A STUDY OF HEAVY METALS IN SOILS OF THE FORMER UNITED STATES NAVAL BASE, ARGENTIA, NEWFOUNDLAND

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ABSTRACT

In contaminated landfill sites, sorption, desorption and mobility of contaminants are important properties that should be studied thoroughly before taking any remedial measures. Ssamples from five soil sections were taken from a landfill site at the former United States Naval facility at Argentia, Newfoundland. Total metal contents were analyzed by XRF and ICP-MS. Available cadmium content was determined by the EDTA extraction method using GF- Atomic Adsorption Spectrometry. High levels of Sr, Zn, Pb, Fe, Ti and Zr were found in these soil samples. Soil samples have variable pH (4.64 to 7.78), organic carbon content (0.03 to 7.49 %), CEC (0.6 to 10.2 cmole(+)/Kg), bulk density (0.994 to 0.638 Mg/m^3) and soil texture (as sandy, sandy loam, sandy clay loam, loamy sand, loam, silty loam and clay loam). They are classified using USDA soil textural classification.

Batch sorption and desorption experiments were carried out for all samples, and Freundlich isotherms and equations were developed. The results showed that Cd sorption increased with increasing depth in two sections and decreased in another section, whereas the other sections showed a variable behavior. Cadmium sorption increased with increasing soil pH, organic carbon content and clay content, whereas it decreased with increasing sand percentage.

The results revealed a possible relationship between Cd sorption and associated anions. In particular, sorption decreased with increasing Cl^- content of the soil samples in section V. This was attributed to the formation of $CdCl^+$, which is less readily sorbed than Cd^{2+}. The results of desorption experiments showed a positive relationship between sand

content and Cd desorption. The amount of Cd retained in profile IV decreased with increasing calcium content, which might be due to the competition of calcium for Cd sorption sites.

A possible relationship between the pH and sand content with Cd mobility was studied by soil thin layer chromatography. The soil samples that showed lower pH values and higher sand percentage also showed high Cd mobility; therefore, the lower the pH and higher the sand percentage, the higher will be the Cd movement to the lower soil layers and groundwater.

ACKNOWLEDGEMENTS

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ARG	Argentia Remediation Group
SLF1	South Landfill Site I
USDA	United States Department of Agriculture
ASV	Anodic Stripping Voltammetry
GF-AAS	Graphite Furnace Atomic Absorption Spectrophotometer
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
XRF	X – ray Fluorescence Spectrometry
CEC	Cation Exchange Capacity
OC	Organic Carbon
C_{org}	Percent Organic Carbon content of soil
Mg/m^3	Mega gram per cubic meter
mè/100g	milli equivalent per 100 gram of soil
SPSS	Statistical Package for the Social Sciences
μM	micro molar
$\mu molL^{-1}$	micro mole per liter
K_d	Freundlich Sorption Constant

CHAPTER 1

INTRODUCTION

The recent increase in disposal of heavy metals into soils has been widely considered as one of the most dangerous environmental hazards. There has been increasing concerns about the accumulation of heavy metals, such as cadmium, lead, arsenic etc. in soils and their subsequent movement to surface water and groundwater (Tiller 1989, Naidu *et al* 1996). The movement of heavy metals in soil profiles has received considerable attention (Li and Shuman, 1997), since even a slow transport through soil and subsoil materials may result in an increased heavy metal content in groundwater.

This increased metal content and mobility in soils has resulted from various anthropogenic practices such as widespread use of sewage sludge as a soil amendment (Lamy *et al.*, 1993) and the use of fertilizers and agrochemicals that contain toxic metals (Jones *et al.*, 1987). Apart from this, leachates from landfills often contain high levels of toxic elements. One of the issues of greatest concern on the impacts of an existing or a proposed landfill is the pollution of groundwaters by landfill leachate (Lisk, 1991 and Lumbsdon *et al.*,1995). Even a small amount of landfill leachate can pollute large amount of groundwater, rendering them unusable for domestic and other purposes. Further, accumulation of salts can influence the release of toxic metals from the landfills to the subsurface soils and groundwater (Lumbsdon *et al.*, 1995)

1.1 Objectives

Cadmium (Cd) is considered one of the common mobile elements in a soil profile, and the movement of Cd in soil is representative of the transport of other metals in soil (Biddappa *et al.* 1982). The fate of Cd that reaches the soil from anthropogenic sources depends essentially on its sorption and mobility in the host medium, which in turn depends on various soil properties such as pH, soil texture, organic carbon content and cation exchange capacity (CEC). Hence, the sorption and mobility of Cd in different types of soil is of potential interest for determining the Cd loading capacity of a given soil and the distribution of this element in the soil profile. These data can also be of further use in predicting subsequent Cd movement to groundwater and to nearby marine environments.

Environmental site assessments conducted by the Argentia Remediation Group (ARG) found that the former US Naval facility located at Argentia, Newfoundland, Canada is contaminated with several heavy metal species and organic pollutants (ARG, 1997). Various military activities had resulted in elevated concentrations of heavy metals, particularly Cd, Pb and Cr, in soils and groundwater. This is considered to be a potential threat for aquatic, plant and human populations. The present work is focused on the main dump site, South Land Fill Area (SLF1) of the former US Naval Base, Argentia. The hypothesis is that the groundwater is impacted by the downward movement of heavy metals in the soil horizons and this depends largely on the nature of the soils.

The major objectives of this research are:

a) To determine the concentration of heavy metals in the soil profile of SLF1 of the former US Naval Base, Argentia.

b) To determine the Cd sorption and desorption behavior of the soil samples.

c) To characterize and classify the soil samples of the study area.

d) To find the relationship between soil texture, pH, CEC, OC content and soil metal sorption.

e) To study the movement of Cd in the soil by thin layer chromatography.

1.2 Argentia Naval Base

1.2.1 History and Topography of the Site

The former US naval base at Argentia, on the western coast of the Avalon Peninsula of Newfoundland, was constructed and operated by the US Navy during World War II. It was one of the biggest US naval bases (4047 hectare) outside of the US. The US Navy closed this base in September 1994 after 54 years of service. They buried a variety of damaged military vehicles and other materials in various landfills located inside the base. Among these, the South Land Fill (SLF1) area was the main dump site. The US Navy reportedly graded the site on closeout and placed 150 mm of topsoil and grass throughout a large portion of SLF1.

The SLF1 site has a relatively flat topography with only a few undulations. Elevations range from sea level to about 9 m above sea level. In general, the topography of the west-central portion of the site gently slopes towards the Placentia Bay coast, whereas in the northern and western portions of the site, elevations drop sharply by 4 to 6 m to sea level. Wet boggy areas are present in the east and south of SLF1 (ARG, 1995).

1.2.2 Previous Studies and Conclusions

A site assessment conducted by the Argentia Remediation Group (ARG) found a wide range of concentrations of toxic metals in SLF1 soil samples (ARG 1995). For Cd, site 514-MW had the maximum of concentration of 19.1 ppm, compared to background soil levels of less than 0.5 ppm. As far as the groundwater is concerned, most of the SLF1

wells showed increasing heavy metal concentrations from 1995 to 1997 (ARG,1997). SLF1 sites 502-MW, 503-MW, 517-MW and S-MW-9 had the greatest increase in metal concentrations. The following are some of the salient conclusions from the ARG site assessment:

- Unacceptable risks to potential human, terrestrial and aquatic receptors exist at SLF1 from a variety of contaminants being discharged from SLF1.

- Erosion of wastes from SLF1 represents a major potential impact on the marine environment within Placentia Bay.

- Most groundwater from SLF1 discharges into Placentia Bay and contains a variety of contaminants including petroleum hydrocarbons, polychlorinated biphenyls (PCBs), dioxins/furans and toxic metals.

- Soils beneath the SLF1 liquid waste disposal ponds are probably extensively impacted by total petroleum hydrocarbons (TPH) and other contaminants, however, the vertical extent of these impacts was not determined.

- A silt unit may underlie much of SLF1, which will likely limit vertical contaminant migration. Further work however is required to confirm its presence. (ARG, 1995)

1.3 Cadmium in Soil

Cadmium in soil comes from both soil parent materials and from various anthropogenic activities such as dumping of industrial wastes and effluents, agricultural applications of sewage sludge (as soil amendments and manures), fertilizers and pesticides. Generally, Cd concentrations in soils exceeding 0.5 mg/kg are considered to be evidence of soil pollution from one or more of the above – mentioned sources.

1.3.1 Occurrence of Cadmium

Cadmium, a heavy metal, has an average natural abundance of 0.1 to 0.2 mg /Kg. In most primary (bedrock) environments, cadmium behaves as a chalcophile element, i.e., one that combines with sulphur to form sulphide minerals. In general, cadmium replaces zinc in many minerals due to the similar bonding behavior of cadmium and zinc. The cadmium content of different rock types is listed in Table 1.1

Table 1.1 Cadmium content (mg/kg or ppm) for different rock types

Rock	Content (mg/kg or ppm)
Ultrabasic rocks	0.1
Basic rocks	0.2
Felsic rocks	0.1
Archean metamorphic and igneous rocks	0.1
Sandstones	0.02
Carbonates	0.05
Shales	0.2
Black organic-rich shales (North America)	4.0
Permian phosphatic shale (USA)	200

Source: Garrett (1996)

Agricultural materials such as phosphatic fertilizers are widely regarded as being the most common source of Cd contamination in agricultural soils. High concentrations of Cd (up to 500 mg/kg) can be found in phosphorites used for the manufacture of fertilizers. Around 70% of the Phosphatic fertilizers used in the USA are produced from the relatively low-Cd Florida phosphorite, whereas Australian fertilizers generally

contain between 25 and 50 mg/kg of Cd. Phosphatic fertilizers with 3-8 mg/kg of Cd. used in long-term field experiments at Rothemsted, UK, contributed 2g Cd/ha/yr to an aerable soil and 7.2 g Cd/ha/yr to the same soil under permanent grass (Jones et al., 1987).

Nonferrous metal production, fossil fuel combustion, iron and steel production and waste incineration are some of the major sources for atmospheric emissions of Cd. The OECD (1994) reported Cd emissions in Belgium, Canada, Sweden and USA. Among these countries, Canada recorded the highest Cd emission due to non-ferrous metal production and iron and steel production (120 and 5 t/year, respectively). The USA released the highest Cd due to fossil fuels (244 t/year), waste incineration (22 t/year) and cement production (13 t/year).

Another important source of Cd is sewage sludge. Sewage vary in their composition and contain different levels of Cd based on their sources. Land application and incineration are the two main pathways through which Cd from sewage sludge enters into the environment (Chandler, 1996). Wastes from the plastic industry is also an important source of Cd. Cadmium is mainly used as an additive in the production of pigments and as a heat stabilizer in the plastic industry. Approximately 80 percent of the Cd pigments consumed in the United States is used in the manufacturing of plastics (Cook and Atherton, 1996). Other major sources of Cd which can cause soil contamination are mining, land fill leachates, ore-dressing and smelting of Cd-containing sulphide ores which can contain up to 5% Cd. Soils severely polluted by Pb-Zn mining and smelting have been found to contain up to 750 mg/kg of Cd (Alloway, 1995).

From a Canadian point of view, the available data compiled by Environment Canada indicates that an estimated total of 159 tonnes of Cd are released into the Canadian environment each year. Approximately 340 tones of Cd slag, sludge and solid waste are estimated to be disposed on land. According to available estimates, base metal smelters (primarily lead and zinc) account for the largest percentage (82%) of total Cd released into the Canadian environment (Canadian Environmental Protection Act, 1994).

1.3.2 Chemistry and Environmental Chemistry of Cd

Cadmium is a member of Group IIB (12) of the periodic table and is a relatively rare metal, being 67th in order of elemental abundance. Cd is mainly found in zinc, lead-zinc and lead-copper-zinc ores. Its geochemical behavior is similar to that of zinc because of the similar electron structures and ionization potentials of the two elements. In nature, Cd is nearly always present in the Cd^{2+} oxidation state.

It is important to be able to identify the forms of metals in soil, particularly in the soil solution, in order to more fully understand the dynamics of the metal in natural and agricultural ecosystems. The toxic effect of a metal is determined by its form as well as by its concentration. The free ion Cd^{2+} is more likely to be adsorbed on the surfaces of soil solids than are neutral or anionic species of Cd (Naidu *et al.*, 1997). Cd^{2+} is the principal species of Cd in the soil solution, but the metal can also form ions such as $CdCl^{+}$, $CdOH^{+}$, $CdCl_4^{2-}$, $Cd(OH)_3^{-}$ and organic complexes (Alloway, 1995). Cd^{2+} is more soluble than Zn^{2+} in acidic oxidizing solutions, and is rated as having medium to high mobility in well-drained acid soils. This high mobility is attributable to the fact that Cd^{2+}

adsorbs rather weakly on organic matter, silicate clays, and oxides unless the pH is higher than 6. Above pH 7, Cd^{2-} can co-precipitate with $CaCO_3$ or precipitate as $CdCO_3$, and Cd phosphates may limit solubility as well. Therefore, mobility and bioavailability of Cd in neutral to alkaline soils is relatively lower than in acid soils (McBride, 1994).

1.3.3 Cadmium in Soils and Soil Profiles

The average abundance levels in soils are in the 0.2 to 0.3 mg Cd/kg range, but can vary significantly in different places due to differing parent material geochemistries and pedological processes (Table 1.2).

Table 1.2 Average Cd content (ppm or mg/kg) for surface soils of different countries

Country		Cd content (mg/kg)
Canada	-Prairies	0.28
	-Ontario	0.56
U.S	-Western Region	0.33
	-North-Central Region	0.37
	-Northeast	0.17
	-Southern	0.16
Austria		0.20
Belgium		0.30
Denmark		0.30
England and Wales		0.24
France		0.74
Germany		0.52
Netherlands		1.76
Norway		0.95
Scotland		0.47
Sweden		1.17

Source: Garrett (1996)

One of the main factors determining the Cd content of soil is the chemical composition of the parent materials. Furthermore, soils developed on rocks containing similar levels of Cd may have significantly different Cd levels by virtue of the amount of clay minerals, Fe and Mg sesquioxides, and organic matter present in different horizons within the developing soil profile.

Recent data on concentrations of Cd in Canadian soils are limited. Bewers *et al.*(1987) reported that mean concentrations of Cd in rural, urban, and agricultural soils from across Canada (more than 350 sites in total) ranged from 0.56 to 1.1 mg/kg. Higher levels have been reported in the vicinity of industrial plants and urban areas, especially near known sources of Cd. Pip (1991) reported that the Cd content of garden soils collected up to 12.8 km away from a copper/zinc smelter in Flin Flon, Manitoba contained a mean concentration of Cd of 5.2 mg/kg. Cadmium levels in peat samples collected from 1.0 to 3.7 km away from a copper smelter (Rouyn-Noranda, Quebec) ranged from 54 to 66 mg/kg, while samples collected 25 to 43 km away from the smelter contained between 5.5 to 7.8 mg/kg (Dumontent *et al.*,1990).

Berrow and Mitchell (1980) observed that Cd, like Zn, was higher in soils formed from basic igneous rocks than in soils formed from other rock types. Adriano (1986) observed Cd levels (<1 mg/kg) were fairly uniform throughout the profile, and apparent mobilization also occurs in very poorly drained profiles. They also noticed that most of the Cd is originally complexed in the upper horizons rich in organic matter. Soils contaminated by smelting operations showed Cd concentrations close to background level at a depth of about 30 to 40 cm. Although high concentrations were observed in the top soil layers, some studies found movement of Cd to a depth of at least 30 cm, and in

one case, to at least a depth of 3.5 m (Adriano, 1986). Streck and Richter (1997a) found Cd displacement to below 0.7 m depth in a wastewater irrigated site in the city of Braunschweig (Germany).

1.4 Cadmium Sorption and Factors Influencing Cd Sorption

Sorption is one of the most important processes which governs the transport of Cd in soil (Boekhold and van Der Zee 1991). Cd entering into soil can be retained by both precipitation and sorption. Normally, precipitation appears to be the predominant process in the presence of anions such as S^{2-}, CO_3^{2-}, OH^- and PO_4^{3-}. Sorption of Cd at soil mineral surfaces may occur by both specific and nonspecific processes. Under the conditions that prevail in soil, the lower the solution Cd concentration and the more sites available for sorption, the more likely sorption/desorption processes will determine the soil solution concentration (Brümmer et al., 1983).

Knowledge about the mechanisms involved in the retention and mobility of Cd is an important precursor for the determination of the permissible loading capacity for a given soil and its distribution in the soil profile. Such information is necessary to predict the environmental impact of Cd from anthropogenic sources (Naidu et al., 1997).

Several studies have revealed significant relationships between Cd sorption and soil properties such as pH, organic carbon content, cation exchange capacity, soil texture, and the presence of other metal ions.

1.4.1 Soil pH

Several researchers have studied the effect of pH on Cd sorption. Filius *et al.* (1998) found increased Cd sorption with an increase in pH of sandy and clayey soils of Northern Germany. Figure 1 clearly shows the effect of soil solution pH on Cd sorption (Naidu *et al.*, 1997).

Bolton and Evans (1996) investigated the retention of Cd on selected Ontario soils with a range of soil properties. Batch sorption experiments were carried out at the actual pH of the soil and at a range of pH values adjusted by the addition of acid or base. They found that for all soils Cd sorption increased with increasing pH and with increasing Cd solution concentration. Bolan *et al.* (1999) found that the Cd sorption increased with increasing pH of selected soils of New Zealand. They also found an increase in surface negative charge with an increase in pH and approximately 50% of the increase in surface charge was balanced by Cd sorption.

Figure 1. Effect of pH on soil Cd sorption (Naidu *etal.*, 1997)

1.4.2 Organic Carbon

Heavy metal sorption, particularly Cd sorption, depends on the organic carbon content of the soil. Streck and Richter (1997b) studied the relationship between organic carbon content and Cd sorption in a North-West German sandy soil irrigated under controlled conditions for 29 years with municipal wastewater. They found high Cd sorption was evidenced in soils having high organic carbon content (high 0.73%) and Cd sorption decreased with decreasing organic carbon content (low 0.06%). Further, Bolton and Evans (1996) and many other authors incorporated organic carbon values in sorption isotherms, and justified the significance of organic carbon in Cd sorption.

1.4.3 Cation Exchange Capacity

Al, Ca, Na and Mg are the most common cations in soils and have significant effects on sorption of Cd. Christensen (1984) found that increasing solution Ca^{2+} concentration from 10^{-3} to $10^{-2}M$ reduced the sorption capacity for Cd of a sandy loam soil by 67%. The effect was likely due to either competition between the cations and the Cd species, or to the ionic strength effect on Cd ion activity. The effect of the index cation on sorption of Cd depends on soil type and the affinity of the soil for Cd. The index cation (Ca^{2+}, Na^+ and Al^{3+}) has a marked effect on the amount of Cd adsorbed in low affinity soils, i.e., those with low negative surface charge densities and a low pH (eg., Oxisols). At constant pH and ion concentration, changing the index cation from Na^+ to Ca^{2-} markedly reduces the amount of Cd adsorbed. This decrease in Cd sorption follows the decrease in net negative surface charge density although this could also be partially

due to increased competition between Ca and Cd for sorption sites. This result contrasts with those for high affinity soils, i.e., those with large surface charge densities such as Vertisols and Mollisols. In these soils, at low Cd levels, the cation has only a very small effect on the amounts of Cd sorbed (Naidu *et al.* 1997).

1.4.4 Ligands

The mobility of elements in soils and sediments is also influenced by complexant ligands including inorganic species, such as Cl^- and SO_4^{2-} ions, as well as by organic acids and low-molecular-weight humic substances. Landfill leachates are often reported to contain high concentrations of both toxic metals and complexant inorganic and organic ligands (Bolton and Evans, 1996). The presence of Cl^- ions has been shown to decrease the sorption of Cd ions on a variety of soils (Boekhold *et al*.,1993). Bolan *et al.* (1999) studied the effect of chloride, sulfate, nitrate, and phosphate anions on the sorption and leaching of Cd in two types of New Zealand soils. They reported that sorption of cadmium by variable charge density soils was affected by the associated anions.

1.4.5 Soil Type

In general, clay soils have more Cd sorption capacity than sandy soils. This is due to greater surface area, higher cation exchange capacity and the presence of organic carbon content in clay soils, whereas Cd mobility or transport is normally high in sandy soils compared to clay soils because of its low sorption capacity. In heavily contaminated

sandy or silty soils, the elements translocated to subsoil and groundwater reach an extent where irreversible damage to the groundwater reservoir is possible.

Investigations of Cd sorption has shown that sorption can vary by nearly 100-fold depending on soil type. In general, Cd sorption increased in the following general order: Oxisol<Inceptisol<Ultisol<Vertisol = Mollisol. The Ultisols, Vertisols, and Mollisols dominated by smectite or other 2:1 (2 tetrahedral sheets : 1 octahedral sheet) minerals, adsorb the largest amounts of Cd. Soils consisting mainly of 2:1 layer silicate minerals with high CEC adsorbed greater amounts of Cd than strongly weathered oxidic soils (Naidu *et al.* 1997). In another study conducted in Ontario soils by Bolton and Evans (1996), a simple correlation between Cd sorption and soil properties revealed that percentage clay was the important property influencing Cd sorption.

In general, an increase in soil solution pH increases the Cd sorption in soils. Similarly, the presence of organic matter also directly enhances Cd sorption. As well, complexation and cation exchange are two other important mechanisms which can affect metal sorption and mobility in soils.

1.5 Cd Desorption

The transportation of metals through the soil profile into groundwater is a prime environmental concern. The movement and availability of heavy metals may vary considerably depending on the nature of sorption-desorption processes in the soils. A number of studies have been conducted to establish sorption isotherms of Cd in soils (Section 1.4). Contrary to sorption, only a few publications deal with desorption of heavy

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metals in soils. Filius *et al.* (1998) studied the desorption behavior of Cd in different soils (with different pH levels) containing elevated levels of Cd. Two different desorption techniques were applied: (i) soils were repeatedly (up to 20 times) extracted with Cd-free 0.01 M $Ca(NO_3)_2$ for 8 hours using a constant soil/solution ratio (1:2.5); (ii) soils were shaken with 0.01 M $Ca(NO_3)_2$ solution for 48 hours using various soil/solution ratios (1:2.5 to 1:1000). Filius *et al.* (1998) found that, with the widening of the soil/solution ratio, different soil pH variants released different amounts of Cd. For example, at the lowest pH (4.60) the soil sample adjusting to a solution concentration of 0.1 μM Cd released 50 μmol Cd per kilogram of soil. At the same solution concentration, the soil with the highest pH (6.81) was, however, still sorbing Cd from the solution. Furthermore, they concluded that the contact time of the seeping soil solution with the soil is long compared with the equilibration time needed for desorption. Backes *et al.* (1995) found that 96 to 98% of Cd adsorbed by geothite over one week was desorbed in 0.01M $Ca(NO_3)_2$ within 5 hours. However, they also found that the desorption of Cd from ferrihydrite and manganese oxide soils ranged from only 8 to 38% under the same conditions. These studies suggest that more than 90% of Cd can rapidly desorbed in substrates with variable charge surfaces and low CEC, impacting both soil-plant transfer and mobility in the soil environment (Naidu *et al.*, 1997).

1.6 Batch Experiments and Sorption Models

A sorption isotherm refers to the relationship of the concentration of contaminant accumulated in the soil with its equilibrium concentration in solution. This is determined

by either batch sorption experiments or column tests. Two models are widely used to describe the results of sorption experiments – Freundlich and Langmuir. The choice of the model is largely based on its usefulness and simplicity. In many cases it has been found that Cd sorption by suspensions of soils or their constituents fits either Freundlich or Langmuir isotherm equations. The choice of the model is not critical in the case of Cd. since Cd is usually well below saturation when realistic concentration ranges are used (Alloway. 1995).

The Freundlich equation is perhaps the simplest approach for quantifying the behavior of retention of reactive solute with the soil matrix and is used in this study.. It is considered one of the oldest of the nonlinear sorption equations and has been used widely to describe solute retention by soils. The Freundlich equation is:

$$S = K_d \, C^b$$

Where 'S' is the amount of solute retained by the soil (mg/kg), 'C' is the solute concentration in solution in μg/mL. 'K_d' is the distribution coefficient (Freundlich sorption constant) and 'b' is an exponent constant (Selim. 1992). There are numerous examples for solute retention. especially cadmium retention, which are described successfully by use of the Freundlich equation (Kookana *et al* ., 1994, Naidu *et al*., 1997. Filius *et al*., 1998 and Bolan *et al.,* 1999).

Batch sorption experiments were carried out by many researchers to find out the solute retention in soils. In one study by Bolan *et al.* (1999). the sorption of Cd was measured using initial concentrations of 0.1 M KCl, 0.1 M K_2SO_4. 0.1 M KNO_3 and 0.1 M KH_2PO_4 solutions. Soil samples were mixed with cadmium solutions at a soil:solution

ratio of 1:30 at room temperature (20°). At the end of the shaking period, the supernatant solution was separated from the soil by centrifugation and filtration and cadmium concentration was measured in the solution using atomic sorption spectrophotometry. The amount of sorbed ions was calculated from the difference between the amount added and that remaining in the solution after equilibration. A variety of matrix solutions, such as $Ca(NO_3)_2$, $CaSO_4$ and Na_2SO_4, were used in the batch experiments. $Ca(NO_3)_2$ is the commonly used electrolyte solution, because Ca^{2+} is the most common cation under aerable conditions.

1.7 Cadmium Mobility

Environmental hazards derived from heavy metals are closely linked to metal mobility and thus to the concentrations of the metals in the soil solution. These heavy metals in the solution can be transported down the soil profile and possibly enter groundwater. Metals and pesticide mobility in soils have been investigated by leaching of soil columns (Boyle and Fuller, 1987) or by thin layer chromatography (Helling and Turner, 1968 and Martén and Camazano, 1993). With Cd in particular, a number of leaching studies has been conducted to establish Cd mobility in soils (Lamy *et al.*, 1993, Schirado *et al.*, 1986 and Li and Shuman 1997). However, only very few references are available on Cd mobility using thin layer chromatography. Martín and Camazano (1993) found that the lower the pH and the clay content, the higher the Cd mobility in soil will be, since high pH values favor the exchange of Cd by other cations and a high clay content favors retention by the constituent minerals.

CHAPTER 2

EXPERIMENTAL

2.1 Reagents

For all experiments. water used (referred to as Nano-pure water) for dilution and rinsing was distilled and then deionised with a NANOpure II system (Barnstead). Fisher Scientific pH buffer solutions (4.0, 7.0 and 10.0) were used for calibrating the pH meters. Potassium chloride (Suprapur) used as electrolyte was purchased from BDH Inc. Concentrated hydrochloric acid, nitric acid and ammonia used for the preparation of solutions and for final rinsing were Seastar double sub-boiling distilled in quartz. Fisher 1000 mg/L atomic absorption spectrometry Cd standard solution was used for preparing Cd standard solution. Fisher Scientific trace metal grade nitric acid was used for cleaning sample bottles. Sodium hydroxide, sodium chloride, hydrogen peroxide, orthophosphoric acid, sodium acetate and potassium dichromate were purchased from BDH Inc and were ACS analytical grade. The following ACS analytical grade reagents were used; calcium chloride (ACP), ferrous ammonium sulphate (Fisher Scientific), ammonium oxalate (Fisher Scientific), calcium nitrate (Anachemia Ltd) and ammonium acetate (Fisher Scientific).

2.2 Materials

A filter holder which held a 0.45 μm millipore filter membrane (HA type, Millipore Corporation) was used with a 10 mL syringe to filter small amounts of sample

before ASV analysis. Whatman® No 1, 5 and 42 filter papers were used for other experiments.

Polyethylene conical centrifuge graduated tubes (45mL VWR Scientific Products) were used for the sorption and desorption experiments. These tubes and the bottles for sample solutions and reagent storage were cleaned in the following way. First, the tubes and bottles were rinsed with tap water and placed in a 5% micro detergent (Cole-Parmer Instrument Company) bath for 24h. Next, they were filled with 6M reagent grade HCl and soaked in a 2M reagent grade HCl bath for 2 weeks. Finally the bottles were rinsed with 2M HNO_3.

2.3 Instruments

2.3.1 pH Meter

A Chemtrix pH meter (type 60A) with a glass electrode (Broadley James Corporation) and a portable Orion pH meter (model 290A) with a glass electrode (model 9107BN) were used to measure the pH of soil samples in the laboratory. The pH meter was calibrated daily using three buffer solutions pH=4.00, pH=7.00 and pH=10.00. For field pH measurement, the same portable Orion pH meter with a glass electrode was used. The pH meter was calibrated before taking the field pH measurement using the same standard solutions.

2.3.2 Anodic Stripping Voltammetry

The Cd content of the soil extractant was analyzed using Anodic Stripping Voltammetry (ASV). The instruments used for this were an EG & G Princeton Applied Research (PAR) model 174A Polarographic Analyzer and a 303A SMDE (Static Mercury Drip Electrode). 10 mL of filtered soil extractant was accurately pipetted into a Teflon cell and 250 μL of 1M HAc/NaAc buffer solution was added to maintain the pH. Then, 250 μL of 1 M KCl (electrolyte) was added to the soil solution/buffer mixture. The solution was purged with N_2 for 8 minutes. A deposition time of 8 min was used. The equipment was controlled using M394 Analytical Voltammetry Software (EG & G Instruments) on a PC computer. Calculations performed on the peaks give the free ion Cd concentration.

2.3.3 Graphite Furnace Atomic Absorption Spectrophotometer

The available Cd content of the soil was determined using a PC-controlled (software: SpectrAA-220 version.3) Varian Spectra AA 220 Zeeman Graphite furnace atomic absorption spectrophotometer. Both single and UltrAA Cd lamps were used in this experiment. A representative aliquot of a sample was placed in the graphite tube in the furnace, evaporated to dryness, charred, and atomized. The following instrument parameters were used for Cd determination.

Instrument mode   : Absorbance

Calibration mode   : Standard additions

Measurement mode   : Peak height

Inert Gas	: Nitrogen
Wavelength	: 326.1nm
Slit width	: 0.5 nm
Lamp current	: 4.0 mA

2.3.4 Inductively Coupled Plasma Mass Spectrometry

Total metal concentrations of digested soil samples were determined by using the Department of Earth Science, Memorial University's Inductively Coupled Plasma Mass Spectrometry (ICP–MS).

2.3.5 X-ray fluorescence spectrometry

The data was collected using a Fisons/ARL (Mississauga, Ontario) model 8420 sequential wavelength - dispersive X-ray spectrometer in the Department of Earth Science, Memorial University . This is equipped with one goniometer, which is capable of holding six analyzing crystals. Either an argon flow-proportional detector (FPC) or scintillation (SC) detector was used with the X-ray tube operated at 3 kW. A rhodium anode end-window X-ray tube was used, and the instrument specimen chamber was operated under vacuum.

2.4 Methods

2.4.1 Sample Collection

Fresh soil samples were collected from SLF1. Surface and near surface (0.45 m deep) samples were collected from three sites (section V, site 1 and II) (Figure 2.1, 2.2,

and 2.3, Plate 2). The sampling sites were selected mainly based on their accessibility and the results from previous studies were also taken into consideration, which have recorded the greatest increase in concentration of metal contents over the years (ARG 1997). A shovel covered with a polyethylene sheet to avoid metal contamination of the soil was used for the sample collection. The soil samples were collected in polyethylene bags and transported to the laboratory.

2.4.2 Soil Processing

Archived soil samples from SLF1 (section I, II, III and IV) (Figure 2.3) were obtained from Newfoundland Geosciences Limited-Jacques Whitford with the approval of Public Works Government Services Canada (PWGSC). The samples were selected based on its previous history about the metal movement in the soil layers and also based on the availability of sample. The samples were air dried in the laboratory at room temperature (around 25°C) for a week and then powdered using a porcelain pestle and mortar. The samples were sieved using a 2mm mesh and these samples were used for most of the analysis. A portion of each soil sample was sieved through a 150 μm mesh for organic carbon estimation and Cd mobility experiments. After this, the soil samples were stored in polyethylene bags to minimize contamination. For safety considerations, the soil samples were measured for their radioactivity using a Beta counter by the Memorial University Safety Department. None of the soil samples had radiation levels above background.

Avalon Peninsula

Argentia

Placentia Bay

Newfoundland

Study Area

N

0   20 Miles

Figure 2.2 Argentia Naval Base
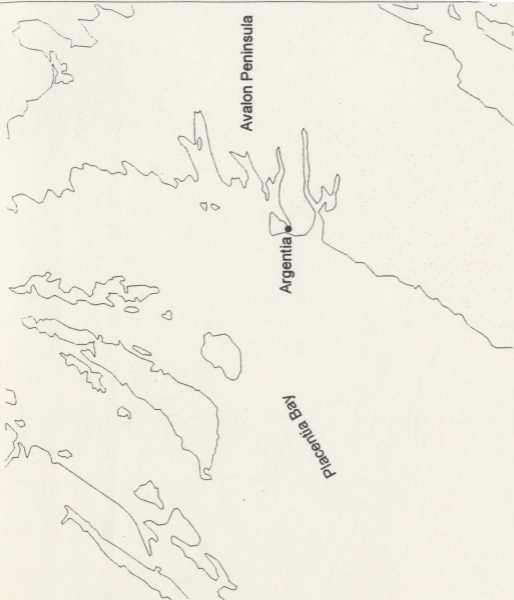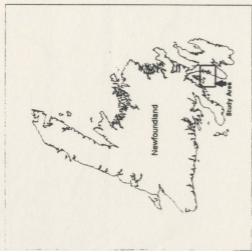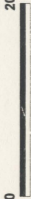
Figure 2.3 Sampling sites

N

PLACENTIA BAY

CARD POND

SHALLOWY POINT

III (2)

IV (3)

II (5)

I (5)

V (2)

26
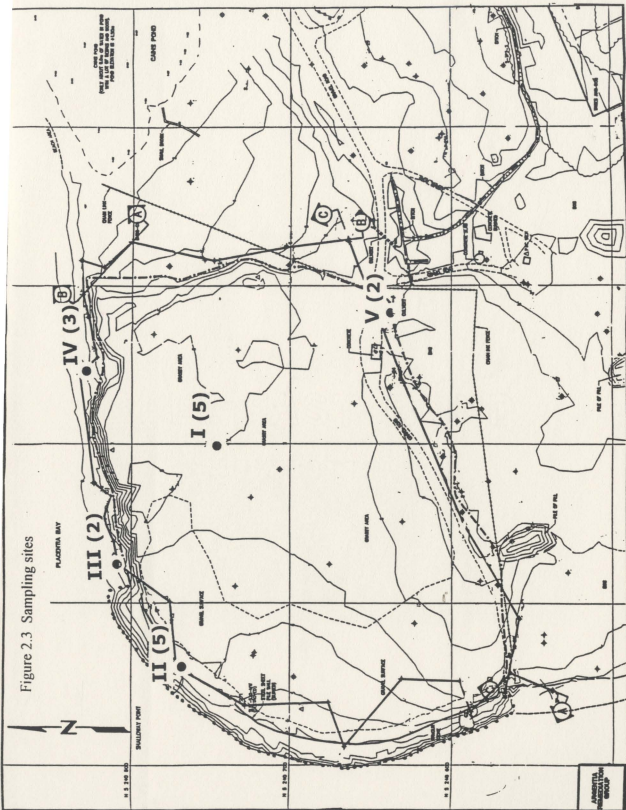
Plate 1 South Land Fill (SLF1) Site

Plate 2 Sample Collection

2.4.3. Soil Properties

2.4.3.1 Soil Texture

There are several methods to analyze soil texture, including the hydrometer method. But in the present study the soil texture was analyzed using a soil texture unit (model 1067, Lamotte Company, Maryland), since the volume of soil available for analysis was limited. The soil texture unit was used for the determination of soil fractions (sand, silt and clay). The experiment was performed by using three capped 50 mL polyethylene tubes held in a plastic stand. The soil sample was added to the first tube and tapped gently on a firm surface to pack the soil and eliminate air spaces until the total soil volume was 15mL. Then 1 mL of texture dispersing reagent containing 2% sodium pyrophosphate deca-hydrate in Nano-pure water was added to the tube containing the soil sample and the mixture was diluted to the 45 mL mark with Nano-pure water. The tube was capped and gently shaken for 2 minutes to mix the soil sample with water. After shaking, the tube was placed in a rack and allowed to stand undisturbed for exactly 30 sec. After 30 sec, all the solution in the first tube was poured into the second tube, and this tube was allowed to stand undisturbed for 30 min. At the end of 30 min, all the solution was poured off from the second tube. The amount of sand was determined by measuring the volume of the remaining sediment in the first tube, and the volume of the sediment in the second tube was considered as silt. The clay content was determined by subtracting the total sand and silt content from the amount of soil (15mL) used during the experiment. Soil texture classification was carried out following the USDA (Soil Survey Staff, 1951) soil textural classification method.

2.4.3.2 Soil pH

Twenty mL of 0.01 M $CaCl_2$ was added to a 20mL beaker containing 10 g of air-dried soil (<2 mm). The suspension was stirred intermittently for 30 min and was then allowed to stand for about 1h. The pH of the soil solution was measured using an Orion pH meter (model 290A) with a glass electrode. The field pH measurement was carried out by the following method. A 1:2 ratio of field soil sample and Nano-pure water was mixed thoroughly and the pH of the sample was measured using the portable Orion pH meter (model 290A) (Hendershot *et al*, 1993).

2.4.3.3 Organic Carbon

A 500mg soil sample was passed through a 150 mm sieve and transferred to a 500mL Erlenmeyer flask. Ten mL of $K_2Cr_2O_7$ solution was added and the flask was allowed to stand for 30 min on an wooden sheet. The solution was then diluted by adding 200 mL of Nano-pure water and 10 mL of 85% H_3PO_4. One mL of diphenylamine indicator was added, and the mixture was back titrated with 0.5N ferrous ammonium sulphate. The excess $K_2Cr_2O_7$ (T) was determined and a blank run (B) was also carried out using the same procedure. The organic carbon content (C_{org}) of the soil sample was calculated using the following formula:

$$ \% \ C_{org} = (0.5)(B-T) \ 0.5* \ x \ 3 \ x \ 0.003 x 1.33** \ (100/mg \ dry \ soil) $$

where 0.5* is the normality of $K_2Cr_2O_7$ solution; 1.3** is the Walkley correction factor (Tan.1996)

2.4.3.4 Cation Exchange Capacity

Ten grams of soil was accurately weighed and added to a 100 mL centrifuge tube. 25mL of NH_4OAc solution was added and the mixture was shaken mechanically for 1h. The supernatant solution was then separated from the soil by centrifugation at 2400 rpm for 30 min. Both the clear supernatant and NH_4^+-saturated soil were collected, and the supernatant was filtered into a 100mL volumetric flask. The NH_4^+-saturated soil was then washed three times with 20 mL of 95% ethanol by shaking and centrifugation. Each washing was then added to the supernatant in the 100mL volumetric flask. The extract was made up to 100 mL with Nano-pure water and used for the determination of the exchangeable cations, Ca, Mg, Na, and K. The concentration of these cations was measured by GF-AAS (Lavkulich, 1981).

2.4.3.5 Total Elemental Analysis - ICP-MS

The powdered soil sample was passed through a 150 µm mesh. 0.1 g of sample powder was weighed accurately into a clean, dry, high pressure (HP) vessel. Three mL of 8 N HNO_3 and 2 mL of 30% HF were added to the vessel. A teflon lid was put in place and the vessel was set into the assembly. Up to 6 HP vessels were assembled and the assembly was placed in the oven at 200°C for 12 to 16 h. After the assembly was sufficiently cooled each container was carefully opened. Two mL of 8 N HNO_3 and 1mL of 2.8% boric acid were added to the sample and the mixture was evaporated to dryness. The addition of HNO_3 and drying step was repeated several times. Finally, 2 mL of 8 N HNO_3 was added and the cap was replaced. The vessel was warmed to dissolve the

residue. The solutions were then transferred to a clean. dry. 120 mL polypropylene container. The HP vessel was rinsed with Nano-pure water and this water was added to the solution. A mixture of 0.665 mL HF/boric acid solution (0.453 N boric acid and 0.108N HF) and 1.35 mL oxalic acid (0.222 N) were added to the above solution. This solution was made up to 60 g with Nano-pure water and the concentration of metals in the solution was determined using ICP-MS.

2.4.3.6 Total Elemental Analysis-XRF

XRF pressed pellets were prepared by the following method. A bottle with two ball bearings were cleaned using ethanol. Five grams of powdered soil were weighed into the bottle. To this. 0.70 g of phenolic resin binder was added and the bottle was closed with a cap. The bottle was swirled for about 10 min using a roller mixer. After mixing. the sample was removed from the bottle. transferred to the pellet press chamber (Herzog. Germany) and pressed for 10 sec at a pressure of 20 tonnes. The pressed pellets were transferred to a baking sheet and placed in an oven at 200°C for 15 min. After baking. the pellets were cooled and labeled for XRF analysis.

2.4.3.7 Available Cadmium Content

Five grams of air-dried (<2 mm) soil was weighed into a 125 mL Erlenmeyer flask and 25mL of 0.05 M EDTA solution was added. The mixture was shaken for 1h at a speed of 120 cycles min^{-1}. After shaking. the solution was filtered through a Whatman$^®$ No.42 filter paper and analyzed for Cd content using GF-AAS.

2.4.3.8 Background Metal Concentrations

Background levels of metals in the study area soils had already been determined and reported by ARG (1995). These results are used as background levels in the present study. The ARG has established the background levels of metals in soils by selecting analytical results for soil samples from test pits, boreholes and monitor wells installed in 1995 in areas around the US Naval facility in those places where there was no evidence of man-made contamination. They have also excavated several test pits in undisturbed areas, specifically to obtain background soil samples. In addition, some 1994 soil analytical data were also included from borehole and monitor wells that were installed specifically to determine background conditions.

2.4.4 Batch Sorption

The Cd sorption experiments were performed using the batch method (Figure 2.4) by equilibrating 10 g of air dried soil with 25 mL 0.01 M $Ca(NO_3)_2$ solution containing varying Cd concentrations (0.00, 0.10, 0.25, 0.50, 1.00, 2.50, 5.0, 10.0, 25.0, 50.0 and 100 µM). Each sample with its supernatant solution was transferred to an acid cleaned 45mL polyethylene tube. The tubes with soil and solution were horizontally shaken (using a Dubnoff metabolic shaking incubator, Model:30C/100C-120. Precision Scientific Group, Chicago) for 48h at room temperature (22 ± 2°C). After this, the samples were centrifuged (2500 rpm) and filtered through Whatman® No.5 and 0.45 µM filter papers. The Cd concentration in the filtrate was determined by the GF-AAS. The concentration of Cd accumulated in the soil (S) was determined using the following equation:

$$S = V_w(C_0 - C)/M_s$$

Where, V_w is the volume of 0.01 M $Ca(NO_3)_2$, C_0 is the initial concentration of Cd used, C is the final Cd concentration after the equilibration and M_s is the mass of soil sample used for the experiment.

Figure 2.4 Flow diagram for cadmium sorption experiment

10 g soil sample (<2 mm)

in 45 mL acid cleaned polyethylene tubes

↓

Addition of 25mL of 0.01M $Ca(NO_3)_2$
Containing varying Cd concentrations
(0.0,0.10,0.25,0.50,1.0,2.5,5.0,10,25,50 & 100 μM)

↓

Continuous horizontal shaking for 48 hours

↓

Centrifuging 10 minutes at 2500 rpm

↓

Filtering the supernatant
(by 0.45 μM and Whatman No.5 filter papers)

↓

Analyzing for Cd content
(using Graphite-AA)
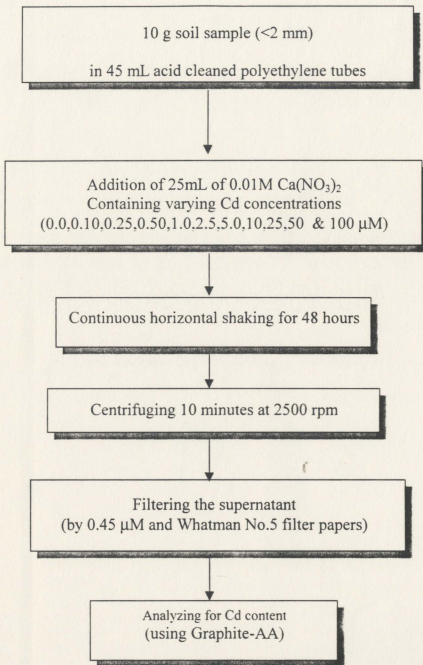
2.4.5 Desorption

The cadmium desorption experiment was performed for all the archived and fresh soil samples as outlined by the flow diagram shown in Figure 2.5. The soil samples were enriched with Cd by placing 10 g of soil in an acid cleaned 45mL polyethylene tube, and adding, 100 μM of Cd solution. The tube was closed using an airtight cap, and the tube with soil solution was shaken continuously for 48 h using a horizontal shaker (Model:30C/100C-120, Precision Scientific Group, Chicago). After the equilibration period, the Cd solution was carefully removed from the tube and the soil sample in the tube was used for the desorption experiment. The desorption experiment was carried out by extracting the Cd enriched soil sample with Cd free 0.01 M $Ca(NO_3)_2$. Then, 25mL of 0.01 M $Ca(NO_3)_2$ was added to the tube containing the soil sample and it was continuously shaken for 12h. After 12h, the solution was carefully removed from the tube, centrifuged, filtered and analysed for Cd content using GF-AAS. The extraction step was repeated up to 6 times (12th, 24th, 48th, 60th, 72nd, 84th hours of shaking).

Figure 2.5 Flow diagram for cadmium desorption experiment

	10 g soil sample (sieved through 2 mm mesh)
Step I	Cd sorption experiment (Cd addition and 48hours shaking)
Step II	Decant supernatants
Step III	Addition of extracting solution (25 mL of 0.01M Ca(NO₃)₂)
Step IV	Shaking for 12 hours, centrifuging, filtering and analyzing for Cd content
	Repeat Step II to IV (every 12 h extraction up to 6 times)
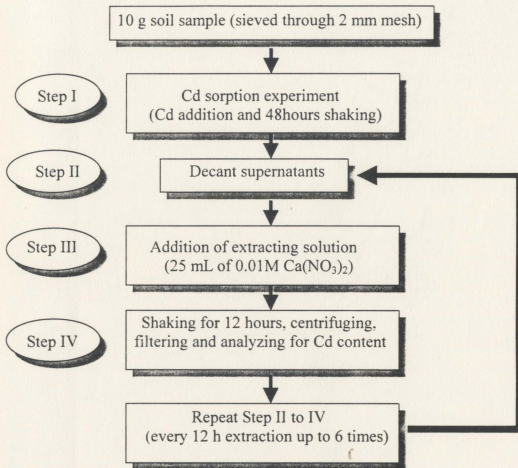
The amount of Cd desorbed from the soil was calculated as follows:

Amount of Cd desorbed = Sum of Cd extracted at $12^{th}, 24^{th}, 48^{th}, 60^{th}, 72^{nd}, 84^{th}$ h of shaking.

The Cd retention capacity was calculated by using the following steps:

Cd sorbed during the sorption experiment (Cd_{sorbed}) =

$$S = (C_o - C) \, V/Ms$$

Where V_w = volume of 0.01 M $Ca(NO_3)_2$.

C_0 = initial concentration of Cd used (11.24 mg/L)

C = final Cd concentration after the equilibration

M_s = mass of soil sample used for the experiment (10g).

Total soil Cd content (Cd_T)   =   available Cd content of soil + (Cd_{sorbed})
(before desorption)

Total Cd desorbed ($Cd_{desorbed}$) = Σ Cd desorbed at $12^{th}, 24^{th}, 48^{th}, 60^{th}, 72^{nd}, 84^{th}$ hours of shaking.

From this, the Cd retention capacity of the soil was calculated as follows:

$$Cd_{retained} = Cd_T - Cd_{desorbed}$$

Figure 2.6 Flow diagram for cadmium mobility

Soil
(Sieved through 160 μm mesh)

↓

Soil water slurry
(7.5 g of soil and 15g of distilled water)

↓

Spread (as a 0.5-mm thick layer)
in a 20- by 5-cm glass plates with the aid of ordinary TLC applicator

↓

Plates air dried and stored in a desiccating chamber

↓

Spotted with 5μL of 0.1 M $CdCl_2$ in ethanol with the aid of micropipette
(drops at a distance of 2 cm from the plate edge)

↓

Plates are allowed to develop for 10 cm in chromatographic tanks
(water as solvent)

↓

Presence of Cd is detected as orange spots
(spraying the plates with 0.05% dithizone in CCl_4)

↓

Cd mobility is measured visually as R_f values

2.4.6 Freundlich Isotherm Model

The Freundlich isotherm model was developed using the results obtained from sorption experiments. The relationship between sorbed Cd content and Cd in the soil solution was determined using this Freundlich isotherm. The Freundlich isotherm graph was obtained by plotting the log of the Cd sorbed concentration in the soil against Cd concentration in solution. The Freundlich equation was derived by plotting log S (log of Cd sorbed) against log C_o (Initial Cd concentration of the $Ca(NO_3)_2$ solution). From this, the Freundlich equation $S = K_d C^b$ was obtained. Here, S is the Cd concentration in the sorbed phase (μmol [kg soil]$^{-1}$), C is the Cd concentration in the solution phase (μmol L^{-1}), K_d is the Freundlich distribution coefficient and b is the Freundlich parameter ($0 < b < 1$).

2.4.7 Statistical Analysis

All the experiments were conducted in triplicate and their mean values and standard deviation are presented. A statistical analysis was performed using SPSS (version 9) statistical software to determine the relationships between log K_d and n values with soil properties (pH, organic carbon, CEC, sand, silt, clay, Cl, Fe_2O_3, Ca and Zn).

2.4.8 Cadmium Mobility

The mobility of Cd was studied by soil thin layer chromatography (TLC) (Figure 2.6). The chromatographic plates were prepared according to Helling and Turner (1968) and Martin and Camazano (1993). The soil samples were powdered and sieved

through a 150 μm mesh. A soil-water slurry was prepared using 10 g of soil and 20 mL of Nano-pure water. This slurry was spread as a 0.5 mm thick layer over a 20x5 cm^2 glass plate with the aid of a TLC applicator. The soil coated plate was then air dried and subsequently stored in a desiccating chamber. The soil plate was then spotted with 5 μL of 0.1 M CdCl$_2$ in ethanol with the aid of a micropipette. The spots were placed at a distance of 2 cm from the plate bottom edge and the plate was then allowed to develop for 10 cm in chromatographic tanks containing Nano-pure water as solvent. After the development, the presence or movement of Cd was detected as orange spots of Cd-dithizone complexes formed by spraying the plates with 0.05 % dithizone in CCl$_4$. For each soil sample, at least two TLC plates were prepared and two spots were made on each plate. The Cd mobility was measured visually as R$_f$ values using the following relation: R$_f$ =R$_1$/R$_2$ where, R$_1$ and R$_2$ denotes the distance traveled by the Cd from its origin (from the spot) and the distance traveled by the solvent (Nano-pure water) from its origin, respectively.

CHAPTER 3.0

SOIL PHYSICAL AND CHEMICAL CHARACTERISTICS

3.1 Introduction

Soil is a complex mixture of substances that vary in composition from area to area. The soil properties which affect metal retention and transport in contaminated soils include texture, organic matter content, bulk density, pH and ion exchange capacity. Texture affects movement of water through soil, and in turn affects movement of dissolved contaminants. The movement of percolating water is faster in case of coarse soils and hence the adsorption of contaminant is less (Naidu *et al.*, 1997). Soils with more clay and organic matter tend to hold water and contaminants longer (Streck and Richter 1997b). These soils also have more surface area on which contaminants can be adsorbed. Soil organic matter influences the amount of water that the soil can hold and the amount of metals adsorbed. The soil pH and CEC have a positive influence on contaminant sorption (Filius *et al.*, 1998) and the bulk density values are used for determining contaminants index of mobility (Baskaran *et al.*, 1994).

3.2 Soil Section Description and Properties

Results of the composition and properties of five sections are presented and discussed. The analysis of soil texture using the soil texture unit, produced results that were closer to previous studies conducted in the same soils by ARG (1999). The depth of sampling and the ARG soil codes of the samples are given in Table 3.1.

3.2.1 Section I

Section I has a top fill layer of 6.0 m with plant roots in the top 0.6 m and very dense grey gravely sand with silt and debris (bricks and concrete), the second layer is characterized as very dense, grey silty sand and gravel, the third layer (at 7.5m) as compact to dense, grey silty sand with sandy silt lenses and the last layer (14.4 m) as hard, reddish grey lean clay with sand and gravel (ARG 1999). The soil samples were classified in the laboratory using the USDA soil textural classification. The top layer (first sample) is classified as sandy soil, this is followed by a sandy loam layer (second sample), a loamy sand layer (third sample) and a sandy clay layer (fourth sample) (Figure 3.1 and Table 3.3).

The spatial distributions and the transport behavior of metals in the soil matrix are strongly dependent on soil parameters. The depth distribution of these soil parameters for section 1 are illustrated in Figure 3.2. The results from the laboratory soil analysis show that the pH of the samples varies from 5.26 to 7.60 (Table 3.2).

Table 3.1 Section details

Section	Sample No	Depth (m)	Sample Code
Section I	1	3.0	MW 98-24-1
	2	6.0	MW 98-24-3
	3	7.5	MW 98-24-4
	4	14.4	MW 98-24-8
Section II	1	12	BH 98-G4-3
	2	13	BH 98-G4-4
	3	14	BH 98-G4-7
	4	15	BH 98-G4-10
	5	19.4	BH 98-G4-16
Section III	1	3.1	BH 98-G5-1
	2	6.0	BH 98-G5-5
Section IV	1	5.0	BH 98 G6-4
	2	6.5	BH 98 G6-7
	3	8.0	BH 98-G6-9
Section V	1*	Surface	MW 98-24 (surface)
	2*	0.45	MW 98-24 (subsurface)
	3	2.0	TP25-1
	4	4.6	TP25-2
site I	1*	Surface	SLF1-514
site II	1*	Surface	SLF1-517

* Indicates field samples (others are archived samples).

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Table 3.2 Soil Properties (moisture, pH, organic carbon)

Section	Depth of sampling	pH (1:2 soil & 0.01M CaCl.2H₂O)	Organic Carbon (%)	Bulk Density (Mg/m³)
Section I	1 (3.0 m)	7.27	0.16	1.610
	2 (6.0 m)	7.31	0.18	1.610
	3 (7.5 m)	5.26	0.03	1.612
	4 (14.4m)	7.60	0.26	1.419
Section II	1 (12m)	7.78	0.18	1.446
	2 (13m)	7.74	1.43	1.455
	3 (14m)	7.66	0.14	1.597
	4 (15m)	7.70	0.08	1.519
	5 (19.4m)	7.77	0.14	1.397
Section III	1 (3.1m)	7.64	0.03	1.563
	2 (6.0m)	7.73	0.26	1.433
Section IV	1 (5.0m)	7.67	0.10	1.468
	2 (6.5m)	7.76	0.07	1.581
	3 (8.0m)	7.66	0.20	1.256
Section V	1 (surface)	5.73	7.49	0.994
	2 (0.45m)	6.58	2.89	1.486
	3 (2.0m)	4.64	0.20	1.638
	4 (4.6m)	5.23	0.10	1.470
site I	1 (surface)	6.68	4.29	1.274
site II	1 (surface)	6.45	3.86	1.285

All experimental values given are mean of three replicates

Figure 3.1 Section I Description

Depth (m)

Depth	Description

FILL:
Plant roots up to 0.6 m: very dense grey gravelly sand with silt and debris (bricks and concrete)[1]

sandy soil[2]

Very dense, grey silty sand and gravel[1]

sandy clay loam[2]

Compact to dense, grey silty **sand** with sandy **silt** lenses[1]

loamy sand[2]

Hard, reddish grey lean **clay** with sand and gravel[1]

sandy clay[2]

[1] ARG (1999) report
[2] laboratory classification

1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0

Figure 3.2 Vertical spatial distributions of pH, organic carbon, clay, silt and sand contents, bulk density and CEC (section I)

Table 3.3 Soil Fraction, Cation Exchange Capacity (CEC) and Available Cadmium Content

Section	Depth of sampling	Soil Fraction				CEC	Available Cd
		Sand (%)	Silt (%)	Clay (%)	Type	(cmole(+)/Kg)	(μg/kg)
Section I	1 (3.0 m)	86.7	10.0	3.3	sandy	18.9	39.2
	2 (6.0 m)	53.3	23.3	23.3	sandy clay loam	21.1	18.0
	3 (7.5 m)	80.0	15.0	5.0	loamy sand	18.8	28.9
	4 (14.4 m)	53.3	3.3	43.3	sandy clay	23.6	24.9
Section II	1 (12.0 m)	33.3	46.7	20.0	loam	22.4	38.2
	2 (13.0 m)	30.0	30.0	40.0	clay loam	17.9	27.4
	3 (14.0 m)	30.0	56.7	13.3	silt loam	18.8	22.8
	4 (15.0 m)	75.0	15.0	10.0	sandy loam	15.8	20.4
	5 (19.4 m)	43.3	20.0	36.7	clay loam	23.9	22.3
Section III	1 (3.1 m)	73.3	20.0	6.7	sandy loam	16.5	26.9
	2 (6.0 m)	56.7	33.3	10.0	sandy loam	20.9	21.2
Section IV	1 (5.0 m)	85.0	13.3	1.7	loamy sand	18.9	20.8
	2 (6.5 m)	91.7	6.7	1.7	sandy	17.7	9.3
	3 (8.0 m)	53.3	13.3	33.3	sandy clay loam	23.3	15.6

Table 3.3 *Continued..*

Section	Depth of sampling	Soil Fraction				CEC	Available Cd (µg/kg)
		Sand (%)	Silt (%)	Clay (%)	Type	(cmole(+)/Kg)	
Section V	1 (surface)	80.0	13.3	6.7	loamy sand	100.2	12.5
	2 (0.45 m)	83.3	13.3	3.3	loamy sand	75.0	12.0
	3 (2.0 m)	93.3	5.0	1.7	sandy	6.0	10.1
	4 (4.6 m)	95.0	3.3	1.7	sandy	1.2	10.4
site I	1 (surface)	66.7	20.0	13.3	sandy loam	78.5	9.8
site II	1 (surface)	73.3	25.3	1.3	loamy sand	69.7	11.4

All experimental values given are mean of three replicates

Table 3.4 Correlation coefficient (r) for selected soil properties of Section 1

Properties	Zn	Ca	Fe$_2$O$_3$	Cl	Clay	Silt	Sand	CEC	OC	pH
pH	0.934	ns	0.951*	ns	ns	ns	ns	ns	0.945	1
OC	ns	ns	ns	ns	0.809	-0.425	-0.661	ns	1	
CEC	ns	ns	ns	ns	0.998**	ns	-0.879	1		
Sand	ns	ns	ns	ns	ns	ns	1			
Silt	ns	-0.976*	ns	ns	ns	1				
Clay	ns	ns	ns	ns	1					
Cl	ns	ns	ns	1						
Fe$_2$O$_3$	0.983*	ns	1							
Ca	ns	1								
Zn	1									

ns = not significant; ** and * indicate significance at 0.01 and 0.05 probability levels, respectively.

An irregular increase in pH distribution with depth is noticed in section I (Figure 3.2 a). The correlation study of pH with soil properties shows a positive relationship with organic carbon, Zn and Fe_2O_3 (significant at 0.05 probability level) values (Table 3.4).

The organic carbon content of the soils of section I ranged from 0.03 % (third layer) to 0.26 % (fourth layer) and its distribution pattern with depth is almost similar to the pH distribution, which shows an irregular increase in OC content with depth (Figure 3.2.b). The organic carbon content shows positive correlation with clay percentage and negative correlation with silt and sand percentages (Table 3.4), but the relationships are not statistically significant. The positive correlation of OC with clay may be due to the binding nature of the clay and its larger surface area. An irregular increase in clay content with depth is noticed in this section. This may be due to the heterogeneous nature of the landfill layers or eluviation of clay to the lower layers, whereas the spatial distribution graph does not show any particular trend for the sand and the silt content with depth (Figure 3.2c). In general, high sand content is found throughout the section which may be due to the weathering nature of the soil parent material. Relatively low CEC is recorded in all the samples and also shows positive correlation with clay content of the soils (Table 3.4). The available Cd content varies from 18.0 to 39.2 µg/kg of soil (Table 3.3). The reason for the low OC of the third sample may be due to the presence of higher sand content, which can hold only small amounts of organic matter because of its smaller surface area compared to clay.

3.2.2 Section II

The description of the soils of section II is presented in the Figure 3.3. This section is categorized as interbeded very stiff to hard, reddish gray lean clay with sand and trace gravel and compact to very dense, gray sandy silt (ARG, 1999). The laboratory soil classification confirmed the presence of considerable silt content throughout the section and the soils are classified as loam, clay loam, silty loam and sandy loam (Table 3.3 and Figure 3.3). The soil pH is uniform throughout the section (Figure 3.5a) and it is above the neutral range. The distribution of organic carbon content is also uniform except for a higher OC value in the second layer. The top and bottom layers have high clay content, whereas the intermediate layer has more sand and silt. The high clay content in the bottom layer may be due to the eluviation of clay from the top layer. In general a higher silt content is found in all the samples and it varies from 15.0 to 56.7 %, this is one of the reasons to classify these soils as loam to clay loam. An irregular increase in bulk density value with depth is noticed (Figure 3.5d) in the section. The CEC values range from 15.8 to 23.9 cmole(+)/kg and these do not show any particular distribution trend with depth. Relatively high available Cd content is found in all samples and the highest value, 38.19 µg/kg, is recorded for the top layer. The results of the correlation study shows a significant negative relationship between sand and Fe_2O_3 values. The pH value shows positive correlation with clay, Cl and CEC, but they are not statistically significant. Other parameters show non-significant relationship (Table 3.5).

Figure 3.3 Section II Description

Depth (m)		Lab classification:
11.0		
12.0		loam
13.0		clay loam
14.0		silty loam
15.0		
16.0		sandy loam
17.0		
18.0		clay loam
19.0		
20.0		

Interbeded very stiff to hard, reddish grey lean **clay** with sand and trace gravel and compact to very dense, grey sandy **silt** (ARG, 1999)
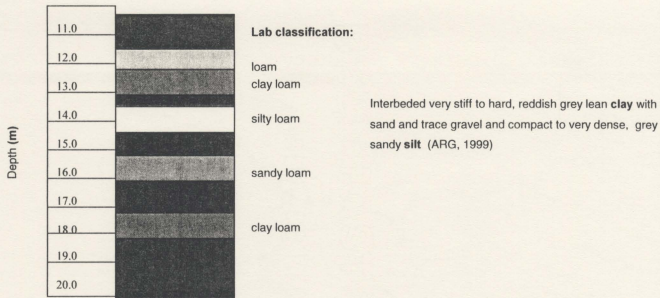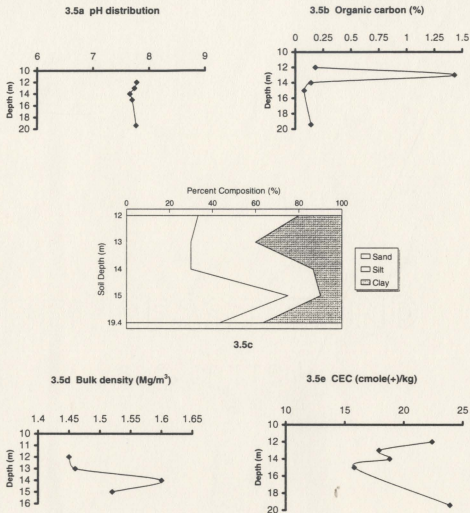
Figure 3.4 Vertical spatial distributions of pH, organic carbon, clay and sand contents, bulk density and CEC (section II)

Table 3.5 Correlation coefficient (r) for selected soil properties of Section II

Properties	Zn	Ca	Fe$_2$O$_3$	Cl	Clay	Silt	Sand	CEC	OC	pH
PH	ns	ns	ns	0.759	0.600	ns	ns	0.700	ns	1
OC	ns	ns	ns	ns	0.674	ns	ns	ns	1	
CEC	ns	ns	ns	ns	ns	ns	ns	1		
Sand	-0.762	ns	-0.923*	-0.676	ns	-0.727	1			
Silt	0.781	0.609	ns	ns	ns	1				
Clay	ns	ns	0.748	ns	1					
Cl	ns	ns	0.773	1						
Fe$_2$O$_3$	ns	ns	1							
Ca	ns	1								
Zn	1									

ns = not significant; * indicates significance at 0.05 probability level.

Figure 3.5 Section III Description

FILL material, grey sand and gravel with silt[1]

Dense to very dense, grey silty **sand** and sandy **silt**[1] sandy loam[2]

Hard reddish grey lean **clay** with silt and fine sand lenses.[1] sandy loam[2]

[1] ARG Report (1999)
[2] Laboratory classification

Depth (m)

1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
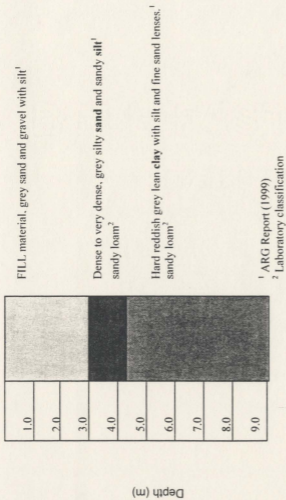
3.2.3 Section III

Section III has fill material containing gray sand and gravel up to 3.0 m depth (ARG 1999) followed by a layer of dense to very dense, gray silty sand and sandy silt. The bottom layer of this section contains hard reddish gray lean clay with silt and fine sand lenses (Figure 3.4). Only two samples (at 3.1m and 6.0m depth) of this section were analyzed for their properties. Both the samples are classified as sandy loam. The samples show a slight increase in pH, OC, clay, silt and CEC with depth. A decrease in the sand and available Cd content with depth is also noticed. A statistical analysis for this section was not carried out because of the limited number of samples.

3.2.4 Section IV

The top layer of the section IV contains very dense, interbeded gray silt sand and sandy silt layer. This is followed by a very stiff to hard, purplish gray lean clay with silt and fine sand lenses layer. Shell fragments were observed below 9.5m depth (ARG 1999) (Figure 3.6). The samples are classified as loamy sand (sample 1), sand (sample 2) and sandy loam (sample 3) (Table 3.3). The pH values are similar for all the three samples, and are alkaline (pH above 7.6). The OC content is low and it does not follow any trend with depth (Figure 3.7b). The clay percentages are lower in the top two layers than the bottom layer. Higher clay content in the bottom layer may be due to the movement of clay particles to the lower layers. High sand content is found in all three samples. The CEC values vary from 17.7 to 23.3 cmole(+)/kg and do not show any particular distribution with depth. The available Cd content varies from 9.33 to 20.80, and the top layer contains the highest Cd content compared to other samples (Table 3.3).

Figure 3.6 Soil Section IV

Depth (m)

4.0	
5.0	
6.0	
7.0	
8.0	
9.0	
10.0	
11.0	
12.0	

Compact to very dense, interbedded grey silty **sand** and sandy **silt**[1]

loamy sand (5.0-5.7 m)[2]

sand (6.4 -7.0 m)[2]

sandy clay loam (8.0 m)[2]

Very stiff to hard, purplish grey lean **clay** with silt and fine sand lenses[1]

Shell fragments below 9.5 m depth[1]

[1] ARG Report (1999)
[2] Laboratory classification

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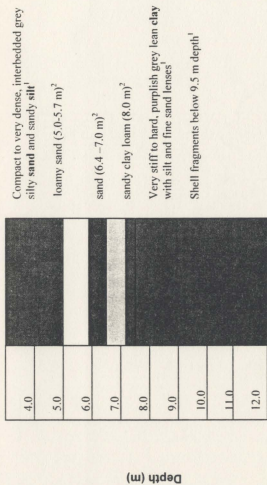
Table 3.6 Correlation coefficient for selected soil properties of Section IV

Properties	Zn	Ca	Fe$_2$O$_3$	Cl	Clay	Silt	Sand	CEC	OC	pH
PH	ns	ns	ns	-0.940	ns	-0.996	ns	ns	ns	1
OC	0.980	0.944	0.967	ns	0.965	ns	-0.995	0.998*	1	
CEC	0.990	0.963	0.981	ns	0.979	ns	-0.999*	1		
Sand	-0.995	-0.973	-0.988	ns	-0.987	ns	1			
Silt	ns	ns	ns	0.967	ns	1				
Clay	0.998*	0.998*	1.000**	ns	1					
Cl	ns	ns	ns	1						
Fe$_2$O$_3$	0.998*	0.997*	1							
Ca	0.991	1								
Zn	1									

ns = not significant; ** and * indicates significance at 0.01 and 0.05 probability levels, respectively.
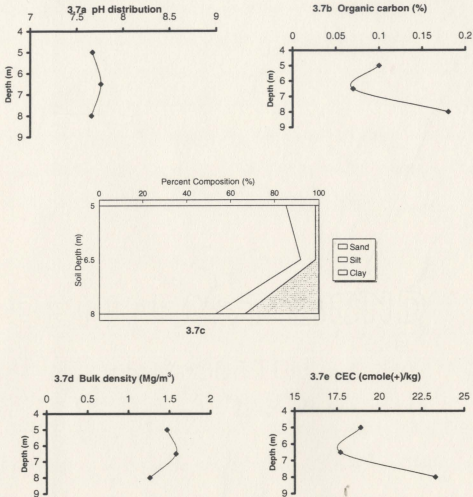
Figure 3.7 Vertical spatial distributions of pH, organic carbon, clay and sand contents, bulk density and CEC (section IV)

The results of correlation analyze between the soil properties are presented in Table 3.6. The pH value shows negative correlations with Cl value and silt percentage, but the relationships are not statistically significant. The OC content correlates positively with CEC (significant at 0.05 probability level), clay, Fe_2O_3, Ca and Zn values, whereas it shows a negative correlation with the sand percentage. The CEC also shows a negative correlation (significant at 0.05 probability level) with the sand percentage, and a positive correlation with clay, Fe_2O_3, Ca and Zn values. The clay content correlates positively with Fe_2O_3 (significant at 0.01), Ca and Zn (significant at 0.05) values.

3.2.5 Section V

In section V, sand, gravel and silt are present in the top fill layer. This is followed by a compact black peat layer and a compact weathered brown sand with gravel and silt layer. The fourth layer is classified as dense, gray sand with gravel and the final layer has compact, brownish gray, silty, fine sand layer (ARG 1999) (Figure 3.8).

The surface and near surface samples of section V were collected during the field trip. The field pH values of these samples were 5.6 and 6.73, respectively. High organic carbon content is found in both the samples which may be due to the presence of plant roots and residues. In general, the pH value decreases with increasing depth. The low pH in the lower layers may be due to downward movement of the leachates from the top fill layer or the production and the movement of organic acid from the immediate top peat layer (Figure3.1.8). The OC content shows a marked decrease with depth (Figure 3.9b). The soils have high sand and low clay percentage (Table 3.3) and the sand content

Figure 3.8 Soil Section V

FILL ,compact, greyish brown **sand** with gravel and silt[1]

Compact black peat[1]

Compact, weathered brown sand with gravel and silt[1]
sandy @ 2.0m[2]

Dense, grey **sand** with gravel[1]
sandy @ 4.6m[2]

Compact, brownish grey silty fine **sand**[1]

[1] ARG Report (1999)
[2] Laboratory classification

Table 3.7 Correlation coefficient for selected soil properties of Section V

Properties	Zn	Ca	Fe_2O_3	Cl	Clay	Silt	Sand	CEC	OC	pH
pH	0.962*	0.904	ns	ns	ns	0.812	-0.735	0.757	ns	1
OC	ns	ns	ns	0.984*	0.999**	ns	-0.922	0.937	1	
CEC	ns	0.889	ns	0.973*	0.920	0.959*	-0.989*	1		
Sand	ns	-0.915	ns	-0.975*	-0.902	-0.983	1			
Silt	ns	0.972*	ns	0.917	ns	1				
Clay	ns	ns	ns	0.975*	1					
Cl	ns	ns	ns	1						
Fe_2O_3	ns	ns	1							
Ca	0.876	1								
Zn	1									

ns = not significant; ** and * indicates significance at 0.01 and 0.05 probability levels, respectively.
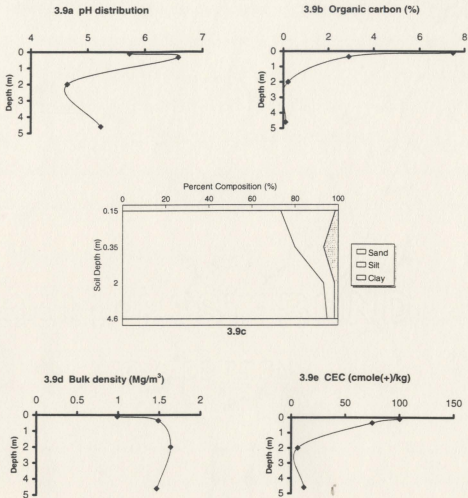
Figure 3.9 Vertical spatial distributions of pH, organic carbon, clay and sand contents, bulk density and CEC (section V)
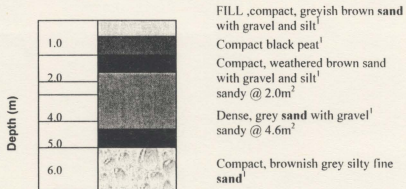
increases with depth (Figure 3.9c). Relatively higher CEC values are found in the surface and near surface samples and the CEC greatly decrease with depth (Figure 3.9e). The reason for the low OC, CEC and available Cd values in the bottom layers is due to the presence of high sand content, which contributes lower surface area and ion adsorption capacity. The results of correlation analysis are presented in Table 3.7. The pH correlates positively with Zn (significant at 0.01 probability), CEC, Ca and silt content. The OC value shows a positive correlation with clay (significant at 0.05), Cl (significant at 0.01) and CEC, but shows negative correlation with sand percentage. Similar relationships are also found between CEC and soil parameters (Table3.1.7).

3.2.6 Field Samples I and II

The surface samples (site-I and II) collected during the field trip have relatively high organic carbon content compared to the archived samples. This is due to the presence of plant roots and residues in the surface soils. These samples have pH values of 6.68 and 6.45. Site-I shows higher clay content than site-II, however both the samples have high sand and moderate silt contents. Site-I and II are classified as sandy loam and loamy sand, respectively. The CEC value of site-I is slightly higher than site-II and these values are higher than the CEC values of archived samples. The available Cd content of site-I and II are 9.75 and 11.41 µg/kg, respectively.

3.3 Soil Total Elements

The total metal and elemental composition of the soil samples were determined using XRF and ICP-MS analysis. For each element, readings from the ICP-MS and XRF were plot in a graph (Appendix A.1). Based on these rationale the XRF data are used for Cl, Ca, V, Cu, Fe$_2$O$_3$ and As contents whereas the ICP-MS data are used for Ca, V, Ni, Ag, Cd, Ce, Pb and Th (Table 3.8). The results of XRF and ICP-MS are presented in Table 3.9 and Table 3.10 respectively.

The section wise concentration of some labile elements such as Cd, Cu, Pb, Zn and Sr are shown in Figures 3.10 to 3.14. High concentrations of Sr and Zn are present in all the five sections. Among these five elements, Cd concentration is lowest. In general, the abundance of these elements in the soil sections show the following order:

Sr > Zn > Pb > Cu > Cd   or   Sr > Zn > Pb = Cu > Cd

The high concentration of Sr and Zn may be due to the presence of these elements in the soil minerals. This is consistent with the results from ARG report (1995), which reported high background concentrations of Sr and Zn in the study area soils.

The concentration and the distribution pattern of Cl, Ca, Cr, Fe$_2$O$_3$, Ni, Cu, Cd, Zn Pb and Sr are discussed below:

The Cl content of the soil sections varies from 552 to 1735 ppm. Fresh field samples have relatively higher Cl content. A regular decrease of Cl content with depth is observed in the section V, whereas there is an irregular decrease in Cl content in section I and II and increase in section III.

Table 3.8 Data Selection (√) from XRF and ICP-MS results

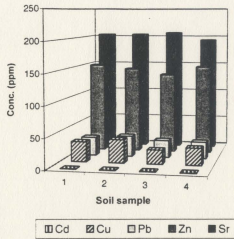| Elements	XRF	ICP-MS
Ca		√
Ti		√
V	√	√
Cl	√	
Cr	√	
Fe		√
Co		√
Ni		√
Cu	√	
Zn		
As	√	
Ga	√	
Ag		√
Cd		√
Rb	√	
Ce		√
Ba	√	
Nb	√	
Zr	√	
Pb		√
Y	√	
Th		√
Sr	√	

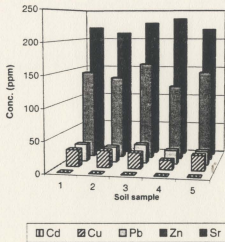**Figure 3.10** Total metal content (Section I)

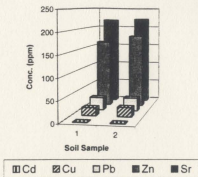**Figure 3.11** Total metal content (Section II)

Figure 3.12 Total metal content (Section III)
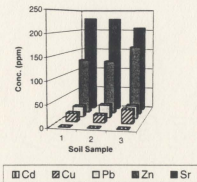

Figure 3.13 Total metal content (Section IV)
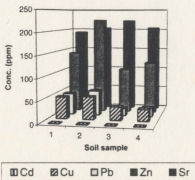
Figure 3.14 Total metal content (Section V)

Table 3.9 Total Elemental Contents (XRF) in mg/kg soil

Section	Depth	Cl (± 2.1%)*	V (± 0.5%)*	Cr (± 2.4%)*	Ni (± 3.5%)*	Cu (± 1.1%)*	Zn (± 2.5%)*	Ga (na)	As (na)
Section I	1 (3.0 m)	764	132	70	15	33	63	17	5
	2 (6.0 m)	743	126	74	14	38	72	17	13
	3 (7.5 m)	688	101	63	8	23	49	14	13
	4 (14.4m)	706	139	74	13	28	62	18	7
Section II	1 (12m)	806	116	63	13	27	53	16	11
	2 (13m)	717	116	84	21	27	56	18	8
	3 (14m)	616	127	63	12	25	47	17	4
	4 (15m)	552	118	62	9	15	52	15	<3
	5 (19.4m)	673	122	73	13	24	58	15	9
Section III	1 (3.1m)	739	109	72	<LD	19	43	14	<LD
	2 (6.0m)	841	119	82	<LD	22	52	14	<LD
Section IV	1 (5.0m)	1302	105	81	<LD	19	50	15	<LD
	2 (6.5m)	1013	113	58	<LD	17	51	13	<LD
	3 (8.0m)	1226	124	72	14	31	62	18	<LD
Section V	1 (surface)	1735	121	74	<LD	50	56	9	<LD
	2 (45 cm)	1336	123	87	10	52	133	16	<LD
	3 (2.0m)	931	110	58	<LD	31	35	13	<LD
	4 (4.6m)	846	116	94	10	24	45	15	<LD
site I	1 (surface)	1644	159	108	22	134	349	13	<LD
site II	1 (surface)	1240	180	105	19	111	281	17	<LD
†Background Concentration (mg/kg)		NA	4.9-39.5	<0.3	1.9-5.0	0.2-35.5	10.7-28.4	NA	2.1-5.7

<LD indicates low detection limit   na – Data not available   * indicates RSD %   † Background concentration - source ARG (1995)

Table 3.9 *Continued.*

Section	Depth	Rb (± 0.2%)*	Sr (± 0.3%)*	Y (± 3.7%)*	Zr (± 0.3%)*	Nb (± 5.7%)*	Ba (± 3.9%)*	Pb (± 3.9%)*	Th (± 7%)*
Section I	1 (3.0 m)	70.6	203.0	31.2	224.3	20.5	687	27	9
	2 (6.0 m)	70.5	203.8	32.5	226.4	15.8	690	38	9
	3 (7.5 m)	60.0	206.6	29.9	219.1	15.0	602	25	4
	4 (14.4m)	84.8	193.6	32.4	246.2	15.4	722	24	7
Section II	1 (12m)	69.1	219.7	30.4	246.9	15.9	599	28	8
	2 (13m)	70.2	210.5	32.7	254.8	17.3	655	22	9
	3 (14m)	63.5	227.9	30.3	232.1	15.3	632	25	8
	4 (15m)	55.6	235.5	28.1	207.1	13.3	576	20	6
	5 (19.4m)	69.9	217.2	27.1	210.1	14.2	702	20	9
Section III	1 (3.1m)	57.5	218.2	28.2	247.0	16.5	509	17	6
	2 (6.0m)	67.4	221.3	30.1	246.7	16.6	615	27	8
Section IV	1 (5.0m)	56.8	228.8	27.6	226.5	15.6	565	22	7
	2 (6.5m)	57.1	227.7	26.1	199.0	13.6	584	24	6
	3 (8.0m)	78.7	205.7	30.1	241.3	15.8	764	27	<LD
Section V	1 (surface)	44.9	192.2	27.8	211.7	18.4	545	41	5
	2 (45 cm)	61.5	203.4	32.6	226.7	19.3	617	53	<LD
	3 (2.0m)	49.4	222.0	28.7	226.4	18.0	453	17	8
	4 (4.6m)	58.5	204.0	31.7	233.3	16.1	580	15	<LD
site I	1 (surface)	53.1	214.9	27.5	200.5	15.4	613	237	5
site II	1 (surface)	55.7	213.4	27.1	215.8	16.3	602	385	5
Background Concentration (mg/kg)		NA	130	NA	NA	NA	4-57.3	1.3-30	NA

<LD indicates low detection limit   * indicates RSD %   NA-data not available   ¹Background concentration - source ARGi (1995)

Table.3.10 Total Elemental Contents (ICP-MS)

Section	Depth	Ca (g/100g)	Ti (g/100g)	V (mg/kg)	Cr (mg/kg)	Fe (g/100g)	Ni (mg/kg)
Section I	1 (3.0 m)	1.77	0.73	122.2	55.6	4.80	33.1
	2 (6.0m)	1.43	0.60	99.9	57.5	3.82	36.3
	3 (7.5 m)	1.59	0.65	99.8	45.1	3.80	21.0
	4 (14.4m)	2.09	0.66	116.3	55.0	4.60	28.3
Section II	1 (12m)	2.43	0.70	110.1	58.8	4.30	31.0
	2 (13m)	2.06	0.67	88.7	42.9	3.93	26.2
	3 (14m)	2.22	0.60	113.9	45.6	3.41	26.3
	4 (15m)	2.15	0.51	98.9	35.9	3.00	19.3
	5 (19.4m)	2.08	0.51	105.1	39.8	3.13	22.4
Section III	1 (3.1m)	2.37	0.73	118.7	54.8	4.08	25.2
	2 (6.0m)	2.40	0.68	123.4	53.4	3.96	25.1
Section IV	1 (5.0m)	2.09	0.52	103.3	44.2	3.18	20.2
	2 (6.5m)	2.17	0.53	96.0	39.4	3.53	17.4
	3 (8.0m)	3.21	0.63	115.8	48.9	4.39	23.9
Section V	1 (surface)	1.75	0.65	95.3	39.0	3.02	21.2
	2 (45 cm)	1.89	0.70	113.8	48.6	4.00	31.8
	1 (2.0m)	1.43	0.61	85.1	36.3	3.21	16.8
	2 (4.6m)	1.38	0.66	99.4	47.6	3.57	27.2
site I	1 (surface)	3.30	0.60	113.2	51.3	3.83	29.5
site II	1 (surface)	2.02	0.71	137.7	89.0	4.07	55.2
Background Concentration[1]		NA	<2.5	4.9-39.5	<0.3	0.15%-3.3%	1.9-5.0

NA-data not available   [1]background concentration - source ARG (1995)

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Table.3.10 *Continued.*

Section	Depth	Cu (mg/kg)	Zn (mg/kg)	As (mg/kg)	Ag (mg/kg)	Cd (mg/kg)	Ce (mg/kg)	Pb (mg/kg)	Th (mg/kg)
Section I	1 (3.0 m)	68.2	150.4	8.3	0.8	0.319	39.6	30.5	5.2
	2 (6.0 m)	68.4	144.5	7.4	0.9	0.430	38.6	34.2	5.3
	3 (7.5 m)	54.1	134.6	9.2	0.9	0.326	34.6	28.4	4.4
	4 (14.4m)	65.2	148.7	8.7	0.9	0.336	38.1	27.5	5.7
Section II	1 (12m)	67.3	143.4	8.9	0.9	0.266	36.3	27.6	5.2
	2 (13m)	57.8	135.1	7.1	0.8	0.253	47.8	24.5	6.4
	3 (14m)	64.1	158.8	9.0	0.9	0.358	33.6	29.9	5.4
	4 (15m)	52.3	121.5	7.2	0.7	0.257	30.4	21.7	4.8
	5 (19.4m)	54.3	145.8	7.5	0.8	0.338	27.8	21.5	4.3
Section III	1 (3.1m)	55.8	162.9	8.2	1.0	0.382	31.2	30.3	4.5
	2 (6.0m)	65.0	179.0	8.7	1.1	0.526	34.5	31.5	5.0
Section IV	1 (5.0m)	55.8	128.4	7.3	0.8	0.280	28.3	24.0	4.1
	2 (6.5m)	57.4	125.8	8.4	0.7	0.293	28.3	28.9	4.5
	3 (8.0m)	58.4	160.9	7.9	0.9	0.415	35.9	29.0	5.5
Section V	1 (surface)	90.9	141.9	6.8	0.8	0.589	25.3	49.2	3.8
	2 (45 cm)	91.8	223.8	8.8	1.0	0.633	22.1	57.3	3.3
	1 (2.0m)	50.7	103.1	5.7	0.7	0.235	19.9	17.1	3.0
	2 (4.6m)	57.0	120.1	5.4	0.8	0.228	21.1	20.3	2.8
site I	1 (surface)	138	447.5	9.9	1.6	1.379	30.3	229	4.4
site II	1 (surface)	132	413.0	11	1.3	1.623	23.1	323	3.4
†Background Concentration (mg/kg)		0.2-35.5	10.7-28.4	2.1-5.7	NA	<0.5	NA	1.3-30	NA

NA-data not available   †Background concentration - source ARG (1995)

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The Ca content of the sections ranges from 1.38 to 3.30 g/100g. All the samples have high Ca concentration and this is due to the proximity of the site to seawater. Section III and IV show considerable increase in Ca content with depth, whereas others show mixed behavior.

The soil Cr content, determined using XRF, varies from 58 to 108 ppm. There is no particular distribution trend observed in Cr content with depth, but relatively high Cr concentrations are found in the lower layers. This may be due to the possible downward movement of Cr in the soil sections. This finding is consistent with the conclusion from the ARG report (1995), which reports possibility of metal movement to the groundwater. A similar movement of Cr through the soil layers and subsequently to the groundwater was also reported by Puls et al (1994).

The total Fe content of the soils varies from 2.95 g/100g to 4.80 g/100g. Section I shows an irregular decrease in Fe_2O_3 content with depth, whereas the other sections show a mixed behavior. The high concentration of Fe_2O_3 may be due to the presence of iron wastes in the landfills.

High Zn content is noticed in all the soils, and it varies from 103.1 to 447.5 ppm. There is no particular distribution trend found in Zn content with depth.

The Ni content of the sections vary from 16.8 to 55.2 ppm. There is an irregular decrease in Ni content is noticed in section II, other sections have no particular Ni distribution trend. The Cu content of the soils ranges from 15 to 134 ppm and there is no trend in Cu distribution in the sections.

The total Cd content of the soils was determined using ICP-MS analysis. The Cd content of the soils vary from 0.228 to 1.623 ppm. A regular increase in Cd content with depth is noticed against background values in section III and IV (Table 3.10). This increase may be due to the downward movement of Cd in the soil sections. The presence of high Cd in the lower layers may be due to the high clay content (Table 3.1.3) of these soils which favors more Cd absorption. Similar results were also reported by Naidu *et al*. (1997), Filius *et al*. (1998) and Hargitai (1995).

A wide range of soil Pb (17.1 to 323 ppm) is noticed in the sections. An irregular decrease in Pb content is observed in section I and II, but sections III and IV show an increase in Pb content with depth. The reason for such an increase and decrease in Pb content is due to the high absorption of Pb in clay layers of the sections.

All the soils have relatively high Sr content and it varies from 192.2 to 235.5 ppm. These samples were checked for their radioactive level using a beta counter, but none of the samples had radioactivity above the background level. The high Sr content may be due to the presence of Sr minerals in soils. Section II. III and V show an irregular increase in Sr content with depth, whereas section IV shows an increase in Sr content. In general, the high Sr content in the lower layers may be due to the weathering nature of soil parent materials and its mineralogical composition. The decrease in Sr content may be due to the low mobile nature of the element. Similar results were also reported by Chamard *et al*. (1993). They found a slow vertical migration of Sr^{90} in soils of Northern Italy.

In general, high average concentrations of Sr, Zn, Pb, Fe, Cr, Cu, Ti, Ni, Zr and V were present in all the sections as compared to the background concentrations reported by ARG (1995) (Table 3.9 and 3.10).

CHAPTER 4

CADMIUM SORPTION, DESORPTION AND RETAINING CAPACITY

Solute retention and release by soil matrix surfaces have been described by equilibrium models or by kinetic (time-dependent) models (Selim, 1992). Equilibrium models assume rapid or instantaneous reactions of the solute with soil matrix. Common approaches are Langmuir models with a maximum sorption term and linear or nonlinear Freundlich models without a maximum sorption term. Kinetic models describe retention and release as a function of time and include irreversible and reversible first-,second-,and n-th order models. The Freundlich equation is the oldest of the nonlinear sorption equations and has been used widely to describe solute retention by soils (Buchter *et al.*, 1989). The Freundlich equation is

$$S = K_d \, C^n$$

where S is the amount of Cd retained by the soil (μmols/kg) and C is the Cd concentration (μM) in the equilibrium solution. This equation allows K_d and n, two characteristic parameters of Cd sorption by the soils concerned, to be readily calculated. In fact, K_d denotes the amount of Cd sorbed at an equilibrium concentration of 1, while n represents the extent to which Cd sorption is dependent on the concentration.

4.1 Section I

Figure 4.1 shows the Cd sorption isotherms of the soils of section I. The pH in this section ranges from 5.25 to 7.60, the organic carbon content from 0.03 to 0.26 % and the CEC from 18.8 to 23.6 cmole(+)/kg (Section 3.1, Tables 3.2 and 3.3). All the log-transformed isotherms in Figure 4.1 are linear proving the suitability of the Freundlich model. All four isotherms are compared in Figure 4.1e and a slight deviation among the isotherms is noticeable at high Cd concentrations, whereas no differences are noted at lower Cd levels. The soil with the lowest pH, 5.26, showed the lowest Cd sorption, indicating a positive relationship between pH and Cd sorption. Similar results were also reported by many authors (Tiller *et al*., 1984, Naidu *et al*., 1997 and Filius *et al*., 1998). Freundlich equations were calculated using these Freundlich isotherm graphs by plotting the logarithmic values of the amount of Cd sorbed (S) vs Cd in the initial $Ca(NO_3)_2$ solution (C_0) (Table 4.1).
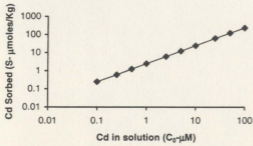
Table 4.1 Freundlich equations for section I

Freundlich equation $S = K_d\, C^n$. S is [Cd] in sorbed phase. C is [Cd] in the soil solution phase and K_d (linear coefficient) and n (exponential coefficient) are constants.

Sample number (Depth)	Freundlich equation	
1 (3.0 m)	$S = 2.47\, C^{0.998}$	(or) $\log S = 0.393 + 0.998 \log C$
2 (6.0 m)	$S = 2.33 C^{0.993}$	(or) $\log S = 0.367 + 0.993 \log C$
3 (7.5 m)	$S = 2.10\, C^{0.951}$	(or) $\log S = 0.322 + 0.951 \log C$
4 (14.4 m)	$S = 2.37\, C^{1.0}$	(or) $\log S = 0.376 + 1.0 \log C$

A statistical analysis was performed to determine the relationships between $\log K_d$ and n values with soil properties. The correlation coefficients (r) for statistically significant and near significant relationships are listed in Table 4.2.
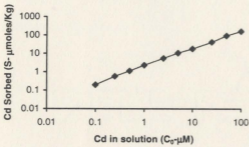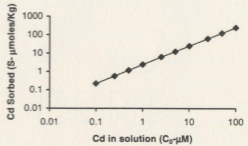
4.1a sample 1 (pH 7.27)

4.1b sample 2 (pH 7.31)
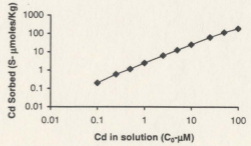
4.1c Sample 3 (pH 5.26)

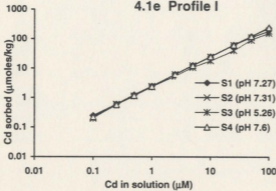4.1d Sample 4 (pH 7.6)

4.1e Profile I

S1 (pH 7.27)
S2 (pH 7.31)
S3 (pH 5.26)
S4 (pH 7.6)

Figure 3.2.1 e

Figure 4.1 Freundlich Isotherm for Section I

Table 4.2 Correlation (r) between soil properties and Freundlich parameters for section l

Properties	Section l				
	K	Log K	n	Cd Retained	Cd Desorbed
pH	0.900	0.912	0.987*	0.713	-0.505
OC	0.754	0.776	0.968*	0.876	-0.729
CEC	ns	ns	0.677	0.830	-0.798
Sand	ns	ns	-0.483	-0.478	0.415
Silt	-0.322	ns	-0.410	-0.790	0.868
Clay	ns	ns	0.636	0.802	-0.779
Cl	0.816	ns	0.538	ns	ns
Fe_2O_3	0.936	0.946	0.982*	0.817	-0.647
Ca	ns	ns	ns	0.903	-0.952*
Zn	0.985*	0.989*	0.949	0.703	ns

ns = not significant, * indicates significance at 0.05 probability level

Both log K and n show a positive correlation with pH values. The organic carbon content is statistically significant and correlates positively with n values but not significantly with log K values. A similar trend is also noticed between Fe_2O_3 content and the Freundlich parameters, whereas the Zn content shows a significant positive relationship with log K and a positive correlation (not significant) with n values. The Cd sorption in soils may be due to binding of Cd by metal oxides such as Fe_2O_3. Similar results were also reported by Buchter et al (1989). Other properties such as CEC, clay and Cl content also correlate with Freundlich parameters but the relationships are not statistically significant.

The relationships between soil properties (pH, OC and Fe_2O_3) and sorption parameters (log K and n) were also performed using regression analysis. The regression lines with equations are presented in Figure 4.2. These equations can be used to estimate the sorption parameters when data for a particular soil property is available. For many
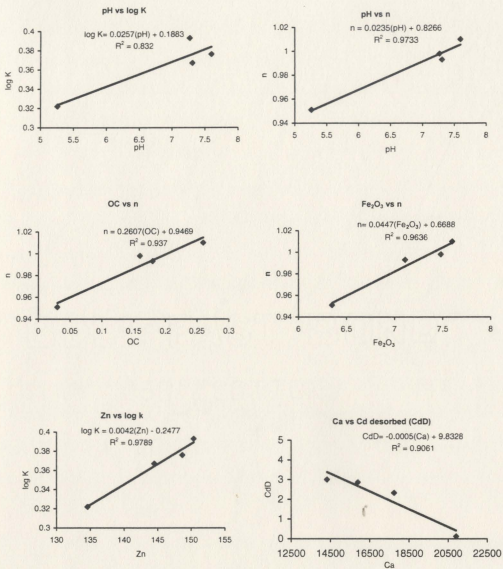
Figure 4.2 Correlation and regression between soil properties and retention parameters (Section I)

purposes such an estimate would be useful, as a first approximation, in describing the sorption characteristics of a soil.

Apart from the soil composition and the metal concentration in the soil solution, soil pH and organic carbon content have strong effects on the sorption behavior of soils (Filius et al 1998), therefore, the soil pH and organic carbon content were included in an extended Freundlich equation expressed as;

$$S = K_d* (pH)^a OC^b C^n \text{ or}$$

$$\text{Log } S = \log K + a \text{ pH} + b \log OC + n \log C \text{ -----------------------------(3.2.1)}$$

The parameters a, b, and n for the extended Freundlich equation were estimated by multiple regression analysis of the log transformed data using the SigmaStat 2.03 statistical package. The data for Cd sorption in all the soil samples of section I were pooled to derive the coefficients for the extended Freundlich expression (Eq.3.2.1). For section I, the organic carbon content does not show any correlation with the Freundlich parameters (log K and n), because of its low content and narrow range in the soils, so the parameter b was eliminated from the extended equation and the equation was calculated as

$$\text{Log } S = 0.0996 + (0.0386 \text{ pH}) + (0.989 \log C) \text{ -----------------------------------(3.2.2)}$$

If sorption in soils of section I is governed by pH only, Eq.(3.2.2) may correctly describe the soil metal sorption behavior.

The results of Cd desorption experiments and stepwise calculations are presented in Appendix A.2. The amount of Cd present in the soil after Cd addition, the amount of Cd desorbed during the serial stepwise extraction experiments and the amount of Cd retained in the soil after the desorption experiment for section I samples are presented in Table 4.3

Table 4.3 Cadmium retaining capacity for section I

Sample	Cd concentration after Cd treatment (mg/kg)	Cd desorbed (mg/kg)	Cd retained in the soil (mg/kg)
1	27.78	2.33	25.45
2	27.67	3.00	24.67
3	26.08	2.86	23.83
4	28.08	0.12	27.96

The soil with high pH and organic carbon content (sample # 4) retained more Cd than the soil with low pH and organic carbon content (sample #3). The soil calcium content showed a significant negative correlation with Cd desorbed values (Table 4.2), whereas, other properties such as pH, organic carbon, CEC, clay, Fe_2O_3 and Zn contents show a negative correlation with Cd desorbed values, but these values are not statistically significant. In general, the Cd sorption and retaining capacities decreased with increasing depth up to the 3rd layer (up to 7.5m depth) and thereafter an increase in Cd sorption and retaining capacity is noticed. This might be due to the variation in soil pH and organic carbon content. The strong positive correlation of these soil properties with Freundlich constants also supports the above mentioned relationship.

4.2 Section II

The sorption isotherms for the soils of section II are presented in Figure 4.3. The pH levels of the soils are uniform throughout the section. The organic carbon content varies from 0.08 to 1.43% and the CEC from 15.8 to 23.9 cmole(+)/kg (Section 3.1, Tables 3.2 and 3.3). The isotherms of these soils show a linear relationship and they are compared in Figure 4.3f. Almost no differences are observed among the isotherms and this graph is basically a single line. The narrow range of pH values of these soils is a possible reason for this lack of difference in isotherms. Martín and Camazano (1993) also reported a similar result.

The Freundlich equations for these samples were calculated and the isotherm graphs are presented in Figure 4.3

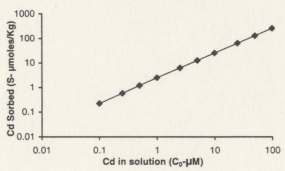**Table 4.4** Freundlich equations for section II

Sample number (Depth)	Freundlich equation
1 (12)	$S = 2.19\ C^{1.0}$ (or) $\log S = 0.354 + 1.0 \log C$
2 (13)	$S = 2.41\ C^{1.0}$ (or) $\log S = 0.381 + 1.0 \log C$
3 (14)	$S = 2.46\ C^{1.0}$ (or) $\log S = 0.391 + 1.0 \log C$
4 (15)	$S = 2.50\ C^{1.0}$ (or) $\log S = 0.398 + 1.0 \log C$
5 (19.4)	$S = 2.50\ C^{1.0}$ (or) $\log S = 0.398 + 1.0 \log C$

The K_d values in the above equations show a slight increase with increasing depth: whereas the value for the exponential coefficient, n, is 1 for all the samples.
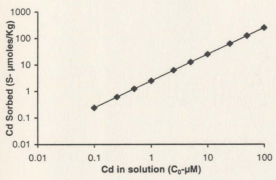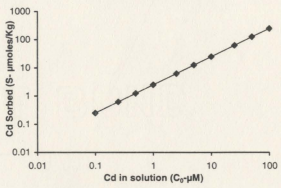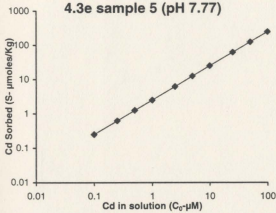
4.3a sample 1 (pH 7.78)
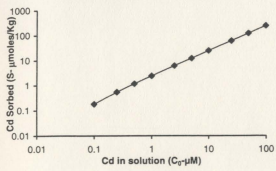
4.3b sample 2 (pH 7.74)

4.3c sample 3 (pH 7.66)

4.3d sample 4 (pH 7.7)

4.3e sample 5 (pH 7.77)

4.3f Prfile II

- S1 (pH 7.78)
- S2 (pH 7.74)
- S3 (pH 7.66)
- S4 (pH 7.7)
- S5 (pH 7.77)

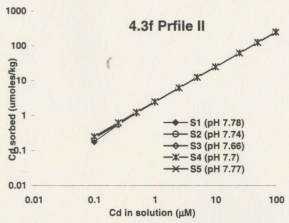Axis labels: Cd Sorbed (S- µmoles/Kg) vs Cd in solution (C_0-µM)
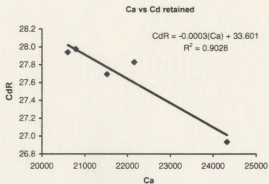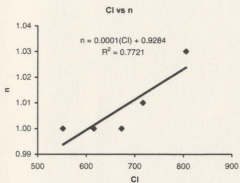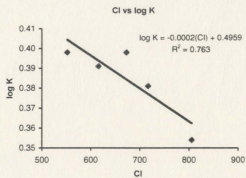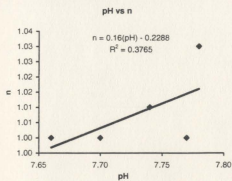
Figure 4.3 Freundlich Isotherm for Section II

Figure 4.4 Correlation and regression between soil properties and retention parameters (Section II)

Table 4.5 shows the results of correlation analysis between the soil properties and the Freundlich coefficients.

Table 4.5 Correlation (r) between soil properties and Freundlich parameters for section II

Properties	Section II			
	Log K	n	Cd Retained	Cd Desorbed
pH	ns	0.614	ns	ns
OC	ns	ns	ns	ns
CEC	ns	ns	ns	ns
Sand	ns	ns	ns	ns
Silt	ns	ns	ns	ns
Clay	ns	ns	ns	ns
Cl	-0.874	0.879*	-0.590	0.676
Fe_2O_3	ns	ns	ns	ns
Ca	-0.797	ns	-0.950*	0.941*
Zn	ns	ns	ns	ns

ns = not significant and * indicates significance at 0.05 probability level

A non-significant correlation is noted between the sorption coefficients (log K and n values) and pH, OC and CEC values. The reason for this lack of correlation may due to a very narrow range of properties in the soils. Soil fractions such as clay, sand and silt percentages also exhibits non-significant correlations with Freundlich coefficients, whereas, the Cl content of the soils correlates negatively with log K values (Table 4.5). The chloride anions can decrease the sorption of Cd by forming $CdCl^+$, which is less readily sorbed than Cd. Similar results were also reported by Lumsdon *et al.* (1995) and Bolan *et al.* (1999). Similarly, the Ca content of the soils also show a negative correlation with the sorption coefficient (log K). The decrease in Cd sorption with increasing Ca

content may be due to the competition with Ca ions. Homann and Robert (1987) also reported that dissolved Ca strongly depressed Cd sorption. The regression lines, with equations, for the soil properties and sorption parameters are presented in Figure 4.4.

The Cd desorption experiment was carried out for all the samples of section II and the results are presented below (Table 4.6)

Table 4.6 Cadmium retaining capacity for section II

Sample	Cd concentration after Cd treatment (mg/kg)	Cd desorbed (mg/kg)	Cd retained in the soil (mg/kg)
1	28.09	1.15	26.93
2	28.08	0.14	27.94
3	28.03	0.20	27.83
4	27.97	0.28	27.69
5	28.09	0.12	27.97

All the samples sorbed high amounts of Cd, and there is no regular increase or decrease in Cd desorbed values with depth. There is a positive correlation between Cl and Ca at the 0.05 probability level with Cd desorption and similarly, a negative correlation of these properties with Cd retention is observed. The presence of competing cations such as calcium is likely to induce the leaching of cadmium from the soil.

4.3 Section III

Two soil samples from section III collected at 3.1m and 6.0m were used for the Cd sorption and desorption experiments. The sorption isotherms for these samples are presented in Figure 4.5. The Freundlich isotherms are linear and the sorption equations are:

For sample 1

$$S = 2.42 \, C^{1.0} \quad \text{(or)} \quad \log S = 0.384 + 1.0 \log C$$

For sample 2

$$S = 2.49 \, C^{1.0} \quad \text{(or)} \quad \log S = 0.397 + 1.0 \log C$$

Statistical analysis was not performed due to insufficient number of samples. The pH values of these samples were very similar as were the CEC values (refer in Section 3.1 Table 3.2 and Table 3.3). The sorption equations for these samples are also similar and this may be due the narrow range of pH and CEC values and the similarity in soil type.

The Cd desorption experiments performed on these soil samples show similar results and are presented in Table 4.7

Table 4.7 Cadmium retaining capacity for section III

Sample	Cd concentration after Cd treatment (mg/kg)	Cd desorbed (mg/kg)	Cd retained in the soil (mg/kg)
1	27.97	0.22	27.75
2	27.96	0.22	27.75

Both the samples retained the same amount of Cd.

4.5a sample 1 (pH 7.64)
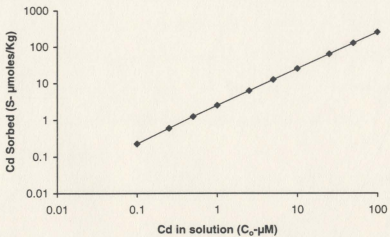
4.5b sample 2 (pH 7.73)

Figure 4.5 Freundlich Isotherm for Section III
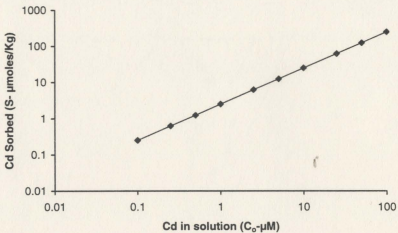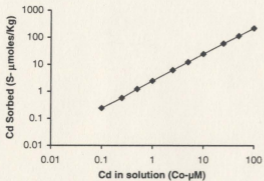
4.4 Section IV

Figure 4.6 shows the Cd sorption isotherms of section IV soils. The pH values are uniform throughout the section, and there is a narrow range of organic carbon content. All the three isotherms are compared and presented in Figure 4.6d A slight difference is noticed at lower Cd concentrations, whereas no differences are noted at higher Cd levels. The Freundlich sorption equations for these samples are given in Table 4.8.

Table 4.8 Freundlich equations for section IV

Sample number (Depth)	Freundlich equation
1 (5.0)	$S = 2.41\ C^{1.0}$ (or) $\log S = 0.382 + 1.0 \log C$
2 (6.5)	$S = 2.37\ C^{1.0}$ (or) $\log S = 0.374 + 1.0 \log C$
3 (8.0)	$S = 2.16\ C^{1.0}$ (or) $\log S = 0.334 + 1.0 \log C$

The K_d value increases with increasing depth, whereas the n values for all the samples are 1. The correlation analysis performed between soil properties and Freundlich coefficients are presented in Table 4.9.

4.6a sample 1 (pH 7.67)

4.6b sample 2 (pH 7.76)
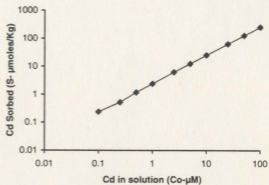
4.6c sample 3 (pH 7.66)

4.6d Profile IV

Figure 4.6 Freundlich Isotherm for Section IV

Table 4.9 Correlation (r) between soil properties and Freundlich parameters for section IV

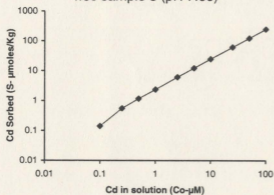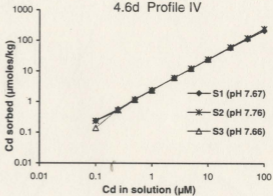| Properties	Section II			
	Log K	**n**	**Cd Retained**	**Cd Desorbed**
pH	ns	ns	-0.952	0.971
OC	-0.912	0.780	0.930	-0.902
CEC	-0.936	0.818	0.905	-0.873
Sand	0.949	-0.840	-0.887	0.853
Silt	ns	ns	0.920	-0.945
Clay	-0.988	0.918	0.800	-0.756
Cl	ns	ns	0.790	-0.831
Fe_2O_3	-0.987	0.914	0.804	-0.761
Ca	-0.996	0.943	0.757	-0.710
Zn	-0.975	0.889	0.838	-0.798

ns = not significant

There is no significant relationship found between the pH values and sorption parameters. This is due to the narrow range of pH values among the soils (Table 3.2), whereas, OC, CEC values and clay percentage shows negative correlations with log K values but are not statistically significant. This is contradictory to the results obtained in other sections and the results reported by other authors (Naidu *et al.*, 1997 and Martín and Camazano, 1993) where these properties positively correlated with log K . The reason for this negative relationship may be due to the influence of other factors such as the presence of Ca, Fe_2O_3 and Cl in the soils. Log K shows a negative correlation with Ca, Zn and Fe_2O_3 values, which may be due to the competition of cations with Cd sorption.
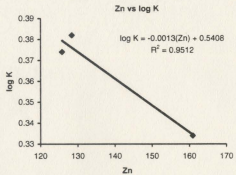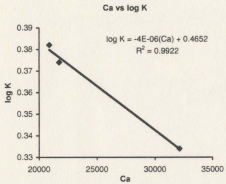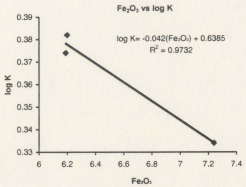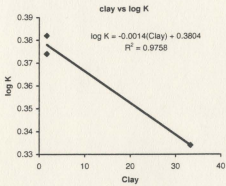
Figure 4.7 Correlation and regression between soil properties and retention parameters (Section IV)

The regression equations and graphs for soil properties and sorption coefficients were calculated and are presented in Figure 4.7.

The results of Cd desorption experiments are presented in Table 4.10 and in Appendix A.2

Table 4.10 Cadmium retaining capacity for section IV

Sample	Cd concentration after Cd treatment (mg/kg)	Cd desorbed (mg/kg)	Cd retained in the soil (mg/kg)
1	27.95	0.203	27.75
2	27.85	0.229	27.62
3	28.02	0.190	27.83

No particular trend in Cd desorption with depth is found for section IV. The amounts of Cd retained in all the three samples are almost similar in values. The results from the correlation studies show a non-significant positive correlation between the Cd retained values and OC, CEC, clay, silt, Cl, Fe_2O_3, Ca and Zn values, whereas a negative correlation is observed between the above parameters and the Cd desorbed values (Table 4.9).

4.5 Section V

Four samples from section V were used for the sorption and desorption experiments. All the samples showed low pH levels and these varied from 4.67 to 6.58. Freundlich isotherms for these samples are presented in Figure 4.8. The isotherm lines for all the samples are compared and presented in Figure 4.8e and all the points lie in a single line. The sorption equations were calculated and presented in Table 4.11.

Table 4.11 Freundlich equations for section V

Sample number (Depth)	Freundlich equation
1 (surface)	$S = 2.16\ C^{1.0}$ (or) $\log S = 0.335 + 1.0 \log C$
2 (25-35cm)	$S = 2.30\ C^{1.0}$ (or) $\log S = 0.362 + 1.0 \log C$
3 (2.0m)	$S = 2.21\ C^{1.0}$ (or) $\log S = 0.343 + 1.0 \log C$
4 (4.6m)	$S = 2.29\ C^{1.0}$ (or) $\log S = 0.361 + 1.02 \log C$

There is a slight increase in Cd sorption with increasing pH levels, but the results from the correlation analysis (Table 4.12) show a non-significant relationship between pH and sorption parameters.
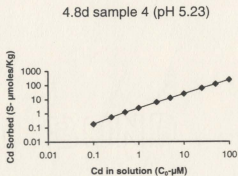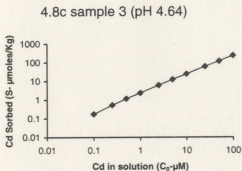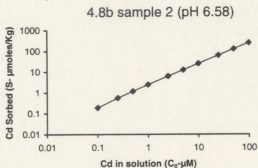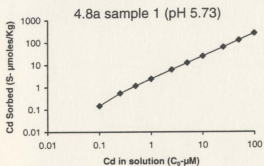
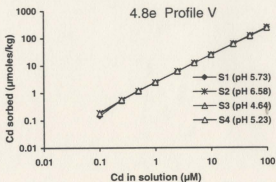Figure 4.8 Freundlich Isotherm for Section V
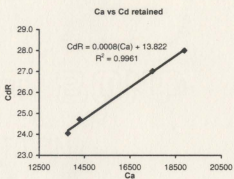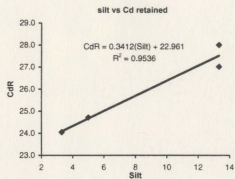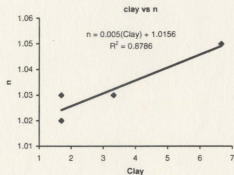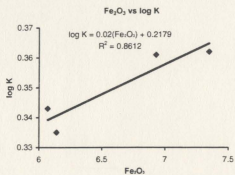
Figure 4.9 Correlation and regression between soil properties and retention parameters (Section V)

Table 4.12 Correlation (r) between soil properties and Freundlich parameters for section V

Properties	Section V			
	Log K	n	Cd Retained	Cd Desorbed
pH	Ns	Ns	0.876	Ns
OC	Ns	0.934	Ns	Ns
CEC	Ns	0.796	0.886	Ns
Sand	Ns	-0.823	-0.920	Ns
Silt	Ns	Ns	0.977*	Ns
Clay	Ns	0.937	Ns	Ns
Cl	Ns	0.915	0.809	Ns
Fe_2O_3	0.928	Ns	Ns	Ns
Ca	Ns	Ns	0.998**	Ns
Zn	Ns	ns	0.858	ns

ns = not significant and * indicate significance at 0.05 probability level

The other parameters such as OC, CEC, sand, silt, clay, Cl, Ca and Zn also show non-significant relationship with log K, whereas, the exponential coefficient n exhibits positive correlation with OC, CEC, clay and Cl values, however neither of these are statistically significant. The regression line and equations for these soils are presented in Figure 4.9

The results of Cd desorption experiment is presented in Table 4.13 and Appendix A.2

Table 4.13 Cadmium retaining capacity for section V

Sample	Cd concentration after Cd treatment (mg/kg)	Cd desorbed (mg/kg)	Cd retained in the soil (mg/kg)
1	28.06	1.048	27.01
2	28.09	0.089	28.00
3	26.27	1.559	24.71
4	26.80	2.751	24.05

The amount of Cd desorbed increases with increasing depth, and it is highest in the bottom layer, thus, more Cd is retained in the top two layers. This may be due to the increase in sand percentage with depth, which sorbs lower amounts of Cd compared to clay particles.

4.6 Site I and II

Freundlich equations and graphs for the site I and II are presented in Figure 4.10 and Table 4.14, respectively. Both the samples had similar pH values and high organic carbon content. The results of Cd desorption experiment and Cd retaining capacity are presented in Table 4.15.

4.10a Site 1 (pH 6.68)
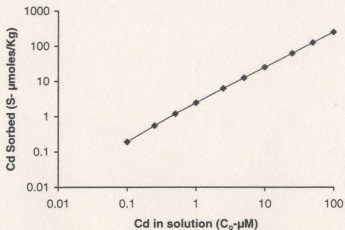
4.10b Site II (pH 6.45)
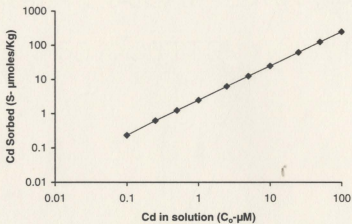
Figure 4.10 Freundlich Isotherm for Site I and II

Table 4.14 Freundlich equations for site I and II

Sample (Depth)	Freundlich equation
Site I (surface)	$S = 2.30 \, C^{1.0}$ (or) $\log S = 0.362 + 1.0 \log C$
Site II (surface)	$S = 2.47 \, C^{1.0}$ (or) $\log S = 0.393 + 1.0 \log C$

Table 4.15 Cadmium retaining capacity for site I and II

Site	Cd concentration after Cd treatment (mg/kg)	Cd desorbed (mg/kg)	Cd retained in the soil (mg/kg)
I	29.00	0.054	28.05
II	28.10	0.072	28.02

4.7 Cadmium Mobility

The mobility of Cd in selected samples from each section was determined using Thin Layer Chromatography (TLC). Few studies (Martín and Camazano, 1993) have been carried out previously to determine Cd mobility using TLC. Cadmium mobility was measured visually as R_f values, i.e. the distance traveled by Cd spots from the origin. The R_f values are presented in Table 4.16.

Table 4.16 Cadmium mobility (R_f) values

Section number (Depth)	pH	Average R_f value with Standard deviation
I (7.5m)	5.26	0.70 ± 0.07
I (14.4m)	7.60	0.48 ± 0.18
II (13.0m)	7.74	0.52 ± 0.07
II (19.4m)	7.77	0.21 ± 0.05
III (3.1m)	7.64	0.59 ± 0.07
IV (5.0m)	7.67	0.40 ± 0.05
V (2.0m)	4.67	1.00 ± 0.00
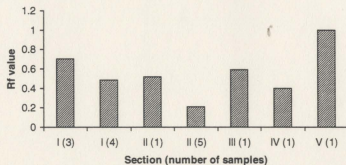
Figure 4.11 Cd Movement in TLC (Rf)

The Rf values range from 0.21 to 1.00, with relatively higher Rf values (more than 0.50) being noted for sections I (at 7.5cm), II (at 13.0m), III (at 3.1m) and V (at 2.0m) (Figure 4.11). R_f values below 0.50 were generally found for soils with a medium to high adsorption capacity (Martín and Camazano, 1993). These soils are generally high in pH, Ca and organic carbon contents (Section 3.1 and 3.2). On the other hand, R_f values above 0.50 correspond to soils of variable sorption capacity and low pH.

The samples that have lower pH values recorded high mobility, whereas the soils which higher pH levels showed relatively low R_f values (Figure 4.11). Therefore, the lower the pH, the higher will be the Cd mobility in soils since high pH values favors the exchange of Cd by other cations. Similarly, low clay content favors mobility of Cd in soils.

4.8 Overall Discussion

Environmental hazards from heavy metals are closely linked to metal mobility, and thus to the concentrations of the metals in the soil solution. The soil samples in the study area were found to have a variety of heavy metals. High concentrations of Sr, Zn, Pb, Fe, Ti and Zr compared to background levels were present in all the sections. The abundance of common mobile metals such as Cd, Sr, Zn, Pb and Cu show the following order: Sr > Zn > Pb ≥ Cu > Cd. Relatively low Cd content was found in all the samples and total Cd content of the soils ranged from 0.228 to 1.623 ppm, the available Cd content of the soils varied from 18.0 to 39.19 µg/kg and are below the CCME guideline value of 5mg/kg.

The sorption and mobility of heavy metals depends not only on the total metal concentration in soil but also on soil properties. In general, Cd sorption and mobility were influenced by soil texture, pH, organic carbon content and CEC. In section-I, the sand layer was present just below the top landfill layer, followed by a clay rich bottom layer. The Cd sorption decreased with increasing sand percentage and the sand layer had high Cd mobility, which favoured contaminant transport to the bottom layer. The bottom clay layer showed high Cd retaining capacity which could act as a potential sink for Cd and for other metals, with slow release of the metals to the groundwater.

In section I and II, the pH and organic carbon content showed a positive relationship with Cd sorption. The CEC value was not significantly related with Cd sorption, likely due to the same range of values in the sections.

Sections I, II, III and IV are located near the sea shore and there is a possibility of releasing sorbed Cd and other metals from the soils to the groundwater and to the near

Figure 4.12 Soil sorption effect on contaminants
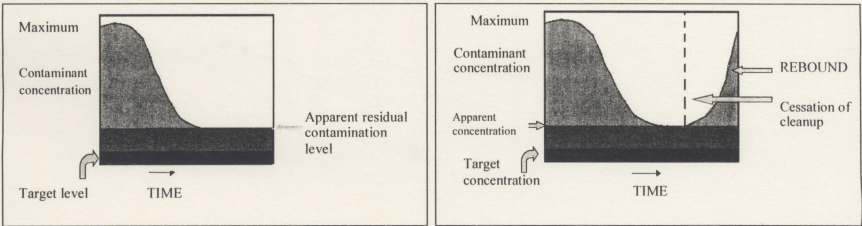
marine environment, especially, if the pH of the soil decreases due to local anthropogenic activities or acid rain.

A relatively high amount of Cd was sorbed by the soils of section II compared to other sections and this might be due to the higher pH values of these soils. Sections I, II, III and IV had high clay percentages in their bottom layers, which could act as a potential sink for contaminants. The intermediate sand and silt layers of these sections showed higher Cd mobility which could in turn transport the contaminants quickly to the lower clay layers.

The section V had a top layer of landfill followed by a black peat layer and then by a sandy layer. Higher sand content was found for all the samples of this section which reduced the Cd sorption and increased the Cd mobility. The pH of these samples was acidic and this might have also reduced Cd sorption. The production of organic acids in the peat layer might be the reason for lowering the soil pH levels in this section.

Sandy soils had higher Cd mobility than the clay soils, likely due to the high leaching and low sorption capacity of sandy soils.

The soil sorbed contaminants in the study area landfills could form a potential and a permanent source for groundwater contamination. There is a possibility of the contaminants being leached out from the soil sorbed phase, even after the removal or cleanup of these landfills. The contaminants from the apparent residual contamination level could rebound after the cessation of cleanup, in the contaminated areas (Figure 4.12). In conclusion, sorption and desorption are two important factors which should be taken into account before remediation of contaminated landfills.

CHAPTER 5

CONCLUSION

A variety of heavy metals were found in the soil samples of the former US Naval Base, Argentia. All of the samples examined showed high Sr, Zn, Pb, Fe, Cr, Cu, Ti, Ni, Zr and V concentrations compared to the background concentrations reported in the ARG report (1995). The average concentration of the heavy metals analyzed in the present study and the background concentrations for the study area soils as reported by ARG (1995) are summarized as :

Elements	This Study	Background Concentration (ARG 1995)
Sr	213	130
Zn	175	10.7-28.4
Pb	54	1.3-30
Cd	0.47	<0.5
Fe	3.78%	0.15-3.3%
Ti	0.63%	<2.5
Zr	227	Not available
Cu	37.7	<0.2-35.5
V	124	4.9-39.5
Cr	76	<0.3
Ni	27	1.9-5.0

The abundance of common mobile elements such as Sr, Cd, Zn, Pb, Cr and Cu in the soil sections were in the following order: Sr > Zn>Cr > Pb > Cd . The total Cd content of the soil samples was found to be below the CCME guideline value of 5 mg/kg. Other metals such as Rb, Y, Nb, Ba, Th, Ti, As, Se, Br, Ag and Ce were also present in the soil samples.

The Cd sorption capacity of the soils was determined using the Freundlich Isotherm model. The isotherms for all samples showed a linear trend and proved the suitability of this model for the present study. The Cd sorption increased with increasing depth in section II and III, and decreased in section IV, whereas, the other sections showed mixed behavior. This was due to the possible influence of soil texture, pH and organic carbon content of the soils. In general, all the sections showed high Cd retaining capacity.

The sorption of Cd by the soils studied was found to be pH dependent and increased with increasing solution Cd concentrations. Simple correlations between the sorption parameters and soil properties revealed a strong relationship between clay, sand and organic carbon content. CEC, silt and other properties also showed some relationship with sorption parameters, but were not statistically significant, likely due to the narrow range of these properties in the sections.

The results also revealed the possible correlation between Cd sorption and associated anions. In particular, the sorption of Cd decreased with increasing Cl^- content of soils of section V, which can be attributed to the formation of $CdCl^+$, which is less readily sorbed than cadmium. Therefore, an increase in Cl^- content in landfill sites containing elevated amounts of heavy metals could enhance the movement of the heavy metals into the subsoil and groundwater. In some soils (section IV), the presence of competing cations, such as calcium, induced the leaching of cadmium.

The results of soil thin layer chromatography (TLC) revealed the possible relationship of Cd mobility with pH and sand content of the soil samples. The samples that showed lower pH and high sand percentage showed higher Cd mobility, therefore,

the lower the clay content and pH value, the higher will be the Cd mobility in the soil layers.

In general, the contaminated soils were characterized and classified using the USDA soil textural classification method. The soils were classified as sandy, loamy sand, sandy loam, sandy clay loam, loam, clay loam and silty clay loam. The majority of the soil samples contained considerable amounts of sand, which favored Cd mobility to the lower layers and subsequently to the groundwater.

In conclusion, the following factors should be considered before recommending any particular remediation measures:

▫ Metal sorption, desorption and retaining capacity of the soils
▫ The depth distribution of soil properties such as pH, organic carbon content, cation exchange capacity and soil fraction
▫ Concentrations of anions and cations with respect to the depth
▫ Type of soil

The results obtained in this study can be used to help formulate remedial measures. Further investigations on the vertical migration of metals would be useful and this could be carried out by conducting batch sorption experiments. The effect of acid rain or any other anthropogenic activities on the contaminant transport to the sub soil layers and groundwater could be established by changing the pH levels of the soil samples and conducting simulation studies.

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Appendix A.1 ICP-MS and XRF comparision

Ca

Ti
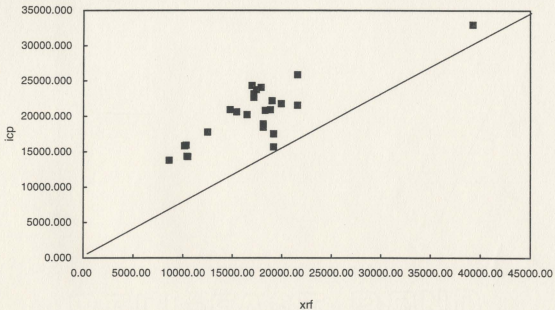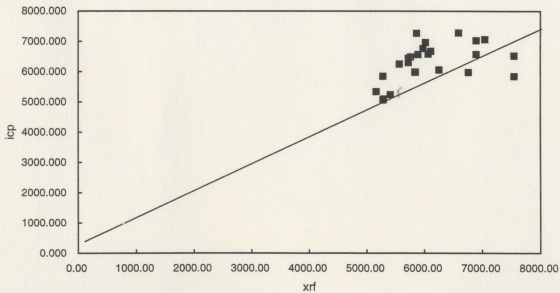
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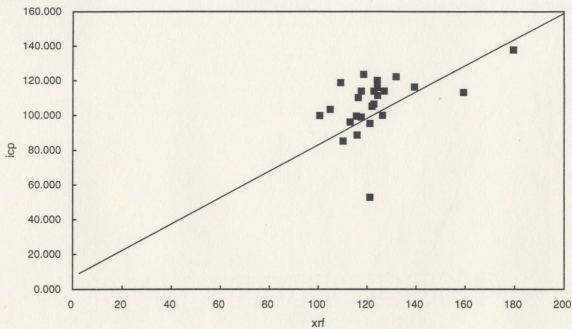
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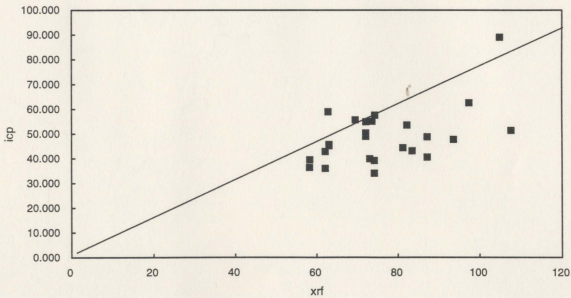
Appendix A.1

Ni
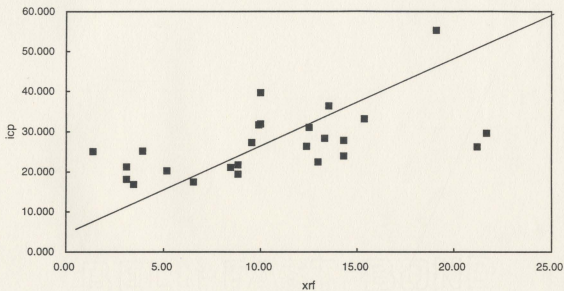
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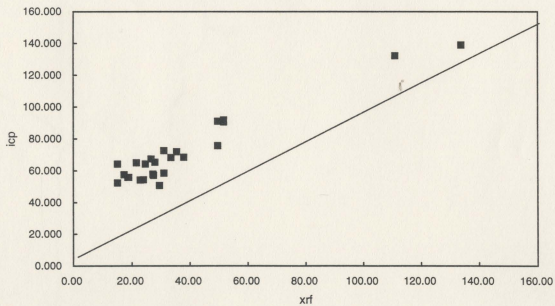
Appendix A.1

Zn

As

Appendix A.1

Ce
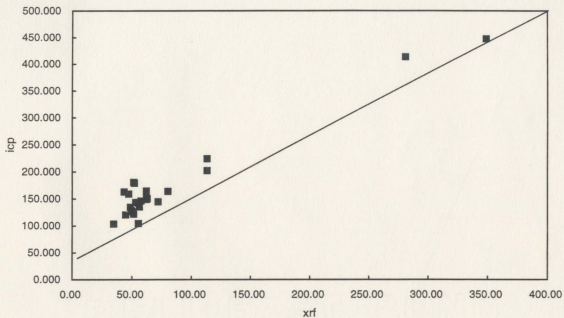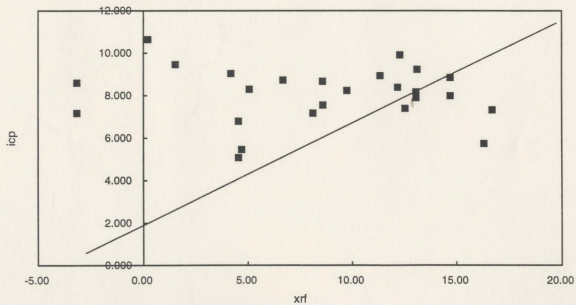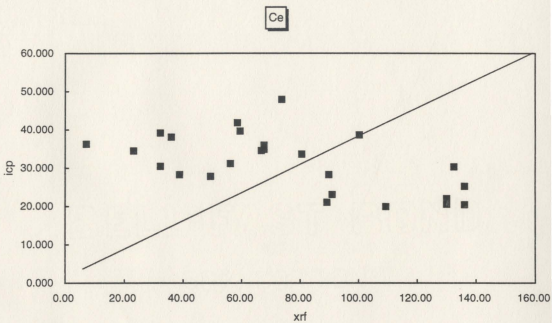
Appendix A.2 Cadmium desorption and retaining capacity

Sample	Cd in the remaining soln.(ug/L)	Desorp I	Desorp II	DesorpIII	DesorpIV	DesorpV	DesorpVI	Total Desorp	Tot.Des (mg/L)	Cd Desorbd (mg/1kg)
I (1)	143.174	58.390	35.820	18.810	18.660	12.060	11.460	155.200	0.155	2.328
I (2)	177.429	81.790	42.940	23.700	21.940	17.990	11.840	200.200	0.200	3.003
I(3)	577.361	102.780	34.050	21.700	11.260	10.470	10.390	190.650	0.191	2.860
I(4)	17.359	10.752	3.019	2.068				15.839	0.016	0.119
II(1)	21.003	16.540	13.440	13.740	13.210	10.580	9.250	76.760	0.077	1.151
II(2)	20.879	10.000	4.244	3.856				18.100	0.018	0.136
II(3)	37.733	15.525	7.580	3.710				26.815	0.027	0.201
II(4)	60.933	24.179	8.050	4.448				36.677	0.037	0.275
II(5)	13.460	8.384	3.425	3.504				15.313	0.015	0.115
III(1)	62.666	20.491	7.577	0.983				29.051	0.029	0.218
III(2)	59.114	12.319	9.962	7.188				29.469	0.029	0.221
IV(1)	69.304	19.135	7.880	0.050				27.065	0.027	0.203
IV(2)	103.660	15.796	8.934	5.845				30.575	0.031	0.229
IV(3)	40.192	12.258	7.604	5.450				25.312	0.025	0.190
V(1)	20.110	12.920	13.400	11.360	13.930	11.290	6.950	69.850	0.070	1.048
V(2)	10.535	6.149	5.761	0.000				11.910	0.012	0.089
V(3)	735.041	50.770	13.870	11.590	11.220	8.390	8.080	103.920	0.104	1.559
V(4)	524.650	140.012	40.919	22.826	10.570	5.720		220.047	0.220	2.751
S1	3.933	3.797	3.401	0.000				7.198	0.007	0.054
S2	6.096	5.093	4.505	0.000				· 9.598	0.010	0.072

Appendix A.2 Continue.
Cd adsorbed in 1 kg of soil (treated with 100uM Cd soution)

Sample	Cd initial Conc(Co) uM	in (mg/L) (a)	Cd in the remaining soln.(ug/L)	Cd in mg/L (b)	S=Amt.of Cd adsorbed(mg/Kg) [(a-b)*0.025/0.01]
I (1)	100	11.24	143.174	0.143	27.742
I (2)	100	11.24	177.429	0.177	27.656
I(3)	100	11.24	577.361	0.577	26.657
I(4)	100	11.24	17.359	0.017	28.057
II(1)	100	11.24	21.003	0.021	28.047
II(2)	100	11.24	20.879	0.021	28.048
II(3)	100	11.24	37.733	0.038	28.006
II(4)	100	11.24	60.933	0.061	27.948
II(5)	100	11.24	13.460	0.013	28.066
III(1)	100	11.24	62.666	0.063	27.943
III(2)	100	11.24	59.114	0.059	27.952
IV(1)	100	11.24	69.304	0.069	27.927
IV(2)	100	11.24	103.660	0.104	27.841
IV(3)	100	11.24	40.192	0.040	28.000
V(1)	100	11.24	20.110	0.020	28.050
V(2)	100	11.24	10.535	0.011	28.074
V(3)	100	11.24	735.041	0.735	26.262
V(4)	100	11.24	524.650	0.525	26.788
SI	100	11.24	3.933	0.004	28.090
S2	100	11.24	6.096	0.006	28.085

Appendix A.2 Continue.

Total amount of Cd (amount of Cd already in the soil as available Cd phase + amount of Cd adsorbed)

Sample	Available Cd (mg/kg) (A)	Amount of Cd adsorbed (mg/kg) (B)	Total Cd in the soil after shaking A+B(mg/kg)
I (1)	0.039	27.742	27.781
I (2)	0.017	27.656	27.674
I(3)	0.029	26.657	26.685
I(4)	0.025	28.057	28.082
II(1)	0.038	28.047	28.086
II(2)	0.027	28.048	28.075
II(3)	0.023	28.006	28.028
II(4)	0.020	27.948	27.968
II(5)	0.022	28.066	28.089
III(1)	0.027	27.943	27.970
III(2)	0.021	27.952	27.973
IV(1)	0.021	27.927	27.948
IV(2)	0.009	27.841	27.850
IV(3)	0.016	28.000	28.015
V(1)	0.012	28.050	28.062
V(2)	0.012	28.074	28.086
V(3)	0.010	26.262	26.273
V(4)	0.010	26.788	26.799
SI	0.010	28.090	28.100
S2	0.011	28.085	28.096

Appendix A.2 Continue.
Cd Retained in the soil (after the desorption)

Sample	Total Cd (mg/kg) (a)	Cd Desorbd(mg/kg) (b)	Cd Retained in the soil (mg/kg) (a-b)
I (1)	27.781	2.328	25.453
I (2)	27.674	3.003	24.671
I(3)	26.685	2.860	23.826
I(4)	28.082	0.119	27.963
II(1)	28.086	1.151	26.934
II(2)	28.075	0.136	27.939
II(3)	28.028	0.201	27.827
II(4)	27.968	0.275	27.693
II(5)	28.089	0.115	27.974
III(1)	27.970	0.218	27.752
III(2)	27.973	0.221	27.752
IV(1)	27.948	0.203	27.745
IV(2)	27.850	0.229	27.621
IV(3)	28.015	0.190	27.825
V(1)	28.062	1.048	27.014
V(2)	28.086	0.089	27.996
V(3)	26.273	1.559	24.714
V(4)	26.799	2.751	24.048
SI	28.100	0.054	28.046
S2	28.096	0.072	28.024