + E_{jpCu} \qquad (Eq.\ 2)$$

Acid-base titrations and copper complex titrations were carried out. The calculations from the acid-base titrations gave the conditional dissociation

constants for the organic acids, carbonic acid and the dissolution constant for carbonate (Eq. 1). The calculation for the copper titrations gave the formation constants for the copper complex with organic material and with carbonate (Eq. 2).

3.5 Metal retention in landfills

Columns with three different treatments of landfill material (original anaerobic, aerated, and combined iron- and heat-oxidised) were used to estimate the capacity to bind metals in landfills. Peat samples were treated in parallel in the same way. A solution containing 1 mg L^{-1} each of cadmium, chromium, cobalt, copper, iron, lead, nickel and zinc was added drop-wise to each column for 65 days at a rate of 1 mL $minute^{-1}$, corresponding to the mean annual precipitation at the site. The leachate samples were collected in 200 mL plastic bottles, which were stored at -20 °C prior to analysis. The content of dissolved organic carbon, sulphur and metals (Cd, Co, Cr, Fe, Ni, Pb and Zn) was analysed after filtration through a 0.45 μm mesh. The content in particles was also estimated (Paper IV).

Estimations of metal speciation were made with the computer programme Medusa and its database Hydra (Puigdomenech, 1983). Medusa calculates the distribution of complex species. The thermodynamic equilibrium constants of the database were extracted from compilations made by IUPAC.

4   Results and discussion

4.1   Characterisation of the landfill

The analysis of the landfill material showed a great variation within the landfill body, both with depth and between sampling sites, and, as expected, large amounts of metals were found (Paper I). This shows that the landfill body is extremely heterogeneous. The analyses showed an increase in water content, organic matter, total sulphur and several metals with increasing depth. This is illustrated for one of the sampling sites in Figure 2. The values obtained were relative values defined as: element concentration at 4.5 m depth of each element = 100 (Figure 2). pH was in the range 7.8-8.5, indicating the presence of a carbonate buffering system in the landfill.

The ranges for water, total carbon and organic matter (loss on ignition) content are given in Table 2. The difference in water content between the upper and lower part of the landfill indicates the possibility of different redox conditions. Analysis of dissolved iron(II) with an colorimetric method, using ferrozine as reagent as an indicator of the redox conditions, showed higher concentration of iron(II) in the lower part compared with the upper part, indicating that there were two layers with different redox conditions (Paper I). Since landfills generally have a very heterogeneous physical structure, water moves downwards in cracks or, if present, gas collecting channels (Fellner *et al.*, 2003).

The difference in redox conditions between the two layers indicated that metals that were released in the upper part of the landfill and transported downwards were eventually precipitated due to the reducing conditions. The observed increase in metal content with increasing depth in the landfill

confirms the occurrence of downward transport of metals. Results from investigation of Finland's largest landfill, which contains municipal solid waste (MSW), show the same pattern with respect to water content (Sormunen *et al.*, 2008). The C/N ratio in soil is an indicator of the maturity of the organic matter – if the ratio is in the range 10-15 the organic material is stabilised as humus (Brady & Weil, 2002). In the landfill at Högbytorp the C/N ratio ranged from 30 to 80, which clearly demonstrates that the carbon in the landfill was not stabilised.
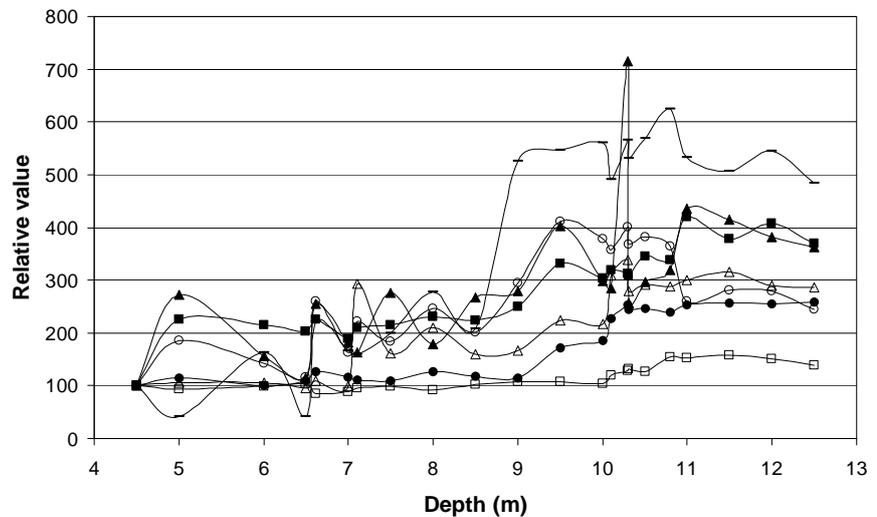

Figure 2. Variation with depth in the landfill in cadmium (-▪-), total sulphur (-■-), copper (-▲-), zinc (-△-), water content (-●-), organic matter as loss on ignition (LOI) (-○-), and iron (-□-) given as relative values. Relative values defined as: element concentration at 4.5 m depth, each element = 100.

Table 2. *Water content, total carbon and organic matter (OM) as loss on ignition in the landfill*

Depth	Water	Total carbon	OM
m	%	% dry matter	% dry matter
<10	25–30	5–10	10–20
> 10	47–65	15–26	25–40

Table 3 presents results from municipal solid waste and industrial waste for comparison. It also shows the metal content in the typical Swedish clay soil used as quality control in the laboratory and the peat soil used as a reference in the incubation experiments in the present work. It is difficult to make direct comparisons since the authors of the reports have used different methods to produce the figures. The values from all three sampling sites at Högbytorp are within the range shown in Table 3. The Finnish study (Assmuth, 1991) is from field studies at 43 different landfill sites, while the Norwegian study (Fossom & Sørum, 1997) uses mean values for the year 1995. Figures in the Swiss investigation (Baccini *et al.*, 1987) are mean values for MSW. The Swedish studies (Flyhammar, 1997; Flyhammar *et al.*, 1998; Aulin, 1998) and the French study (Prudent *et al.*, 1996) are based on values from investigation of specific samples.

Table 3. *Metal contents of landfills of various origin*

Origin of landfill	Fe g kg⁻¹	Zn g kg⁻¹	Cd mg kg⁻¹	Cr mg kg⁻¹	Cu mg kg⁻¹	Pb mg kg⁻¹	Ni mg kg⁻¹	Reference
Högbytorp	50 – 109	0.9 – 6.4	0.1 – 5.2	40 – 109	200 – 2000	80 – 3900	40 – 170	Paper I
Swiss MSW	40	1.4	12		300	400		Baccini *et al.*, 1987
Mixed MSW and industri		0.18-1.2	0.3-4.3		41-950	80-450		Assmuth, 1991
French MSW		0.38	4	350	77	230	57	Prudent *et al.*, 1996
Norwegian MSW	8.8	1.1	5.3	21		446		Fossom & Sorum, 1997
Fresh Swedish MSW	12	2.7	6	16	139	216	25	Flyhammar, 1997
Degraded Swedish MSW	10	1.7	3	53	173	420	21	Flyhammar, 1997
Mixed Swedish MSW (95 sewage sludge		1.3	8.3	250	400	750	80	Flyhammar *et al.*, 1998
Clay soil	36	0.12	0.2	50	33	24	37	Paper I
Peat	14	0.27	0.3	17	24	17	23	Paper I

The values shown in Table 3 demonstrate that landfills contain large amounts of deposited metals and that the amount varies both with depth and sampling site. The metal content at Högbytorp is in most cases higher than in comparable landfills. The heterogeneity of the material from Högbytorp is evident (Paper I). This landfill contains large amounts of industrial and construction waste, which probably explains the high levels of copper, iron, lead and nickel. Copper and lead were visible as scrap metal during sampling and preparation before analysis. The study in Finland also included landfills with high amounts of lead and copper which may originate from industrial waste (Assmuth, 1991). The study by Prudent *et al.* (1996) showed that copper and nickel predominantly originated from scrap metal. In that study lead predominantly came from wood wastes, which is a difference compared with the waste from Högbytorp. Flyhammar (1997) shows the difference over time in metal content in fresh waste (from 1994–1995) and degraded material (from 1974). The difference can probably be explained by better source separation in 1995.

4.2 Influence of the ageing processes in landfills

4.2.1 Effects on solid material

The aeration of landfill material causes decomposition of organic matter, and carbon dioxide and acids are produced (Mårtensson *et al.*, 1999; Bozkurt *et al.*, 2000). Carbon dioxide is released to the air and to some extent dissolved as bicarbonate in the aqueous phase. The acids are neutralised by the bicarbonate present but when the bicarbonate is consumed the pH decreases. The remaining organic material is more resistant to degradation and is stabilised as humus-like substances (Persson, 1996; Prantl *et al.*, 2006). The landfill material and the peat soil used in this experiment had an organic matter content based on loss on ignition of around 30% and 70% of dry matter, respectively.

The artificial ageing of landfill material conducted as aeration over 14 months resulted in an increase in the cation-binding capacity (sodium–binding capacity) and an increase in the ability to bind divalent copper ions (Paper II). The peat soil that was used as a reference did not show any increase in sodium-binding capacity, but the copper-binding capacity proved to be considerably lower, approximately 60% of the sodium–binding capacity. This is explained by the ability of copper to form strong complex bonds with organic material, and therefore it is not possible to recover the

added copper ions. The ability to form strong complexes has been described previously (Gregor *et al.*, 1989; Logan *et al.*, 1997; Österberg *et al.*, 1999; Brown *et al.*, 1999). Logan *et al.* (1997) also show that peat and humic acid have a higher capacity to bind Pb^{2+} than Cu^{2+}. The increased capacity of the landfill material to bind copper ions is explained by the formation of secondary minerals such as FeOOH that have oxide surfaces with a negative charge. The formation of FeOOH and the ability to bind metals have also been commented on in several reports (Bozkurt *et al.*, 2000; Kendall, 2003; Ettler *et al.*, 2008). Poorly humified peat has a good capacity to bind metals (Ringqvist & Öborn, 2002; Ringqvist *et al.*, 2002). According to Bozkurt *et al.* (2001), peat is a potential analogue to landfill organic material, so the metal-binding capacity can also be explained by that, although FeOOH is the most likely explanation.

The sequential analysis of the landfill material showed a transformation in distribution between the extracted fractions (Paper II). More sulphur was water-soluble in the aerated landfill material, indicating that sulphides had been dissolved. A small increase in metals in the aerated landfill material (Zn > Cu, Cd, Ni,) was found in the exchangeable and oxidisable fractions. This indicates a risk for increased mobility when the landfill is oxidised. An investigation by Flyhammar & Håkansson (1999) in which the material was oxidised for 15 days showed a small increase in more reactive binding forms of Pb, Cd, Zn and Fe. Their finding of Fe in a more reactive form is not consistent with the results for landfill material in Paper II, where Fe was found in the residual fraction. In the peat soil used as reference, a proportion of the Fe was found in the oxidisable fraction. The differences between the investigations may originate from differences in treatment time or material. In this investigation Pb was found in the residual fraction, both in the original and in the aerated landfill material. In the investigation conducted by Prudent *et al.* (1996), Pb was found in more soluble fractions. The difference in results between the investigations can be explained by differences in the original wastes. Prudent *et al.* (1996) found most of the Pb in wood waste, while at Högbytorp the scrap metal content influenced the Pb speciation. The sequential analysis of the peat soil did not show any changes in the distribution between the fractions.

Aeration of landfill material has been utilised by several authors to simulate the ageing process in landfills whereby oxygen is expected to intrude dissolved in rain water or in air (Mårtensson *et al.*, 1999; Heyer *et al.*, 2005; Prantl *et al.*, 2006). A risk of increased metal release when oxygen

intrudes into landfill was indicated in studies by Mårtensson *et al.* (1999) and Bozkurt *et al.* (2000). Prudent *et al.* (1996) concluded from their investigations that the origin of the contaminating metal is crucial for its rate of release. In German studies by Hantsch *et al.* (2003), Heyer *et al.* (2005) and Ritzkowski *et al.* (2006), aeration was carried out in order to stabilise the organic material and prevent methane production. No increased leaching of metals was reported in those studies. The work presented in Paper II demonstrated that the aerated ('aged') landfill material had a higher capacity to bind copper ions (divalent) than original landfill material, but also that the more easily soluble fractions were augmented. The effect on the solid landfill material appears to be that the increased binding capacity achieved compensates for the dissolved sulphides.

A study on the composition of material in the landfill at Högbytorp by Aulin & Neretnieks (1996), based on recording of incoming wastes, showed that the total metal content was approximately 71 10^3 tonnes. Deposited sulphur was considered to contribute to the binding of 5% of the metals as sulphides. The calculations in Paper I based on total analyses of three randomly chosen sampling sites showed that approximately 30% of the metals could be bound as sulphides. Sequential leaching performed by Ecke & Lagerkvist (1993) and Flyhammar (1997) revealed that hydroxides and carbonates are also important factors for metal retention. These findings are supported by this thesis. In the present work, calculations with the computer programme Medusa indicated the importance of hydroxides and carbonates in retaining metals in the landfill. The calculations also indicated that pH is a key factor in maintaining stability.

4.2.2 Effects in the aqueous phase

The aqueous phase of landfills contains a mixture of dissolved inorganic and organic carbon species (DIC and DOC, respectively), inorganic macrocomponents and dissolved metal ions. DOC in leachate has been characterised in several studies (Calace *et al.*, 2001; Kang *et al.*, 2002) which show that the humic acid content increases with increasing age of the landfill. Investigations carried out on leachate water have shown that colloidal particles are also present in the leachate (Jensen & Christensen, 1999; Baun & Christensen 2004; Paper III). According to the literature, DOC and colloids bind and transport metal ions. In this investigation we found that the majority of the DOC in the aqueous phase occurred as low molecular weight compounds. During aeration DOC and DIC are largely removed, so that less than 5% remains of the original organic substance

(Table 4). This work confirmed that DOC and colloids bind and transport metal ions. It also showed that artificial ageing by aeration degrades DOC, which means that the dominant transporting ligand is missing.

Table 4. *Effects of ageing landfill material on content of dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) before and after dialysis (cut-off 8000 Da)*

	Before dialysis		After dialysis	
Sample	DOC	DIC	DOC	DIC
	mg C L^{-1}	mg C L^{-1}	mg C L^{-1}	mg C L^{-1}
Original landfill material	2700	160	220	22
Aerated landfill material	100	40	40	7

Acid–base titrations were performed to determine the proton-binding capacity of the material in the aqueous phase. In the aqueous phase of the original material, the dissociation constant pK_a for organic material was found to be 4.8 ± 0.1 for aliphatic acids, a group of short-chain acids that includes acetic acid, and pK_a 3.1 ± 0.1 for other organic material. The titration also indicated pK_a 6.3 for carbonic acid. In addition, particles of calcium carbonate were found. In the aqueous phase of the artificially 'aged' (aerated) material, the low molecular weight carbon was consumed, but it was possible to determine pK_{a1} for high molecular weight material. Carbonic acid was also present but at a lower concentration. Values of pK_a in the range observed here are confirmed by Bergelin *et al.* (1997).

The copper titrations showed that copper ions in the original landfill formed complexes with carbonate and to some extent with the low molecular weight organic material. In the aged landfill, where the low molecular weight compounds were consumed, high molecular weight material increased the importance of the metal-complexing agent, here illustrated by copper complexation. Inorganic complexes form as long as the pH is appropriate.

Paper III showed that the original leachate water contained large amounts of low molecular weight DOC that can bind and transport metal ions. In the aerated ('aged') landfill the low molecular weight DOC had been consumed and thus the main transport agent for metal ions was absent.

The titration analysis showed that recovered organic and inorganic carbon in the aqueous phase of material used in the experiment had the

ability to bind and transport metals. This finding confirms the results of other studies that DOC and carbonate are important ligands for dissolved metals in leachate plumes (Jensen & Christensen, 1999; Christensen *et al.*, 2001). The oxidation of the landfill material reduces the DOC content as well as the carbonate content in the aqueous phase (Paper III). This means that transporting ligands decrease in the aqueous phase when landfills are oxidised.

4.2.3 Transport and retention of metals

The leaching experiment showed that only small amounts of the metals added were recovered in the leachate. The leachate from the original landfill material contained visible amounts of particles, the amount decreasing with time during the leaching period. The first leachate collected was rust-red, followed by leachates with less intensive colour. The amount of particles visible in the leachate from original landfill material also decreased over time. The leachate from the aerated landfill material was colourless and did not contain visible particles. The pH in the landfill leachate was in the range 7.3-7.8 and in the leachate from the peat soil 4.9-5.3. Analysis of the filtered leachate showed decreasing DOC values over time and decreasing values of sulphur and metals, recovered at concentrations above the detection limit of the ICP equipment used. The decrease in DOC was probably caused by wash-out during leaching. As expected, the two factors that controlled the redox conditions in the landfill, DOC and iron, changed during aeration. The DOC content decreased and iron was precipitated in the landfill. The dissolution of particles in the leachate from the original landfill showed high iron contents in the particle fraction. Dissolution also revealed copper and nickel to be bound to particles >0.45 μm. In the filtered leachate from both original and aerated landfill material, there was a strong positive correlation between DOC and Ni and Cu. For Cd, Cu, Fe, Ni and Pb, the dissolution of particles >0.45 μm indicated that particulate transport is important. The leaching experiment also showed the sulphur content in the leachate from the aerated landfill material to be higher than in that from the original landfill material. This indicates that dissolution of sulphides in landfill material is a slow process. Table 5 shows changes in DOC, S, Fe, Cd, Cu, Ni and Pb due to aeration and also estimated content in particles. The leachate from the column with peat soil had a low content of metals, which showed that the organic material had a high capacity to retain metals even though pH ranged from 4.9 to 5.3 in the leachate.

Table 5. *Effect of ageing of a landfill on changes in dissolved organic carbon (DOC), S, and some metals in leachates (range in which values decreased over time)*

Material	Leachate treatment	DOC	S	Fe	Cd	Cu	Ni	Pb
		mgL^{-1}	mgL^{-1}	mgL^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}
Original landfill	Leachate <0.45 µm	110-2900	13 – 120	0.4-35	<1	<15	<6-24	<10
Aerated landfill	Leachate <0.45 µm	25-150	220-1000	<0.1-0.1	<1	<15-53	10-58	<10
Original landfill	With dissolved particles			50-220	<1-1.5	<15-75	<6-50	<10-15
Aerated landfill	With dissolved particles			<1	<1-1.2	<15-80	6-115	<10-13
Aerated peat	Leachate <0.45 µm	170 – 310	16 – 450	0.9-1.2	<1-1	<15-39	13-14	<10

The results from the column leaching experiment are presented in greater detail in Paper IV. Overall, the experiment showed that landfill material had the capacity to bind metals. The amounts of Cu and Ni were slightly higher in leachate (filtered 0.45 µm) from the oxidised landfill and both elements had a strong correlation with DOC. Cu and Ni were transported bound to organic particles. The titration described in Paper III also indicates binding to carbonate. It is probable that both inorganic and organic colloids transport copper. The distribution calculation identified the formation of inorganic copper complexes in the leachate water as the most likely form at the ambient pH, and with particles >0.45 µm. This conclusion confirms findings by Øygard *et al.* (2007). According to the distribution calculation, nickel is bound to organic ligands. Prudent *et al.,* (1996) emphasised the risk of contamination by trace metals bound to organic matter in fine particles. The levels of Cd and Pb were not affected by the aeration and no correlation with organic material was found. Dissolution of particles revealed particulate transport. The small amount of metal ions that was not retained in the material was transported as carbonates, colloids, hydroxides or with organic ligands depending on the preference of the transported metal. The particulate transport of metals has been reported by others (Ward *et al.*, 2005; Baumann *et al.*, 2006; Øygard *et al.*, 2007). Baumann *et al.* (2006) also reported that the colloids formed can contribute to a self-sealing system in the landfill.

In the leaching experiment the lowest metal concentrations were found in the last leachate collected (after 65 days). The slow kinetics contributed to

metal retention. Table 6 presents the mean annual values in leachate from the Högbytorp landfill.

Table 6. *Chemical oxygen demand (COD), sulphate and concentrations of some metals in leachate from the Högbytorp landfill (Miljörapport 1997-2000)*

Year	COD	SO_4^{2-}	Fe	Cd	Cu	Ni	Pb
	$g\ L^{-1}$	mgL^{-1}	mgL^{-1}	$\mu g\ L^{-1}$	$\mu g\ L^{-1}$	$\mu g\ L^{-1}$	$\mu g\ L^{-1}$
2000	2.50	104	7	0.9	26	440	22
2001	1.56	n.a	n.a.	0.6	110	170	20
2002	1.23	n.a	n.a.	0.02	31	440	5.8
2003	1.95	n.a	n.a.	0.6	110	170	20
2004	8.00	n.a	n.a.	<0.45	39	530	11
2005	2.40	n.a	n.a.	0.33	34	300	14

n.a. = not analysed

The variation in metal concentrations in the leachate is considerable. The mean values for 2000 were based on 10 sampling occasions and the variation observed for Cd was 0.08-3.9 $\mu g\ L^{-1}$, for Cu 3.7-51 $\mu g\ L^{-1}$, for Ni 23-3300 $\mu g\ L^{-1}$ and for Pb 0.8-22 $\mu g\ L^{-1}$. In 2001 the corresponding variation in metal concentration for Cd was 0.16-1.5 $\mu g\ L^{-1}$, for Cu 15-440 $\mu g\ L^{-1}$, for Ni 15–340 $\mu g\ L^{-1}$ and for Pb 4.5-54 $\mu g\ L^{-1}$. The leachate flow varies throughout the year, with the mean values 1988-2001 showing a minimum in the summer, with a monthly leachate flow around 4000 m^3, and a maximum in the winter, with a monthly flow of 10 000 m^3 (Miljörapport Högbytorp, 1997–2006). The metals that were present in high concentrations in the leachate water from the landfill were the most mobile and were more readily released from the landfill material.

4.2.4 Current status of the landfill

During the ageing process, the low molecular weight organic material is consumed. The more resistant material is transformed to humus-like substances. During this transformation the redox buffer changes from low molecular weight material that constitutes the redox buffer region around pe -5 (reducing conditions) to the humic buffer with pe 3 (slightly oxidising). When this occurs the sulphides dissolve. As long as carbonate is present in abundance the metals will be re-precipitated as carbonates and also as hydroxides. The humic material formed will also be able to bind metals. This transformation has also been described by others (Bozkurt *et al.*, 2000; Fannin & Roberts, 2006; Prantl *et al.*, 2006). It is difficult to predict the time for stabilisation of the organic material in the landfill under the current anaerobic conditions, but it is known that it will take generations. Bozkurt *et*

al. (2000) have simulated oxidisation of 10-m thick landfill in different scenarios and have found that in uncovered landfill it will take 600 years, in covered landfill 30 000 years and in fully water-saturated covered landfill it will take >500 000 years.

As demonstrated, the landfill at Högbytorp consists of two layers, an upper part that is not fully saturated with water and a lower saturated part. The water level is at present at approximately 10 m below the landfill surface. Continuous degradation of organic material will produce water but it is not clear at present whether the amount of water produced will be sufficient to maintain the groundwater at its current 10 m level. Assuming that the calculations made by Bozkurt *et al.* (2000) are correct, complete oxidation of the Högbytorp landfill will take more than 30 000 years, with the composition of the cover determining the actual rate. Whether oxidation of the landfill takes 30 000 or 100 000 years is perhaps not the most critical question. This generation has deferred the responsibility for solving this problem to future generations.

In the coming decades the methane production will most likely continue, since it was found that the substrate (DOC) is abundant. When the methane production ceases and the landfill starts to oxidise, a risk of a slight increase in metal release is indicated by my study of binding forms (Paper II), but the levels will still be very low. An interesting observation is that when humic compounds begin to dominate, the redox conditions probably will transform to more oxidising with pe ≈3 where sulphides starts to dissolve. If DOC is still present then metal transport can increase. The column experiment conducted showed decreasing metal release over time (Paper IV). When the landfill has stabilised it can be concluded that the metal leaching will cease since the metals are retained in the landfill. An increase in sulphate in the leachate will almost certainly occur.

Stigliani *et al.* (1991) describes the Chemical Time Bomb, meaning the chemical load created by man in the 200 years since the beginning of the industrial revolution. The main effect is climate change and the associated changes in chemical and biological conditions in soils. The acidification of soils will release metals currently bound in soils, but the question is whether this is applicable to landfills and whether changes in chemical conditions will trigger a sudden release of metals from landfills. Flyhammar *et al.* (1998) and Bozkurt *et al.* (2000) concluded in their investigations that landfills have a high buffering capacity that will maintain their stability for very long time.

From data presented here I conclude that the organic material, when stabilised as humus, acts as a powerful buffer and also as a powerful complexing agent for metal retention. The critical factor with respect to metal transportation out of the landfill is DOC, which also complexes and transports metals.

Stabilised organic material contributes to landfill stability in terms of metal leaching through its ability to form stable humic compounds. One environmental concern with landfills containing organic material is the emission of greenhouse gases. Another is the fact that in old landfills there is a high possibility of finding persistent organic compounds that have now been phased out from use.

A landfill such as that investigated here, representing a common type in Sweden and containing large amounts of old industrial and construction wastes and sludge from different sources (Aulin & Neretnieks 1996), will be an environmental concern regarding production of xenobiotic end-products, although several have been found to be degradable (Christensen *et al.*, 2001).

From the results obtained here, two possible ways to manage old landfills in the future can be suggested. One way is to continue as at present, allowing slow anaerobic degradation of the organic material and collecting the methane to minimise the environmental impact. This will result in a need for management and monitoring as long as methane is produced. Another management strategy could be to apply forced oxidation, which will end methane production. This will temporally increase the release of metals but the leaching of metals will most probably cease thereafter. After oxidation is completed the metals will be bound as carbonates, hydroxides or bound to charged oxide surfaces as long as the pH is maintained around 7.5. If pH should decrease the stabilised organic material will control the retention of metals. As described earlier, the 'breaking point' in the distant future under current management, when the organic compounds change the redox conditions and thereby the metal binding form, will require environmental monitoring. The organic material in the landfill acts both as a friend and foe depending on the circumstances.

5 Conclusions

- In the Swedish landfill studied here, it was possible to distinguish two distinct layers with different characteristics as regards water, carbon and metal content. As a consequence, different chemical processes regulate the fate of metals in the upper part and the lower part of the landfill.

- Landfill material has the capacity to bind additional metal ions as well as those dissolved at present.

- Metal transport relies on inorganic and organic colloids or carbonate, depending on the preferences of the individual metal. Therefore reducing the transporting ligands is an effective way to reduce metal transport.

- The stability of metals in the landfill is regulated by the pH and the redox buffer.

- Oxide surfaces such as FeOOH are important for metal retention. Since iron is abundant in landfills, oxidation provides many binding sites for metals.

- The stabilised organic material in landfills retains metals in landfills and in that respect the organic material is a friend.

- Dissolved organic carbon can bind and transport metal ions and is thus a foe in the environmental perspective.

6 References

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