AN EVALUATION OF DEDICATED LAND DISPOSAL PRACTICES FOR SEWAGE SLUDGE

by

JE Herselman, PW Wade, CE Steyn and HG Snyman

Report to the Water Research Commission on the Project
“An evaluation of dedicated land disposal practices for sewage sludge "

WRC Report No. 1209/1/05
ISBN No : 1-77005-288-7

MARCH 2005

EXECUTIVE SUMMARY

This research project forms part of a research program funded by the Water Research Commission that started in 2001 to critically assess the South African sludge legislation and revise the guidelines if necessary. This multidisciplinary research program includes the following projects:

- **WRC Project Number 1209:** An evaluation of dedicated land disposal practices for sewage sludge
- **WRC Project Number 1210:** Laboratory and field scale evaluation of agricultural use of sewage sludge
- **WRC Project Number 1240:** A technical and financial review of sludge treatment technologies
- **WRC Project Number 1283:** A metal content survey of South African sewage sludge and an evaluation of analytical methods for their determination in sludge
- **WRC Project Number 1339:** Survey and methodology for analyzing organic pollutants in South African sewage sludge

The results of the research projects will form the knowledge base to start a participative process in 2003 to develop Edition 2 of the Permissible utilization and disposal of sewage sludge guidelines.

The main aim of this study was to determine the current and future impact of DLD practices on the environment. The outcome of the study can serve as input for the revision of the guidelines for sludge disposal. The objectives of the study were as follows:

1. To evaluate the extent of the current practice of disposing of sewage sludge on dedicated land.
2. To evaluate the potential pollution risk this practice poses to the water environment at selected sites.
3. To estimate the future impact of dedicated land disposal of sewage sludge on the water environment.

Most of the wastewater treatment facilities in South Africa dispose of their sewage sludge on dedicated land disposal (DLD) sites (sacrificial lands), since this is the quickest and cheapest way to get rid of the waste. The sludge is regularly applied at high rates to the surface soils. No crops are grown and the land is only used for the disposal of sewage sludge. The impact of this practice on the environment is believed to be negative, but very little research has been done to determine the extent of the damage to the soil and water resources. Negative impact can be caused by erosion and run-off after rainstorms that will cause surface water pollution. The groundwater may also be contaminated due to the movement of heavy metals and nitrogen through the soil. It should also be determined whether the same set of guidelines for the maximum permissible levels of heavy metals in soils should be used for DLD areas as for agricultural land.

A survey in conjunction with WRC project number 1283 was executed to determine to what extent sacrificial land disposal is currently used in SA. The selection of the sites included sites from all the major cities, as well as smaller towns with and without industries. Questionnaires were used to determine amounts of sludge, application methods, time intervals between applications and other important information. Topsoil samples were collected at each site and analysed. The analyses included a semi-quantitative analysis (scan) of the total metal content (EPA 1050 digestion) of the soil sample to estimate the heavy metal concentrations, as well as analyses for essential plant nutrition elements (K, Ca, Mg and Na; total N; Total P), pH (H_2O), organic carbon content and particle size distribution (7 fractions).

The extent of dedicated land disposal (DLD) practices in South Africa is widespread. Stockpiling is the practice used by most of the sewage treatment facilities (40%), either as the only disposal method or a means to store the dried sludge until it is utilized by farmers and municipalities, disposed of in landfills or composted. Liquid sludge is applied to soils by 40% of the remaining disposal sites. This includes practices like irrigation, flooding, sludge ponds, instant lawn irrigation and paddies.

Thirty percent of the DLD sites were on sandy soils (<10% clay) with a high leaching potential while only 11% were on sandy clay and clay soils (>35% clay) where the adsorption capacity of the soils may impede groundwater pollution. The majority of topsoil samples had above average macronutrient and organic carbon contents, and 65% of the samples had pH(H_2O) values <6.5. Groundwater pollution at these sites with the low pH values is a possibility because many heavy metals are mobile under acid conditions.

The heavy metal analyses indicated that 88% of the topsoil samples had at least one element that exceeded the maximum permissible level (MPL) for soils that are used beneficially (Dept. Nat. Health & Pop. Dev., 1991). Nickel is the main element that was too high in most of the samples, followed by Zn and Pb. Other elements that were present in high concentrations were Cd, Cr and Cu.

It should be kept in mind that the MPL for heavy metals in soils was set for the beneficial use of sewage sludge for agricultural purposes and not for DLD practices. A separate set of guidelines should be considered for DLD practices after the completion of this study.

From the information collected during the initial survey, 40 sites were selected for further detailed studies. These sites included sewage works with different soil properties, application techniques, metal concentrations and period of sludge application. Soil samples were collected at three different locations and at five depths (to determine the mobility of metals and other elements) at each of the selected wastewater treatment facilities. Water samples were collected from boreholes where possible and analysed for the same elements as the soil. Four extraction methods were used to determine the metal content of the soil samples, *aqua regia* and EPA 3050 digestion (total), NH_4EDTA extractions (potentially bio-available fraction) and NH_4NO_3 extractions (soil solution fraction). The samples were analysed according to the information collected during the survey.

The selection of sites for the detailed study consisted of 14 sites with wet sludge application without beneficial use, 5 sites with sludge irrigation onto instant lawn (beneficial use) and 21 sites with dry sludge application (stockpile and belt press dewatered sludge). Seven of the sampled sites receive only domestic wastewater.

The total P content of 23 sites was above the average for normal soil (0.1%; Brady, 1984). None of the soil samples had above average total N (>1.5%; Sparks, 1996) even in the top 100mm of the soil profile. However, the analysis data of the groundwater samples had high NO_3 concentrations, which indicates leaching of nitrate. Sixty percent of the sampled sites had organic carbon contents higher than 1.2%, due to high organic matter application.

Correlations for all analytical methods were done for all the samples, only topsoil samples and subsoil samples (lowest soil layer sampled) to determine where the strongest correlation would be. The correlations indicated that the EPA 3050 and *aqua regia* methods could be used interchangeably for all the metals, except Ni, because of the were very strong (r^2 >0.82) correlations. The correlation between the NH_4EDTA and NH_4NO_3 extraction methods were strong for Cr, Ni and Cd. For Zn, Cd and Pb the correlation between the total methods (EPA 3050 and *aqua regia*) and NH_4EDTA were also strong.

Of the 40 selected sites, 35 sites had at least one heavy metal that exceeded the MPL for South African soils (Dept. Nat. Health & Pop. Dev., 1991). The total topsoil concentration of Cr was above the MPL for South African soils (80 mg kg^{-1}) in 50-53% of the sampled sites, followed by Ni (45-48% > 50 mg kg^{-1}), Zn (40-45% > 185 mg kg^{-1}), Pb (35-38% > 56 mg kg^{-1}), Cu (30-35% > 100 mg kg^{-1}), Co (25-33% > 20 mg kg^{-1}) and Cd (25-30% > 2 mg kg^{-1}). The percentage samples exceeding the MPL for South African soils (Nat. Dept. Health & Pop. Dev., 1991) decreased in the lower soil layers indicating accumulation in the surface layers due to surface application of sludge.

The high total metal concentrations in many of the soils, especially those that receive only domestic wastewater, may be due to high background concentrations of these elements in South African soils (Herselman & Steyn, 2001) and not only sludge application. Detailed studies of these sites, including surrounding areas to determine the baseline concentration of the area, is advised.

The NH_4EDTA extractable metal fraction gives an indication of the potentially bio-available or medium term risk of metals entering the environment. None of the sites (all soil layers) had NH_4EDTA extractable Cr and Pb concentrations above the NH_4EDTA threshold values. The potentially available topsoil Cd, Zn, Co, Cu and Ni concentrations in respectively 20% (Cd, Zn), 13% (Co, Cu) and 10% (Ni) of the sites exceeded the NH_4EDTA threshold values (Bruemmer & van der Merwe, 1989). There is thus a small medium term risk for environmental pollution.

The exchangeble (NH_4NO_3 extractable) Ni, Zn and Cd concentrations are reason for concern because 23-45% of the sites had concentrations above the NH_4NO_3 guidelines set for groundwater protection (Baden-Wurttemberg, 1993) in the topsoil and 23-25% sites had elevated concentrations of these metals in the 400-500mm soil layer, indicating a short term risk for groundwater pollution.

The lack of groundwater monitoring at most of the wastewater treatment facilities should be addressed. Seven of the 9 groundwater samples that could be obtained showed high NO_3 concentrations (>6 mg l^{-1}). This would probably be the case at most of the treatment facilities. The organic C in the top 200mm of the soil profile may adsorb some nitrogen, but the rest is mobile and leach through the soil. Therefore, the soil analyses do not show high total N concentrations. In some cases, where NH_4NO_3 extractable metal concentrations in the 300-500mm soil layers are high, groundwater pollution by heavy metals may even be possible, especially if the soil has low clay content.

Some degree of leaching of the heavy metals occurred at some of the sampling sites and the average depth of leaching was 100-200mm. Deeper than 300mm the metal concentrations in most soil samples reached background concentrations. The elements that leached in most soils were Co and Ni. The leaching of the metals, in spite of the high organic carbon content of the soils, was due to the extremely low soil pH(H_2O) of most sites.

Statistics of the data indicate no significant differences between sludge type (wet or dry) and leaching, or age of the disposal sites and leaching. It should be kept in mind that most of the sampled sites receive industrial effluent, therefore the metal loading of the sludge at these sites is probably very high. Taking into account the age of the disposal sites, the frequency of sludge application and the metal load of the sludge, the depth of leaching is surprisingly shallow in most soils, in spite of the low soil pH(H_2O) and clay content.

There is a need to be able to predict the impacts of the practice of amending soils with sewage sludge on aquifers. The current investigation explores the feasibility and utility of chemical fate and transport modelling as a means of predicting the mobility of metals inherent in sludge-soil mixtures, under a number of specific environmental conditions.

A very extensive literature survey revealed that many famous scientists have attempted the task of modelling the migration of metals in sludge-amended soils. To date, no satisfactory predictive model has been developed. Published experimental data is in conflict with respect to relative strengths of binding of metal ions to sludge-soil matrices, and with respect to potential mobility of the metals in the environment. Not only are sludge and soils highly site-specific in their chemical nature, but so is the nature of biota (species and community structures) responsible for degrading organic material in the sludge/soil mixtures into potentially metal-binding soluble material. Despite the difficulties, some headway has been made in determination of metal binding constants by thermodynamic means.

A chemical model was constructed using PhreeqC, a geochemical fate and transport modelling package extensively used in the groundwater field. The model was constructed from published thermodynamic data, and calibrated against simple conceptual models of the behavior of soils, and natural organic matter. A subset of the field results from this study was analysed statistically to determine a Reference Behavior Pattern to benchmark the model against. The model was further calibrated against the extractions of metals from the sludge/soil samples by NH_4NO_3 and NH_4EDTA.

Literature and modelling studies indicated that the organic carbon component of the sludge/soil matrix is principally responsible for the fate of metals. Scenarios were modelled, using cadmium as a representative metal ion. The scenarios are presented below with the results of the simulations:

- Elution with dilute saline solution at pH 7 - metals were not mobilized
- Elution with dilute saline solution at pH 6.5 - metals were not mobilized
- Elution with dilute saline solution at pH 5.0 - metals were completely mobilized
- Effect of maintaining carbon content of sludge layer - microbial decomposition of organic carbon will continuously produce soluble organic matter, which will bind metals and mobilize the metals
- Effect of maintaining high pH through liming - addition of lime involves the addition of calcium ion which out-competes toxic metal adsorption to sludge/soil matrix, resulting in substantial mobilization of metals

- Effect of cessation of sludge addition - metals would be mobilized in the short term, due to continuous production of soluble, metal-binding organic matter, but will cease in the long-term. Literature suggests that after ten years, metals will cease to be mobile

In general only a few of the disposal sites have sound management practices in place. Most of the disposal sites are not fenced off and are very close to populated areas. General access by the public occurs and in some cases the local people harvest edible plants that grow on the disposal sites.

The majority of the disposal sites are on even terrain, but most of those that are on a slope have no erosion control measures in place even though they are near surface water bodies. Surface water monitoring at these sties is recommended.

Generally the larger cities and metropolitan councils were found to be knowledgeable in sludge management and legislative requirements but this was not the case in other towns. Many plant managers didn't really care where they put the sludge, as long as it is disposed of. No systems exist at most wastewater treatment facilities to manage the disposal of the sludge. At two wastewater treatment facilities raw sewage was disposed of on the disposal site.

The following recommendations should be considered:

- Clear demarcation of sludge disposal areas with restrictive access
- Continuous groundwater and surface water monitoring should be enforced
- Erosion control measures where necessary
- Sound management practices at the disposal site to regulate disposal
- Prerequisites for permit – no disposal on sandy soils, safe distance from water bodies etc.
- Nitrogen should be considered in the guideline for sludge disposal because it poses a bigger threat than the metals
- Guidelines should be set for DLD specifically

Acknowledgements

The research in this report emanated from a project funded by the Water Research Commission and entitled:

"AN EVALUATION OF DEDICATED LAND DISPOSAL PRACTICES FOR SEWAGE SLUDGE"

The Steering Committee responsible for this project, consisted of the following persons:

Mr HM du Plessis	Water Research Commission (Chairman)
Mr GN Steenveld	Water Research Commission
Mr P Gaydon	Umgeni Water
Mr KS Fawcett	City of Cape Town
Mr FB Stevens	Ethekwini (Durban) Water Services
Ms M Hinsch	Department of Water Affairs and Forestry
Mr CE Steyn	Agricultural Research Council - ISCW
Dr DJ Jaganyi	University of Natal
Prof GA Ekama	University of Cape Town
Mr GB Saayman	Tshwane Metro
Mr R Avis	Johannesburg Water
Prof RO Barnard	Agricultural Research Council - ISCW
Dr AR Pitman	Johannesburg Water
Mr D Makwela	Department of Health
Mr AT van Coller	National Department of Agriculture
Prof MV Fey	University of Stellenbosch
Mr DJ van Nieuwenhuizen	National Department of Agriculture
Mr CJ Marx	Africon Engineering International
Mr JW Wilken	ERWAT

The financing of the project by the Water Research Commission and the contribution of the members of the Steering Committee is acknowledged gratefully.

This project was only possible with the co-operation of many individuals and institutions. The authors therefore wish to record their sincere thanks to the following project team members and their organisations:

Mrs E Lazenby	Agricultural Research Council – ISCW
Mr WFA Kirsten	Agricultural Research Council - ISCW
Mr A Loock	Agricultural Research Council - ISCW
Mrs M Smit	Agricultural Research Council – Biometry Unit
Mr S Narain	Agricultural Research Council - ISCW

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

List of acronyms and abbreviations

AD	**anaerobic digested**
ARC	**Agricultural Research Council**
As	**Arsenic**
B	**Boron**
C	**carbon**
Cd	**Cadmium**
Co	**Cobalt**
Cr	**Chromium**
Cu	**Copper**
d	**day**
DLD	**dedicated land disposal**
dom	**domestic**
DWAF	**Department of Water Affairs and Forestry**
EPA	**Environmental Protection Agency**
ERWAT	**East Rand Water Care Company**
EU	**European Union**
Hg	**Mercury**
ICP-MS	**Inductively Coupled Plasma – Mass Spectrophotometer**
Ind	**industrial**
ISCW	**Institute for Soil, Climate and Water**
IT	**investigation threshold**
K	**Potassium**
mg kg^{-1}	**milligram per kilogram**
Mn	**Manganese**
Mo	**Molybdenum**
MPL	**maximum permissible level**
N	**Nitrogen**
Ni	**Nickel**
NO_3	**Nitrate**
P	**Phosphorus**
Pb	**Lead**
PTME	**Potentially Toxic Metal or Element**
SD	**Standard Deviation**
Se	**Selenium**
Sn	**Tin**
t	**ton**
Tl	**Thallium**
U	**Uranium**
UK	**United Kingdom**
USA	**United States of America**
V	**Vanadium**
WAS	**waste activated**
WRC	**Water Research Commission**
WWTP	**Wastewater Treatment Plants**
yr	**year**
Zn	**Zinc**

CHAPTER 1

INTRODUCTION

1.1 SCOPE

The potential benefits of the application of sewage sludge for agricultural purposes and as a soil conditioner for rehabilitating land have been well demonstrated in many parts of the world. The main limitation of this practice is the high metal content of sewage sludge, which can pose a risk to the environment, as well as high nutrient contents (N, P & K), which can leach to the groundwater if present in high concentrations. According to the Addendum to Edition 1 (1997) of the Permissible utilization and disposal of sewage sludge (WRC, 2002) and a study conducted by Snyman, Herselman & Kasselman (2003), very few wastewater treatment facilities in South Africa can comply with the standards to use sludge on agricultural land. Therefore most of the wastewater treatment plants in South Africa dispose of their sewage sludge on dedicated land disposal (DLD) sites (sacrificial lands), since this is the quickest and cheapest way to dispose of sewage sludge. The sludge is regularly applied at high rates to the surface soils. No crops are grown and the land is only used for the disposal of sewage sludge. The scope of this study is on these sewage treatment facilities that use DLD practices.

There is a lot of controversy concerning DLD practices. The impact of this practice on the environment is believed to be negative, but little research has been done to determine the extent of the damage to the soil and water resources. Negative impact can be caused by erosion and run-off after rainstorms that will cause surface water pollution. The groundwater may also be contaminated due to the leaching of heavy metals and nitrogen. It should also be determined whether the same set of guidelines for the maximum permissible levels of heavy metals in soils should be used for DLD areas as for agricultural land.

The main aim of the study is to determine the current and future impact of DLD practices on the environment. The outcome of the study can also serve as input for the revision of the guidelines for sludge disposal.

1.2 OBJECTIVES

1. To evaluate the extent of the current practice of disposing of sewage sludge on dedicated land.
2. To evaluate the potential pollution risk this practice poses to the water environment at selected sites.
3. To estimate the future impact of dedicated land disposal of sewage sludge on the water environment.

1.3 APPROACH

This study was conducted in three phases, starting with an assessment of the extent of the practice and concluding with an in-depth evaluation of its real and potential impact on the water environment.

1.3.1 Survey to determine the extent to which sacrificial land disposal is used in SA

A survey in conjunction with another WRC project (WRC Project nr. 1283, entitled: "A metal content survey of South African sewage sludge and an evaluation of analytical methods for their determination in sludge") was executed to determine to what extent sacrificial land disposal is currently used in SA. The selection of the sites included sites from all the major cities, as well as smaller towns with and without industries. Questionnaires were used to determine amounts of sludge, application methods, time intervals between applications and other important information. Soil samples (topsoil) were collected at each site and analysed. The analyses included a semi-quantitative analysis (scan) of the total metal content (EPA 1050 digestion; Test Methods for Evaluating solid wastes, 1986) of the soil sample to estimate the heavy metal concentrations, as well as analyses for essential plant nutrition elements (K, Ca, Mg and Na with Ammonium acetate method; total N & P), pH (H_2O), organic carbon content and particle size distribution (7 fractions), using analytical methods as described by The Non-Affiliated Soil Analysis Work Committee (1990).

1.3.2 Detailed study of selected sites

From the information collected during the initial survey, 40 sites were selected for further detailed studies. These sites include wastewater treatment facilities (WWTP) with different soil properties, application techniques, metal concentrations and period of sludge application. Soil samples were collected at three different locations and at five depths (to determine the mobility of metals and other elements) at each of the selected wastewater treatment facilities. Water samples were collected from boreholes where possible and analysed for the same elements as the soil.

Four extraction methods were used for metal determination in the soil samples, *viz:*

- *aqua regia* (total; Bigham & Bartels, 1996)
- EPA 3050 digestion (total; Test Methods for Evaluating solid wastes, 1986)
- NH_4EDTA extractions (potentially bio-available, medium term risk; The Non-Affiliated Soil Analysis Work Committee, 1990)
- NH_4NO_3 extractions (soil solution, exchangeable fraction; Bigham & Bartels, 1996) (see Chapter 4.1 for more detail).

Soils were also analysed for total N and P, organic C, pH(H_2O) and clay content, using analytical methods as described by The Non-Affiliated Soil Analysis Work Committee (1990).

1.3.3 Estimation of the potential future impact of dedicated land disposal of sewage sludge on the water environment

All the information collected were evaluated and a geochemical contaminant fate-and-transport model were used to simulate the risk of dedicated land disposal on the water environment should the conditions change over a period of time. The model simulate the transport and fate of the contaminants under realistic environmental scenarios, which could alter the hydrology, as well as the chemistry of the soils.

CHAPTER 2

LITERATURE REVIEW

2.1 The problem

Sewage sludge is an organic solid, semi-solid or liquid by-product of the wastewater treatment process that contains human faecal waste as well as waste products and contaminants from homes, industries and businesses. The characteristics of sludge depend on the waste stream of each treatment facility as well as the treatment processes used (Marriott, 1998).

The growth in human population results in an increase in waste products, including organic wastes like sewage sludge, compost and manure. The world is striving to find ways to dispose of the escalating amount of waste products. Especially around large towns and cities the disposal of wastes is an increasing problem.

According to baseline studies on waste generation in South Africa (DWAF, 1997) every person in South Africa produces approximately 50 g of dry sludge per day, thus a total of 309 556 tons per annum for South Africa. Waste treatment in South Africa (sewage sludge) account for only 0.06% of the total waste generated in the country (Figure 2.1). The general approach in South Africa has been to plough the sludge into land specifically designated for this purpose or stockpiling at sewage treatment plants in dry heaps or liquid lagoons (paddies) (Ekama, 1993). Due to industrialisation and urbanisation, municipalities and industries in South Africa produce increasing amounts of sludge. The current disposal routes are becoming increasingly unacceptable from an environmental point of view.

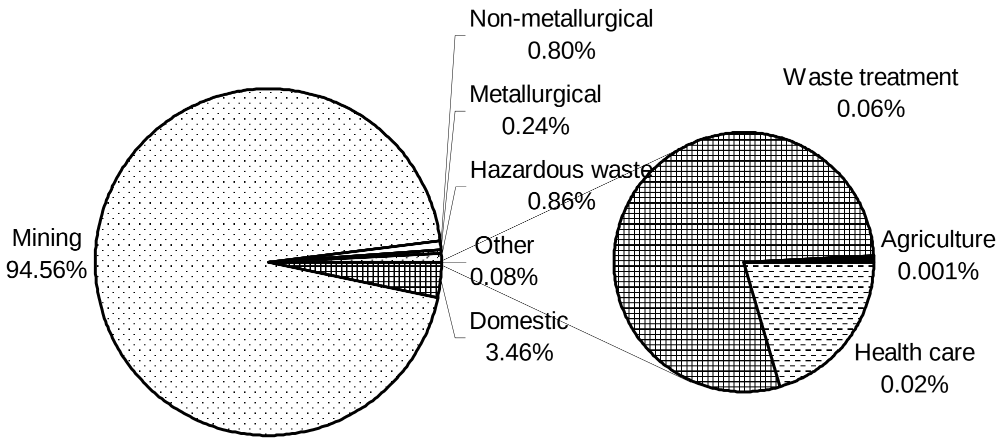


Figure 2.1: Waste generation in South Africa (DWAF, 1997)

2.2 Dedicated land disposal (DLD)

According to Lue-Hing, Zenz & Kuchenrither (1992) there are two distinct classifications of dedicated land disposal: dedicated disposal sites and dedicated beneficial use sites.

Dedicated disposal sites are land set aside specifically for sewage sludge disposal. The sludge solids are regularly applied at high rates to the top of the soil profile where microorganisms and chemical processes degrade the sludge organic matter. Organic pollutants are degraded or, along with the metals and other elements, bound to the soil colloids. Generally no vegetative cover is produced and therefore the nutrient content and the conditioning properties of the sludge are not utilized due to the high application rates necessary to dispose of all the sludge produced. These sites are generally owned or leased in the long term by the treatment facilities and public access is limited to minimize the risk of adverse human health effects due to exposure to sludge-borne pollutants or pathogens.

At dedicated beneficial use sites the objective of achieving maximal sludge loading rates is balanced with the objective of deriving beneficial use of the land-applied sludge, which normally involves vegetation growth. Usually the crops that are grown are not directly ingested by humans but rather used for animal feed because cumulative soil pollutant loadings become high after years of operation. Instant lawn is also a popular option. The sludge is used beneficially because it is applied to land to improve poor soils or to reclaim disturbed soils and it supplies nutrients to plants. Crops are then used to generate income for the treatment facility.

Sewage sludge can be applied either as dewatered sludge or liquid sludge. Dewatered sludge application is usually used when the disposal site is far from the treatment facility. The sludge can be dewatered by mechanical processes (belt press or centrifugation) or by putting it into lined drying beds and allowing it to dry over time through evaporation. In high rainfall areas drying beds are often not an option. Once the sludge is dry, it is put onto the soil and ploughed in or just stored in heaps on site (stockpiled). Landfilling is also used to dispose of dried sewage sludge.

It is perceived to be cheaper to apply sludge in the liquid state if the sludge disposal site is located near the treatment facility because there is no need for a dewatering facility. Liquid sludge can be applied over a large surface with high-pressure nozzles connected to liquid sludge pipelines. The soil surface must be ploughed regularly to assure maximum application rates and to maintain vector and odour control. Surface runoff from DLD sites must be strictly controlled to ensure that surface water bodies are not polluted (Lue-Hing *et al*., 1992). Other methods of disposing of liquid sludge on soil are sludge ponds, paddies, flooding and instant lawn (see paragraph 3.1 for a more detailed discussion).

2.3 The advantages and disadvantages of DLD

From an environmental view point DLD has little advantages, but for the wastewater treatment facility there are advantages. These include cheap disposal over large areas. In some cases, where liquid sludge is disposed, money can be saved on drying equipment.

A major disadvantage for the environment is leaching of heavy metals through the soil, causing groundwater pollution if care is not taken. This can be as disastrous as surface water contamination. Nitrogen is another element present in sewage sludge that can cause soil and water pollution, therefore the application rate of sewage sludge should ideally be based on the N content of the sludge rather than the metal content. The amount of total N in sewage sludge available to plants during the first year of application is 30% with 15% and 5% during the second and third years respectively (WRC, 1997). Other plant nutrients (P, K, Ca & Mg) can also leach to the groundwater if present in high concentrations and cause groundwater pollution.

2.4 The potential pollution problem

Repeated sludge application to soil can result in elevated metal concentrations that persist in the plough layer or topsoil. Most natural soils act as a repository sink for metals without obvious effects on soil biological behaviour, but the accumulated heavy metals are depleted slowly by leaching, plant uptake, erosion or deflation (Kabata-Pendias & Pendias, 1992). The transportation of metals and other pollutants is affected by the capacity of the soil to impede the passage of the contaminants to the groundwater and to subsurface runoff, and the physical and chemical properties of the soil determine this capacity of the soil to attenuate movement of contaminants (Wong, Cheung & Wong, 2000).

Various studies have been executed to determine the mobility of heavy metals after sludge application on agricultural land as well as DLD sites (McGrath *et al*., 1995; Herselman, 1998; Herselman & du Preez, 2000). These studies indicate that in most cases the metals will stay in the plough layer even after numerous sludge applications because they are strongly held by the soil particles with little removal by plant uptake or movement down the soil profile. Soil erosion and run-off are probably the main pathways for metal loss from the soil.

As was mentioned earlier, other elements applied with sewage sludge (N, P, K, Ca, Mg & Na) can also cause pollution. Although most of these elements are essential to all life forms, if present in excess they will leach through the soil profile and pollute the groundwater as well as surface water due to runoff. Especially in the case of DLD practices, where there are no restrictions on application rates of sewage sludge, nitrogen leaching poses a serious pollution problem. A study conducted by Lötter & Pitman (1997) at various waste water treatment facilities in Johannesburg, Gauteng, clearly indicated that continuous sludge disposal to dedicated land areas cause groundwater pollution.

2.5 International approach to sludge disposal

Table 2.5 gives a summary of sludge production and disposal methods in various countries during the last decade. The disposal of sewage sludge on land, either for beneficial or non-beneficial use, is the most popular disposal method in most countries. DLD does not take advantage of the nutrient value and soil-building properties of sludge, but it is the unavoidable choice if the sludge is contaminated with industrial waste. In Canada and Japan 47% and 55% of the sludge load respectively is incinerated. From a environmental view point this should be a limited disposal option since the ash produced should be treated as hazardous waste because it contains high levels of heavy metals (www.unep.or.jp).

Table 2.5: Sludge production and disposal methods in various countries

Country	Annual production (1000 dry tons)	Disposal method (% of total)			
		Agriculture	Landfill / DLD	Incineration	Other
Austria [a]	320	13	56	31	0
France [a]	700	50	50	0	0
Germany [a]	2500	25	63	12	0
Italy [a]	800	34	55	11	0
United Kingdom [a]	1075	51	16	5	28
USA [a]	5357	36	38	16	10
Canada [b]	389	43	4	47	6
Japan [c]	1133	8	35	55	2
Australia [c]	300	9	76	2	13
South Africa [d]	310	30	67	-	3

a – www.unep.or.jp

b – Apadaile, 2001

c – Priestley, 1990

d – Lötter & Pitman, 1997

2.5.1 Australia

Approximately 60% of the Australian population live in large metropolitan areas, resulting in large volumes of sludge produced in a few centralized locations. Sewage sludge disposal in Australia are mainly in open lagoons (67% of produced sludge) within the boundaries of the treatment plant. The dried sludge is then stockpiled. To reduce odour problems the sludge is anaerobically digested before drying and the lagoon is surrounded by a considerable buffer zone. Problems associated with this method is weather conditions which are not favourable for drying of sludge and residential development which begin to encroach on the buffer zone surrounding the disposal areas. There are currently no guidelines protecting the environment against this disposal method.

During 1989 the NSW Agriculture and Fisheries Department issued guidelines for the utilisation of sewage sludge on agricultural land, dictating application rates and the degree of sludge pre-treatment. Only 9% of sewage sludge in Australia is used for agricultural purposes. Intensive research has been undertaken to promote this disposal option to take advantage of the nutrients and soil conditioning properties of the sludge (Priestley, 1990).

2.5.2 Canada

The treatment and disposal of sewage sludge is provincially regulated in Canada. Certificates of approval are required for all land application sites and include explicit management conditions. All dischargers in the country are regulated to ensure that hazardous wastes are not discharged into sewage treatment systems (Apediale, 2001).

Sewage sludge have been used in agriculture for more than 40 years (43% of produced sludge; 1.5 million m^3 per annum) in Canada. This disposal method is strictly regulated by guidelines for the safe use of sludge on agricultural land to protect ground- and surface water and to ensure a balance of nutrients. These guidelines include criteria for metals in dewatered sludge, soil conditions (pH >6) and separation distances from water bodies and residential areas (Toronto, 2002).

Incineration is another common practice in Canada (47% of produced sludge). The organic material is converted into a hot combustion gas, which is used as a source of energy. The residual ash can be used as concrete blocks, road material and lanfill cover. Only 4% of the produced sludge is sent to landfill and these sites are monitored for groundwater impact. Most municipalities move away from incineration and landfill disposal due to environmental concerns (Apediale, 2001).

2.5.3 Europe

The annual sewage sludge produced in Europe reached 6.8 million tons dry weight in 1999 and will reach 9.4 million tons in 2005 (Laturnus, 2002). Germany, France and Italy produced the highest amounts of sludge in Europe. Landfilling of sludge is the most common practice for disposal. There are two types of landfill: mono-deposits (sludge only) and mixed-deposits (sludge and municipal waste). Up to now it's been an inexpensive method of disposal but due to national restrictions and the proposed EU Landfill Directive, it will become more expensive in future. A serious disadvantage of landfill is the generation of leachate which ultimately affect human health and ecosystems (Chateauvert *et al.*, 2002). Some sludge is incinerated (mono-incineration) and the ash used for landfilling. Due to supplementary fuel needed to burn the sludge, this method is less economical.

Agricultural application of sewage sludge has become a wide spread method of disposal and is the most economical outlet for both liquid and dried sludge. However, there are concerns on long-term build-up of heavy metals and toxic organic compounds that can damage the agricultural soil and the groundwater. Both EU and national regulations are setting limits for contaminant concentrations to protect the soil, water and humans from pollution (Laturnus, 2002).

2.5.4 United Kingdom

In the UK 1.5 million tons of dry sludge is produced annually. Agricultural land application of sludge is the principle outlet for sludge at present, accounting for half of the produced sludge. However, less than 1% of agricultural land in the UK receives sewage sludge (Nadim, 2000).

Other disposal methods used in the UK is incineration (5%) and landfill (16%). As a consequence of the Urban Wastewater treatment Directive the additional treatment required will result in significant increase in sludge production and disposal. Recent predictions suggests that by 2005 the proportions of sludge disposed on agricultural land will be 60%, incineration 36% and landfill 4%. Incineration is an increasingly popular disposal method because electricity can be generated. The residual ash containing heavy metals and the atmospheric emissions still pose a problem. Landfilling is not such a popular disposal method because it requires large areas of land and has adverse environmental impact on soil and groundwater (Nadim, 2000).

2.5.5 USA

The United States produce approximately 5.5 million tons dry sludge annually and use a number of disposal methods for sewage sludge. The commonly used methods are land application (36%), other beneficial uses (concrete production, landfill cover; 10%), incineration (16%) and surface disposal/landfill (38%).

For sludge application to agricultural land the sludge quality, pollution limits (metals), application rates, pathogen and vector properties and environmental conditions under which land application is permitted are specified in the provisions of Part 503 (EPA Standards for the use or disposal of sewage sludge (40 CFR Part 503); A plain English guide to the EPA Part 503 Biosolids Rule, 1994). The regulations specify sampling and analyses of sewage sludge as well as record keeping requirements for land application facilities.

Under the provisions of Part 503, facilities using surface disposal/landfill must comply with pollutant limits, management practices and operational standards as well as other requirements related to the frequency of monitoring, record keeping and reporting. In terms of pollutants, the regulation established limits for As, Cr and Ni for unlined disposal sites with no leachate collection system. If sewage sludge is placed in a municipal landfill, the local government is responsible for ensuring that the sludge meets the provisions of 40 CFR Part 258.

The general requirements for surface disposal are:

- Disposal is prohibited in wetlands and unstable areas
- No pollutant limits for surface disposal sites with liners and leachate collection systems
- Pollutant limits for As, Cr and Ni for disposal sites without liners and leachate collection systems. The limits depend on distance from property boundaries
- Runoff must be collected
- Required management practices and continuous monitoring requirements
- No crops may be grown on site
- No animals may graze on site
- Public access must be restricted
- Sewage sludge must not contaminate an aquifer.

2.6 Guidelines for potentially toxic metals and elements (PTME) in soil and water

During 1991 the Department of Health published a document “Guide: Permissible utilisation and disposal of sewage sludge” by which sludge application to land is managed in terms of the Health Act. This guide included guidelines on the PTME levels in sewage sludge as well as maximum permissible metal and inorganic contents in soil (MPL). No extraction and analyses methods were stipulated in the document and it is assumed that the MPL for South African soils is based on total content of the soil. The 1991 guidelines were subject to considerable debate, as all the government departments that had an interest in sludge application to land; i.e. Department of Health, Department of Water Affairs and Forestry, Department of Agriculture and the Department of Environment Affairs and Tourism did not reach consensus. The 1991 guideline was therefore used as an interim guideline while negotiations were taking place between the government departments.

The “Permissible utilisation and disposal of sewage sludge, Edition 1” known as the 1997 Sludge Guidelines, was finally published in 1997 and was aimed to assist organisations involved in sewage treatment to promote safe handling, disposal and utilisation of sewage sludge (WRC, 1997). The guideline was perceived to be overly restrictive, specifically with regard to some of the PTME standards for sewage sludge. However, when the origin of these limits were investigated, after publication of the guidelines, it was found that from the way the concentrations were calculated, they appeared to be the available PTME fraction and not the total extractable PTME fraction as originally interpreted. This was not stipulated in the guideline. The MPL of Cu, Pb and Zn in soils were considerably lower in the 1997 guidelines (WRC, 1997) (Table 2.6a). The reason for this decrease is not clear and again no extraction methods or analyses methods were stipulated in the document.

Table 2.6a: Maximum permissible total metal content in soil (mg kg^{-1})

Metal	**Maximum permissible metal and inorganic content in soil (mg kg^{-1})**		**Metal**	**Maximum permissible metal and inorganic content in soil (mg kg^{-1})**	
	1991 [a]	**1997** [b]		**1991** [a]	**1997** [b]
Cd	2	2	**Pb**	56	6.6
Co	20	20	**Zn**	185	46.5
Cr	80	80	**As**	2	2
Cu	100	6.6	**Se**	2	2
Hg	0.5	0.5	**B**	10	10
Mo	2.3	2.3	**F**	50	200
Ni	15	50			

a - Dept. Nat. Health & Pop. Dev., 1991
b - (WRC, 2002), 1997

Herselman & Steyn (2001) calculated a baseline concentration range for Cd, Cr, Ni, Pb, Zn, Cu and Co from geometric means and standard deviations, excluding values lying outside the 5th and 95th percentiles. The data used was a major inventory of some 4500 soil profiles in South. Surface soil horizons were analysed by inductively coupled plasma – mass spectrometry for total (acid-extractable) and available (NH_4EDTA extractable) fractions. These supposedly natural, background values were used to set investigation threshold values based on total digestion of the soil (EPA 3050 method). The baseline concentrations and the suggested investigation threshold values are presented in Table 2.6b.

Table 2.6b: Baseline concentration range of metals in South African soils and suggested investigation threshold values for soil (mg kg^{-1}) (from Herselman & Steyn, 2001)

	EPA 3050 digestion		**NH_4EDTA extractable**		
	SA Baseline conc.	**Suggested Investigation threshold**	**SA Baseline conc.**	**Threshold [a]**	**Suggested Investigation threshold**
Cd	0.62 - 2.74	3	0.89 - 1.17	1	1
Cr	5.82 - 353	150	0.87 - 4.52	50	5
Ni	3.43 - 159	80	0.57 - 9.78	20	10
Pb	2.99 - 65.8	70	0.93 - 11.9	100	15
Zn	12.0 - 115	120	0.62 - 6.03	100	10
Cu	2.98 - 117	120	0.84 - 10.6	60	15
Co	1.51 - 68.5	70	0.64 - 16.1	10	20

a – Brummer & van der Merwe, 1989

After consideration of the baseline concentration of metals in South African soils as well as the two sets of published guidelines, it was decided to use the limits set in the 1991 guidelines (Nat. Dept. Health & Pop. Dev., 1991) as guideline for the total metal content in soil for the purposes of this study. The suggested investigation threshold is also used throughout the report.

In an internal report to the Soil and Irrigation Institute, now ARC-ISCW, Bruemmer G.W. & van der Merwe A.J. (1989) suggested NH_4EDTA threshold values for metals in soil to protect the plant environment and food-chain against metal pollution. After calculation of the baseline NH_4EDTA concentration of metals in South African soils, Herselman & Steyn (2001) suggested new investigation threshold values for NH_4EDTA extractable metals in soil (Table 2.6b).

In Germany guidelines were set by the Government in Baden-Wurttemberg (1993) for NH_4NO_3 extractable metals in soil to protect groundwater from pollution. A different set of guidelines was published for topsoil and subsoil. For the purposes of this study the guidelines for topsoil were used (Table 2.6c).

The South African Water Quality Guidelines (DWAF, 1996) were used as guidelines to determine the quality of the groundwater sampled during this study. Guidelines for both domestic use and irrigation were used where applicable.

Table 2.6c: Guidelines for NH_4NO_3 extractable metals in soil for groundwater protection (mg kg^{-1}) and water quality guidelines (mg l^{-1})

Metal	Topsoil[a]	Subsoil[a]	Drinking water[b]	Irrigation water[b]
As	0.14	0.07	0.01	0.1
Cd	0.1	0.03	0.005	0.01
Cr	0.13	0.13	0.05	0.1
Co	-	-	NA	0.05
Cu	1.2	0.45	1	0.2
Hg	0.007	0.007	0.001	NA
Ni	1.2	0.7	NA	0.2
Pb	3.5	0.25	0.01	0.2
Zn	5.0	1.5	3	1
NO_3	-	-	6	0.5 (N)

a - Baden-Wurttemberg, 1993

b – DWAF, 1996

2.7 Modelling of metal migration in sludge ammended soils

2.7.1 Metal Contaminant Mobility and bioavailability in soils

An valuable source of information of potential metal mobility in soils is the literature on soil toxicology of metals. The form of the metal that is mobile is the form that is soluble in the aqueous solution that percolates through the soil. This is the dissolved fraction.

There is some justification for the use of the Free Ion Activity Model of bioavailability to explain effects of metals in soils on biota. It is a reasonable assumption that there is a correlation between the total dissolved fraction of the metal and the free ion activity of the metal for a given soil type. Thus, there may be a case for inferring metal mobility in a soil from toxicity studies on soil. The parameter of interest here is the Kd, or partitioning coefficient of the metal between soil and interstitial aqueous phases in the soil.

It has been shown that multiple regression models relating soil pH and total metal content to plant uptake resulted in statistically significant predictions with respect to arsenic, cadmium, copper, lead, mercury, nickel and zinc (Efroymson *et al.*, 2001).

2.7.2 Metal ion complexing capacity in sewage-associated water

It is assumed that the interstitial waters in freshly applied sewage will have the same chemical qualities as sewage works effluents. Sewage works effluents were analysed in terms of their copper complexing capacity and other chemical variables (van Veen *et al.*, 2002). A very strong relationship is evident between DOC and CC for the final effluents, suggesting that this may be a useful parameter for estimating the free ion concentration from total metal concentrations in the interstitial waters. Sewage effluents contain substantial concentrations of copper- complexing ligands that were present in a three- to eightfold excess of total dissolved copper concentration. Sewage treatment works final effluent can have a significant impact on the toxicity of copper to aquatic biota.

The tolerance of Daphnia magna to dissolved copper concentrations was found in one study (van Veen *et al.*, 2002) to be more than quadrupled, and the increase in tolerance was related to complexing capacity and DOC. Ligand concentrations in effluents were found to correlate strongly with effluent DOC concentration, but no such relationship was observed in surface waters. On mixing with river water, sewage-derived ligands seem to behave conservatively. Such sewage-derived ligands are relatively stable over time scales of up to 10 days, though some indication of degradation exists over longer periods in waters of low DOC concentration.

The free metal ion in interstitial soil/sewage/water solution is expected to be the principal adsorbent to soil phases. The decrease in toxicity in the sewage effluents as DOC increases implies decrease in free metal ion concentration. Thus, higher DOC in soil/sewage interstitial waters would lead to higher complexation by dissolved ligands, and thus higher potential mobility of the metals through the soil column.

2.7.3 Movements of metals within soil profiles

Davies et al., (1988) found that in the short term, mobility of metals in sludged soils was generally limited to the top 5-10cm of the soil, with 87% in the top 5 cm. Increased acidity was observed over time, with increased metal availability to plants, but did not increase metal mobility. Fiskell *et al.* (1984) found that in an acid, sandy soil, most metals remained in the top 7cm of soil, displaying some slight movement in the first 6-30 months. Harris and Urie (1986) found that a large proportion of metals were immobilised in the humus layer, with the underlying soil matter playing no part in metal complexation for at least the first 5 years after application.

Some higher mobilities were observed by Darmody *et al.* (1983), on a silt loam soil, where zinc and copper migrated down to 75cm, with most of the movement in the first year, at the highest sludge application rates. Copper was found to be particularly mobile. Most metals were found in the 0-15 cm fraction though, with some moving below this horizon, 3 years after dredging. On a coarse textured, sandy soil (with presumably no organic matter and iron), three years after sludging, the following metals had migrated the following distances in centimetres: Cd: 60-80; Ni: 40-60; Pb: 20-40, Cr: 0-10. On chalky boulder clay, several metals were found to have moved to the 50-100 cm level. Overall, it has been found that the local climate heavily influences the mobility of metals in sludge-amended soils (Alloway and Jackson, 1991).

Antoniadis & Alloway (2002) found that Cd, Ni, and Zn leaching was considered to be severe, having moved 8 cm in a short time. They suggested that there was a risk of the metals moving beyond incorporation zone due to Sludge DOM. Keefer and Singh (1986) investigated the fractionation of metals in sludge-amended soils by a sophisticated system of extractants and ion-exchange resins, and found that pH was a major determinant in the mobility of Cd, Cr, Ni and Zn, with secondary factors being the concentrations of Illite, chlorite and fine clay (<0.2um). They noted that there was significant unexplained variance, which underlined the need for classifying sludges.

2.7.3.1 Effect of pH

Sorption of heavy metals is strongly pH-dependent. In general, sorption increases with increasing pH. The lower the pH-value the more metal can be found in solution and thus, the more metal is mobilized. When pH falls to below 5, mobility is enhanced as a result of the increased proton concentration. At pH-values above 7 some heavy metals tend to form hydroxy-complexes which will increase the solubility of the metal in question. Also, the solubility of a number of compounds is pH-dependent.

2.7.3.2 Chromium

Dudka and Chlopeka (1990) report that chromium is associated with the organic fraction in sludge-treated soils.

2.7.3.3 Sulphur

Sewage sludge may contain reduced sulphur compounds, sometimes even elemental sulphur. Tyagi *et al.* (1994) studied the behaviour of thiobacilli in sewage sludges, and noted that the presence of thiosulphate compounds in sludges caused the bacteria to use them as a substrate, yielding sulphuric acid. This can have the effect of eroding the pH buffering capacity of soil components such as carbonates, when sludge is applied to soils.

2.7.3.4 Copper

Berggren (1992b) studied the mobilization of copper in soil solutions and found that copper migrates as inorganic and organically bound forms, with the latter predominating (90-98%). Even where the DOC was low, at 50cm depth, copper existed as the organically complexed form (62-83%). Results indicated that solution pH affected copper mobilization in cases where the soluble DOC concentration was relatively low, and increased pH seemed to increase the amount of copper bound per gram DOC. This indicates that copper is bound to acid-binding sites on the fulvic acids, such as carboxylates or phenolates.

2.7.3.5 Aluminium

Berggren (1992a) notes that the processes governing the mobilization of aluminium and cadmium differ markedly between different soil types, with the nature of the plants growing on the soils being a confounding factor. He finds that formation of complexes with dissolved organic acids is a very important determinant of metal mobility in the soils, with pH being very important in controlling the behaviour of the free aluminium ion in solution. As the soil solution percolated through the soil, humic substances and their complexed metals were precipitated and/or adsorbed in the upper horizons. Inorganic forms of both aluminium and cadmium were predominant in soil solutions collected by lysimeters at 50 cm. the findings agreed with the "fulvate theory" of podzolization, where organic compounds chelate aluminium and iron and migrate downwards to where adsorption/precipitation occurs. The concentration of aluminium ion in soil solution was not controlled by precipitation or dissolution of mineral phases.

2.7.3.6 Cadmium

Information available in the literature regarding interactions between dissolved cadmium and naturally occurring organic ligands (humic and fulvic acids) is ambiguous. Weber and Posselt (1974) reported that cadmium can form stable complexes with naturally occurring organics, whereas Hem (1972) stated that the amount of cadmium occurring in organic complexes is generally small and that these complexes are relatively weak. Pittwell (1974) reported that cadmium is complexed by organic carbon under all pH conditions encountered in normal natural waters. Levi-Minzi *et al.* (1976) found cadmium adsorption in soils to be correlated with soil organic matter content. In a critical review of the literature, Giesy (1980) concluded that the complexation constants of cadmium to naturally occurring organic matter are weak because of competition for binding sites by calcium, which is generally present in much higher concentrations. - EPA 402-R-99-004B.

Fu and Allen (1992), in their attempts to understand the adsorption of cadmium by oxic sediments, were forced to invoke a multi-site binding model with weakly acidic functional groups. The binding model incorporates the effect of pH. The model assumes four types of binding sites, with pKa's of about 4.0, 5.8, 7.8 and 9.8. Cadmium is mostly associated with the Fe-Mn oxide component of the soil (Dudka and Chlopeka, 1990).

In computer modelling with the program GEOCHEM, Mahler *et al.* (1980) found that the free Cd^{2+} ion was predominant in topsoil solutions. Mullins and Sommers, (1988) arrived at the same conclusion using liquid chromatography. Tills and Alloway (1983) used liquid chromatography to reveal that Cd also underwent substantial organic complexation (13%). Cadmium carbonates have also been found to be responsible for immobilization of cadmium in natural soils (Alloway and Jackson, 1991).

2.7.3.7 Zinc

The free zinc ion was found to be predominant in natural soils by GEOCHEM modelling of Mahler *et al.*, (1980) and Mullins and Sommers (1988). This result was also obtained by Tills and Alloway (1983). Mench *et al.* (2000) found that the K_d for zinc (measured as zinc in sludge-amended soil (mg/kg) / zinc in 0.1M calcium nitrate extract (mg/l)) ranged from 67.4 to 1724 l/kg, the minimum value being for the control soil, which had no further amendments other than sewage.

2.7.3.8 Lead

Solid organic matter such as humic material in soils is known to adsorb lead (Rickard and Nriagu, 1978; Zimdahl and Hassett, 1977). Additionally, soluble organic matter such as fulvates and amino acids are known to chelate soluble lead and affect its adsorption on soils (Rickard and Nriagu, 1978). Correlative relationships between the organic matter content of soils and its effect on lead adsorption have been established by Gerritse *et al.* (1982) and Soldatini *et al.* (1976). Lead adsorption by a subsurface soil sample from Hanford, Washington was investigated by Rhoads *et al.* (1992). Adsorption data from these experiments showed that K_d values increased with decreasing lead concentrations in solution (from 0.2 mg/l to 0.0062 mg/l) (EPA 402-R-99-004B).

2.7.3.9 Microbial Influences

It was once believed that the rate of decomposition of soil organic matter was constant. Experimental studies by Janssen (1984) yielded an equation relating the decomposition rate of soil organic matter with time. Decomposition rates were found to decrease predictably over time, provided the "apparent initial age" of the organic matter was known, varying from one year for green matter to 14 years for some peats. It was demonstrated that apparent differences in soil organic matter quality, found after 25 years of different fertilizing practices, were related to the proportion of young soil organic matter.

Microbial degradation is a very important factor in the metal-binding aspects of sludge (Yamada el al, 1984, Neal and Sposito, 1986). Two metal exchange sites in sludge organic matter have been determined by Fletcher & Beckett (1987), one predominantly binding Ca, Mg, Zn, Ni, Co, Mn, Cd, Pb, Fe, and one predominantly binding Cu, Pb, and H. In sludged soils, it has actually been found that microbial degradation rates increase over time (within the first five years at least), being the lowest in the first year. Dudley *et al.* (1987) determined that the soluble organic ligands decreased in size as a function of time (this implies that they increased in water-solubility). NTA increases the solubility and mobility of metals in sludged soils, particularly Cd, Cu, Mn, Ni, Pb, and Zn, implying that the sites on the sludged soils that immobilized the metals are weaker metal binders than NTA. This may give a clue that is useful in modelling exercises.

Effects on microbial activity have been observed by McGrath *et al.* (1988) from a soil which had last received sludge 20 years previously, including a 50% reduction in N2 fixation, acetylene reduction reduced by 50% and dehydrogenase, phosphatase activity reduced. The inhibitions were related to metal concentrations, which were in turn influenced by biological activity resulting in the degradation of organic matter and the release of complexing ligands, accompanied by a pH-change and a redox change.

2.7.3.10 Role of Sludge Organic Matter

The sludge organic matter is a very important determinant of metal mobility (Alloway and Jackson, 1991). The organic matter is largely in the solid state, with soluble, low molecular weight organic ligands being produced by microbial degradation. Garnett *et al.* (1987) found that copper and nickel is complexed to high molecular weight ligands, while manganese is unbound to organics. Zinc was found to be present in both organic and inorganic forms.

Ribet *et al.*, 1995, note that organic materials such as sewage sludge can reductively dissolve metal oxides and mobilise them through soil. Ferric oxyhydroxide was observed to decompose. This implies that the Eh that results from application of sewage sludge is lower than that required to reduce ferric ion.

Vengosh *et al.*, (1996) studied the impact of a sewage reclamation plant in Israel that operated for 16 years. They note that while the original sewage composition was modified, particularly during early stages of effluent migration in the unsaturated zone, by cation-exchange and adsorption reactions, the soil sorption capacity is finite, and once the system reached a steady state the inorganic composition of the contaminated groundwater became similar to that of the recharge water. Decomposition of organic matter released carbon dioxide, which dissolved carbonate minerals. The solid organic material in sewage sludge, when mixed with soil, is 55-80% resistant to decomposition, with a turnover time of hundreds of years (Terry *et al.*, 1979)

2.7.3.11 Role of sludge iron and manganese

Iron and manganese are important metals in the retention of other metals in sludged soils, though this depends on their conversion to the iron and manganese oxide states, which can be halted or reversed by flooding of the sludge-amended soils.

CHAPTER 3

EXTENT OF DEDICATED LAND DISPOSAL IN SOUTH AFRICA

3.1 Background Information

A database received from DWAF with information on the sewage and water treatment facilities on their records was used to select the 100 sampling points required for Phase 1 of this study. The database contained information such as addresses, telephone numbers and contact persons for each facility. A questionnaire was compiled in collaboration with ERWAT to collect all applicable data from the sewage treatment facilities. The sites were selected by telephonically contacting the facilities, asking a few questions from the questionnaire in order to determine if they could be used as sampling sites. A total of 234 sewage treatment facilities were contacted in order to identify 100 suitable sites for sampling.

3.1.1 Telephonic survey

The telephonic survey indicated that a wide variety of disposal options are used in South Africa (Figure 3.1.1). The disposal option used by most of the treatment facilities is **stockpiling** (33%), either as the only disposal method or a temporarily measure before it is removed to a landfill or utilized beneficially. The sludge is dried in drying beds or paddies and then put on heaps until the municipalities' parks division, farmers or the public utilizes it.

Another popular disposal option is **sludge ponds** where they continuously pump the sludge into a dam that may or may not be lined. None of these sites was sampled because the ponds are permanently wet and no soil samples could be taken below the sludge. **Irrigation** of soil with liquid sewage sludge with high-pressure nozzles connected to a sludge line is a popular option if sufficient soil is available, while some facilities **flood** the soil with the liquid sludge. At 10% of the sites the sludge was dried on drying beds and then **composted** while 9% of the treatment facilities had **oxidation ponds** where no soil samples could be taken due to the wet state and depth of the sludge.

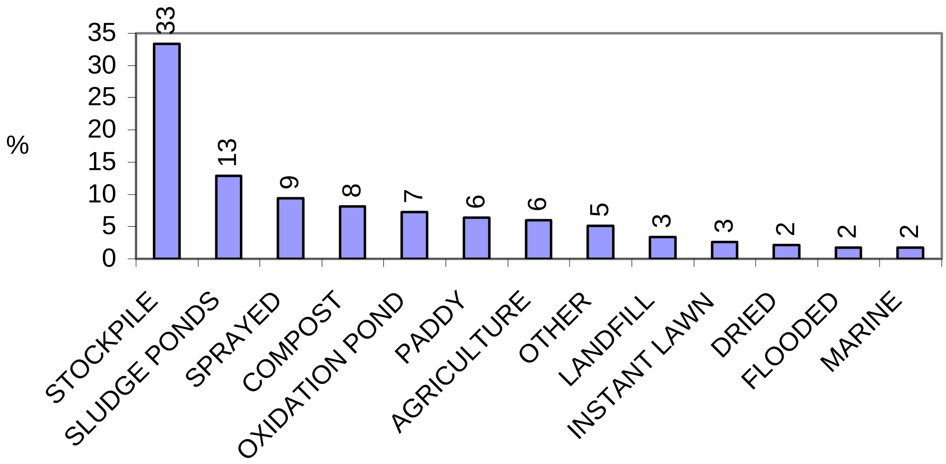


Figure 3.1.1: Disposal options used by 234 different sewage treatment facilities (% of total)

A number of treatment facilities used **paddies** (6%) to dry the sludge. Paddies are shallow, bounded disposal dams into which wet sludge is pumped. There are a number of these paddies at one site that are used alternatively in order to allow the sludge to dry out. The **agricultural** sector uses the sludge of 6% of the treatment facilities contacted while 3% used **landfill** to dispose of the sludge. **Instant lawn** is a disposal method that can generate income while disposing of the sludge and is used by 3% of the consulted facilities.

Other disposal methods used are dumping into the ocean, use it for brick making purposes, incineration, pumping the sludge to other treatment facilities or pumping it into old mine shafts.

3.2 Survey of 100 selected sites

Six types of dedicated land disposal practices were identified where soil samples could be taken underneath the sludge: stockpile, irrigated onto soil and ploughed, paddy systems, instant lawn, flooded onto soil and ploughed as well as dried sludge put onto the soil and ploughed.

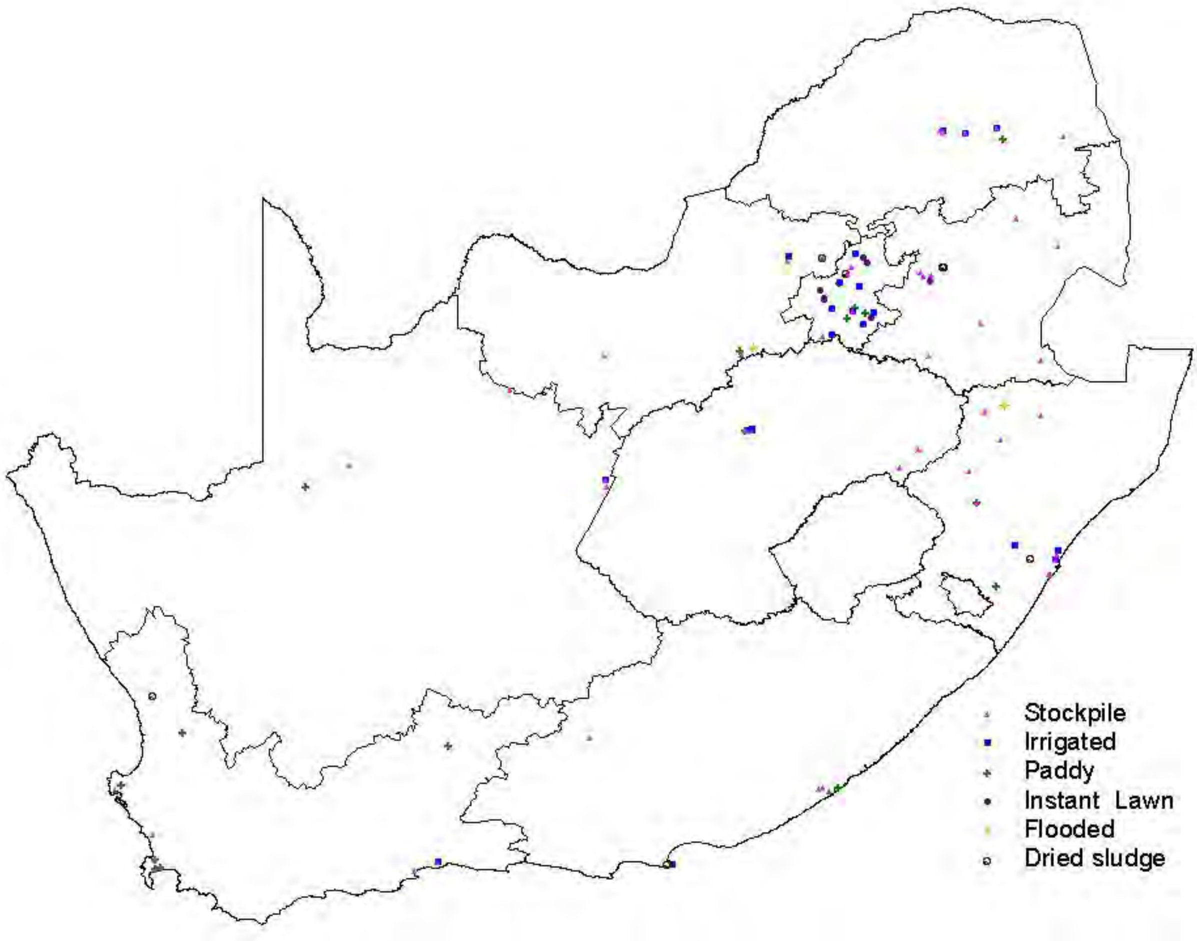


Figure 3.2a: Location of the 100 selected sampling sites

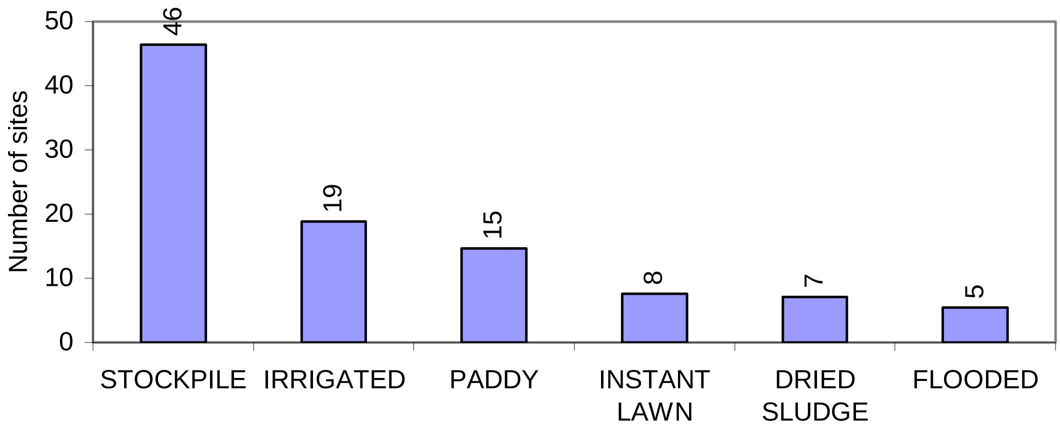


Figure 3.2b: Disposal options of the 100 sites selected for soil sampling

Figure 3.2b indicates the disposal options of the 100 sites that were selected form the telephonic survey for soil sampling. It would have been very useful if the data could be presented as mass of sludge per disposal option because of the big variation in the masses of sludge produced by different sewage treatment facilities. This could not be achieved because of the ignorance on the part of the persons in charge of the treatment facilities. The questionnaires indicated that only 66% of the responsible persons knew the amount of raw sewage inflow they received, 63% knew their COD levels and only 26% knew how much sludge they produced. Therefore it was impossible to calculate the mass of sludge per disposal option. Some other important statistics of the selected sites, as captured by the questionnaires, are presented in Table 3.2.

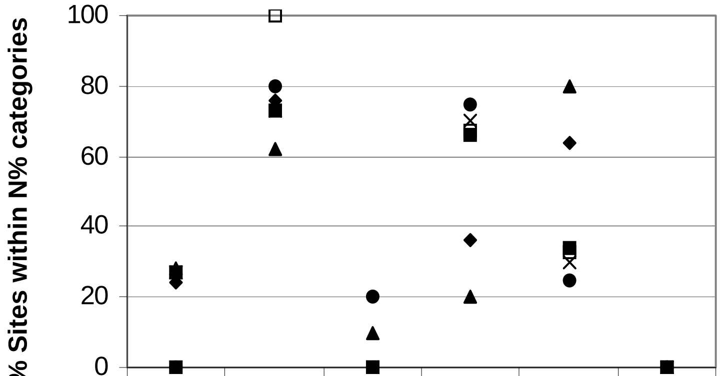
Table 3.2: Statistics on the type of sludge disposed and industrial effluent received at the 100 selected sites (number of sites)

Type of sludge disposed				
Waste activated (WAS)	**Combined Bio-Filter & WAS**	**Anaerobic Digested**	**Combined Anaerobic digested & WAS**	**Other**
20	12	16	41	11

Industrial effluent					
Receive effluent	**<10%**	**10-25%**	**25-50%**	**>50%**	**Unknown**
75	9	23	12	9	22

3.2.1 Macronutrient content of soil samples

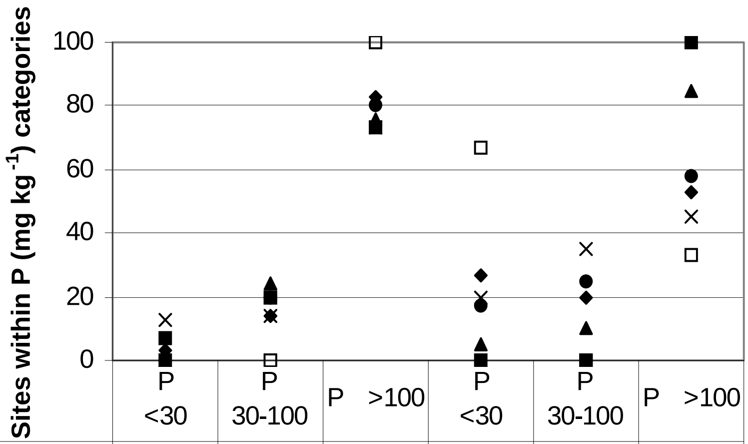
The total N concentrations of the soil samples were lower than would be expected after sludge application. In total only 3 soil samples had a total N content >1.5% which, according to Sparks (1996), is high in soils (Figure 3.2.1a).



	N <0.1 (Industrial)	N 0.1-1.5 (Industrial)	N >1.5 (Industrial)	N <0.1 (Domestic)	N 0.1-1.5 (Domestic)	N >1.5 (Domestic)
◆ Stockpile	24	76	0	36	64	0
■ Instant lawn	27	73	0	66	34	0
▲ Irrigated	28	62	10	20	80	0
× Paddy	27	73	0	70	30	0
□ Flooded	0	100	0	67	33	0
● Dried sludge	0	80	20	75	25	0

Figure 3.2.1a: Graph and table of % of soil samples within different total N% categories for different disposal methods (both industrial and domestic sludge)

The majority of the soil samples had above average Bray I extractable P concentrations of 30-100 mg kg-1 (Brady, 1984) (Figure 3.2.1b). The application of sewage sludge to the soils, both from domestic and industrial origin, in many cases resulted in an increase in the Ca, Mg and K content of the soils. Only a small number of soils (18 samples) had Ca levels <200 mg kg^{-1} which is regarded as low in soils by the FSSA (1997). The majority of samples had 200-3000 mg kg^{-1} Ca (adequate according to FSSA, 1997).



	Industrial			Domestic		
	P <30	P 30-100	P >100	P <30	P 30-100	P >100
◆ Stockpile	3	14	83	27	20	53
■ Instant lawn	7	20	73	0	0	100
▲ Irrigated	0	24	76	5	10	85
× Paddy	13	14	73	20	35	45
□ Flooded	0	0	100	67	0	33
● Dried sludge	0	20	80	17	25	58

Figure 3.2.1b: Graph and table of % of soil samples within different P categories for different disposal methods (both industrial and domestic sludge)

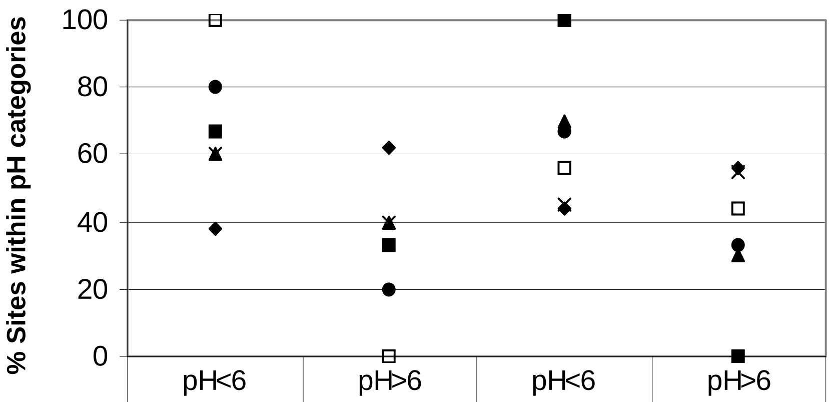
The Mg content of the majority of soil samples was also within the adequate range of 50-300 mg kg^{-1} as suggested by the FSSA (1997). The K content of the soils were raised by the sludge application, 66% of the soil samples had high K concentrations (>250 mg kg^{-1}; FSSA, 1997). There were no significant differences between the macronutrient contents of soil samples from different disposal methods.

3.2.2 pH(H_2O) of soil samples

The average soil pH(H_2O) value of all the samples was 6.1 and a total of 65% of the soil samples had a pH (H_2O) < 6 which can be classified as acid soils. Since many of these samples were taken in areas with naturally low pH(H_2O) values (high rainfall areas) it cannot be concluded that the sewage sludge application caused the acidification although it could play a role. There were no significant differences between the average pH(H_2O) values of the different disposal methods although the average pH(H_2O) of the instant lawn samples was the lowest (Table 3.2.2). There were also no significant difference in the average pH(H_2O) of the soil samples receiving industrial and domestic sludge of each disposal method.

Table 3.2.2: Average pH(H2O) of the soil samples from 100 selected sites

	Stockpile		**Instant lawn**		**Irrigated**		**Paddy**		**Flooded**		**Dried sludge**	
Ave pH(H_2O)	6.3		5.5		5.8		6.4		5.9		5.9	
Industrial effluent	**Yes**	**No**	**Yes**	**No**	**Yes**	**No**	**Yes**	**No**	**Yes**	**No**	**Yes**	**No**
Ave pH(H_2O)	6.4	6.2	5.5	5.1	5.9	5.7	6.1	6.4	5.8	5.9	5.2	5.9



	Industrial pH<6	Industrial pH>6	Domestic pH<6	Domestic pH>6
◆ Stockpile	38	62	44	56
■ Instant lawn	67	33	100	0
▲ Irrigated	60	40	70	30
× Paddy	60	40	45	55
□ Flooded	100	0	56	44
● Dried sludge	80	20	67	33

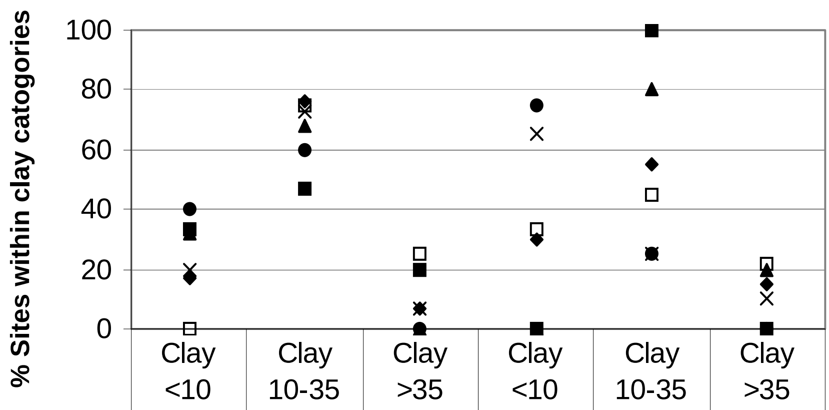
Industrial **Domestic**

Figure 3.2.2: Graph and table of % of soil samples within different pH(H_2O) categories for different disposal methods (both industrial and domestic sludge)

The majority of soil samples (receiving both industrial and domestic sludge) at all disposal sites, except stockpiled sites, had pH(H_2O) levels <6 (Figure 3.2.2). Groundwater pollution at the sites where the soil pH(H_2O) is below 6 is a possibility because most heavy metals are mobile under these acid conditions.

3.2.3 Clay content of soil samples

The clay contents of the soils was determined mainly to give an indication of the sites where groundwater pollution is more likely to occur due to low clay content of the soils as well as sites where pollution is less likely to occur due to high clay content. Figure 3.2.3 present the clay content data of the different disposal options. At 30% of the sampling sites the clay content of the soil was <10% (sandy soils; high leaching probability) and 11% of the sites had clay contents of >35% (sandy clay to clay soils; lower leaching probability).



	Clay <10	Clay 10-35	Clay >35	Clay <10	Clay 10-35	Clay >35
◆ Stockpile	17	76	7	30	55	15
■ Instant lawn	33	47	20	0	100	0
▲ Irrigated	32	68	0	0	80	20
× Paddy	20	73	7	65	25	10
□ Flooded	0	75	25	33	45	22
● Dried sludge	40	60	0	75	25	0

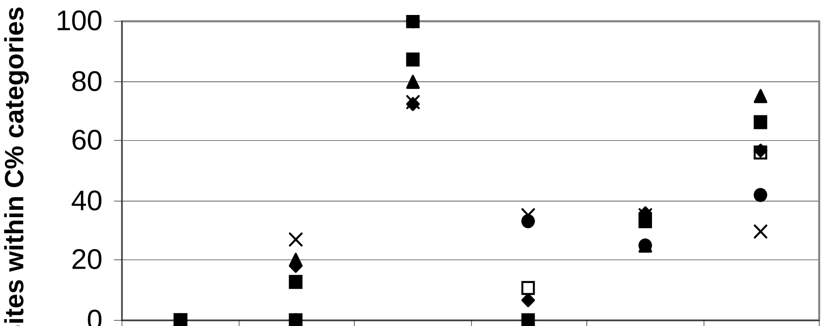
Industrial **Domestic**

Figure 3.2.3: Graph and table of % of soil samples within different clay categories for different disposal methods (both industrial and domestic sludge)

Where the soils with low clay content also have low pH values, which is true for 15% of the samples, the possibility of groundwater pollution becomes most likely if the heavy metal content of the soils is higher than the MPL for South African soils (Nat. Dept. Health & Pop. Dev., 1991). These disposal sites were sampled again during Phase 2 to determine the depth to which the metals have already leached into the soils.

3.2.4 Organic carbon content of soil samples

The application of sewage sludge to the soils had a large influence on the organic carbon content. In South Africa most soils contain between 0.3 - 1.2 %C (FSSA, 1997) and 64% of the samples taken had more than 1.2 % organic carbon and 28% of the samples even contained more than 5%C (Figure 3.2.4).



	C <0.3	C 0.3-1.2	C >1.2	C <0.3	C 0.3-1.2	C >1.2
◆ Stockpile	0	18	72	7	36	57
■ Instant lawn	0	13	87	0	34	66
▲ Irrigated	0	20	80	0	25	75
× Paddy	0	27	73	35	35	30
□ Flooded	0	0	100	11	33	56
● Dried sludge	0	0	100	33	25	42
	Industrial			Domestic		

Figure 3.2.4: Graph and table of % of soil samples within different C% categories for different disposal methods (both industrial and domestic sludge)

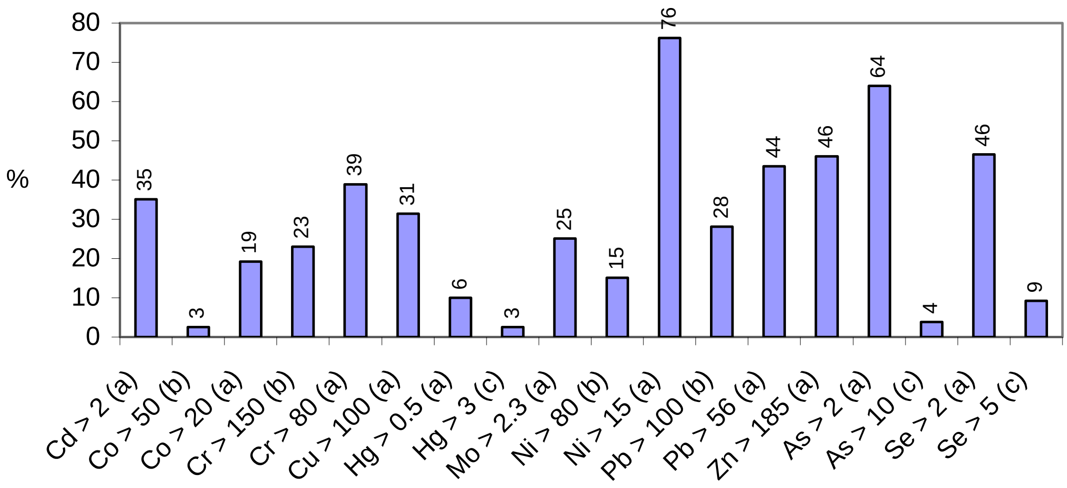
Some of the samples had extremely high organic carbon contents (>30%) but in these cases it was difficult to sample the soil without any sewage sludge and therefore the organic C content of the soil samples were very high.

3.2.5 Heavy metal content of soil samples

The soil samples were digested with the EPA 3050 method and scanned with an ICP-MS in order to estimate the total heavy metal content. The 1991 guidelines (Dept. Nat. Health & Pop. Dev., 1991) were used as guide of the maximum permissible level (MPL) for soils. The new suggested threshold values set by Herselman & Steyn (2001) after a study on the natural background concentrations of heavy metals in South African soils was also used. In some cases (Hg, As and Se) the guidelines for other parts of the world were used, as presented by Kabata-Pendias & Pendias (1992).

The majority of soil samples (88%) had at least one element that exceeded the MPL for soils (Dept. Nat. Health & Pop. Dev., 1991). Figure 3.2.5 indicates the percentage of samples that exceeded the levels set by different authors. However, the set guidelines are for the beneficial use of sewage sludge for agricultural purposes and not for DLD practices. Additional guidelines should probably be considered for DLD sites.

The heavy metals that are reason for concern in South African sewage sludge will be discussed individually.



a – 1991 Guidelines b – Herselman & Steyn, 2001 c – Kabata-Pendias & Pendias, 1992

Figure 3.2.5: Soil samples (%) from 100 sites exceeding the MPL for soils

3.2.5.1 Cadmium

Although Cd is not essential for plant growth, it is effectively absorbed by roots and leaves (Kabata-Pendias & Pendias, 1992). Human and animal life is threatened at Cd concentrations in the plant well below phytotoxicity levels (McLaughlin *et al*., 2000) and its accumulation in food crops at sub-toxic levels is a cause for concern due to the risk to the food chain and consumers (Alloway, 1995). Cadmium is mainly adsorbed by clay and organic matter and the adsorption capacity of soils for Cd is highest at pH levels between 6 and 7. Therefore, the lower the pH and clay content, the higher the mobility of Cd will be (Alloway, 1995).

Sewage sludge contains Cd from various sources like human excretion, Zn-containing domestic products, storm water containing particles of rubber tyres as well as industrial effluents (electroplating, batteries, alloys, iron and steel production) (Alloway, 1995; Korte, 1999).

According to Kabata-Pendias & Pendias (1992) the world-wide mean of Cd in soils is 0.6 – 1.1 mg kg^{-1} and Herselman & Steyn (2001) found the total concentration of Cd in South African soils to be between 0.62 and 2.74 mg kg^{-1}.

Results from this survey indicate that 35% of the soil samples exceeded the 2 mg kg^{-1} guideline value (Dept. Nat. Health & Pop. Dev., 1991). The median concentrations of total Cd at all the sites exceed the median baseline concentration in South Africa (0.1 mg kg^{-1}; Herselman & Steyn, 2001). The sites receiving industrial effluent had significantly higher average and median total Cd concentrations than the sites receiving only domestic sludge. The soil samples from the sites disposing of liquid sludge (irrigated, flooded, paddies and instant lawn) had the highest average Cd contents (Table 3.2.5.1) in the topsoil while the 90^{th} percentiles of the flooded, instant lawn and irrigated sites were all extremely high.

Table 3.2.5.1: Statistics of total (EPA 3050) Cd in the topsoil of the 100 selected sites (mg kg^{-1})

	Industrial sludge				Domestic sludge			
	n	**Ave**	**Median**	**90^{th} %tile**	**n**	**Ave**	**Median**	**90^{th} %tile**
Stockpile	29	1.8	1.4	3.7	81	1.3	0.8	2.9
Dried sludge application	5	0.9	0.7	2.1	12	1.4	1.1	2.8
Flooded with sludge	4	6.7	7.4	11.3	9	0.3	0.0	0.9
Instant lawn	15	5.2	0.9	18.9	3	0.1	0.1	0.2
Paddy systems	15	4.2	2.1	8.6	20	2.3	2.6	2.8
Irrigated with sludge	25	15.5	2.6	34.2	20	2.6	1.5	6.8
All disposal methods	93	6.6	1.4	11.5	145	1.6	0.9	3.5
All samples (ind & dom)	238	3.5	1.1	5.0				

3.2.5.2 Cobalt

Cobalt is mainly present in horizons rich in organic matter and clays and is immobile in alkaline conditions, but leaches through the soil profile under acid conditions (Alloway, 1995). Plant uptake of Co is a function of the Co concentration in the soil solution and it is readily taken up (Kabata-Pendias &

Pendias, 1992) although only a few plant species accumulate significant cobalt levels to cause severe phytotoxicity.

Herselman & Steyn (2001) suggested a new threshold value of 70 mg kg^{-1} for Co, after the total baseline concentration of Co in South African soils was determined to be 1.51-68.5 mg kg^{-1} (median 8.44 mg kg^{-1}). Only 2.5% of the samples exceeded this value while 19% of the samples exceeded the 1991 guideline value of 20 mg kg^{-1} (Table 3.5.2.2). The sites that receive industrial effluent had higher Co concentrations than the sites that receive only domestic sludge. The 90th percentile values of Co at all the studied sites are well below the 70 mg kg^{-1} threshold value, which indicates that Co is probably not a major contaminant in South African sewage sludge.

Table 3.5.2.2: Statistics of total (EPA 3050) Co in the topsoil of the 100 selected sites (mg kg^{-1})

	Industrial sludge				Domestic sludge			
	n	**Ave**	**Median**	**90th %tile**	**n**	**Ave**	**Median**	**90th %tile**
Stockpile	29	11.9	10.5	23.8	81	13.7	11.1	25.6
Dried sludge application	5	9.5	7.4	14.5	12	5.7	3.4	10.5
Flooded with sludge	4	30.7	28.4	54.6	9	8.4	8.3	15.1
Instant lawn	15	19.6	20.7	38.8	3	7.2	5.3	10.7
Paddy systems	15	26.1	22.2	58.1	20	8.0	6.2	15.2
Irrigated with sludge	25	17.4	9.2	41.0	20	10.4	8.6	19.2
All disposal methods	93	17.6	11.2	40.9	145	11.3	9.3	20.5
All samples (ind & dom)	238	13.8	9.9	26.9				

3.2.5.3 Chromium

In nature Chromium occurs as Cr(III) and Cr(VI). Cr(III) is only slightly mobile in very acid conditions and its compounds are considered stable in soils, but Cr(VI) is very unstable in soils, easily mobilized and toxic to plant, animals and humans. Soluble Cr(VI) is readily converted to Cr(III) under normal soil conditions and therefore soil Cr is not available for plant uptake and therefore unlikely to reach phytotoxic concentrations in soils (Kabata-Pendias & Pendias, 1992; Korte, 1999; McLaughlin *et al*., 2000).

Chromium gets into the sewage system mainly via industrial effluents released by metal plating, ink manufacture, dyes, pigments, glass, ceramics, glues, tanning, wood preserving and textile industries. Both Cr(III) and Cr(VI) can be present in the effluents but many of the effluents are treated on site to decrease the potential toxic load in the wastewater or at the sewage treatment plants where Cr(VI) is reduced by organic matter to Cr(III) (Alloway, 1995).

The guidelines referred to are Cr(III) levels, although the extraction method used for this study (EPA3050) extracts both Cr(III) and Cr(VI). The total background concentration of Cr in South African soils is 5.82-353 mg kg^{-1} (median 46.3 mg kg^{-1}; Herselman & Steyn, 2001).

Table 3.5.2.3: Statistics of total (EPA 3050) Cr in the topsoil of the 100 selected sites (mg kg^{-1})

	Industrial sludge				Domestic sludge			
	n	**Ave**	**Median**	**90^{th} %tile**	**n**	**Ave**	**Median**	**90^{th} %tile**
Stockpile	29	45.4	31.6	89.9	81	89.8	60.4	186.6
Dried sludge application	5	56.9	45.6	102.4	12	83.3	25.8	236.3
Flooded with sludge	4	216.1	242.3	347.11	9	51.8	44.8	85.2
Instant lawn	15	173.2	150.1	320.6	3	33.2	37.7	43.0
Paddy systems	15	142.3	128.5	315.7	20	43.1	25.6	86.9
Irrigated with sludge	25	189.7	101.3	511.2	20	131.7	72.9	298.7
All disposal methods	93	128.4	74.6	311.9	145	85.1	51.8	217.6
All samples (ind & dom)	238	102.1	62.9	233.2				

The chromium content of the soil samples was rather high with 39% of the samples exceeding the 1991 guideline value of 80 mg kg^{-1} and 23% exceeding the threshold value of 150 mg kg^{-1} suggested by Herselman & Steyn (2001). The 90^{th} percentile values of all the disposal options, especially the sites that dispose of liquid sludge from industrial origin, are well above the MPL and threshold values and suggest that Cr is a major problem in South African sewage sludge with a negative influence on the topsoil at the disposal sites (Table 3.5.2.3). The median total Cr content of the stockpile and dried sludge application sites were the only one's not exceeding the median concentration of 46.3 mg kg^{-1} in South African soils.

3.2.5.4 Copper

Copper is one of the more immobile heavy metals since it is adsorbed by clay minerals as well as organic material. Copper in the soil profile usually accumulates in the top horizons, which reflects its accumulation by organic matter and probable anthropogenic sources of the element. The mobility of Cu is related to the pH of the soil, the lower the pH the more mobile the Cu will be (Kabata-Pendias & Pendias, 1992).

All around the world the Cu content of sewage sludge is high (84-17000 mg kg^{-1}). Sources of Cu pollution that can be added to sewage sludge via surface run-off or industrial effluents are fly ash due to burning of coal for electricity, combustion of wood products and fossil fuels, fungicides as well as plating and chemical industries (Alloway, 1995).

The baseline total concentration of Cu in South African soils is 2.98-117 mg kg^{-1}. In this study, 31% of the soil samples had Cu concentrations above the MPL of 100 mg kg^{-1} (Dept. Nat. Health & Pop. Dev., 1991). The median concentration of all the disposal sites, whether they receive industrial effluent or only domestic sewage, was significantly higher than the South African median concentration (17.7 mg kg^{-1}; Herselman & Steyn, 2001) (Table 3.5.2.4). The 90^{th} percentile values of all the sites receiving industrial effluent exceed the MPL for South African soils (Nat. Dept. Health & Pop. Dev., 1991) and the 120 mg kg^{-1} suggested threshold value of Herselman & Steyn (2001). It is clear that the Cu content of South African sewage sludge, both from industrial and domestic origin, pose a threat to the environment.

Table 3.5.2.4: Statistics of total (EPA 3050) Cu in the topsoil of the 100 selected sites (mg kg^{-1})

	Industrial sludge				Domestic sludge			
	n	Ave	Median	90th %tile	n	Ave	Median	90th %tile
Stockpile	29	124.2	51.4	295.7	81	120.2	42.9	274.1
Dried sludge application	5	106.6	63.5	232.6	12	54.4	12.6	151.8
Flooded with sludge	4	289.8	320.1	464.8	9	27.9	29.1	43.7
Instant lawn	15	86.9	48.7	207.8	3	17.5	17.5	21.8
Paddy systems	15	153.8	90.4	354.2	20	56.4	26.6	100.7
Irrigated with sludge	25	173.8	73.6	519.7	20	122.3	76.0	309.2
All disposal methods	93	142.4	73.3	398.1	145	98.4	38.9	242.5
All samples (ind & dom)	238	115.4	47.6	302.7				

3.2.5.5 Nickel

Nickel is not a cumulative toxin in animals or humans. The Ni status of soils is highly dependant on the Ni content of the parent material, since Ni is easily mobilized during weathering, and is the highest in soils with a high clay content. It is a phytotoxic element with no essential role in plant metabolism and, when present in soluble form, is readily absorbed by plant roots (Kabata-Pendias & Pendias, 1992). The mobility of Ni in the soil profile increases when pH decreases.

Nickel is used for the manufacturing of stainless steel, electroplating, alloys, batteries, electronic equipment and petroleum products. If these industries do not clean their wastewaters then Ni gets into the sewage system. Tanneries are another main contributor of Ni to the sewage system (Alloway, 1995). The Ni in sewage sludge is mainly present in organic forms and readily available for plant uptake as well as leaching.

After a study on the background concentration of Ni in South African soils (3.43-159 mg kg^{-1}; median 21.3 mg kg^{-1}; EPA 3050 extractable), Herselman & Steyn (2001) suggested a new threshold of 80 mg kg^{-1} total concentration for Ni in soils while in the 1991 guidelines the MPL was 15 mg kg^{-1}. 15% of the soil samples exceeded the 80 mg kg^{-1} level while 76% exceeded the 15 mg kg^{-1} level. The average and median Ni concentrations of the site that receive industrial effluent are significantly higher than that of the sites that receive only domestic sewage. The sites that dispose of liquid sludge had the highest average and median Ni concentrations (Table 3.5.2.5) in the topsoil.

Table 3.5.2.5: Statistics of total (EPA 3050) Ni in the topsoil of the 100 selected sites (mg kg^{-1})

	Industrial sludge				Domestic sludge			
	n	**Ave**	**Median**	**90th %tile**	**n**	**Ave**	**Median**	**90th %tile**
Stockpile	29	35.4	26.7	75.0	81	62.9	29.1	114.4
Dried sludge application	5	38.6	42.6	60.3	12	24.9	14.8	49.3
Flooded with sludge	4	54.6	61.7	75.2	9	20.1	24.3	30.7
Instant lawn	15	68.1	48.0	118.2	3	10.7	10.0	13.6
Paddy systems	15	65.8	61.9	109.8	20	25.4	18.1	46.6
Irrigated with sludge	25	71.7	44.9	200.2	20	50.4	38.4	87.9
All disposal methods	93	56.3	37.4	115.8	145	49.2	27.9	88.9
All samples (ind & dom)	238	51.9	30.4	109.7				

3.2.5.6 Lead

The natural Pb content of soils is inherited from the parent material and it occurs mainly in the top horizon. Lead is reported to be the least mobile of the heavy metals, it is mainly associated with clay minerals, hydroxides and organic matter and is more soluble under acid conditions. Because plants are able to take up Pb only to a limited extent from the soil, it is unlikely to reach phytotoxic concentrations in soils, while airborne Pb, a major source of Pb pollution, is readily taken up by plants (Kabata-Pendias & Pendias, 1992; McLaughlin *et al.*, 2000). The main source of Pb pollution is from smelters, automobile exhausts and paints. Sewage sludge has high Pb concentrations because of old lead water pipes and run-off from roads and gardens as well as industrial effluents from above mentioned industries (Alloway, 1995).

According to Herselman & Steyn (2001) the total baseline concentration of Pb in South African soils is 2.99-65.8 mg kg^{-1} (median 13.1 mg kg^{-1}) and the new suggested threshold value is 100 mg kg^{-1}, while the MPL according to the 1991 guidelines is 56 mg kg^{-1}. Twenty eight percent of the samples had > 100 mg kg^{-1} and 44% had > 56 mg kg^{-1} Pb. The disposal sites that dispose of liquid sewage sludge had the highest median total Pb content (Table 3.5.2.6). The total Ni content of the sites that receive industrial effluent was significantly higher than that of the sites receiving only domestic sewage.

Table 3.5.2.6: Statistics of total (EPA 3050) Pb in the topsoil of the 100 selected sites (mg kg^{-1})

	Industrial sludge				Domestic sludge			
	n	**Ave**	**Median**	**90th %tile**	**n**	**Ave**	**Median**	**90th %tile**
Stockpile	29	92.9	45.5	207.6	81	118.3	39.4	368.3
Dried sludge application	5	26.1	19.4	44.2	12	36.9	12.4	96.8
Flooded with sludge	4	301.0	341.1	458.0	9	27.9	14.9	70.9
Instant lawn	15	59.9	41.9	141.1	3	33.8	32.8	39.5
Paddy systems	15	136.4	91.6	269.9	20	75.0	21.7	214.5
Irrigated with sludge	25	256.7	85.1	659.9	20	162.5	59.5	481.0
All disposal methods	93	144.0	61.5	303.7	145	104.3	32.8	363.7
All samples (ind & dom)	238	119.6	44.1	359.1				

3.2.5.7 Zinc

Zinc is an essential trace element for humans, animals and higher plants. (Alloway, 1995). Zinc is easily adsorbed by clay and organic components and accumulates in most soils in the top horizon from where plants can take it up relatively easily. The mobility of Zn increases when the soil pH decreases (Kabata-Pendias & Pendias, 1992; Alloway, 1995; Korte, 1999).

The major sources contributing to Zn pollution are the burning of coal and other fossil fuels and smelting of non-ferrous metals. The sewage system contains high Zn concentrations due to various household products and chemicals as well as house dust and run-off (Alloway, 1995). The Zn added to soils with sewage sludge is organically bound, soluble and easily available.

The total background concentration of Zn in South African soils is 12-115 mg kg^{-1} (Herselman & Steyn, 2001; median 38.1 mg kg^{-1}). The MPL for South African soils is 185 mg kg^{-1} (Dept. Nat. Health & Pop. Dev., 1991) and 46% of the soil samples in this study exceeded this value. The average concentration of Zn in soils of all the different disposal options (industrial and domestic) greatly exceeded the MPL for South African soils (Table 3.5.2.7). The sites with dried sludge application and instant lawn as disposal options had lower Zn concentrations in the topsoil than the other sites. The reason may be that the grass utilize some of the Zn in the topsoil.

Table 3.5.2.7: Statistics of total (EPA 3050) Zn in the topsoil of the 100 selected sites (mg kg^{-1})

	Industrial sludge				Domestic sludge			
	n	**Ave**	**Median**	**90th %tile**	**n**	**Ave**	**Median**	**90th %tile**
Stockpile	29	269.4	128.8	598.7	81	454.6	175.5	1260.6
Dried sludge application	5	143.1	80.0	280.7	12	228.3	61.9	638.1
Flooded with sludge	4	964.3	869.6	1676.8	9	136.8	39.4	375.2
Instant lawn	15	474.2	84.1	1706.3	3	190.9	211.0	219.1
Paddy systems	15	362.7	186.3	787.2	20	191.2	86.8	473.0
Irrigated with sludge	25	585.9	247.5	1835.7	20	501.9	265.2	1453.2
All disposal methods	93	425.7	175.3	1161.1	145	380.9	151.3	1053.9
All samples (ind & dom)	238	399.2	163.7	1083.1				

3.2.5.8 Other elements

The semi-quantitative analyses of the soil samples gave estimated concentrations of other elements in the soil samples as well. Table 3.5.2.8 gives an indication of the estimated concentration of various other elements. These elements will not be discussed at length in this report. The very high average concentration of Thallium is due to 2 samples from different sites that receive industrial effluent, which contained excessive Tl concentrations.

Table 3.5.2.8: Semi-quantitative concentration of other elements in the topsoil of the 100 selected sites (mg kg^{-1})

	Industrial sludge (n=93)			Domestic sludge (n=145)			All samples (n=238)		
	Ave	Median	90th %tile	Ave	Median	90th %tile	Ave	Median	90th %tile
Arsenic	6.9	3.9	8.4	3.8	2.3	6.5	5.0	2.9	7.1
Mercury	3.9	1.8	3.3	1.2	0.4	3.6	6.4	2.0	4.8
Beryllium	8.0	6.6	12.9	6.4	5.7	10.7	7.0	5.9	11.3
Boron	41.0	19.9	114.2	25.8	12.3	41.2	31.7	14.6	55.29
Titanium	157.6	167.9	228.9	157.2	161.9	268.3	158.2	165.2	252.7
Molybdenum	3.4	1.5	4.8	2.3	1.3	4.3	2.9	1.4	3.9
Vanadium	57.6	52.9	109.6	54.8	52.3	103.1	55.8	52.5	104.9
Manganese	989.5	191.3	1221.7	267.9	193.6	552.4	546.4	191.4	754.0
Bromine	13.9	14.5	17.7	11.6	13.3	25.1	12.4	13.8	24.2
Selenium	12.4	2.6	4.9	2.1	1.6	4.8	6.4	2.0	4.8
Strontium	53.8	27.9	103.5	57.6	18.9	161.2	55.9	24.1	147.7
Tin	11.6	2.0	28.1	9.4	1.6	24.6	10.2	1.7	26.9
Antimony	1.4	0.2	2.3	0.6	0.2	2.14	0.95	0.18	2.17
Tellurium	3.1	0.1	2.2	0.5	0.1	2.3	1.6	0.13	2.3
Iodine	4.4	3.0	7.2	3.1	1.5	7.0	3.6	1.9	7.2
Barium	126.8	106.2	264.7	143.9	100.7	274.1	137.2	105.0	269.6
Tungsten	3.1	0.3	4.7	0.9	0.1	3.2	1.8	0.19	3.3
Platinum	2.0	0.02	2.9	0.7	0.1	2.9	1.23	0.05	2.9
Thallium	64.5	1.9	3.4	1.3	0.4	3.0	25.9	0.63	3.2
Bismuth	14.0	4.6	9.5	3.8	2.9	8.6	7.7	3.6	9.2
Uranium	4.8	1.4	11.2	2.8	1.1	5.5	3.6	1.2	7.4

3.3 Conclusions from the survey on 100 selected sites

As expected, the application of sewage sludge to soil increased the organic carbon content and the Bray I extractable P of the soil above the average for South African soils. However, the total N of the topsoil samples was lower than would be expected after sludge application.

Most of the topsoil samples (88%) had at least one element exceeding the MPL for South African soils (Nat. Dept. Health & Pop. Dev., 1991). Industrial effluent clearly has an influence on the metal content of the sludge that is spread onto the soil during disposal. The total metal concentrations in the topsoil of the water treatment facilities that dispose of liquid sludge are higher than those that dispose of dry sludge, especially when the facility receives industrial effluent.

CHAPTER 4

CASE STUDIES TO DETERMINE MOBILITY OF SLUDGE CONSTITUENTS AT 40 SELECTED DISPOSAL SITES

4.1 Background to Site selection and sampling

Data and information collected during the initial survey of 100 disposal sites were used to select the 40 sites that would be visited for the detailed study. These sites included wastewater treatment facilities with different:

- application techniques (stockpile, instant lawn, paddy, irrigated, flooded and dried sludge application)
- sludge types (waste activated (WAS), anaerobically digested (AD), combinations (WAS & AD)
- soil properties (clay content, pH(H_2O), soil type)
- sizes (large, medium and small treatment facilities with industrial and domestic sludge from metro areas and smaller towns)
- period of sludge disposal
- metal concentrations

Table 4.1 indicates the number of sites within a range of variables that were considered for the selection.

Soil samples were collected at three different locations at each of the selected sites in order to have three replicates for analyses. At each location soil samples were taken at 5 different depths (100mm intervals) where possible, to determine the mobility of the metals and other elements (P, N etc).

Groundwater samples were also collected from sites that have accessible boreholes to determine if any groundwater pollution occurred at the site. Only 9 groundwater samples could be obtained from the 40 sites.

Table 4.1: Number of sites within some variables for selection of 40 sites for detailed studies

Sludge type			**Origin**		**Metro area**	**Size (Ml/d)**	**Clay %**	**pH (H_2O)**
WAS	**AD**	**WAS & AD**	**Industrial**	**Domestic**				
Stockpile (19 sites)								
7	4	8	14	5	6	(8) <10 (7) 10-25 (3) 25-80 (1) >80	(8) <10 (10) 10-35 (1) >35	(8) <6 (11) >6
Instant lawn (5 sites)								
2	-	3	5	-	4	(3) 10-25 (2) 25-80	(4) 10-35 (1) >35	(4) <6 (1) >6
Paddy (4 sites)								
1	1	2	3	1	4	(1) <10 (1) 10-25 (1) 25-80 (1) >80	(2) <10 (2) 10-35	(2) <6 (2) >6
Irrigated (7 sites)								
2	-	5	6	1	5	(2) <10 (1) 10-25 (3) 25-80 (1) >80	(1) <10 (5) 10-35 (1) >35	(4) <6 (3) >6
Flooded (2 sites)								
-	1	1	2	-	1	(1) <10 (1) 10-25	(2) 10-35	(2) <6
Dried (3 sites)								
2	-	1	3	-	2	(1) <10 (1) 10-25 (1) 25-80	(1) <10 (2) 10-35	(3) <6

4.2 Background to Analytical Methods

Many different methods exist to do trace element or heavy metal analysis. The interpretation of the data is influenced by the analytical methods used during analyses. If the method is omitted results are impossible to interpret.

Most analytical methods for heavy metals in soil have two main parts. Firstly the elements are brought into solution and then, secondly an analytical instrument is used to determine the concentration of elements in the solution. Instruments most commonly used are Atomic Absorption (AA), Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES) and Inductively Coupled Plasma – Mass Spectrometry (ICP-MS). These instruments should give very similar results, although each one has its particular limitations.

Knowledge of the total concentration of heavy metals in soils provides only limited information when considering the potential risk to the environment because the risk is determined more by chemical form than simply by total concentration. Nevertheless, if total elemental concentrations are greatly in excess of those expected for a particular soil type, it might be a sign of pollution or risk to the environment. The Environmental Protection Agency method 3050 (EPA method 3050) acid digestion procedure (United States Environmental Protection Agency, 1986), is defined as the "so called total" or "pseudo-total" element concentration and recovers more than just the potentially bio-available fraction of heavy metals from soil samples. It also includes firmly bound elements that will not become bio-available in the near future. The *aqua regia* method ($HCl + HNO_3$) is another method often used to predict the "so called total" concentration. These methods are named "so called total" or "pseudo-total" concentrations because they do not dissolve silicates or silica completely but are vigorous enough to dissolve the heavy metals not bound to silicate phases.

Trace element bio-availability to plants and soil organisms is a function of the concentration of elements in the soil solution and the ability of the soil to buffer concentration in solution. The quantity of heavy metals that can be exchanged and the rate at which they are exchanged is dependant on the buffer capacity of the soil. The 0.2 mol dm^{-3} Di-ammonium Ethylenediaminetetraacetic Acid (NH_4EDTA) extraction method (The Non-Affiliated Soil Analysis Work Committee, 1990) is recommended by Bruemmer & van der Merwe (1989) as the best method to use when predicting the pollution danger of heavy metals in soils. This extraction method predicts the potential bio-available fraction of heavy metals in the soil, or in other words, the quantity of heavy metals available for exchange, depending on soil conditions. It can, therefore, be used to indicate the potential risk of heavy metals that can enter the food chain. Soil composition and environmental factors will influence the rate of exchange to the soil solution.

The apparent (current) risk is best predicted by the concentration of an element in the soil solution. The concentration of heavy metals in the soil solution is generally very low and difficult to determine routinely. It has been found that weak, unbuffered salt solutions (NH_4NO_3, $CaCl_2$, $NaNO_3$, etc.) are most likely to give the best estimate of the immediate bio-availability and therefore current risk.

For legislation purposes, total methods such as EPA method 3050 and *aqua regia* are mostly used and compared with threshold values. This is probably an over- prediction and over simplification of risk. The NH_4EDTA method will give a better indication of the potential medium term risk for heavy metals to the environment. If this method shows potential risk then the current risk should be determined by using weak salt extractions (e.g. ammonium nitrate).

The methods used in this study were EPA 3050 and *aqua regia* (total), NH_4EDTA (potentially bio-available) and NH_4NO_3 (soil solution). The metals that were studied are Cr, Co, Ni, Cu, Zn, Cd, and Pb. In this chapter the average of the data of the three locations at each sampling site were used for the figures. The sludge data referred to in the report were collected from a WRC report on the Project “A metal content survey of South African sewage sludge and an evaluation of analytical methods for their determination in sludge" (Snyman, Herselman & Kasselman, 2003).

The guideline values that were used for this study were:

- maximum permissible level (MPL) for South African soils according to the 1991 sludge guidelines (Dept. Nat. Health & Pop. Dev., 1991)
- NH_4EDTA extractable guideline values set by Bruemmer & van der Merwe (1989)
- NH_4NO_3 guidelines for groundwater protection (Baden-Wurttemberg, 1993).
- investigation thresholds suggested by Herselman & Steyn (2001) for total concentrations of metals in soils
- median metal concentrations (total) determined by Herselman & Steyn (2001) during a study of the baseline metal concentrations in South African soils

4.3 Correlations between analytical methods

The data of all the analytical methods for all the elements were correlated to determine the r^2 values (Table 4.3). The correlations were done for all the samples, only topsoil samples and subsoil samples (lowest soil layer sampled) to determine where the strongest correlation would be. The correlation between EPA 3050 and *aqua regia* for all the metals, except Ni, were very strong (r^2 >0.82). There are very small differences between the correlations of the topsoil and subsoil samples. These two analytical methods can thus be used interchangeably since both give an indication of the total metal content of the soil.

Table 4.3: Correlation matrix of different analytical methods for all metals of all samples, only topsoil samples and only subsoil samples

		Cr			Co		
		EPA	Aqua regia	NH_4EDTA	EPA	Aqua regia	NH_4EDTA
All samples	Aqua regia	0.82			0.90		
	NH_4EDTA	0.56	0.35		0.60	0.60	
	NH_4NO_3	0.42	0.23	0.69	0.28	0.32	0.46
Only topsoil	Aqua regia	0.80			0.90		
	NH_4EDTA	0.63	0.42		0.69	0.73	
	NH_4NO_3	0.62	0.43	0.79	0.42	0.56	0.70
Only subsoil	Aqua regia	0.88			0.90		
	NH_4EDTA	0.43	0.30		0.57	0.62	
	NH_4NO_3	0.27	0.16	0.87	0.15	0.11	0.43
		Ni			Cu		
All samples	Aqua regia	0.40			0.84		
	NH_4EDTA	0.34	0.16		0.55	0.67	
	NH_4NO_3	0.36	0.15	0.91	0.12	0.14	0.17
Only topsoil	Aqua regia	0.50			0.85		
	NH_4EDTA	0.41	0.26		0.44	0.72	
	NH_4NO_3	0.31	0.21	0.80	0.25	0.25	0.19
Only subsoil	Aqua regia	0.51			0.78		
	NH_4EDTA	0.36	0.15		0.61	0.53	
	NH_4NO_3	0.35	0.14	0.95	0.06	0.10	0.40
		Zn			Cd		
All samples	Aqua regia	0.85			0.97		
	NH_4EDTA	0.78	0.75		0.86	0.88	
	NH_4NO_3	0.25	0.24	0.53	0.79	0.78	0.78
Only topsoil	Aqua regia	0.89			0.97		
	NH_4EDTA	0.80	0.87		0.92	0.94	
	NH_4NO_3	0.13	0.30	0.42	0.82	0.82	0.81
Only subsoil	Aqua regia	0.74			0.63		
	NH_4EDTA	0.83	0.59		0.37	0.25	
	NH_4NO_3	0.29	0.08	0.46	0.40	0.14	0.57
		Pb					
All samples	Aqua regia	0.86					
	NH_4EDTA	0.83	0.80				
	NH_4NO_3	0.41	0.21	0.45			
Only topsoil	Aqua regia	0.80					
	NH_4EDTA	0.72	0.74				
	NH_4NO_3	0.61	0.24	0.53			
Only subsoil	Aqua regia	0.99					
	NH_4EDTA	0.92	0.82				
	NH_4NO_3	0.25	0.20	0.25			

The correlation between the NH_4EDTA and NH_4NO_3 extraction methods are strong for Cr, Ni and Cd (Table 4.3) but not for the other elements. For Zn, Cd and Pb the correlation between the total methods (EPA 3050 and *aqua regia*) and NH_4EDTA are also strong (r^2>0.78 and r^2>0.75 respectively) but for the other elements it is not that strong (r^2>0.45). In the case of Cd even the correlation between the total methods and NH_4NO_3 are strong, but for all the other elements it is weak (r^2<0.41), with better correlations for the topsoil than the subsoil.

4.4 Macronutrients and other elements in soil samples of 40 selected sites

The application of sewage to soil resulted in high Bray I extractable P content of the soils. At all the sites the P content of the soil are higher than the average of 30-100 mg kg^{-1} for normal soils (Brady, 1984; Table 4.4).

Table 4.4: Number of sites of each disposal method that fall within guideline ranges for Bray I P, total N and organic C

Bray I P (mg kg^{-1}) [a]			**Total N % [b]**			**Total organic C % [c]**		
<30	**30-100**	**>100**	**<0.1**	**0.1-1.5**	**>1.5**	**<0.3**	**0.3-1.2**	**>1.2**
Stockpile (19 sites)								
-	-	19	12	5	-	2	13	4
Instant lawn (5 sites)								
-	-	5	4	1	-	-	4	1
Paddy (4 sites)								
-	-	4	2	2	-	-	4	-
Irrigated (7 sites)								
-	-	7	3	4	-	1	3	3
Flooded (2 sites)								
-	-	2	-	2	-	-	1	1
Dried (3 sites)								
-	-	3	-	3	-	-	1	2

a – Brady, 1984

b – Sparks, 1996

c – FSSA, 1997

The total N of the soil samples where within the normal and low ranges of agricultural soils in South Africa (Sparks, 1996) and it seems that sludge application did not significantly increase the total N content of the soils (Table 4.4). The soil samples at the majority of sites were in the normal to high ranges according to the FSSA (1997).

The distributions of P, N and C in the soil profiles of selected sites of each disposal method are displayed in Figure 4.3. The sites that were selected for the figure were the sites with the highest P concentration of each disposal method. The Bray I extractable P concentration of the instant lawn site was the highest followed by the irrigated site. At both these sites the concentration was highest in the topsoil and decreased significantly with depth. In the case of all the other sites the P distribution in the soil profile stayed consistent.

The total N content of the topsoil of the irrigated and dried sites were the highest and decreased significantly with depth. At the instant lawn site the total N in the topsoil was lower than in the 100-200mm layer. This may be because of the N uptake of the grass from the topsoil layer. At the rest of the sites the N were distributed evenly through the soil profile.

The organic C content of the irrigated site and the dried application were the highest because these sites are ploughed and the sludge incorporated into the soil. Thus, it was impossible to remove all sludge from the topsoil samples. At the instant lawn site the organic C were also high in the top 200mm of soil. The distributions of C in the rest of the disposal sites were consistent through the profile.

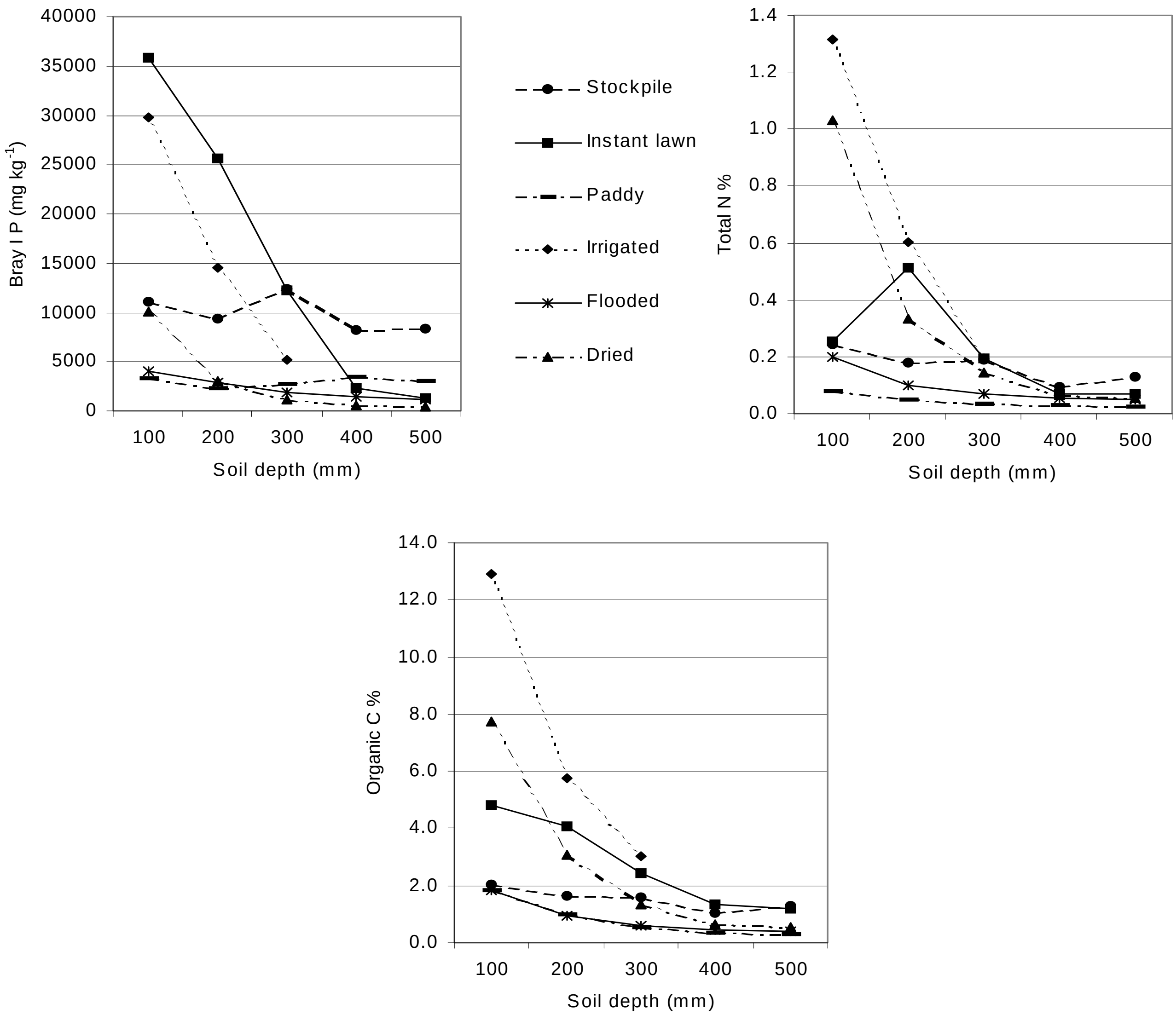


Figure 4.3: Distribution of Bray I P, total N and organic C in the soil profiles of selected sites from each disposal method

4.5 Metals in the sludge and soil samples of 40 selected sites

The metal content of all the different disposal sites were studied extensively and these data and discussions are in Appendix A. For the purposes of the general report only some of the sites and metals are discussed.

Table 4.5a indicates the number of sites of each disposal method with topsoil metal concentrations above the guideline levels set for the particular analytical method.

Table 4.5a: Number of sites with topsoil metal concentrations exceeding the guideline levels set for the different analytical methods

		Guideline mg kg^{-1}	Stockpile	Instant lawn	Paddy	Irrigated	Flooded	Dried
Cr	**NH_4EDTA [a]**	**50**	0	0	0	0	0	0
	NH_4NO_3 [b]	**0.13**	2	1	0	2	0	1
	MPL [c]	**80**	6	3	3	5	1	2
	IT [d]	**150**	3	2	1	4	0	1
Co	**NH_4EDTA [a]**	**10**	1	1	2	0	1	0
	MPL [c]	**20**	3	2	2	2	1	0
	IT [d]	**70**	0	0	0	0	0	0
Ni	**NH_4EDTA [a]**	**20**	0	2	1	1	0	0
	NH_4NO_3 [b]	**1.2**	7	3	2	3	2	1
	MPL [c]	**15**	13	5	4	7	2	2
	IT [d]	**80**	5	1	0	1	0	0
Cu	**NH_4EDTA [a]**	**60**	2	1	0	1	1	1
	NH_4NO_3 [b]	**1.2**	4	1	1	2	1	2
	MPL [c]	**100**	6	2	1	3	1	1
	IT [d]	**120**	5	2	0	3	1	1
Zn	**NH_4EDTA [a]**	**100**	1	1	1	2	1	2
	NH_4NO_3 [b]	**5**	5	2	1	3	2	2
	MPL [c]	**185**	7	1	2	4	2	2
Cd	**NH_4EDTA [a]**	**1**	1	2	2	2	1	0
	NH_4NO_3 [b]	**0.1**	3	2	0	3	1	0
	MPL [c]	**2**	4	1	2	3	1	1
	IT [d]	**3**	0	1	1	3	1	1
Pb	**NH_4EDTA [a]**	**100**	0	0	0	0	0	0
	NH_4NO_3 [b]	**3.5**	1	0	0	0	0	0
	MPL [c]	**56**	6	1	2	3	1	1
	IT [d]	**70**	6	1	2	3	1	1

a - Bruemmer & van der Merwe, 1989 b – Baden-Wurttemberg, 1993
c – Nat. Dept. Health & Pop. Dev., 1991 d – Herselman & Steyn, 2001

The Ni concentrations (all analytical methods) in topsoil samples of the majority of sites are higher than the guideline values. This is also the case for Zn, Cu, Pb and Cr although to a lesser extend. These seem to be metals that are reason for concern at the DLD sites in South Africa.

The sludge at the majority of the 40 selected sites were analysed in a study conducted by Snyman, Herselman & Kasselman (2003). Analyses results of the total metal content of the sludge are presented in Table 4.5b for reference purposes.

Table 4.5b: Total metal content (*aqua regia*) of sewage sludge at the selected 40 sites (mg kg^{-1})

	Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**		**Cd**	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
Site 1	3.8	5.1	270	275	172	157	1098	**Site 20**	15.0	24.1	459	1645	229	321	4486
Site 2	3.5	3.9	173	339	178	140	1344	**Site 21**	4.7	22.8	1650	439	141	214	3874
Site 3	5.4	16.7	113	208	42	297	1238	**Site 22**	3.4	35.2	411	265	298	105	4549
Site 4	4.0	6.4	82	271	151	211	1000	**Site 23**	1.3	15.6	296	137	137	107	640
Site 5	3.7	5.3	145	341	105	178	1851	**Site 24**	41	12.7	979	1024	526	278	17373
Site 6	6.4	10.1	119	574	177	545	3159	**Site 25**	11.7	10.6	912	865	471	286	5538
Site 7	4.7	30.9	322	582	201	201	3239	**Site 27**	12.9	37.5	456	505	253	239	3179
Site 8	5.2	9.9	377	1310	270	219	2150	**Site 28**	73	333	1483	1435	1043	897	12843
Site 9	10.8	79	1589	2244	660	182	4524	**Site 29**	71	178	2791	2920	600	3758	20533
Site 10	19.2	102	1085	951	399	1297	5441	**Site 30**	7.8	11.9	179	346	117	286	1852
Site 11	3.7	10.6	193	370	159	150	2222	**Site 31**	4.4	63	259	335	185	150	1451
Site 12	7.3	17.8	292	858	364	377	4197	**Site 32**	2.3	10.5	105	277	190	153	1371
Site 13	1.9	4.9	438	365	247	276	1470	**Site 34**	1.7	5.6	3681	292	292	200	1090
Site 14	3.9	5.3	78	269	131	218	867	**Site 35**	7.2	30.0	1129	276	126	154	1685
Site 16	2.6	8.3	62	379	245	186	1216	**Site 36**	22.3	75	950	954	380	735	5387
Site 17	4.8	5.2	265	525	179	258	1508	**Site 39**	15.5	7.8	205	1575	279	151	2613
Site 18	4.8	8.7	87	641	158	259	2081	**Site 40**	0.7	3.0	52	109	48	16	474
Site 19	3.3	19.7	63	454	213	499	1868								

4.6 Mobility of metals in soil samples of 40 selected sites

Soil samples were taken at 5 different depths (100mm increments) to determine the depth of metal movement in the soil profile. All the soil samples were analysed with the different analytical methods and the correlations between the analytical methods were discussed in paragraph 5.3. Figure 4.6 is an example of 2 graphs indicating the depth of metal mobility. The metal concentration in the soil profile with the total methods (EPA 3050 and *aqua regia*) did not decrease significantly with depth probably because the total baseline concentrations of the metals are also high. The metal concentrations with the NH_4EDTA and NH_4NO_3 methods decreased with depth until the baseline concentrations were reached. Therefore only the NH_4EDTA extractable metal concentration will be used for further discussions.

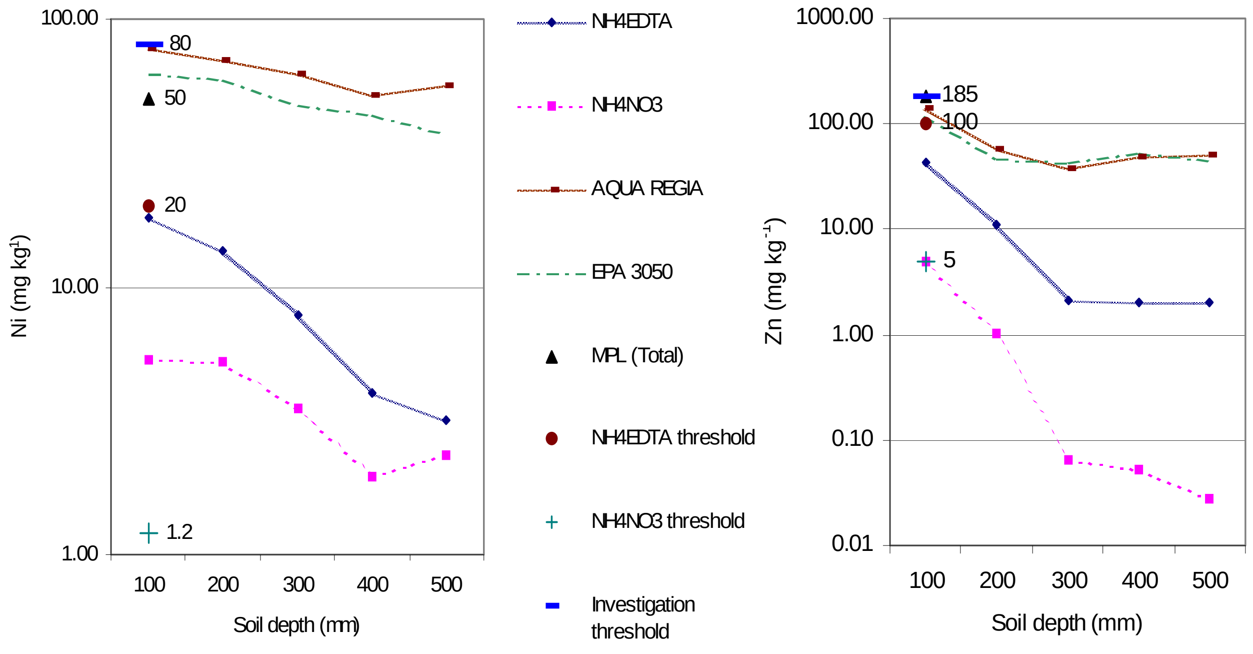


Figure 4.6: Examples of the mobility of metals in the soil profile with the different analytical methods

4.6.1 Stockpile sites

A total of 19 stockpile sites were sampled. These include 4 sites where WAS is disposed of, 2 sites with AD sludge and 7 sites that dispose of combined WAS and AD (Table 4.6.1). The soil samples were taken at the footprint of the stockpiles after removing the sludge. Six of the sites had sandy soils (<10% clay) and only one site had a clay soil (>35% clay). Nine of the sites had soil pH(H_2O) levels <6.

Table 4.6.1: General information of 19 stockpile sites

	Sludge type			Origin		Metro area	Size (Ml/d)	Clay %	C %	pH (H_2O)
	WAS	AD	WAS & AD	Ind	Dom					
Site 1			✓		✓	✓	10-25	2	0.81	7.5
Site 2			✓	✓		✓	>80	4	2.79	7.5
Site 3		✓		✓			10-25	20	0.82	6.3
Site 4	✓			✓			<10	4	0.56	5.9
Site 5	✓			✓			25-80	5	0.25	5.5
Site 6			✓	✓			10-25	7	1.17	7.3
Site 7			✓		✓		<10	17	1.98	3.6
Site 8	✓			✓			<10	10	1.76	4.4
Site 9	✓			✓			<10	20	2.04	5.7
Site 10			✓	✓		✓	25-80	25	1.05	5.4
Site 11		✓			✓		<10	12	0.99	6.7
Site 12			✓	✓			25-80	45	0.56	7.3
Site 13			✓	✓			<10	7	1.44	5.9
Site 14			✓	✓		✓	<10	15	1.48	5.9
Site 15	✓				✓		10-25	12	0.17	5.1
Site 16		✓		✓		✓	<10	19	4.51	4.7
Site 17	✓			✓		✓	10-25	3	0.53	5.6
Site 18	✓				✓		10-25	5	0.71	7.4
Site 19		✓		✓			10-25	16	0.97	7.7

Seven stockpile sites, with different types of sludge (both domestic and industrial) and soil properties, were selected for discussion. The metal contents of the soils that receive sludge from industrial origin (sites 2, 12, 17 and 19) are higher than the soils that receive sludge from domestic origin (sites 1, 11 and 15; Figure 4.6.1). The sites that received WAS (15 & 17) had the highest metals concentration in the topsoil and an even distribution in the subsoil layers. Metals moved deeper in the soil profile at the sites that received AD sludge (11 & 19). This phenomenon was also found during research done by Snyman & Kasselman (personal communication, HG Snyman). They found that the metals are associated with the solid phase for WAS sludge and with the liquor for AD sludge. Therefore the metals are more mobile when AD sludge is applied to soil.

The influence of clay content on the mobility of the metals is also clear when site 1 and 12 is compared (Figure 4.6.1). Both these sites received combined WAS and AD sludge from industrial origin with respectively 172 and 364 mg kg^{-1} Ni and 275 and 858 mg kg^{-1} Cu (see Table 4.5b). The soil pH(H_2O) of the sites are 7.5 and 7.3 respectively. The Ni and Cu concentrations of the soil from site 12 are highest in the topsoil and decrease significantly with depth. The same metals are equally distributed in the soil profile of site 1, indicating that the metals leached through the profile.

The metal concentrations in the topsoil of site 2 are significantly higher than in the subsoil because of the high C content of the topsoil (2.79%), which adsorbed the metals and immobilized it even though the clay content of the soil was only 4%.

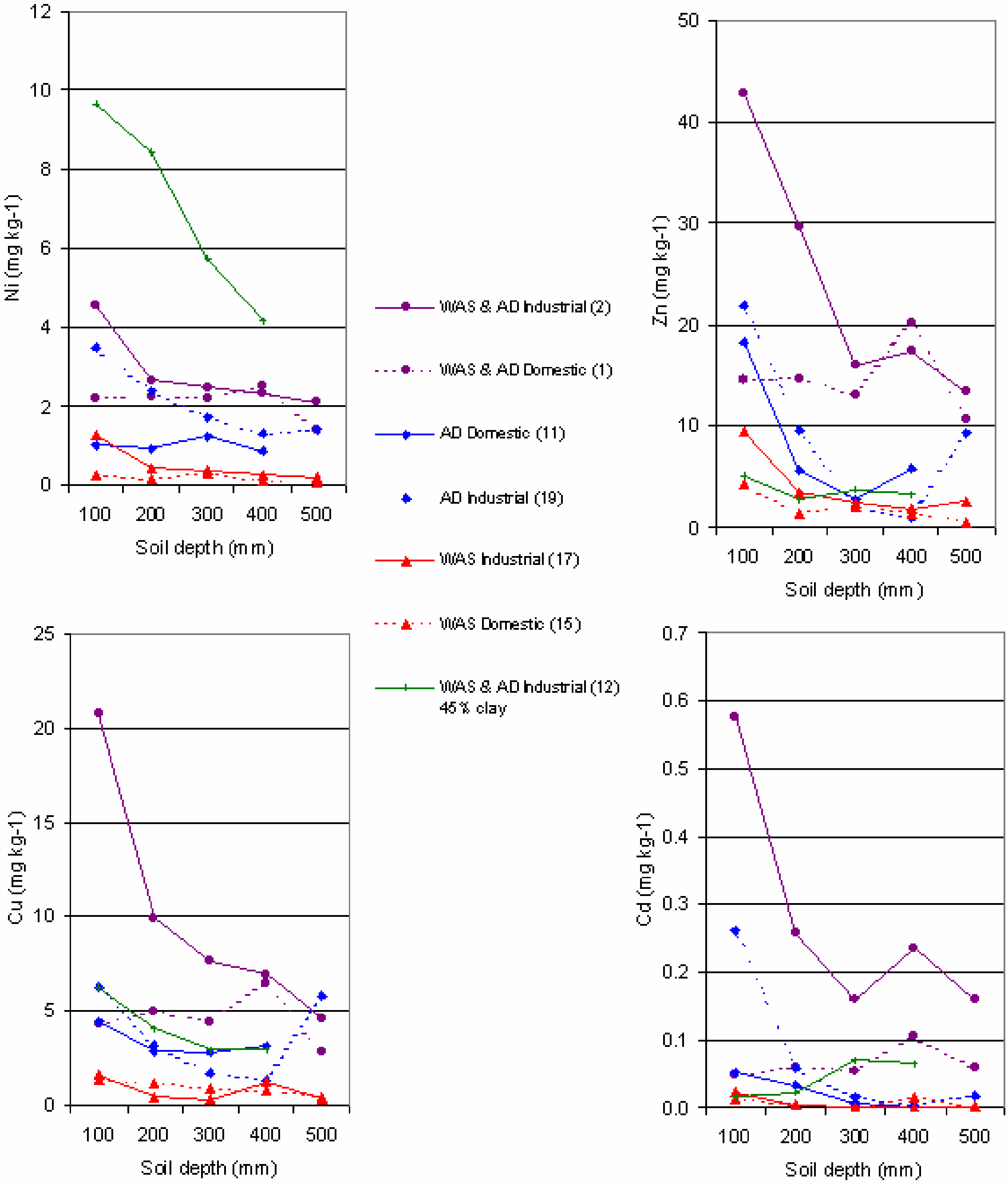


Figure 4.6.1: NH_4EDTA extractable Ni, Zn, Cu and Cd in the soil profiles of 7 selected stockpiled sites (sites 1,2,11,12,15,17 and 19)

4.6.2 Instant lawn sites

Soil samples were taken at 5 instant lawn disposal sites. Two of these sites produce WAS and 3 produce combined WAS and AD, all from industrial origin. The clay content of the sites ranged between 11 and 34%, the pH(H_2O) between 4.1 and 5.9 and the organic C content were between 0.88 and 4.82 (Table 4.6.2). The soil samples were taken after the grass was harvested.

Table 4.6.2: General information of 5 instant lawn sites

	Sludge type			Origin		Metro area	Size (Ml/d)	Clay %	C %	pH (H_2O)
	WAS	AD	WAS & AD	Ind	Dom					
Site 20			✓	✓		✓	10-25	19	2.31	5.9
Site 21	✓			✓			10-25	34	1.25	4.9
Site 22			✓	✓		✓	25-80	12	0.88	4.3
Site 23			✓	✓		✓	10-25	11	1.28	4.1
Site 24	✓			✓		✓	25-80	21	4.82	4.3

The Ni, Cu and Cd concentrations of sites 22 and 23 were distributed evenly through the soil profile, indicating leaching of these metals. Both these sites had low clay contents (11-12%) and pH(H_2O) between 4.1 and 4.3. The high metal concentrations in the topsoil of sites 20 and 24 are a result of the high organic C of the topsoil at the sites (2.31 and 4.82% respectively). The metals are bound by the carbon and rendered immobile even though the clay content of the sites are not that high (19-21%) and the pH(H_2O) are low.

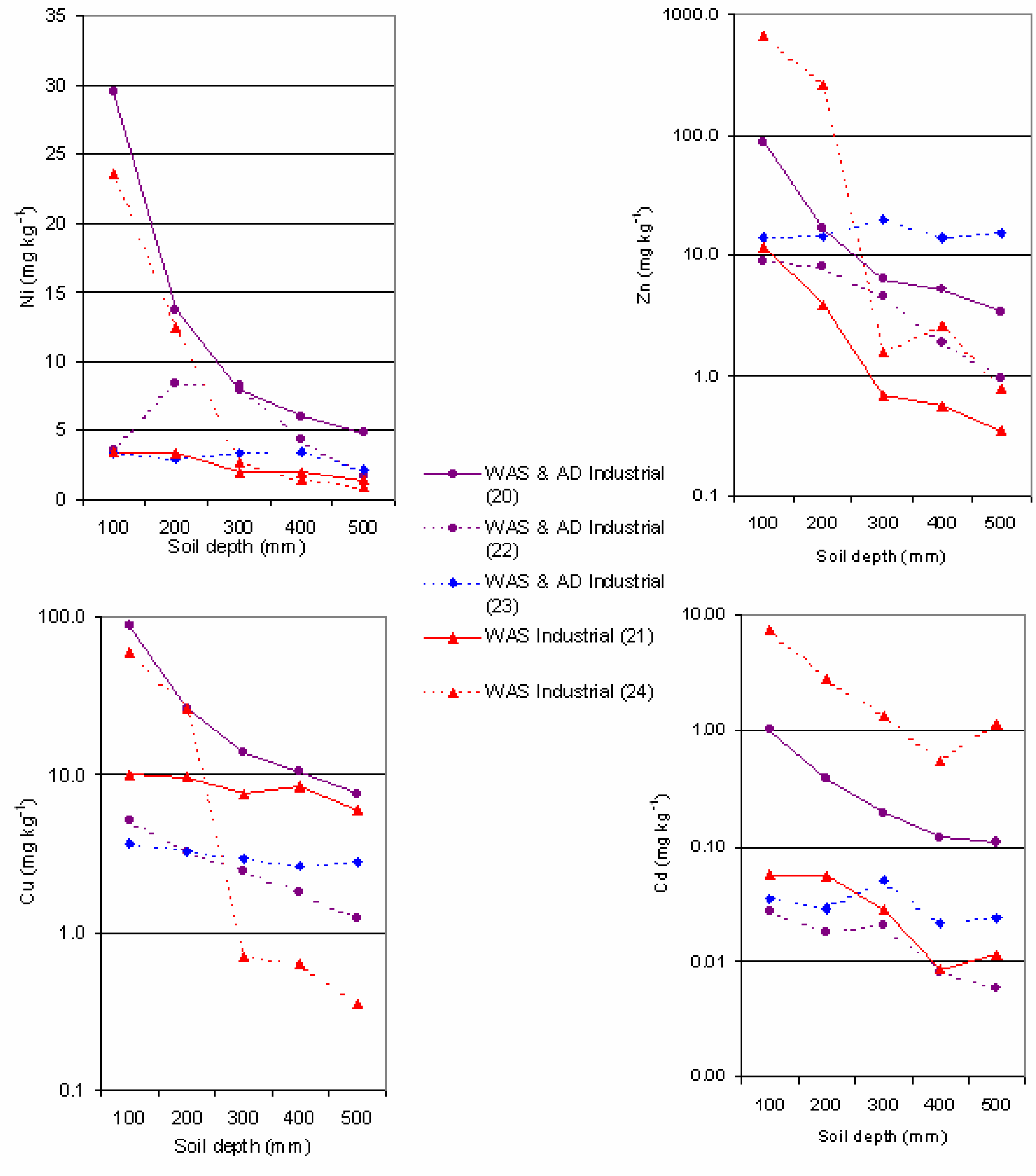


Figure 4.6.2: NH_4EDTA extractable Ni, Zn, Cu and Cd in the soil profiles of the 5 instant lawn sites

4.6.3 Paddy system sites

Four sites that dispose of their sludge in paddies were selected for detailed studies. Soil samples were taken in dry paddies after the sludge was removed. All the sites were in large metropolitan areas. Two of the sites dispose of combined WAS and AD (one from industrial origin and the other from domestic origin) and the other two produce WAS and AD respectively (both from industrial origin). The clay content, organic C and pH(H2O) of the different site are presented in Table 4.6.3.

The site that received industrial WAS and AD (site 27) did not have higher Zn, Cu and Cd concentrations than the site that received domestic WAS and AD (site 25), as would be expected (Figure 4.6.3). The metal content of the domestic sludge was higher than the industrial sludge (see Table 4.5b).

Table 4.6.3: General information of 4 paddy sites

	Sludge type			**Origin**		**Metro area**	**Size (Ml/d)**	**Clay %**	**C %**	**pH (H_2O)**
	WAS	**AD**	**WAS & AD**	**Ind**	**Dom**					
Site 25			✓		✓	✓	10-25	4	1.87	6.4
Site 26	✓			✓		✓	<10	4	0.62	7.8
Site 27			✓	✓		✓	>80	25	0.89	6.5
Site 28		✓		✓		✓	25-80	19	1.83	3.9

The metals were more mobile at the site that received AD sludge (site 28) than at the site that received WAS sludge (site 26; Figure 4.6.3) even though site 28 had higher clay and organic C content than site 26 (29% vs 4%). An explanation for this may be that the metals associated with AD sludge is in the liquor and therefore more mobile.

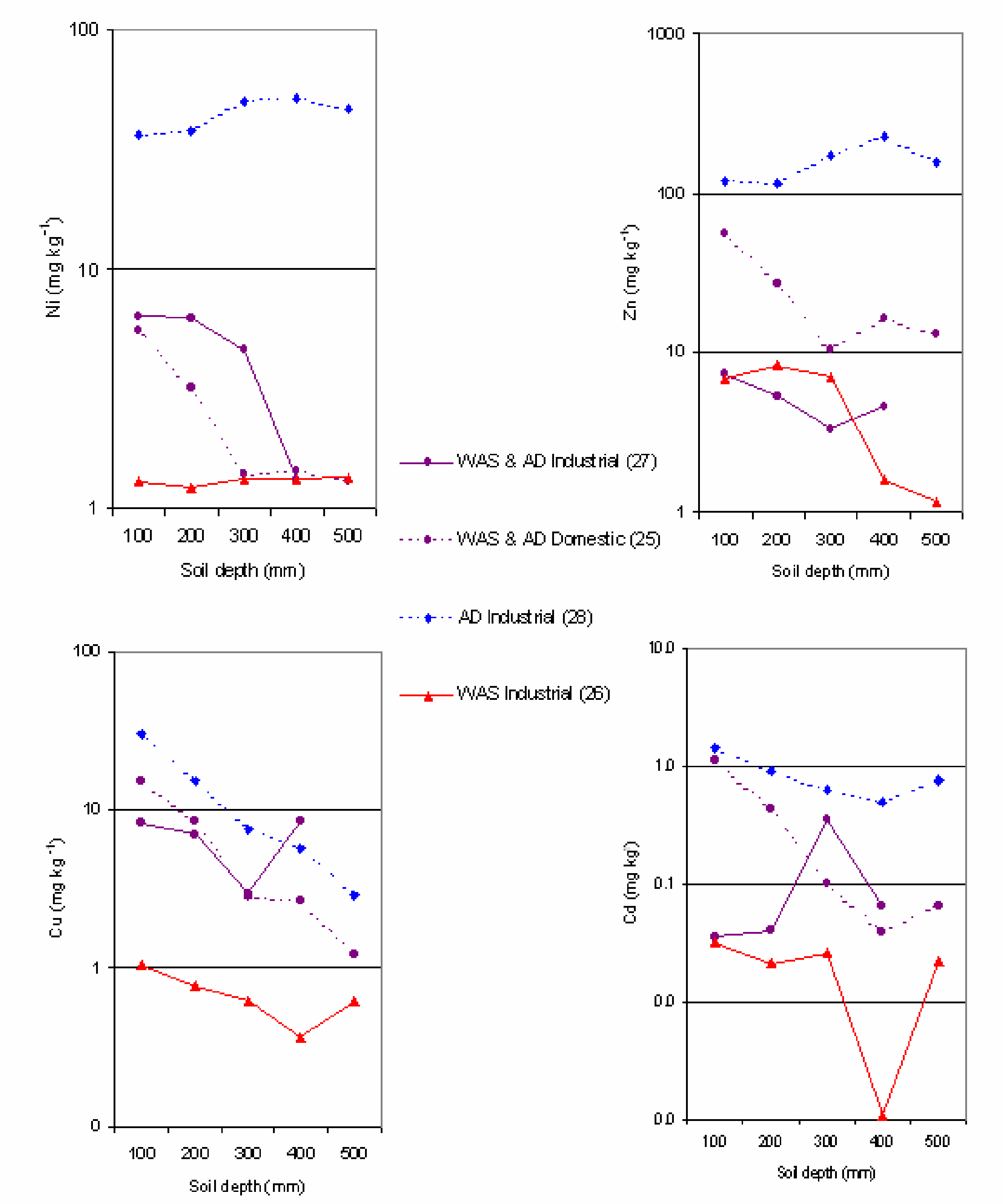


Figure 4.6.3: NH_4EDTA extractable Ni, Zn, Cu and Cd in the soil profiles of the 4 sites using paddies as disposal method

4.6.4 Irrigation sites

Seven sites were chosen that dispose of liquid sludge on land by irrigation. Five of these sites dispose of combined WAS and AD and the rest dispose of WAS sludge. All the sludge, except one site, are from industrial origin. The clay and organic C content as well as pH(H_2O) of the soils are represented in Table 4.6.4.

Table 4.6.4: General information of 7 irrigation sites

	Sludge type			Origin		Metro area	Size (Ml/d)	Clay %	C %	pH (H_2O)
	WAS	**AD**	**WAS & AD**	**Ind**	**Dom**					
Site 29			✓	✓		✓	25-80	24	4.90	4.6
Site 30			✓	✓			25-80	28	1.90	4.9
Site 31			✓	✓		✓	>80	14	5.72	3.6
Site 32			✓		✓		10-25	30	1.39	7.7
Site 33			✓	✓		✓	25-80	12	12.91	5.8
Site 34	✓			✓		✓	<10	3	0.82	7.8
Site 35	✓			✓		✓	<10	22	1.56	5.1

The metal content of the site that receives combined WAS and AD sludge from domestic origin (site 32) is significantly lower than the site that receives industrial WAS and AD sludge (site 33). The organic matter in the topsoil of site 33 (13%) adsorbed the metals in the soil and, although the clay content of the soil is low, the metals do not move deeper than 300mm down the soil profile (Figure 4.6.4).

Sites 34 and 35 received the same type of sludge with small differences in metal content (see Table 4.5b). The major difference between these sites are their clay content (3% and 22% respectively) and pH(H_2O) levels. Site 35 with its higher clay content adsorbed most of the metals in the topsoil and render it immobile, thus have the highest metal concentration in the topsoil with a significant decrease with depth. The high metal contents in the top 200mm of soil are because the site is ploughed frequently. The metals at site 34 did not moved as far in the soil profile as was expected from a soil with only 3% clay. The organic

C content of the topsoil may have adsorbed some metals, but the main reason for the immobility is probably the high pH(H_2O) of the soil.

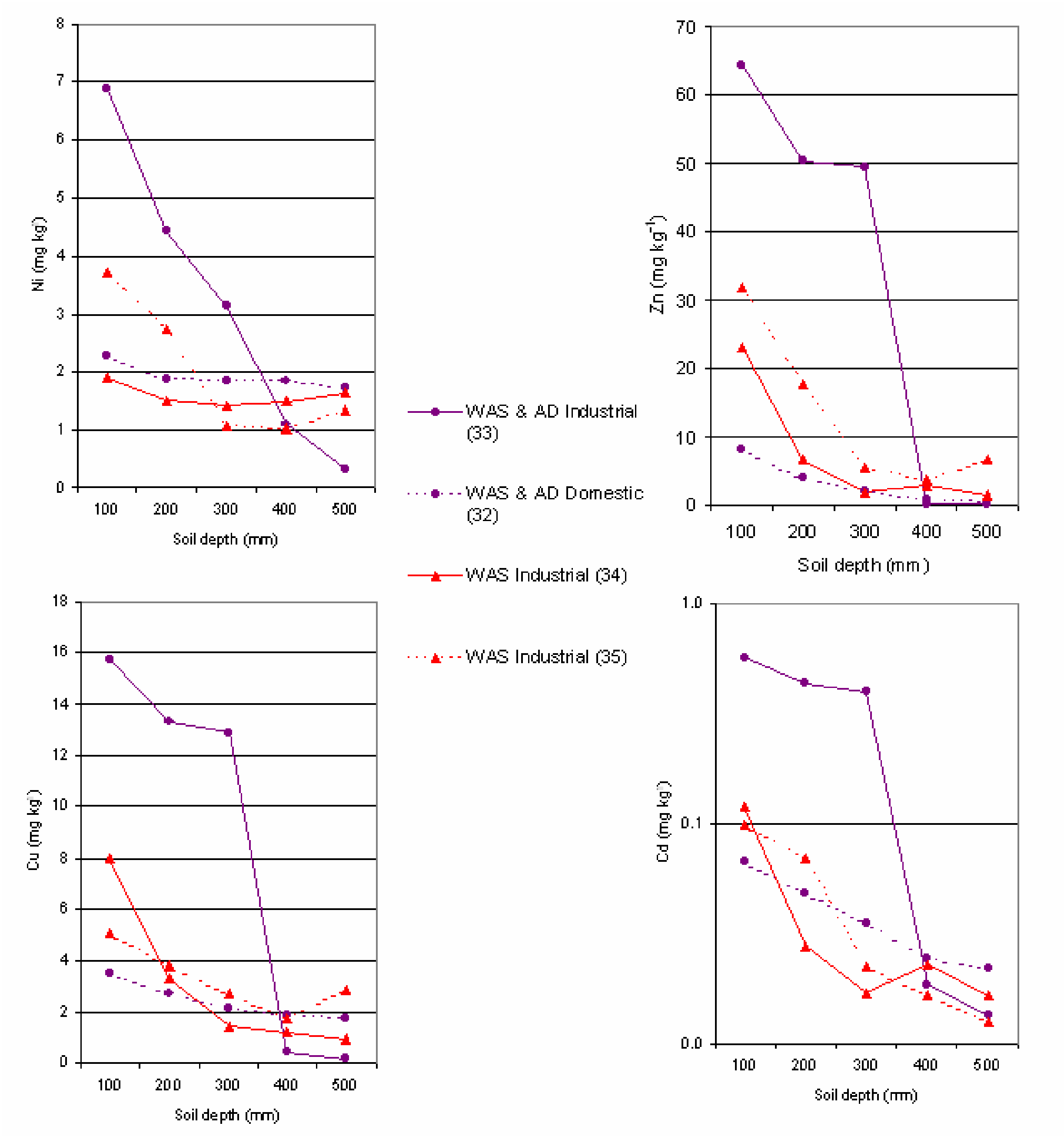


Figure 4.6.4: NH_4EDTA extractable Ni, Zn, Cu and Cd in the soil profiles of 4 selected irrigation sites (sites 32, 33, 34 and 35)

4.6.5 Flooded sites

Only two sites were sampled that dispose of sludge by flooding it onto the soil. the general information of the sites are in Table 4.6.5. The metals were mobile in the soil profile of site 37 with its very low pH(H_2O) and clay content. Another reason for the mobility of the metals at site 37 is that AD sludge is applied to soil with the metals in the liquor of the sludge. At site 36 the organic C in the topsoil adsorbed the metals little movement occurred (Figure 4.6.5).

Table 4.6.5: General information of 2 flooded sites

	Sludge type			**Origin**		**Metro area**	**Size (Ml/d)**	**Clay %**	**C %**	**pH (H_2O)**
	WAS	**AD**	**WAS & AD**	**Ind**	**Dom**					
Site 36		✓		✓		✓	10-25	18	3.04	5.1
Site 37			✓	✓			<10	12	1.82	4.4

4.6.6 Dried application sites

General information of the 3 sites with dried sludge application to land is presented in Table 4.6.6. All the sludge applied to the soil are from industrial origin but the metal content of the sludge at site 40 are much lower than that at site 39 (see Table 4.5b).

Table 4.6.6: General information of 3 dried application sites

	Sludge type			**Origin**		**Metro area**	**Size (Ml/d)**	**Clay %**	**C %**	**pH (H_2O)**
	WAS	**AD**	**WAS & AD**	**Ind**	**Dom**					
Site 38	✓			✓			10-25	16	3.27	5.4
Site 39			✓	✓		✓	25-80	11	7.75	4.4
Site 40	✓			✓		✓	<10	8	1.95	5.0

The mobility of the metals at all the sites was low. The metals are adsorbed in the topsoil by the organic C and rendered immobile although the clay content and

$pH(H_2O)$ of the soil are low (Figure 4.6.6). Another reason for the low mobility is that dewatered sludge is added to the soil.

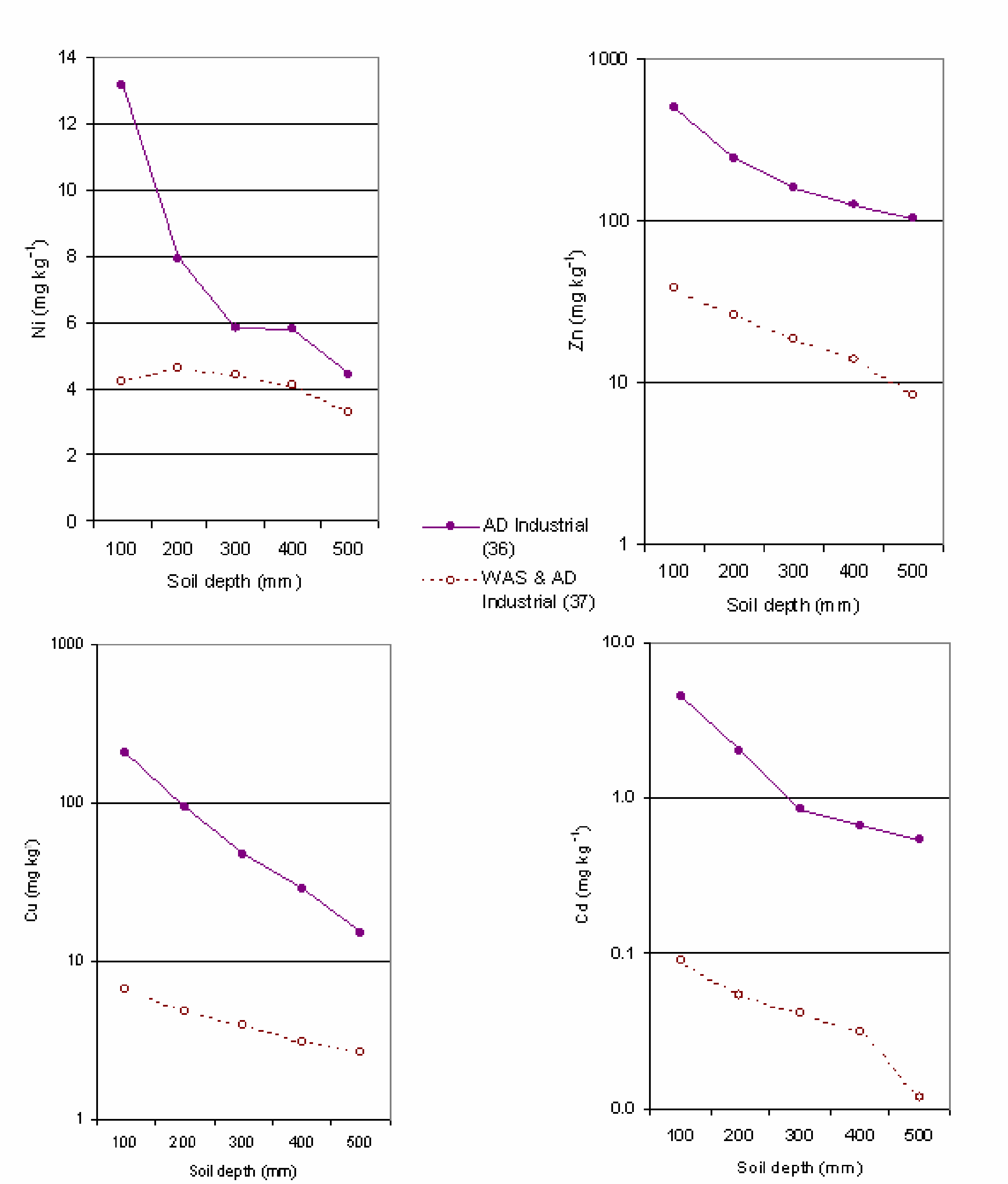


Figure 4.6.5: NH_4EDTA extractable Ni, Zn, Cu and Cd in the soil profiles of the flooded sites

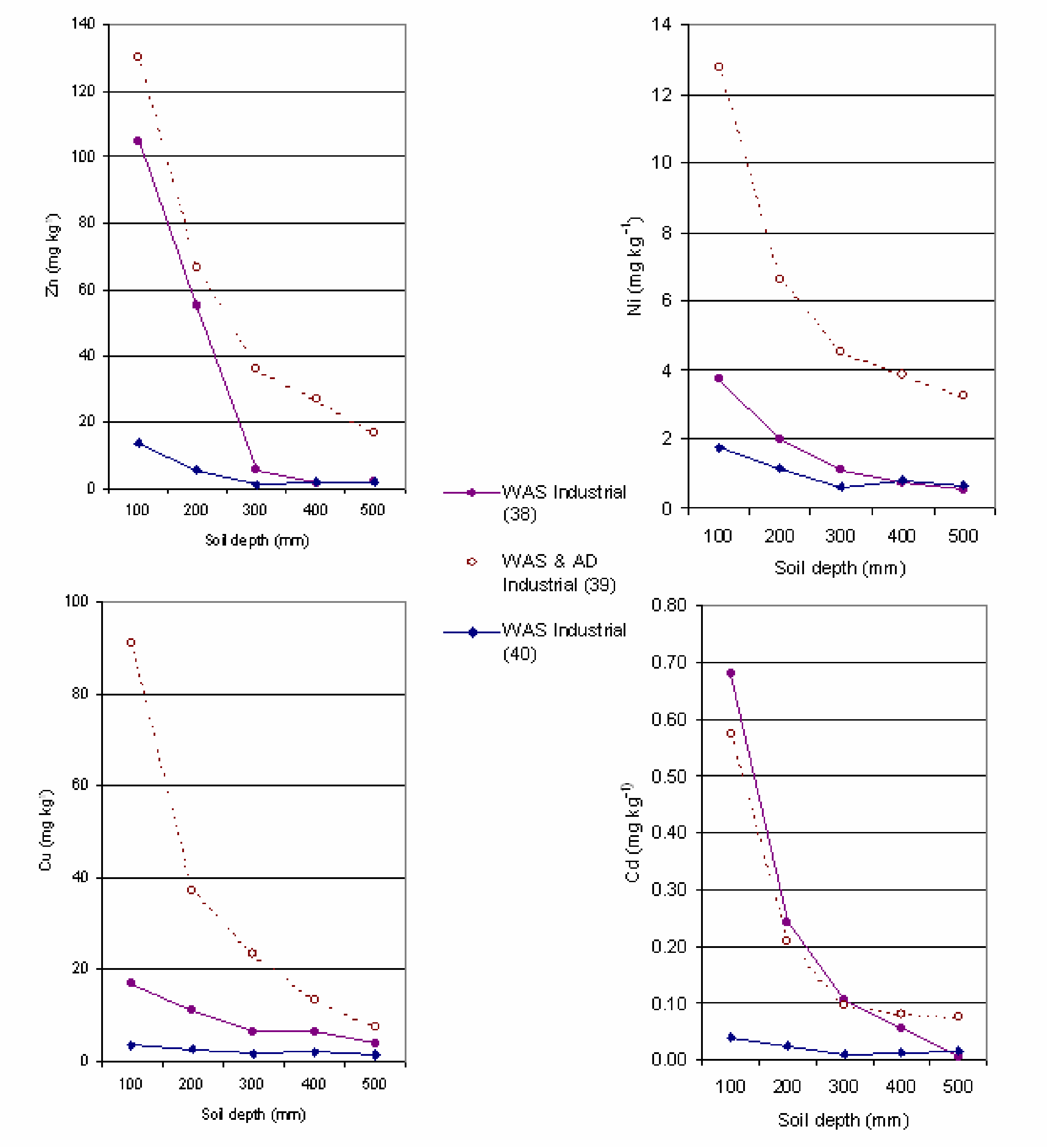


Figure 4.6.6: NH_4EDTA extractable Ni, Zn, Cu and Cd in the soil profiles of the dried application sites

4.6.7 Comparison between different types of disposal

The sites with the highest metal contents were selected for this comparison with Zn as the indicator metal (Figure 4.6.7). All these sites received sludge with high metal contents (see Table 4.5b). The Zn content was highest at the instant lawn

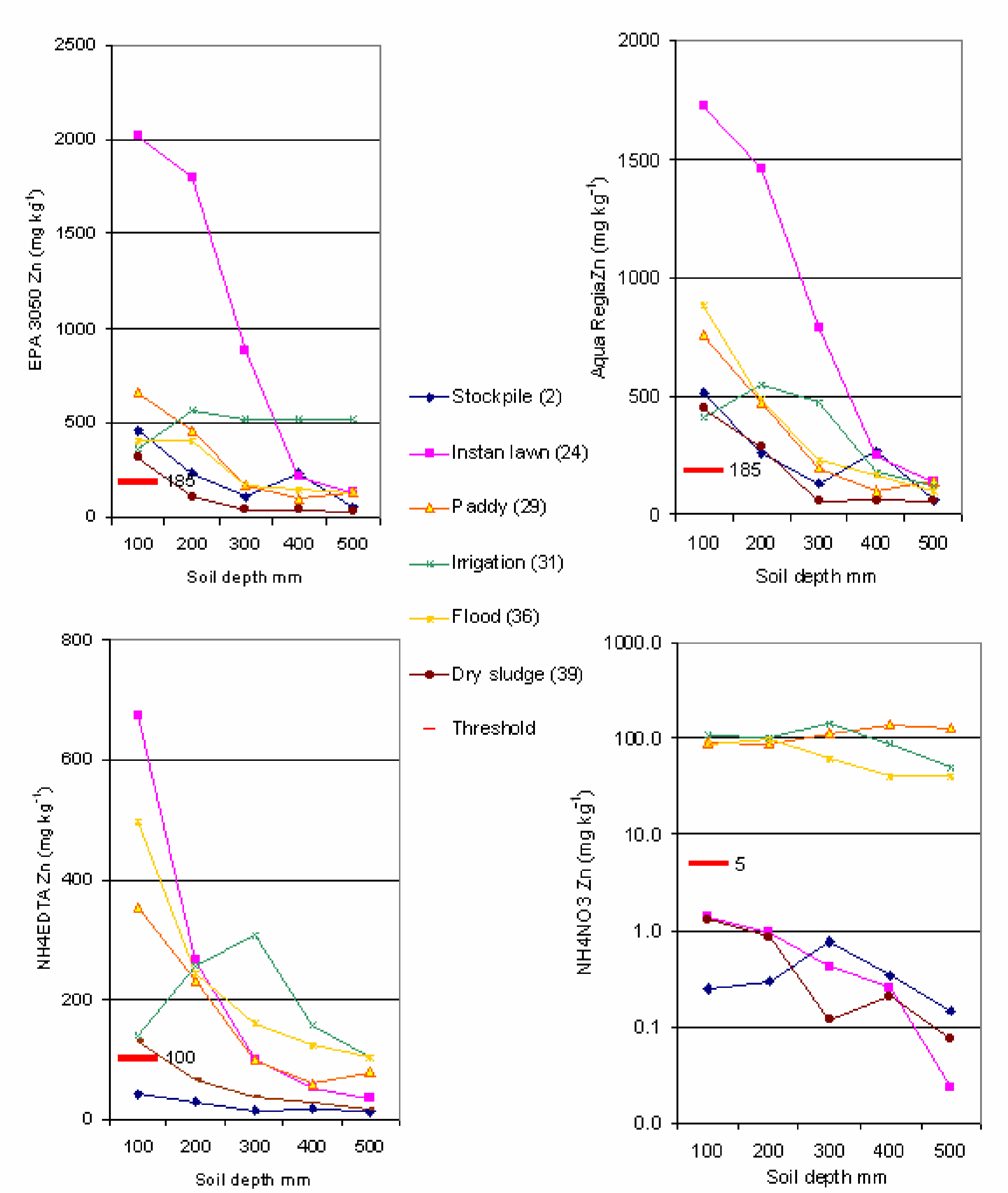


Figure 4.6.7: Zn concentrations with all analytical methods in the soil profiles of the most contaminated sites from each disposal method

site followed by the other sites that dispose of liquid sludge and the concentration decreased with depth in the soil profile. The metal concentrations in the soils of the sites that apply dewatered sludge to the soil were lowest. The *aqua regia*, EPA 3050 and NH_4EDTA analytical methods show similar distribution patterns of the Zn in the soil profile but the Zn distribution of the NH_4NO_3 analytical method was significantly different. The soluble Zn in the soils that received liquid sludge was much higher than those that received dewatered sludge, except at the instant lawn site. This may be because some of the Zn in the soil were taken up by the grass.

4.7 Groundwater samples

Groundwater samples could be obtained at only 9 of the selected 40 disposal sites. There were various reasons for this. At 5 sites there were boreholes but the pump were either out of order or stolen. At 3 sites the boreholes were dry and the rest (23 sites) did not have any boreholes. The metal concentrations of all the groundwater samples were lower than the DWAF guidelines (DWAF, 1996; Appendix B). Other elements (Ca, Mg, Na, K and Cl) were also lower than the guidelines. The only element that was higher than the DWAF (1997) guidelines was NO_3 (Figure 4.7).

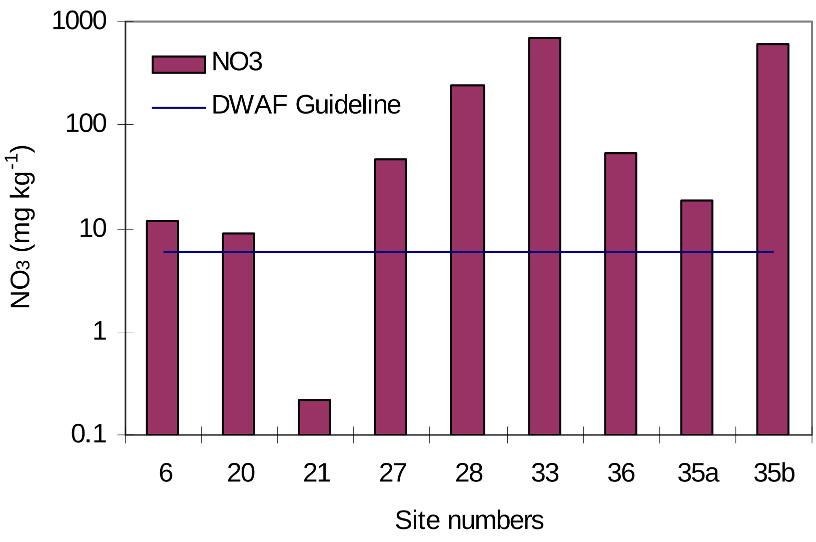


Figure 4.7: NO_3 contents of groundwater samples at 9 sites

From the data presented above it is clear that NO_3 leaching is a serious problem at most disposal sites and should be monitored carefully. It is also advised that nitrogen be included in new guidelines for MPL in South African soils.

4.8 General observations and concerns

Many of the disposal sites is situated on soils with <35% clay (37% of sites) and even <10% clay (17% of sites; Plate 4.8a) and the pH(H_2O) of the soils is generally <6. These soil properties indicate soils with a high probability for leaching. Given this information, only 9 of the studied disposal sites have a groundwater monitoring system in place. Of these 9 sites, 7 had NO_3 concentrations above the DWAF (1996) water quality guidelines. This is really reason for concern.

Most of the disposal sites are not fenced off and very near to populated areas. General access by the public occurs and in some cases the local people harvest edible plants that grow on the disposal sites. Some sites are also used for animal grazing (Plate 4.8b)

The majority of the disposal sites are on even terrain, but most of those that are on a slope have no erosion control measures in place even though they are near surface water bodies (Plate 4.8c). Surface water monitoring and erosion and run-off control measures at these sties are recommended.

Generally the larger cities and metropolitan councils were found to be knowledgeable in sludge management and legislative requirements but this was not the case in other towns. Many plant managers didn't really care where they put the sludge, as long as it is disposed of. No systems exist at most wastewater treatment facilities to manage the disposal of the sludge. At two wastewater treatment facilities raw sewage was disposed of on the disposal site (Plate 4.8d).

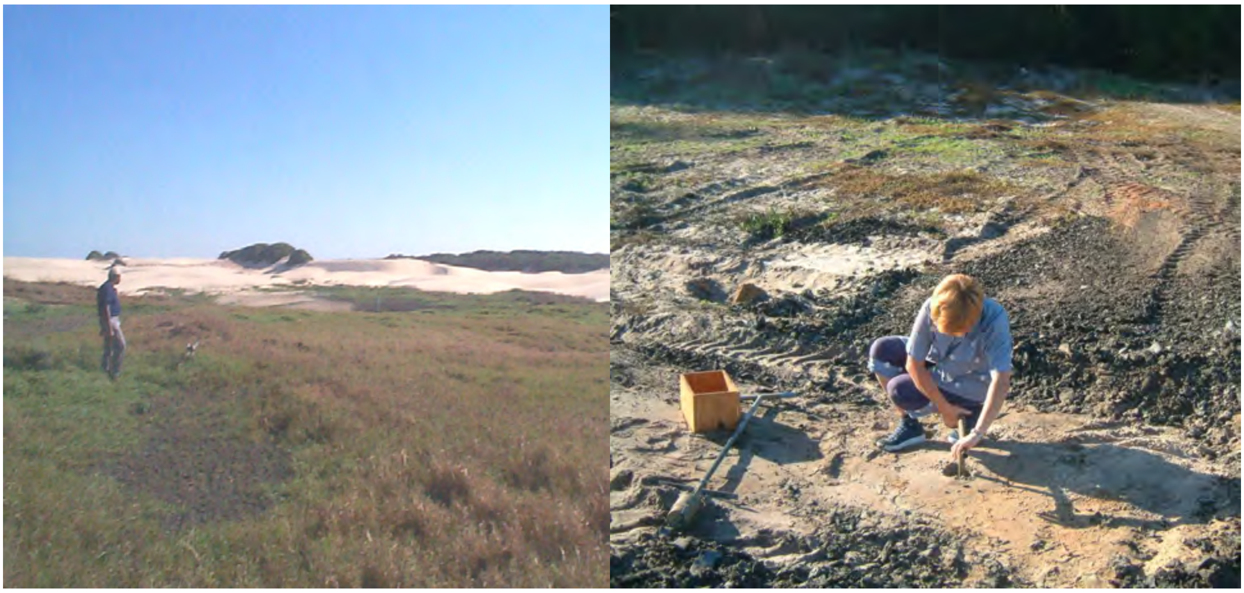


Figure 4.8a: Photographs of two sites situated on soils with low clay content (<5%).

Figure 4.8b: Photographs of two sites without fences, one very near a populated area and the other with cattle grazing on the disposal site

Figure 4.8c: Photograph of a site situated on a slope near a surface water body without any erosion and run-off control measures

Figure 4.8d: Photograph of a site with poor management practices (raw sewage is disposed on disposal site)

CHAPTER 5

MODELLING OF METAL MIGRATION IN SLUDGE-AMENDED SOILS

5.1 Description of the Modelling Problem

Included in the description of the modelling problem should be the following:

- the purpose of the modelling investigation
- the reference behaviour pattern that is to be modelled
- how to interpret results
- how to characterise uncertainty and variability
- scenarios to be modelled

5.1.1 The purpose of the modelling investigation

The situation to be modelled in the current study is as follows. A soil column consisting of a number of horizons experiences infiltration of water from above. The very top layer of the soil experiences mixture with solid sewage sludge, which contains heavy metals. The source of the heavy metals is natural depuration from humans, and resulting from co-disposal of industrial effluents with sewage, prior to treatment of the sewage.

The identity and concentration of the heavy metals depend on the locality of the sludge-amended soils. Water infiltrating from the top of the soil column may pick up heavy metals from the sludge, and may mobilise the metals through the soil column to groundwaters, thereby contaminating aquifers.

5.1.2 The reference behavior pattern that is to be modelled

In this case, the Reference Behaviour Pattern of the modelling problem is the known hydro-geochemistry of metals in various kinds of soils, with and without sludge amendment.

To this end, a literature survey was undertaken on the expected behaviour of a range of metals in soils. This literature survey is presented as a separate section.

5.1.3 How to interpret results

The results of the modelling exercises will take the form of projected concentration-vs-depth profiles as a function of time. The extent of movement of a metal along a depth profile would be considered prediction of mobility of the metal. The degree of mobility would be related to hazard of groundwater contamination.

5.1.4 How to characterize uncertainty and variability

Variability in ingress of water depends on periodicity, frequency, intensity and duration of rainfall events, and anthropogenic recharge events such as deliberate irrigation regimes.

5.1.5 Scenarios to be modelled

The scenarios with respect to fate-and-transport in sludge-amended soils fall into two categories - scenarios with respect to nature (chemical and hydrological) of influent water, and scenarios with respect to changing chemical characteristics of the soil as a result of the sewage amendment.

The infiltrating water may change pH to more acidic values due to impacts on atmospheric chemistry by industrialisation (“acid rain”). The salinity may increase in the case of irrigation with various waste-waters.

Microbial activity in sewage has been reported to significantly decrease the pH of pore waters. Chemical processes responsible for the acidification include the oxidation of ammonia and sulphide, with concomitant release of protons. If the soil has a significant carbonate composition, the pH may be buffered at high values for as long as the carbonate phase lasts.

5.2 Determination of the Reference Behavior Pattern

The parameter that metals are most sensitive to in normal soils with respect to changed mobility is pH (Allen *et al*., 1995).

As mentioned in the literature survey, sludge-amended soils are expected to tend towards the anoxic. Heavy metals bind to the CEC-determining components of anoxic soils in the following descending order (Ankley *et al*., 1994; Zhuang *et al*., 1994; Paterson *et al*., 1991):

- sulphide
- organic matter (particulate and dissolved humic substances) (especially Cu binding)

The following components may be present, but binding to them is negligible by comparison to that of the iron sulphide and organic matter (*ibid.*).

- hydrous metal oxides
- aluminium silicates
- clay minerals
- calcium carbonate

In normal (not sludge-amended) soils, the mobility of metals is known to be strongly pH-dependent. Model phases of metal precipitates and organically bound metal were used to corroborate the nature of metal species found in sewage sludge by a sequential chemical extraction scheme (Rudd *et al*., 1988). Model phase extractions supported the identification of the major species of Cd and Ni as carbonate (EDTA-extractable), Zn as organically bound ($Na_4P_2O_4$-extractable) and Pb as organically-bound or carbonate, although considerable overlap of fractions was apparent. Identification of the major species of Cu as sulphide (HNO_3-extractable) could not be confirmed. The selectivity and efficiency of certain reagents was found to differ when used in sequence with other reagents, as opposed to being applied individually to model metal phases. Sample preparation was found to influence metal fractionation profiles in a model organic phase. These conclusions are compared with those of previous workers in Table 5.2a.

Table 5.2a: Summary of speculations of metal solid phases in sludge-amended soils

Metal	**Predominant metal species**					
	Stover *et al*. (1976)	**Emmerich *et al*. (1982)**	**Legret *et al*. (1983)**	**Oake *et al*. (1984)**	**Lake *et al*. (1985)**	**Rudd *et al*. (1988)**
Cu	S	Org	Org	S	S	S
Cd	CO_3	CO_3	Oxid	CO_3	CO_3	CO_3
Ni	CO_3	CO_3	Org	CO_3	Exch/CO_3	CO_3
Pb	CO_3	-	Res	Org/CO_3	Org/CO_3	Org/CO_3
Zn	org	CO_3	oxid	org	org	Org

Sequential extractions were used on soils from a long-term experiment treated with either metal-contaminated sewage sludge or inorganic fertilizers between 1942 and 1961 (McGrath and Cegarra, 1992). The four extractants used were $CaCl_2$, NaOH, EDTA and aqua regia. These showed that large increases in the proportions of Pb, Cu, Zn, Ni and Cd in at least one of the first three fractions occurred during the first 10 years of sewage sludge additions. Cr always remained predominant in the aqua regia-soluble fraction.

For 30 years after this, including a period of more than 20 years after application of sludges to the field had ceased, there was very little change in the percentage of each metal extracted by each reagent. Although the 'residual' (aqua regia-soluble) and EDTA fractions usually contained the largest amount of metals in either sludge- or fertilizer-treated soils, there were clear differences between the metals: Pb represented the largest fraction of any metal extracted by $CaCl_2$. The same extractions were made of the sewage sludges that were applied to the field, and the distributions of the metals differed from those found in the treated soils. It was particularly apparent that more Pb and Cu was present as the 'residual' (aqua regia) fraction in sludges than in the soils.

These observations (summarised in Table 5.2b) were used in attempts to derive a reference behaviour pattern for modelling the behavior of metals in sludges in ths project.

Table 5.2b: Speculations of operationally defined metal solid phases in sludge-amended soils (McGrath & Cegarra, 1992)

Metal	**Predominant metal species**
Cr	Resid.
Cu	NaOH
Cd	EDTA > CaCl2
Ni	EDTA > CaCl2
Pb	EDTA >>> CaCl2, NaOH
Zn	EDTA > CaCl2

The complexes formed between either Cd(II) or Pb(II) and fulvic acids extracted from sewage sludge mixtures were investigated by potentiometric titration of K/H fulvate (Sposito *et al*., 1981). Formation functions were calculated from the titration data and analysed by Scatchard plots. The results were similar to those obtained previously for sludge-fulvic acid complexes of Ca(II) and Cu(II) in that two classes of complex were found for both Cd(I)) and Pb(II).

The common logarithms of the measured conditional stability constants for the two types of complexes with sludge-derived fulvic acid were hypothesised to be linearly correlated with the Misono softness parameter, which is a quantitative measure of the tendency to covalent bonding on the part of the metal cations. The resulting linear correlation equations had r^2-values greater than 0.99 and, therefore, were used to predict conditional stability constants of complexes of sludge-derived fulvic acid with Mg(II), Mn(II), Fe(II), Ni(II) and Zn(II), which cannot be investigated by the method of potentiometric titration. The conditional stability constants are presented in Table 5.2c.

Table 5.2c: Conditional stability constants for metals bound to sewage-amended soils (Sposito *et al*., 1981).

Metal Cation	**LogK(Site1)**	**LogK(Site2)**
Mg	2.71	0.69
Ca	3.12	1.23
Mn	3.93	2.23
Fe	3.96	2.28
Ni	3.81	2.08
Cu	3.88	2.11
Zn	3.54	1.74
Cd	3.04	2.27
Pb	4.22	2.62

Chemical models of trace metal complexation by fulvic acid extracted from sewage sludge were incorporated into the computer program GEOCHEM and were compared in illustrative speciation calculations (Sposito *et al*., 1982). The calculations were performed for 21 saturation extracts obtained from three acid soils that had been amended with sewage sludge. The Mixture Model consisted of a set of nine organic acids whose metal complexing functional groups were expected to simulate closely the distribution and complexation behaviour of the groups in the ligands of the fulvic acid fraction of sewage sludge. The Fulvate Model comprised 18 metal-fulvic acid complexes whose stability constants had been either measured in the laboratory or estimated by linear correlation analysis. The two models were in general accord on the overall speciation of Cd(II), and were found to be in good agreement with measured values in the extracts obtained with a Cd electrode. The results indicated that the Mixture Model could be used in conjunction with computer estimates of Cd(II) speciation in soil solutions, but should not be applied to help speciate metals, such as Cu(II), which are expected to form strong fulvic acid complexes, but evidently do not. The organic acids in the Mixture Model are in Table 5.2d.

Table 5.2d: The organic acids in the Mixture Model of Sposito *et al*. (1982), with their acidity constants.

Organic acid	**pKa's**
Arginine	9.7, 2.3
Benzenesulfonic	~3.7
Citric	6.4, 4.8, 3.1
Lysine	11, 8.5, 2.5
Maleic	6.1, 1.9
Ornithine	10.7, 9.0, 1.6
Phthalic	5.4, 2.9
Salicylic	13, 2.9
Valine	9.6, 2.3

Some characteristics of the binding of the ions Ca(II), Mg(II), Cu(II), Co(II), Ni(II), Zn(II), Mn(II), Pb(II), and Fe(II) on the soluble organic matter in a digested sewage sludge were determined using ion-selective electrodes (Fletcher and Beckett, 1987b). This work builds on the foundation laid in thermodynamic investigations of Cu(II) bound to sludge extracts (Fletcher and Beckett, 1987a). Results showed that ion exchange with protons is a principal component in metal binding and that copper and lead can replace more protons from the soluble organic matter than can the other ions.

It appeared that the soluble organic matter contained two distinguishable groups of exchange sites. One group of sites was capable of binding all of the above ions plus protons, whereas the second set could bind Cu(II), Pb(II) and protons only. A numerical description of their uptake characteristics, based on two set of ion exchange constants for each element, was able to predict the measured values of cation activity to within about 10% in the pH range 5.7-7.0. This thermodynamic data was in reasonable agreement with the general concepts of coordination chemistry and values for the proton displacement constants were derived (Table 5.2e).

Table 5.2e: Conditional constants for metals with sludge-amended soils (Fletcher and Beckett, 1987b).

Metal	**LogK**	
	Site 1	**Site 2**
Cu(II)	-8.084	-8.769
Pb(II)	-7.570	-8.377
Ca(II)	-9.552	
Mg(II)	-9.886	
Zn(II)	-9.065	
Ni(II)	-8.889	
Cd(II)	-8.642	
Co(II)	-9.240	
Mn(II)	-9.349	
Fe(III)	-13.500	
Fe(II)	-9.165	
Cu(I)	-4.149	
Density (mol/g)	6.38E-03	2.40E-03

The concentrations of calcium and magnesium in sewage sludge are high enough to compete so strongly with other metal ions that only copper, lead and cadmium will be bound significantly. Consequently, the model was simplified to predict the ion uptake behaviour of soluble organic matter, in the presence of high concentrations of calcium, using a limited set of analytical expressions (analogous to adsorption equations) rather than the complete set of equilibrium constants.

Electron spin resonance (ESR) spectroscopy was used to study the binding of Cu(II) by humic acid (HA) extracted from sewage sludge (Boyd *et al*., 1983). The ESR data were consistent with Cu^{2+} forming a chelate with two equatorial bonds with HA oxygen donor ligands. The copper ion also appeared to form axial bonds with HA donor ligands originating from proteinaceous materials associated with the sludge HA fraction. Characterisation of an adduct with glycylglycine shoes that the dipeptide formed coordinate bonds with Cu^{2+} bound to HA involving the terminal amino group and peptide carbonyl oxygen of glygly. This is consistent with an earlier study (Boyd *et al*., 1979), where IR techniques were used to demonstrate that metal ions were bound to proteinaceous materials present in sewage sludge.

In an ESR study by Senesi *et al*. (1985) on the binding of copper(II) with fulvic acids (FA) extracted from sewage sludge, it was found that at low copper binding, the copper was quadridentate, nearly square-planar with FA donor ligands. At "intermediate" ratios, mixed Cu-FA-H_2O complexes became more evident. Analysis of the ESR suggested the formation of inner-sphere, polydentate complexes, with Cu(II) coordinated equatorially by oxygenated and nitrogenated FA ligands, the binding sites involving both 4O and 2O, 2N ligand atoms, as well as a minor, more nitrogenated site (1O, 3N). A significant rearrangement of the Cu-FA systems was suggested to take place upon air-drying of the solutions.

Sequential extraction was utilized (Dudka and Chlopecka, 1990) for partitioning Cd, Cr, Ni, and Zn, in soil and sludge samples into the operationally defined fractions: exchangeable, bound to carbonates, bound to Fe and Mn-oxides, bound to organic matter and residual. The highest amounts of Cd, Ni and Zn, expressed as percent of the total, were found in the Fe-Mn oxide fraction of the sewage sludge.

Cr was significantly associated with the organic fraction of the sludge. The residue was the most abundant fraction for all metals studied in the untreated soil, and for Cd and Ni in the sludge-treated soil. The concentration of exchangeable Cd and Cr was relatively low in the untreated soil and did not change much after sludge application, whereas the concentrations of exchangeable Zn increased about 50 times and the concentrations of exchangeable Ni doubled in the sludge-treated soil. The assumption that mobility and biological availability are related to metal speciation was confirmed by the agreement between the distribution patterns of Cd, Cr, Ni and Zn in the solid, the uptake of the metals by plants, and their capacity for leaching out from the soils.

In an attempt to explain metal reactions in soils to which sewage sludges had been added, Keefer and Singh (1986) mixed two anaerobically digested municipal sludges (one pre-treated with chlorine), and one aerobically digested municipal sludge with soils at the rate of 300 metric tons per hectare, and incubated for one month. DMF extracts were prepared, and fractionated on nonpolar, non-ionic macroreticular and ion exchange resins into acidic, neutral and basic hydrophilic solute fractions and acidic, neutral an basic hydrophobic solute fractions and analysed for Cu, Cd, Cr, Ni, Pb and Zn. Soil properties most closely associated ($r > 0.73$) with Cd, Cr, Ni and Zn in the various fractions were pH and the amounts of illite, chlorite and fine clay.

The leachability of Cd, Ni and Zn was studied by Vasileios and Alloway (2002) in repacked 40 cm soil columns. The hypotheses tested were that DOC would influence the metal movement, and that this would be increased with water application rates. Sludge was placed at the top of the columns at rates of 0, 10 and 50 t/ha, and two water regimes were applied, equivalent to 450mm and 900mm per year. It was found that at 50 t/ha, the total concentrations of Cd and

Zn were significantly hither than the control down to a depth of 8 cm, while Ni moved to 10cm. In the leachates collected underneath the columns, soluble forms of Ni and Zn were found in significantly higher concentrations at 50 t/ha than in the control.

5.2.1 Regression and Correlation Studies

The results of the chemical and soil analyses of the first 20 sludged soil samples were subjected to correlation analysis by multiple regression (Table 5.2.1a). Maximum metal concentrations for most sites are in top 10cm of soil profile. Sites where deeper leaching has occurred are presented in Table 5.2.1b.

In order to fully explore the relationship between metal ion retention on sludged soil and soil properties, cross-correlations within soil properties were determined, to avoid confounding factors.

Table 5.2.1a: Pearson correlation coefficients within soil properties. Numbers in bold font are statistically significant.

	Org_ C %	**pH (H2O)**	**S Total %**	**N Total %**	**Clay %**	**Sand %**	**Silt %**
Org_ C %	1.00	-0.35	**0.57**	**0.95**	-0.18	-0.14	**0.58**
pH (H2O)	-0.35	1.00	-0.25	-0.30	0.22	-0.12	-0.17
S Total %	**0.57**	-0.25	1.00	0.49	0.39	**-0.63**	0.74
N Total %	**0.95**	-0.30	0.49	1.00	-0.21	-0.10	0.53
Clay %	-0.18	0.22	0.39	-0.21	1.00	-0.81	0.36
Sand %	-0.14	-0.12	**-0.63**	-0.10	-0.81	1.00	**-0.71**
Silt %	**0.58**	-0.17	**0.74**	0.53	0.36	**-0.71**	1.00

Table 5.2.1b: Depths to which maxima of metal plumes have traveled, as a function of interstitial water pH and organic matter concentration (%)

Site No.	**Depth**	**Mean pH**	**Mean %Corg**
4	10	5.793	1.43
8	10	4.903	0.85
10	10	5.217	1.67
11	10	4.632	0.57
15	10	5.510	0.85
17	10	5.053	0.19
27	10	6.696	0.89
30	10	4.176	0.81
34	10	7.278	0.60
37	10	4.415	2.67
38	10	4.718	2.32
42	10	4.631	2.77
3	20	4.608	0.74
16	20	7.487	1.12
24	20	3.827	3.36
28	20	4.459	1.28
43	30	4.646	0.69
31	40	7.403	0.54
39	40	5.403	0.74
45	40	5.110	1.53
29	50	5.960	1.08

The above table indicates that organic carbon is very strongly correlated with nitrogen concentration, implying a pertinacious origin for the organic matter. A weaker correlation of organic matter with sulphur content may hint at cysteine residues, or at active biological processes fixing sulphide from sulphate by utilizing the carbon.

The weak correlation between organic carbon and silt fractions may indicate that low-molecular weight organic carbon molecules are adsorbing to the high surface area of the silt fraction. Correlations were then determined between concentrations of metals extracted, and soil properties, so as to form hypotheses of the phase of the sludge/soil system that may have been retaining the metals (Table 5.2.1c).

For the purposes of understanding the chemistry of binding of metals to sewage sludge, the extraction data were initially grouped into two sets:

- those metal concentrations corresponding to hypothesized “weak” binding sites, i.e. those from which the metals were extracted by a solution of NH_4NO_3 (1.0 mol dm^{-3}).
- those metal concentrations corresponding to hypothesized “strong” binding sites, i.e. those from which the metals were *only* extracted by a solution of Di-ammonium Ethylenediaminetetraacetic Acid ($H_2(NH_4)_2EDTA$) (0.2 mol dm^{-3}). These metal concentrations would be determined by subtracting the NH_4NO_3 extraction results from the $H_2(NH_4)_2EDTA$ results.

Metals only extractable by the US Environmental Protection Agency method 3050 (EPA method 3050) acid digestion procedure are considered uninteresting, because not only does the procedure recover more than just the potentially bio-available fraction of trace elements from soil samples, but it also extracts firmly bound elements that will not become bioavailable in the near future.

This analysis was used in deriving the Reference Behaviour Pattern with respect to the sludge extracts (see paragraph 5.3).

Table 5.2.1c: Pearson correlation coefficients for soil properties with concentrations of metals extracted by different methods (significant correlations are presented in bold font)

Extraction method	Property	Cr	Co	Ni	Zn	Cu	Cd	Hg	Pb
EDTA	Org_ C %	**0.64**	-0.06	0.29	**0.56**	**0.68**	**0.66**	0.06	0.47
	pH (H2O)	-0.31	-0.13	-0.35	-0.37	-0.30	-0.38	-0.03	-0.11
	S Total %	0.33	0.24	0.43	**0.57**	0.33	**0.53**	0.30	0.16
	N Total %	0.63	-0.12	0.28	0.46	0.66	0.52	0.04	0.43
	Clay %	-0.22	0.24	-0.06	-0.14	-0.27	-0.07	0.36	-0.23
	Sand %	0.04	-0.16	-0.12	-0.17	0.04	-0.18	-0.31	0.09
	Silt %	0.25	0.04	0.31	**0.57**	0.34	0.54	0.20	0.16
EPA5050	Org_ C %	0.44	0.11	0.34	**0.88**	**0.64**	**0.69**	0.47	**0.74**
	pH (H2O)	-0.05	-0.07	-0.10	-0.40	-0.34	-0.35	-0.20	-0.27
	S Total %	0.52	0.52	**0.70**	0.51	**0.67**	**0.58**	0.12	0.34
	N Total %	0.41	0.02	0.29	0.88	0.55	0.59	0.52	0.71
	Clay %	0.32	0.52	0.45	-0.16	-0.06	-0.09	-0.18	-0.23
	Sand %	-0.50	-0.47	-0.63	-0.11	-0.30	-0.21	0.10	0.02
	Silt %	**0.63**	0.36	**0.72**	0.52	**0.68**	0.59	0.10	0.34
NH4NO3	Org_ C %	**0.67**	0.34	0.26	0.33	0.23	**0.59**	-0.03	**0.59**
	pH (H2O)	-0.31	-0.35	-0.44	-0.42	-0.20	-0.54	-0.11	-0.31
	S Total %	0.41	0.41	0.46	0.11	0.62	0.55	0.02	0.19
	N Total %	0.68	0.28	0.26	0.33	0.18	0.52	-0.03	0.59
	Clay %	-0.21	0.16	-0.08	-0.13	0.08	-0.03	-0.13	-0.23
	Sand %	-0.05	-0.22	-0.08	0.10	-0.34	-0.18	0.13	0.09
	Silt %	0.38	0.34	0.28	0.06	0.55	0.50	-0.16	0.19

5.3 Modelling Method - Operational Philosophy

The following steps are generic to modelling studies of the nature of the current investigation:

- Construction of the model with all available thermodynamic data.
- Calibration of the chemical model against previous modelling exercises in similar systems (interpolation within realm of experience).

- Modelling of the chemical system of interest (extrapolation beyond realm of experience).
- Validation of modelling results against field results.
- Adjustment of the chemical model to reproduce field results.
- Interpretation of field results in terms of model structure.
- Prediction of new field results.
- Generation of new field results

5.4 Model Selection

A literature study into the availability and application of chemical modelling software revealed that a number of choices of inexpensive and available software were available via the internet from US government sources such as the US Environmental Protection Agency (US EPA) and the US Geological Survey (USGS).

The principal modelling parameters, based on the literature, and based on the correlations observed in the previous chapter, were chosen to be pH and organic matter. The modelling software originally proposed for the task of determining the risk of pollution of aquifers due to sludge-amendment of soils was CHEMTARD. CHEMTARD is a program developed for use in risk assessments of nuclear facilities post-closure, and is approved by Her Majesties' Inspectorate of Pollution (HMIP UK) for use in this domain.

Subsequent to a detailed literature survey, it was established that the hydrogeochemical modelling code, PhreeqC, was superior to CHEMTARD, in a number of aspects (dealt with below). During the execution of the modelling phase of the current study, another promising modelling package became available, namely CHAIN2_D. CHAIN2_D is sufficiently demanding in data input and sophistication of user that it was resolved to push on with preliminary modelling using PhreeqC, and then to possibly use CHAIN2_D as a modelling tool when more experience in utilization of this software had been gained. Subsequently, it was revealed that CHAIN2_D cannot simulate competition for protons, and is thus not applicable in prediction of metal mobility. It was resolved thus to rather perform the hydrogeochemical hazard assessment calculations using PhreeqC, issue number 2.4.2.

The advantages of using PhreeqC are multiple. PhreeqC (in all its forms, e.g. PhreeqE, PhreeqM, HarPhreeqe, etc.) has been widely used, and thus the advantages and limitations to modelling with PhreeqC are recognised by many, resulting in a more sympathetic readership of scientific publications using the chemical package. Having been widely used by the groundwater fraternity, PhreeqC has been parameterised for use in many and various circumstances. More thermodynamic parameters have been published for use in PhreeqC than have been published for CHEMTARD.

In addition, PhreeqC sports (through the associated thermodynamic database, Wateq4f) a substantial embedded collection of data on the chemistry of hydrous ferric oxide (HFO), an important component of many soils. Both weak and strong HFO binding sites are represented and data exists for Ca, Sr, Ba, Cd, Cu, Zn and Pb as cationic species, and fluoride, phosphate, borate, carbonate and sulphate as anionic species.

PhreeqC has embedded algorithms for the simulation of solution equilibria, solution chemical kinetics, advective transport, diffusion, dispersion, cation exchange, surface complexation, and mineral equilibria. Included in the facility for advective transport is the ability to simulate transport in dual porosity media, such as a soil which may have channels through which infiltrating water advects, and blind pores that exchange solution constituents by diffusion.

The versatility with which data input for PhreeqC may be generated lends to simulation of multiple soil horizons, with multiple boundary options. PhreeqC does, however, not represent the detailed chemistry of a number of metal ions. The physical constants describing the behaviour of these ions are not embedded in PhreeqC, and have to be retrieved from other sources and input explicitly into calculation input files. Some, though, may view this as an advantage, in that addition of complex chemistry describing site-specific behaviour of metal ions is an explicit task, causing the mind to become more focussed. This would result in more explicit descriptions of the contexts under which the study using PhreeqC is published.

Another, more severe, disadvantage of PhreeqC is the fact that thermodynamic constants employed in PhreeqC are only reasonably accurate at low concentrations of metal ions. PhreeqC may be used to simulate reactions in seawater, but simulations in more concentrated NaCl solutions, and in solutions of similar concentration but with different ions are subject to greater scrutiny for inaccuracies.

5.5 Model Construction

The solution phase in the system of interest consists of the pore waters in the soil, and the infiltrating water. Reactions in the solution phase were generic enough to use the Wateq4f database that is packaged with PhreeqC.

The solid phase of the system consists of a number of compounds, of greater or lesser reactivity to metals. Soil components likely to influence the chemistry of infiltrated metals most are sulphides, carbonates, hydrous ferric oxides, and particulate organic matter. The thermodynamic constants of the reactions partitioning the metals between solution and sludge phase were taken from the "Fulvate Model" of Sposito *et al*. (1981b).

The problem to be modelled consists of solution flowing from above, around solid soil components of heterogeneous size and chemical constitution. Thus, the flow is tortuous. The simplification is often made, to model a tortuous flow path as a linear advection, with the flow rate of the advection being related to the forward (or downward) velocity component of the average particle in the flow path. The tortuosity of the flow is modelled as dispersion of the infiltrating water, and diffusion of the infiltrating water into solution-filled pores in the receiving matrix.

In the current study, infiltration rate is not known for any of the sites of study, and a simplified model system was constructed consisting of 51 cells, one centimetre in length, making up the maximum 5m length of core that was extracted from sites in the associated field.

The initial state of the system was modelled as follows. The soil column has uniform chemical characteristics of solid components throughout. The pore waters in all cells of the column are identical in all but the uppermost cell. The uppermost cell of the column contains the metal of interest, which is in equilibrium with the solid adsorbing phases in the soil column.

Flow was considered to be continuous from above and unhindered below the column - i.e. there are no discontinuities in flow. Dispersion and diffusion was not modelled. If required, it is possible to model the solution of in the pores as “dead” zones in the flow path, i.e. impervious to advection, but interacting with the infiltrating advected water by means of dispersion and diffusion.

Advection rate is currently not known, and thus was expressed as displacement of pore volumes by plug flow, as opposed to in average velocity.

The porosity of the soils is currently not known, and thus a simple model is used in which advection as described above has the information about the porosity embedded.

5.6 Model Parameterization

5.6.1 Methods

Models were initially parameterised by inserting values of constants and representative concentrations of constituents of system components derived from the literature.

5.6.2 Solid phase

Thermodynamic data was located in publications dealing with the behaviour of soils. However, the bulk of the thermodynamic information results from studies on metal partitioning in sediments, as a result of the thrust to ensure protection of benthic fauna by the US EPA.

A number of thermodynamic constants have been derived for marine sediments, which would be similar to the more anoxic, wet soils. The adsorption models most used in the literature to describe soil and sediment metal partitioning are the Langmuir and Freundlich isotherms. Use of the Langmuir isotherms requires a guess at the maximum sorption capacity of the solid phase for immobilisation of the metals in question, the thermodynamic binding constant of the metal to the site on the solid surface, and the pH.

Kd's, or partition constants have also been determined for a number of compounds. These parameters are useful when modelling metal binding to environmental phases at low metal loading (when the Kd's are equivalent to the above isotherm binding constants).

5.6.2.1 Organic Carbon

Environmental organic carbon in solution can be categorised into humic acids and fulvic acids. Inspection of thermodynamic databases describing binding to the solution phase organic carbon reveals that metal binding strength is generally regarded as equivalent between humic and fulvic acids, i.e. both types of organic matter bind metals in a roughly equivalent way.

A number of Kd values have been determined for partitioning to solid (or particulate) organic carbon in sediments, and have been incorporated into US EPA legislation. Constants were found which described the binding of cadmium, copper and lead to organic carbon in this legislative context.

The restriction on the use of the Langmuir and Freundlich isotherms to a particular pH regime is unfortunate, since the pH may change during an infiltration event, requiring significant user intervention in the modelling process to ensure reasonable accuracy of predictions.

A more robust way of representing the binding of metals to solid surfaces is the use of the multisite surface-complexation method, which explicitly models the influence of pH through the competitive binding of the hydrogen ion to the metal-accepting surface. Fu and Allen (1992) published a multisite model of Cd binding to soil organic matter. The model chosen here to represent the sludge/soil system was the Fulvate model, specifically derived for the sludge/soil system by Sposito *et al*. (1981b).

5.6.2.2 Sulphide

Sulphide is by far the strongest binding agent as far as toxic heavy metals is concerned. The US EPA published sediment quality criteria in which the relative proportions of sulphide and toxic metals are of critical importance. Soil sulphur, particularly that of sludge-amended soil, may exist in many forms, although it is probably safe to identify the sulphur content of anoxic, carbon rich soils with sulphide content. Were it possible to determine the redox status of the pore waters of soils, the probability of sulphur existing exclusively as sulphide may be more rationally determined. The binding constants of cadmium, copper, nickel, lead and zinc with sulphides have been published in the US EPA sediment quality criteria.

5.6.2.3 Hydrous Ferric Oxides (HFO)

Hydrous Ferric Oxides (HFO's) are a strong contributor to the binding of metals in oxic soils. A highly detailed investigation into the binding of cations and anions by HFO was published by Dzombak and Morel (1990). This compilation of thermodynamic constants is embedded in the Wateq4f database. The Wateq4f database is the one used in the current modelling study.

5.6.3 Liquid phase

The liquid phases of the system consist of the initial pore water, and the recharge water.

5.6.3.1 Initial Pore water

The pH of the pore waters has been characterised empirically in the current study. However, the remainder of the chemical characteristics of the pore water will have to be assumed by reference to some model system.

5.6.3.1.1 Redox status

The redox status of the pore waters is an important determinant of the chemical behaviour, and thus the mobility of metals in the system of interest. Redox status of soil pore waters is difficult to measure in the field, and usually not measured in the lab.

A useful approximation of the redox status of soil pore waters may be determined by modelling the published behaviour of chromium in soils under various conditions. Chromium undergoes conversion from Cr(III) to Cr(VI) under environmental conditions, and the oxidation potential (Eh / mV) at which this conversion occurs is a function of pH. If the pH is known, and the dominant chromium species is known, one can infer in what zone of the Pourbaix diagram for Cr the system is. Thus, a guess at the redox status of the system is guided by measurement.

5.6.3.1.2 Sewage plant effluent

In the initial stages of the sewage-amended soil system, it may be assumed in some cases that the dominant contributor to the pore waters is sewage plant effluent entrained in the sludge which percolates throughout the soil column, either as a result of direct advection, in the case of a wet sludge application, or by mixing with rainwater, followed by advection, in the case of a relatively dry sludge application.

5.6.3.1.3 Peat water

In the case of an aged sewage-amended soil system, in which there has been a substantial contribution to the system of organic matter, the soil pore waters may resemble peat waters, a study of the chemical fractionation of which was published by Read and Hooker (1992).

5.6.3.2 Recharge water

Recharge water may be principally rain water, or irrigation water.

5.6.3.2.1 Redox status

The redox status of the infiltrating waters is an important determinant of the chemical behaviour, and thus the mobility of metals in the system of interest. Infiltrating water may be assumed to be in equilibrium with atmospheric oxygen. Redox status is characterised by the pH of the infiltrating water, and the oxygen / hydroxide coupled chemical reaction, the thermodynamic constants of which are embedded in the Wateq4f database.

5.6.3.2.2 Rain water

The chemical characteristics of rain water depend on the location. Inland, rain water is relatively dilute in salts. Near the coast, there can be a significant contribution of seawater to rain water, and near industrial centres, the rain water may contain a significant acidic component (acid rain). The chemical characteristics of these types of rain water may be estimated from publications of chemical analyses.

5.6.3.2.3 Irrigation water

The chemical characteristics of the irrigation water are highly site-dependent. A useful generalisation may be to use sewage plant effluent as a guess for the chemical characteristics of the irrigation water.

5.7 Model Calibration

There are three phases to model calibration, namely

- Reproduction of conceptual models
- Reproduction of previous modelling results in a similar environment
- Reproduction of previous field study results in a similar environment.

Initially, the model is to be calibrated against expected behaviour of metals in the soil environment.

5.7.1 Reproduction of conceptual models

5.7.1.1 Reproduction of known chemistry of the system

The properties of metals that are relevant in the current study are those that underlie the behaviour of transport or retention of a metal in a soil matrix, with aqueous solution advected through the soil matrix.

5.7.1.1.1 Solution Chemistry

Metals bind to compounds (called ligands) in solution to form complexes, which are entities more or less stable, depending on the energetics of binding. The higher the energy of binding of metals with ligands, the more stable the complex, and the more prevalent the metal will be in the condition of attachment to the ligand.

Thus, if the ligands in solution are sufficiently strongly binding of the metal, the metal would “prefer” to remain in solution form, as opposed to being adsorbed to a solid phase.

5.7.1.1.2 Retention mechanisms

Mechanisms whereby metals may be retained in the solid phase of the soil matrix include adsorption, precipitation, surface complex formation and occlusion. On a molecular level, it is difficult to distinguish between these processes, and they may be seen to be states in the continuum between metal in solution, and metal embedded in a solid.

Adsorption is seen to be the “sticking” of a metal ion to a surface. This is viewed as a weak, easily reversible condition. The metal ion is significantly hydrated, and still very similar to the metal ion in solution. If the energetics is favourable, the adsorbed metal ion sheds water molecules of hydration, and proceeds to bind to a site on the surface to which it was adsorbed. The binding of the metal is usually accompanied by the release from the surface site of a cation that was previously chemically bound. This process is referred to as surface complex formation.

If the bulk solid, the surface of which is involved in the surface complex formation is chemically identical to the adsorbed metal species, the process of immobilisation is called precipitation and the reverse process is called dissolution. If the bulk solid is of a different chemical form, and precipitation of this chemical form buries the “surface complexed” metal ion, the metal ion is considered to have been occluded in the adsorbent solid.

A form of occlusion that has been given a different name occurs when the occluding solid is hydrous ferric oxide (HFO). This process is referred to as coprecipitation. Coprecipitation with HFO is relatively fast by comparison with other occlusion processes, e.g. those involving precipitation of highly crystalline phases such as calcite.

5.7.1.1.3 Influence of biological activity

Microbial activity resulting in the degradation of organic matter in soil (particularly prevalent in sludge-amended soils) can have an effect on metal mobility by two mechanisms - pH adjustment and the release of strongly complexing ligands. As organic carbon, nitrogen and sulphur is oxidized by certain strains of bacteria, there is a concomitant release of hydrogen ions from the water that was split to yield the oxygen for the oxidation process. These hydrogen ions can successfully compete for metal binding sites on “inert” substrates, or can actively dissolve substrates such as HFO and carbonates, thereby releasing occluded metals.

As the bacteria chew up the complex humic materials in soils, they can release compounds with functional groups like phenols, catecholates and carboxylic acids. These water-soluble compounds may bind to the metals of interest. If the resulting complex is water soluble (as it often is), the result is that metals are stabilised in the solution phase and may be advected away from their site of temporary immobilisation.

A change in pH often results in a concomitant change in Eh, or redox potential in the soil system. This change of redox potential may stabilise one oxidation state of a metal over another, thus resulting in a metal ion with different solution chemistry or adsorbing properties than the one that was previously in the system.

5.7.1.2 Modelling Simulations

In preparation for the simulations, the literature was reviewed for hints on the most relevant initial simulations that might be performed.

The metal chosen for the initial simulations was cadmium, since the chemical speciation is relatively simple, being a d10 metal, and acting much like a p-block element. Cadmium represents a good average of chemical properties of the toxic metals focussed on in this study - it has a hardness between that of zinc and lead, it has an ionic size between that of zinc and lead, and a “medium” preference for binding to oxygen and nitrogen functional groups.

The substrate on which the cadmium is to be bound in the simulations is HFO, since it is reported by Dudka and Chlopeka (1990) that in sludge-treated soils, cadmium is mostly associated with the Fe-Mn oxide component of the soil, as opposed to e.g. chromium, which is associated with the organic fraction.

The surface site density of the HFO was calculated as follows: assuming a density of rock/soil to be 2.7 kg/l, then a 2% iron content of the sandy soil is equivalent to 3.4 mol/l Fe. Most diagenetic iron exists in the form of goethite and haematite, which are somewhat crystalline and have a low reactive site density. If 10% of the iron is in the form of HFO, this corresponds to 0.34 mol/l Fe. With an average of 0.2 surface sites per mole of iron (Dzombak and Morel, 1990), the number of moles of active sites per litre is 0.07. The gram formula weight of HFO averages at 89 g/mol, leading to a mass of 30g/l HFO, and the specific surface area is 600 m^2/g (Dzombak and Morel, 1990).

Three simulations were performed, each on a column of sand with HFO adsorbed to it, and corresponding broadly to the 'ingress water' scenarios so far identified as those most likely to impact the sludge-amended land.

The first cell of the column was polluted with chromium. The column was eluted with a dilute salt solution in one simulation, a dilute salt solution with dilute natural organic matter, represented here as humic materials, and a dilute salt solution with a dilute mineral acid (HCl = pH 3). The results of the simulations may be seen in the following figures.

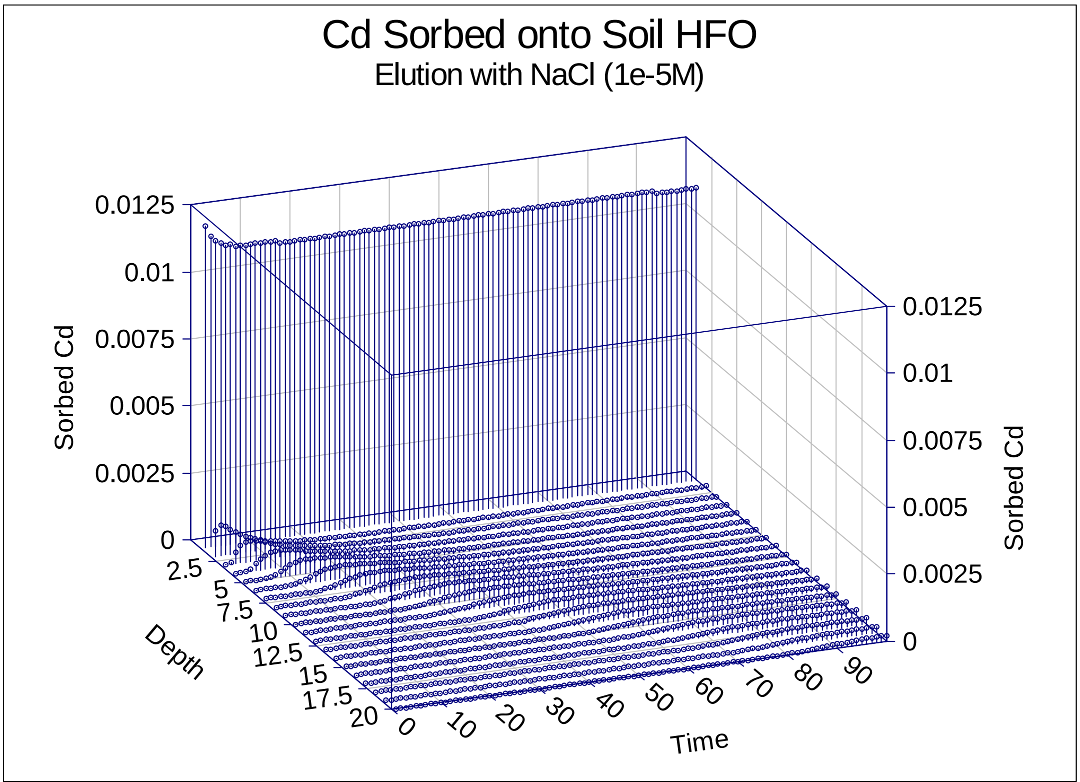


Figure 5.7.1.2a: Elution of a soil column of 20 cells depth by 100 pore volumes of a dilute salt solution. The soil consists mainly of sand, with hydrous ferric oxide adsorbed to it.

When the soil column is eluted with dilute salt solution (Figure 5.7.1.2a), the majority of the cadmium remains on the surface of the soil column. The cadmium that was initially in the pore waters, in equilibrium with the adsorbed cadmium, is transported along the column as a function of time. The distribution of the cadmium along the column is “smeared out” due to interaction of the mobilised cadmium with adsorbed HFO. The reason why the mobile cadmium does not permanently adsorb to the upper layers of the column is that the sodium concentration in the eluate is so high that the sodium competitively displaces adsorbed cadmium.

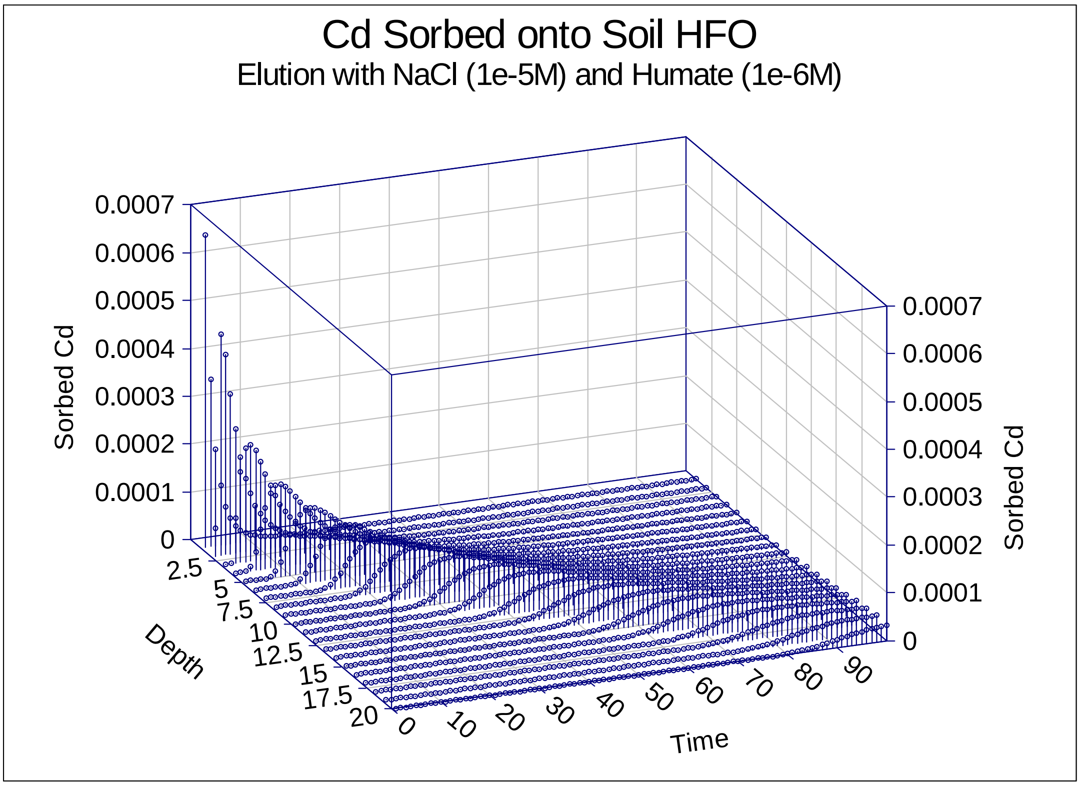


Figure 5.7.1.2b: Elution of a soil column of 20 cells depth by 100 pore volumes of a dilute salt solution containing a small concentration of humic acids (pH = 7). The soil consists mainly of sand, with hydrous ferric oxide adsorbed to it.

In Figure 5.7.1.2b, humic acid is seen to mobilise the initial pulse of cadmium along the column. The “smearing out” over many cells of the cadmium contained initially only in one cell indicates that at a concentration of 10-6M active sites in humate, the competition for cadmium between surface HFO and solution humate is strong enough for some Cd to remain behind on the surface phase after equilibrium with the solution phase.

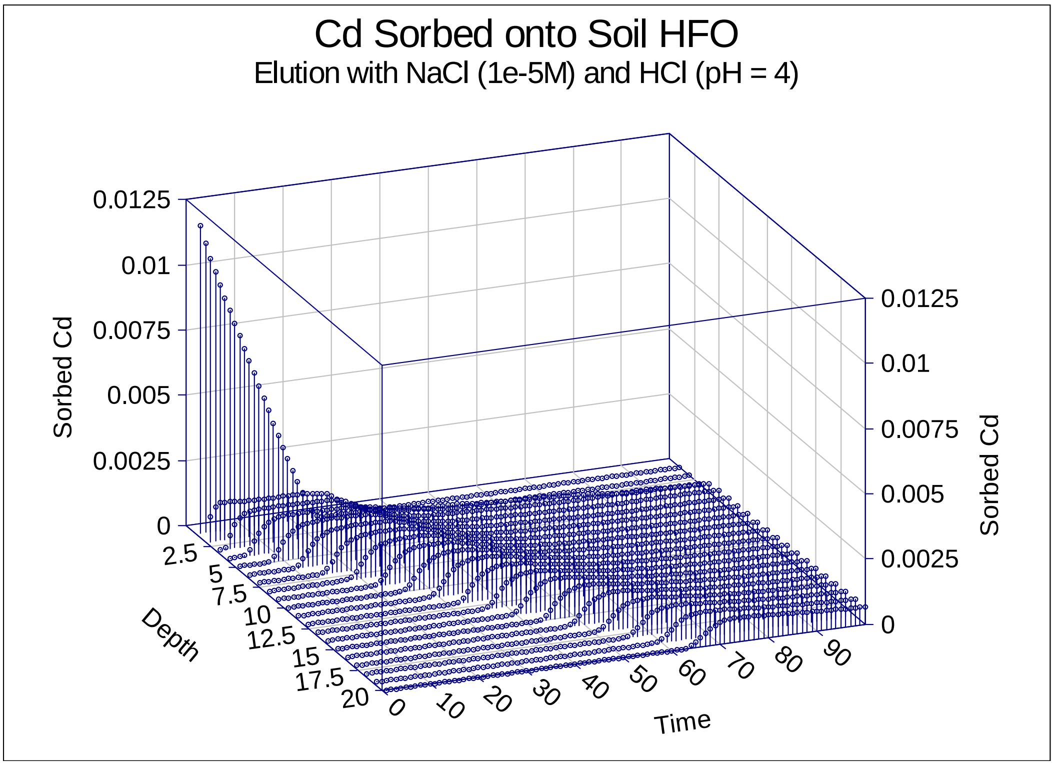


Figure 5.7.1.2c: Elution of a soil column of 20 cells depth by 100 pore volumes of a dilute salt solution containing dilute mineral acid (pH = 3). The soil consists mainly of sand, with hydrous ferric oxide adsorbed to it.

The dilute mineral acid at pH 3 is able to mobilise adsorbed cadmium (Figure 5.7.1.2c). The cadmium is very “smeared out” by the elution water, since the binding strengths of HFO to the hydrogen ion and cadmium are log K = -7.2 and -3.0, and at pH 3 there is as much free hydrogen ion as total cadmium in the first cell, giving the acid water a very slight edge in mobilising cadmium, but not enough to strip it totally off the column.

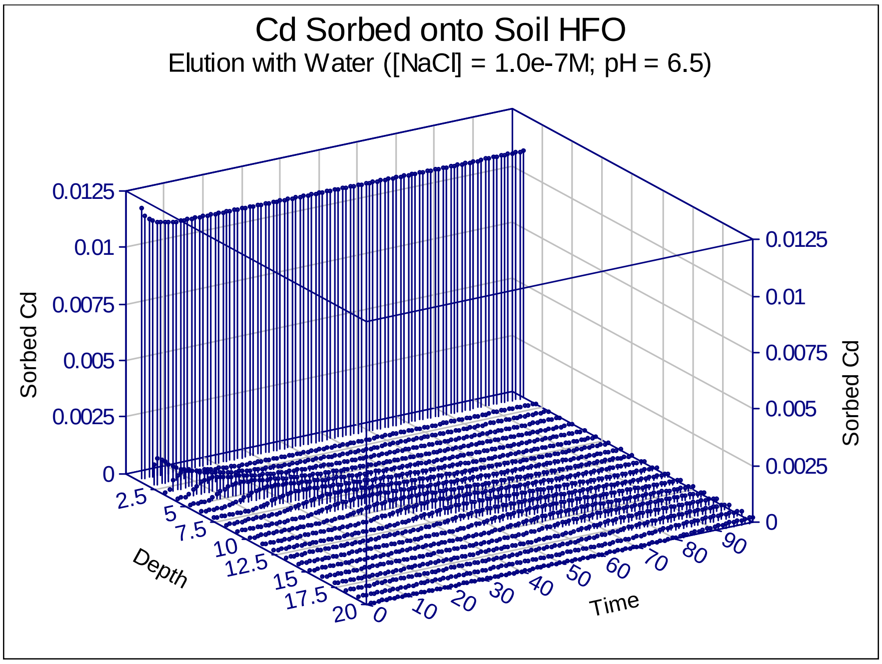


Figure 5.7.1.2d: Elution of a soil column of 20 cells depth by 100 pore volumes of a dilute salt solution at approximately neutral pH. The soil consists mainly of sand, with hydrous ferric oxide adsorbed to it.

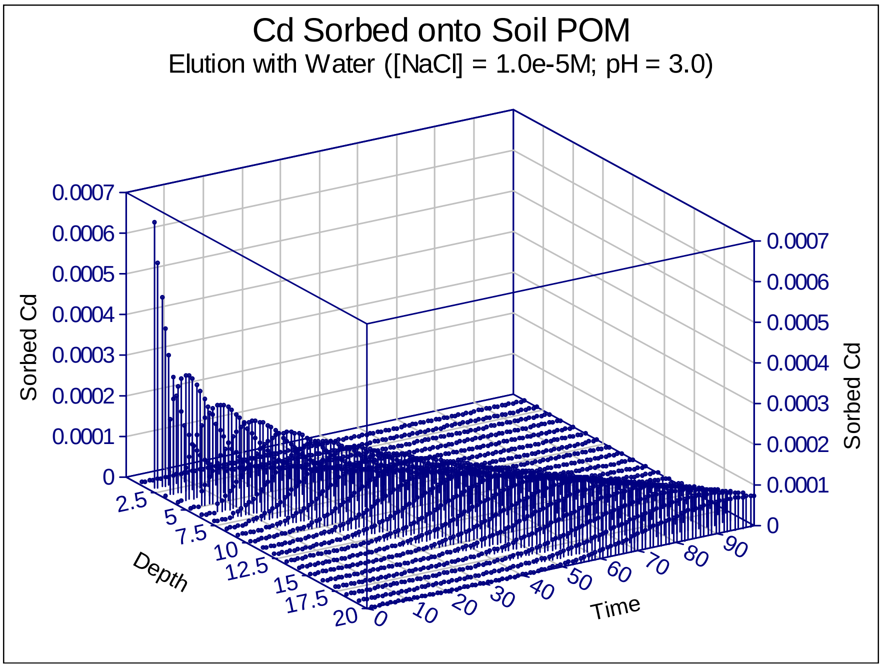


Figure 5.7.1.2e: Elution of a soil column of 20 cells depth by 100 pore volumes of a dilute salt solution at acidic pH. The soil consists mainly of sand, with particulate organic matter adsorbed to it.

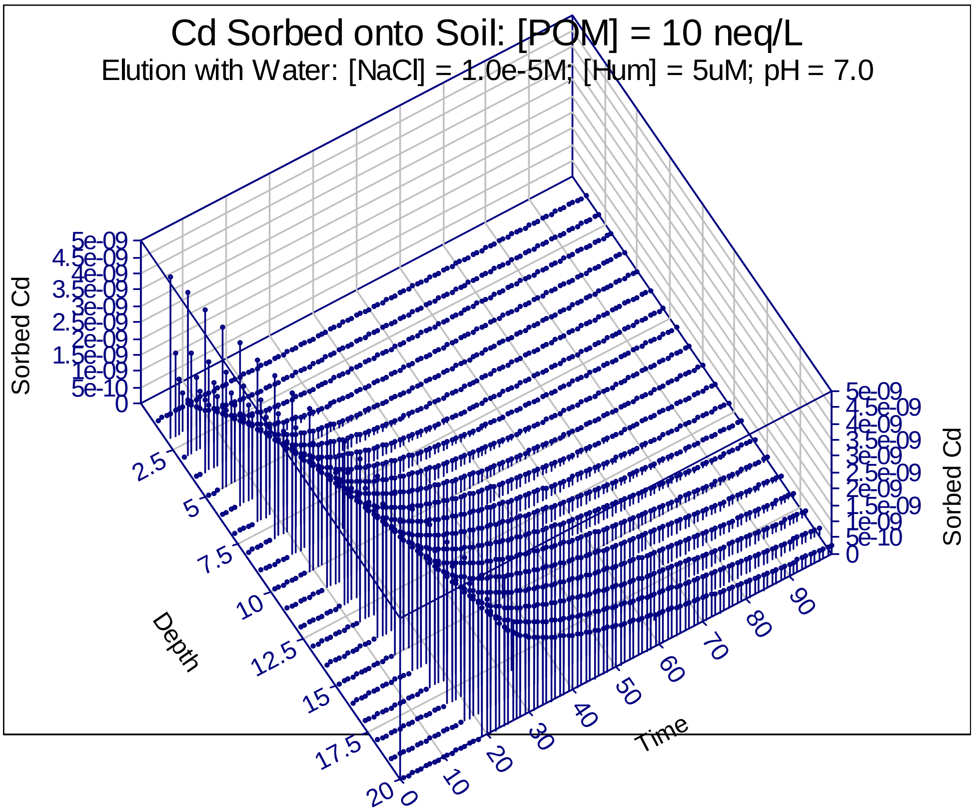


Figure 5.7.1.2f: Elution of a soil column of 20 cells depth by 100 pore volumes of a dilute salt solution at neutral pH, containing sludge-derived humic acid. The soil consists mainly of sand, with particulate organic matter adsorbed to it.

The calibration exercise resulting in the figure above is a simulation of a sandy soil, with the only organic matter in the system coming from the sludge itself. Over time, the ability of the system to retain the metal is eroded.

5.7.2 Reproduction of previous field study results in a similar environment

The field study of greatest relevance to the modelling exercise is the one that is presented in this report. It does look very much like cheating to use the "verification data" for calibration of the model. However, what is planned as a calibration exercise is the characterisation of the broad categories of "weak" and "strong" binding sites in the soils for the metals of interest. The "weak" sites will be the ones that are stripped of metals by ammonium nitrate solution (please see

Section: Model Verification). The "strong" sites will be the ones stripped only by EDTA solution.

Another field study of interest is the one of Sidle *et al*. (1977), in which soil adsorption characteristics were determined prior to sludge amendment. The mobility of the heavy metals in the soil column was measured and reported. It would be good to be able to explain the observations of these authors. It is perceived that they erred in not adjusting their soil adsorption characteristics for the influx of organic material from the sludge. Reproduction of their results by our model would provide justification for continuing to use our model in the study of the next 20 samples.

5.8 Model Verification

The results of the first field study are used to verify the predictions of the model. The mobilities of the metals in the soil are roughly measured as the extent to which the maximum of the metal "plume" has moved, i.e. the depth at which the maximum metal concentrations are measured. Due to the fact that we are dealing with sectioned cores, the mobilities are represented as ranges (in cm) in the following tables (Table 5.8a-c)

The tables represent the extraction of metals by the methods: extraction by NH_4EDTA, total metal extraction by the aggressive EPA 3050 method, and extraction by ammonium nitrate (NH_4NO_3) solution. The NH_4NO_3 method is expected to remove the metals "weakly" adsorbed to the soils, i.e. to surfaces such as clays and hydrous ferric oxides (HFO's). The NH_4EDTA extraction is expected to pluck metals from stronger binding sites, such as phenolic and carboxylic acid groups as well as from the same weak sites that the NH_4NO_3 method will yield.

Thus, the difference between the metal concentrations derived by the NH_4EDTA extraction method and the NH_4NO_3 method will yield the metals removed only during the NH_4EDTA extraction.
By similar reasoning, the difference between the metal concentrations derived by the EPA 3050 extraction method and the NH_4EDTA method will yield the metals removed only during the EPA 3050 extraction.

Of most relevance to the modelling exercises will be the metal concentrations derived from the NH_4NO_3 extraction method (weakly chemically bound), and those yielded as the difference between the metal concentrations derived by the NH_4EDTA extraction method and the NH_4NO_3 method (strongly, but reversibly chemically bound).

Table 5.8a-c above shows that the vast majority of the metals remained in the first ten centimetres of the soil. An important part in the model verification procedure was the reproduction of the laboratory extraction results. If we assume that overall the EDTA extractions removed the metals bound to strong sites, as well as those bound to weak sites, then the average soil being simulated will have the metal loadings and bulk characteristics presented in Table 5.8d.

Table 5.8a: NH_4EDTA extraction: Core depths (cm) at which maximum concentrations of metals were found

Site number	Cr	Co	Ni	Cu	Zn	Cd	Hg	Pb
6	~	~	~	~	~	~	~	~
8	~	~	~	~	~	~	~	~
9	0-10	10-20	30-40	10-20	10-20	10-20	~	10-20
10	0-10	30-40	0-10	0-10	0-10	0-10	~	0-10
12	30-40	0-10	0-10	0-10	0-10	0-10	0-10	0-10
15	~	30-40	20-30	0-10	0-10	0-10	0-10	0-10
19	~	~	~	~	~	~	~	~
20	0-10	30-40	0-10	0-10	0-10	0-10	0-10	0-10
21	~	0-10	0-10	0-10	0-10	0-10	0-10	0-10
22	0-10	30-40	10-20	0-10	0-10	0-10	0-10	0-10
23	0-10	10-20	30-40	0-10	20-30	20-30	20-30	20-30
26	~	0-10	30-40	0-10	30-40	30-40	~	30-40
27	0-10	30-40	0-10	0-10	0-10	0-10	~	0-10
29	0-10	40-50	0-10	0-10	0-10	0-10	0-10	0-10
30	0-10	20-30	20-30	0-10	0-10	0-10	0-10	0-10
31	10-20	20-30	20-30	10-20	20-30	20-30	20-30	20-30
35	0-10	10-20	0-10	0-10	0-10	0-10	~	0-10
36	10-20	0-10	0-10	0-10	0-10	0-10	0-10	0-10
38	~	30-40	0-10	0-10	0-10	0-10	0-10	0-10
39	~	~	~	~	~	~	~	~

Table 5.8b: EPA 3050 extraction: Core depths (cm) at which maximum concentrations of metals were found

Site Number	Cr	Co	Ni	Cu	Zn	Cd	Hg	Pb
6	~	~	~	~	~	~	~	~
8	~	~	~	~	~	~	~	~
9	10-20	10-20	10-20	10-20	10-20	10-20	~	10-20
10	0-10	0-10	0-10	0-10	0-10	0-10	0-10	0-10
12	0-10	0-10	0-10	0-10	0-10	~	~	0-10
15	0-10	0-10	0-10	0-10	0-10	0-10	0-10	0-10
19	~	~	~	~	~	~	~	~
20	0-10	0-10	0-10	0-10	0-10	0-10	0-10	0-10
21	0-10	0-10	0-10	0-10	0-10	0-10	0-10	0-10
22	0-10	0-10	0-10	0-10	0-10	0-10	0-10	0-10
23	20-30	20-30	~	20-30	20-30	20-30	20-30	20-30
26	30-40	30-40	30-40	30-40	30-40	30-40	30-40	30-40
27	0-10	0-10	0-10	0-10	0-10	0-10	~	0-10
29	0-10	0-10	0-10	0-10	0-10	0-10	0-10	0-10
30	0-10	0-10	0-10	0-10	0-10	0-10	0-10	0-10
31	20-30	20-30	20-30	20-30	20-30	20-30	20-30	20-30
35	0-10	0-10	0-10	0-10	0-10	0-10	~	0-10
36	0-10	0-10	0-10	0-10	0-10	0-10	0-10	0-10
38	0-10	0-10	0-10	0-10	0-10	0-10	~	0-10
39	~	~	~	~	~	~	~	~

Table 5.8c: NH_4NO_3 extraction: Core depths (cm) at which maximum concentrations of metals were found

Site Number	Cr	Co	Ni	Zn	Cu	Cd	Hg	Pb
6	~	~	~	~	~	~	~	~
8	~	~	~	~	~	~	~	~
9	10-20	10-20	10-20	10-20	10-20	10-20	10-20	10-20
10	0-10	0-10	0-10	0-10	0-10	0-10	0-10	0-10
12	~	0-10	0-10	0-10	0-10	0-10	~	~
15	0-10	0-10	0-10	0-10	0-10	0-10	0-10	0-10
19	~	~	~	~	~	~	~	~
20	0-10	0-10	0-10	0-10	0-10	0-10	0-10	0-10
21	0-10	0-10	0-10	0-10	0-10	0-10	0-10	~
22	0-10	0-10	0-10	0-10	0-10	0-10	0-10	0-10
23	~	20-30	20-30	20-30	20-30	20-30	20-30	20-30
26	~	30-40	30-40	30-40	30-40	30-40	~	30-40
27	0-10	0-10	0-10	0-10	0-10	0-10	0-10	0-10
29	0-10	0-10	0-10	0-10	0-10	0-10	0-10	0-10
30	~	0-10	0-10	0-10	0-10	0-10	0-10	0-10
31	20-30	20-30	20-30	20-30	20-30	20-30	20-30	20-30
35	0-10	0-10	0-10	0-10	0-10	0-10	0-10	0-10
36	0-10	0-10	0-10	0-10	0-10	0-10	0-10	0-10
38	0-10	0-10	0-10	0-10	0-10	0-10	0-10	0-10
39	~	~	~	~	~	~	~	~

Table 5.8d: Metal loadings and characteristics of the average soil to be simulated

Cr	Co	Ni	Zn	Cu	Cd	Hg	Pb
0.21	6.30	9.62	72.54	22.15	0.56	0.22	8.46
P	**Ca**	**K**	**Mg**	**Na**	**Tot N%**	**Tot S%**	**C %**
2569.74	1292.51	264.57	297.48	48.44	0.12	0.23	1.27
pH(H_2O)	**Clay %**	**Sand %**	**Silt %**				
5.26	21.50	58.09	18.78				

The initial calculation of cadmium with particulate organic matter at pH 7 exhibited an almost 100% loading of cadmium onto the organic fraction.

5.8.1 Batch Extraction with Ammonium Nitrate

NH_4NO_3 removes the percentages of metals presented in Table 5.8.1.

Table 5.8.1a: Percent available metal retained in sludge/soil after extraction with ammonium nitrate solution

Cr	**Co**	**Ni**	**Zn**	**Cu**	**Cd**	**Hg**	**Pb**
26%	15%	55%	27%	91%	40%	7%	1%

Cadmium is removed to 26% by ammonium in batch reaction, Pb is removed to 27% and Cu to 78% by ammonium in batch reaction. These modelling results represent a tradeoff of a number of unknowable entities, such as the acidity constants of the ligands in the sludge and the soil. The agreement of model with observation is therefore tolerable, given the uncertainties.

5.8.2 Batch Extraction with EDTA

All metals are completely stripped by NH_4EDTA solution (see Figure 5.8.2). The model is now constructed and calibrated with respect to the batch extraction studies.

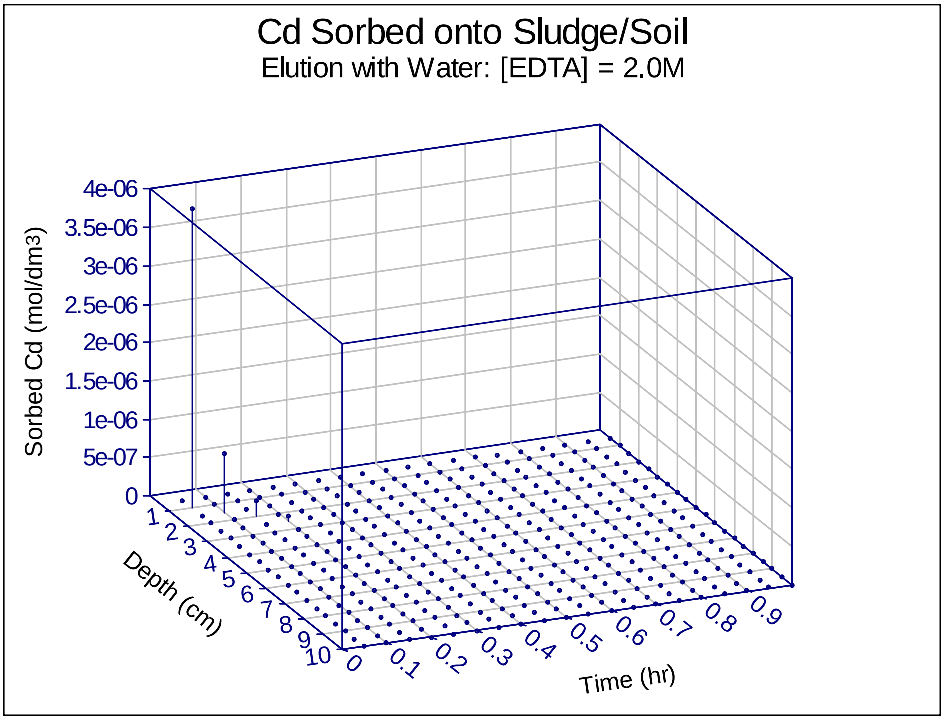


Figure 5.8.2: Elution of a soil column of 20 cells depth by 100 pore volumes of a diammonium EDTA solution. The soil consists mainly of sand, with particulate organic matter adsorbed to it.

5.9 Scenario Modelling

The thermodynamic “Fulvate Model” constants of Sposito *et al*. (1981b) were used to simulate the sludge chemical system. The average weight percent of organic carbon is 1.27% = 12.7 g/kg mixture. The density of exchange site type 1, defined by Fletcher and Beckett (1987b) is $6.38x10^{-3}$ mol/g C. If a calculation cell height is 5 mm, the area of the cell would be 2 cm^2, to make the cell volume one cubic centimetre. The column is 20 cells deep, making the entire column 10 cm deep (Table 5.9).

Table 5.9: Transport parameters for kinetic column model

Length of column	10 cm
Bulk density	1.5 kg/l
Porosity	0.3
Carbon	1.27%
Grams of solid per litre	5.00e3 g/l
Grams of Carbon per litre	63.5 g/l
Exchange Site density (mol/g)	6.38e-3 mol/g
Exchange Site concentration (eq/litre)	0.405
Pore water velocity	10 cm/hr

After 1 hour (20 shifts of 1/20 hours time steps), one pore volume has flushed through the column. After 5 hours (the length of the simulation), five pore volumes have flushed through the column.

The following scenarios modelled include leaching of sludge-amended soils containing cadmium, with soils containing hydrous ferric oxide, or particulate organic carbon as stationary phases.

5.9.1 Scenario 1: Elution of column with dilute salt solution

Once biological action has ceased to yield soluble organic ligands that may mobilise metals, it is hypothesised that the metals will remain immobile, even when contacted with dilute salt solution.

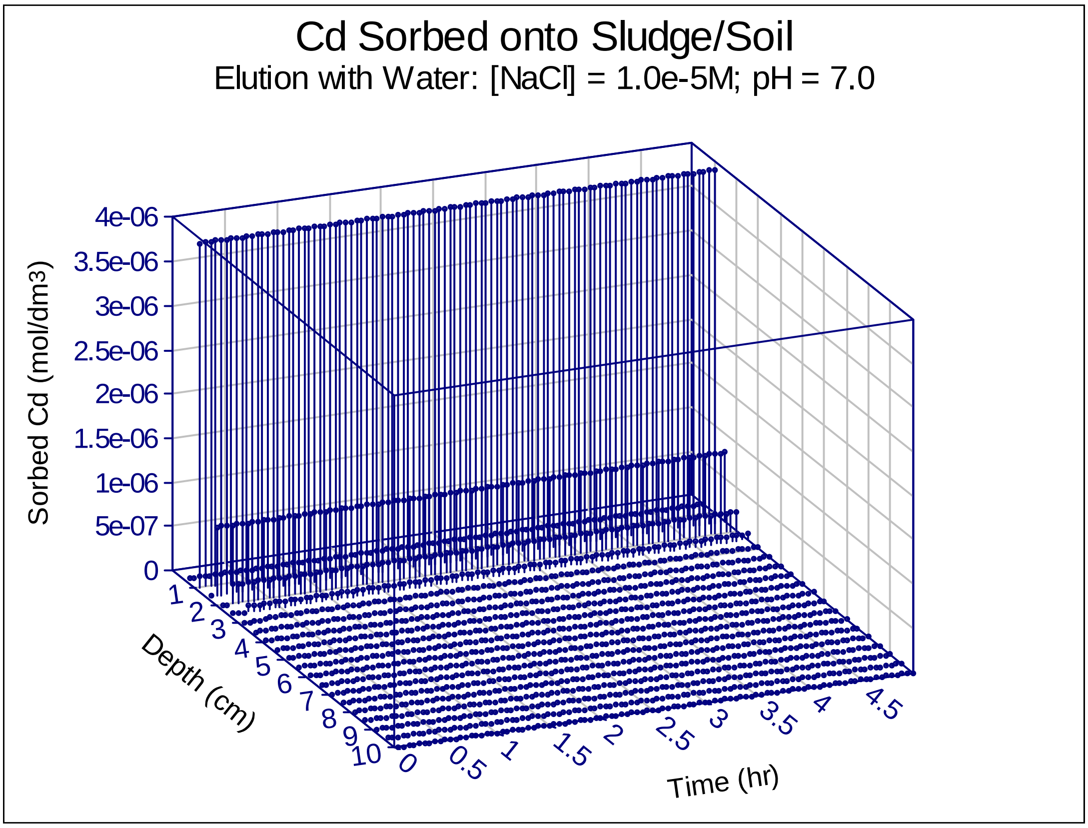


Figure 5.9.1: Elution of a soil column of 20 cells depth by 100 pore volumes of a dilute salt solution at neutral pH. The soil consists mainly of sand, with particulate organic matter adsorbed to it.

From the above figure, it may be seen that the cadmium concentration at the top of the sludge/soil column remains reasonably constant over time and space.

5.9.2 Scenario 2: Influx of acidic water

If even mildly acidic water were to contact the soil column, it is hypothesised that the metals will be mobilised. This could occur if the sludged soil were irrigated with acidic water, or if biological activity was such that carbon degradation yielded high concomitant acid production.

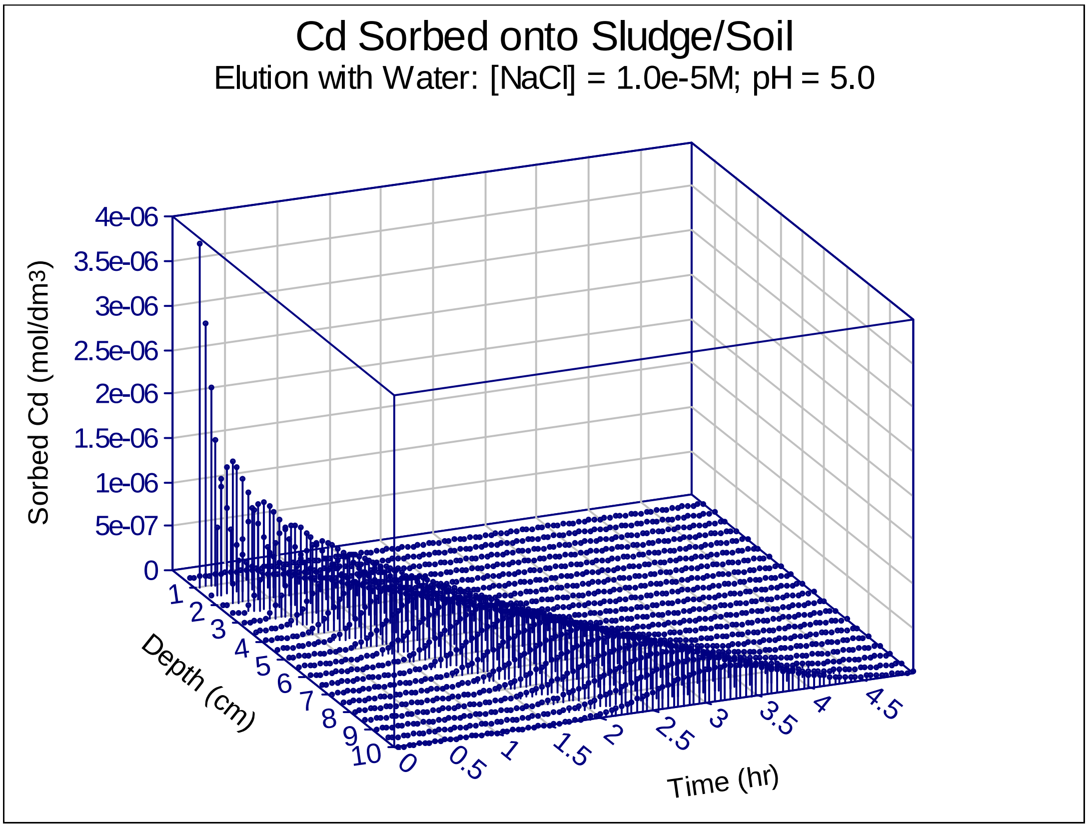


Figure 5.9.2a: Elution of a soil column of 20 cells depth by 100 pore volumes of a dilute acidic solution. The soil consists mainly of sand, with particulate organic matter adsorbed to it.

Reference to the figure above suggests that water at a pH of 5 is fully capable of mobilising cadmium from the sludge/soil matrix. Of interest is the question – is a pH of 6.5 adequate to immobilise metals? The following simulation adds information to the discussion.

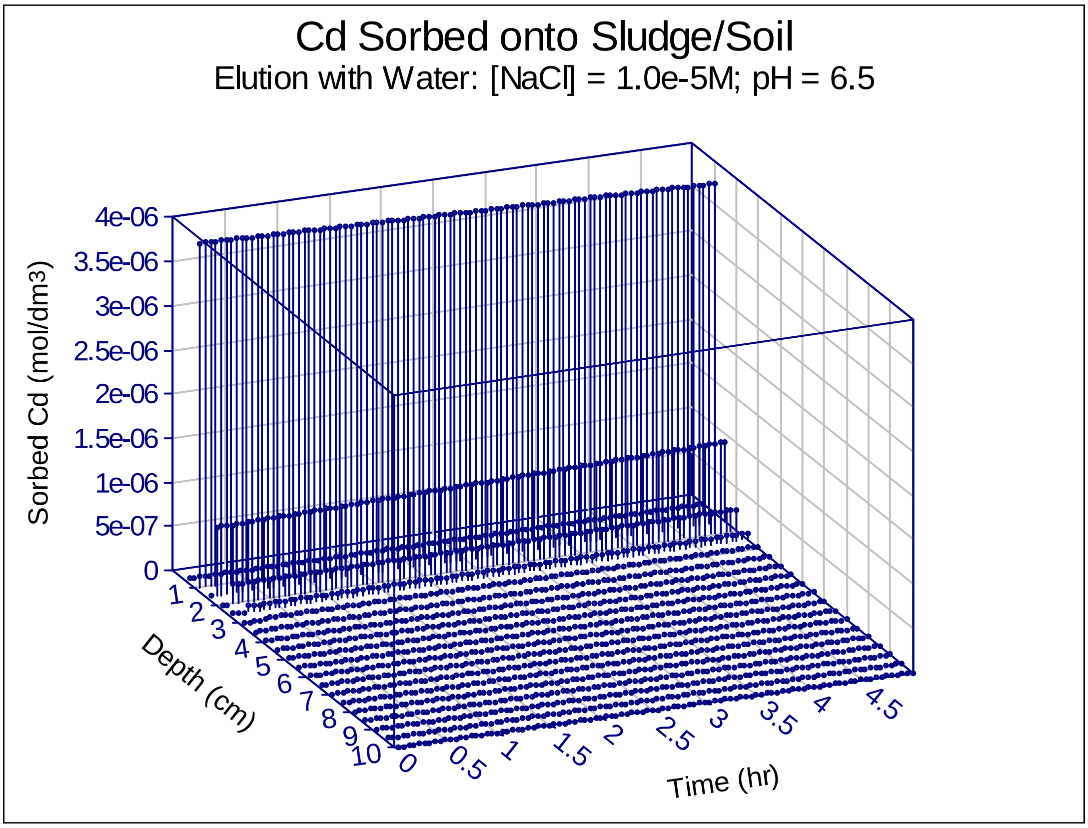


Figure 5.9.2b: Elution of a soil column of 20 cells depth by 100 pore volumes of a near-neutral solution. The soil consists mainly of sand, with particulate organic matter adsorbed to it.

The figure above suggests that a pH of 6.5 is NOT capable of leaching metal from the sludge/soil matrix. This is a comforting result, since many knowledgeable people believe that a pH of 6.5 is safe.

5.9.3 Scenario 3: The effect of maintaining the organic carbon content of the top layer

As naturally occurring, and sludge-organic carbon is microbially degraded, organic molecules of low molecular weight, with high solubility and metal-mobilising properties may be produced. The following simulation was performed to see if constant addition of organic matter is reasonably safe.

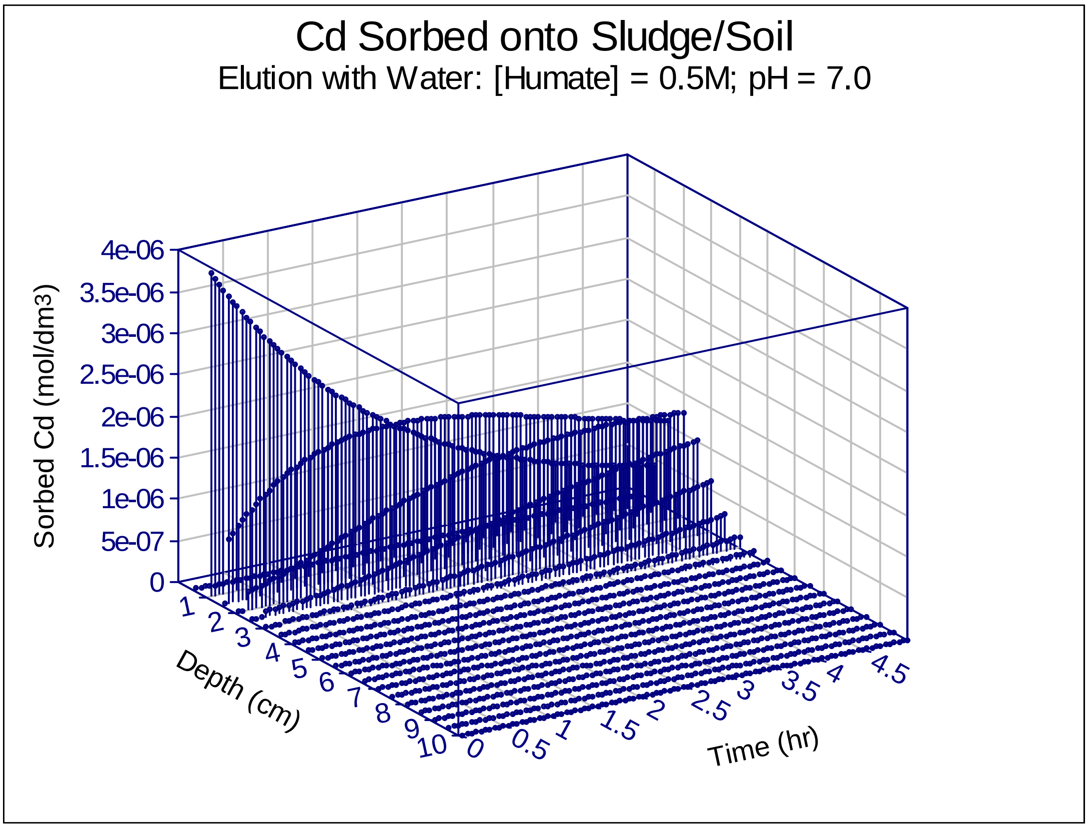


Figure 5.9.3: Elution of a soil column of 20 cells depth by 100 pore volumes of a solution in contact with decaying organic matter. The soil consists mainly of sand, with particulate organic matter adsorbed to it.

Reference to the figure above indicates that Fulvate Model predicts elution of metal from the sludge/soil matrix by natural organic matter. Thus, if carbon is added continuously to maintain low redox conditions, care must be taken to avoid the formation of soluble humic fractions by microbial decay.

5.9.4 Scenario 4: Effect of adding lime to maintain higher pH

The simulation proves that even at high pH, metals may be mobilised from sludge/soil matrices by the addition of a sufficient concentration of a competing metal ion, e.g. calcium in lime (Figure 5.9.4).

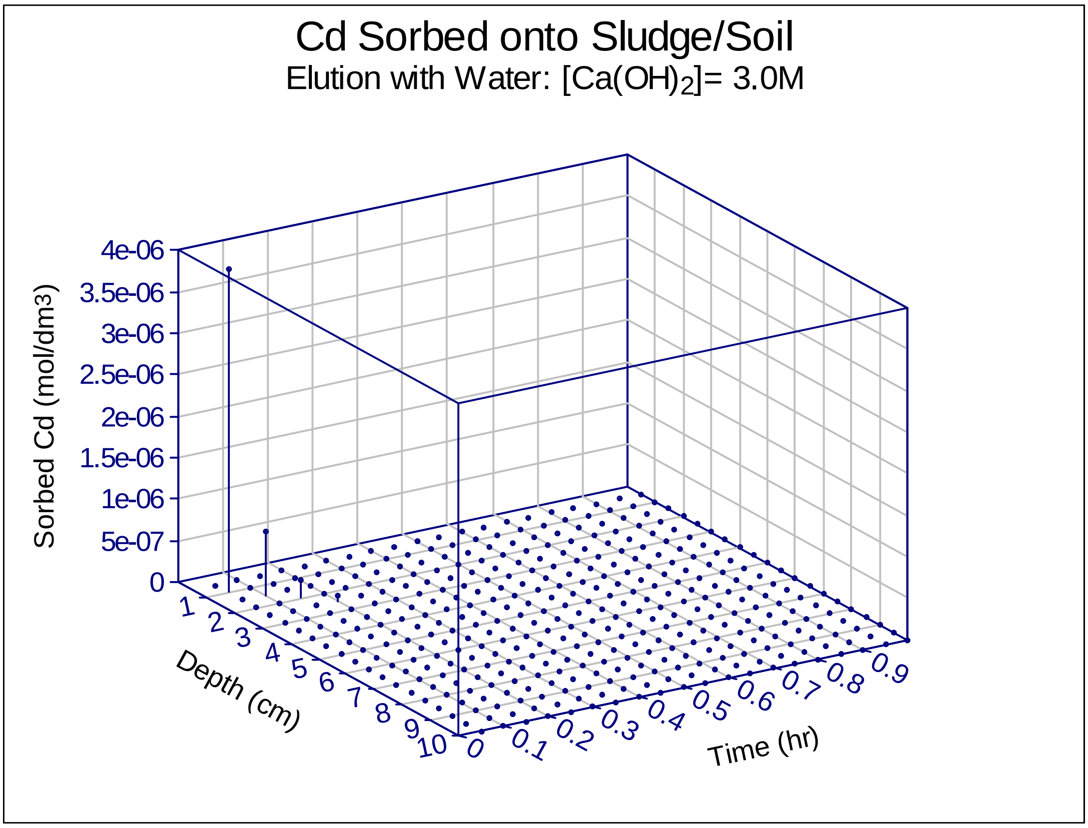


Figure 5.9.4: Elution of a soil column of 20 cells depth by 100 pore volumes of a solution of moderately concentrated lime ([Ca] = 5.0M). The soil consists mainly of sand, with particulate organic matter adsorbed to it.

5.9.5 Scenario 5: Termination of sludge application

It is very difficult at this stage to incorporate microbial degradation kinetics into the model. This is due primarily to the lack of knowledge of the compounds making up the sludge/natural organic carbon mix, which itself is a function of origin of both the sludge and the natural organic carbon, as well as the community structure of microbes present, which depend on the presence of other contaminants and nutrients present.

Suffice to say, however, that the work published by McGrath and Cegarra (1992) suggests that metal slowly leaches from the sludged soil over a decade, as the readily decomposable organic fraction is consumed, whereafter the system settles down, and no more metal is released from the soils.

5.10 Conclusions from the Modelling Studies

Inspection of Figure 5.7.1.2a to Figure 5.9.4 reveals that only when the soil has an appreciable amount of particulate organic matter in it, does the metal ion remain attenuated in the upper soil layers. Organic matter may be destroyed by microbial action. Hydrous ferric oxide, on its own, will not suffice to immobilise metals, even when only eluted with dilute salt water.

Sludge-derived humic and fulvic acids are fully capable of mobilizing metals down the soil column and into the groundwater. This modelling result is in accordance with experimental evidence gleaned from literature studies. Excessive liming of sludged soils will mobilise heavy metals.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Extent of DLD practices in South Africa

The extent of DLD practices in South Africa is widespread. Stockpiling is the practice used by most (40%) of the WWTP surveyed telephonically, either as the only disposal method or a means to store the dried sludge until it is utilized by farmers and municipalities, disposed of in landfills or composted. Liquid sludge is applied to soils by 40% of the remaining disposal sites. This includes practices like irrigation, flooding, sludge ponds, instant lawn irrigation and paddies.

The majority of soil samples from the 100 selected disposal sites had above average macronutrient and organic carbon contents, and 65% of the samples had pH(H_2O) values <6.5. Groundwater pollution at these sites with low pH values is a possibility because many heavy metals are mobile in acid conditions. Thirty percent of the DLD sites were on sandy soils with a high leaching potential while only 11% were on sandy clay and clay soils where the adsorption capacity of the soils may impede leaching, and thus, groundwater pollution.

The heavy metal analyses indicated that 88% of the soil samples used for this study had at least one element that exceeded the MPL for soils (Dept. Nat. Health & Pop. Dev., 1991). Nickel is the main element that was high in most of the samples, followed by Zn and Pb. Other elements that were present in high concentrations were Cd, Cr and Cu.

The soil samples irrigated with liquid sewage sludge had the highest heavy metal content, followed by instant lawn, paddies and flooded soils. Therefore, it seemed as if liquid sludge poses a bigger pollution risk than dried sludge application, especially when the sludge is from industrial origin.

It should be kept in mind that the MPL for heavy metals in soils was set for the beneficial use of sewage sludge for agricultural purposes and not for DLD practices. A separate set of guidelines should probably be considered for DLD practices after the completion of this study.

6.2 Case studies

The selection of sites that were sampled consisted of 14 sites with wet sludge application without beneficial use, 5 sites with sludge irrigation onto instant lawn (beneficial use) and 21 sites with dry sludge application (stockpile and belt press dewatered sludge). Seven of the sampled sites receive only domestic wastewater.

The P contents of the topsoil of 23 sites were above the average for normal, agricultural soil (>0.1%; Brady, 1984). None of the soil samples had above average total N (>1.5%; Sparks, 1996) even in the top 100mm of the soil profile. However, the analysis data of the groundwater samples had high NO_3 concentrations, which indicate leaching of nitrate. Sixty percent of the sampled sites had organic carbon contents higher than 1.2%, which is high by South African standards (FSSA, 1997).

Correlations for all analytical methods were done for all the samples, only topsoil samples and subsoil samples (lowest soil layer sampled) to determine where the strongest correlation would be. The correlations indicated that the EPA 3050 and *aqua regia* methods could be used interchangeably for all the metals, except Ni, because of the were very strong (r^2 >0.82) correlations. The correlation between the NH_4EDTA and NH_4NO_3 extraction methods were strong for Cr, Ni and Cd. For Zn, Cd and Pb the correlation between the total methods (EPA 3050 and *aqua regia*) and NH_4EDTA were also strong.

Of the 40 selected sites, 35 sites had at least one heavy metal that exceeded the MPL for South African soils (Dept. Nat. Health & Pop. Dev., 1991). Table 6.2 presents the percentage of samples in each soil layer that exceeded the guideline values set for each analytical method. The *aqua regia* and EPA 3050 methods gave similar metal concentrations at 26 sites. It seems as if certain soil properties influence the results of the digestion methods and should be studied further. Only the Ni concentration between the two methods differs significantly ($p=0.01$).

The total topsoil concentration of Cr was above the MPL for South African soils in 50-53% of the sampled sites, followed by Ni (45-48%), Zn (40-45%), Pb (35-38%), Cu (30-35%), Co (25-33%) and Cd (25-30%). The percentage samples exceeding the MPL for South African soils (Nat. Dept. Health & Pop. Dev., 1991) decreased in the lower soil layers. The high total metal concentrations in many of the soils, especially those that receive only domestic wastewater, may be due to high background concentrations of these elements in South African soils (Herselman & Steyn, 2001) and not only to sludge application. Detailed studies of these sites, including surrounding areas to determine the baseline concentration of the area, is advised.

None of the sites (all soil layers) had bio-available Cr and Pb concentrations above the NH_4EDTA threshold values. The topsoil bio-available Cd, Zn, Co, Cu and Ni concentrations in, respectively, 20% (Cd, Zn), 13% (Co, Cu) and 10% (Ni) of the sites exceeded the NH_4EDTA threshold values (Bruemmer & van der Merwe, 1989). There is thus a small medium term risk for environmental pollution because of the buildup of metals.

Table 6.2: Percentage of samples in each soil layer that exceeded the guideline values set for each analytical method

0-100mm soil layer													
EPA 3050							***Aqua Regia***						
Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**	**Cd**	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
30	25	50	35	45	35	45	25	33	53	30	48	38	40
NH_4EDTA							**NH_4NO_3**						
Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**	**Cd**	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
20	13	0	13	10	0	20	23	-	15	11	45	5	38
100-200mm soil layer													
EPA 3050							***Aqua Regia***						
Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**	**Cd**	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
15	30	45	30	38	23	28	15	35	50	23	40	17	30
NH_4EDTA							**NH_4NO_3**						
Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**	**Cd**	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
10	10	0	7	7	0	15	28	-	7	25	45	0	28
200-300mm soil layer													
EPA 3050							***Aqua Regia***						
Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**	**Cd**	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
7	28	43	15	35	15	15	13	35	48	20	43	15	28
NH_4EDTA							**NH_4NO_3**						
Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**	**Cd**	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
5	7	0	2	7	0	13	25	-	5	20	30	0	17
300-400mm soil layer													
EPA 3050							***Aqua Regia***						
Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**	**Cd**	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
5	20	35	2	25	5	13	2	25	28	5	40	2	15
NH_4EDTA							**NH_4NO_3**						
Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**	**Cd**	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
0	13	0	0	5	0	10	23	-	2	13	25	0	15
400-500mm soil layer													
EPA 3050							***Aqua Regia***						
Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**	**Cd**	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
5	15	33	2	20	2	17	5	28	33	7	33	2	13
NH_4EDTA							**NH_4NO_3**						
Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**	**Cd**	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
0	5	0	0	5	0	10	23	-	0	13	25	0	13

The lack of groundwater monitoring at most of the wastewater treatment facilities should be addressed. All the groundwater samples that could be obtained showed high NO_3 concentrations (>6 mg l^{-1}). This would probably be the case at most of the treatment facilities. The organic C in the top 200mm of the soil profile may adsorb some nitrogen, but the rest is mobile and leach through the soil. Therefore, the soil analyses do not show high total N concentrations.

Some degree of leaching of heavy metals occurred at some of the sampling sites and the average depth of leaching was 100-200mm. Deeper than 300mm the metal concentrations in the soil samples reached background concentrations. More leaching occurred at the sites that dispose of liquid sludge from industrial origin, especially when the sludge disposed of is AD sludge (metals in liquor phase). The elements that leached in most soils were Co and Ni. The leaching of the metals, in spite of the high organic carbon content of the soils, was due to the low soil pH(H_2O) and clay content of most sites.

Taking into account the age of the disposal sites and the frequency of sludge application, the depth of leaching is surprisingly shallow, in spite of the low soil pH(H_2O) and clay content.

6.3 Modelling of metal migration in sludge-amended soils

The modelling results revealed that, only when the soil has an appreciable amount of particulate organic matter in it, does the metal ion remain attenuated in the upper soil layers. Organic matter may be destroyed by microbial action. Hydrous ferric oxide, on its own, will not suffice to immobilise metals, even when only eluted with dilute salt water. Sludge-derived humic and fulvic acids are fully capable of mobilizing metals down the soil column and into the groundwater. This modelling result is in accordance with experimental evidence gleaned from literature studies. Excessive liming of sludged soils will mobilise heavy metals.

Scenarios were modelled, using cadmium as a representative metal ion. The scenarios are presented below with the results of the simulations:

- Elution with dilute saline solution at pH 7 - metals were not mobilised
- Elution with dilute saline solution at pH 6.5 - metals were not mobilised
- Elution with dilute saline solution at pH 5.0 - metals were completely mobilised
- Effect of maintaining carbon content of sludge layer - microbial decomposition of organic carbon will continuously produce soluble organic matter, which will bind metals and mobilise the metals
- Effect of maintaining high pH through liming - addition of lime involves the addition of calcium ion which out-competes toxic metal adsorption to sludge/soil matrix, resulting in substantial mobilisation of metals
- Effect of cessation of sludge addition - metals would be mobilised in the short term, due to continuous production of soluble, metal-binding organic matter, but will cease in the long-term. Literature suggests that after ten years, metals will cease to be mobile

6.4 Recommendations

The following recommendations should be considered:

- Clear demarcation of sludge disposal areas with restrictive access
- Continuous groundwater and surface water monitoring should be enforced
- Erosion control measures where necessary
- Sound management practices at the disposal site to regulate disposal
- Prerequisites for permit – no disposal on sandy soils, safe distance from water bodies etc.
- Nitrogen should be considered in the guideline for sludge disposal because it poses a bigger threat than the metals
- Guidelines should be set for DLD specifically

REFERENCES

ALLEN H.E., CHEN Y.T., LI Y., HUANG C.P. & SANDERS P.F. 1995. Soil partition coefficients for Cd by column desorption and comparison to batch adsorption measurements. Environmental Science and Technology, Vol. 29, pp 1887-1891.

ALLOWAY, B.J. 1995. Heavy metals in soils. 2nd edn. Blackie, London.

ANKLEY, G.T., THOMAS N.A., DI TORO D.M., HANSEN D.J., MAHONY J.D., BERRY W.J., SWARTZ R.C., HOKE R.A., GARRISON A.W., ALLEN H.E. & ZARBA C.S. 1994. Assessing Potential Bioavailability of Metals in Sediments: A Proposed Approach. Environ. Management Vol. 18 (no. 3) pp 331-337.

APEDAILE, E. 2001. A perspective on biosolids management. The Canadian Journal of Infectious Diseases. Vol 12 Number 4. Canadian Infectious Disease Society, Ottowa, Ontario.

BADEN-WURTTEMBERG. 1993. Umweltschutz in Baden-Wurttemberg: Boden. Druck & Verlagshaus, Balingen.

BIGHAM, J.M. AND BARTELS, J.M. (eds). 1996. Methods of Soil Analysis. Part 3: Chemical Methods. SOIL SCIENCE SOCIETY OF AMERICA and AMERICAN SOCIETY OF AGRONOMY. Madison, Wisconsin, USA.

BOYD S.A., SOMMERS L.E., NELSON D.W. & WEST D.X. 1979. Copper(II) Binding by Humic Acid Extracted from Sewage Sludge: an Electron Spin resonance Study. J. Am. Soil Sci. Soc., Vol. 47, pp 43-46.

BRADY, N.C. 1984. The nature and properties of soils. Macmillan Publishing Company, New York.

BRUEMMER, G.W. & VAN DER MERWE, A.J. 1989. Report on a visit to the Soil and Irrigation Research Institute, Pretoria in connection with soil pollution in the RSA and the future research requirements. Unpublished report, ISCW, Pretoria.

CHATEAUVERT, A., FUNG, K., STEWART, B., IANIERO, K. & SKENDERIS, V. 2002. Asurvey of past practice in disposal practices for manure and sewage sludge around the world. www.bordeaux.uwaterloo.ca

DEPARTMENT OF NATIONAL HEALTH AND POPULATION DEVELOPMENT. 1991. Guide: Permissible utilization and disposal of sewage sludge. Ref: A11/2/5/4 (2nd Draft). Unpublished report, Dept. of Nat. Health and Pop. Dev., Pretoria.

DEPARTMENT OF WATER AFFAIRS AND FORESTRY. 1996. South African water quality guidelines. 2nd ed. Pretoria Department of Water Affairs and Forestry.

DEPARTMENT OF WATER AFFAIRS AND FORESTRY. 1997. Waste Management Series. Waste generation in South Africa: Baseline studies. Pretoria Department of Water Affairs and Forestry.

DEPARTMENT OF WATER AFFAIRS AND FORESTRY. 1998. Waste Management Series. *Minimum Requirements for the Handling, Classification and Disposal of Hazardous Waste.* Pretoria Department of Water Affairs and Forestry.

DUDKA, S & CHLOPECKA, A. 1990. Effect of Solid-Phase Speciation on Metal Mobility and Phytoavailability in Sludge-Amended Soil. Water, Air, Soil Pollut., Vol. 51, pp 153-160

DZOMBAK, D.A. & MOREL, F.M.M. 1990. Surface complexation modelling. Hydrous ferric oxide. Wiley & Sons, New York.

EKAMA, G.A. (ed). 1993. Sewage sludge utilization and disposal: Information document. WRC, Pretoria.

EMMERICH W.E., LUND L.J., PAGE A.L. & CHANG A.C. 1982. Solid phase forms of heavy metals in sewage sludge-treated soil. J. Environ. Qual., Vol. 11, pp 178-181.

EVANS, L.J. 1989. Chemistry of metal retention by soils. Environ. Sci. Technol. Vol. 23 (no. 9) pp1046-1056.

FARLEY, K.J., DZOMBAK D.A. & MOREL, F.M.M. 1985. A surface precipitation model for the sorption of cations on metal oxide. J. Colloid. Interfac. Sci. Vol. 106, pp 226-242.

FLETCHER P. & BECKETT P.H. 1987a. The Chemistry of Heavy Metals in Digested Sewage Sludge 2. Heavy Metal Complexation with Soluble Organic Matter. Water Res., Vol. 21, pp 1163-1172.

FLETCHER P. & BECKETT P.H.T. 1987b. The Chemistry of Heavy Metals in Digested Sewage Sludge 1. Copper(II) Complexation with Soluble Organic Matter. Water Res., Vol. 21, (no. 10) pp 1153-1161.

FSSA. 1997. Fertilizer Handbook. 5th ed. Fertilizer Society of South Africa, Pretoria.

FU, G. & ALLEN, H.E. 1992. Cadmium Adsorption by Oxic Sediment, Wat. Res. Vol 26, No.2. pp. 225-233.

GOLDEN, D.C., DIXON J.B. & CHEN C.C. 1986. Ion exchange, thermal transformations, and oxidizing properties of birnessite. Clays Clay Miner. Vol. 34, pp 511-520.

GOODDY, D.C., SHAND P., KINNIBURGH D.G. & VAN RIEMSDIJK W.H. 1995. Field-based partition coefficients for trace elements in soil solutions. Eur. J. Soil Sci. Vol. 46, pp 265-285.

GU, B., SCHMITT, J., CHEN, Z., LIANG, L. & MCCARTHY, J.F. 1994. Adsorption of natural organic matter on iron oxide: Mechanisms and models. Environ. Sci. Technol. Vol. 28, pp 38-46.

HERSELMAN, J.E. 1998. Adsorption capacity of selected South African soils for heavy metal disposal. MSc thesis, UNISA, Pretoria

HERSELMAN, J.E. & DU PREEZ, H.G. 2000. Field experiments to determine the leaching of heavy metals through the soil profile of sludge applied soils. Report no. GW/A/2000/9, ISCW, Pretoria.

HERSELMAN, J.E. & STEYN, C.E. 2001. Predicted concentration of trace elements in South African soils. Report no. GW/A/2001/14, ISCW, Pretoria.

KABATA-PENDIAS, A. & PENDIAS, H., 1992. Trace elements in soils and plants. 2nd edn. CRC Press, London.

KEEFER R.F. & SINGH R.N. 1986. Correlation of metal-organic fractions with soil properties in sewage-sludge-amended soils. Soil. Sci., Vol. 145, (no. 1) pp 20-26.

KINNIBURGH, D.G., JACKSON M.L. & SYERS J.K. 1976. Adsorption of alkaline earth, transition, and heavy metals cations by hydrous oxide gels of iron and aluminum. Soil Sci. Soc. Am. J. Vol. 40, pp 796-799.

KORENTAJER. 1991. A review of the agricultural use of sewage sludge: benefits and potential hazards. *Water SA* 17, 189-196.

KORTE, N. 1999. A guide for the technical evaluation of environmental data. Technomic Publishing Co., Lancaster, USA

LAKE D.L., KIRK P.W.W. & LESTER J.N. 1985. The Effects of Anaerobic Digestion on Heavy Metal Distribution of Sewage Sludge. Water Pollut. Control, Vol. 84, pp 549-558.

LATURNUS, F. 2002. Sewage sludge in Europe – What's the problem? www.infoweb.unit.liu.se

LEGRET M., DEMARE D. & MARCHANDISE P. 1983. Speciation of Heavy Metals in Sewage Sludges. Proc. of The 4th Int. Conf. Heavy Metals in the Environment . CEP, Edinburg. pp 350-353.

LOEPPERT, R.H., WEI L. & OCUMPAUGH W.R. 1994. Soil factors influencing the mobilization of iron in calcareous soils. in: Biochemistry of metal micronutrients in the rhizosphere. J.A. Manthey, D.E. Crowley and D.G. Luster (eds.). Lewis Publishers Inc, Arm Arbor, pp. 343-360.

LÖTTER, L.H. & PITMAN, A.R. 1997. *Aspects of Sewage Sludge Handling and Disposa*l. WRC Report No 316/1/97. Water Research Commission.

LUE-HING, C., ZENZ, D.R. & KUCHENRITHER, R. (eds.) 1992. Municipal sewage sludge management: Processing, utilization and disposal. Technomic Pub. Co., Lancaster.

MARRIOT, B.A. 1998. Land spreading of sludge in New Hampshire: Report to the UNH Sludge Task Force. **http://ceinfo.unh.edu**

MASSCHELEYN, P.H., DELAUNE R.D. & PATRICK W.H. Jr. 1991. Effect of redox potential and pH on arsenic speciation and solubility in a contaminated soil. Environ. Sci. Technol. 25 (no. 8): 1414-1419.

McBRIDE, M.B. 1994. Environmental chemistry of soils. Oxford Univ. Press. New York.

McBRIDE, M.B. 1985. Sorption of copper(H) on aluminum hydroxide as affected by phosphate. Soil Sci. Soc. Am. J. Vol. 49, pp 843-846.

MCGRATH S.P. & CEGARRA J. 1992. Chemical Extractability of Heavy Metals during and after long-term Applications of Sewage Sludge to Soil. J. Soil Sci., Vol. 43, pp 313-321.

McGRATH, S.P., CHAUDRI, A.M. & GILLER, K.E. 1995. Long-term effects of metals in sewage sludge on soils, microorganisms and plants. *Journal of Industrial Microbiology* 14, 94-104.

McLAUGHLIN, M.J., HAMON, R.E., McLAREN, R.G., SPEIR, T.W. & ROGERS, S.L. 2000. Review: A bioavailability-based rationale for controlling metal and metalloid contamination of agricultural land in Australia and New Zealand. *Aust. J. Soil Res*. 38: 1037-1086.

NADIM, A. 2000. Sludge treatment and disposal. www.ourworld.compuserve.net

OAKE R.J., BOOKER C.S. & DAVIS R.D. 1984. Fractionation of Heavy Metals in Sewage Sludges. Water Sci. Technol., Vol. 17, pp 587-598.

PATERSON, E., GOODMAN B.A. & FARMER V.C. 1991. The chemistry of aluminum, iron and manganese oxides in acid soils. Soil Acidity. pp97-124. Paterson, E., Goodman B.A., and Farmer V.C., (1991) The chemistry of aluminum, iron and manganese oxides in acid soils. Soil Acidity. pp97-124.

PEDERSON, BETH M., LOUIS J. THIBODEAUX, KALLIAT T. VALSARAJ & DANNY D. REIBLE, 2001. Testing A Multimedia Compartmental Model With Monitoring Data. Environmental Toxicology And Chemistry, Vol. 20, No. 9, Pp. 2114–2121.

PRIESTLEY, A.J. 1990. Report on sewage sludge treatment and disposal – Environmental problems and research needs from an Australian perspective. www.eidn.com.au/ukcsirosewagesludge.htm

RAI, D., EARY, L.E. & ZACHARA, J.M. 1989. Environmental chemistry of chromium. Sci. Total Environ. Vol 86, pp 15-23.

READ, D. AND HOOKER, P. 1992. Using data from natural environments to improve models of uranium speciation in groundwaters. J.Geochem.Expl Vol 46, pp63-81.

RUDD T., CAMPBELL J.A. & LESTER J.N. 1988. The Use of Model Compounds to Elucidate Metal Forms in Sewage Sludge. Environmental Pollution, Vol. 50, pp 225-242.

SAGER, M. 1992. Chemical speciation and environmental mobility of heavy metals in sediments and soils. in: Hazardous metals in the environment. M.

SCHUMAN, L.M., 1986. Effect of ionic strength and anions on zinc adsorption by two soils. Soil Sci. Soc. Am. J. Vol. 50, pp 1438-1442.

SCHWAB, A.P. & LINDSAY W.L. 1983. Effect of redox on the solubility and availability of iron. Soil Sci. Soc. Am. J. Vol. 47, pp 201-205.

SENESI N., BOCIAN D.F. & SPOSITO G. 1985. Electron Spin Resonance Investigation of Copper(II) Complexation by Fulvic Acid Extracted from Sewage Sludge. Soil Sci. Soc. Am. J., Vol. 49, pp 119-126.

SENESI, N. 1992. Metal-humic substances complexes in the environment. Molecular and mechanistic aspects by multiple spectroscopic approach. in: Biogeochemistry of trace metals. D.C. Adriano (ed.). Lewis Publishers, Arm Arbor, pp. 429-496.

SIDLE, R.C., KARDOS, L.T. & VAN GENUCHTEN, M.Th. 1977. Heavy metals transport model in a sludge-treated soil, J. Environ. Qual., Vol 6, pp. 438-443

SMITH, R. & VASILOUDIS, H. 1991. Importance, determination and occurrence of inorganic chemical contaminants and nutrients in South African municipal sewage sludges. *Water SA* 17, 19-29.

SNYMAN, H.G., HERSELMAN, J.E. & KASSELMAN, G. WRC Report on the Project “A metal content survey of South African sewage sludge and an evaluation of analytical methods for their determination in sludge ". In press.

SPARKS, D.L. (ed). 1996. Soil Science Society of America Book Series 5. Methods of soil analysis. Part 3: Chemical methods. SSSA Inc., Wisconsin, USA.

SPOSITO G., HOLTZCLAW K.M. & LEVESQUE-MADORE C.S. 1981. Trace Metal Complexation by Fulvic Acid Extracted from Sewage Sludge: I. Determination of Stability Constants and Linear Correlation Analysis. J. Am. Soil Sci. Soc., Vol. 45, pp 465-468.

SPOSITO G., BINGHAM F.T., YADAV S.S. & INOUYE C.A. 1982. Trace Metal Complexation by Fulvic Acid extracted from Sewage Sludge: II. Development of Chemical Models. J. Am. Soil Sci. Soc., Vol. 46, pp 51-56.

SPOSITO G. 1986a. Sorption of Trace Metals by Humic Materials in Soils and Natural Waters. CRC Crit. Reviews in Environ. Control, Vol. 16, pp 193-229.

SPOSITO G. 1986b. Distinguishing adsorption from surface precipitation. In: J.A. Davies, Hayes K.F. (eds.) Geochemical processes at mineral surfaces. (ACS Symposium Series), Vol 323. ACS, Washington pp 217-228.

STEYN, C.E. 1994. The bioavailability of certain heavy metals in selected organic products. MSc(Agric) thesis, Univ. of Pretoria.

STOEPPLER (ed.). Elsevier Science Publ., Amsterdam, pp. 133-175.
STUMM, W. & SULZBERGER, B. 1992. The cycling of iron in natural environments:considerations based on laboratory studies of heterogenous redox processes. Geochim. Cosmochim. Acta 56pp 3233-3257.

STOVER R.C., SOMMERS L.E. & SILVIERA D.J. 1976. Evaluation of metals in wastewater sludge. J. Water Pollut. Control Fed., Vol. 48, pp 2165-2175.

TEST METHODS FOR EVALUATING SOLID WASTES. 1986. 3rd edn. US Environmental Protection Agency, Washington, DC.

THE NON-AFFILIATED SOIL ANALYSIS WORK COMMITTEE. 1990. Handbook of standard soil testing methods for advisory purposes. Soil Science Society of South Africa, Pretoria.

TIPPING, E. & COOKE, D. 1982. The effect of adsorbed humic substances on the surface charge of goethite (ci-FeOOH) in freshwaters. Geochim. Cosmochim. Acta Vol. 46, pp 75-80.

USEPA Standard Methods. 1986. Environmental Protection Agency. *Test methods for evaluating solid waste, physical/chemical methods (SW-846): Method 3050 Acid digestion of sediments, sludges and soils.* Washington DC. USA. Environmental Protection Agency

VAN DER WATT, H.v.H & VAN ROOYEN, T.H. 1990. A glossary of soil science. Soil Science Society of South Africa. V & R Printing Works, Pretoria.

VAN VEEN, E., BURTON, N., COMBER, S. & GARDNER, M. 2002. Speciation Of Copper In Sewage Effluents And Its Toxicity To *Daphnia Magna,* Environmental Toxicology And Chemistry, Vol. 21, No. 2, Pp. 275–280,

VASILEIOS A. & ALLOWAY B.J. 2002. Leaching of Cadmium, Nickel and Zinc down the Profile of Sewage Treated Soil. Commun. Soil Sci. Plant Anal., Vol. 33, (no. 1&2) pp 273-286.

WEI, Q.F., LOWERY, B. & PETERSON, A.E. 1985. Effect of sludge application on physical properties of a silty clay loam soil. *J. Environ. Qual.* 14, 178-180.

WONG, J.W.C. & HO, G.E. 1991. Effects of gypsum and sewage sludge amendment on physical properties of fine bauxite refining residue. *Soil Sci*. 153, 326-332.

WONG, J.W.C., CHEUNG, K.C. & WONG, M.H. 2000. Environmental implication of soils amended with anaerobically digested sewage sludge in Hong Kong. *Water, Air and Soil Pollution* 124, 23-36.

WRC. 1997. Permissible utilisation and disposal of sewage sludge. 1st ed. WRC, Pretoria.

WRC. 2002. Department of Agriculture, Department of Health. Department of Water Affairs and Forestry. Water Research Commission. Sludge Consultant. *Addendum No, 1 to Edition 1 (1997) of Permissible Utilisation and Disposal of Sewage Sludge.* TT 150/01 Pretoria. Water Research Commission.

www.unep.or.jp Newsletter and Technical publications. Freshwater Management Series No 1. Biosolids management: An environmentally sound approach for managing sewage treatment plant sludge.

ZHUANG, Y., ALLEN, H.E. & FU, G. 1994. Effect of aeration of sediment on cadmium binding. Environ. Toxicol. Chem. Vol 13 (no. 5), pp 717-724.

APPENDIX A

Case Studies

5.1 Stockpile sites

5.1.1 Site 1

The first site is situated on a deep, sandy soil with very low clay content (2%) of the Fernwood soil form (orthic A, regic sand). The treatment facility has an average inflow of 30–40 Ml/day and both waste activated and digested sludge is produced. It is an old disposal site (>30 years) where sludge are dried on drying beds and stockpiled. For the last few years the sludge have been dried mechanically and transported to a landfill site. Samples were taken at the old stockpile site. No groundwater monitoring occurs at this site.

The data in Table 5.1 show higher total P, N and organic C in the 200-400mm soil samples than in the topsoil, indicating leaching of these elements from the topsoil into the subsoil. The low clay content of the soil is probably the main reason for the leaching. The pH(H_2O) of the soil profile is mildly alkaline (van der Watt & van Rooyen, 1990). The heavy metal content of the sludge is below the guidelines for Type D sludge (WRC, 2002).

Table 5.1: Site 1 general soil and sludge data

Soil depth (mm)	Total P %	Total N %	C %	Clay %	pH (H_2O)	
0-100	0.08	0.11	0.81	2.00	7.46	
100-200	0.08	0.12	0.87	2.00	7.53	
200-300	0.09	0.13	0.80	2.00	7.55	
300-400	0.14	0.20	1.66	2.00	7.49	
400-500	0.08	0.14	1.19	2.00	7.68	
SLUDGE	0.61	2.63	55	-	6.27	
Sludge data (*aqua regia*) mg kg^{-1}						
Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
3.79	5.05	269.9	275.4	171.8	157.4	1098

The only element that exceeds the MPL for South African soils is Ni (Figure 5.1) with the EPA 3050 digestion method. Nickel is the only element that is relatively high in the sludge. The results of the other digestion and extraction methods are al below the relevant threshold levels (Bruemmer & van der Merwe, 1989; Baden-Wurttemberg, 1993). The constant distribution of Ni throughout the soil profile, indicate leaching through the soil profile because of the very low clay content of the soil. All other elements occur in low concentrations in the soil but are also distributed in equal amounts through the soil profile. This disposal site has been in use for 30+ years and groundwater should be monitored to determine the NO_3 and metal content and possible groundwater contamination at the site.

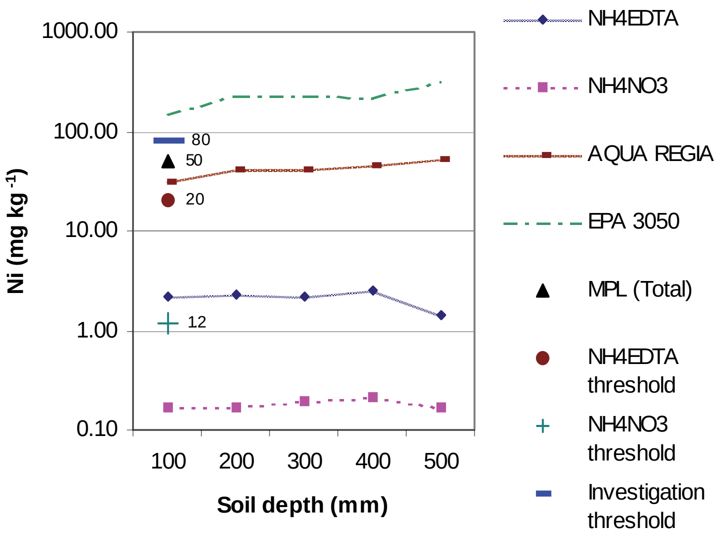


Figure 5.1: Ni content of the soil profile at Site 1

5.1.2 Site 2

Both waste activated and digested sludge is produced at this large water treatment facility with an average daily inflow of 200 Ml of which 20-30% is of industrial origin. The disposal site is on a Fernwood soil (orthic A, regic sand) with low clay content (3-4%). The sludge is mainly dried mechanically but due to the size of the facility, all sludge cannot be handled this way. The excess sludge is pumped into lagoons and stockpile when it's dry. Samples were taken at the footprint of a stockpile. Data on groundwater monitoring is still awaited from the site manager.

Table 5.2 contains data of the total P, N and organic C of the soil profile as well as the clay content and pH(H_2O). These data indicate a buildup of P, N and C in the top 400mm of the soil profile with very high total P and organic carbon concentrations for South African soils (MVSA, 1997). The pH(H_2O) of the soil is mildly to moderately alkaline (van der Watt & van Rooyen, 1990). The high organic C content keeps most of the P and N in the top 200mm, but leaching down the profile still occur, most likely due to the low clay content, and therefore the low attenuation capacity, of the soil.

Table 5.2: Site 2 general soil and sludge data

Soil depth (mm)	**Total P %**	**Total N %**	**C %**	**Clay %**	**pH (H_2O)**
0-100	0.25	0.19	2.79	3.33	7.52
100-200	0.15	0.09	1.03	3.33	7.58
200-300	0.08	0.04	0.62	4.00	7.95
300-400	0.13	0.09	0.99	4.00	8.12
400-500	0.04	0.06	0.59	3.33	8.15
SLUDGE	2.0	4.43	51	-	5.99

Sludge data (*aqua regia*) mg kg^{-1}						
Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
3.5	3.9	173.4	338.7	178.2	140.2	1344.2

The total Cr, Ni, Cu, Zn, Cd and Pb (EPA 3050 and *aqua regia* digestions) concentrations in the topsoil all exceed the MPL for South African soils (Nat. Dept. Health & Pop. Dev., 1991), and the Ni, Cu, Zn and Cd concentrations even exceed the investigation threshold levels suggested by Herselman & Steyn

(2001) (Figure 5.2). There is a decrease in total metal concentrations down the soil profile with higher concentrations at the 400mm soil layer.

The NH_4EDTA as well as the NH_4NO_3 extractable concentrations of all the elements are below the NH_4EDTA threshold values (Bruemmer & van der Merwe, 1989) and NH_4NO_3 guidelines (Baden-Wurttemberg, 1993) respectively.

Figure 5.2 shows the higher metal concentrations in the topsoil and the decrease with depth. There is adsorption of the metals in the top soil layers due to the high organic C content of the topsoil, but it also indicates leaching of the metals down the soil profile. The leaching of the metals are a lot less than expected for a sandy soil and is probably inhibited by the high organic C content and high $pH(H_2O)$ of the soil (Kabata-Pendias & Pendias, 1992). This site is contaminated

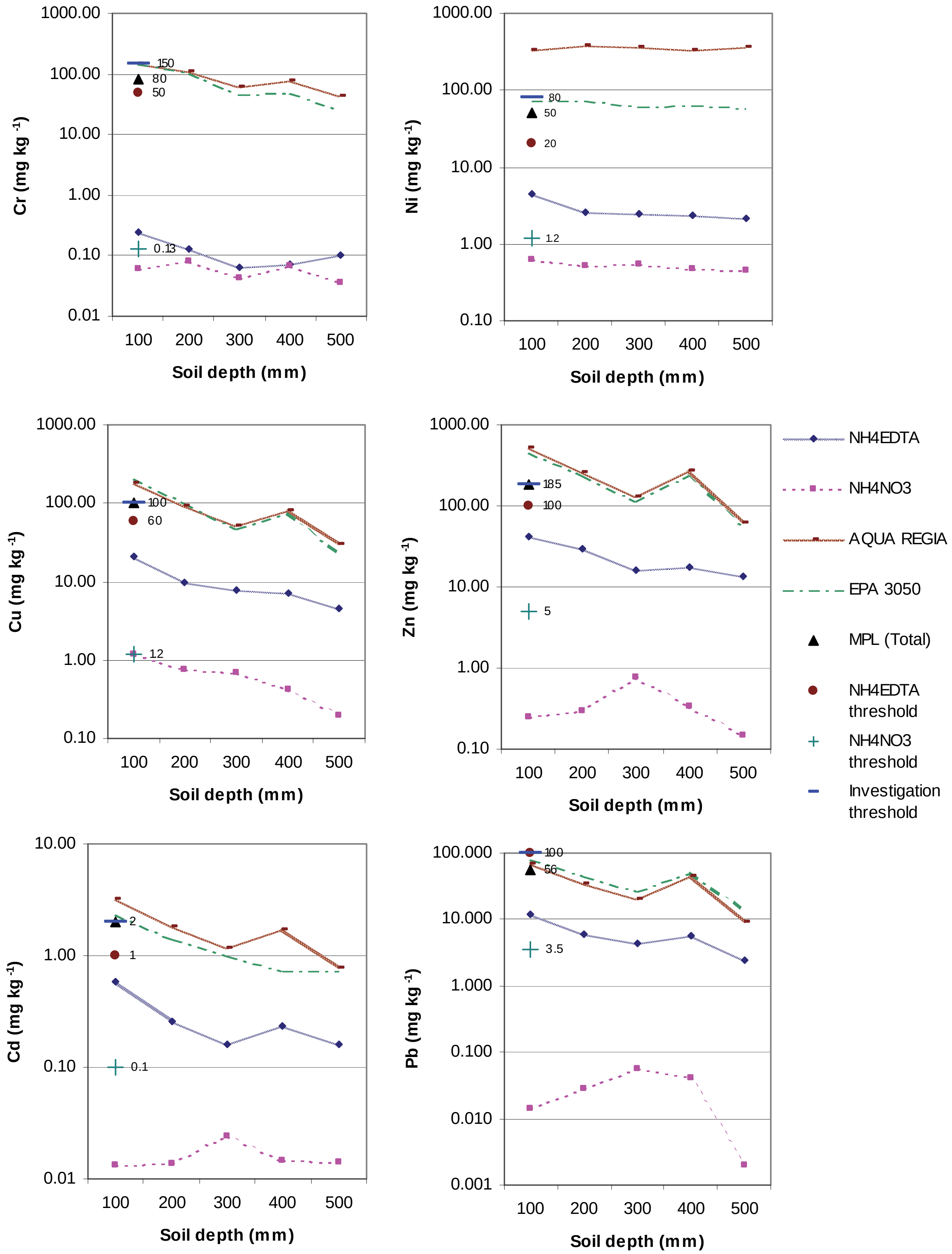


Figure 5.2: Cr, Ni, Cu, Zn, Cd and Pb contents of the soil profile at Site 2

and should be monitored closely to protect the groundwater against contamination.

5.1.3 Site 3

Site 3 is a medium sized wastewater treatment facility with an average daily inflow of 30Ml of which half is from industrial origin (breweries, mining, fats and oils). The anaerobic digested sludge has been dried on drying beds and stockpiled at the disposal site for more than 30 years. There are no boreholes on site and the nearest surface water body is 1km from the site. The underlying soil is a deep loam with 18-25% clay and the soil form is Clovelly (orthic A, Yellow-brown apedal B).

The data in Table 5.3 show elevated total P and organic C contents in the top 100mm with a gradual decrease downward. The total N is slightly higher in the 100-300mm soil layers. The pH(H_2O) of the topsoil is slightly acid, but the rest of the soil is mildly alkaline (van der Watt & van Rooyen, 1990). The metal content of the sewage sludge is below the guidelines (WRC, 2002).

Table 5.3: Site 3 general soil and sludge data

Soil depth (mm)	**Total P %**	**Total N %**	**C %**	**Clay %**	**pH (H_2O)**	
0-100	0.08	0.05	0.82	19.33	6.30	
100-200	0.03	0.10	0.56	18.33	7.39	
200-300	0.02	0.08	0.46	20.33	7.54	
300-400	0.02	0.07	0.44	22.33	7.35	
400-500	0.02	0.07	0.44	25.67	7.14	
SLUDGE	1.14	2.34	54	-	6.3	
Sludge data (*aqua regia*) mg kg^{-1}						
Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
5.4	16.7	113.4	208.3	42.4	296.9	1237.55

Results of all the extraction procedures are below the guideline levels set for each method. The total Zn and Cd concentrations in the top 100mm of soil are just below the MPL for South African soils (Nat. Dept. Health & Pop. Dev., 1991) of 185 mg kg^{-1} and 2 mg kg^{-1} respectively (Figure 5.3) and decrease with depth. The NH_4EDTA and NH_4NO_3 extractable Zn and Cd are also higher in the top 200mm soil layer but decrease rapidly with depth, indicating little leaching below 400mm. Groundwater contamination with metals is unlikely to be a cause for concern at this site, but should be monitored for NO_3 contamination.

After 30 years of industrial sludge application to the soil, one would expect much more leaching than that occurred in this soil. This may be due the clay content of the soil profile, the higher organic C content of the topsoil and the high pH(H_2O) of the soil. The metals are thus adsorbed in the top soil layers and rendered immobile (Kabata-Pendias & Pendias, 1992; Alloway, 1995).

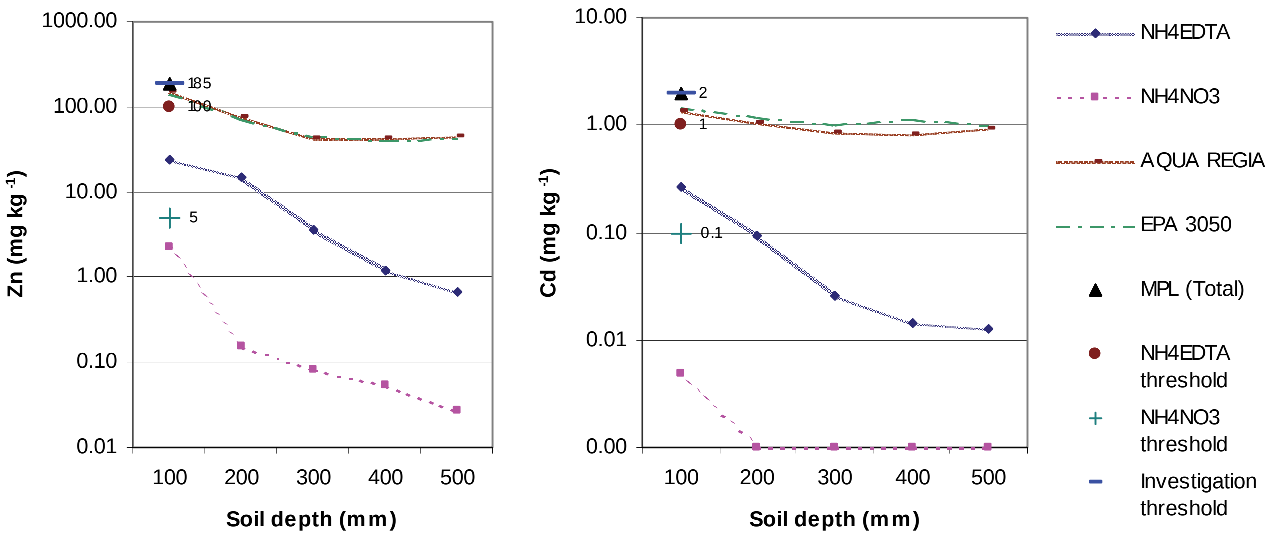


Figure 5.3: Zn and Cd contents of the soil profile at Site 3

5.1.4 Site 4

This wastewater treatment facility is very small (3Ml/day) and receives 20% of the inflow from industries (metal plating). It produces waste activated sludge that is dried on drying beds and stockpiled on site. It is situated on a deep, sandy (2-6% clay), Fernwood soil (orthic A, regic sand). There are no boreholes on site and it's 300m from the nearest surface water body.

Table 5.4 contains the general soil data of Site 4. The data show slightly higher total P, N and organic C concentrations in the top soil with a gradual decrease with depth. The pH(H_2O) of the soil is slightly to medium acid (van der Watt & van Rooyen, 1990). The metal content of the sludge is below the guidelines (WRC, 2002).

Table 5.4: Site 4 general soil and sludge data

Soil depth (mm)	**Total P %**	**Total N %**	**C %**	**Clay %**	**pH (H_2O)**	
0-100	0.03	0.06	0.56	6.00	5.99	
100-200	0.02	0.06	0.53	4.00	5.93	
200-300	0.02	0.05	0.36	2.67	5.91	
300-400	0.02	0.04	0.28	3.33	6.11	
400-500	0.02	0.03	0.26	2.67	6.50	
SLUDGE	2.06	4.81	50	-	6.43	
Sludge data (*aqua regia*) mg kg^{-1}						
Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
4.0	6.43	81.9	270.6	150.5	211.0	999.8

The results of all extraction methods used are well below the appropriate guideline levels (Bruemmer & van der Merwe, 1989; Nat. Dept. Health & Pop. Dev., 1991; Baden-Wurttemberg, 1993). Figure 5.4 show the distribution of Cu and Zn in the soil profile. The metal concentrations are slightly higher in the topsoil with a steady distribution down the soil profile, indicating that the elements added to the soil move through the profile with only a slight buildup in the topsoil. The low clay content and acid conditions in the soil profile lead to the leaching of the metals. Groundwater monitoring is advised at the site because the low clay content and pH(H_2O) of the soil lead to leaching of elements.

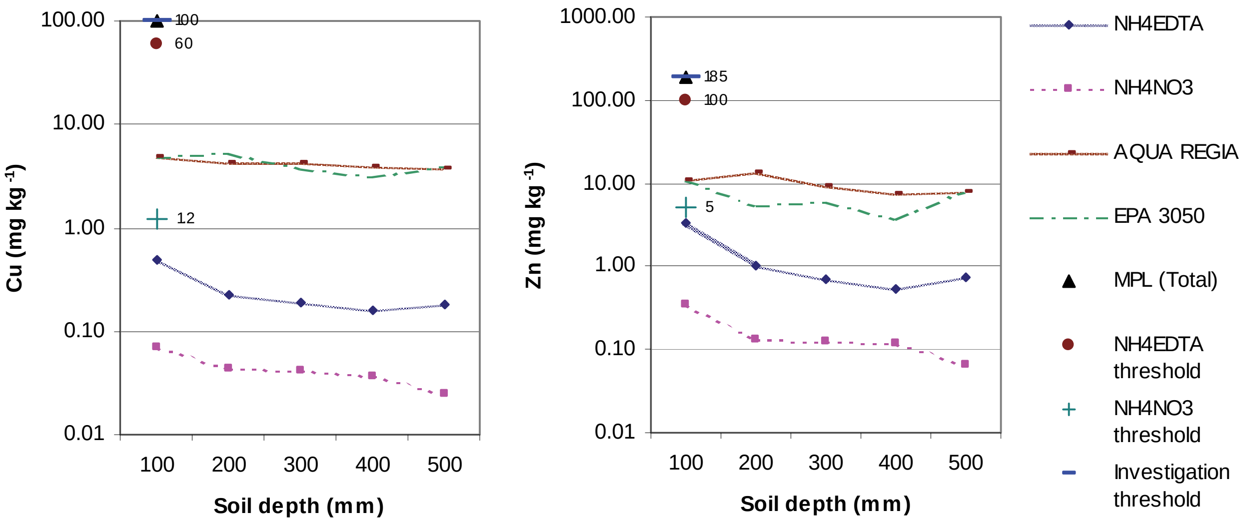


Figure 5.4: Cu and Zn contents of the soil profile at Site 4

5.1.5 Site 5

Situated on a deep, sandy Hutton soil (orthic A, red apedal B), this site receives an average inflow of 30Ml/day with 10% industrial effluent. Waste activated sludge is produced which is dried in drying beds and stockpiled on site since the 1980's. The site is 2km from the nearest open water body and there is no groundwater monitoring.

Table 5.5: Site 5 general soil and sludge data

Soil depth (mm)	Total P %	Total N %	C %	Clay %	pH (H_2O)
0-100	0.06	0.06	0.25	4.00	5.51
100-200	0.05	0.04	0.19	4.67	5.75
200-300	0.04	0.03	0.15	4.67	5.87
300-400	0.03	0.03	0.12	4.67	5.94
400-500	0.02	0.02	0.10	5.33	5.98
SLUDGE	0.84	5.27	51	-	6.46

Sludge data (*aqua regia*) mg kg^{-1}						
Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
3.7	5.3	144.8	340.7	104.7	177.6	1850.5

Data in Table 5.5 indicate higher concentrations of all elements in the top 200mm soil layers and a gradual decrease with depth. The pH(H_2O) of the soil is medium acid (van der Watt & van Rooyen, 1990). The movement of P, N and organic C down the soil profile are due to the low pH(H_2O) and clay content of the soil. The metal content of the sludge is within the guidelines (WRC, 2002). Groundwater contamination with NO_3 is a possibility since the total N in the soil and the total N in the sludge do not correspond, indicating leaching through the soil profile. groundwater monitoring is advised.

None of the analysed metals exceed the guideline levels set for the different extraction methods (Bruemmer & van der Merwe, 1989; Nat. Dept. Health & Pop. Dev., 1991; Baden-Wurttemberg, 1993). Figure 5.5 shows higher concentration of Zn in the top soil layers, decreasing with depth. This tendency is the same for all the metals at Site 5. Metals leached to a depth of 300mm because of the low clay content and low pH(H_2O) of the soil, and the natural baseline concentration is reached at 500mm.

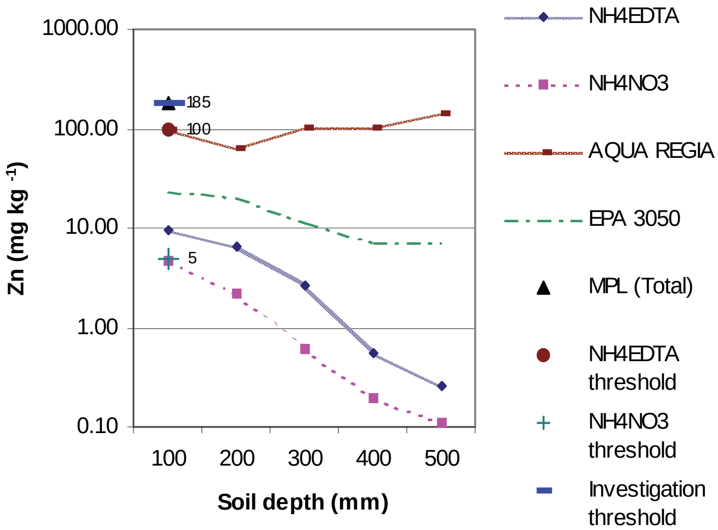


Figure 5.5: Zn content of the soil profile at Site 5

5.1.6 Site 6

Site 6 is situated on shallow (<300mm), loamy sand with low clay content (<10%). The soil form is Glencoe (orthic A, yellow-brown apedal B, hard plinthic B). The facility receives 14Ml/day inflow (10% industrial) and produces waste activated, as well as anaerobically digested sludge, which is air-dried on drying beds and then stockpiled on site. The soil samples were taken on the footprint of the stockpile, but could only be taken up to 300mm because of the shallow soil. This disposal practice has been in use for 20+ years on the same piece of land where the terrain is even and the nearest open water body is 200m away. A groundwater sample was collected at the disposal site.

The total P, N and organic C are highest in the 100-200mm soil samples and decrease rapidly at the next depth. The pH(H_2O) of the soil is neutral to mildly alkaline (Table 5.6). The sludge data indicate Zn and Pb concentrations exceeding the guideline values for type D sludge (WRC, 2002). The analysis data of the groundwater sample indicate that the water is suitable for irrigation but not for human consumption because the NO_3 in the water is above the water quality guideline of 6 mg l^{-1} (DWAF, 1996). The rest of the elements are all below the water quality guideline levels.

Table 5.6: Site 6 general soil, sludge and groundwater data

Soil depth (mm)	Total P %	Total N %	C %	Clay %	pH (H_2O)
0-100	0.06	0.09	1.17	8.7	7.33
100-200	0.15	0.15	1.90	7.3	7.37
200-300	0.02	0.02	0.30	6.0	7.76
SLUDGE	1.49	3.63	44	-	6.43

Sludge data (*aqua regia*) mg kg^{-1}						
Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
6.42	10.1	119.0	574.0	176.8	544.6	3158.9

Water data								
Cd ($\mu g\ l^{-1}$)	**Cr ($\mu g\ l^{-1}$)**	**Co ($\mu g\ l^{-1}$)**	**Cu ($\mu g\ l^{-1}$)**	**Pb ($\mu g\ l^{-1}$)**	**Ni ($\mu g\ l^{-1}$)**	**Zn ($\mu g\ l^{-1}$)**	**NO_3 (mg l^{-1})**	**pH**
0.55	3.47	1.85	7.6	nd	7.74	31.61	11.97	6.35

The total Zn (EPA 3050) and Pb (EPA 3050 and *aqua regia*) concentrations of the topsoil exceed the MPL for South African soils (Dept. Nat. Health & Pop. Dev., 1991) and decrease with depth (Figure 5.6). Very little leaching occurred deeper than 200mm, due to the high pH(H_2O) and organic C content of the soil, even though the soil has very low clay content (Kabata-Pendias & Pendias, 1992; Alloway, 1995).

The bio-available Zn and Pb are lower than the NH_4EDTA threshold values of Bruemmer & van der Merwe (1989). Due to the low NH_4NO_3 extractable concentrations of all metals, the risk for groundwater pollution with heavy metals is low. The NO_3 concentration in the groundwater is high, which indicate leaching of N into the groundwater. The organic material adsorbed some of the nitrogen, but the excess leach through the soil profile, therefore the soil analyses data do not show high levels of nitrogen.

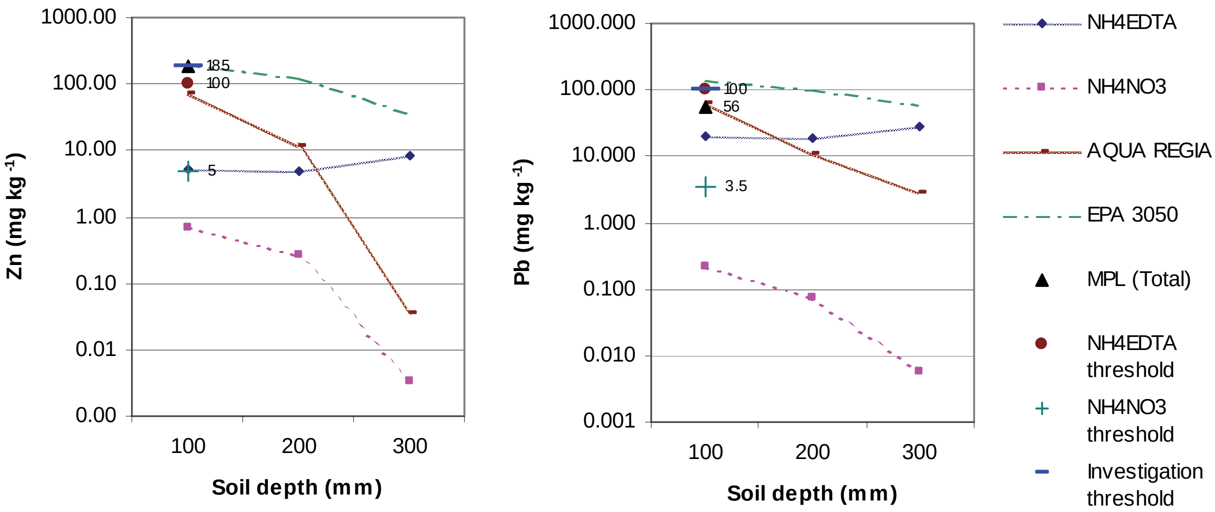


Figure 5.6: Zn and Pb contents of the soil profile at Site 6

5.1.7 Site 7

This water purification facility is situated on a shallow (<400mm), sandy clay loam Westleigh soil (orthic A, soft plinthic B) with 13-20% clay. The facility receives an average of 8Ml domestic wastewater per day and produces waste activated and digested sludge. The sludge has been air dried on drying beds and stockpiled on site for the past 20 years. There is no groundwater monitoring and the nearest surface water body is 200m from the disposal site.

Table 5.7: Site 7 general soil and sludge data

Soil depth (mm)	**Total P %**	**Total N %**	**C %**	**Clay %**	**pH (H_2O)**	
0-100	0.19	0.22	1.98	13.33	3.60	
100-200	0.07	0.07	0.74	17.33	5.92	
200-300	0.03	0.04	0.34	18.00	6.68	
SLUDGE	1.2	3.31	43	-	6.08	
Sludge data (*aqua regia*) mg kg^{-1}						
Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
4.7	30.9	321.6	581.8	200.9	201.0	3238.8

The data in Table 5.7 indicate a slight buildup of total P, N and organic C in the top 200mm soil layers with a decrease lower in the soil profile. The pH(H_2O) of the topsoil is extremely acid and increase to neutral at 300mm (van der Watt & van Rooyen, 1990). The Ni and Zn contents of the sludge is higher than the guideline values (WRC, 2002).

The total Cr, Co and Ni concentrations (*aqua regia* and EPA 3050 digestions) of the whole soil profile are well above the MPL for South African soils (Nat. Dept. Health & Pop. Dev., 1991), while the total Zn concentration in the topsoil is equal to the MPL concentration, decreasing with depth (Figure 5.7).

The NH_4EDTA extractable fractions of all these elements are below the NH_4EDTA threshold values suggested by Bruemmer & van der Merwe (1989), while the NH_4NO_3 extractable Ni and Zn concentrations in the top 200mm soil layers are higher than the NH_4NO_3 guidelines (Baden-Wurttemberg, 1993), but decrease towards the 300mm soil layer.

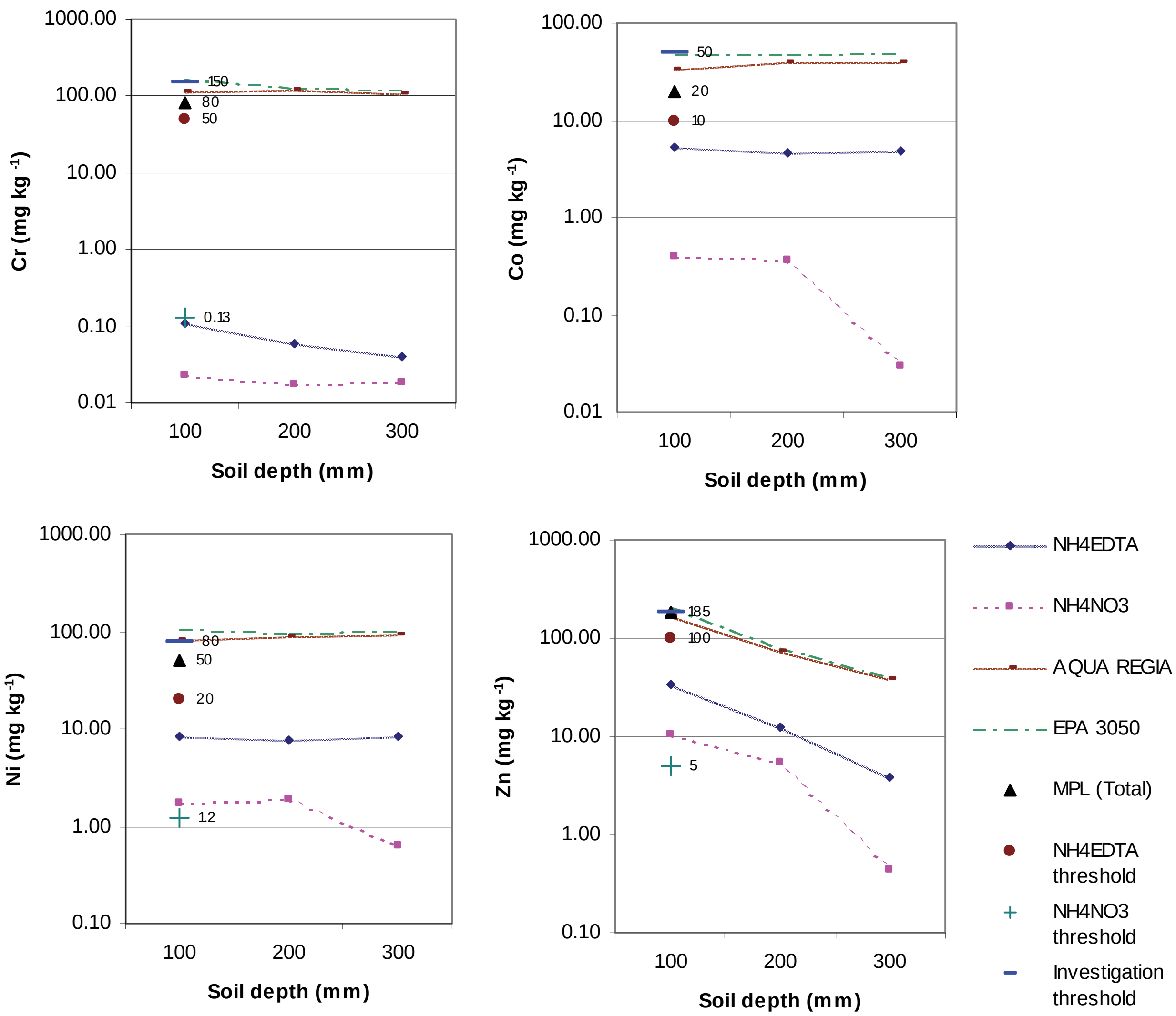


Figure 5.7: Cr, Co, Ni and Zn contents of the soil profile at Site 7

Since this is a domestic wastewater treatment facility with low Cr and Co concentrations in the sludge, the constant distribution of these metals in the soil indicates that these concentrations are probably due to high baseline concentrations in the soil (Herselman & Steyn, 2001) rather than sludge application. The higher Ni and Zn concentrations in the topsoil, decreasing down the soil profile indicate adsorption of Ni and Zn and some leaching due to the low pH(H_2O) of the topsoil (Kabata-Pendias & Pendias, 1992).

5.1.8 Site 8

This site is situated on a very shallow, sandy loam, Glenrosa soil (orthic A, lithocutanic B). It is a small sewage treatment facility (5 Ml/day inflow) that receives 35% industrial effluent. The waste activated sludge is pumped into drying beds and, once dry, it is stockpiled on site. The disposal site is on a level plain with no boreholes on site. Due to the shallow soil, samples could be taken at only three depths from the stockpile footprint.

The data in Table 5.8 show that the whole soil profile is enriched with P, N and organic C. The total N buildup is not as high as expected with 4.87%N added on top of the soil. The low soil pH(H_2O) indicates extreme acidity (below 4.5).

Table 5.8: Site 8 general soil and sludge data

<table>
<tr><th>Soil depth (mm)</th><th>Total P %</th><th>Total N %</th><th>C %</th><th>Clay %</th><th>pH (H_2O)</th></tr>
<tr><td>0-100</td><td>0.17</td><td>0.17</td><td>1.76</td><td>10.0</td><td>4.39</td></tr>
<tr><td>100-200</td><td>0.08</td><td>0.09</td><td>0.98</td><td>10.7</td><td>4.43</td></tr>
<tr><td>200-300</td><td>0.09</td><td>0.10</td><td>1.09</td><td>14.0</td><td>4.56</td></tr>
<tr><td>SLUDGE</td><td>1.46</td><td>4.87</td><td>55</td><td>-</td><td>6.32</td></tr>
</table>

<table>
<tr><th colspan="7">Sludge data (aqua regia) mg kg^{-1}</th></tr>
<tr><th>Cd</th><th>Co</th><th>Cr</th><th>Cu</th><th>Ni</th><th>Pb</th><th>Zn</th></tr>
<tr><td>5.2</td><td>9.9</td><td>377.0</td><td>1310.1</td><td>269.5</td><td>219.4</td><td>2150.1</td></tr>
</table>

The total Cr and Cu concentrations of the top 200mm of the soil profile exceed the MPL for South African soils (Dept. Nat. Health & Pop. Dev., 1991), decreasing slightly with depth (Figure 5.8). The very low soil pH(H_2O), as well as the low clay content of the soil is the reason for the mobility of the Cr and Cu to a depth of 200mm.

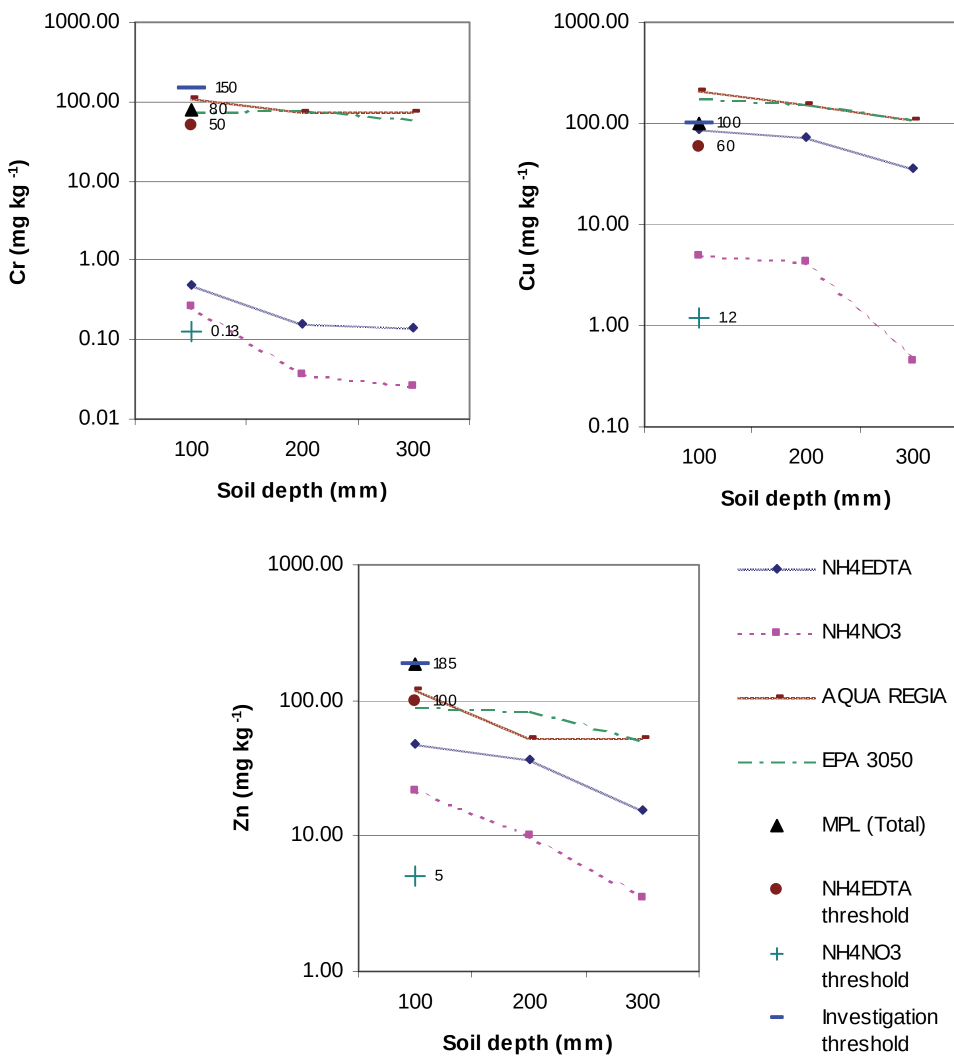


Figure 5.8: Cr, Cu and Zn contents of the soil profile at Site 8

The bio-available Cr and Zn are well below the threshold value (Bruemmer & van der Merwe, 1989), but the bio-available Cu exceeds this value. The Cr, Cu and Zn concentrations in the NH_4NO_3 soil extract in the top 200mm soil layers exceed the guideline values of Baden-Wurttemberg (1993), but decrease significantly with depth. This indicates that the attenuation capacity of the topsoil is exceeded and that these metals move downward in the soil profile, with potential future risk for groundwater pollution. Nitrate pollution of the groundwater is also a probability because there is no correspondence between the amount of N added and the amount present in the soil.

5.1.9 Site 9

Site 9 is situated on a Glenrosa soil (orthic A, lithocutanic B) with <25% clay. It is a waste activated wastewater treatment facility, receiving an average of 10Ml/day wastewater of which 20% are industrial effluent (powder coating, metal plating, litho-plating, paint, dye, breweries, food and beverage, pulp and paper). The sludge is dried on drying beds and the dried sludge is stockpiled on site. The soil samples were taken on the stockpile footprint. The disposal site is on a flat surface and 800m from a river. There are no boreholes on site.

The total P and N concentrations in the top 300mm of the soil profile are above average as is the organic C content of the whole soil profile (Table 5.9) (Sparks, 1996; MVSA, 1997). The pH(H_2O) of the soil profile is medium acid in the top soil layers and extremely acid in the 300-500mm soil layers (van der Watt & van Rooyen, 1990). The Cu, Ni and Zn concentrations in the sludge is higher than the guideline values for type D sludge (WRC, 2002).

Table 5.9: Site 9 general soil and sludge data

Soil depth (mm)	Total P %	Total N %	C %	Clay %	pH (H_2O)	
0-100	1.11	0.25	2.04	18.7	5.69	
100-200	0.94	0.18	1.65	20.7	5.77	
200-300	1.23	0.19	1.60	15.3	5.80	
300-400	0.81	0.10	1.06	24.0	4.17	
400-500	0.84	0.13	1.30	22.0	4.12	
SLUDGE	1.56	3.41	56	-	6.77	
Sludge data (*aqua regia*) mg kg^{-1}						
Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
10.8	79.4	1589.4	2243.6	659.8	181.7	4524.4

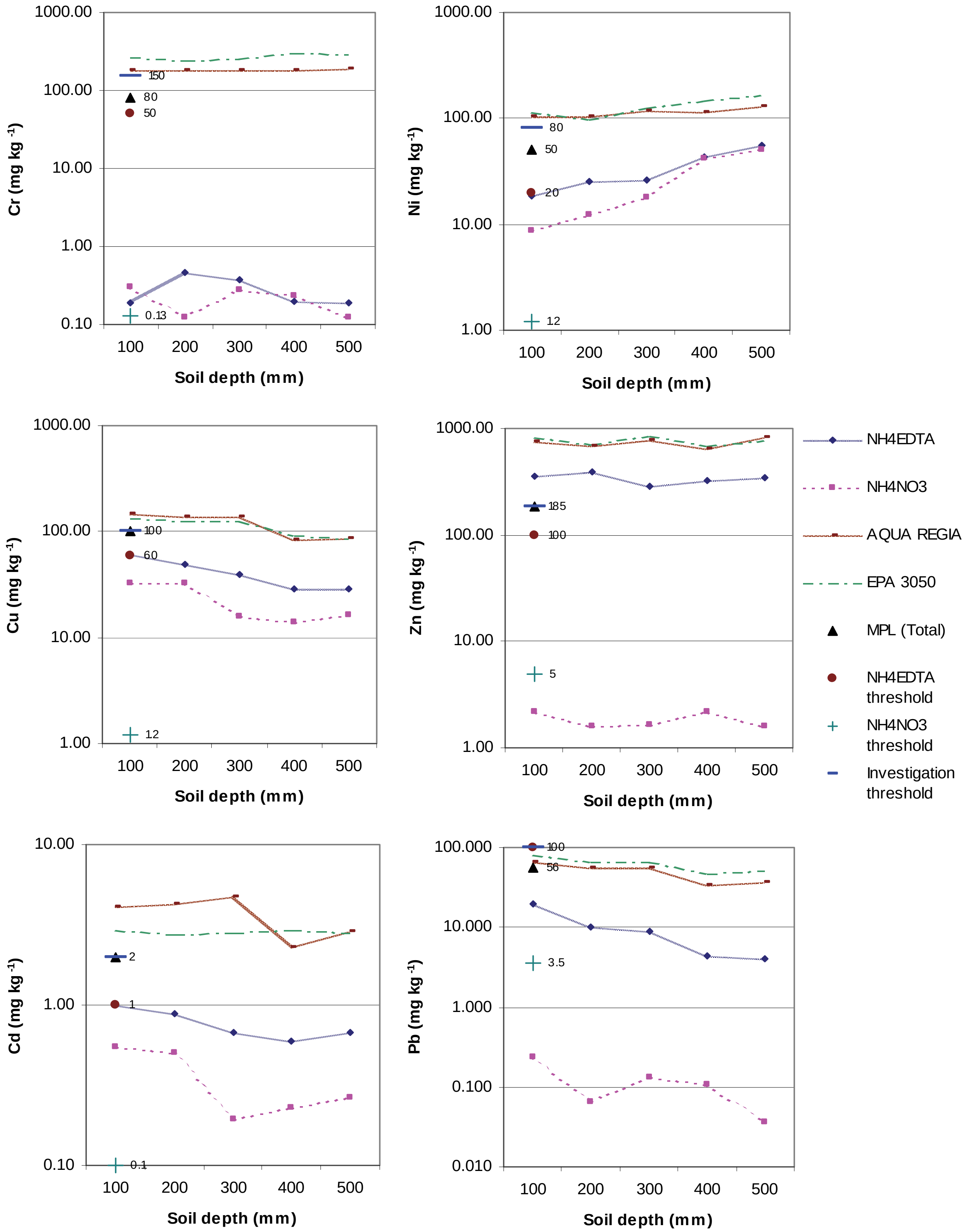


Figure 5.9: Cr, Ni, Cu, Zn, Cd and Pb contents of the soil profile at Site 9

Figure 5.9 shows that the total concentrations of Cr, Ni, Cu, Zn, Cd and Pb in the whole soil profile exceed the MPL for South African soils (Dept. Nat. Health & Pop. Dev., 1991) as well as the suggested investigation threshold levels (Herselman & Steyn, 2001). The decrease in Cu, Zn, Cd and Pb concentrations below 300mm indicates that the concentration in the topsoil is due to sludge application and the movement of the metals to a depth of 300mm. The leaching mainly occur due to the low pH(H_2O) of the soil which renders the metals mobile (Kabata-Pendias & Pendias, 1992) and the high metal load added to the soil.

The bio-available Ni, Cu, Zn and Cd exceed the threshold values for NH_4EDTA extractable metals (Bruemmer & van der Merwe, 1989) and the NH_4NO_3 extractable Ni, Cu and Cd concentrations in the whole soil profile exceed the guideline values set for groundwater protection (Baden-Wurttemberg, 1993) and are reason for concern. Groundwater should be monitored to, especially since the subsoil pH(H_2O) is very low and the N and metal load are very high.

5.1.10 Site 10

Site 10 is situated on a Westleigh soil (orthic A, soft plinthic B) with <28% clay. A quarter of the inflow is from an industrial area (food and beverage, textile). It is a waste activated treatment plant with anaerobic digesters. The sludge is pumped to drying beds and the dry sludge is stockpiled on site. Some of the dry sludge is used, together with other materials, for compost. The soil samples were taken on the footprint of a stockpile after removing the sludge. The terrain is level and the disposal site is 1km from a river. No groundwater monitoring takes place at this site.

There is only a slight increase in the total P and N concentrations in the top 100mm soil layer (Table 5.10). The organic C content of the soil is normal for South African soils and decrease gradually with depth. The soil pH(H_2O) indicates a strongly acid soil. The concentrations of Co, Cu, Ni, Pb and Zn in the sludge exceed the guidelines levels for type D sludge and the Cd concentrations is just below the guideline value(WRC, 2002).

Table 5.10: Site 10 general soil and sludge data

Soil depth (mm)	Total P %	Total N %	C %	Clay %	pH (H_2O)
0-100	0.11	0.10	1.05	26.0	5.40
100-200	0.04	0.04	0.75	26.0	4.53
200-300	0.04	0.04	0.64	24.0	4.55
300-400	0.04	0.04	0.58	28.0	4.46
400-500	0.04	0.04	0.45	28.0	4.30
SLUDGE	2.36	1.87	25	-	7.12

Sludge data (*aqua regia*) mg kg^{-1}						
Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
19.2	102.2	1085.3	950.7	399.4	1296.9	5441.2

The total (*Aqua regia* & EPA 3050) Cr and Ni concentrations exceed the MPL for South African soils (Dept. Nat. Health & Pop. Dev., 1991) (Figure 5.10). The bio-available fractions of all heavy metals are below the threshold values for NH_4EDTA extractable metals (Bruemmer & van der Merwe, 1989), but the NH_4NO_3 extractable Cu concentration of the whole soil profile is above the NH_4NO_3 guidelines set for groundwater protection by Baden-Wurttemberg (1993). The concentrations of the metals are uniformly spread through the soil profile with no significant decreases with depth. This indicates movement of the metals in the profile, probably due to the extremely low pH(H_2O) of the soil. The clay can only adsorb limited amounts of metals before the attenuation capacity of the soil is exceeded. The groundwater at this site should be monitored since the soluble Cu content of the soil is very high.

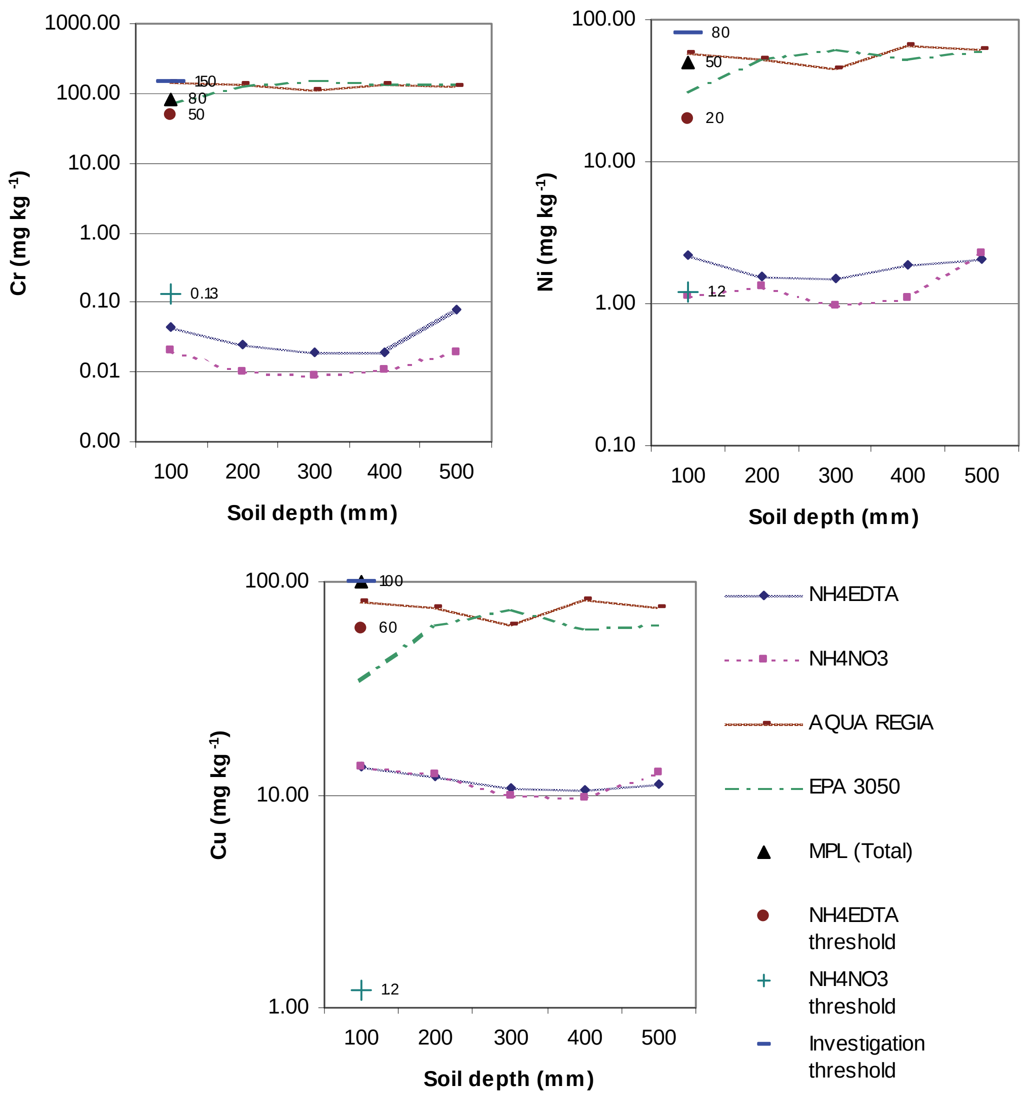


Figure 5.10: Cr, Ni and Cu contents of the soil profile at Site 10

5.1.11 Site 11

Wastewater treatment facility 11 is a new bio-filter and anaerobic digester plant. It is a small facility (4Ml/day) and receives only domestic wastewater, with a low metal load (Table 5.11). The sludge is dried in drying beds and has been stockpiled for the past 4 years. The local municipality uses the dry sludge for fertilizer on a golf course and other gardens in town. It is situated on a Hutton soil with low clay content (<12%) and the slope of the disposal site is minimal. There is no borehole on site and the nearest river is >5km from the disposal site.

Table 5.11: Site 11 general soil and sludge data

Soil depth (mm)	Total P %	Total N %	C %	Clay %	pH (H_2O)	
0-100	0.06	0.08	0.99	8.0	6.73	
100-200	0.04	0.04	0.40	12.0	6.81	
200-300	0.02	0.03	0.36	12.0	7.64	
300-400	0.03	0.05	0.66	10.0	7.94	
SLUDGE	0.73	3.17	45	-	5.99	
Sludge data (*aqua regia*) mg kg^{-1}						
Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
3.74	10.6	192.9	370.1	158.5	149.6	2222.3

Table 5.11 contains the general soil data and indicates that the top 100mm of soil has a slightly higher organic C content than the other soil samples, as well as higher total P and N concentrations. The pH(H_2O) of the soil profile is neutral (top 200mm) to mildly alkaline (van der Watt & van Rooyen, 1990).

The concentrations of all metals with all extraction methods are below the respective guideline values (Bruemmer & van der Merwe, 1989; Nat. Dept. Health & Pop. Dev., 1991; Baden-Wurttemberg, 1993). Only the total Cr concentration is near the MPL for South African soils and stays constant through the soil profile (Figure 5.11). The fact that the total Cr concentration of a new treatment facility that receives only domestic wastewater exceeds the MPL for South African soil, indicates that the Cr concentration may be due to the high background concentration of Cr in South African soils (Cr – 5.82-353 mg kg^{-1}) (Herselman & Steyn, 2001).

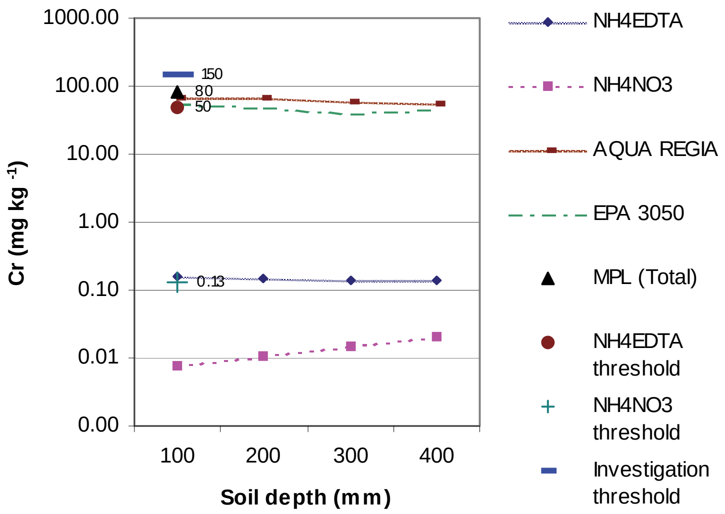


Figure 5.11: Cr content of the soil profile at Site 11

5.1.12 Site 12

Site 12 is situated on an Arcadia soil (vertic A) with high clay content (38 – 46%). Waste activated as well as anaerobic digested sludge is produced and dried on drying beds. The dry sludge has been stored in stockpiles on site for 30+ years and used by farmers and the local municipality. Soil samples were taken on the footprint of a stockpile. The plant receives 10% industrial effluent of 26Ml/day inflow from various factories (breweries, food and beverage, fats, oils and grease). The disposal site is 4ha, on even terrain and 800m from a river with no borehole on site.

The soil analysis data (Table 5.12) show no real elevation in total P, N or organic C in the top 200mm of the soil profile, although large amounts are added with the sludge. The soil pH(H_2O) is mildly alkaline. The sludge data indicate high concentrations of Cu, Ni and Zn.

The total Cr, Co and Ni concentrations in the whole soil profile exceed the MPL for South African soils (Dept. Nat. Health & Pop. Dev., 1991), and the investigation thresholds suggested by Herselman & Steyn (2001) (Figure 5.12). There is only a slight decrease in the metal content of the soil profile with depth.

Table 5.12: Site 12 general soil and sludge data

Soil depth (mm)	Total P %	Total N %	C %	Clay %	pH (H_2O)	
0-100	0.05	0.04	0.56	44.0	7.33	
100-200	0.04	0.04	0.55	46.0	7.34	
200-300	0.06	0.03	0.61	45.0	7.45	
300-400	0.03	0.03	0.44	38.0	7.50	
SLUDGE	1.94	4.11	52	-	6.19	
Sludge data (*aqua regia*) mg kg^{-1}						
Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
7.34	17.8	291.9	858.4	363.7	376.8	4196.8

The NH_4EDTA and NH_4NO_3 extractable fractions of all metals are below the thresholds set by Bruemmer & van der Merwe (1989) and Baden-Wurttemberg (1993) except the NH_4NO_3 extractable Ni, which is above the guideline level in the topsoil.

Although the clay content and pH(H_2O) of this soil is high, the attenuation capacity of the soil is probably exceeded after 30+ years of sludge application with high metal and nitrogen loads, and leaching is possible. Groundwater monitoring is advised.

5.1.13 Site 13

Situated in a deep, sandy Fernwood soil (orthic A, regic sand), Site 13 receives 3Ml/day raw sewage per day of which half is from industries. In the past the waste activated sludge were dried in drying beds and stockpiled on site but during the last 5 years the sludge is removed and disposed of by another wastewater treatment facility nearby. The soil samples were taken at the footprint of the old stockpile.

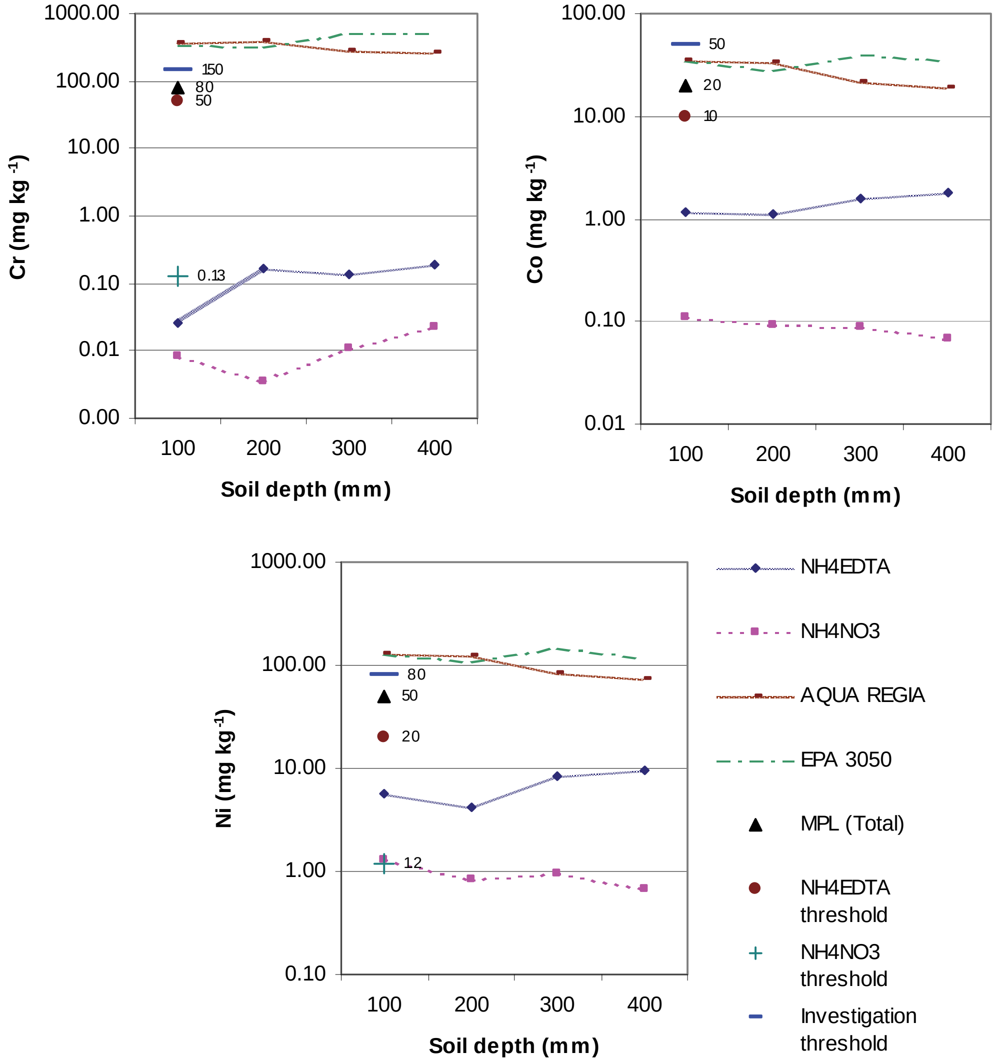


Figure 5.12: Cr, Co and Ni contents of the soil profile at Site 12

The general soil data (Table 5.13) show higher total P, N and organic carbon contents in the topsoil with a gradual decrease with depth in the soil profile. The pH(H_2O) of the soil is medium acid (van der Watt & van Rooyen, 1990). All metals in the sludge, except Ni, are within the guideline levels (WRC, 2002).

Table 5.13: Site 13 general soil and sludge data

Soil depth (mm)	Total P %	Total N %	C %	Clay %	pH (H_2O)
0-100	0.11	0.07	1.44	6.67	5.97
100-200	0.04	0.05	0.50	8.67	6.59
200-300	0.03	0.01	0.15	7.33	6.77
300-400	0.02	0.05	0.11	6.67	6.62
400-500	0.02	0.01	0.10	6.00	6.36
SLUDGE	0.57	3.17	43	-	5.29

Sludge data (*aqua regia*) mg kg^{-1}						
Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
1.9	4.9	438.1	365.3	246.8	276.0	1470.3

The total Ni, Cu and Zn concentrations of the topsoil are higher than the MPL for South African soils (Nat. Dept. Health & Pop. Dev., 1991) but decrease considerably with depth in the soil profile (Figure 5.13). The bio-available fractions of all elements are below the NH_4EDTA threshold values suggested by Bruemmer & van der Merwe (1989), but the NH_4NO_3 extractable Ni and Zn of the topsoil is higher than the guidelines set to protect groundwater (Baden-Wurttemberg, 1993).

Technically, all metals added to this soil should leach easily due to the low clay content and low pH(H_2O) of the soil (Kabata-Pendias & Pendias, 1992; Alloway, 1995). However, leaching in this soil occurred only to a depth of 300mm. The only explanation is that small amounts of dry sludge, with a low metal load, are disposed of on site and the organic C in the top 200mm soil adsorbs the metals and renders it immobile. Groundwater should be monitored because it is a sandy soil with low pH(H_2O) and nitrogen may leach through the profile.

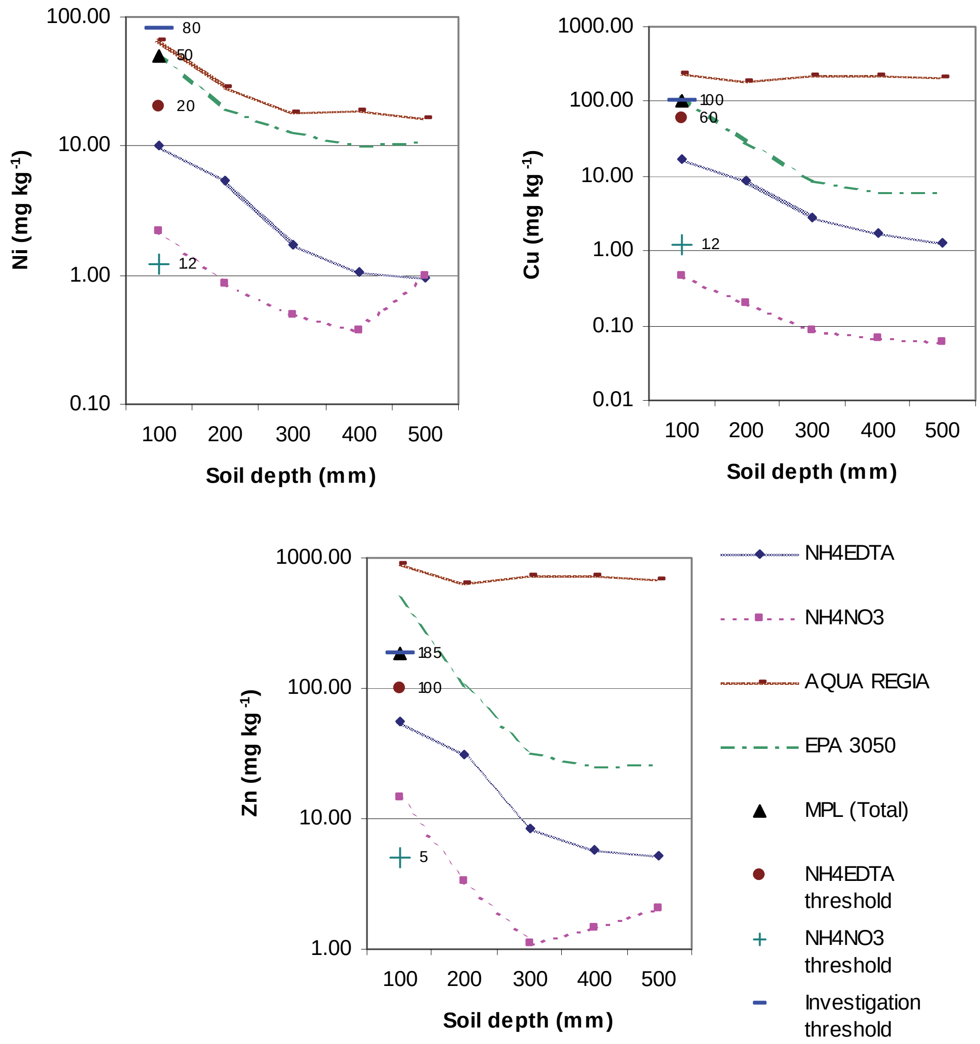


Figure 5.13: Ni, Cu and Zn contents of the soil profile at Site 13

5.1.14 Site 14

This wastewater treatment facility has been in operation for more than 30 years. The facility has bio-filters, anaerobic digesters and a waste activated sludge part. The site is situated on a sandy loam Bainsvlei soil (orthic A, red apedal B, soft plinthic B). The sludge is dried on drying beds and stockpiled on site.

Table 5.14: Site 14 general soil and sludge data

Soil depth (mm)	Total P %	Total N %	C %	Clay %	pH (H_2O)	
0-100	1.28	0.26	1.48	15.00	5.98	
100-200	0.40	0.18	1.26	15.00	6.96	
200-300	0.11	0.10	0.96	15.00	7.14	
SLUDGE	0.97	3.75	49	-	6.51	
Sludge data (*aqua regia*) mg kg^{-1}						
Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
3.9	5.3	77.9	269.2	130.7	217.9	866.9

There are higher total P and N concentrations in the top 200mm of soil than lower in the profile. The organic C content is high in the whole profile and the pH(H2O) are medium acid in the topsoil increasing to neutral at 300mm (Table 5.14). The concentrations of all metals are within the guidelines for type D sludge (WRC, 2002).

After 30 years of sludge application, the total Ni, Cu, Zn and Pb concentrations are above the MPL for South African soils (Nat. Dept. Health & Pop. Dev., 1991) and decrease with depth. The bio-available concentrations of all the metals are well below the NH_4EDTA threshold values (Bruemmer & van der Merwe, 1989) and only the soluble Ni concentration is higher than the NH_4NO_3 guidelines (Baden-Wurttemberg, 1993).

There is an accumulation of metals in the topsoil and leaching to 200mm. The organic material in the topsoil adsorb some metals but leaching still occur due to the low pH(H_2O) and clay content of the soil and groundwater monitoring is advised.

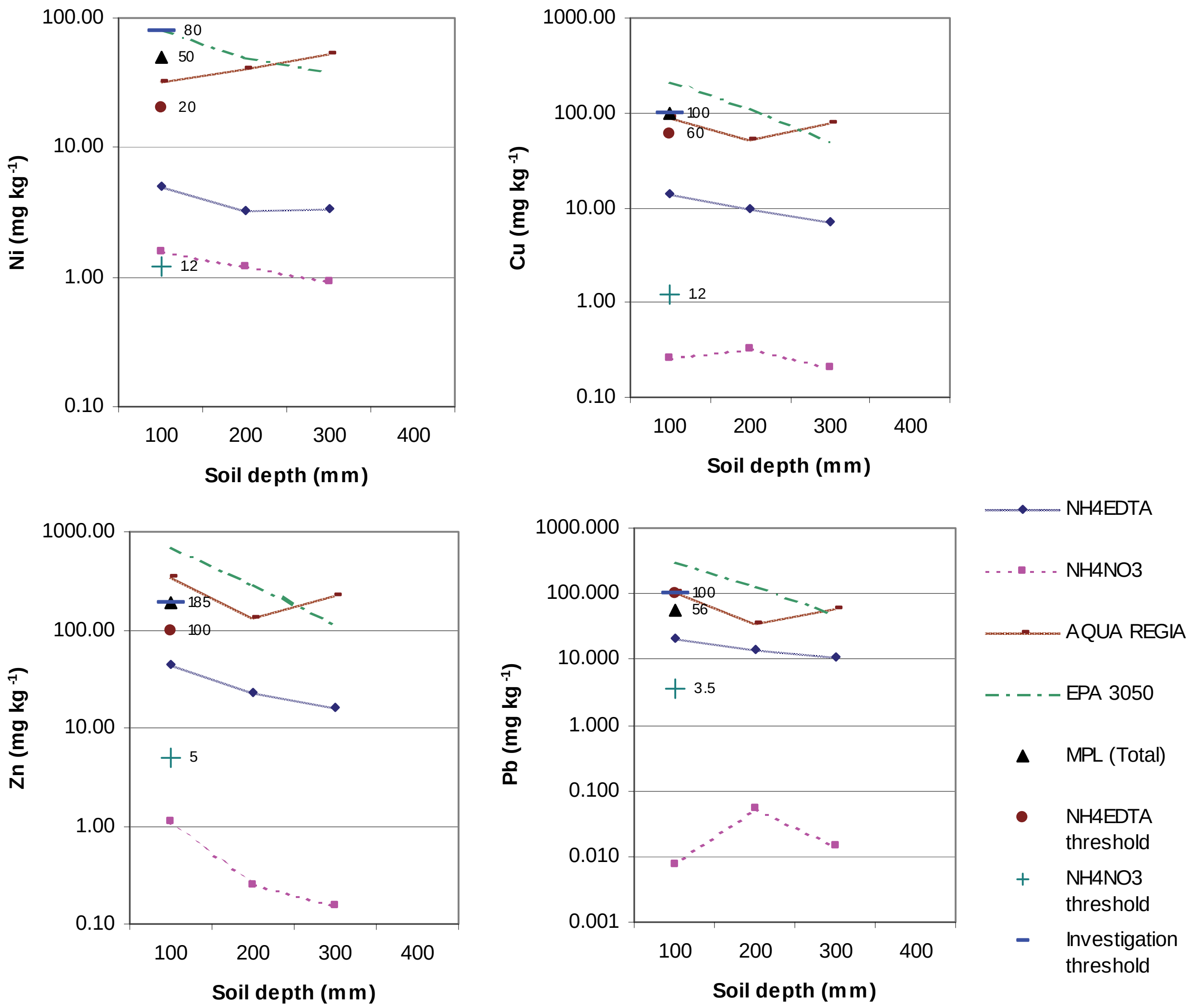


Figure 5.14: Ni, Cu, Zn and Pb contents of the soil profile at Site 14

5.1.15 Site 15

Site 15 receives only domestic inflow (12Ml/day) and produces combined bio-filter and activated sludge. The sludge is dried on drying beds and stockpiled on site. It is a new water purification plant and has been in use for 3 years. Although there is a river near the disposal site (300m), the slope is very gentle and the possibility for run-off is minimal. No groundwater sample could be obtained because the pump was out of order.

Because of the age of the disposal site, no buildup of organic C or other elements occurred (Table 5.15). The site is on a Clovelly soil (orthic A, yellow-brown apedal B) with low clay content (<15%). The low pH(H_2O) of the soil indicates acidity.

Table 5.15: Site 15 general soil data

Soil depth (mm)	Total P %	Total N %	C %	Clay %	pH (H_2O)
0-100	0.02	0.03	0.17	11.0	5.01
100-200	0.02	0.03	0.19	12.0	5.78
200-300	0.02	0.02	0.15	13.0	5.18
300-400	0.02	0.02	0.27	13.0	4.57
400-500	0.02	0.02	0.18	13.0	4.74

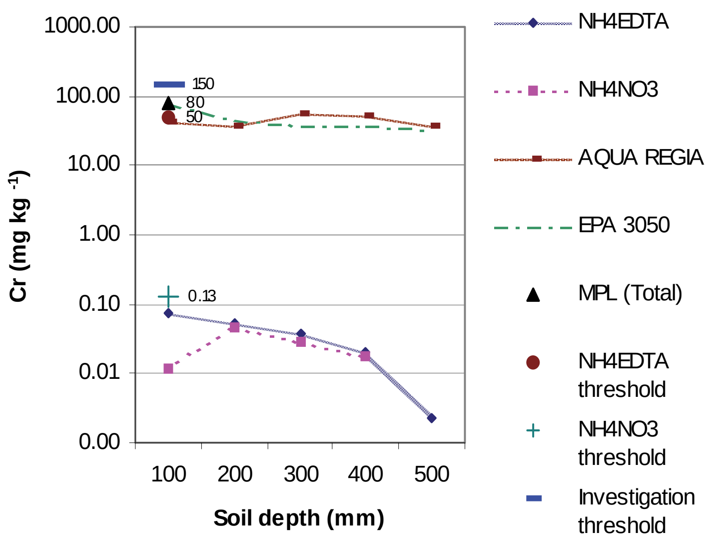


Figure 5.15: Cr content of the soil profile at Site 15

Only the total concentration of Cr (top 100mm) exceeds the MPL for South African soils (Dept. Nat. Health & Pop. Dev., 1991) and the concentration slightly decrease down the soil profile (Figure 5.15). The high total Cr concentration in the soil may be due to the high background concentration of Cr in South African soils (5.82-353 mg kg^{-1}) (Herselman & Steyn, 2001). The bio-available and soil solution fractions are well below the threshold values of Bruemmer & van der Merwe (1989) and Baden-Wurttemberg (1993). Due to the low clay content and pH(H_2O) of the soil, groundwater monitoring is advised.

5.1.16 Site 16

Site 16 is a small wastewater treatment facility that receives an average of 5Ml/day raw wastewater of which 25% is of industrial origin. For the past 25 years the facility produced anaerobic digested sludge, which have been air-dried on drying beds and stockpiled on site. The underlying soil is Milkwood (melanic A, hard rock) with 14-20% clay. Soil sampling was executed at the footprint of a stockpile.

The data in Table 5.16 indicate a buildup of total P and N in the topsoil with a gradual decrease with depth. The organic C content of the whole soil profile is high, which is a requirement for a melanic horizon. The much higher organic C in the topsoil is probably due to the sewage sludge disposal. The total metal concentrations in the sludge are within the guideline values (WRC, 2002).

Table 5.16: Site 16 general soil and sludge data

Soil depth (mm)	**Total P %**	**Total N %**	**C %**	**Clay %**	**pH (H_2O)**	
0-100	0.19	0.44	4.51	20.00	4.67	
100-200	0.09	0.26	2.69	19.33	5.74	
200-300	0.07	0.19	2.02	14.00	6.64	
SLUDGE	0.57	3.4	51	-	5.82	
Sludge data (*aqua regia*) mg kg^{-1}						
Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
2.6	8.3	62.4	378.5	244.6	186.3	1215.5

The total Ni, Cu, Zn, Cd and Pb concentrations of the whole soil profile are above the MPL for South African soils (Nat. Dept. Health & Pop. Dev., 1991) and the suggested investigation threshold levels (Herselman & Steyn, 2001), but

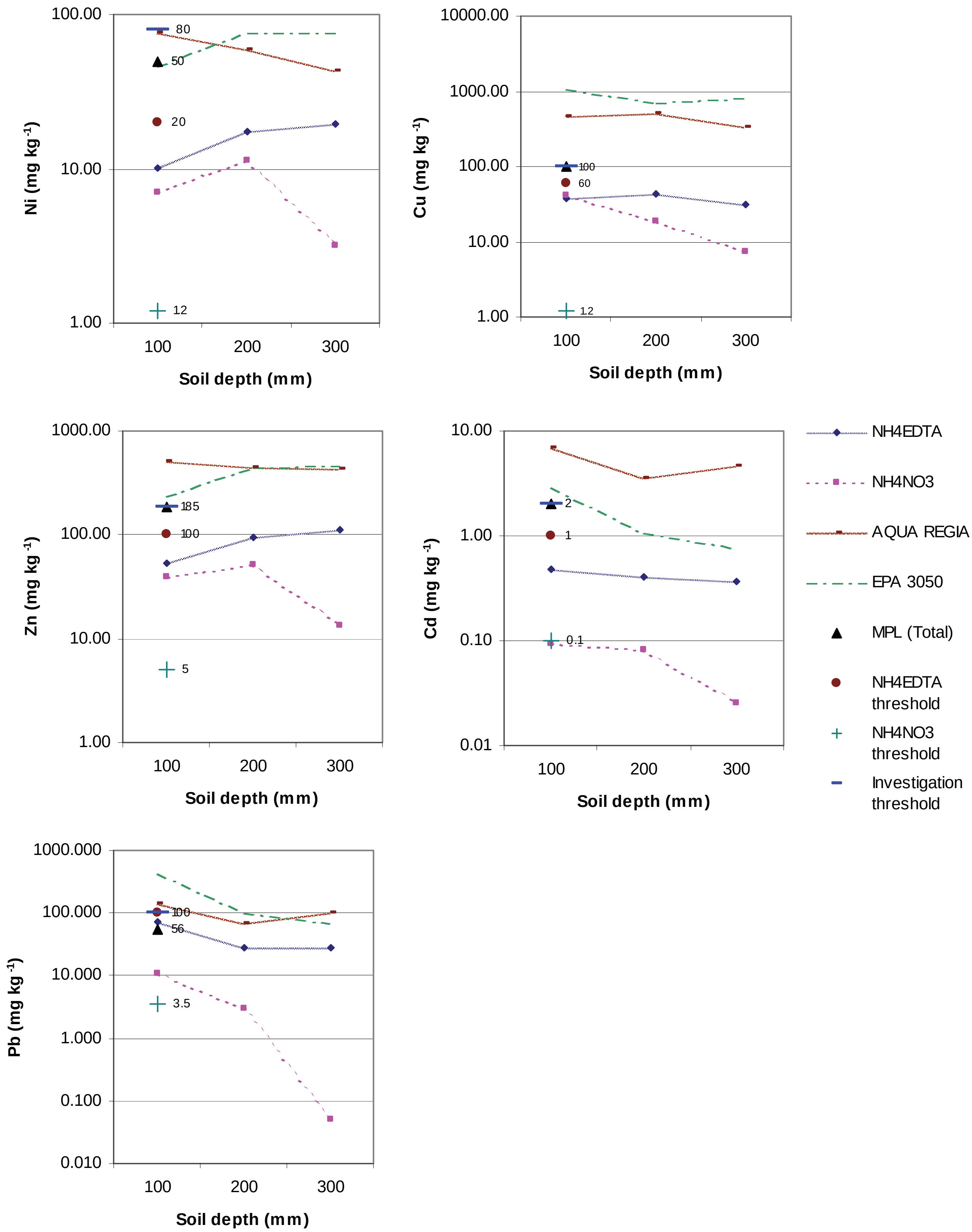


Figure 5.16: Ni, Cu, Zn, Cd and Pb contents of the soil profile at Site 16

gradually decrease with depth in the profile (Figure 5.16). The bio-available concentrations of these elements are almost at the NH_4EDTA threshold values of Bruemmer & van der Merwe (1989). The soluble fractions (NH_4NO_3 extractable) of the mentioned elements are all higher than the NH_4NO_3 guidelines (Baden-Wurttemberg, 1993).

The data indicate slow leaching of the metals in the soil profile. The high organic carbon in the soil probably adsorb most of the metals and only small amounts are mobile even though the clay content and pH(H_2O) are low (Kabata-Pendias & Pendias, 1992; Alloway, 1995). Although the soluble metal concentrations decrease with depth in the soil profile, the high Ni, Cu and Zn concentrations of the whole soil profile indicate risk to the groundwater. Groundwater monitoring is suggested at this site.

5.1.17 Site 17

Site 17 is situated on a deep, sandy Clovelly (orthic A, yellow-brown apedal B) with a very low clay content. It is a small water purification facility, which receives only 5% industrial effluent. The waste activated as well as digested sludge is dried on drying beds and stockpiled on site. Data on groundwater monitoring is still awaited from site manager.

The general soil data show only a very slightly higher total P and N content in the topsoil (Table 5.17). There is an accumulation of organic material in the top 200mm soil layers with a gradual decrease with depth in the soil profile. The pH(H_2O) of the soil is strongly acid. The total metal concentration of the sludge are within the guidelines for type D sludge (WRC, 2002).

Table 5.17: Site 17 general soil and sludge data

Soil depth (mm)	Total P %	Total N %	C %	Clay %	pH (H_2O)
0-100	0.02	0.04	0.53	3.33	5.58
100-200	0.01	0.03	0.33	2.67	5.28
200-300	0.01	0.02	0.27	2.67	5.07
300-400	0.01	0.02	0.18	2.00	5.02
400-500	0.01	0.02	0.19	2.00	5.10
SLUDGE	1.42	5.02	65	-	5.92

Sludge data (*aqua regia*) mg kg^{-1}

Cd	Co	Cr	Cu	Ni	Pb	Zn
4.8	5.2	265.4	525.3	179.4	258.3	1508.2

The total, bio-available and soluble fractions of all elements are well below the respective guidelines set by various authors (Bruemmer & van der Merwe, 1989; Nat. Dept. Health & Pop. Dev., 1991; Baden-Wurttemberg, 1993). Figure 5.17 gives an indication of the distribution of Zn and Pb in the soil profile. The concentrations are generally higher in the topsoil and decrease with depth.

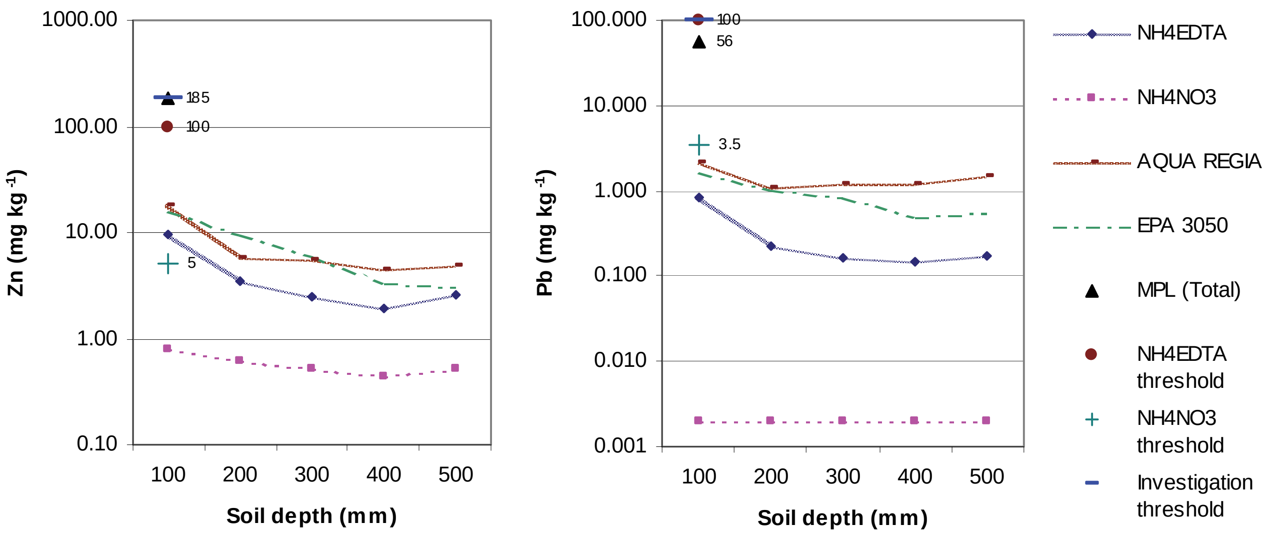


Figure 5.17: Zn and Pb contents of the soil profile at Site 17

According to Kabata-Pendias & Pendias (1992) and Alloway (1995), the low clay content and pH(H_2O) of the soil should lead to leaching of metals in the soil profile. The attenuation capacity of the topsoil has probably not been exceeded, therefore there is no movement of heavy metals in the soil profile. the groundwater should be monitored for NO_3 contamination due to the high lad of application.

5.1.18 Site 18

Site 18 is situated on a shallow, sandy Mispah (orthic A, hard rock). The facility produces combined waste activated and digested sludge, which is dried on drying beds and stockpiled on site. There are no boreholes on site and the nearest surface water body is 2km from the disposal site. Samples were taken on the footprint of the stockpile, but only to a depth of 200mm due to the shallow soil.

Data in Table 5.18 indicate accumulation of P, N and organic C in the top 200mm, probably due to the impermeable layer underneath. The pH(H_2O) is mildly alkaline. The metal load of the sludge is below the (WRC, 2002) guidelines for type D sludge (2002).

Table 5.18: Site 18 general soil and sludge data

Soil depth (mm)	Total P %	Total N %	C %	Clay %	pH (H_2O)
0-100	0.09	0.09	0.71	4.00	7.42
100-200	0.11	0.08	0.67	5.33	7.81
SLUDGE	1.06	3.99	45	-	5.97

Sludge data (*aqua regia*) mg kg^{-1}

Cd	Co	Cr	Cu	Ni	Pb	Zn
4.8	8.7	86.9	641.3	157.6	258.9	2081.1

The total Cu and Zn concentrations of the soil profile are almost at the MPL for South African soils (Nat. Dept. Health & Pop. Dev., 1991) and stay constant in the 200mm soil (Figure 5.18). The bio-available and soluble fractions are below the guideline levels set for these extraction methods (Bruemmer & van der

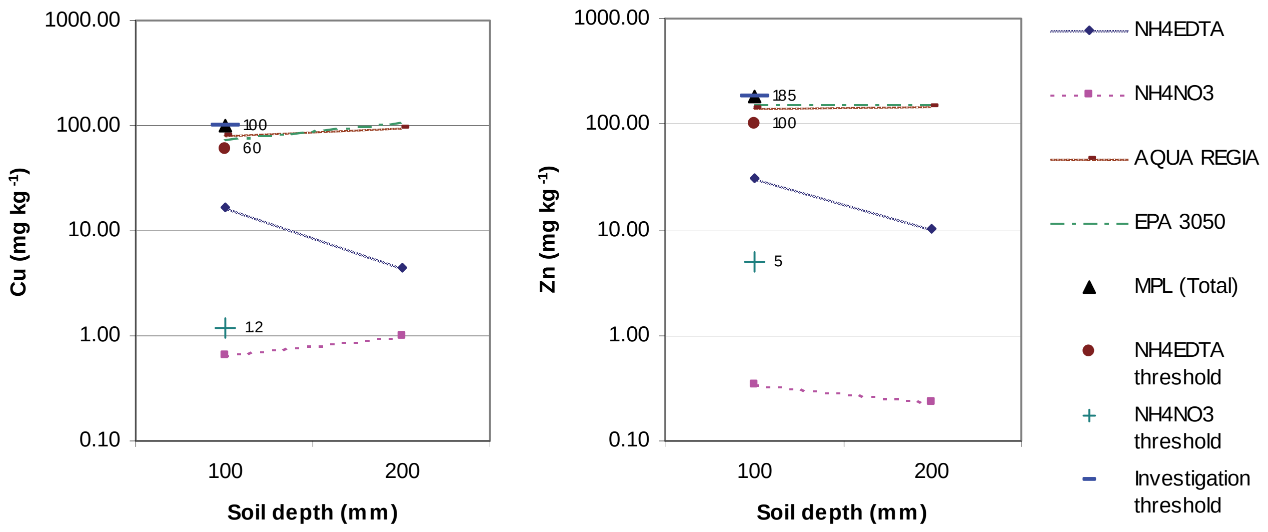


Figure 5.18: Cu and Zn contents of the soil profile at Site 18

Merwe, 1989; Baden-Wurttemberg, 1993) and decrease with depth. The high pH(H_2O) of the soil should render the metals immobile and the impermeable layer could protect the groundwater at this site, but groundwater monitoring is still advised.

5.1.19 Site 19

This site produces anaerobic digested sludge, which has been air-dried and stockpiled on site for more than 20 years. The site receives 8% industrial effluent from engineering works. The underlying soil is Hutton (orthic A, red apedal B) with 12-17% clay. There is a borehole on site, but the pumps were stolen and no groundwater sample could be obtained. The terrain is even and the disposal site is 1km from a dam.
The general soil data (Table 5.19) indicate an accumulation of total P, N and organic C in the top 100mm soil layer, decreasing with depth. The pH(H_2O) of the soil is mildly alkaline (van der Watt & van Rooyen, 1990).

Table 5.19: Site 19 general soil and sludge data

Soil depth (mm)	Total P %	Total N %	C %	Clay %	pH (H_2O)
0-100	0.06	0.09	0.97	16.00	7.66
100-200	0.02	0.05	0.43	17.33	7.89
200-300	0.02	0.04	0.29	16.67	7.76
300-400	0.01	0.04	0.29	12.67	7.56
400-500	0.01	0.05	0.31	12.00	7.38
SLUDGE	0.61	2.96	41	-	6.35

Sludge data (*aqua regia*) mg kg^{-1}						
Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
3.3	19.7	63.2	454.3	212.8	499.0	1868.4

The total Pb concentration (the only metal with a high concentration in the sludge) (Figure 5.19) in the topsoil is at the MPL for South African soils (Nat. Dept. Health & Pop. Dev., 1991) and decrease significantly with depth. The bio-available and soluble fractions are also well below the guideline levels set (Bruemmer & van der Merwe, 1989; Baden-Wurttemberg, 1993).

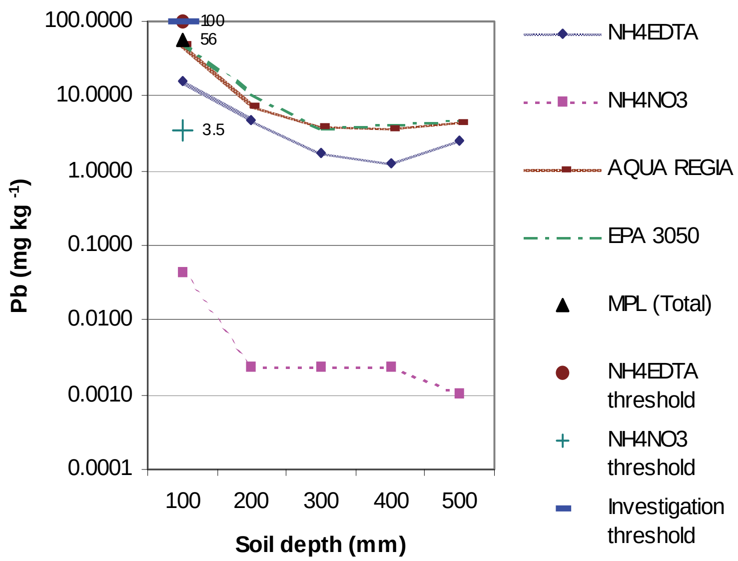


Figure 5.19: Pb content of the soil profile at Site 19

The distributions of all the metals follow the same trend in the soil than Pb. The accumulation of metals in the topsoil and the limited movement down the profile can be ascribed to the alkaline pH(H_2O) of the soil as well as the organic C and clay, which adsorb the metals (Kabata-Pendias & Pendias, 1992).

5.2 Instant lawn sites

5.2.1 Site 20

Site 20 is situated on a deep Hutton soil (orthic A, red apedal B) with <25% clay. This wastewater treatment facility receives 50% of its inflow from metal plating, paint and textile industries. The waste activated sludge and anaerobically digested sludge is mixed and irrigated daily onto instant lawn. The disposal area of 45ha is on level terrain and has been utilized for 30+ years.

Table 5.20: Site 20 general soil, sludge and groundwater data

Soil depth (mm)	**Total P %**	**Total N %**	**C %**	**Clay %**	**pH (H_2O)**
0-100	0.18	0.21	2.31	15.3	5.95
100-200	0.06	0.06	0.88	19.3	6.60
200-300	0.04	0.04	0.56	22.7	6.87
300-400	0.04	0.03	0.39	23.3	6.99
400-500	0.04	0.03	0.30	18.0	7.07
SLUDGE	2.20	3.33	70	-	6.4

Sludge data (*aqua regia*) mg kg^{-1}						
Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
15.0	24.1	458.9	1644.9	228.7	320.9	4486.3

Water data								
Cd (µg l^{-1})	**Cr (µg l^{-1})**	**Co (µg l^{-1})**	**Cu (µg l^{-1})**	**Pb (µg l^{-1})**	**Ni (µg l^{-1})**	**Zn (µg l^{-1})**	**NO_3 (mg l^{-1})**	**pH**
0.30	0.17	1.93	25.73	0.16	17.02	41.01	9.09	6.95

The topsoil is enriched with P, N and organic C but not as much as would have been expected after 30 years of sludge application (Table 5.20). This is probably due to the removal of a thin layer of soil with the harvesting of the instant lawn.

The pH(H_2O) of the soil profile is slightly acid (top 300mm) to neutral. Sludge data indicate Cu, Ni and Zn concentrations above the guideline values (WRC, 2002). The analysis data of the groundwater sample indicate that the water is suitable for irrigation but not for human consumption because the NO_3 in the water is above the water quality guideline of 6 mg l^{-1} (DWAF, 1996). The rest of the metals are all below the levels of water quality guidelines.

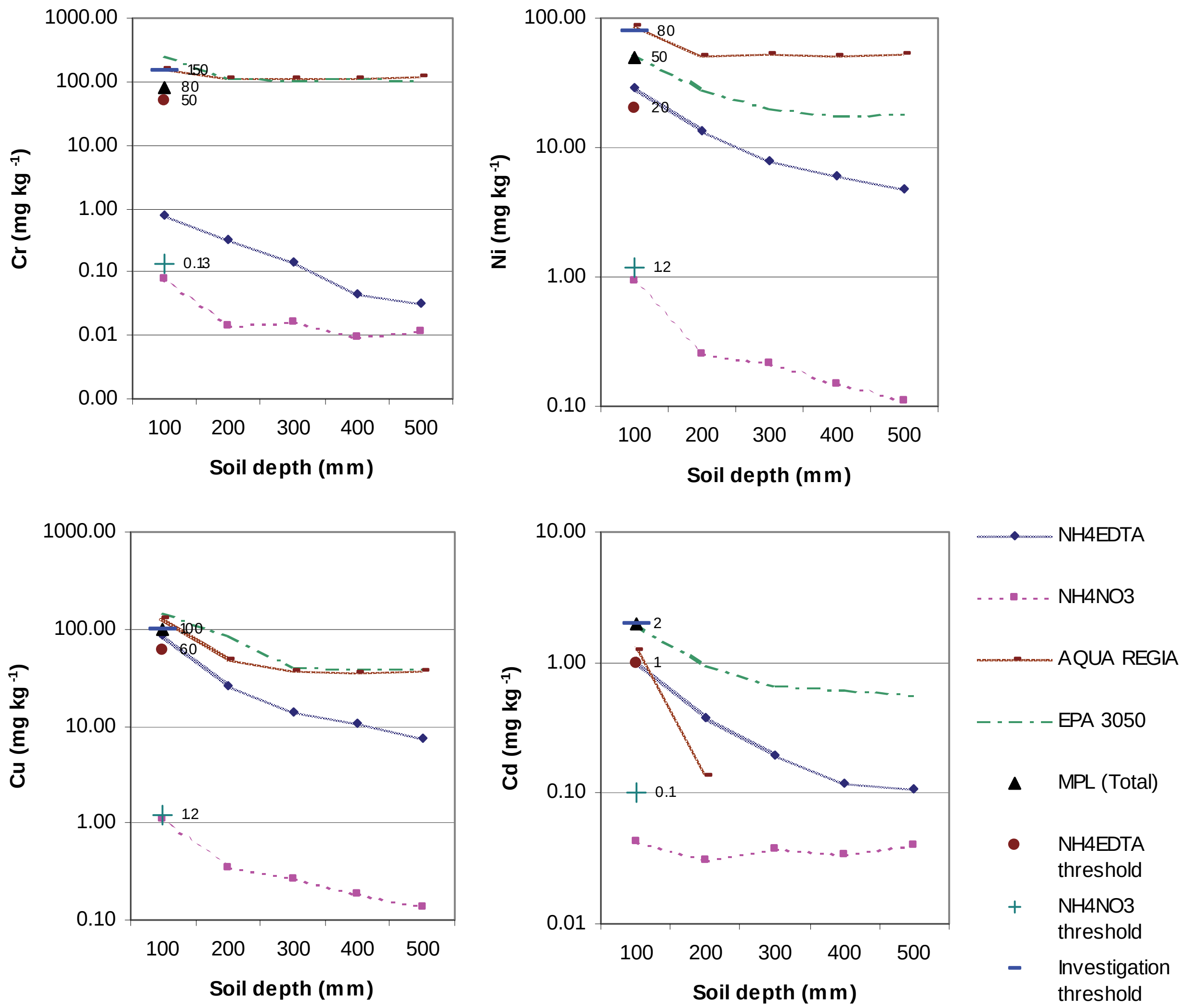


Figure 5.20: Cr, Ni, Cu and Cd contents of the soil profile at Site 20

The total concentration of Cr in the whole soil profile exceeds the MPL for South African soils (Dept. Nat. Health & Pop. Dev., 1991), decreasing slightly with depth. The concentrations of Ni, Cu and Cd in the topsoil exceed the MPL for South African soils, but there is a significant decrease with depth in the soil profile (Figure 5.20) and the background concentration is reached at 300mm. The adsorption of heavy metals by the topsoil is due to the high organic C content and the high pH(H_2O) of the soil (Kabata-Pendias, 1992; Alloway, 1995).

The bio-available Cr concentration in the soil are below the threshold set by Bruemmer & van der Merwe (1989), but that of Ni and Cu exceed these thresholds. The concentrations of all metals in the soil solution are below the guideline values for NH_4NO_3 extractable metals (Baden-Wurttemberg, 1993). The risk for groundwater pollution with heavy metals is thus limited, but the risk for groundwater pollution with N is a reality as is indicated by the analyses of the groundwater sample.

5.2.2 Site 21

This sewage treatment facility receives industrial effluent from various industries (textile, dyes, fats, oils and grease) and produces waste activated sludge that has been irrigated onto 30ha of instant lawn on a daily basis for the past 5 years. The site is situated on a deep, sandy clay loam soil (Hutton; orthic A, red apedal B) with 30-38% clay. The disposal site is on level terrain with the nearest open water body more than 2km away. A groundwater sample was taken from the borehole at the disposal site.

The data in Table 5.21 indicate slightly elevated organic C contents in the top 300mm. The total P and N are evenly distributed through the whole soil profile. The pH(H_2O) is strongly acid in the top 300mm and medium acid lower down the soil profile (van der Watt & van Rooyen, 1990). The groundwater is suitable for irrigation and domestic use since no elements exceed the DWAF (1996) water quality guidelines. Only the Zn concentration of the sludge exceeds the WRC (2002) guideline for a type D sludge.

Table 5.21: Site 21 general soil, sludge groundwater data

Soil depth (mm)	Total P %	Total N %	C %	Clay %	pH (H_2O)
0-100	0.04	0.07	1.25	30.0	4.92
100-200	0.03	0.05	1.01	30.7	5.11
200-300	0.02	0.04	0.82	34.0	5.49
300-400	0.02	0.04	0.64	36.0	5.89
400-500	0.02	0.03	0.55	38.0	6.15
SLUDGE	1.54	3.17	61	-	6.00

Sludge data (*aqua regia*) mg kg^{-1}						
Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
4.7	22.8	1649.9	438.7	140.7	213.6	3873.9

Water data								
Cd (μg l^{-1})	**Cr (μg l^{-1})**	**Co (μg l^{-1})**	**Cu (μg l^{-1})**	**Pb (μg l^{-1})**	**Ni (μg l^{-1})**	**Zn (μg l^{-1})**	**NO_3 (mg l^{-1})**	**pH**
0.29	13.04	8.27	32.26	9.01	10.28	16.83	1.42	7.83

Even though the disposal site has only been in use for 5 years, the total Cr and Co concentrations in the whole soil profile exceed the MPL for South African soils (Dept. Nat. Health & Pop. Dev., 1991) as well as the investigation threshold levels (Herselman & Steyn, 2001), with a slight decrease with depth (Figure 5.21). The relatively low Cr and Co content of the sludge and the constant high total concentrations of these metals in the soil profile indicate that it is probably

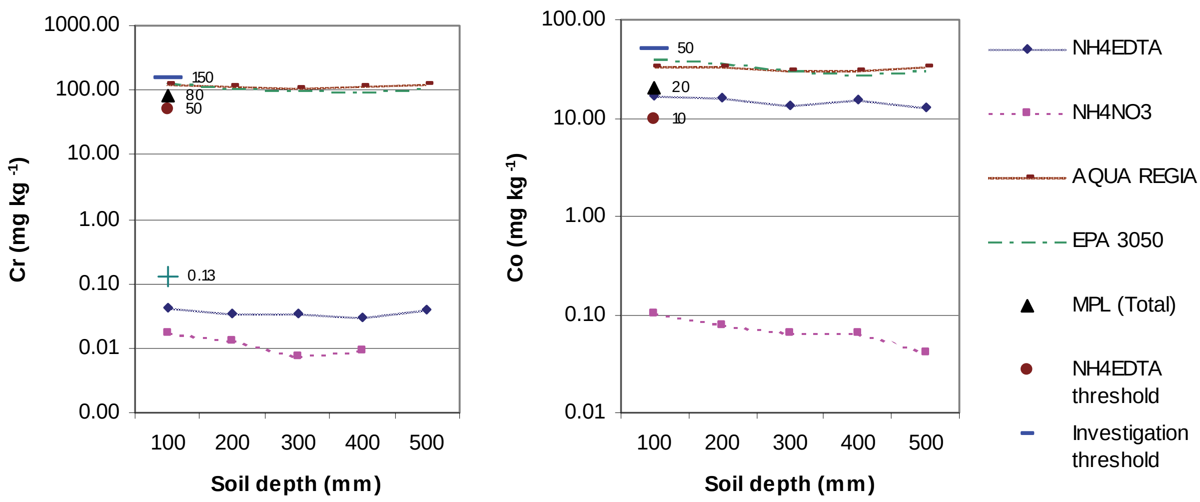


Figure 5.21: Cr and Co contents of the soil profile at Site 21

due to the high background concentrations of these elements in South African soils (Herselman & Steyn, 2001).

However, the NH_4EDTA and NH_4NO_3 extractable fraction of Cr are below the threshold levels set by Bruemmer & van der Merwe (1989) and Baden-Wurttemberg (1993). The NH_4EDTA extractable Co is higher than the threshold value and could be cause for concern.

5.2.3 Site 22

Site 22 is situated on a relatively shallow (<1m) Avalon soil form (orthic A, yellow-brown apedal B, soft plinthic B) with low clay content (<15%). This wastewater treatment facility receives half of its inflow from an industrial area (powder coating, litho-plating, metal plating, paint, battery, pulp and paper, breweries, petrochemical, food and beverage and mining effluent). It produces waste activated sludge, which is irrigated onto instant lawn. The area of disposal is 60ha, which has been utilized for 30+ years. The disposal site has a gradual slope, is 200m from a river and there is no borehole on site.

Table 5.22: Site 22 general soil and sludge data

Soil depth (mm)	Total P %	Total N %	C %	Clay %	pH (H_2O)
0-100	0.07	0.06	0.88	9.3	4.31
100-200	0.06	0.03	0.64	10.7	4.57
200-300	0.03	0.03	0.52	12.0	4.98
300-400	0.02	0.03	0.45	10.0	4.91
400-500	0.01	0.03	0.34	15.0	4.40
SLUDGE	1.61	2.78	47	-	6.65

Sludge data (*aqua regia*) mg kg^{-1}						
Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
3.4	35.2	410.7	264.5	297.5	105.1	4549.4

The topsoil is only slightly enriched with P, N and organic C (Table 5.22), but not as much as would have been expected after 30 years of sludge application. This is probably due to the removal of a thin layer of soil with the harvesting of the instant lawn. The pH(H_2O) of the soil profile is very strongly acid (<5) (van der Watt & van Rooyen, 1990).

The total metal content of the site is low even though the sludge has high Ni and Zn concentrations. The total Cr concentration is at the MPL for South African soils (Dept. Nat. Health & Pop. Dev., 1991) and is uniformly spread in the soil profile (no significant decrease with soil depth) (Figure 5.22). The bio-available and soluble Cr concentration in the soil is below the guidelines set for these extraction methods (Bruemmer & van der Merwe, 1989; Baden-Wurttemberg, 1993). There are very little movement of Cr down the soil profile, even though the pH(H_2O) are very low. This may be an indication that the high total Cr concentration could be due to high background concentrations at the site. The background concentration of Cr in South African soils is 5.82-353 mg kg^{-1}. Groundwater monitoring is advised since the clay content and pH(H_2O) of the soil are very low.

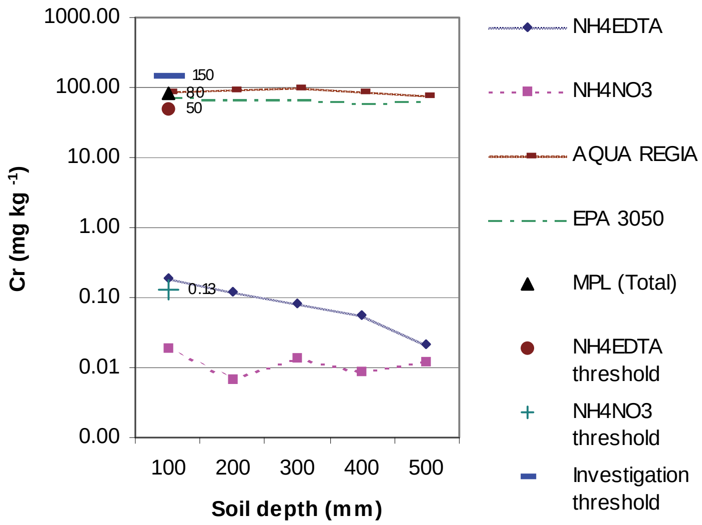


Figure 5.22: Cr content of the soil profile at Site 22

5.2.4 Site 23

This site is situated on a sandy loam (12% clay), Hutton soil (orthic A, red apedal B). It is a bio-filter treatment facility with anaerobic digesters and the sludge has been irrigated onto 34ha of instant lawn for the past 8 years. The treatment facility receives industrial effluent from a motor manufacturer. The slope at the site is gradual and the run-off possibility is minimal. The soil samples were taken after removing the grass on top of the soil. No water sample could be obtained from the borehole since the pump was out of order.

The low pH(H_2O) values of all soil samples (Table 5.23) indicate that the whole profile is strongly acid. The data indicate no significant increase in total P, N and organic C in the topsoil (0-100mm). During the harvesting of the instant lawn a thin layer of topsoil is removed and that may be the reason for this phenomenon.

Table 5.23: Site 23 general soil and sludge data

Soil depth (mm)	Total P %	Total N %	C %	Clay %	pH (H_2O)
0-100	0.07	0.09	1.28	8.7	4.07
100-200	0.08	0.05	0.89	10.0	4.26
200-300	0.09	0.05	0.71	11.3	4.62
300-400	0.09	0.03	0.51	12.7	4.88
400-500	0.09	0.02	0.33	14.0	5.21
SLUDGE	0.94	2.46	53	-	6.58

Sludge data (*aqua regia*) mg kg^{-1}						
Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
1.3	15.6	296.0	137.0	137.0	107.3	639.9

None of the total heavy metal concentrations exceed the investigation thresholds suggested by Herselman & Steyn (2001) and only the Cr concentration is at the MPL for South African soils (Dept. Nat. Health & Pop. Dev., 1991) (Figure 5.23). The NH_4EDTA extractable heavy metals are all below the threshold values suggested by Bruemmer & van der Merwe (1989), but the NH_4NO_3 extractable Ni and Zn concentrations exceed the guidelines set by and Baden-Wurttemberg (1993) for groundwater protection.

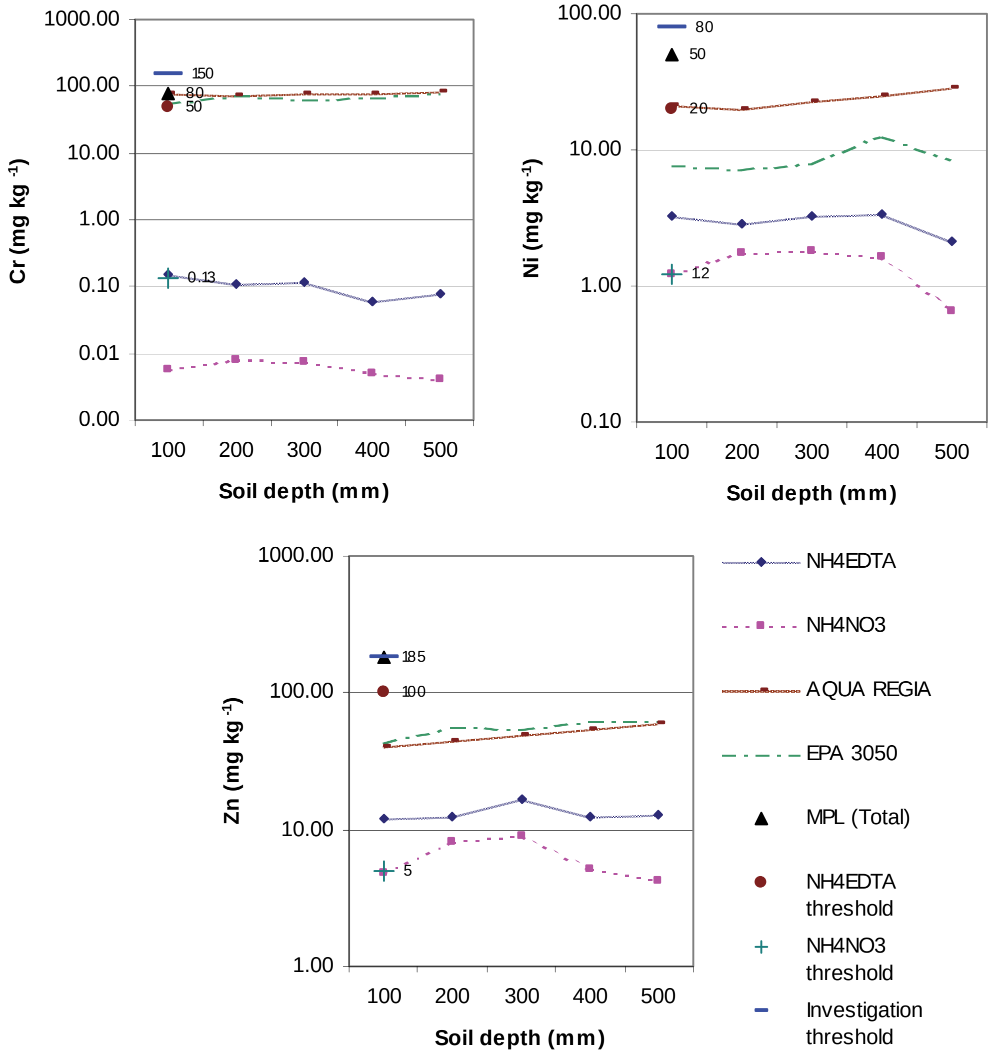


Figure 5.23: Cr, Ni and Zn contents of the soil profile at Site 23

The metals in the soil profile leach due to low clay content and pH(H_2O) levels. Even though the total concentrations of the metals do not exceed the MPL for South African soils, the high soluble Ni and Zn levels in the soil are reason for concern and continuous groundwater monitoring at the site is advised.

5.2.5 Site 24

Waste activated sludge has been irrigated daily onto 32ha of instant lawn for the past 10 years. The disposal area is on even terrain, 2km from a river. The treatment facility receives a large amount of inflow from various industries (powder coating, metal plating, paint, dye, breweries, food and beverage). The underlying soil is a Shortlands (orthic A, red structured B) with high clay content in the subsoil.

The soil data (Table 5.24) indicate high total P, N and organic C in the top 300mm of the soil profile, although a thin layer of topsoil is removed with the harvesting of instant lawn. The pH(H_2O) of the top 300mm of soil indicates that the soil is acid (<5). The sludge data indicate excessively high concentrations of Cd, Cu, Ni and Zn, well above the guideline values (WRC, 2002).

Table 5.24: Site 24 general soil and sludge data

Soil depth (mm)	**Total P %**	**Total N %**	**C %**	**Clay %**	**pH (H_2O)**
0-100	3.58	0.25	4.82	16.0	4.26
100-200	2.56	0.51	4.06	21.3	4.78
200-300	1.22	0.20	2.45	44.0	4.96
300-400	0.23	0.07	1.32	59.3	5.22
400-500	0.13	0.07	1.18	63.3	5.36
SLUDGE	3.06	5.29	58	-	6.21

Sludge data (*aqua regia*) mg kg^{-1}						
Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
41.3	12.7	978.9	1023.7	526.1	277.6	17373

The total concentrations of most heavy metals (Cr, Ni, Cu, Zn, Cd and Pb; Figure 5.24) in the whole soil profile exceed the MPL for South African soils (Dept. Nat. Health & Pop. Dev., 1991), as well as the investigation thresholds suggested by Herselman & Steyn (2001). The total concentration of Cd in the top 300mm of soil is especially high. The higher values of all mentioned metals in the top 300mm soil layers indicates adsorption by the topsoil.

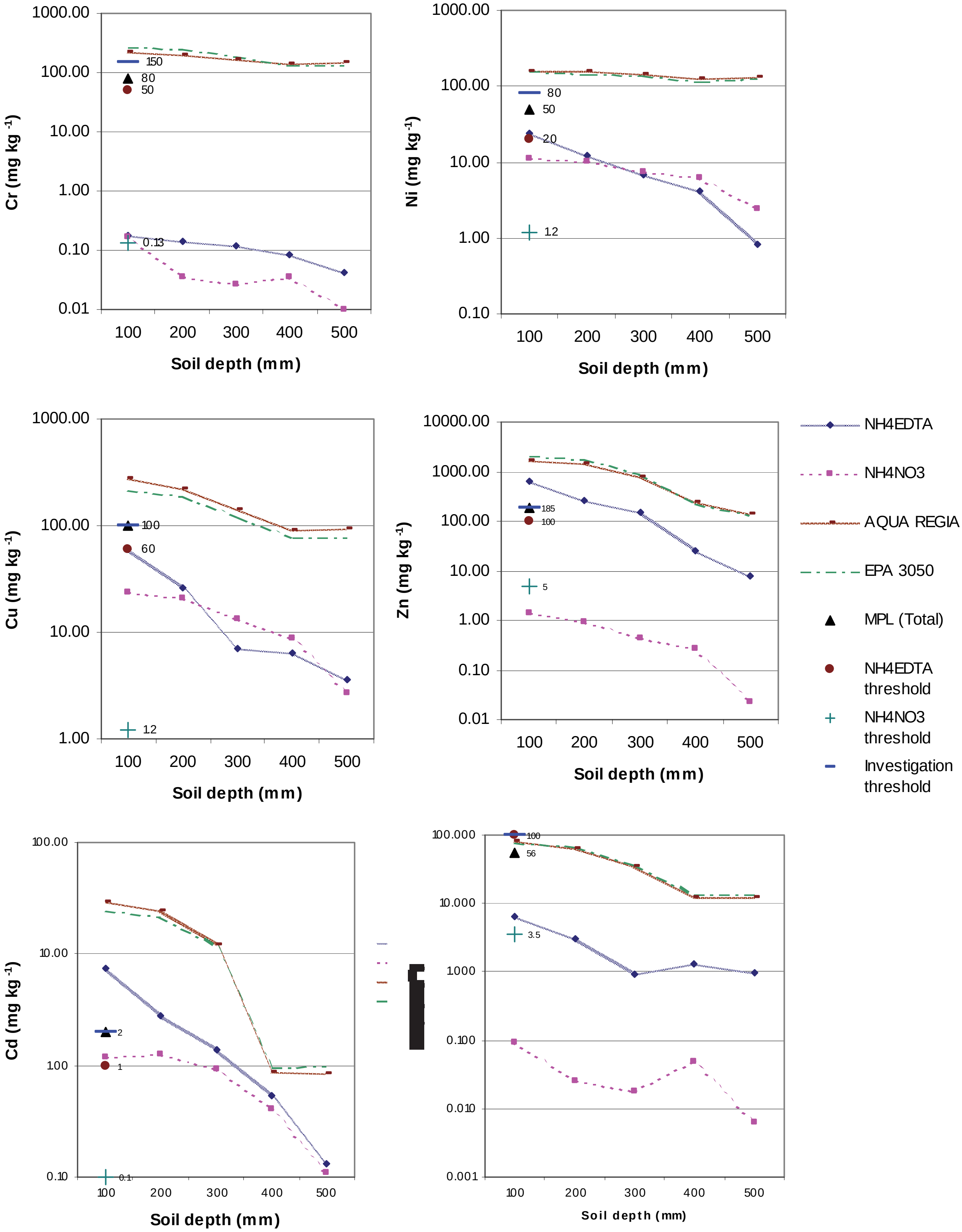


Figure 5.24: Cr, Ni, Cu, Zn, Cd and Pb contents of the soil profile at Site 24

The bio-available Cr and Pb are low, but the concentrations of NH_4EDTA extractable Ni, Cu, Zn and Cd exceed the threshold set by Bruemmer & van der Merwe (1989). The Cd concentration is especially high (4 mg kg^{-1}) in the top 300mm of soil (Figure 5.24). The NH_4NO_3 extractable concentrations of Ni, Cu and Cd exceed the guideline values for NH_4NO_3 extractable metals set by Baden-Wurttemberg (1993). Although there is a decrease with depth, the concentrations in the whole profile are higher than the guideline values and groundwater pollution is a possibility at this site.

The higher metal concentrations in the top 300mm soil layers indicate adsorption of the metals by the organic C. After 10 years of application of sludge with a high metal and N load, the attenuation capacity of the topsoil has been exceeded and leaching occur down the soil profile.

5.3 Paddy system sites

5.3.1 Site 25

Situated on a deep, sandy Fernwood (orthic A, regic sand), this site receives only domestic wastewater (13Ml/day) and produces waste activated and digested sludge. For the past 20+ years the sludge has been pumped into lagoons and left to dry. The dry sludge is then mechanically removed and dumped at a landfill site. The soil samples were taken at the footprint of a lagoon where the dry sludge has been removed. There are no boreholes at the disposal site.

Table 5.25 contains general soil and sludge data of Site 25. There is an accumulation of total P, N and organic C in the topsoil with a gradual decrease with depth. The organic C of the whole profile is higher than expected for a sandy soil.

Table 5.25: Site 25 general soil and sludge data

Soil depth (mm)	Total P %	Total N %	C %	Clay %	pH (H_2O)
0-100	0.12	0.15	1.87	5.33	6.41
100-200	0.04	0.05	0.95	4.00	6.91
200-300	0.02	0.02	0.40	3.33	7.14
300-400	0.03	0.04	0.95	4.00	7.00
400-500	0.02	0.03	1.02	4.00	7.10
SLUDGE	2.56	5.03	67	-	6.61

Sludge data (*aqua regia*) mg kg^{-1}						
Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
11.7	10.6	912.1	865.3	470.8	285.8	5538.0

The total Cu, Zn, Cd and Pb concentrations in the top 100mm soil layer are higher than the MPL for South African soils (Nat. Dept. Health & Pop. Dev., 1991), but decrease significantly with depth, reaching a plateau at 300mm (Figure 5.25). The bio-available Cd and soluble Zn are at the guideline values set for these extraction methods (Bruemmer & van der Merwe, 1989; Baden-Wurttemberg, 1993). All the other elements are below the guideline levels.

The data indicate adsorption of the metals in the topsoil with gradual leaching down the soil profile. The adsorption in the topsoil is mainly due to the high organic carbon content of the top 200mm soil layers. One would expect much more leaching of the metals because it is a sandy soil, but leaching is limited due to the neutral pH(H_2O) and the relatively high organic C content of the soil, which immobilize the metals (Kabata-Pendias & Pendias, 1992; Alloway, 1995).

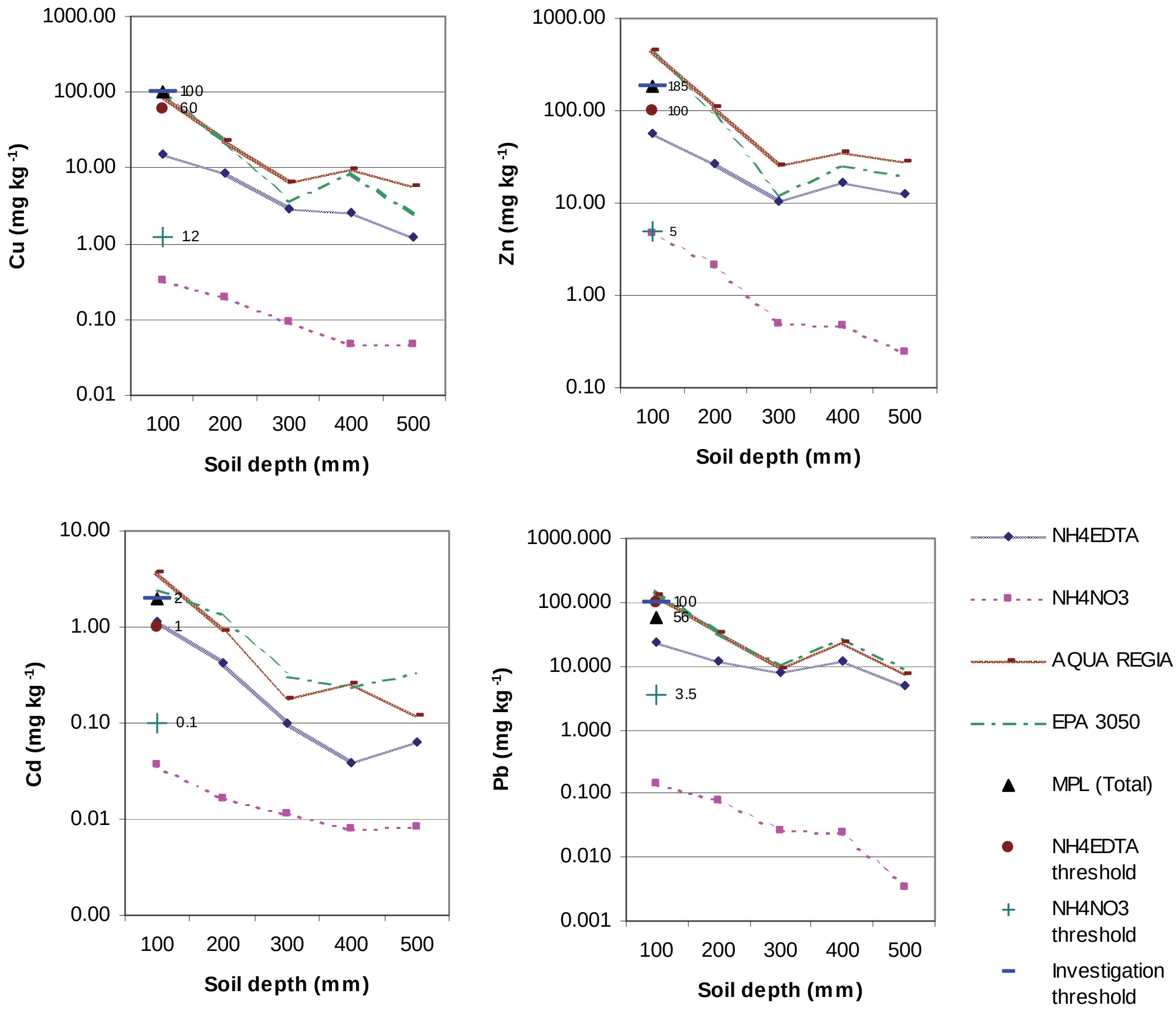


Figure 5.25: Cu, Zn, Cd and Pb contents of the soil profile at Site 25

5.3.2 Site 26

Site 26 is situated on a deep, sandy Clovelly (orthic A, yellow-brown apedal B). This wastewater treatment facility receives 9Ml/day inflow of which 5% is industrial effluent. The waste activated and digested sludge is pumped into sludge dams. Once these dams are full, the sludge is left to dry and then mechanically removed. This disposal site has been utilized for the past 9 years. The nearest open water body is 300m from the disposal site and no groundwater monitoring occur.

Table 5.26: Site 26 general soil data

Soil depth (mm)	Total P %	Total N %	C %	Clay %	pH (H_2O)
0-100	0.06	0.23	0.62	5.33	7.85
100-200	0.06	0.04	0.36	4.67	7.86
200-300	0.06	0.03	0.27	4.00	7.93
300-400	0.06	0.03	0.26	4.00	7.99
400-500	0.06	0.03	0.25	4.00	8.01

There is an accumulation of total N and organic C in the topsoil with a decrease in depth down the soil profile (Table 5.26). The total P content stays constant through the profile and the pH(H_2O) of the soil is moderately alkaline.

Results of the *aqua regia* digestion are higher than the EPA 3050 digestion and the Ni, Cu and Zn concentrations exceed the MPL for South African soils (Nat. Dept. Health & Pop. Dev., 1991). The NH_4EDTA and NH_4NO_3 extractable concentrations of all metals are below the guidelines set by Bruemmer & van der Merwe (1989) and Baden-Wurttemberg (1993).

The soils in the area where this site is located have high baseline concentrations of Cu and Zn (Herselman & Steyn, 2001) and may be the reason for the high total Cu and Zn concentrations at the site. Leaching of the metals should be limited by the neutral soil pH(H2O) and organic C content of the soil (Kabata-Pendias & Pendias, 1992).

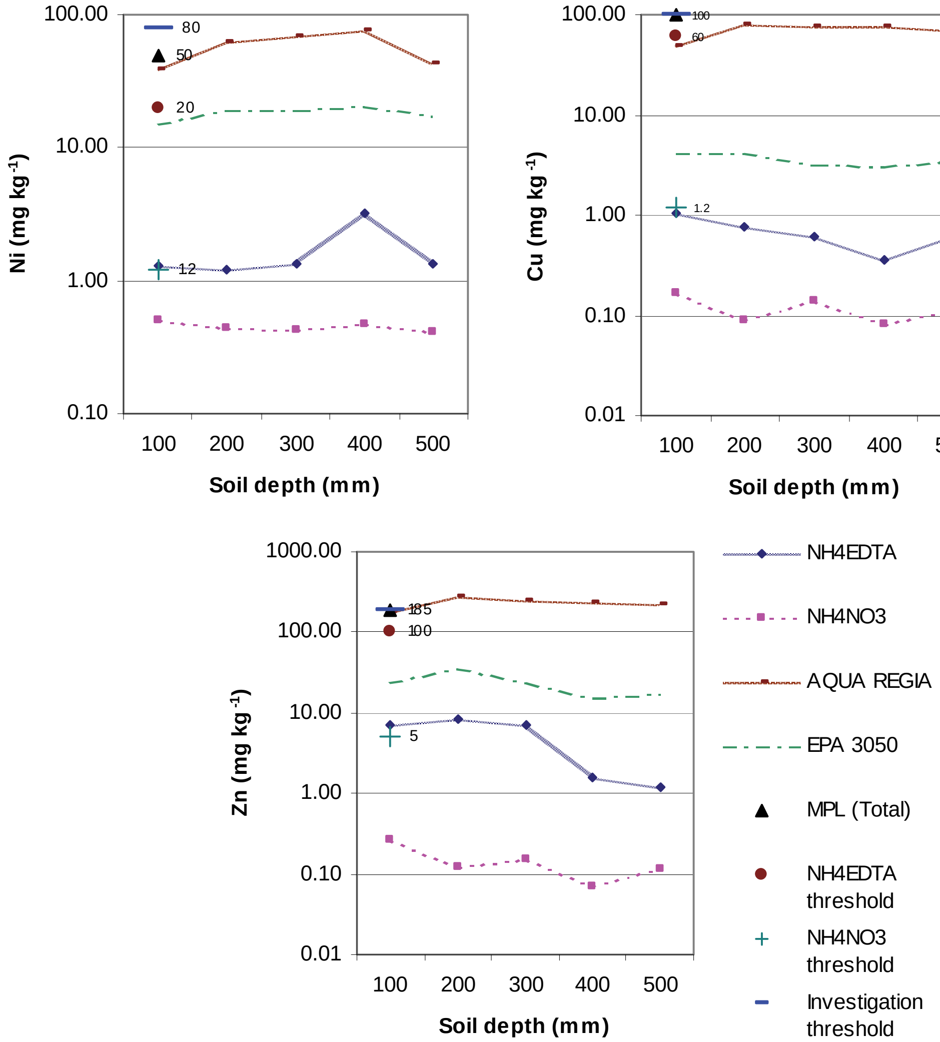


Figure 5.26: Ni, Cu and Zn contents of the soil profile at Site 26

5.3.3 Site 27

Wastewater treatment facility 27 produces waste activated sludge that is pumped into paddies to dry. The dry sludge is stockpiled on site. The disposal area is 40ha, on smooth terrain and has been in use for 30+ years. The facility receives 20% if it's inflow of 105Ml/day from various factories (powder coating, metal plating, paint, dye, breweries, food and beverage). The soil samples were taken on the footprint of a paddy where the dry sludge has been removed recently. It is situated on a Glencoe soil form (orthic A, yellow-brown apedal B, hard plinthic B) with 24-27% clay.

The soil data (Table 5.27) indicate buildup of total N and organic C in the topsoil, decreasing with depth. The soil pH(H_2O) indicates acidification of the soil and the total Ni and Zn concentration of the sludge exceed the guidelines for type D sludge (WRC, 2002).

Table 5.27: Site 27 general soil and sludge data

Soil depth (mm)	Total P %	Total N %	C %	Clay %	pH (H_2O)
0-100	0.05	0.09	0.89	27.0	6.49
100-200	0.05	0.06	0.77	27.0	5.04
200-300	0.05	0.04	0.66	24.0	5.02
300-400	0.04	0.03	0.64	24.0	5.07
SLUDGE	2.12	2.28	43	-	7.23

Sludge data (*aqua regia*) mg kg^{-1}						
Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
12.9	37.5	456.2	505.0	253.1	239.4	3178.8

The total Cr, Co and Ni concentrations of the whole soil profile exceed the MPL for South African soils (Dept. Nat. Health & Pop. Dev., 1991), and increase with depth (Figure 5.27). The bio-available fractions of Cr and Ni are below the threshold values (Bruemmer & van der Merwe, 1989), but that of Co exceeds these values through the whole soil profile. The NH_4NO_3 extractable Cr and Co is very low, but that of Ni exceed the NH_4NO_3 guidelines set for groundwater protection (Baden-Wurttemberg, 1993).

The increase in the total metal concentration with depth indicate leaching of the metals due to the low soil pH(H_2O). After 30 years of sludge application the attenuation capacity of the soil, a function of the high clay and organic carbon content, are most probably exceeded and no more metals can be adsorbed

(Kabata-Pendias & Pendias, 1992). Groundwater monitoring is advised at the site.

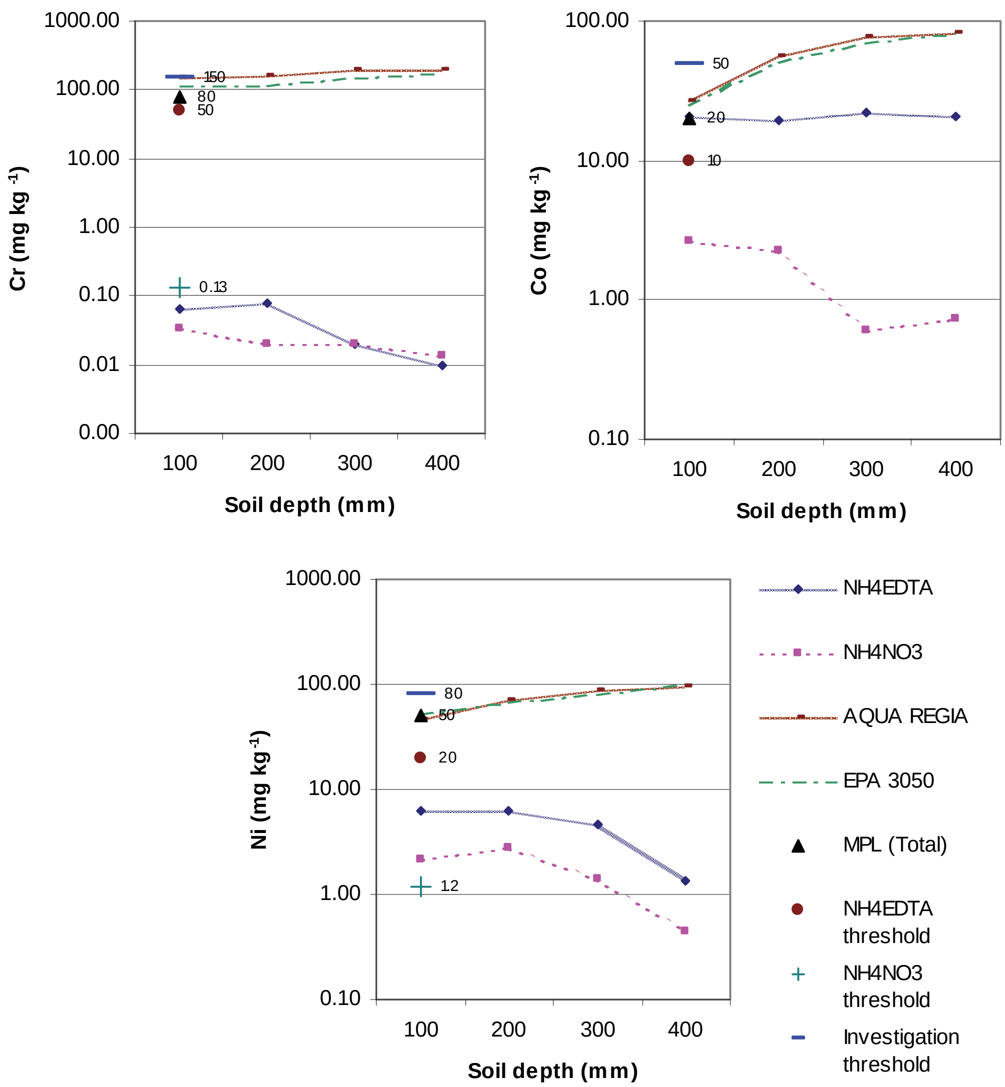


Figure 5.27: Cr, Co and Ni contents of the soil profile at Site 27

5.4 Irrigation sites

5.4.1 Site 28

Site 28 has a 75ha disposal area where waste activated sludge is flooded onto the land and ploughed frequently. This disposal method has been in use for the past 15 years and the disposal area is on even terrain. A large percentage of the inflow of this facility originates from industries (metal plating, paint, dye, battery, pulp and paper, fats, oils and grease). The soil form is Hutton with a loam texture and 16-24% clay. The soil is extremely acidic (pH<4.5) with elevated total P and organic C contents (Table 5.28). The total metal content of the sludge, except Cr, is extremely high and far above the guidelines (WRC, 2002). The NO_3 content of the groundwater sample is extremely high and the water is not suitable for any use according to the water quality guidelines of DWAF (1996). The metal content of the water sample is within the limits set by DWAF.

Table 5.28: Site 28 general soil, sludge and groundwater data

Soil depth (mm)	Total P %	Total N %	C %	Clay %	pH (H_2O)
0-100	0.33	0.08	1.83	16.0	3.89
100-200	0.23	0.05	1.00	20.0	3.88
200-300	0.27	0.04	0.57	19.3	4.17
300-400	0.35	0.03	0.36	22.0	4.39
400-500	0.30	0.03	0.30	24.0	4.56
SLUDGE	3.11	2.79	45	-	6.52

Sludge data (*aqua regia*) mg kg^{-1}						
Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
72.6	333.1	1483.3	1434.6	1042.5	896.6	12843

Water data								
Cd (µg l^{-1})	**Cr (µg l^{-1})**	**Co (µg l^{-1})**	**Cu (µg l^{-1})**	**Pb (µg l^{-1})**	**Ni (µg l^{-1})**	**Zn (µg l^{-1})**	**NO_3 (mg l^{-1})**	**pH**
0.66	13.18	6.62	34.17	2.51	10.96	26.72	238.44	7.75

The total heavy metal concentrations of the whole soil profile show reasons for concern because all metals, except Co, exceed the MPL for South African soils

(Nat. Dept. Health & Pop. Dev., 1991) and the suggested investigation threshold levels (Herselman & Steyn, 2001). The total Cd and Pb concentrations show significant decrease with soil depth (Figure 5.28), while the other metals decrease only slightly down the soil profile.

The bio-available fractions of Ni, Zn and Cd exceed the threshold concentration for NH_4EDTA extractable metals (Bruemmer & van der Merwe, 1989). In the case of Ni, Cu, Zn and Cd the NH_4NO_3 extractable fraction is also above guidelines set for NH_4NO_3 extractable metals (Baden-Wurttemberg, 1993) and gives reason for concern for groundwater pollution.

This soil has received very high metal loads with the sludge for the past 15 years and the extremely low pH(H_2O) of the soil is the main reason for the leaching of the metals. The attenuation capacity of the topsoil is most probably exceeded even though the clay content and organic carbon content of the top soil layers are high. Continuous groundwater monitoring and a detailed study at this site is recommended.

5.4.2 Site 29

Site 29 is situated on a Westleigh soil (orthic A, soft plinthic B) with <36% clay. The facility receives 25% of its inflow from an industrial area (food and beverage, textile). It is a waste activated treatment plant with anaerobic digesters. The sludge is irrigated daily onto dedicated land which is ploughed frequently. The disposal site is on level terrain, 1km from a river.

The top 300mm of soil is enriched with total P and N as well as organic C (Table 5.29) and the values are all extremely high for South African soils (Sparks, 1996; MVSA, 1997). The pH(H_2O) of the soil indicates acidification (<5). The total metal content of the sludge is extremely high and the concentrations of all the studied metals exceed the guideline values (WRC, 2002).

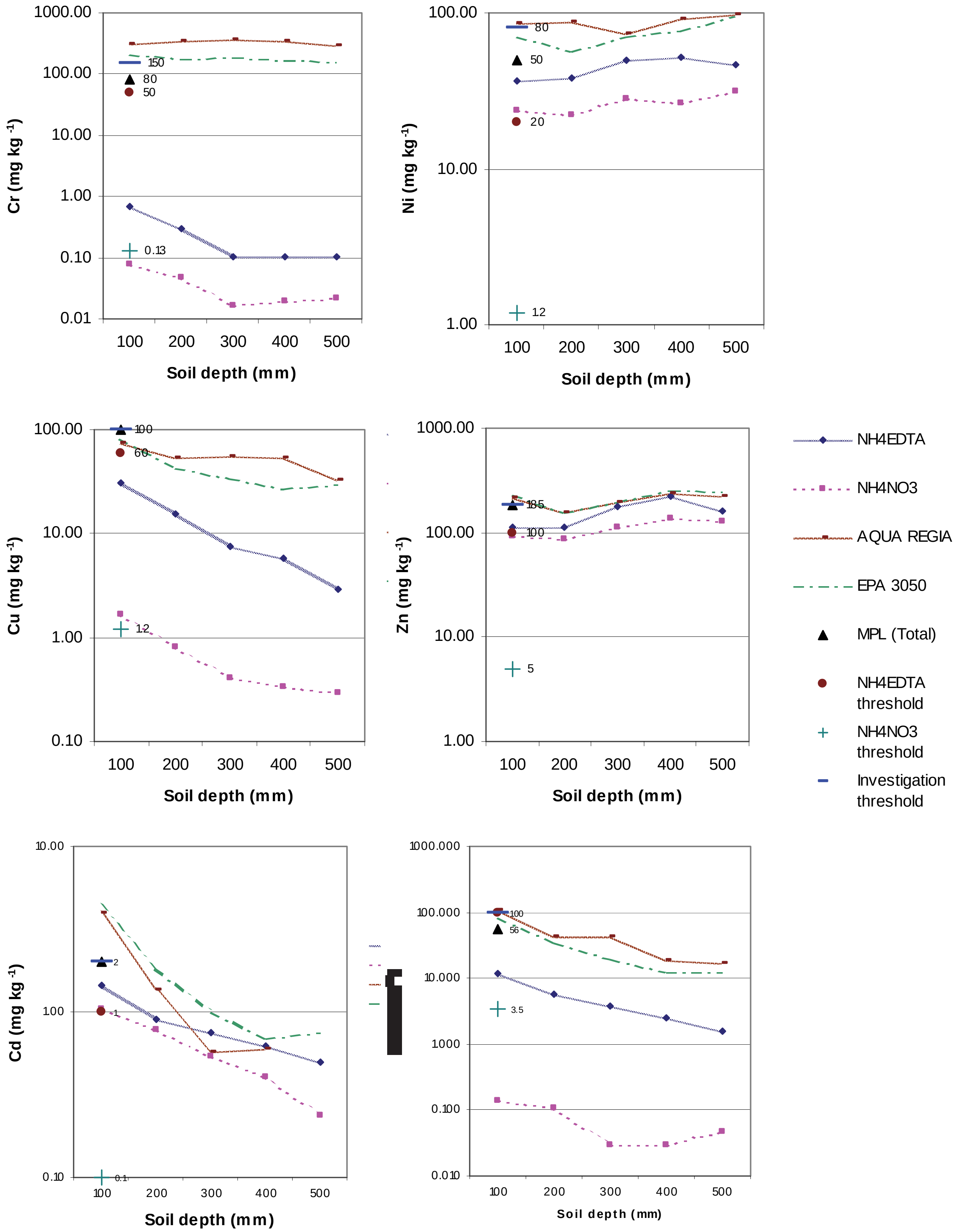


Figure 5.28: Cr, Ni, Cu, Zn, Cd and Pb contents of the soil profile at Site 28

Table 5.29: Site 29 general soil and sludge data

Soil depth (mm)	Total P %	Total N %	C %	Clay %	pH (H_2O)	
0-100	0.88	0.52	4.90	20.7	4.56	
100-200	0.61	0.38	3.44	24.0	4.52	
200-300	0.20	0.12	1.54	30.0	4.63	
300-400	0.12	0.07	0.84	36.0	5.04	
400-500	0.18	0.08	0.86	24.0	4.84	
SLUDGE	2.88	2.68	63.5	-	6.46	
Sludge data (*aqua regia*) mg kg^{-1}						
Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
70.9	178.3	2791.0	2920.0	600.3	3758.1	20533

The total Cr, Ni and Cu concentrations of the whole soil profile exceed the MPL for South African soils (Dept. Nat. Health & Pop. Dev., 1991) and the suggested investigation threshold values (Herselman & Steyn, 2001) with only a slight decrease down the soil profile. The total Zn, Cd and Pb concentrations in the topsoil also exceed the MPL for South African soils, but there is a significant decrease with depth (Figure 5.29). The Cd concentration especially is very high (9mg kg^{-1}).

The bio-available fractions of Zn and Cd exceed the threshold values for NH_4EDTA extractable metals (Bruemmer & van der Merwe, 1989) and decrease significantly with depth. The NH_4NO_3 extractable concentrations of Cr, Ni, Zn and Cd exceed the NH_4NO_3 guidelines for groundwater protection (Baden-Wurttemberg, 1993).

There is adsorption of metals in the top 200mm of soil due to the high clay and organic C content, but leaching still occurred due to the extremely low pH(H_2O) of the soil (Kabata-Pendias & Pendias, 1992). The risk for groundwater pollution is high and detailed investigation at this site is proposed to determine the extent of pollution.

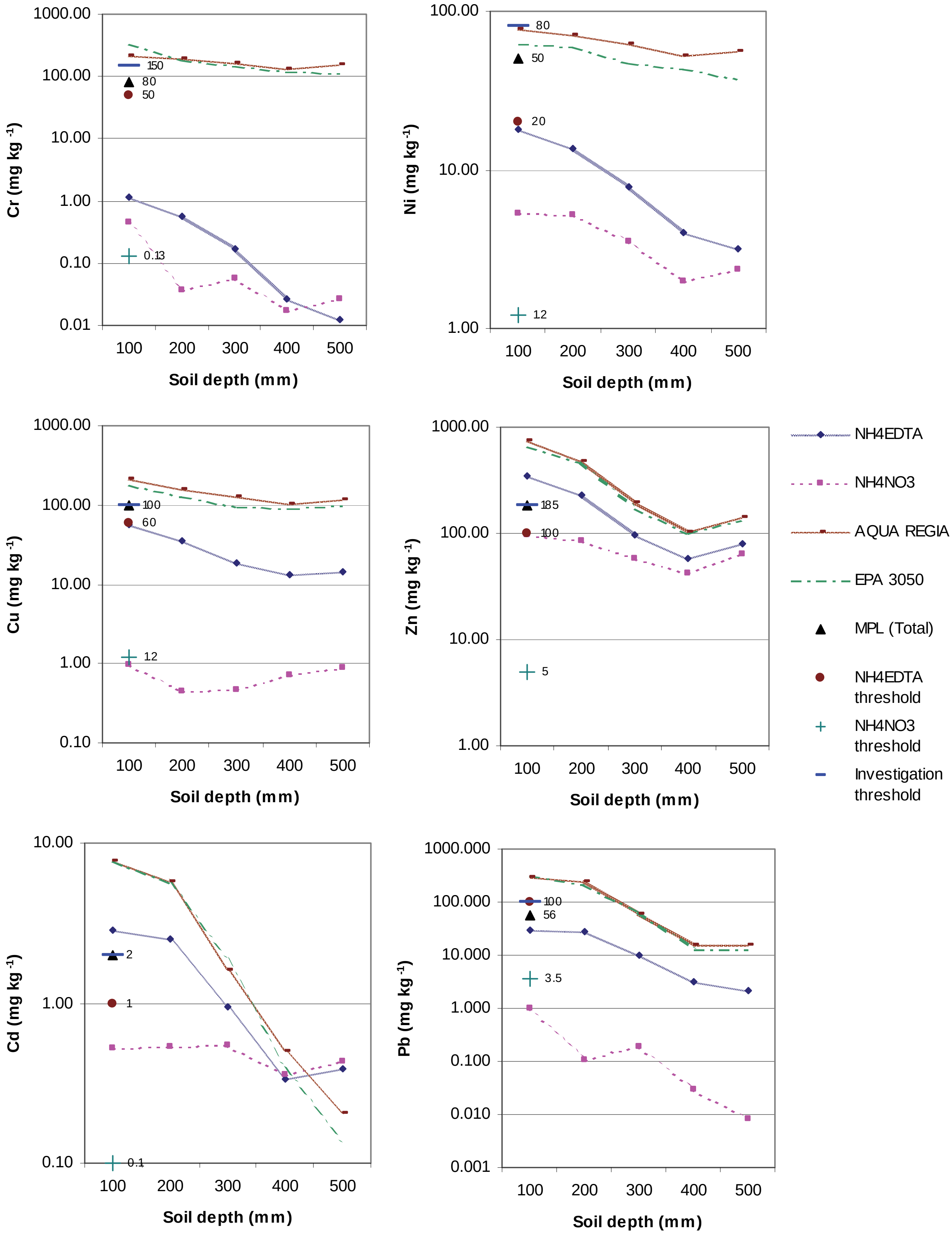


Figure 5.29: Cr, Ni, Cu, Zn, Cd and Pb contents of the soil profile at Site 29

5.4.3 Site 30

This site receives industrial effluent from breweries, food and beverage industries and fats, oils and grease. The facility produces anaerobic digested as well as waste activated sludge. The sludge is irrigated daily onto 10ha of dedicated land that is ploughed frequently. There is no borehole on the disposal site, which is on a uniform surface. This disposal option has been followed for 30+ years. The underlying soil is an Arcadia (vertic A) with 30-45% clay and a medium to slightly acid pH(H_2O) (5.5 – 6.5). The top 200mm of the soil profile is enriched with P and N and the top 300mm has elevated organic C content (Table 5.30). This enrichment is, however, much lower than would be expected for 30+ years of sludge application. The total metal concentration in the sludge is within acceptable limits (WRC, 2002).

Table 5.30: Site 30 general soil and sludge data

Soil depth (mm)	Total P %	Total N %	C %	Clay %	pH (H_2O)
0-100	0.20	0.19	1.90	28.0	4.99
100-200	0.10	0.09	1.25	27.3	5.42
200-300	0.07	0.06	0.99	30.7	6.09
300-400	0.07	0.06	0.67	45.0	6.59
400-500	0.07	0.06	0.58	37.0	6.72
SLUDGE	1.63	3.62	37	-	6.22

Sludge data (*aqua regia*) mg kg^{-1}						
Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
7.8	11.9	178.7	345.7	116.6	286.1	1851.9

The *aqua regia* Ni content of the whole soil profile is above the MPL for South African soils (Nat. Dept. Health & Pop. Dev., 1991). The total Zn concentration (*aqua regia* and EPA 3050) of the topsoil is also above the MPL, but decrease with depth. The NH_4EDTA extractable metals are all much lower than the thresholds set by Bruemmer & van der Merwe (1989). The soluble Ni and Zn are at the NH_4NO_3 guidelines (Baden-Wurttemberg, 1993) (Figure 5.30).

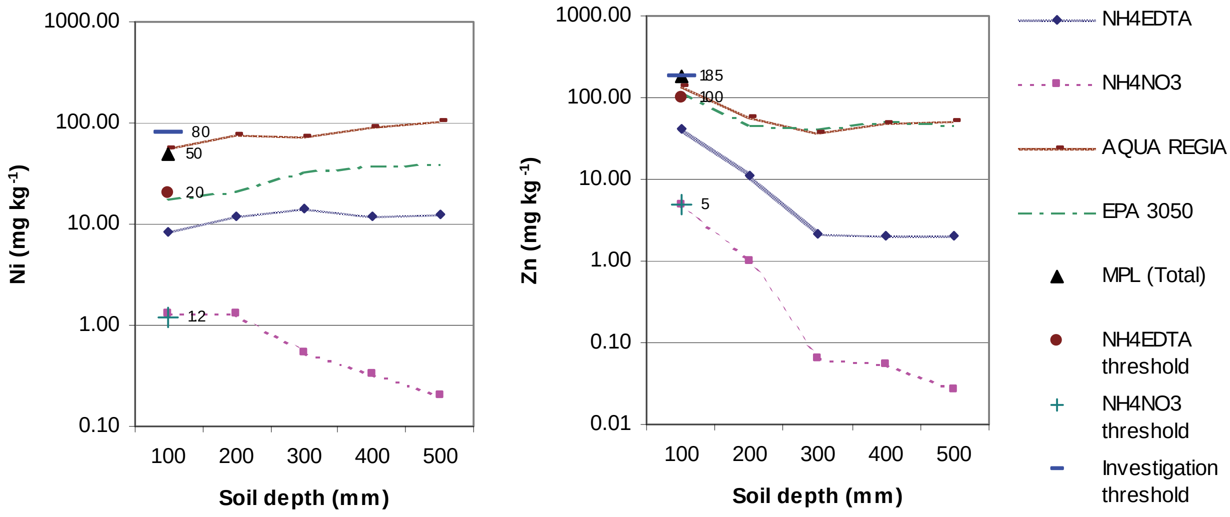


Figure 5.30: Ni and Zn contents of the soil profile at Site 30

At this site it seems that, even after 30 years of sludge application, leaching of metals only occurred to a depth of 300mm. The high clay content and organic C content of the topsoil is probably the main reason for the immobility of the metals (Kabata-Pendias & Pendias, 1992; Alloway, 1995). The low correlation between the total N in the sludge and the total N in the soil are reason for concern and groundwater monitoring is advised.

5.4.4 Site 31

Site 31 is situated on a deep Hutton soil. The average daily inflow at this facility is 160Ml and industrial effluent is received from various industries. Waste activated sludge is produced. The sludge is currently dewatered with a belt press and used for compost. Previously it was pumped onto land and left to dry, without any ploughing. The soil samples were taken on this land, which was in use for 15 years. The disposal site is on even terrain, 500m from a river. The borehole is out of commission and no groundwater sample could be collected.

The organic C content of the whole soil profile is high and the top 300mm shows buildup of P and N (Table 5.31). These high values are due to the fact that no ploughing occurred, which slowed down the organic breakdown. The pH(H_2O) of the soil is extremely acid (van der Watt & van Rooyen, 1990) and the total metal content of the sludge is low (WRC, 2002).

Table 5.31: Site 31 general soil and sludge data

Soil depth (mm)	**Total P %**	**Total N %**	**C %**	**Clay %**	**pH (H_2O)**	
0-100	0.68	0.66	5.72	10.0	3.63	
100-200	0.89	0.68	5.25	10.7	3.67	
200-300	0.76	0.43	3.91	14.0	3.76	
300-400	0.25	0.10	1.10	16.0	4.01	
400-500	0.19	0.07	0.83	20.7	4.06	
SLUDGE	2.71	3.05	53	-	5.4	
Sludge data (*aqua regia*) mg kg^{-1}						
Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
4.4	62.82	259.4	335.4	184.7	149.9	1450.8

The total concentrations of most heavy metals (Cr, Ni, Cu, Zn, Cd and Pb) in the soil profile are above both the MPL for South African soils (Dept. Nat. Health & Pop. Dev., 1991) and suggested investigation thresholds (Herselman & Steyn, 2001), and decrease with depth (Figure 5.31). The concentrations of metals in the soil samples deeper than 300mm are lower than the samples on top, but still higher than the MPL for South African soils. This indicates leaching down the soil profile up to at least 300mm.

Even the NH_4EDTA extractable Cu, Zn, Cd and Pb are higher than the MPL for South African soils, based on total concentrations. There is only a slight decrease in the metal concentration deeper than 300mm. The leaching is probably due to the low pH(H_2O) and clay content of the soil. Some adsorption occurred in the top 300mm due to the high organic C content.

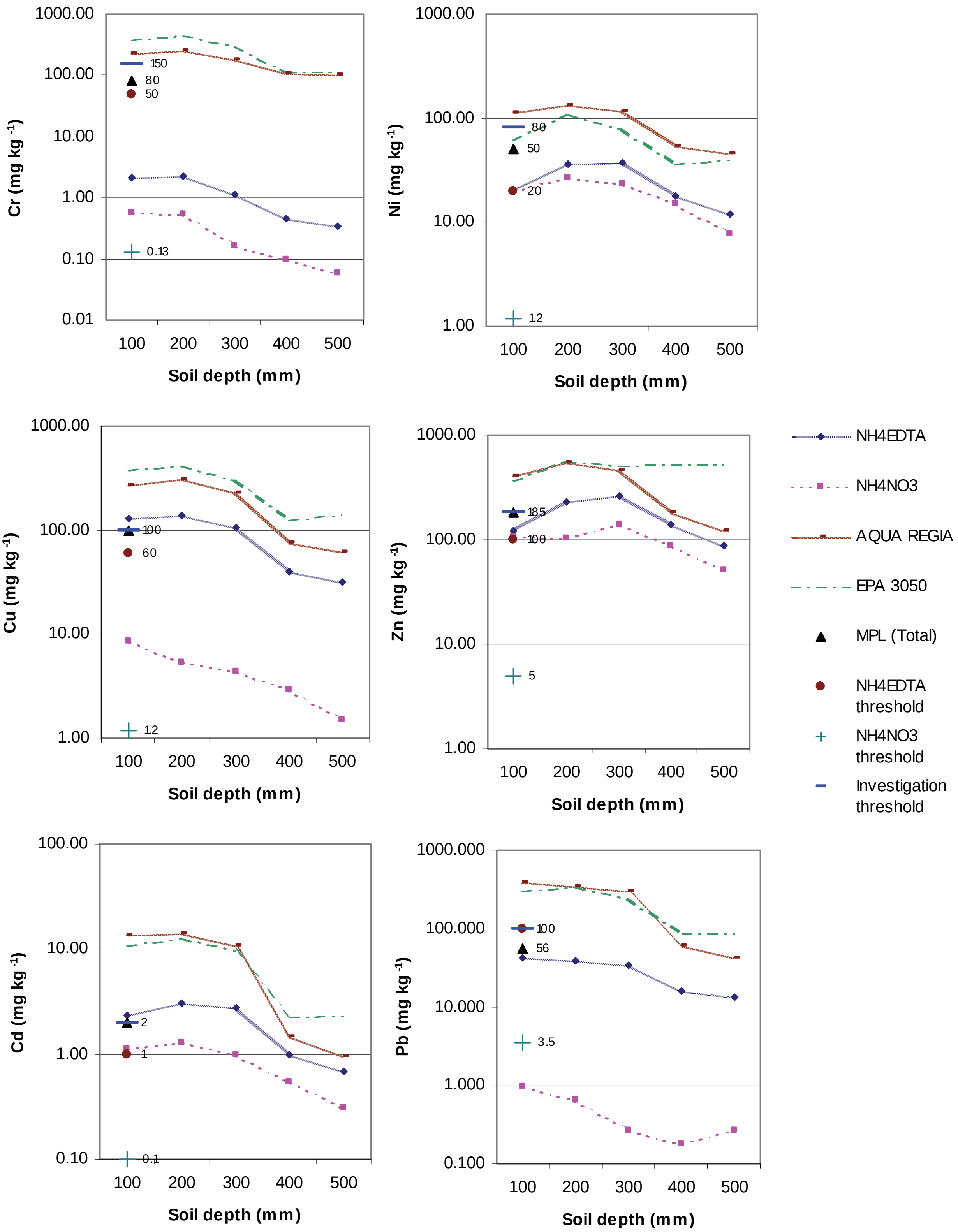


Figure 5.31: Cr, Ni, Cu, Zn, Cd and Pb contents of the soil profile at Site 31

The high concentration of metals in the soil solution (NH_4NO_3 extractable) is certainly of great concern. The concentration of NH_4NO_3 extractable Cr, Ni, Cu, Zn and Cd exceed the guidelines set in Germany for NH_4NO_3 extractable metals (Baden-Wurttemberg, 1993). A further detailed study at the site and groundwater monitoring is recommended in order to determine the actual depth of pollution.

5.4.5 Site 32

Site 32 receives an average of 23Ml/day raw wastewater (all domestic). Waste activated and digested sludge is produced which are mixed and dried on drying beds. The excess sludge is irrigated onto dedicated lands and ploughed from time to time. The disposal site has only been in use for 4 years and is 100m from a river. The soil is a silty clay loam (27-46% clay) of the Pinedene soil from (orthic A, yellow-brown apedal B, gleykutanic B). There are no boreholes at the disposal site.

Data in Table 5.32 show elevated total P, N and organic C in the topsoil with a gradual decrease with depth in the soil profile. The pH(H_2O) of the soil profile is moderately alkaline. The sludge data indicate no excessive metal levels.

Table 5.32: Site 32 general soil and sludge data

Soil depth (mm)	Total P %	Total N %	C %	Clay %	pH (H_2O)
0-100	0.12	0.18	1.39	27.67	7.67
100-200	0.09	0.13	0.91	30.33	7.88
200-300	0.08	0.12	0.84	30.33	7.92
300-400	0.07	0.11	0.72	43.00	8.07
400-500	0.06	0.10	0.61	46.33	8.14
SLUDGE	1.1	3.68	48	-	6.13

Sludge data (*aqua regia*) mg kg^{-1}						
Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
2.3	10.5	104.8	276.9	190.2	152.9	1370.8

The total Ni concentration of the whole profile is higher than the MPL for South African soils (Nat. Dept. Health & Pop. Dev., 1991) (Figure 5.32), but all other elements are below these guideline values. There are only slight decreases of metal content with depth. The bio-available and soluble metal content of the soil are well below the guidelines set for NH_4EDTA extraction (Bruemmer & van der Merwe, 1989) and NH_4NO_3 extraction (Baden-Wurttemberg, 1993).

Leaching in this soil should be limited due to the high clay content and pH(H_2O) of the soil (Kabata-Pendias & Pendias, 1992).The high total Ni content in the soil profile after only 4 years of sludge disposal may be due to high Ni baseline concentration in the area as well as sludge application, since this wastewater treatment facility receives only domestic wastewater with an acceptable Ni content.

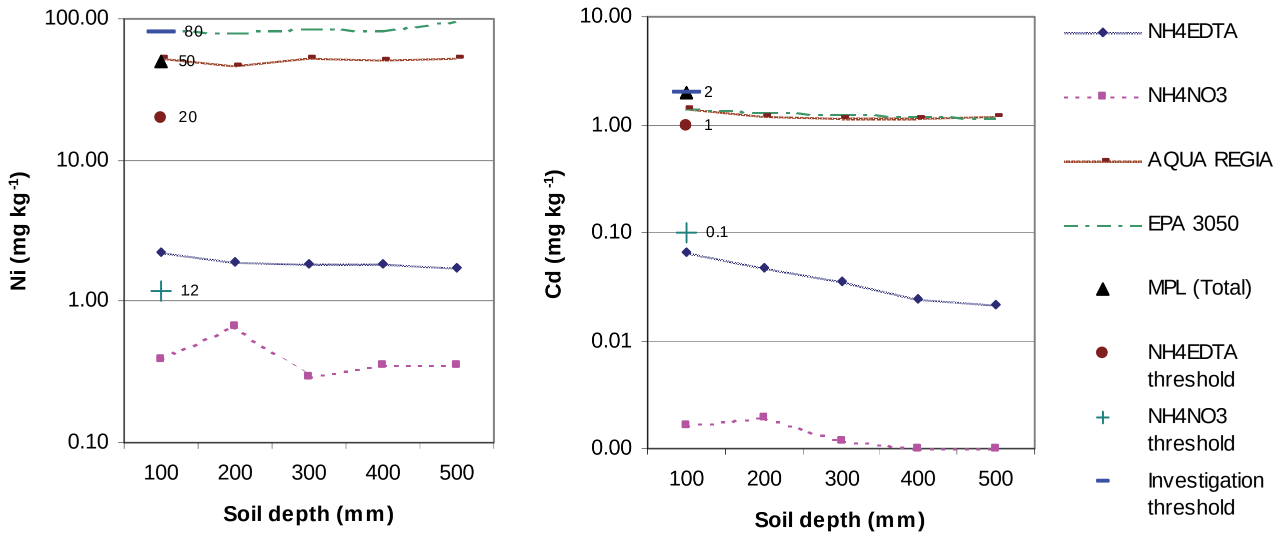


Figure 5.32: Ni and Cd contents of the soil profile at Site 32

5.4.6 Site 33

Receiving 70Ml/day average raw wastewater inflow with a small percentage industrial effluent, this site produces waste activated and digested sludge. The sludge is irrigated onto 50ha land that is covered with grass. This practice has been followed for 30+ years. It is situated on a shallow (<400mm) Glencoe (orthic A, yellow-brown apedal B, hard plinthic B), 400m from the nearest open water body.

The general soil data in Table 5.33 indicate an accumulation of total P, N and organic C in the soil profile. All these contents are much higher than normal for South African soils (Sparks, 1996; MVSA, 1997). The metal content of the groundwater sample is well below the water quality guidelines but the NO_3 content is extremely high (DWAF, 1996), and the water is unsuitable for any use.

Table 5.33: Site 33 general soil data and groundwater data

Soil depth (mm)	**Total P %**	**Total N %**	**C %**	**Clay %**	**PH (H_2O)**
0-100	2.97	1.32	12.91	9.00	5.81
100-200	1.45	0.60	5.75	15.00	6.70
200-300	0.52	0.20	3.04	11.33	6.72

Water data

Cd ($\mu g\ l^{-1}$)	**Cr ($\mu g\ l^{-1}$)**	**Co ($\mu g\ l^{-1}$)**	**Cu ($\mu g\ l^{-1}$)**	**Pb ($\mu g\ l^{-1}$)**	**Ni ($\mu g\ l^{-1}$)**	**Zn ($\mu g\ l^{-1}$)**	**NO_3 ($mg\ l^{-1}$)**	**pH**
-	1.13	4.86	10.28	9.03	19.27	22.00	699.78	8.45

The total Zn and Pb concentrations (*aqua regia* and EPA 3050) in the whole profile greatly exceed the MPL for South African soils (Nat. Dept. Health & Pop. Dev., 1991) (Figure 5.33). The results of the *aqua regia* digestions show an increase with depth in the profile and the concentrations of Cr, Ni, Cu and Cd at the 300mm soil layer also exceed the MPL. The bio-available fractions of all the metals are lower than the NH_4EDTA threshold values (Bruemmer & van der Merwe, 1989) and only the soluble Zn concentration exceeds the NH_4NO_3 guidelines (Baden-Wurttemberg, 1993).

There are adsorption of metals in the topsoil by the organic matter, but leaching still occur due to the low clay content and pH(H_2O) of the topsoil. The low soluble

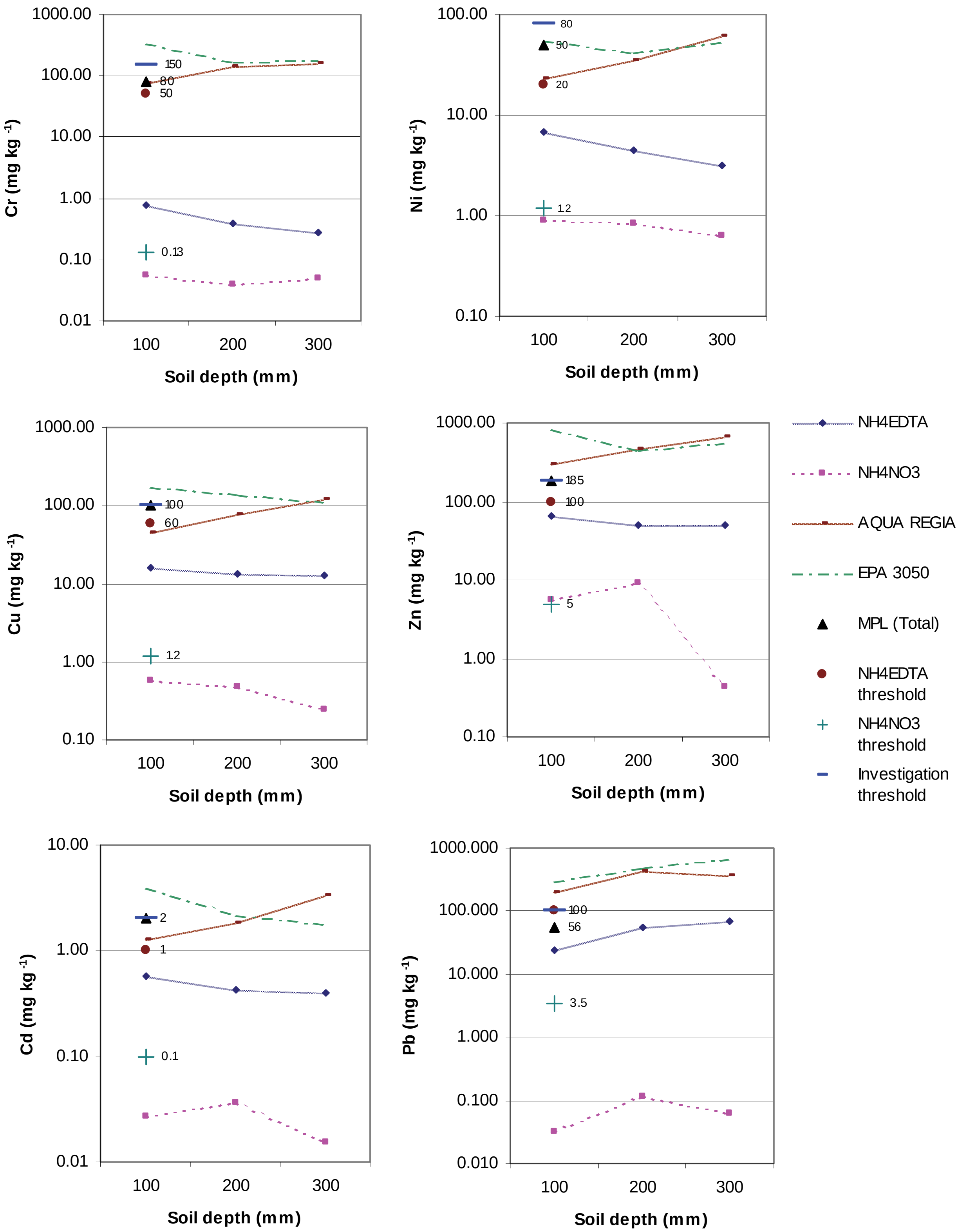


Figure 5.33: Cr, Ni, Cu, Zn, Cd and Pb contents of the soil profile at Site 33

metal concentrations indicate no immediate risk for groundwater contamination with metals but the groundwater data indicate NO_3 pollution.

5.4.7 Site 34

The disposal site of this wastewater treatment facility is situated on a deep, sandy Clovelly soil. The Site receives 10Ml/day inflow (2% industrial) and produces waste activated and digested sludge. The sludge is irrigated onto land covered with grass (no ploughing), 10km from a river.

General soil data indicate higher total P, N and organic C contents in the topsoil, decreasing with depth (Table 5.34). The pH(H_2O) of the soil is moderately alkaline and the clay content is very low.

Table 5.34: Site 34 general soil and sludge data

Soil depth (mm)	Total P %	Total N %	C %	Clay %	pH (H_2O)
0-100	0.24	0.13	0.82	4.00	7.78
100-200	0.09	0.03	0.14	3.33	8.02
200-300	0.08	0.01	0.07	2.67	8.23
300-400	0.08	0.01	0.10	3.33	8.21
400-500	0.04	0.01	0.04	4.00	8.31
SLUDGE	0.84	2.72	64	-	6.53

Sludge data (*aqua regia*) mg kg^{-1}						
Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
1.7	5.6	3680.5	291.9	291.9	200.3	1090.3

The total Ni concentration in the whole profile exceeds the MPL for South African soils (Nat. Dept. Health & Pop. Dev., 1991) and the *aqua regia* digestion even exceed the suggested investigation threshold (Herselman & Steyn, 2001). The total Zn concentration in the topsoil also exceeds these guidelines, but decrease significantly with depth. The bio-available and soluble fractions of all elements are below the guideline levels set for NH_4EDTA (Bruemmer & van der Merwe, 1989) and NH_4NO_3 extractions (Baden-Wurttemberg, 1993).

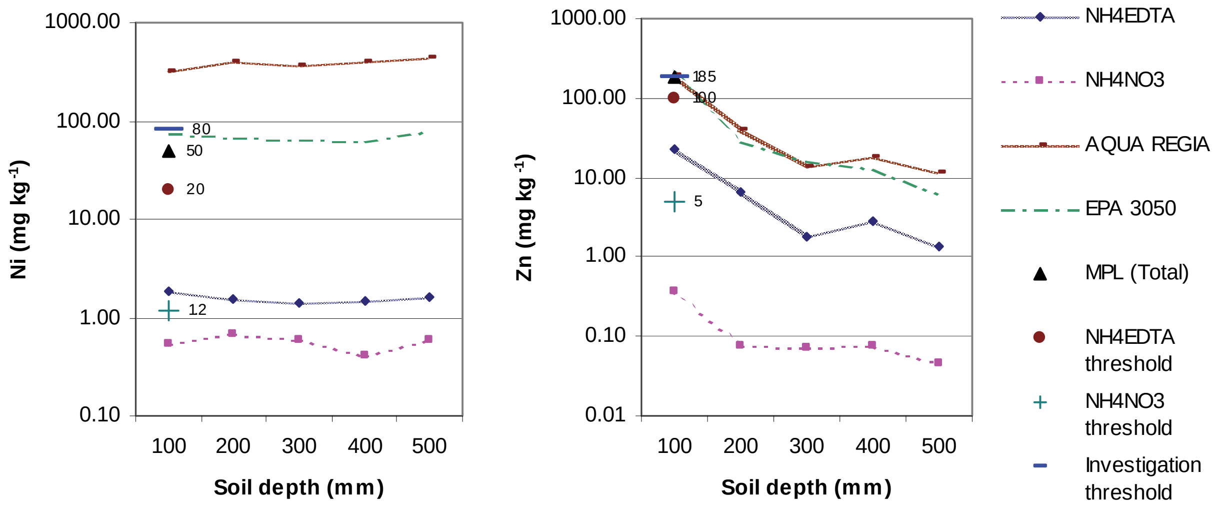


Figure 5.34: Ni and Zn contents of the soil profile at Site 34

The alkaline pH(H_2O) of the soil inhibit the mobility of the metals although the clay content of the soil is low. The metals get adsorbed in the topsoil due to the higher organic C content of the topsoil (Kabata-Pendias & Pendias, 1992). Groundwater monitoring is recommended because the clay content of the soil is very low and therefore NO_3 leaching is possible.

5.4.8 Site 35

Site 35 is situated on a deep, sandy loam, Clovelly soil (orthic A, yellow-brown apedal B). The treatment facility receives industrial effluent (<5%) from a soft-drink factory and produces waste activated sludge. The sludge is irrigated onto 7ha of land, which is ploughed frequently. The disposal area has been in operation for the past 8 years, is on even terrain (minimal run-off) and the nearest open water body is 1km from the site. There is no borehole at the disposal site and a groundwater sample was obtained from the treatment facility.

Table 5.35: Site 35 general soil, sludge and groundwater data

Soil depth (mm)	**Total P %**	**Total N %**	**C %**	**Clay %**	**pH (H_2O)**
0-100	0.07	0.18	1.56	19.3	5.12
100-200	0.03	0.10	0.89	22.0	4.79
200-300	0.03	0.04	0.70	25.3	4.68
300-400	0.03	0.04	0.58	24.0	4.90
400-500	0.03	0.04	0.50	27.3	5.04
SLUDGE	2.26	4.15	49	-	6.42

Sludge data (*aqua regia*) mg kg^{-1}						
Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
7.2	30.0	1128.8	275.5	125.9	153.8	1684.9

Water data								
Cd (µg l^{-1})	**Cr (µg l^{-1})**	**Co (µg l^{-1})**	**Cu (µg l^{-1})**	**Pb (µg l^{-1})**	**Ni (µg l^{-1})**	**Zn (µg l^{-1})**	**NO_3 (mg l^{-1})**	**pH**
-	7.45	1.87	12.9	3.48	-	9.16	611.83	7.28

The data in Table 5.35 indicate an increase in the total carbon content of the top 200mm relative to the deeper soil samples. The total P content of the topsoil is also higher than lower down the soil profile, as is the total N concentration. The pH(H_2O) of the soil is strongly acid. The NO_3 concentration in the groundwater is much higher than the 6mg l^{-1} DWAF (1996) guideline. The metal concentrations are all well below the guideline values for water.

The total Cr content of the soil from this site exceeds the MPL for South African soils (Dept. Nat. Health & Pop. Dev., 1991), but is lower than the investigation threshold suggested by Herselman & Steyn (2001). The Ni content of the topsoil is just below the guideline value. There is a slight decrease in the total Cr and Ni contents of the soil samples down the profile, but the concentrations stay in the high ranges. All the other elements' total concentrations are below the guideline values. The high total concentration of Cr and Ni may be due to the high background concentrations of these elements in South African soils (Herselman & Steyn, 2001).

The NH_4EDTA and NH_4NO_3 extractable Cr and Ni well below the NH_4EDTA threshold values (Bruemmer & van der Merwe, 1989) and NH_4NO_3 guidelines

(Baden-Wurttemberg, 1993) (Figure 5.3). There seem to be movement of metals up to 300mm in the soil profile due to the low pH(H_2O) of the soil, but because the concentrations are so low there are no immediate danger for groundwater pollution with metals, but NO3 contamination is a reality as indicated by the groundwater data.

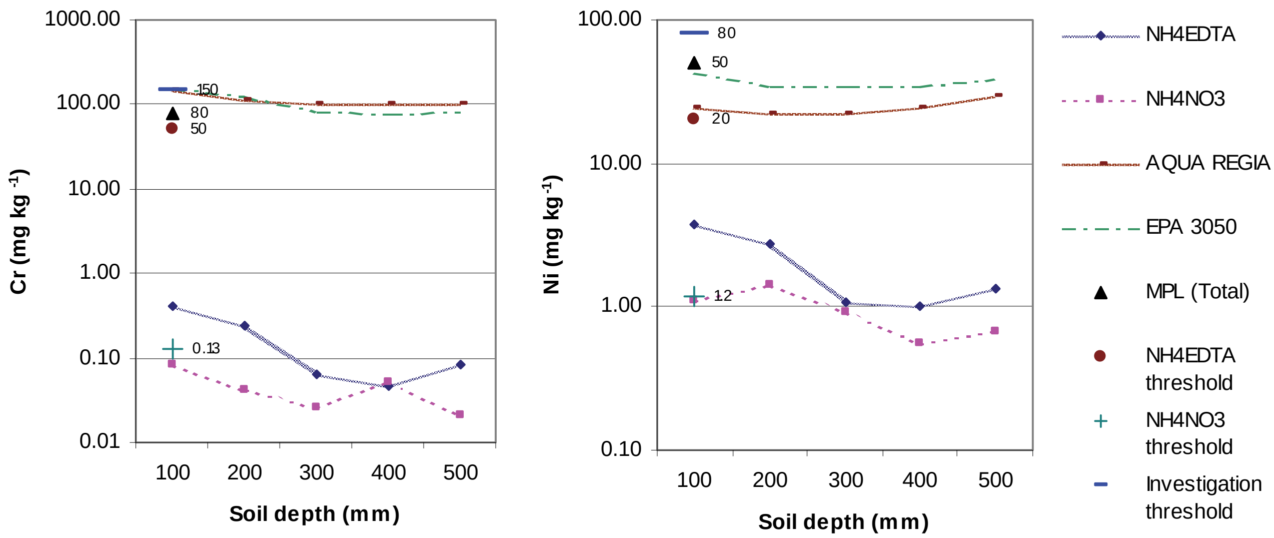


Figure 5.35: Cr and Ni contents of the soil profile at Site 35

5.5 Flooded sites

5.5.1 Site 36

This treatment facility produces anaerobically digested sludge, which is pumped onto land and left to dry. The disposal area is approximately 29ha and has been used for the past 30 years. The facility receives a large amount of industrial effluent (>50%) from various industries (metal plating, textiles, dyes, pulp and paper). The soil form is Pinedene (orthic A, yellow-brown apedal B, unspecified material). The slope is gradual and the nearest open water body is more than 2km away.

The top 200mm of the soil profile has elevated levels of organic C, total P and N (Table 5.36). The pH(H_2O) of the top soil layers is slightly lower than the rest, but the whole soil profile is strongly acidic. The total concentration of all studied metals, except Co and Cr, exceed the guideline values for type D sludge (WRC, 2002).

Table 5.36: Site 36 general soil and sludge data

Soil depth (mm)	Total P %	Total N %	C %	Clay %	pH (H_2O)
0-100	0.39	0.26	3.04	14.7	5.09
100-200	0.20	0.13	1.73	18.0	5.07
200-300	0.06	0.06	0.65	20.7	5.24
300-400	0.03	0.04	0.52	22.0	5.42
400-500	0.02	0.04	0.47	25.0	5.27
SLUDGE	3.22	3.04	46	-	6.88

Sludge data (*aqua regia*) mg kg^{-1}						
Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
22.3	74.9	949.5	953.6	379.6	735.1	5386.6

The total concentrations of Cr, Cu, Zn, Cd and Pb in the top 200mm of soil are above the MPL for South African soils (Dept. Nat. Health & Pop. Dev., 1991) and the suggested investigation thresholds (Herselman & Steyn, 2001), but the concentrations of all these elements decrease with depth in the soil profile (Figure 5.36).

In the case of Cu, Zn and Cd even the NH_4EDTA extractable fractions exceed the MPL for South African soils, which is based on total concentrations, as well as the threshold values set by Bruemmer & van der Merwe (1989). The NH_4NO_3 extractable fractions of Cu, Zn and Cd are also higher than guidelines set in Germany for NH_4NO_3 extractable metals (Baden-Wurttemberg, 1993).

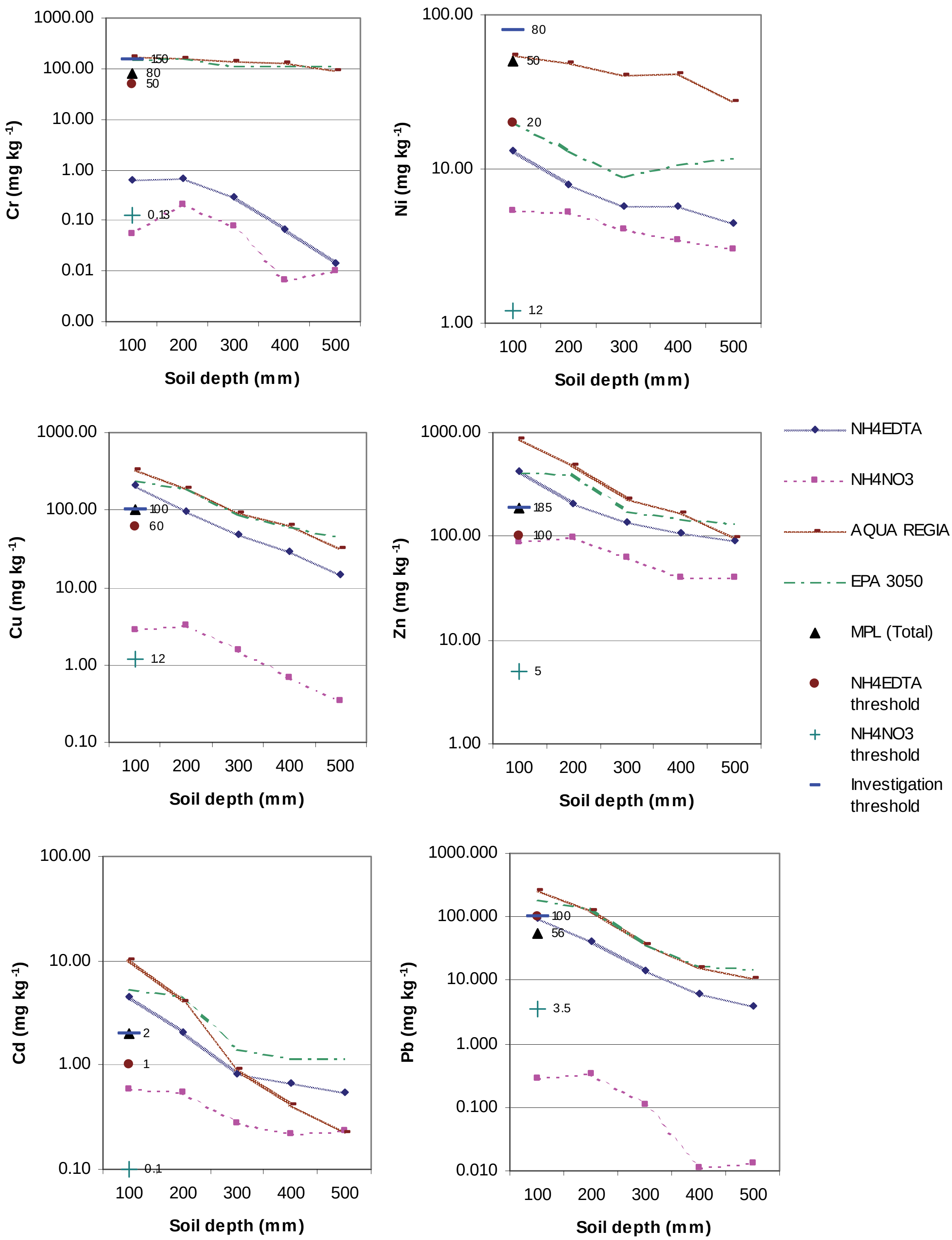


Figure 5.36: Cr, Ni, Cu, Zn, Cd and Pb contents of the soil profile at Site 36

A large percentage of the metals are associated with the organic C in the topsoil (top 300mm), but some leaching occurred through the lifetime of the disposal site due to the low pH(H_2O) and clay content of the soil. Groundwater monitoring is recommended to protect the groundwater.

5.5.2 Site 37

Waste activated and digested sludge have been flooded onto a Hutton soil (orthic A, red apedal B) for >40 years at this disposal site. The disposal area is ploughed occasionally. The site receives only domestic wastewater (7Ml/day) and is situated 4km from the river. No groundwater monitoring occur on site.

Table 5.37: Site 37 general soil data

Soil depth (mm)	**Total P %**	**Total N %**	**C %**	**Clay %**	**pH (H_2O)**
0-100	0.40	0.20	1.82	12.67	4.39
100-200	0.30	0.10	0.96	8.67	4.97
200-300	0.19	0.07	0.62	11.33	5.16
300-400	0.15	0.06	0.46	15.33	5.36
400-500	0.12	0.05	0.38	17.33	5.50

The top 200mm soil layers have much higher total P, N and organic C contents than lower down the soil profile and the pH(H_2O) of the soil is strongly acid (Table 5.37).

The total concentration (*aqua regia* and EPA 3050) of all the metals except Zn (topsoil sample) are below the MPL for South African soils (Nat. Dept. Health & Pop. Dev., 1991) (Figure 5.37). The bio-available concentrations are also below the NH_4EDTA threshold values (Bruemmer & van der Merwe, 1989), while only the soluble Ni and Zn concentrations exceed the NH_4NO_3 guidelines (Baden-Wurttemberg, 1993).

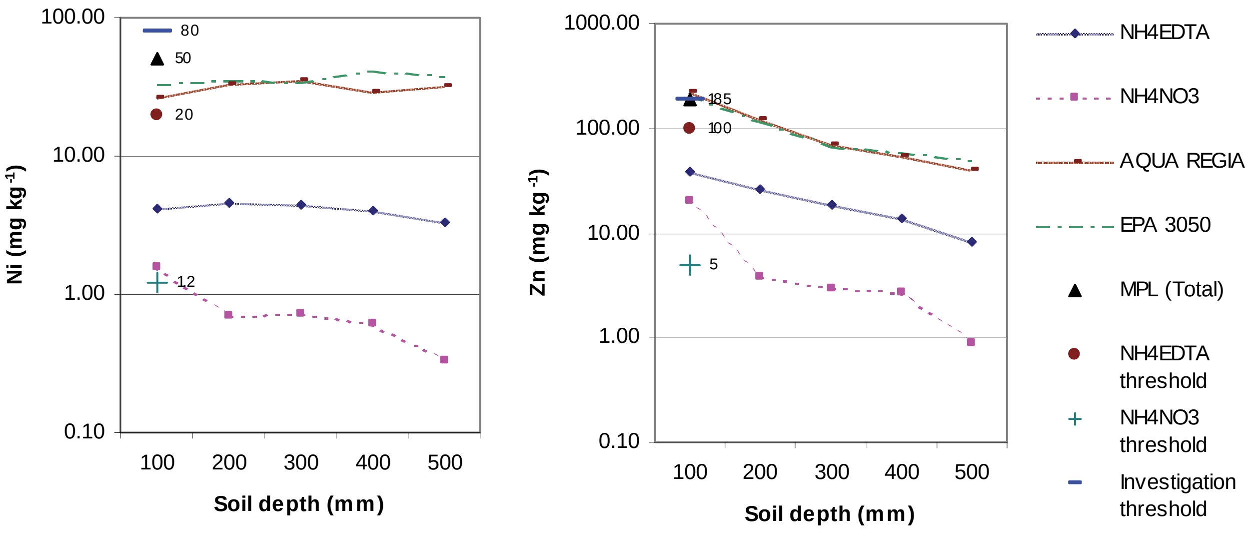


Figure 5.37: Ni and Zn contents of the soil profile at Site 37

Although this site receives only domestic wastewater there are high Ni and Zn concentrations in the soil and leaching occur due to the low clay content and acid pH(H_2O) of the soil (Kabata-Pendias & Pendias, 1992).

5.6 Dried application sites

5.6.1 Site 38

This site is on a deep, Hutton soil with 16-28% clay. It is a waste activated wastewater treatment facility that receives industrial effluent from a stainless steel factory. The sludge is dewatered with a belt press and the sludge cake is then applied to land, which is ploughed quarterly. This practice has been followed for 2 years. The disposal site is on level terrain and 2km from the nearest surface water body. There is no borehole on site and no groundwater sample could be obtained.

Table 5.38 indicates the organic C buildup in the topsoil due to the sludge application and ploughing of the topsoil. The soil pH(H_2O) of the whole soil profile is medium acid with the lowest pH in the topsoil. The total P content of the soil is also much higher in the topsoil than at the lower soil depths.

Table 5.38: Site 38 general soil data

Soil depth (mm)	Total P %	Total N %	C %	Clay %	pH (H_2O)
0-100	0.51	0.07	3.27	16.0	5.43
100-200	0.16	0.21	1.61	16.0	5.68
200-300	0.04	0.16	0.97	24.0	5.70
300-400	0.04	0.06	0.75	28.0	5.66
400-500	0.04	0.04	0.55	17.0	6.49

The total Cr, Cu and Zn concentrations in the top 100mm of soil exceed the MPL for South African soils (Dept. Nat. Health & Pop. Dev., 1991) and the total Pb concentration is just below these guidelines (Figure 5.38). The bio-available concentrations of Cr, Cu and Pb are well below the NH_4EDTA threshold values (Bruemmer & van der Merwe, 1989), but the bio-available Zn concentration in the topsoil is near the guideline value. The soluble fraction of Ni, Zn and Cu in the topsoil exceed the NH_4NO_3 guidelines for groundwater protection (Baden-Wurttemberg, 1993).

The concentrations of all the mentioned elements decrease with depth in the soil profile with the highest concentrations in the top 100mm and reaching the background concentration at 300mm. Leaching occur because of the low pH(H_2O) and clay content of the soil but is limited to a degree by the high organic C content of the topsoil (Kabata-Pendias & Pendias, 1992; Alloway, 1995).

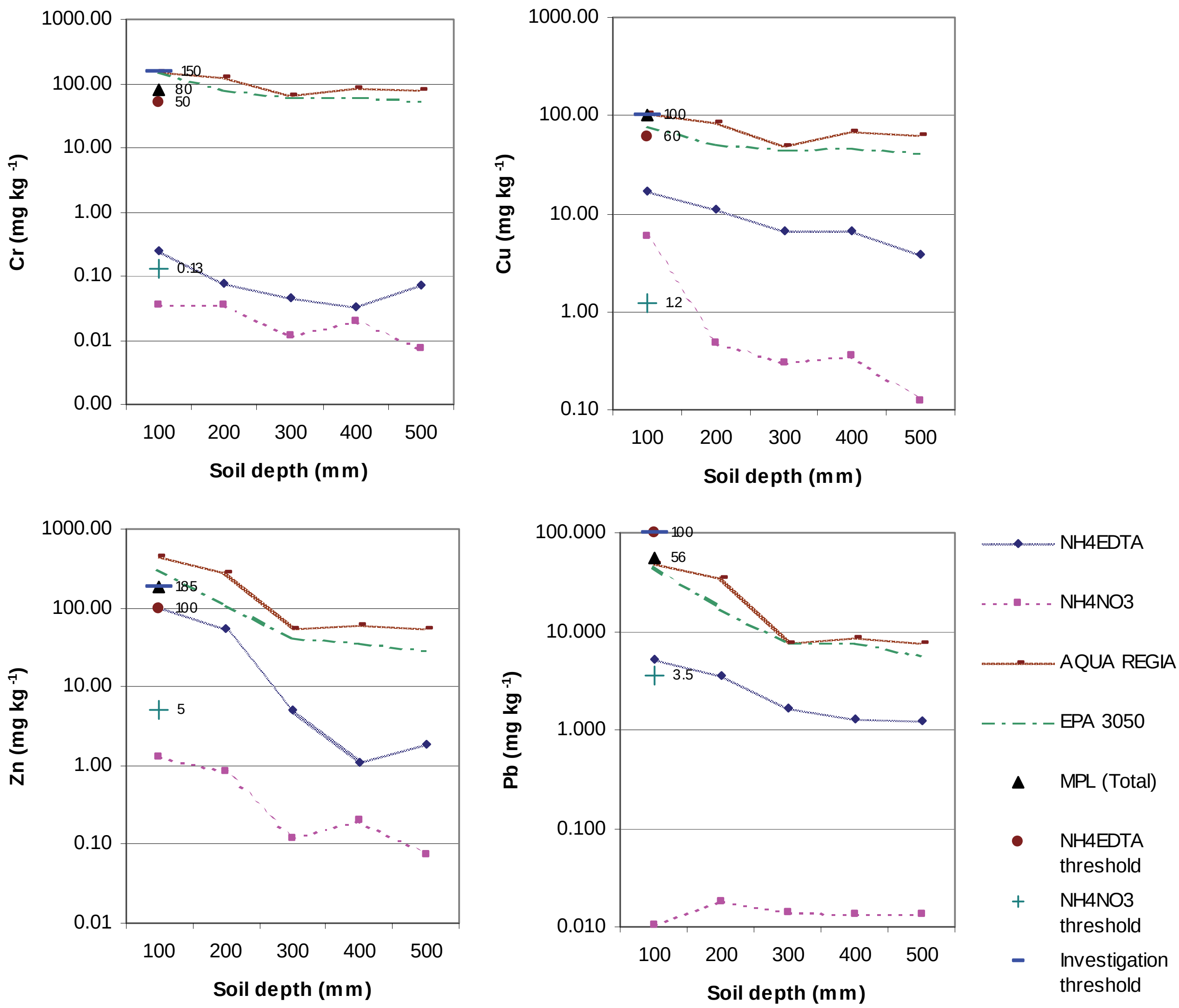


Figure 5.38: Cr, Cu, Zn and Pb contents of the soil profile at Site 38

5.6.2 Site 39

Site 39 receives 20% of its inflow from industries (metal plating, breweries, fats, oils and grease) and produces waste activated as well as anaerobic digested sludge. The sludge is dewatered with a belt press and the sludge cake is spread on 8ha of dedicated land, which is ploughed twice every year. This disposal practice has been in use for 5 years. The disposal site is situated on a flat surface, 200m from a river and there is no borehole on site. The underlying soil is a Hutton with low clay content (9-17%).

Table 5.39 presents the soil data of the site. There is a significant buildup of organic C, total P and total N in the top 300mm of the soil profile. The pH(H_2O) of the soil is extremely acid (<4.5). The organic C buildup is probably because the site is only ploughed twice a year, therefore the organic matter breakdown is slow. The total Cu and Ni content of the sludge exceed the guideline values (WRC, 2002).

Table 5.39: Site 39 general soil and sludge data

Soil depth (mm)	Total P %	Total N %	C %	Clay %	pH (H_2O)
0-100	1.01	1.03	7.75	8.7	4.43
100-200	0.30	0.33	3.07	8.7	4.73
200-300	0.11	0.15	1.33	11.3	4.30
300-400	0.06	0.06	0.67	13.3	4.36
400-500	0.04	0.05	0.54	16.7	4.26
SLUDGE	3.64	5.03	61	-	6.79

Sludge data (*aqua regia*) mg kg^{-1}						
Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
15.5	7.8	205.3	1574.5	279.1	150.9	2613.4

After only 5 years of sludge application, all total heavy metal contents of the top 200mm soil samples are above the MPL for South African soils (Dept. Nat. Health & Pop. Dev., 1991) and decrease with depth. The Cu, Zn and Cd concentrations in particular are very high (Figure 5.39). Adsorption of metals in the topsoil occurred due to the high organic C content, but leaching occurred due to the low pH(H_2O) and clay content of the soil. The high Cr and Ni concentrations in the whole soil profile may be due to the high background concentrations of these metals in South African soils (Herselman & Steyn, 2001).

The NH_4EDTA extractable Cr, Cd and Pb are well below the NH_4EDTA threshold values (Bruemmer & van der Merwe, 1989), but the bio-available concentrations of Cu and Zn in the topsoil exceed these values. The NH_4NO_3 extractable concentrations of Ni, Cu, Zn and Cd exceed the guideline values for NH_4NO_3

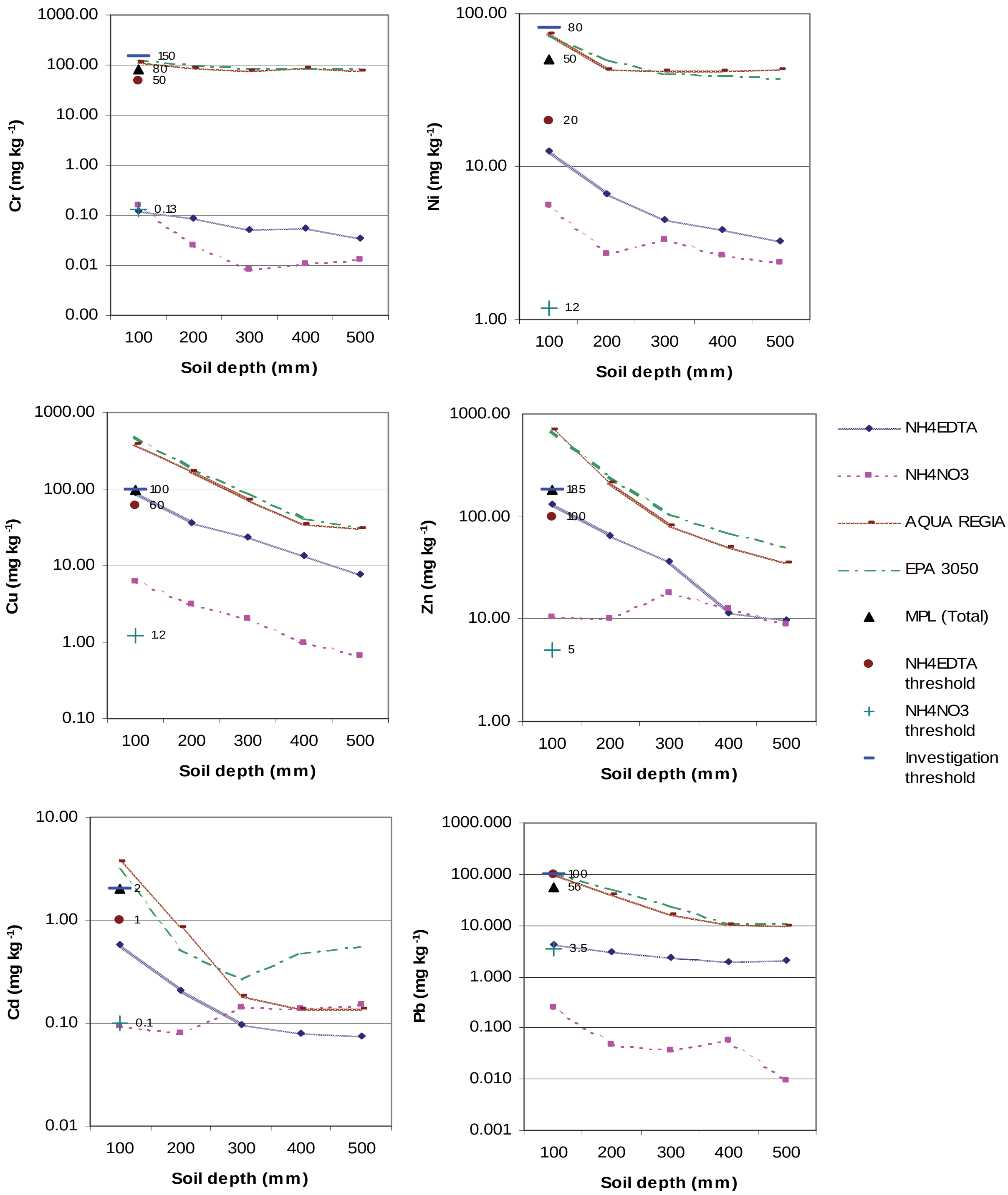


Figure 5.39: Cr, Ni, Cu, Zn, Cd and Pb contents of the soil profile at Site

extractable metals (Baden-Wurttemberg, 1993). Groundwater monitoring is advised at the site because of the high soluble concentrations of metals in the whole soil profile as well as the high nitrogen loading of the sludge.

5.6.3 Site 40

Site 40 receives mainly industrial wastewater and produces waste activated sludge. The sludge is mechanically dried and disposed of on 16ha land and ploughed occasionally. The disposal site is situated on a deep Hutton soil with <10% clay. The disposal site is on a slope, 100m from a stream. The groundwater data is still awaited.

There is an accumulation of total P, N and organic C in the top 200mm soil layers, decreasing gradually down the soil profile (Table 5.40). The pH(H_2O) of the soil is very strongly acid (van der Watt & van Rooyen, 1990). The metal content of the sludge is very low.

Table 5.40: Site 40 general soil and sludge data

Soil depth (mm)	**Total P %**	**Total N %**	**C %**	**Clay %**	**pH (H_2O)**
0-100	0.27	0.26	1.95	7.33	5.04
100-200	0.13	0.15	1.52	8.67	5.02
200-300	0.02	0.04	0.54	9.33	4.79
300-400	0.02	0.04	0.53	9.33	4.86
400-500	0.02	0.03	0.44	9.33	5.06
SLUDGE	1.6	4.88	60	-	6.91

Sludge data (*aqua regia*) mg kg^{-1}						
Cd	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
0.65	3.01	51.9	109.3	48.2	15.7	474.3

The total concentrations of all studied metals are below the MPL for South African soils (Nat. Dept. Health & Pop. Dev., 1991). Figure 5.40 show the distribution of Ni and Zn in the soil profile. The EPA 3050 extractable Ni and Zn are higher in the top 200mm soil layers and reach the background concentration at 300mm. The *aqua regia* extractable Ni and Zn are more uniformly distributed through the soil. The 500mm soil sample were probably contaminated, therefore the high concentrations.

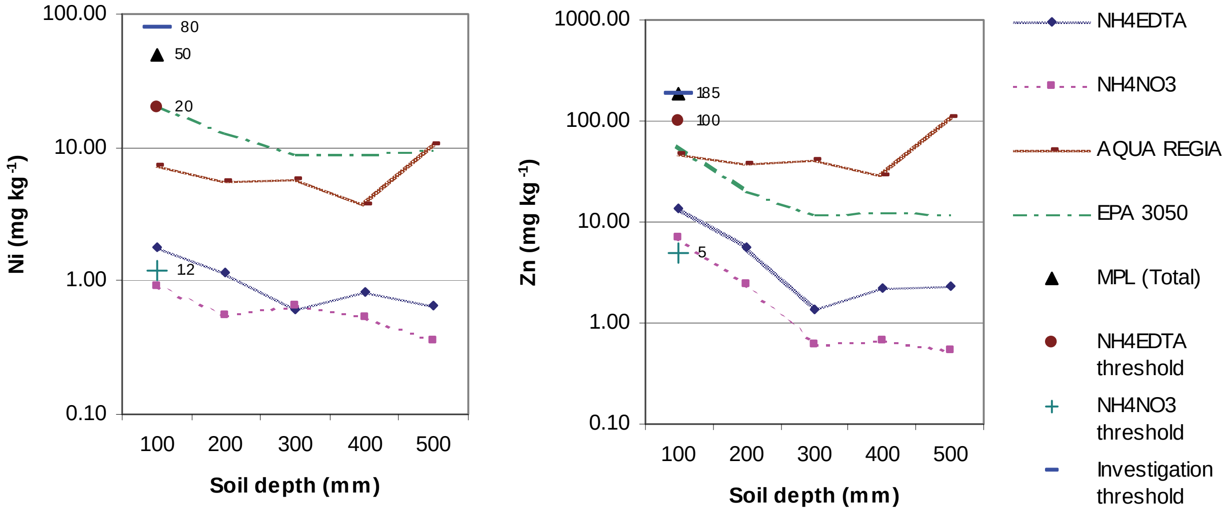


Figure 5.40: Ni and Zn contents of the soil profile at Site 40

The bio-available concentrations of all studied metals are below the NH_4EDTA threshold values (Bruemmer & van der Merwe, 1989). Only the soluble Zn concentration exceeds the NH_4NO_3 guidelines (Baden-Wurttemberg, 1993). Leaching of the metals occur to a depth of 300mm due to the very low soil pH(H_2O) and clay content. The low soluble concentrations of the metals in the soil indicate no immediate risk for metal pollution of the groundwater, but NO_3 contamination may be a possibility.

5.7 General observations and concerns

Many of the disposal sites is situated on soils with <35% clay (37% of sites) and even <10% clay (17% of sites) and the pH(H_2O) of the soils is generally <6. These soil properties indicate soils with a high probability for leaching. Given this information, only 9 of the studied disposal sites have a groundwater monitoring system in place. Of these 9 sites, 7 had NO_3 concentrations above the DWAF (1996) water quality guidelines. This is really reason for concern.

Most of the disposal sites are not fenced off and very near to populated areas. General access by the public occurs and in some cases the local people harvest edible plants that grow on the disposal sites.

The majority of the disposal sites are on even terrain, but most of those that are on a slope have no erosion control measures in place even though they are near surface water bodies. Surface water monitoring at these sties is recommended.

Generally the larger cities and metropolitan councils were found to be knowledgeable in sludge management and legislative requirements but this was not the case in other towns. Many plant managers didn't really care where they put the sludge, as long as it is disposed of. No systems exist at most wastewater treatment facilities to manage the disposal of the sludge. At two wastewater treatment facilities raw sewage was disposed of on the disposal site.

APPENDIX B: SOIL DATA

100 INITIAL SITES

MACRO ELEMENTS

EPA 3050 EXTRACTABLE METALS

Site number	WRC NUMBER	pH(H2O)	Ca mg/kg	K mg/kg	Na mg/kg	Mg mg/kg	Bray I P mg/l	Total N %	Org C %	Clay %
1	WRC 1283 32	8.84	4218	79	53	60	147.5	0.181	14.14	2.64
1	WRC 1283 32	8.25	4213	17	29	21	137.69	0.041	1.05	1.25
1	WRC 1283 32	7.68	4204	40	41	29	137.6	0.144	11.02	4.94
2	WRC 1283 31	7.84	4454	55	74	79	144.7	0.089	2.09	0.76
2	WRC 1283 31	8.06	4180	21	47	39	146.7	0.053	2.2	0.75
3	WRC 1283 26	5.73	1517	674	33	119	520	0.257	2.49	11.21
3	WRC 1283 26	4.92	3642	744	32	148	471	0.548	10.92	21.38
4	WRC 1283 63	7.32	3244	357.75	323	205.54	119.76	0.054	0.56	13.27
4	WRC 1283 63	6.44	1866	339.5	278	167.29	99.31	0.083	0.4	10.87
4	WRC 1283 63	6.73	9360	765	579	510.01	189.66	0.74	10.32	10.23
5	WRC 1283 74	5.85	371	158	7	29	284.79	0.056	0.37	4.01
5	WRC 1283 74	5.46	143	106	8	12	116.35	0.043	0.34	3.76
5	WRC 1283 74	5.29	166	114	6	13	23.86	0.042	0.32	4.76
6	WRC 1283 23	7.32	5884	187	63	979	192	0.81	39.15	13.09
6	WRC 1283 23	7.18	3261	82	11	180	365	0.221	2.64	9.76
7	WRC 1283 69	8.38	2857	194	181	114	237.8	0.124	1.44	15.99
7	WRC 1283 69	6.73	907	206	167	73	22.74	0.091	0.68	17.73
8	WRC 1283 49	5.23	2000	449	45	498	833	0.449	8.68	19.22
8	WRC 1283 49	4.73	1423	489	45	289	768	0.315	3.45	12.53
8	WRC 1283 49	5.18	724	327	51	136	399	0.733	1.13	9.55
9	WRC 1283 55	7.71	6866	483	115	617	487.3	0.03	0.83	35.37
9	WRC 1283 55	5.68	3466	1318	311	1530	383.3	1.13	57.55	0.55
9	WRC 1283 55	7.78	3326	1381	108	653	498.1	0.178	1.32	38.50
10	WRC 1283 02	6.07	1185	308.9	142	124	45.56	0.146	0.98	33.77
11	WRC 1283 52	6.39	624	178	17	72	30.44	0.108	0.58	13.31
11	WRC 1283 52	4.67	530	84	16	66	334	0.142	0.7	12.26
11	WRC 1283 52	5.28	1840	251	17	94	355	0.861	14.38	19.41
12	WRC 1283 53	7.06	13656	516	228	1960	245.9	0.219	3.05	49.95
12	WRC 1283 53	7.32	7163	248	241	726	295.87	0.174	2.06	29.11
12	WRC 1283 53	6.18	10076	627	264	1434	283.3	0.529	8.2	54.18
13	WRC 1283 43	7.63	2942	154	76	114	165.3	0.11	13.48	2.89
13	WRC 1283 43	5.67	297	353	5	76	202	0.042	0.43	12.82
13	WRC 1283 43	6.77	1376	70	55	98	158.4	0.062	1.81	5.98
14	WRC 1283 56	7.21	2618	239	126	614	237.5	0.295	2.7	16.30
14	WRC 1283 56	6.15	2007	121	72	324	227.7	0.154	1.45	13.94

15		5.44	95	49	2	6	10	0.028	0.4	7.58
15		5.17	28	17	2	2	4.75	0.011	0.16	3.81
15		5.47	68	149	6	9	6.82	0.031	0.53	10.56
16	WRC 1283 61	5.47	2756	117.86	119	336.13	32.07	0.239	2.27	28.82
16	WRC 1283 61	6.65	5474	191.32	170	229.07	142.58	0.614	13.3	23.43
17	WRC 1283 34	5.64	307	21	16	18	129.3	0.024	1.81	0.25
17	WRC 1283 34	5.33	685	93	37	76	137.7	0.127	1.85	1.22
18		7.44	4628	282.57	328	340.02	137.93	0.228	2.47	6.32
18		8.16	9132	865	768	1562	47.99	0.153	2.15	21.81
19	WRC 1283 15	4.83	526	599	8	21	428	0.198	2.22	10.84
19	WRC 1283 15	5.96	2841	770	406	359	335	0.395	3.55	34.25
19	WRC 1283 15	5.65	760	208	11	80	106.6	0.079	0.66	10.06
20	WRC 1283 21	6.18	1225	129	85	58	154.9	0.139	3.05	12.73
20	WRC 1283 21	6.36	1057	212	34	66	118.23	0.139	2.39	12.26
20	WRC 1283 21	6.67	1547	233	76	119	174.8	0.116	1.98	23.05
21	WRC 1283 08	6.39	1257	366.9	175	167	15.06	0.094	1.8	31.78
21	WRC 1283 08	5.45	572	250.8	85.9	55.3	33.01	0.134	1.51	29.22
21	WRC 1283 08	5.51	354	151.1	75	45.1	55.32	0.133	1.31	26.74
22	WRC 1283 22	6.32	421	93	30	54	150.7	0.052	0.97	7.04
22	WRC 1283 22	4.92	178	155	25	34	170.3	0.065	1.81	9.27
22	WRC 1283 22	4.93	187	132	21	33	165.5	0.052	1.09	8.01
23	WRC 1283 12	5.46	343	384.2	59.9	107	71.85	0.201	3.01	6.69
23	WRC 1283 12	5.1	447	717	117	150	243.49	0.341	9.22	13.87
23	WRC 1283 12	4.6	297	184.2	34.74	85.2	116.65	0.221	3.21	7.70
24		4.84	1229	1386	155	216.2	245.96	0.45	10.24	35.40
24		5.26	1518	1741	172	261	247.33	0.562	12.3	35.17
24		5.2	1953	1776	194	468	248.75	0.573	12.7	35.34
25	WRC 1283 27	5.64	2863	239	82	118	148.1	0.463	59.15	10.91
25	WRC 1283 27	5.4	157	17	23	18	153.5	0.025	0.23	0.40
25	WRC 1283 27	7.52	1193	69	83	92	148.8	0.04	1.33	1.82
26	WRC 1283 06	7.94	7752	57.91	53	96.95	45.85	0.035	0.23	1.90
26	WRC 1283 06	8.21	7754	35.25	42.8	64.84	17.92	0.023	0.17	3.50
26	WRC 1283 06	7.57	9347	27.68	287	223.2	185.39	0.017	0.19	4.64
26	WRC 1283 06	8.34	7564	9.01	39.25	55.85	28.58	0.022	0.27	2.35
27	WRC 1283 05	6.23	2841	968	265	341	336.99	1.041	60.65	29.35
27	WRC 1283 05	6	3179	592	269	403	261.73	0.325	9.84	16.84

27	WRC 1283 05	6.3	937	430.6	89	104	258.53	0.389	10.02	17.34
28	WRC 1283 30	5.88	477	189.8	109	21.5	265.27	0.379	9.4	15.95
28	WRC 1283 30	7.11	1737	319.2	141	138	61.02	0.085	1.04	14.98
28	WRC 1283 30	6.46	933	176.8	56.8	81.1	19.88	0.096	0.66	20.86
29	WRC 1283 03	4.93	901	426.9	84.8	117	268.2	0.355	8.6	21.09
29	WRC 1283 03	5.05	960	463.7	61.6	100	167.58	0.242	2.93	20.65
30	WRC 1283 47	7.94	1834	552	138	224	143	0.179	1.45	26.32
30	WRC 1283 47	5.23	2273	1487	307	725	671	0.633	11.32	43.44
31	WRC 1283 18	4.36	1750	1285	34	75	161.9	1.138	65.8	21.53
31	WRC 1283 18	4.57	1784	953	35	143	160.7	0.838	43	19.21
31	WRC 1283 18	5.36	625	622	14	90	159.5	0.305	9.12	8.99
32	WRC 1283 72	7.68	15502	330	672	277	17.31	0.092	1.05	29.13
32	WRC 1283 72	7.9	15202	415	928	218	7.22	0.13	1.31	24.72
33	WRC 1283 42	4.62	792	813	58	76	138.5	0.358	9.56	21.68
33	WRC 1283 42	5.11	1334	815	165	173	139.8	0.378	9.92	20.66
33	WRC 1283 42	4.86	1527	794	111	171	185.8	0.477	11.94	24.20
34	WRC 1283 80	7.61	6023	48.69	131	79.26	150.66	0.12	0.59	0.15
34	WRC 1283 80	7.83	6099	36.73	110	81.79	126.78	0.062	0.47	0.15
34	WRC 1283 80	6.96	5921	171.37	230	249.44	242.21	0.371	1.61	2.78
35	WRC 1283 07	5.45	801	339.5	160	124	189.93	0.286	3.49	15.84
35	WRC 1283 07	5.31	344	178.2	84.4	70.5	30.59	0.102	1.94	18.85
35	WRC 1283 07	5.93	422	103.5	7.79	140.5	58.8	0.112	1.27	21.96
36	WRC 1283 04	5.78	1288	192.3	86.4	115	265.45	0.308	9.36	19.47
36	WRC 1283 04	5.98	1678	187.7	90.1	126	264.47	0.328	10.12	21.04
36	WRC 1283 04	5.67	1611	171.9	83.6	151	263.49	0.593	13.36	15.74
37		4.27	184	289	49	44	292.32	0.148	1.78	11.13
37		4.16	491	595	136	56	279.47	0.434	8.48	17.18
37		4.4	733	586	164	51	286.83	0.581	8.12	45.26
38		4.33	322	562	44	74.03	436.4	0.162	2.48	8.25
38		4.41	113	257	20	22	74.87	0.083	0.81	6.30
38		5.67	158	281	19	33	213.9	0.106	0.8	7.41
39	WRC 1283 16	7.04	1609	956	159	817	184.8	0.73	11	24.45
39	WRC 1283 16	5.14	1947	743	69	522	198.7	0.742	14.64	28.36
40	WRC 1283 41	6.01	2152	473	196	122	132.8	0.624	13.66	7.48
40	WRC 1283 41	4.58	925	715	300	112	127.9	1.5	80.55	32.09
40	WRC 1283 41	5.1	578	271	185	100	138.1	0.249	3.72	7.31

41	5.64	1029	495	36	524	158.4	0.271	3.04	8.02
41	4.82	345	177	16	164	157.2	0.059	0.84	5.82
42	7.23	248	26	36	25	120.2	0.056	1.12	4.41
42	6.52	582	57	40	38	137.8	0.086	1.02	4.82
42	6.64	371	29	54	26	124.9	0.049	0.75	5.58
43	4.21	5469	273	122	180	222.8	0.896	48.35	23.85
44	7.36	6508	947	528	517	133.5	0.173	0.88	30.53
44	7.34	4376	386	139	129	159.6	0.118	1.17	11.96
45	5.26	1107	586	95	212	141.6	0.179	1.56	16.30
45	6.1	1107	618	84	238	133.04	0.106	0.93	23.90
46	5.94	2719	113	36	330	137.6	0.108	1.48	39.44
46	7.93	3394	523	14	157	127.4	0.144	2.02	32.07
47	6.31	5204	1013	152	470	137.8	1.28	71	35.09
47	7.68	2703	397	339	396	138.8	0.146	0.91	29.15
48	5.3	2869	90	48	159	128.7	0.333	14.26	10.53
48	5.26	6010	274	113	285	137.9	0.955	72.35	29.84
49	5.6	4325	271	130	230	179.5	0.948	45.05	34.08
49	6.59	6720	250	626	538	189.2	1.358	3.02	18.15
50	5.75	2967	825	556	889	221.5	0.695	52.85	48.24
51	6.98	1335	151	45	290	390.2	0.057	0.67	35.77
51	5.74	1119	198	27	182	404.3	0.098	1.15	32.94
52	7.26	3168	78.59	116	363.02	181.76	0.079	0.72	12.96
52	5.74	3151	81.43	208	490.87	242.9	0.274	2.15	14.57
53	6.94	1157	77.74	270	616.62	11.03	0.071	0.61	23.21
53	5.8	1901	86.07	46.03	166.27	79.34	0.296	3.72	25.59
54	8.83	7531	23.08	40.85	48.82	14.37	0.017	0.08	0.95
54	8.69	7471	39.99	44.67	58.02	12.62	0.022	0.19	0.90
55	8.72	4347	377.39	1424	744.58	24.93	0.041	0.14	16.92
55	8.8	6331	375.13	3002	764.6	10.09	0.02	0.08	20.62
56	8.13	9063	563	390	671	13.33	0.07	0.23	13.38
56	8.15	6235	443.15	417	593.64	72.66	0.075	0.42	18.58
57	7.98	7031	110.44	52.78	158.24	57.18	0.069	0.88	5.21
57	8.63	7939	170.18	63.55	213.73	16.75	0.055	0.76	4.80
58	5.65	1905	115.4	38.23	82.96	191.46	0.17	1.73	2.39
58	5.26	197	42.7	16.74	21.25	181.89	0.024	0.13	0.30
59	5.42	301	112.03	21.03	36.54	116.79	0.037	0.17	0.75

59	8.18	3588	177.55	60.86	170.23	45.16	0.036	0.38	5.11
59	8.18	514	191.66	30.01	99.94	44.89	0.027	0.22	1.47
60	5.74	342	92.99	23.07	36.86	116.24	0.06	0.31	1.20
60	6.56	2601	254.42	221	427.47	66.16	0.097	0.54	7.99
60	5.03	1562	354.5	287	279.8	129.34	0.158	0.87	7.96
61	5.21	2347	241.5	39.98	128.79	48.3	0.11	1.06	22.53
61	4.3	3420	376.15	164	205.57	76.56	0.27	69.75	13.36
62	5.69	8088	2193	791	1612	161.96	1.567	3.03	34.81
62	5.81	7850	2361	795	1613	150.55	1.383	69.35	35.07
62	5.12	6811	1769	414	621.91	1.58	2.324	54.9	28.31
63	4.87	752	144.08	25.63	67.11	133.22	0.111	1.65	27.18
63	4.58	825	70.59	41.11	61	134.77	0.127	1.77	24.53
63	4.29	780	341.43	27.72	57.83	138.33	0.808	34.35	24.48
64	7.56	9925	1058	27	221	187.36	0.183	1.8	19.00
64	6.92	8938	668	158	176	258.93	0.252	1.81	18.08
64	6.31	5403	872	261	270	68.99	0.156	1.36	35.89
65	7.86	4866	237	60	164	58.22	0.101	1.13	11.69
65	7.92	3875	284	108	240	68.65	0.094	1.04	14.71
66	6.23	593	223	60	52	65.44	0.084	0.87	20.27
66	5.46	765	191	59	53	193.2	0.099	1.23	18.95
66	5.87	744	392	184	83	56.97	0.135	1.24	25.26
67	4.73	196	69	58	34	274.2	0.072	1.09	24.54
67	5.31	863	234	21	60	280.49	0.155	1.83	15.75
67	5.18	283	90	54	38	278.79	0.084	1.21	26.92
68	4.84	232	103	50	35	288.3	0.086	1.06	25.90
68	4.36	7896	1063	125	71	283.81	1.481	65.05	36.31
68	4.72	8807	710	38	20	279.33	0.833	9.08	13.11
69	5.27	687	64	233	48	292.98	0.247	3.44	20.59
69	6.34	963	71	384	88	44.06	0.124	2.62	14.20
69	5.6	1187	257	131	90	287.5	0.366	9.96	19.29
70	7.01	197	140	178	85	5.03	0.066	0.33	6.82
70	6.84	535	240	61	112	17.53	0.109	1.15	7.75
70	7.21	347	114	201	89	4.53	0.042	0.47	6.68
71	7.03	685	343	55	153	19.09	0.179	2.14	22.32
71	7.62	157	234	23	43	6.91	0.107	1.51	9.79
71	5.57	1498	430	169	87	458	0.414	3.65	4.47

72	6.27	533	77	7	14	223.1	0.088	1.29	2.22
72	7.56	999	169	14	74	42.1	0.068	1.09	11.58
72	6.13	492	164	14	75	7.41	0.115	1.82	6.79
73	5.86	378	462	12	80	8.49	0.08	1.21	27.35
73	6	448	368	18	75	4.51	0.079	1.17	32.25
74	5.33	1933	140	138	239	39.76	0.086	0.8	35.14
74	6.08	1454	168	150	419	3.56	0.118	1.17	25.53
74	6.95	859	197	32	241	10.59	0.066	0.95	32.15
75	7.21	3679	333	50	174	4.25	0.086	1.15	19.40
75	6.16	1407	142	40	73	13.24	0.143	1.62	25.21
75	4.63	5272	491	157	165	13.41	0.882	11.66	20.34
76	4.6	173	29	7	13	33.44	0.05	0.67	1.65
76	5.28	222	41	9	17	18.96	0.048	0.37	4.90
76	5.21	38	8	3	2	7.74	0.019	0.22	3.00
77	4.67	1522	198	27	87	237	0.565	42.75	17.97
77	4.6	1430	265	39	117	195	0.122	1.42	38.89
78	5.63	1726	421.2	114	359	23.53	0.155	2.74	33.95
78	5.96	2184	385.1	142	417	94.24	0.172	3.08	56.54
78	5.5	1380	373.1	74.4	198	210.57	0.192	3.34	28.26
79	6.57	1693	364.2	26.7	141	69.1	0.1	2.15	22.65
79	7.02	1205	350.1	8.95	193	77.63	0.122	2.44	26.71
79	6.78	2369	115.5	83.8	187	93.69	0.184	3.72	23.50
80	3.97	848	1088	123	260	280.22	0.817	48.95	21.01
80	5.07	579	153.5	6.28	43.6	51.64	0.085	1.8	19.72
81	6.22	5502	466.3	78.81	791	104.6	1.037	3.29	30.13
81	5.63	4683	873	57.9	684	286.18	0.726	40.1	33.76
81	6.86	2591	673	29.1	342	64.72	0.165	2.39	34.97
82	5.92	16571	473	165	273	287	0.242	1.55	16.97
82	6.33	2303	391	68	69	426	0.249	1.83	5.48
82	6.33	978	117	53	133	51	0.102	0.8	6.78
83	5.36	2852	232	74	606	34	0.148	1.63	52.93
84	4.02	1525	386	48	194	418	1.175	49.3	41.96
84	5.1	783	117	26	57	203	0.282	3	29.93
85	4.41	3755	261	82	372	287	0.765	13.04	30.58
85	4.58	1757	196	47	293	47	0.14	1.27	37.50
86	5.14	456	684	16	75	590	0.124	1.05	12.40

86	7.04	1126	620	85	297	66	0.087	0.63	23.23
86	5.67	297	353	5	76	202	0.042	0.43	12.82
86	6.77	1376	70	55	98	158.4	0.062	1.81	5.98
87	5.42	439	347	60	109	282	0.034	0.26	13.54
87	6.14	636	282	131	141	76.6	0.037	0.18	13.41
87	8.13	1416	413	325	289	73.96	0.076	0.5	21.87
88	7.28	284	50	50	68	2.5	0.033	0.65	8.06
88	6.23	88	29	6	13	3.02	0.019	0.15	0.72
88	8.6	4477	343	189	352	4.89	0.079	1.09	6.26
89	6.47	5150	501	330	706	185.7	0.723	52.55	33.54
89	5.6	4925	1127	1435	2315	208.1	1.38	76.65	47.59
90	5.69	2117	639	40	209	137.6	0.329	3.08	40.99
91	7.94	3796	534	36	210	156.04	0.076	1.49	3.71
92	5.15	532	225	25.81	129	43.74	0.117	1.59	18.18
93	4.98	5831	1825	338	584	1017.3	0.07	40.2	21.75
93	5.26	3802	1284	207	366	995.8	0.05	9.44	21.90
93	5.04	7083	1959	317	649	1309.4	0.05	14.78	32.44
94	7.57	15004	805	230	173	136.76	0.194	1.73	28.78
94	7.89	8219	728	224	239	57.8	0.195	1.79	27.38
95	4.27	2158	1588	200	676	673	0.644	11.24	37.19
96	4.83	3592	361	45	149	494	0.375	8.96	18.98
97	7.89	4435	116	120	140	138.4	0.168	9.92	2.95
98	5.49	3087	432.5	121	207	283.07	1.209	55.95	28.90
99	4.44	613	229	13	56	294	0.286	3.07	42.99
100	6.57	744	436	344	102	3.04	0.1	1.49	27.67

Site number	WRC NUMBER	Lithium	Beryllium	Boron	Titanium	Vanadium	Chromium	Manganese	Cobalt	Nickel
1	WRC 1283 32	1.720	1.329	20.167	212.090	7.150	10.770	43.320	1.648	12.809
1	WRC 1283 32	1.650	1.166	8.959	213.890	4.512	6.120	16.570	1.060	6.302
1	WRC 1283 32	6.967	2.721	14.426	270.480	16.609	21.836	89.656	2.665	38.545
2	WRC 1283 31	1.374	0.938	16.859	213.780	15.441	31.170	28.680	4.873	14.142
2	WRC 1283 31	1.151	0.941	9.579	247.190	11.992	22.950	19.730	2.073	14.502
3	WRC 1283 26	5.925	4.491	12.420	103.520	33.119	45.850	115.020	6.732	26.153
3	WRC 1283 26	9.232	2.973	8.175	127.900	28.121	53.526	167.170	9.055	33.250
4	WRC 1283 63	20.111	21.907	121.440	33.624	56.533	86.834	142.430	11.160	121.780
4	WRC 1283 63	23.180	26.981	60.672	36.372	50.583	33.631	164.920	10.356	22.833
4	WRC 1283 63	0.906	2.462	54.762	89.131	4.393	7.660	53.129	1.787	7.585
5	WRC 1283 74	4.575	3.413	6.154	138.270	25.063	27.377	782.330	2.491	9.124
5	WRC 1283 74	2.995	1.800	4.312	99.236	19.454	20.257	665.320	2.249	7.990
5	WRC 1283 74	3.704	2.102	4.981	116.990	20.553	24.237	526.120	3.355	46.169
6	WRC 1283 23	8.481	4.227	48.998	200.000	27.280	57.600	35693.900	10.331	28.927
6	WRC 1283 23	6.550	5.314	19.056	175.740	20.418	31.640	6999.490	6.556	14.124
7	WRC 1283 69	7.427	5.806	5.744	282.490	71.500	109.010	684.160	25.579	43.145
7	WRC 1283 69	10.788	5.466	15.314	374.850	86.675	153.410	799.430	37.938	167.480
8	WRC 1283 49	4.200	4.975	24.789	184.020	71.107	183.410	172.000	7.386	36.605
8	WRC 1283 49	4.713	5.739	21.779	165.890	65.990	150.950	162.290	7.709	38.220
8	WRC 1283 49	5.044	7.770	16.016	98.039	55.896	69.830	459.300	8.438	34.209
9	WRC 1283 55	11.509	4.626	30.458	36.444	98.448	65.770	911.700	43.070	111.570
9	WRC 1283 55	6.809	5.557	16.962	195.670	127.160	243.720	503.290	15.391	82.767
9	WRC 1283 55	11.373	4.115	9.320	312.190	200.020	152.950	202.370	40.577	92.411
10	WRC 1283 02	17.041	14.813	23.872	32.462	107.760	148.140	1493.770	18.781	54.590
11	WRC 1283 52	6.688	5.381	30.542	162.150	44.222	50.720	104.180	6.167	26.033
11	WRC 1283 52	7.138	4.538	38.384	211.300	43.280	56.400	71.670	3.785	28.363
11	WRC 1283 52	8.553	5.727	21.082	195.780	44.775	73.510	255.540	6.553	38.820
12	WRC 1283 53	8.644	6.120	10.040	201.250	92.330	206.610	816.060	32.194	142.980
12	WRC 1283 53	9.076	7.579	0.000	200.200	102.510	268.830	692.330	27.912	127.370
12	WRC 1283 53	8.372	6.442	24.626	191.070	91.805	265.260	757.880	31.393	132.910
13	WRC 1283 43	8.778	6.979	28.101	9.766	68.890	683.100	986.030	111.370	168.670
13	WRC 1283 43	6.697	4.382	44.355	128.360	33.830	47.110	344.560	5.533	15.750
13	WRC 1283 43	5.732	7.114	31.682	189.540	52.786	47.110	449.900	10.603	57.753
14	WRC 1283 56	8.497	7.804	23.974	217.400	53.593	46.770	380.700	16.813	35.013
14	WRC 1283 56	4.159	5.717	3.124	179.510	39.553	29.710	87.420	7.847	20.179

15		3.524	1.655	2.827	108.850	36.995	44.205	57.349	2.108	10.035
15		3.135	0.540	3.037	71.282	23.462	27.775	38.686	1.654	4.929
15		2.671	3.184	3.346	125.280	53.867	59.839	120.100	3.317	4.687
16	WRC 1283 61	7.236	11.311	293.150	196.060	25.857	25.389	168.810	11.962	23.497
16	WRC 1283 61	0.035	2.684	264.770	212.700	29.130	52.427	165.580	11.943	27.140
17	WRC 1283 34	0.453	0.554	6.637	41.075	1.819	4.010	9.530	0.194	5.191
17	WRC 1283 34	0.473	0.426	0.000	37.273	10.244	23.950	16.620	0.351	26.724
18		7.534	3.143	8.040	209.210	29.742	25.003	167.890	5.146	14.342
18		18.747	6.377	16.420	214.500	51.463	42.276	177.890	10.548	23.798
19	WRC 1283 15	5.586	1.856	13.230	86.630	17.058	25.479	53.475	4.724	28.797
19	WRC 1283 15	8.326	4.822	37.056	121.980	31.522	55.990	90.380	4.948	20.156
19	WRC 1283 15	4.042	2.551	11.496	82.540	17.991	26.380	132.200	2.838	10.525
20	WRC 1283 21	14.710	5.778	14.537	206.210	72.523	485.560	597.410	56.085	142.880
20	WRC 1283 21	15.501	5.678	0.000	209.020	88.443	357.830	532.250	22.059	119.090
20	WRC 1283 21	15.700	7.217	29.535	219.490	104.890	152.670	1397.970	30.282	99.089
21	WRC 1283 08	16.553	11.291	36.414	0.905	145.550	210.240	2506.340	44.505	77.805
21	WRC 1283 08	13.275	8.543	26.090	31.835	112.600	125.220	1130.230	24.674	48.031
21	WRC 1283 08	13.238	8.391	40.204	44.954	110.730	150.140	845.790	20.736	40.498
22	WRC 1283 22	6.649	4.231	0.000	154.680	56.898	83.140	36.180	3.468	41.286
22	WRC 1283 22	7.108	3.497	15.622	107.870	39.060	53.210	41.130	3.186	24.160
22	WRC 1283 22	7.594	4.340	4.307	145.910	50.731	63.990	131.280	9.188	31.477
23	WRC 1283 12	5.913	4.540	23.012	160.920	53.195	131.110	124.850	3.780	34.571
23	WRC 1283 12	5.967	4.057	29.233	161.350	50.447	118.990	138.260	3.579	37.716
23	WRC 1283 12	2.735	2.671	10.216	152.790	45.224	70.680	121.940	3.443	23.688
24		7.131	5.896	10.460	306.370	158.740	153.890	191.250	21.279	75.533
24		8.093	10.780	42.191	143.010	185.670	264.800	391.620	28.593	116.950
24		5.214	6.733	11.778	298.090	162.430	177.190	250.910	19.693	109.340
25	WRC 1283 27	4.192	3.004	45.056	176.240	64.046	221.920	144.860	16.492	79.503
25	WRC 1283 27	0.322	0.584	64.607	24.457	3.921	6.090	8.350	0.503	4.761
25	WRC 1283 27	1.206	0.948	0.000	53.126	3.793	6.760	20.300	0.878	6.774
26	WRC 1283 06	0.000	2.468	325.480	197.550	10.141	16.397	157.950	4.340	16.983
26	WRC 1283 06	0.000	2.471	341.680	199.330	8.331	12.353	58.352	2.712	10.829
26	WRC 1283 06	6.171	9.614	306.720	143.590	25.957	33.134	139.960	16.386	42.394
26	WRC 1283 06	0.000	2.065	300.920	196.750	7.031	10.590	126.690	4.625	12.280
27	WRC 1283 05	6.016	2.700	15.615	142.670	59.994	181.450	247.160	26.145	89.362
27	WRC 1283 05	9.791	5.549	42.336	136.190	55.070	159.530	364.670	23.002	61.904

27	WRC 1283 05	9.515	5.562	21.242	127.340	60.162	195.710	267.920	18.027	62.816
28	WRC 1283 30	12.916	16.034	16.321	183.530	79.899	474.720	1464.320	115.580	224.410
28	WRC 1283 30	20.937	19.993	38.785	64.236	141.800	395.750	12402.010	79.473	107.860
28	WRC 1283 30	20.723	6.245	13.892	335.010	114.300	152.460	97.283	25.711	111.170
29	WRC 1283 03	14.752	9.914	13.268	158.410	90.132	286.770	1240.320	15.482	45.574
29	WRC 1283 03	19.243	14.800	37.758	47.334	115.870	232.150	2683.660	27.183	62.554
30	WRC 1283 47	9.128	5.383	27.443	183.750	72.297	144.470	273.380	13.183	64.318
30	WRC 1283 47	18.905	8.481	28.553	211.030	78.675	186.550	527.210	15.814	83.698
31	WRC 1283 18	6.044	2.589	9.780	132.370	66.834	225.350	172.780	48.809	247.740
31	WRC 1283 18	8.499	8.217	37.718	213.090	64.450	730.500	424.980	47.279	329.710
31	WRC 1283 18	8.805	7.009	18.157	213.880	92.909	254.480	248.470	20.868	128.960
32	WRC 1283 72	22.653	16.305	24.821	88.688	29.571	26.105	353.700	11.959	26.943
32	WRC 1283 72	20.105	15.175	39.211	125.860	32.065	30.346	398.040	11.574	35.831
33	WRC 1283 42	6.769	8.912	37.564	196.820	66.952	95.380	711.980	27.443	27.402
33	WRC 1283 42	7.133	9.286	19.891	199.720	68.633	92.610	757.167	31.551	44.859
33	WRC 1283 42	8.112	8.878	19.915	176.170	74.471	100.210	952.840	23.782	31.103
34	WRC 1283 80	0.000	2.399	150.480	223.200	5.280	8.366	44.671	3.131	13.423
34	WRC 1283 80	0.000	1.972	146.610	229.540	4.149	6.620	29.970	2.593	10.582
34	WRC 1283 80	0.000	1.780	122.450	221.930	3.922	6.372	27.850	2.406	10.134
35	WRC 1283 07	11.369	4.540	10.314	169.360	83.304	218.110	247.100	10.791	84.933
35	WRC 1283 07	1.619	41.928	8.224	11.499	8.035	155.860	206.210	4.645	20.421
35	WRC 1283 07	16.324	6.715	26.952	162.890	55.358	104.030	246.360	6.343	25.101
36	WRC 1283 04	30.944	14.361	45.915	153.080	90.825	353.580	1147.050	44.406	72.511
36	WRC 1283 04	29.381	13.245	50.176	174.830	83.743	332.010	1000.070	58.903	76.323
36	WRC 1283 04	15.511	7.102	14.385	192.690	69.973	152.620	213.650	12.472	50.970
37		10.836	6.782	12.561	128.390	50.812	63.079	405.960	8.253	30.379
37		7.527	7.153	17.126	107.720	44.303	44.630	345.240	6.997	20.075
37		7.379	7.345	12.394	78.523	36.648	44.786	348.740	9.781	29.337
38		2.202	1.871	3.584	89.487	24.639	25.460	123.850	2.244	9.428
38		1.875	1.653	1.037	91.588	21.240	21.002	64.172	1.499	10.131
38		2.648	1.883	0.531	113.060	26.565	26.096	49.350	1.554	8.876
39	WRC 1283 16	10.969	4.027	12.980	289.740	51.962	72.724	71.079	12.788	63.738
39	WRC 1283 16	10.882	7.703	38.718	219.970	70.683	120.850	730.090	13.091	67.977
40	WRC 1283 41	2.632	3.065	50.508	172.190	73.246	24.900	187.390	7.361	19.032
40	WRC 1283 41	2.675	4.897	21.500	140.010	151.820	45.620	62.310	5.448	42.569
40	WRC 1283 41	2.670	3.775	9.269	142.360	39.759	18.330	162.100	6.088	14.619

41	23.476	9.784	40.203	206.090	36.176	41.100	286.940	9.899	37.361
41	5.152	3.649	0.000	101.360	18.430	17.550	52.240	4.253	9.071
42	2.933	1.766	30.282	87.716	14.273	6.240	22.560	0.571	4.982
42	2.530	1.410	22.175	66.007	14.511	6.060	22.360	0.459	47.946
42	3.626	2.073	18.064	80.247	15.130	8.000	19.790	0.763	2.680
43	9.502	5.131	19.767	137.230	20.515	31.813	161.460	4.159	36.972
44	19.974	11.435	60.083	238.650	46.626	22.580	340.420	11.243	24.074
44	8.540	6.917	85.423	233.290	23.010	14.100	99.060	6.231	12.806
45	9.888	9.007	0.000	182.480	33.936	20.350	93.240	6.881	21.961
45	8.931	7.748	5.407	138.240	28.603	17.630	71.750	5.476	27.482
46	9.370	11.794	34.857	184.910	59.294	39.080	339.220	16.208	34.487
46	7.409	6.734	10.749	82.842	80.258	64.440	269.830	13.113	35.290
47	5.203	5.307	19.497	219.510	35.904	32.720	726.910	16.459	20.576
47	21.376	31.340	11.552	117.230	43.782	24.090	666.420	22.195	28.725
48	4.561	6.769	9.645	216.550	46.141	44.230	533.370	9.232	27.643
48	5.730	7.549	15.623	215.140	48.137	55.060	891.360	10.303	35.784
49	5.328	7.657	8.221	145.460	28.804	21.220	253.350	6.468	19.500
49	6.262	8.870	8.402	186.380	31.665	18.670	249.280	7.107	16.521
50	13.769	11.730	17.765	167.400	55.065	68.880	266.530	10.143	36.560
51	21.988	11.765	37.323	41.557	123.540	326.760	406.680	26.853	140.610
51	23.142	11.348	8.495	56.563	120.450	296.210	342.850	23.797	132.640
52	5.410	8.492	243.220	204.810	29.958	26.390	149.710	10.499	12.730
52	6.392	10.314	222.330	194.580	29.573	25.186	173.410	8.944	13.824
53	8.084	10.284	193.700	211.110	24.660	17.682	160.190	12.993	14.114
53	8.819	10.637	159.080	89.479	30.694	30.616	12.127	23.546	40.964
54	0.000	2.066	111.800	192.160	4.758	7.223	27.758	3.375	15.507
54	0.000	2.224	105.820	205.200	4.789	7.444	30.293	3.358	15.074
55	15.879	8.652	121.450	171.100	43.127	51.036	198.160	8.921	16.810
55	16.692	8.657	108.390	121.660	47.586	51.798	187.330	9.014	17.775
56	47.849	9.411	71.702	101.000	35.975	30.487	181.060	10.126	19.664
56	31.990	8.976	63.218	117.860	34.633	29.357	190.990	9.862	19.168
57	0.351	3.039	42.474	55.168	4.341	5.173	26.596	1.868	4.269
57	0.201	3.436	38.363	82.265	3.806	4.228	21.044	1.731	3.642
58	0.000	1.939	33.295	32.265	3.445	4.368	22.022	1.195	2.709
58	0.000	1.670	25.519	16.587	3.764	3.258	8.066	1.043	4.437
59	0.493	2.892	25.206	64.766	11.999	13.511	28.465	1.867	3.490

59	16.313	6.736	21.661	53.022	37.270	28.384	170.140	8.674	14.481
59	1.234	3.363	17.269	75.368	13.664	15.690	56.630	2.289	4.597
60	0.535	3.096	13.980	61.636	12.805	14.356	35.682	2.107	3.377
60	53.677	11.371	11.253	7.017	66.733	45.565	155.180	15.023	21.797
60	28.917	10.858	8.807	7.953	51.329	31.906	154.410	9.329	15.835
61	4.993	5.819	7.749	54.758	54.907	73.671	193.590	8.333	21.191
61	5.804	2.853	4.471	114.820	46.873	70.714	156.260	9.102	27.887
62	5.063	7.961	12.310	206.230	76.788	222.810	178.750	6.329	58.720
62	5.303	9.111	12.054	213.690	77.352	225.330	176.290	7.348	59.473
62	7.342	8.441	14.576	183.250	84.419	254.080	208.370	10.344	60.295
63	4.150	5.718	4.085	205.540	85.241	152.240	120.720	8.701	44.181
63	3.452	5.427	4.002	175.340	75.361	129.900	156.220	8.193	35.551
63	13.195	4.698	8.490	241.650	112.680	321.420	287.650	8.418	52.007
64	8.131	4.158	7.933	311.500	59.811	113.550	437.830	11.300	72.745
64	7.117	2.295	3.032	291.020	61.542	119.250	428.580	11.185	71.920
64	17.905	9.721	33.237	256.340	88.903	203.380	697.960	17.115	98.504
65	7.766	4.139	9.720	312.930	55.129	102.750	391.580	17.241	131.050
65	9.365	4.456	13.950	393.230	61.744	126.250	440.590	18.882	114.360
66	5.849	5.934	10.435	161.480	57.287	83.762	382.290	7.776	30.345
66	4.887	4.936	11.824	161.240	55.273	75.334	296.650	7.816	31.770
66	8.930	6.255	5.698	183.050	69.408	115.740	565.150	12.807	50.788
67	5.202	4.665	5.504	94.961	31.566	44.353	140.390	4.228	7.712
67	2.449	5.070	4.375	53.075	13.677	17.436	331.030	12.109	14.497
67	4.216	5.879	5.438	67.688	29.845	37.665	91.434	5.264	10.035
68	4.664	4.484	6.084	86.814	32.429	45.912	67.521	2.770	7.507
68	2.809	36.004	6.139	165.230	58.332	38.868	257.020	16.084	37.244
68	3.869	39.304	20.494	227.950	54.288	63.008	385.040	16.884	55.028
69	10.641	6.765	5.734	176.990	206.130	78.413	223.590	5.721	27.990
69	5.212	3.299	4.454	176.020	103.520	50.227	134.010	3.523	10.637
69	5.022	3.156	10.720	324.560	174.190	83.392	279.300	5.942	12.928
70	6.216	9.062	9.534	168.790	38.407	31.696	197.890	13.355	13.627
70	6.265	6.914	4.084	57.720	27.564	25.242	200.020	9.415	11.699
70	7.940	8.851	1.572	48.182	30.022	26.640	197.240	11.123	16.593
71	8.567	7.156	0.015	221.300	90.769	60.080	195.900	24.458	30.484
71	4.622	4.194	0.000	200.560	81.113	47.435	143.850	23.499	17.251
71	7.534	7.217	12.262	293.250	60.393	89.452	182.060	14.823	45.453

72	3.365	3.566	4.897	145.580	32.262	44.782	190.890	9.370	19.974
72	7.226	6.223	6.645	87.584	54.797	42.064	187.630	16.970	11.501
72	6.296	4.728	0.000	71.211	31.295	25.116	56.988	3.149	7.809
73	9.667	7.691	8.158	228.290	61.308	75.863	181.160	14.529	24.273
73	10.692	8.382	3.947	241.070	66.254	82.492	187.930	14.541	26.156
74	14.769	9.559	1.026	100.510	76.400	79.288	187.290	20.368	29.070
74	22.868	13.087	0.180	104.030	52.687	56.496	206.490	13.315	28.747
74	11.674	9.489	1.026	138.790	64.835	64.821	209.450	14.970	20.489
75	17.151	8.166	3.930	133.530	30.844	40.313	109.980	10.872	17.045
75	8.619	6.536	2.534	111.300	35.092	43.663	172.980	11.745	15.371
75	6.854	6.353	4.538	212.350	64.351	169.300	122.970	8.491	33.491
76	0.969	0.735	3.246	36.633	15.800	14.371	32.272	0.709	10.745
76	1.707	0.996	1.939	37.883	16.550	12.927	27.074	0.778	4.255
76	0.995	0.865	5.528	37.819	15.867	12.285	12.865	0.394	7.908
77	10.048	7.370	7.607	187.970	75.798	239.910	201.080	10.338	34.161
77	20.584	10.063	9.395	263.080	68.907	92.397	208.740	14.687	31.735
78	18.088	10.217	21.077	187.690	92.000	128.540	473.850	24.850	67.641
78	16.856	10.518	27.549	140.580	86.051	109.020	629.360	23.546	76.158
78	5.401	4.725	14.158	252.570	61.230	149.850	154.420	7.570	46.249
79	8.987	3.995	4.765	135.680	50.054	101.290	248.810	16.964	67.008
79	26.214	10.173	24.526	167.930	52.919	131.870	333.320	10.947	58.890
79	11.596	4.666	5.817	88.853	44.603	68.061	202.980	9.202	66.934
80	3.345	6.560	40.954	175.060	72.037	318.260	161.510	7.060	48.117
80	4.511	8.583	14.639	202.170	56.279	77.920	256.870	8.263	23.744
81	9.020	10.775	18.932	178.620	92.074	119.950	531.100	24.805	56.322
81	8.786	9.004	48.456	214.110	90.293	157.260	434.320	43.211	73.208
81	9.129	9.433	6.828	226.240	80.868	102.210	139.080	31.443	82.357
82	14.171	7.592	18.573	349.200	109.270	78.767	225.920	15.531	975.290
82	13.088	5.330	12.961	232.100	86.432	211.110	242.080	12.230	856.550
82	5.242	3.061	32.374	161.600	32.435	60.370	179.770	5.563	41.929
83	7.241	4.257	20.049	74.479	152.460	239.690	753.670	36.691	128.190
84	8.893	7.822	33.577	93.927	89.900	77.930	221.710	11.870	46.152
84	9.385	7.450	16.830	143.430	64.113	72.440	440.960	18.679	38.054
85	12.926	8.662	15.171	132.770	78.092	182.270	350.680	13.602	40.863
85	15.857	10.331	10.408	144.820	78.895	106.200	475.810	26.436	44.040
86	5.028	2.030	7.280	76.768	22.657	31.311	48.903	3.545	10.425

86	12.119	6.147	22.488	101.790	40.204	51.180	218.360	5.141	21.495
86	6.697	4.382	44.355	128.360	33.830	47.110	344.560	5.533	15.750
86	5.732	7.114	31.682	189.540	52.786	47.110	449.900	10.603	57.753
87	4.105	3.061	1.564	251.850	49.835	69.228	157.180	12.389	26.177
87	4.010	3.141	2.090	254.750	53.150	84.543	200.150	17.360	26.436
87	4.472	3.469	2.695	253.240	52.332	102.440	145.340	13.000	24.746
88	2.975	2.161	0.338	59.619	17.615	23.943	52.831	1.183	6.641
88	1.956	1.780	1.106	38.175	18.037	15.029	24.435	0.901	5.246
88	9.073	12.928	12.735	203.490	19.643	20.373	35.353	2.379	6.752
89	13.334	10.807	13.436	203.790	53.576	64.290	443.240	9.337	33.490
89	12.723	10.671	12.797	180.320	52.906	62.860	450.640	11.381	36.679
90	11.311	9.881	29.507	182.660	38.546	25.970	167.730	6.998	18.525
91	15.084	10.293	40.011	120.690	71.953	639.870	4090.210	98.633	347.480
92	9.313	6.551	13.033	217.380	67.561	74.590	1288.650	15.366	48.721
93	4.968	3.347	21.747	322.330	112.260	227.260	211.290	10.547	45.825
93	4.563	4.087	18.682	325.130	104.840	146.070	191.520	9.631	38.498
93	4.847	3.089	21.937	324.600	122.820	237.280	189.490	8.275	49.712
94	17.798	9.890	23.159		37.593	35.644	437.220	9.083	29.761
94	17.923	10.983	17.461	142.360	53.327	47.050	645.660	9.774	82.880
95	18.157	8.283	45.496	207.150	76.631	179.810	398.570	14.733	80.876
96	10.443	3.708	13.371	111.080	26.611	46.938	157.440	11.371	126.230
97	4.045	2.609	4.453	235.750	38.388	71.600	52.380	7.961	29.970
98	0.967	43.676	6.711	5.219	4.321	821.520	326.630	3.421	15.177
99	10.390	10.650	22.243	30.744	131.360	94.080	353.860	20.648	42.698
100	12.980	9.461	4.168	275.990	75.422	96.008	151.410	17.211	32.115

Zinc	Copper	Arsenic	Bromine	Selenium	Strontium	Molybdenum	Cadmium	Tin	Antimony	Tellurium	Iodine
176.730	66.070	2.550	2.751	1.474	265.680	1.400	0.511	2.112	0.346	0.060	4.223
33.760	6.740	1.127	1.263	0.316	308.780	0.241	0.291	1.815	0.029	0.251	1.228
515.620	92.542	4.202		-2.659	201.550	0.993	1.658	52.668	0.231	-0.954	0.952
92.760	36.520	0.967	1.458	0.253	263.380	0.743	0.447	2.537	0.538	0.110	2.360
91.130	30.170	1.110	1.952	0.879	317.940	0.817	0.662	3.156	0.613	0.059	1.891
349.840	73.260	6.236	17.936	3.326	29.625	1.415	3.295	0.000	0.082	0.193	2.592
595.970	177.510	9.861		4.212	38.826	1.535	3.752	10.113	0.463	-1.009	0.624
90.011	21.030	10.725	26.462	7.163	28.018	33.710	4.401	2.028	2.156	2.464	0.831
92.978	20.733	8.877	24.624	7.364	26.849	4.370	2.664	2.067	2.188	2.229	1.822
151.040	51.354	5.123	58.090	5.096	96.510	4.619	3.137	2.654	2.774	2.003	11.045
148.220	10.347	0.821	25.020		2.429		0.626	3.270	0.140		
142.060	7.463		14.787		3.054		0.685	1.413			
1474.500	49.913	0.885	21.985		3.893	0.275	1.139	2.245	0.174	0.533	
609.830	265.790	3.042	14.893	3.429	105.270	5.131	2.351	5.301	0.610	0.211	1.901
230.210	78.980	1.953	13.657	3.356	27.222	2.756	1.220	0.000	0.044	0.193	1.645
147.310	42.939	1.795	33.624	1.960	10.978		0.980	0.884	0.173		0.909
3548.100	149.180	1.823	54.249	0.346	13.288	0.347	1.936	1.834	0.248	3.482	
186.590	134.120	2.181	21.735	3.955	41.046	1.336	1.336	0.000	0.054	0.185	15.743
159.020	310.560	2.579	21.709	3.521	38.017	1.321	1.226	0.000	0.043	0.160	12.593
71.840	134.590	1.537	18.527	3.065	16.282	0.624	0.885	0.000	0.000	0.207	6.243
109.040	42.200	0.919	0.000	0.070	44.380	0.301	0.312	3.701	0.000	0.000	0.898
754.570	207.560	1.840	0.000	0.000	58.865	3.011	1.508	19.529	0.259	0.000	1.714
210.140	177.550	0.835		-4.745	37.550	0.881	1.110	41.366	0.305	-0.557	0.632
100.500	112.520	2.806	18.059	2.916	8.556	1.226	1.093	0.000	0.000	0.127	4.163
67.830	12.030	1.539	14.403	2.996	7.365	0.307	0.777	0.000	0.000	0.151	1.918
88.070	34.700	1.611	13.764	2.734	7.279	0.741	0.965	0.000	0.000	0.145	1.791
570.940	136.430	2.045	13.348	3.360	31.483	1.687	1.956	0.000	0.283	0.197	3.863
254.650	91.410	1.542	2.032	0.042	64.425	0.949	0.508	5.553	0.086	0.149	3.498
112.090	42.430	1.520	0.000	0.000	44.299	0.726	0.411	0.534	0.024	0.015	0.886
160.290	77.620	1.503	0.000	0.810	49.540	1.437	0.754	5.730	0.054	0.000	2.815
1889.590	430.890	19.977	2.029	2.213	146.540	77.917	9.238	40.423	5.804	0.000	2.000
47.870	10.880	2.749	13.325	2.686	5.655	0.696	0.879	0.000	0.000	0.130	2.226
568.710	114.450	3.120	1.491	0.000	23.429	2.593	1.601	21.543	0.578	0.000	2.307
194.960	58.300	3.181	0.029	0.000	24.915	1.229	0.477	1.918	0.072	0.000	2.769
195.760	18.870	1.214	0.260	0.495	13.297	0.585	0.088	0.727	0.000	0.005	4.135

186.450	15.469	1.279	42.568	2.693	2.288	0.562	1.269	0.949	0.200		0.653
104.360	8.871	0.692	32.764		1.676		0.400	1.103	0.073		0.095
97.210	14.421	0.768	28.864		1.931			0.512	0.027	0.468	0.414
120.780	771.740	8.286	17.462	5.428	38.060	2.713	3.667	47.513	2.196	2.358	3.277
26.839	24.223	5.827	16.200	5.003	293.400	1.671	2.670	2.629	2.103	2.329	0.688
51.220	1.800	0.579	0.894	0.042	12.368	0.102	0.033	2.514	0.197	0.135	1.390
124.490	54.140	0.565	1.346	0.030	16.104	0.338	0.185	0.952	1.827	0.100	1.022
304.970	250.930	5.459	12.791	4.846	81.652	2.813	3.133	4.828	2.258	2.142	3.134
135.200	46.378	6.590	21.901	5.389	131.270	2.356	2.825	0.839	2.169	2.232	3.278
480.050	169.130	2.071		-1.233	11.527	0.865	2.132	10.777	0.675	-1.267	0.417
168.960	63.980	3.932	14.461	2.578	31.616	1.320	1.137	0.000	0.111	0.113	5.941
128.760	18.980	1.715	12.112	2.558	6.259	0.434	1.257	0.000	0.000	0.143	2.077
242.690	164.670	8.823	2.572	1.103	18.012	1.659	9.320	18.098	0.565	0.000	5.302
110.840	82.780	8.098	1.705	0.866	7.939	1.100	1.843	5.948	0.160	0.139	4.340
69.710	64.360	7.459	2.138	1.510	5.223	1.100	0.949	3.438	0.136	0.077	5.901
84.070	81.060	3.787	16.375	3.469	7.170	1.043	0.903	0.000	0.000	0.100	7.193
66.420	47.440	2.588	16.557	2.814	4.031	0.676	0.779	0.000	0.000	0.142	4.213
76.600	46.260	2.751	16.444	3.105	3.607	0.643	0.758	0.000	0.000	0.149	4.989
43.150	16.300	3.910	2.102	0.000	2.840	0.731	0.167	1.450	0.076	0.000	1.807
43.570	14.780	2.660	0.957	0.234	2.047	1.112	0.019	1.329	0.090	0.113	1.471
37.190	19.720	3.061	1.027	0.000	1.861	0.757	0.000	1.870	0.012	0.000	1.510
100.090	39.300	4.386	16.319	2.621	10.714	1.834	0.918	0.000	0.106	0.152	6.897
206.750	48.650	4.610	15.574	3.053	19.126	2.031	1.049	0.000	0.092	0.121	8.910
57.120	23.260	2.728	15.638	2.479	8.312	1.277	0.886	0.000	0.018	0.144	5.643
1210.800	169.230	0.429		-4.065	17.841	-0.060	13.289	11.706	0.007	-1.877	2.117
2036.590	233.460	1.564	16.973	4.314	35.698	2.096	22.615	24.019	0.102	0.153	15.098
2726.980	251.830	1.348	17.254	4.115	41.357	2.037	24.347	28.374	0.133	0.329	14.293
1091.850	294.700	6.437	1.246	0.861	127.300	7.698	11.620	5.647	3.581	0.056	3.987
23.590	7.370	0.416	0.000	0.000	5.155	0.299	0.538	2.126	0.255	0.167	0.588
89.890	18.060	1.277	3.910	0.000	31.539	0.333	0.526	0.945	0.527	0.000	0.564
15.167	6.696	5.095	23.535	3.872	312.740	1.585	2.613	3.465	2.152	2.334	1.728
18.912	4.409	5.324	23.685	4.284	345.180	1.538	2.767	1.953	2.138	2.344	1.103
468.310	445.790	8.031	14.206	5.584	66.271	3.578	4.517	71.571	2.223	2.243	5.726
18.369	23.388	5.061	11.835	4.203	312.420	1.658	2.640	3.544	2.155	2.321	0.722
1285.300	443.220	2.849		-0.297	51.372	7.043	9.013	75.062	4.053	-1.096	1.386
349.800	200.010	3.750	16.692	3.444	28.573	3.937	3.828	0.000	1.396	0.163	3.409

552.960	280.190	3.622	17.203	3.486	30.572	4.241	5.151	0.894	3.208	0.104	4.389
943.400	277.550	24.080	15.717	13.141	38.039	6.885	19.372	31.846	1.272	0.171	5.048
175.320	107.100	8.446	15.662	3.491	13.172	2.091	1.849	0.000	0.037	0.151	5.719
283.980	90.427	3.031		-4.078	4.246	0.550	0.670	6.413	0.226	-0.795	0.317
417.950	123.430	4.727	18.005	3.125	24.296	3.510	4.326	5.148	0.268	0.149	6.398
271.910	127.880	5.202	17.612	3.341	18.590	2.969	3.104	1.200	0.158	0.234	5.999
66.930	42.530	2.046	15.808	3.105	9.029	0.507	0.855	0.000	0.000	0.175	3.856
267.500	88.670	4.100	29.155	3.985	49.008	1.704	1.768	4.168	0.021	0.192	21.102
1989.800	563.240	5.112		0.143	69.834	4.839	26.572	113.680	1.637	-1.890	5.838
1604.570	717.710	4.465	2.563	4.356	82.522	7.099	26.463	94.957	5.100	0.126	11.280
496.130	217.380	5.769	0.678	1.172	22.251	2.165	6.106	21.060	0.984	0.212	4.374
297.170	33.752	6.340	23.067	8.877	319.350	1.633	0.420	1.428	0.092	1.765	0.233
384.870	33.748	4.356	20.328	2.852	370.390	2.111	0.852	1.444		1.268	1.611
171.240	70.890	4.918	1.454	0.031	28.485	2.951	0.723	3.412	0.241	0.000	3.625
226.820	104.010	5.487	1.580	1.405	32.492	3.049	1.063	3.663	0.134	0.000	6.088
247.520	61.710	4.485	1.050	1.392	32.540	2.597	1.159	8.504	0.164	0.011	7.103
66.022	14.484	6.740	16.359	4.451	398.480	1.623	2.562	0.386	2.210	2.131	1.650
34.777	8.543	6.681	15.780	5.318	400.950	1.572	2.643	1.212	2.268	2.667	1.173
55.800	16.401	5.780	14.942	3.985	378.350	1.729	2.715	0.813	2.348	2.308	1.537
597.910	164.550	2.165		-2.552	8.543	0.829	0.596	3.782	0.119	-2.226	1.607
60.660	21.180	116.880	146.900	464.130	5.384	51.275	39.343	31.523	21.412	127.500	22.311
78.690	18.420	2.057	16.485	2.588	4.382	0.508	0.825	0.000	0.000	0.143	4.475
962.110	419.370	5.577	17.105	3.897	47.203	4.550	9.972	5.971	0.461	0.182	3.630
1983.140	484.220	5.251	16.893	3.919	58.916	5.459	11.816	3.003	0.366	0.180	2.900
777.170	220.730	2.913		-0.557	28.687	3.130	4.747	14.195	0.539	-1.113	2.746
467.670	37.815	2.862	25.355		6.922	0.529	0.896	1.451	0.166	1.036	1.653
195.600	36.946	1.641	30.429		13.843	0.658	0.428	1.727	0.459		2.770
352.130	45.158	2.954	15.168	0.143	21.402	1.323	0.962	1.568	0.328	0.164	6.175
95.060	14.361	0.920	0.000	0.000	2.912	0.288	0.079	6.124	0.000	0.000	0.000
30.144	6.885	0.998	0.000	0.029	1.558	0.000	0.044	4.558	0.000	0.000	0.000
45.664	10.865	0.714	0.000	0.000	2.651	0.046	0.007	4.030	0.000	0.000	0.000
494.200	293.830	2.397		-1.300	36.616	1.938	1.558	26.772	0.127	-1.982	0.642
401.440	337.140	4.311	16.937	5.774	36.527	2.940	2.649	11.502	0.246	0.454	10.596
66.740	32.510	2.270	3.406	1.362	28.259	1.442	0.148	0.235	6.916	0.129	2.015
99.520	75.820	3.340	13.820	2.111	51.022	3.304	0.658	0.392	14.069	0.261	3.750
80.010	24.030	1.624	3.455	0.000	15.961	0.985	0.181	0.032	2.315	0.096	2.814

178.850	47.630	1.774	0.886	1.918	23.110	0.814	6.069	7.661	0.263	0.000	5.385
28.320	6.720	0.773	0.449	0.000	3.324	0.221	0.709	14.728	0.004	0.000	2.652
111.240	2.800	1.362	0.617	0.000	7.258	0.138	0.000	0.459	0.034	0.226	0.882
576.740	376.090	0.745	0.296	0.000	6.020	0.171	0.136	0.913	0.006	0.000	0.797
26.580	1.540	0.907	0.000	0.000	5.980	0.242	0.049	0.925	0.024	0.000	1.375
1013.600	274.130	7.018		1.376	106.620	2.912	2.482	34.591	0.527	0.195	2.987
71.650	20.950	5.920	1.499	0.000	49.141	0.545	0.377	0.690	0.071	0.000	7.106
40.500	9.840	3.111	0.000	1.153	36.985	0.518	0.296	1.309	0.068	0.010	5.590
76.350	11.860	2.902	0.226	0.000	11.094	0.445	0.106	1.114	0.063	0.210	2.667
267.930	92.120	4.193	0.232	1.349	10.976	0.415	0.170	0.525	0.000	0.077	1.445
85.970	27.640	9.867	0.363	0.565	24.337	0.262	0.259	0.268	0.001	0.160	1.326
77.090	51.200	1.375	0.000	0.299	16.337	0.401	0.304	0.666	0.028	0.151	1.756
438.830	198.050	6.510	0.000	1.110	80.269	1.306	0.634	1.535	0.063	0.000	0.713
85.590	37.900	5.045	2.359	0.464	23.998	0.552	0.301	0.178	0.000	0.199	2.900
464.910	112.610	75.495	0.949	0.972	41.727	3.321	0.861	4.320	0.297	0.000	5.776
625.850	174.450	27.889	2.806	1.516	59.109	2.583	1.422	2.768	0.298	0.000	10.655
184.880	75.890	4.078	2.550	2.091	24.209	2.151	0.648	0.634	0.186	0.000	4.393
87.060	32.740	3.884	0.768	2.035	24.788	1.419	0.403	0.684	0.079	0.034	3.431
475.340	203.690	5.555	0.922	2.585	56.847	4.961	2.644	12.864	0.127	0.023	6.498
46.550	30.570	2.458	0.000	0.523	8.355	0.680	0.000	0.783	0.045	0.058	1.785
68.240	35.850	2.101	0.000	0.000	6.312	0.537	0.084	1.127	0.086	0.066	3.247
108.340	25.383	7.283	9.092	4.366	47.134	2.050	2.695	2.402	2.186	2.349	1.565
322.880	35.585	7.049	10.865	3.659	49.403	2.109	2.961	1.559	2.154	2.158	1.566
60.108	29.320	8.011	16.353	4.054	27.890	1.702	2.567	0.515	2.176	2.241	3.032
378.390	119.790	8.059	16.431	4.505	47.856	2.127	3.078	1.195	2.168	2.460	6.297
37.312	6.346	6.634	15.688	3.672	370.270	1.584	2.831	0.000	2.143	2.159	0.861
20.564	6.017	6.712	15.024	4.843	385.340	1.673	2.784	0.000	2.151	2.578	0.414
60.708	18.421	7.006	13.002	4.423	140.940	2.649	2.759	0.386	2.112	2.158	1.102
53.512	19.849	7.968	16.693	4.512	120.860	3.090	2.731	0.000	2.131	2.194	0.265
85.419	27.438	6.454	16.688	5.817	381.090	1.680	2.713	0.000	2.125	2.262	1.377
99.757	26.464	6.477	11.325	4.318	195.580	1.757	2.769	0.000	2.129	2.310	1.610
16.723	5.889	4.645	15.249	3.907	22.983	1.496	2.569	0.000	2.134	2.340	1.516
8.927	3.901	4.719	15.895	3.828	41.483	1.592	2.586	0.000	2.113	2.307	2.949
69.475	50.809	4.339	19.589	4.289	21.398	2.459	2.711	1.706	2.454	2.288	0.944
34.235	11.815	4.462	17.906	3.934	6.417	2.001	2.654	0.000	2.141	2.171	0.000
16.806	6.452	5.197	17.623	4.039	8.226	1.888	2.610	0.000	2.147	2.168	0.122

58.787	20.343	5.632	17.004	4.783	22.950	1.907	2.734	0.585	2.132	2.441	0.000
65.179	6.425	5.376	16.349	4.654	10.379	1.785	2.608	0.000	2.189	2.278	0.000
24.768	9.312	5.077	19.845	3.647	7.458	1.923	2.638	0.000	2.143	2.267	0.035
143.770	32.094	6.240	13.894	5.274	28.307	1.804	2.822	3.073	2.118	2.521	0.000
120.450	34.121	5.362	15.403	5.932	17.966	1.832	2.751	2.801	2.178	2.212	0.000
122.480	51.604	5.687	19.232	4.018	10.046	1.942	2.734	0.998	2.136	2.379	1.446
397.690	170.690	3.283		0.833	27.344	3.106	1.679	37.056	0.678	-1.946	2.431
1554.400	307.550	2.444		1.356	76.202	9.410	8.286	55.928	1.631	-1.546	21.896
1402.000	328.410	2.094		-2.174	71.491	10.170	6.650	54.183	1.776	-1.437	25.878
1441.900	302.690	4.105		5.222	77.941	8.801	8.039	26.680	1.308	-1.424	29.012
135.160	76.168	7.152	17.267	5.545	7.015	3.393	3.895	2.936	2.153	2.281	2.879
132.830	69.291	6.616	11.970	4.130	5.852	3.233	3.564	1.325	2.156	2.511	2.338
295.030	323.960	3.378		1.908	16.577	5.510	3.707	3.509	0.936	-1.879	10.114
671.460	42.589	1.420	6.456		18.333	1.601	1.181	9.288	0.274	0.266	2.258
561.850	40.175	1.215	12.859		13.747	1.299	0.481	6.937	0.419	0.628	1.837
1291.000	55.947	1.679	18.236	1.174	9.327	0.359	0.495	3.083	0.119		0.873
489.640	66.420	0.371	25.193		50.150	0.536	0.358	1.730	0.262	0.383	0.489
241.830	62.766	0.669	38.249		44.249		0.994	2.660	0.303	2.706	1.048
435.400	26.740		15.253		7.825	0.260		0.947		1.316	
353.210	21.435		25.082		7.880	0.548	0.761	0.033		0.047	0.352
819.480	38.938	1.576	26.877	5.776	10.077	-0.264	1.026	1.185	0.144	0.623	0.307
140.790	12.218	4.105	13.567	0.635	4.290	0.288	0.130	0.488	0.166	0.318	0.015
221.080	22.810	0.665	16.286		13.591		0.147	1.716	0.386		0.198
211.010	17.501	4.051	22.997	1.442	5.292		0.167	1.150	0.322	0.267	0.741
125.140	12.052	4.051	23.803		3.856		0.359	1.147	0.246	1.758	0.581
1080.900	226.200	2.648	24.376	5.380	137.660	6.370	2.485	12.157	0.657	0.371	5.609
1797.500	320.890	3.380	25.020	7.334	158.160	7.704	3.684	29.811	0.630	0.907	1.492
567.640	67.063	1.679	20.328	0.866	21.942	-0.302	0.573	4.781	-0.054	0.073	1.211
175.530	18.243	1.078	39.087	2.687	12.717		0.065	1.649	0.226	0.824	2.543
296.420	38.994	1.483	19.108	2.837	27.229	0.246	1.128	4.454	0.133	0.006	1.963
57.580	17.024	1.287	0.000	0.498	7.229	0.294	0.000	1.981	0.000	0.000	0.595
39.068	12.157	0.901	0.000	0.000	11.442	0.132	0.000	1.842	0.000	0.000	0.339
38.567	12.442	1.043	0.000	0.680	14.011	0.148	0.000	1.087	0.000	0.000	0.174
88.659	45.264	0.771	0.000	0.580	6.647	0.000	0.000	1.884	0.000	0.000	0.352
36.372	29.952	0.453	0.000	0.336	4.347	0.000	0.000	1.477	0.000	0.000	0.000
1260.600	362.400	3.697	0.000	2.066	89.308	4.552	3.240	84.307	0.402	0.000	1.368

515.740	665.210	0.466	0.000	0.000	18.342	2.409	0.616	16.027	0.140	0.000	0.000
107.180	51.142	1.785	0.000	0.114	8.753	0.480	0.048	2.898	0.263	0.000	1.019
46.021	19.366	0.489	0.000	0.000	7.655	0.000	0.086	1.721	0.000	0.000	0.365
38.568	24.168	0.898	0.000	0.535	6.697	0.000	0.000	1.293	0.000	0.000	0.196
38.151	23.253	0.728	0.000	0.819	6.299	0.000	0.000	0.891	0.000	0.000	0.074
80.730	30.304	1.299	0.000	0.000	13.328	0.010	0.000	0.479	0.000	0.000	0.359
81.865	30.583	1.888	0.000	0.502	37.613	0.010	0.000	0.460	0.000	0.000	0.317
59.552	34.694	1.348	0.000	0.000	16.139	0.076	0.000	0.841	0.000	0.000	0.000
108.630	35.698	5.157	0.000	0.431	25.125	0.233	0.018	1.657	0.000	0.000	0.344
151.250	24.109	2.178	0.000	0.000	14.055	0.056	0.000	0.858	0.000	0.000	0.028
1290.600	229.850	4.844	0.000	0.943	108.940	5.478	3.762	124.050	0.525	0.000	1.989
185.520	155.040	0.000	0.000	0.000	3.487	0.000	0.098	4.799	0.000	0.000	0.000
27.193	9.189	0.142	0.000	0.000	1.824	0.136	0.000	2.052	0.000	0.000	0.000
27.581	16.496	0.097	0.000	0.000	0.784	0.000	0.000	1.121	0.000	0.000	0.000
751.130	151.480	2.414	0.000	1.591	40.420	2.172	1.519	13.120	1.236	0.000	3.237
205.360	37.534	3.044	0.000	1.392	13.594	0.983	0.040	1.279	0.249	0.000	0.799
186.310	71.720	1.936	17.643	3.321	19.348	0.779	7.904	0.000	0.000	0.163	5.082
163.670	77.440	2.690	14.856	3.195	20.608	0.615	4.722	0.000	0.000	0.145	3.596
467.170	403.510	0.811		-3.049	44.383	1.072	0.475	7.761	0.084	-1.344	3.411
215.670	73.551	0.758		1.637	5.969	0.210	-0.143	2.546	0.209	-1.122	1.165
118.320	39.420	1.973	16.188	2.900	64.997	0.828	0.961	0.000	0.000	0.111	6.881
411.990	115.240	1.649		0.015	9.804	0.214	0.576	1.621	0.068	-2.117	0.981
365.730	194.670	2.934	16.858	3.410	36.879	4.427	4.977	42.560	0.322	0.181	17.705
115.820	44.030	3.157	15.641	4.235	6.477	0.824	1.474	1.494	0.029	0.319	4.969
305.910	146.630	6.944	15.151	3.102	56.228	2.141	1.394	0.652	0.334	0.135	6.344
733.260	302.950	7.194	18.733	3.960	109.880	3.124	3.017	24.597	0.605	0.186	7.171
395.040	162.350	5.847		2.153	65.057	1.484	1.248	8.016	0.349	-0.656	0.409
3869.700	1122.700	21.129		1.500	244.200	6.786	7.808	235.330	0.830	-0.059	-0.031
3324.400	1399.000	4.241		1.800	163.180	4.028	4.896	71.407	0.993	-0.892	0.837
41.960	25.850	1.428	14.871	2.650	9.942	0.460	0.857	0.000	0.000	0.121	2.336
88.170	84.410	2.213	16.836	3.637	18.920	0.429	0.874	0.000	0.000	0.191	7.131
463.980	174.390	3.399	15.062	4.825	38.365	2.685	2.872	57.651	0.398	0.211	11.826
161.720	81.490	2.121	18.276	3.421	11.510	0.984	1.110	2.815	0.098	0.160	5.166
365.110	108.560	2.577	15.988	3.505	26.962	1.513	1.411	0.000	0.000	0.182	7.022
168.700	33.130	2.582	14.407	3.033	12.328	0.520	0.824	0.000	0.000	0.176	5.879
255.040	52.224	1.780			10.541	1.396	0.562	1.318	0.266	0.361	1.835

43.610	14.870	3.155	17.700	3.155	8.750	0.352	0.792	0.000	0.000	0.154	3.386
47.870	10.880	2.749	13.325	2.686	5.655	0.696	0.879	0.000	0.000	0.130	2.226
568.710	114.450	3.120	1.491	0.000	23.429	2.593	1.601	21.543	0.578	0.000	2.307
35.302	11.648	0.823	0.000	0.398	4.993	0.000	0.000	0.761	0.000	0.000	0.834
48.214	31.122	0.637	0.000	0.000	5.545	0.000	0.000	0.598	0.000	0.000	0.742
54.135	14.585	0.834	0.000	0.535	10.397	0.000	0.000	0.546	0.000	0.000	0.682
30.339	6.826	0.218	0.000	0.000	4.974	0.000	0.000	0.904	0.000	0.000	0.138
11.710	4.081	0.446	0.000	0.197	1.027	0.000	0.041	0.577	0.000	0.000	0.000
39.429	43.341	0.868	0.000	1.284	109.250	0.000	0.000	1.082	0.000	0.000	0.000
545.190	182.250	6.036	1.308	0.889	93.737	4.868	4.067	7.391	0.334	0.087	5.269
766.170	196.820	5.596	2.976	1.082	61.265	6.756	4.177	12.461	0.282	0.053	16.196
134.840	34.770	2.987	0.177	1.767	25.439	0.558	0.205	2.639	0.084	0.000	2.195
3976.310	739.250	6.361	0.707	3.259	192.440	6.300	216.020	250.840	8.651	0.070	2.600
67.840	63.540	2.850	14.528	2.945	5.675	1.126	1.050	0.000	0.000	0.203	5.813
566.110	155.140	1.559	0.000	0.508	42.496	3.283	0.489	9.277	0.018	0.000	9.399
402.960	91.536	1.500	0.000	2.300	30.693	2.075	0.474	9.334	0.000	0.000	4.264
646.140	121.380	1.384	0.000	0.355	51.578	3.385	0.733	11.125	0.077	0.000	6.399
389.990	32.892	3.540	12.785	5.796	167.580	0.171	0.082	0.114	0.208	0.480	1.685
1633.700	61.677	2.198	16.379		62.224	0.813	1.408	1.519	0.031		0.181
275.330	92.690	3.704	31.035	4.120	41.631	1.622	1.676	3.550	0.022	0.228	23.814
1387.300	417.010	13.430		1.518	51.824	1.989	5.485	11.779	0.055	1.200	0.756
253.890	133.190	4.642	2.151	2.137	309.890	2.023	1.389	3.410	0.845	0.031	5.405
2059.790	454.380	122.440	152.300	486.290	5.356	55.323	42.082	33.412	23.523	139.160	23.555
180.620	73.550	2.293	15.054	3.677	10.878	0.919	1.216	3.361	0.010	0.201	8.351
57.371	29.087	0.763	0.000	0.000	9.648	0.146	0.000	0.750	0.000	0.000	1.596

Barium	Tungsten	Platinum	Mercury	Thallium	Lead	Bismuth	Uranium
66.162	0.594	0.055	2.533	0.195	60.890	2.079	0.355
12.322	0.209	0.162	2.089	0.000	12.536	0.300	0.341
122.660	0.806	0.393	0.000	0.655	214.190	4.011	0.131
46.009	0.295	0.000	2.160	0.030	33.150	1.107	0.489
35.178	0.440	0.040	2.282	0.163	32.743	0.763	0.437
106.170	0.000	0.000	1.938	2.911	73.526	6.750	10.917
119.780	4.899	0.067	14.134	0.647	303.890	4.070	23.975
71.559	3.381	3.058	0.170	3.577	41.751	4.200	8.833
66.623	3.269	2.897	0.277	3.585	45.470	4.456	9.719
30.222	3.426	3.014	0.588	2.880	152.170	5.027	4.026
141.870	0.045		0.692	0.086	14.456	0.236	0.180
122.720				0.173	14.447	0.207	0.046
121.320	0.396	0.029		0.406	131.920	0.081	0.164
334.660	12.189	0.001	2.493	3.068	263.130	7.087	0.738
108.660	0.980	0.000	0.369	3.445	114.830	5.235	0.715
135.710	0.334		0.316	0.369	24.344	0.941	2.506
138.600	0.101	0.555		0.367	356.750	0.152	1.136
87.011	0.000	0.000	0.373	3.429	49.295	5.443	2.546
80.107	0.000	0.000	0.297	2.385	50.776	5.645	1.975
50.589	0.000	0.000	0.000	2.807	14.289	4.656	1.002
131.580	0.016	0.000	2.136	0.058	32.427	0.280	0.292
145.060	0.228	0.038	2.300	0.252	116.270	2.140	1.023
180.490	0.447	0.700	1.313	0.604	124.750	2.862	-0.367
164.720	0.000	0.020	0.000	2.310	26.820	4.642	1.049
33.689	0.000	0.000	0.000	2.325	9.504	4.494	0.187
28.235	0.000	0.011	0.000	3.394	7.948	4.440	0.547
109.960	0.000	0.000	2.633	3.109	49.881	6.899	0.919
180.000	0.015	0.071	2.832	0.179	75.842	2.835	0.819
125.150	0.000	0.030	2.310	0.265	39.393	0.998	0.708
162.490	0.035	0.057	2.788	0.165	86.599	2.859	0.680
180.600	0.695	0.051	6.873	18.102	1491.300	35.755	0.921
44.202	0.000	0.000	0.457	2.187	14.223	4.505	1.187
144.550	0.035	0.028	2.275	1.311	391.630	3.114	1.326
176.660	0.058	0.013	2.561	0.424	106.330	2.225	0.987
74.784	0.000	0.039	2.086	0.071	30.323	0.459	0.826

14.224		0.134		0.206	22.280	0.052	1.312
11.163	0.024	0.178		0.399	14.126	0.185	0.404
21.075		0.231		0.084	20.452	0.233	1.863
119.230	3.263	2.934	0.011	3.158	193.650	4.136	4.332
36.047	3.190	3.030	0.000	2.817	4.082	3.479	3.512
7.700	0.055	0.009	2.167	0.042	6.679	0.117	0.063
12.284	0.457	0.038	1.866	0.000	14.629	0.295	0.111
66.410	3.378	2.939	1.161	2.935	110.170	5.563	9.543
91.969	3.206	2.981	0.346	3.008	37.220	4.409	12.535
98.131	1.379	0.234	2.897	0.619	498.540	5.074	10.119
134.740	0.000	0.000	2.859	5.719	114.670	53.539	24.193
34.303	0.000	0.000	0.000	2.502	70.645	5.536	3.211
143.100	2.188	0.082	4.033	0.416	130.830	12.354	11.278
55.204	0.896	0.026	2.482	0.135	49.605	2.758	6.738
76.566	0.410	0.027	2.266	0.278	30.214	1.630	4.650
193.640	0.000	0.000	0.000	2.624	28.662	4.621	0.957
82.351	0.000	0.000	0.000	2.606	19.496	4.540	0.762
61.220	0.000	0.000	0.000	3.172	21.809	4.524	0.868
25.936	0.282	0.039	2.159	0.133	11.379	0.225	1.030
22.953	0.147	0.043	2.066	0.016	12.615	0.268	0.786
39.650	0.123	0.000	2.048	0.110	18.117	0.364	1.389
90.035	0.000	0.000	1.006	2.954	178.520	8.544	1.154
104.680	0.000	0.000	0.549	2.596	147.900	7.168	1.315
50.788	0.000	0.000	0.000	2.154	41.962	4.684	0.603
120.620	0.245	0.009	-0.354	0.486	61.985	3.993	0.403
171.740	0.000	0.000	0.607	2.413	71.079	6.623	1.099
175.440	0.000	0.000	0.628	3.197	75.091	7.383	1.199
253.510	2.137	0.005	6.161	2.854	803.760	10.568	1.205
9.338	0.319	0.000	2.118	0.000	23.303	0.308	0.092
4.056	0.501	0.042	2.058	0.034	7.661	0.143	0.257
10.210	3.396	2.957	0.277	2.832	2.824	3.501	3.722
6.266	3.346	2.948	0.207	2.852	2.215	3.458	3.639
157.400	3.302	2.960	0.984	3.017	748.530	5.911	4.203
9.863	3.188	2.932	0.058	2.810	6.506	3.488	3.523
228.330	3.688	0.326	1.488	0.548	303.030	4.827	3.905
129.110	0.393	0.059	0.696	3.111	167.200	5.877	2.981

127.750	0.383	0.035	0.645	2.764	220.100	6.303	3.213
173.160	11.365	0.056	0.989	2.262	218.230	6.788	32.708
123.340	0.000	0.006	0.000	3.933	91.595	4.634	3.526
172.120	0.577	0.107	2.608	0.785	61.157	2.694	5.854
199.410	0.422	0.000	0.322	2.590	194.890	4.971	1.871
238.040	0.000	0.004	0.117	2.821	148.300	5.033	2.073
54.043	0.000	0.000	0.000	2.964	13.804	4.659	0.728
171.810	0.000	0.000	0.764	3.455	78.954	6.459	3.929
400.600	40.591	0.120	9.176	0.673	648.020	16.580	13.144
385.650	80.725	0.000	8.494	3.427	667.830	32.427	14.199
189.620	13.478	0.082	4.440	0.997	232.110	13.888	7.321
178.960	0.175	0.289		0.580	47.255	0.615	4.057
234.770			0.798	0.249	53.772	0.482	2.905
255.430	0.379	0.011	2.536	0.814	167.390	5.094	1.319
273.950	0.261	0.000	3.353	1.276	188.810	5.248	1.391
265.660	0.197	0.000	2.721	0.426	78.628	1.729	1.385
10.962	3.221	3.055	0.513	2.841	9.488	3.881	4.080
5.928	3.202	2.935	0.037	2.824	5.278	3.610	3.671
11.421	3.250	2.932	0.011	2.806	9.472	4.016	3.646
60.273	1.772	0.236	-0.247	0.753	125.100	2.855	0.993
11.101	24.872	74.194	97.454	2913.500	1326.100	404.380	44.138
39.285	0.000	0.000	0.000	1.887	30.484	4.549	1.381
323.350	0.010	0.024	1.917	2.550	467.930	9.967	2.249
323.890	0.135	0.055	2.314	3.638	434.800	9.176	2.114
225.130	1.053	-0.164	-0.733	0.631	247.330	5.093	0.815
183.570	0.082	0.404	4.532	0.112	71.000	0.394	12.623
219.630		0.007	12.280	0.305	41.403	1.471	25.642
236.430	0.119		7.222	0.306	70.991	1.612	35.046
24.995	0.245	0.201	0.034	0.107	10.956	0.651	0.447
17.057	0.103	0.009	0.367	0.068	6.789	0.368	0.189
21.304	0.086	0.206	0.000	0.035	9.445	0.538	0.367
173.810	0.531	0.247	-0.373	0.698	113.340	5.338	0.894
169.600	0.000	0.163	1.273	9.293	59.953	8.043	1.136
66.274	0.132	0.000	2.279	0.033	15.859	0.266	0.554
102.880	0.176	0.077	3.006	0.106	19.369	0.451	1.091
82.316	0.045	0.008	2.295	0.142	14.474	0.320	0.530

101.330	1.134	0.067	2.442	0.580	46.951	1.584	3.044
20.376	0.471	0.032	2.102	0.266	39.812	0.564	0.560
13.780	0.023	0.000	1.983	0.003	7.198	0.031	0.356
13.162	0.059	0.000	1.844	0.111	62.721	0.317	0.358
13.341	0.036	0.018	1.967	0.000	8.408	0.021	0.519
331.160	1.181	0.098	3.584	0.905	417.840	12.988	1.358
136.800	0.049	0.016	2.150	0.334	22.153	0.755	0.625
59.659	0.009	0.015	2.192	0.297	17.331	0.414	0.532
76.817	0.042	0.020	2.181	0.174	23.383	0.694	1.171
67.659	0.000	0.018	1.931	0.183	27.419	0.411	0.953
180.100	0.016	0.052	2.140	0.338	30.781	0.806	1.082
111.130	0.011	0.016	2.032	0.361	61.504	0.495	0.763
173.030	3.310	0.036	2.125	0.318	44.056	0.739	0.661
360.680	0.132	0.058	1.918	0.805	53.907	1.197	1.134
213.140	0.104	0.059	3.607	0.522	94.128	3.877	1.231
277.470	0.051	0.015	4.638	0.432	138.680	4.965	1.166
153.280	0.375	0.027	2.419	0.360	73.469	2.279	1.076
121.170	0.108	0.006	2.109	0.294	34.902	1.337	1.153
321.840	0.256	0.025	4.057	1.153	368.310	13.612	1.506
65.279	0.056	0.032	2.115	0.439	22.573	0.405	0.789
63.667	0.065	0.065	1.894	0.305	28.730	0.481	0.693
89.593	3.290	3.008	0.353	2.864	38.634	5.166	3.786
128.420	3.286	2.954	0.834	2.881	43.820	4.101	3.998
156.430	3.143	2.979	0.000	3.040	36.264	3.766	4.736
199.870	3.129	3.040	0.638	2.999	89.592	5.005	4.470
4.880	3.199	3.002	0.000	2.820	5.029	3.474	4.081
5.084	3.129	2.939	0.000	2.851	4.428	3.491	4.360
80.513	3.267	2.999	0.116	3.005	15.359	3.623	6.104
106.670	3.191	2.944	0.266	2.949	17.967	3.618	5.541
87.136	3.257	3.052	0.254	2.952	18.436	3.620	5.508
77.415	3.188	2.962	0.120	2.958	20.182	3.678	4.612
6.650	3.149	2.954	0.021	2.868	5.497	3.507	3.179
7.873	3.109	2.954	0.226	2.936	3.480	3.453	3.085
16.951	3.147	2.974	0.316	2.830	24.999	4.208	3.488
6.034	3.139	2.981	0.186	2.847	6.637	3.561	3.247
7.743	3.100	2.940	0.082	2.828	6.636	3.537	3.224

40.121	3.162	2.963	0.019	3.100	16.256	3.665	6.883
13.899	3.176	2.909	0.000	2.866	13.801	3.512	3.228
8.240	3.149	2.947	0.116	2.843	7.185	3.661	3.122
74.859	3.237	2.991	0.410	3.726	24.252	3.655	6.708
62.050	3.247	2.946	0.193	3.800	27.617	3.951	8.706
63.890	3.121	3.068	2.074	3.014	75.704	6.293	4.034
189.150	0.455	0.148	8.237	0.536	486.630	20.928	0.082
798.990	5.340	0.412	3.847	0.539	527.740	12.555	3.880
775.350	4.958	0.303	4.329	0.538	475.770	12.235	3.101
756.640	4.085	0.339	4.196	0.737	561.780	10.751	3.703
139.730	3.423	3.003	0.531	2.915	53.561	4.127	4.542
97.360	3.363	3.007	0.479	3.041	48.927	4.008	4.132
262.610	4.222	0.285	1.448	0.570	200.150	7.158	1.619
69.216	1.050	-0.160	1.085	1.750	68.986	4.294	1.214
63.494	0.595		1.922	1.685	60.802	3.599	1.079
105.380	0.202	0.099	1.076	0.396	111.670	0.219	0.694
127.610	0.063		1.411	0.291	65.289	1.506	0.528
124.360	0.185	0.051		0.283	33.470	1.242	0.565
62.676	0.365			0.319	28.362	0.255	0.825
72.457	0.026		0.220	0.334	33.449	0.607	0.696
96.367	0.243			0.279	75.642	0.695	1.135
90.231	0.142			0.471	27.511	0.719	1.330
113.850	0.097	0.201		0.192	41.176	0.670	1.005
60.136	0.340	0.503		0.300	32.801	0.552	0.871
68.064				0.210	24.023	0.415	1.426
801.480	0.325			0.099	154.200	11.739	6.663
1152.800	0.450	0.435		1.100	226.260	21.524	8.545
129.430	0.193	0.478			94.493	1.923	1.280
36.938	0.095	0.504	0.614	0.592	29.787	1.278	1.326
108.020		0.116	0.091	0.564	85.075	1.847	0.786
85.517	0.000	0.112	0.031	0.110	18.546	0.112	1.332
114.110	0.000	0.117	0.000	0.100	16.382	0.025	1.040
147.390	0.000	0.143	0.132	0.162	18.443	0.005	1.139
100.680	0.022	0.165	0.000	0.045	24.049	0.102	2.135
65.725	0.000	0.039	0.000	0.051	20.603	0.000	1.253
435.240	0.386	0.081	0.641	0.287	402.430	18.932	5.403

154.110	0.226	0.095	1.530	0.017	245.370	5.624	0.610
93.934	0.000	0.127	0.024	0.145	41.854	1.808	1.038
65.610	0.000	0.083	0.000	0.029	19.795	0.436	0.872
71.350	0.061	0.006	0.000	0.142	14.796	0.000	0.991
68.060	0.000	0.067	0.000	0.147	14.881	0.187	0.785
128.660	0.000	0.042	0.016	0.157	22.141	0.178	1.011
269.160	0.053	0.085	0.246	0.158	30.342	0.264	1.281
142.370	0.000	0.104	0.052	0.224	26.409	0.505	1.054
290.890	0.000	0.132	0.000	0.229	42.334	1.036	0.665
147.320	0.000	0.111	0.000	0.091	27.652	0.411	0.474
496.620	0.711	0.083	1.318	0.108	290.880	6.203	2.604
22.152	0.001	0.021	0.000	0.000	16.737	0.202	0.471
18.466	0.000	0.027	0.000	0.000	6.482	0.000	0.377
9.751	0.000	0.028	0.000	0.000	5.521	0.000	0.219
251.010	0.137	0.040	0.855	0.187	155.190	9.185	1.503
144.190	0.000	0.000	0.000	0.327	28.347	0.678	1.218
98.898	0.000	0.022	0.297	2.424	35.013	4.561	0.962
92.655	0.000	0.011	0.149	3.128	40.523	4.734	1.130
117.810	0.375	-0.102	0.101	0.741	122.270	4.861	2.611
54.243	0.593	0.004	0.599	0.800	45.562	2.678	0.853
133.910	0.000	0.000	0.419	2.453	85.087	8.877	1.932
69.033	0.309	0.031	0.439	0.529	83.093	3.124	0.342
178.640	0.210	0.000	1.314	3.320	220.930	7.793	1.776
104.400	0.000	0.069	0.000	5.845	35.853	5.240	1.133
162.670	0.000	0.000	1.180	2.855	61.126	7.472	2.070
260.770	0.033	0.003	4.940	3.293	143.820	9.640	1.974
292.600	0.688	0.171	0.587	0.676	101.830	6.150	1.392
690.740	1.116	0.020	1.014	1.064	550.770	13.173	41.382
420.080	0.837	-0.069	0.507	0.789	449.580	5.848	17.592
38.790	0.000	0.000	0.000	2.227	11.508	4.530	0.535
84.355	0.000	0.000	0.000	2.699	8.889	4.640	0.026
177.360	0.000	0.003	1.788	2.356	217.540	7.476	0.848
95.999	0.000	0.000	0.944	3.143	65.507	5.327	0.612
152.480	0.000	0.003	1.024	3.415	60.179	7.756	0.930
150.250	0.000	0.000	0.000	2.204	18.497	4.855	0.948
56.769	1.256		1.366	1.659	35.802	3.714	8.512

59.172	0.000	0.000	0.000	2.806	8.101	4.437	1.978
44.202	0.000	0.000	0.457	2.187	14.223	4.505	1.187
144.550	0.035	0.028	2.275	1.311	391.630	3.114	1.326
50.076	0.059	0.024	0.000	0.000	7.925	0.000	0.735
36.682	0.000	0.117	0.000	0.003	11.558	0.000	0.811
49.021	0.000	0.217	0.090	0.067	8.924	0.000	0.869
23.276	0.000	0.141	0.000	0.016	5.723	0.000	0.258
14.983	0.033	0.071	0.000	0.000	5.050	0.000	0.152
124.120	0.082	0.000	0.000	0.000	11.108	0.082	0.598
307.810	0.307	0.000	3.592	1.277	400.700	14.972	1.478
319.430	0.553	0.018	3.855	0.963	370.610	14.643	1.493
146.400	0.018	0.010	2.230	0.307	53.908	1.182	1.159
297.310	5.938	0.068	2.167	3.216	641.450	36.820	15.016
81.580	0.000	0.000	0.000	3.216	20.642	4.940	0.574
180.980	0.147	0.114	0.149	0.116	95.400	1.900	0.920
111.470	0.181	0.064	0.516	0.083	60.807	0.990	0.730
181.160	0.337	0.137	0.618	0.075	96.927	2.227	0.855
194.330		0.246		0.496	52.908	2.303	1.167
207.230		0.188		0.372	142.810	4.165	1.523
168.730	0.000	0.013	0.937	2.767	82.648	6.835	3.679
143.840	8.155	-0.032	23.066	0.612	490.760	4.667	39.592
101.620	0.642	0.006	2.446	0.263	104.680	2.545	1.129
9.709	25.474	76.480	93.671	2923.900	1321.600	401.930	42.921
98.445	0.000	0.000	0.211	2.879	72.871	5.373	0.906
80.669	0.009	0.041	0.000	0.261	15.794	0.103	0.771

APPENDIX C: SOIL DATA

DETAILED CASE STUDIES

MACRO ELEMENTS

METALS

Aqua regia

EPA 3050

NH4EDTA

NH4NO3

Groundwater data

site number	location at site	Depth mm	Bray I P mg/kg	Ca mg/kg	K mg/kg	Mg mg/kg	Na mg/kg	Org_ C %	pH (H2O)	S Total %	N Total %	Clay %
1	1	0-100	918.8	7304	45	118	112	0.92	7.33	0.042	0.112	2
1	1	100-200	1032.2	6800	47	128	122	0.91	7.30	0.056	0.115	2
1	1	200-300	1858.3	6996	66	140	130	1.17	7.21	0.054	0.224	2
1	1	300-400	1346.0	7237	66	118	120	1.10	7.27	0.053	0.166	2
1	2	0-100	689.8	7003	43	95	101	0.75	7.49	0.054	0.112	2
1	2	100-200	346.0	7160	41	95	100	0.71	7.80	0.052	0.094	2
1	2	200-300	258.4	6615	38	93	99	0.56	7.92	0.053	0.063	2
1	2	300-400	267.5	4350	49	87	81	0.69	7.95	0.063	0.081	2
1	2	400-500	223.9	4139	28	78	65	0.69	7.86	0.058	0.094	2
1	3	0-100	933.6	4081	48	90	76	0.76	7.57	0.054	0.097	2
1	3	100-200	1064.0	4102	44	87	65	0.99	7.48	0.058	0.136	2
1	3	200-300	821.0	4120	37	90	66	0.66	7.53	0.050	0.091	2
1	3	300-400	2637.1	4033	44	131	78	3.18	7.26	0.061	0.358	2
1	3	400-500	1498.3	4169	32	109	75	1.69	7.50	0.052	0.188	2
2	1	0-100	3418.6	4900	53	105	71	3.25	7.16	0.033	0.330	2
2	1	100-200	1083.3	4688	17	69	48	0.59	7.34	0.046	0.067	2
2	1	200-300	300.8	4682	7	67	51	0.09	8.18	0.040	0.008	4
2	1	300-400	268.8	4573	7	67	51	0.07	8.56	0.044	0.009	4
2	1	400-500	641.0	4663	17	75	57	0.53	8.26	0.052	0.109	4
2	2	0-100	2037.8	4580	26	89	60	3.51	7.72	0.043	0.145	4
2	2	100-200	1503.4	4700	22	80	69	1.15	7.74	0.039	0.101	4
2	2	200-300	486.1	4457	11	81	47	0.46	8.16	0.029	0.032	4
2	2	300-400	290.4	7332	8	91	77	0.34	8.34	0.030	0.020	4
2	2	400-500	377.3	7506	11	92	78	0.75	8.14	0.042	0.041	2
2	3	0-100	2054.4	7567	46	100	109	1.60	7.67	0.060	0.089	4
2	3	100-200	2034.5	7281	49	99	99	1.36	7.66	0.044	0.112	4
2	3	200-300	1730.9	4408	35	86	66	1.31	7.52	0.044	0.093	4
2	3	300-400	3395.1	4723	98	157	69	2.56	7.47	0.054	0.239	4
2	3	400-500	276.6	4630	17	83	58	0.49	8.06	0.041	0.040	4
3	1	0-100	1485.4	2815	258	211	58	1.19	5.72	0.139	0.014	16
3	1	100-200	318.9	4767	296	282	71	0.55	7.18	0.102	0.135	21
3	1	200-300	239.5	2349	263	242	64	0.49	7.20	0.086	0.074	21
3	1	300-400	191.2	1827	284	269	64	0.46	6.92	0.095	0.068	25
3	1	400-500	149.6	2583	349	345	78	0.43	6.71	0.108	0.073	31
3	2	0-100	347.2	5927	512	281	97	0.71	7.52	0.093	0.074	23
3	2	100-200	364.8	5110	550	308	99	0.72	7.67	0.095	0.091	21
3	2	200-300	303.8	5689	676	337	139	0.50	7.83	0.090	0.095	21
3	2	300-400	251.0	5453	637	304	155	0.43	7.82	0.095	0.073	21
3	2	400-500	152.7	3686	587	264	163	0.45	7.72	0.090	0.068	21

3	3	0-100	796.3	1728	169	117	36	0.56	5.67	0.104	0.067	19
3	3	100-200	250.0	5570	277	247	55	0.42	7.32	0.098	0.069	13
3	3	200-300	233.3	4557	243	261	68	0.40	7.60	0.091	0.058	19
3	3	300-400	158.1	1800	248	249	60	0.42	7.32	0.091	0.061	21
3	3	400-500	156.8	2517	306	325	73	0.43	7.00	0.096	0.071	25
4	1	0-100	242.3	585	123	98	88	0.61	5.17	0.049	0.066	10
4	1	100-200	174.4	465	102	87	71	0.50	4.98	0.049	0.052	4
4	1	200-300	156.1	407	99	85	74	0.32	5.01	0.049	0.038	4
4	1	300-400	171.9	380	100	80	72	0.28	5.04	0.053	0.039	4
4	1	400-500	191.2	405	103	78	70	0.27	5.62	0.048	0.032	
4	2	0-100	352.8	1399	233	193	265	0.62	5.46	0.062	0.093	4
4	2	100-200	173.7	846	166	162	272	0.48	5.41	0.051	0.082	4
4	2	200-300	152.0	622	132	139	271	0.38	5.21	0.051	0.066	2
4	2	300-400	178.0	481	110	120	242	0.28	5.20	0.051	0.037	4
4	3	0-100	199.9	556	65	170	45	0.44	7.33	0.045	0.035	4
4	3	100-200	174.1	476	97	169	197	0.62	7.39	0.051	0.035	4
4	3	200-300	165.0	462	111	157	357	0.39	7.50	0.053	0.035	2
4	3	300-400	162.5	541	145	164	389	0.29	8.10	0.052	0.030	2
4	3	400-500	138.0	346	129	131	330	0.23	8.36	0.054	0.028	4
5	1	0-100	724.6	363	155	125	46	0.34	4.64	0.100	0.052	4
5	1	100-200	550.8	297	131	115	30	0.24	4.96	0.100	0.039	6
5	1	200-300	375.6	324	123	113	45	0.20	5.26	0.110	0.041	6
5	1	300-400	280.8	301	96	97	40	0.15	5.40	0.106	0.032	6
5	1	400-500	169.6	271	90	84	23	0.12	5.44	0.099	0.026	6
5	2	0-100	845.3	396	72	92	27	0.24	4.54	0.091	0.054	4
5	2	100-200	634.7	432	94	101	22	0.18	4.76	0.091	0.042	4
5	2	200-300	538.0	459	87	109	16	0.14	5.02	0.095	0.031	4
5	2	300-400	395.7	429	82	103	31	0.10	5.12	0.100	0.026	4
5	2	400-500	212.4	431	89	108	29	0.08	5.16	0.096	0.022	4
5	3	0-100	180.0	377	100	77	33	0.18	7.34	0.075	0.064	4
5	3	100-200	174.7	420	82	82	17	0.14	7.53	0.079	0.048	4
5	3	200-300	179.9	405	63	86	27	0.12	7.34	0.079	0.028	4
5	3	300-400	125.4	470	63	89	32	0.12	7.30	0.080	0.025	4
5	3	400-500	134.5	437	57	83	22	0.10	7.35	0.079	0.025	6
6	1	0-100	137.9	1119	84	83	18	0.39	7.37	0.078	0.03	12
6	1	100-200	119.71	1143	73	80	16	0.3	7.83	0.064	0.024	10
6	2	0-100	113.18	1911	59	77	13	0.24	7.84	0.066	0.021	8
6	2	100-200	123.45	1664	48	80	11	0.25	7.8	0.068	0.021	6
6	2	200-300	168.41	2657	54	103	17	0.3	7.76	0.055	0.02	6
6	3	0-100	1438.21	3334	66	85	17	2.89	6.77	0.065	0.221	6

6	3	100-200	4309.38	4639	112	193	30	5.14	6.49	0.073	0.401	6
7	1	0-100	4228.5	2844	315	326	32	4.46	4.90	0.260	0.493	4
7	1	100-200	1342.2	1812	169	268	29	1.39	4.93	0.156	0.132	12
7	1	200-300	338.0	1652	108	309	45	0.50	5.99	0.127	0.055	20
7	1	300-400	273.1	1361	76	284	52	0.42	6.34	0.118	0.049	20
7	2	0-100	1065.5	1024	489	252	102	0.80	5.83	0.309	0.095	16
7	2	100-200	693.0	1155	208	265	87	0.62	5.74	0.309	0.063	20
7	3	0-100	469.9	1223	157	214	43	0.69	.06	0.131	0.081	20
7	3	100-200	206.7	1477	55	335	48	0.22	7.10	0.118	0.024	20
7	3	200-300	241.8	1697	55	487	53	0.18	7.36	0.173	0.017	16
8	1	0-100	1685.77	937	541	536	57	2.25	4.36	0.143	0.237	10
8	1	100-200	1063.71	694	328	345	36	1.37	4.59	0.142	0.131	12
8	1	200-300	861.89	955	302	380	45	1.09	4.56	0.174	0.104	14
8	2	0-100	2400.12	1005	266	227	13	2.07	3.98	0.163	0.206	10
8	2	100-200	762.51	542	189	130	8	0.84	4.15	0.141	0.069	10
8	3	0-100	908.74	433	341	120	16	0.95	4.83	0.129	0.072	10
8	3	100-200	532.72	399	244	110	14	0.74	4.54	0.117	0.057	10
9	1	0-100	2346.53	3557	615	756	49	2.16	7.27	0.295	0.156	24
9	1	100-200	755.78	3217	471	615	57	1.08	7.5	0.237	0.081	24
9	1	200-300	732.55	3939	432	858	94	1.02	7.68	0.277	0.073	26
9	2	0-100	14318.88	9823	613	286	73	1.69	4.27	0.917	0.246	6
9	2	100-200	15809.04	7439	501	356	87	2.32	4.16	0.693	0.253	12
9	2	200-300	12639.8	6929	477	428	99	1.77	4.12	0.552	0.271	20
9	2	300-400	8137.63	4215	374	453	86	1.06	4.17	0.285	0.096	24
9	2	400-500	8416.54	7779	427	514	25	1.3	4.12	0.847	0.131	22
9	3	0-100	16730.48	1808	383	313	29	2.26	5.53	0.313	0.337	26
9	3	100-200	11684.15	2124	169	255	43	1.56	5.64	0.259	0.207	26
9	3	200-300	23573.86	6468	153	154	53	2.01	5.61	0.528	0.222	0
10	1	0-100	527.29	410	164	55	27	0.8	5.24	0.189	0.071	26
10	1	100-200	399.37	406	71	46	17	0.74	4.39	0.166	0.025	26
10	1	200-300	346.2	383	73	43	19	0.66	4.46	0.163	0.041	24
10	1	300-400	400.24	488	68	45	18	0.56	4.42	0.163	0.037	28
10	1	400-500	418.19	1015	55	42	16	0.45	4.3	0.182	0.037	28
10	2	0-100	1621.43	572	198	82	42	1.3	5.56	0.184	0.133	26
10	2	100-200	487.15	476	85	78	36	0.76	4.67	0.177	0.045	26
10	2	200-300	382.85	442	84	62	25	0.61	4.63	0.169	0.039	24
10	2	300-400	360.13	349	80	46	20	0.59	4.49	0.181	0.04	28
11	1	0-100	972.25	497	144	66	8	0.81	5.24	0.083	0.071	12
11	1	100-200	764.83	472	159	65	3	0.48	5.14	0.077	0.048	14
11	2	0-100	305.4	591	663	160	30	0.7	7.3	0.063	0.067	12

11	2	100-200	187.78	397	702	141	24	0.38	7.56	0.065	0.03	12
11	2	200-300	186.68	310	628	124	18	0.34	7.44	0.063	0.023	12
11	3	0-100	644.24	1084	906	303	40	1.47	7.64	0.095	0.113	0
11	3	100-200	212.85	400	697	169	30	0.35	7.73	0.062	0.04	10
11	3	200-300	237.89	391	758	192	34	0.38	7.83	0.067	0.036	12
11	3	300-400	286.53	436	744	175	33	0.66	7.94	0.063	0.053	10
12	1	0-100	427.44	6754	206	1873	164	0.54	7.29	0.192	0.033	42
12	1	100-200	374.32	7480	275	2201	205	0.56	7.27	0.202	0.035	48
12	1	200-300	692.35	7870	322	2387	204	0.68	7.46	0.241	0.036	48
12	2	0-100	490.19	8824	164	2642	185	0.57	7.36	0.283	0.04	46
12	2	100-200	495.34	7319	160	2256	147	0.53	7.4	0.209	0.038	44
12	2	200-300	436.41	6503	150	2132	160	0.53	7.44	0.194	0.03	42
12	2	300-400	326.95	5772	148	1862	140	0.44	7.5	0.15	0.031	38
13	1	0-100	990.9	378	114	124	28	1.09	4.61	0.076	0.084	6
13	1	100-200	466.2	513	74	129	31	0.67	5.79	0.063	0.049	10
13	1	200-300	274.4	527	56	116	40	0.35	6.54	0.057	0.025	8
13	1	300-400	238.9	390	32	82	28	0.25	6.60	0.056	0.145	8
13	1	400-500	242.3	391	29	86	47	0.22	6.41	0.057	0.017	8
13	2	0-100	729.9	2362	195	138	46	1.92	7.14	0.093	0.020	8
13	2	100-200	483.7	1278	117	80	32	0.61	7.50	0.053	0.076	10
13	2	200-300	320.6	375	88	55	32	0.07	7.48	0.056	0.009	8
13	2	300-400	274.5	341	87	54	17	0.05	7.38	0.037	0.008	6
13	2	400-500	253.5	334	84	55	33	0.04	7.31	0.051	0.007	6
13	3	0-100	1468.1	672	48	94	29	1.30	6.16	0.094	0.106	6
13	3	100-200	286.4	478	29	73	42	0.22	6.49	0.050	0.033	6
13	3	200-300	189.8	273	24	57	26	0.04	6.28	0.039	0.007	6
13	3	300-400	207.9	247	24	60	28	0.03	5.87	0.037	0.005	6
13	3	400-500	218.2	246	35	58	27	0.03	5.36	0.040	0.004	4
14	1	0-100	25016.4	4295	569	584	225	2.55	6.12	0.277	0.395	10
14	1	100-200	7733.8	5357	94	471	121	2.09	7.05	0.102	0.246	10
14	1	200-300	1801.8	4454	48	373	81	1.58	7.33	0.093	0.148	10
14	1	300-400	4404.8	5984	65	660	109	1.83	7.12	0.160	0.480	16
14	2	0-100	485.3	2162	133	416	78	0.41	5.84	0.203	0.120	20
14	2	100-200	315.2	2494	80	626	73	0.42	6.86	0.171	0.118	20
14	2	200-300	362.6	2340	93	583	80	0.33	6.94	0.168	0.054	20
15	1	0-100	136.59	195	55	34	14	0.06	5.44	0.071	0.024	14
15	1	100-200	201.73	13	18	4	4	0.02	5.46	0.062	0.007	12
15	1	200-300	224.7	31	27	7	4	0.13	4.08	0.065	0.011	12
15	1	300-400	254.54	53	45	15	2	0.47	4.21	0.059	0.032	12
15	1	400-500	175	22	46	8	0	0.32	4.63	0.055	0.023	12

15	2	0-100	211.87	146	60	44	14	0.28	4.57	0.055	0.04	8
15	2	100-200	213.49	111	63	35	14	0.36	6.09	0.059	0.056	12
15	2	200-300	189.62	49	62	37	11	0.16	6.28	0.059	0.036	14
15	2	300-400	222.26	22	17	33	8	0.06	4.93	0.061	0.014	14
15	2	400-500	229.37	27	17	31	5	0.03	4.84	0.06	0.009	14
16	1	0-100	2880.3	891	106	102	55	6.19	4.60	0.275	1.037	20
16	1	100-200	1123.7	699	108	128	55	3.49	4.76	0.153	0.378	20
16	1	200-300	1341.1	2636	90	246	79	3.03	6.58	0.174	0.333	16
16	2	0-100	1035.6	600	86	104	85	3.24	4.54	0.144	0.239	20
16	2	100-200	1414.5	2595	85	138	96	2.67	6.29	0.194	0.233	18
16	2	200-300	412.8	1650	78	199	115	1.68	6.78	0.158	0.130	20
16	3	0-100	1679.8	598	97	99	59	4.11	4.86	0.174	0.047	20
16	3	100-200	297.9	1462	83	131	68	1.92	6.18	0.169	0.161	20
16	3	200-300	197.4	1469	60	158	77	1.34	6.56	0.148	0.107	6
17	1	0-100	299.8	436	27	71	26	0.85	5.70	0.070	0.080	4
17	1	100-200	101.1	211	13	51	29	0.32	5.24	0.059	0.019	4
17	1	200-300	131.1	181	13	49	26	0.23	4.96	0.064	0.019	4
17	1	300-400	112.6	154	12	46	23	0.21	4.87	0.056	0.012	2
17	1	400-500	120.4	168	12	46	23	0.27	4.93	0.065	0.019	2
17	2	0-100	123.1	177	21	49	21	0.27	5.69	0.066	0.026	2
17	2	100-200	106.8	162	18	49	30	0.27	5.41	0.065	0.020	2
17	2	200-300	108.4	147	13	48	20	0.19	5.10	0.065	0.021	2
17	2	300-400	100.4	144	14	49	24	0.13	5.00	0.060	0.015	2
17	2	400-500	86.8	143	14	47	26	0.10	5.26	0.059	0.011	2
17	3	0-100	108.0	255	15	52	18	0.46	5.34	0.076	0.011	4
17	3	100-200	80.8	248	14	52	21	0.41	5.18	0.070	0.036	2
17	3	200-300	78.0	221	12	52	29	0.38	5.14	0.071	0.027	2
17	3	300-400	73.4	182	11	50	27	0.19	5.18	0.056	0.026	2
18	1	0-100	917.1	828	258	275	281	0.32	7.20	0.153	0.035	4
18	1	100-200	2317.6	4238	366	599	580	1.23	7.67	0.081	0.123	4
18	2	0-100	1021.0	4844	342	451	712	1.04	7.54	0.070	0.119	4
18	2	100-200	567.1	5309	322	548	689	0.49	7.94	0.101	0.072	8
18	3	0-100	865.2	3090	549	247	187	0.76	7.52	0.071	0.103	4
18	3	100-200	517.0	1745	452	209	163	0.29	7.83	0.064	0.048	4
19	1	0-100	411.4	817	3296	233	289	0.77	7.98	0.072	0.087	24
19	1	100-200	270.3	976	3034	209	272	0.51	8.38	0.067	0.053	20
19	1	200-300	200.9	567	1736	139	168	0.27	8.40	0.061	0.031	20
19	1	300-400	163.5	629	1465	141	173	0.27	8.21	0.059	0.029	12
19	1	400-500	141.8	588	920	142	172	0.28	7.86	0.063	0.041	8
19	2	0-100	1092.6	1274	3395	300	398	1.80	6.86	0.228	0.154	14

19	2	100-200	338.1	1220	2469	235	271	0.44	7.95	0.074	0.059	20
19	2	200-300	168.8	1085	1619	228	239	0.25	7.96	0.052	0.033	16
19	2	300-400	127.5	459	627	129	142	0.21	7.74	0.054	0.024	8
19	2	400-500	157.8	572	342	156	145	0.27	7.60	0.068	0.038	8
19	3	0-100	181.4	360	1944	150	262	0.33	8.14	0.074	0.040	10
19	3	100-200	138.9	420	1826	149	278	0.34	7.34	0.074	0.040	12
19	3	200-300	133.8	590	1473	176	260	0.35	6.91	0.072	0.041	14
19	3	300-400	126.7	972	960	243	259	0.40	6.74	0.076	0.054	18
19	3	400-500	139.7	1325	622	220	210	0.38	6.67	0.080	0.060	20
20	1	0-100	3634.36	2672	287	197	31	3.66	6.18	0.325	0.327	18
20	1	100-200	714.15	1704	183	142	74	1.31	6.63	0.193	0.095	26
20	1	200-300	440.68	1344	175	129	68	0.78	6.72	0.194	0.058	28
20	1	300-400	423.55	978	146	105	57	0.54	6.74	0.173	0.039	28
20	1	400-500	360.36	821	140	92	59	0.37	6.8	0.17	0.032	28
20	2	0-100	874.53	1152	102	95	80	1.26	6.04	0.162	0.089	16
20	2	100-200	490.75	845	61	90	54	0.45	6.7	0.17	0.033	18
20	2	200-300	400.81	724	44	101	44	0.32	7.04	0.155	0.026	22
20	2	300-400	337.31	744	27	105	36	0.25	7.25	0.162	0.025	24
20	2	400-500	421.95	737	26	108	38	0.21	7.32	0.171	0.019	26
20	3	0-100	785.82	1245	57	83	58	2.01	5.64	0.125	0.219	12
20	3	100-200	469.31	871	28	71	62	0.88	6.47	0.115	0.063	14
20	3	200-300	335.87	846	16	93	70	0.58	6.86	0.11	0.041	18
20	3	300-400	333.64	729	15	87	45	0.38	6.97	0.111	0.027	18
20	3	400-500	385.97	754	14	94	42	0.32	7.08	0.106	0.025	0
21	1	0-100	334.75	543	308	121	45	1.25	5	0.48	0.063	28
21	1	100-200	290.2	548	223	141	58	1	5.19	0.324	0.054	30
21	1	200-300	245.3	485	166	137	89	0.84	5.58	0.371	0.042	34
21	1	300-400	219.47	602	101	112	40	0.64	6.1	0.34	0.038	36
21	1	400-500	192.56	633	54	108	45	0.54	6.34	0.341	0.029	38
21	2	0-100	410.71	555	137	73	62	1.26	4.57	0.406	0.073	30
21	2	100-200	315.19	691	78	91	63	0.98	4.99	0.414	0.052	30
21	2	200-300	210.32	751	77	122	79	0.77	5.42	0.322	0.042	34
21	2	300-400	228.7	644	63	130	80	0.64	5.67	0.334	0.034	34
21	2	400-500	216.39	650	42	138	36	0.57	5.94	0.335	0.035	36
21	3	0-100	380.78	703	171	150	69	1.23	5.18	0.444	0.065	32
21	3	100-200	297.96	739	58	184	119	1.06	5.16	0.414	0.054	32
21	3	200-300	263.66	845	43	153	250	0.85	5.46	0.453	0.039	34
21	3	300-400	200.58	914	37	166	181	0.63	5.89	0.397	0.035	38
21	3	400-500	207.62	1020	40	180	116	0.55	6.16	0.352	0.035	40
22	1	0-100	712.5	119	100	44	7	0.89	4.05	0.126	0.056	10

22	1	100-200	694.79	249	82	76	11	0.59	4.93	0.112	0.032	12
22	1	200-300	422.45	306	82	98	14	0.64	5.24	0.124	0.028	12
22	1	300-400	254.21	241	26	82	20	0.59	5.47	0.096	0.038	0
22	2	0-100	962.46	169	197	75	36	0.76	4.65	0.096	0.046	8
22	2	100-200	555.83	102	110	52	45	0.6	4.21	0.095	0.037	10
22	2	200-300	373.86	131	115	50	49	0.46	4.72	0.096	0.025	12
22	2	300-400	291.74	144	132	48	48	0.4	4.73	0.08	0.03	16
22	2	400-500	124.94	112	121	51	45	0.38	4.14	0.09	0.028	16
22	3	0-100	495.33	143	114	45	15	0.98	4.23	0.117	0.07	10
22	3	100-200	507.56	124	33	38	8	0.74		0.098	0.03	10
22	3	200-300	222.88	147	27	35	8	0.47		0.088	0.027	12
22	3	300-400	138.36	87	24	23	5	0.37	4.52	0.096	0.034	14
22	3	400-500	126.72	0	0	0	0	0.29		0.09	0.024	14
23	1	0-100	444.47	38	117	31	12	0.85	3.64	0.096	0.095	6
23	1	100-200	675.3	132	142	57	20	0.58	4.37	0.094	0.034	10
23	1	200-300	666.05	213	128	78	19	0.28	5.09	0.077	0.024	12
23	1	300-400	528.08	206	97	82	15	0.21	5.18	0.067	0.019	12
23	1	400-500	502.56	228	92	98	19	0.17	5.21	0.071	0.02	12
23	2	0-100	792.71	197	142	107	37	1.2	3.93	0.133	0.048	10
23	2	100-200	888.36	173	131	87	29	0.65	3.94	0.105	0.035	8
23	2	200-300	1311.14	242	158	145	27	0.51	4.53	0.112	0.034	14
23	2	300-400	1296.75	358	167	162	26	0.5	5.14	0.11	0.029	18
23	2	400-500	997.98	547	202	172	31	0.42	5.48	0.129	0.026	18
23	3	0-100	970.25	400	364	193	77	1.8	4.63	0.127	0.141	10
23	3	100-200	798.37	299	153	158	82	1.45	4.46	0.126	0.086	12
23	3	200-300	780.23	257	137	159	98	1.34	4.24	0.135	0.079	8
23	3	300-400	894.49	238	122	163	89	0.81	4.33	0.126	0.028	8
23	3	400-500	1322.43	318	151	228	96	0.39	4.95	0.126	0.027	12
24	1	0-100	76301.73					7.34		0.745	0.039	10
24	1	100-200	52772.5	3383	2227	1233	101	6.71	5.57	0.691	0.789	12
24	1	200-300	28592.27	2661	1487	1207	22	4.94	5.97	0.612	0.443	22
24	1	300-400	914.55	1771	818	769	41	1.56	6.24	0.505	0.08	54
24	1	400-500	647.59	1489	584	736	44	1.37	5.83	0.508	0.083	62
24	2	0-100	12457.98	1042	909	349	51	3.48	4.06	0.584	0.307	16
24	2	100-200	10241.77	1309	747	325	95	2.87	4.02	0.679	0.484	28
24	2	200-300	5864.25	1066	520	279	39	1.2	3.92	0.56	0.073	54
24	2	300-400	5009.73	1240	552	303	38	1.25	4.53	0.511	0.068	62
24	2	400-500	2373.16	1324	510	351	34	1.21	4.97	0.513	0.064	64
24	3	0-100	18608.98	965	1056	713	61	3.65	4.46	0.698	0.413	22
24	3	100-200	13785.15	1217	786	902	62	2.6	4.74	0.552	0.26	24

24	3	200-300	2112.98	1100	383	680	82	1.21	4.98	0.523	0.07	56
24	3	300-400	1100.43	1200	395	531	68	1.16	4.9	0.517	0.063	62
24	3	400-500	815.41	1282	394	506	57	0.97	5.27	0.522	0.057	64
25	1	0-100	2682.2	2638	87	160	185	3.21	6.21	0.126	0.283	4
25	1	100-200	612.1	1108	13	89	72	1.08	6.79	0.038	0.063	4
25	1	200-300	184.4	993	10	74	139	0.16	7.42	0.040	0.014	2
25	2	0-100	490.3	367	96	77	74	0.73	5.44	0.052	0.047	6
25	2	100-200	461.7	449	71	76	50	0.92	5.62	0.055	0.044	4
25	2	200-300	281.4	329	45	58	42	0.62	5.81	0.055	0.032	4
25	2	300-400	411.0	784	91	118	80	1.64	5.76	0.064	0.060	6
25	2	400-500	372.3	1192	112	168	87	1.88	6.21	0.085	0.053	6
25	3	0-100	430.3	1259	228	212	186	1.68	7.58	0.077	0.118	6
25	3	100-200	115.0	471	95	130	83	0.84	8.31	0.040	0.042	4
25	3	200-300	107.2	280	61	74	60	0.42	8.18	0.029	0.025	4
25	3	300-400	106.8	253	57	58	61	0.25	8.24	0.038	0.020	2
25	3	400-500	114.9	234	47	55	54	0.16	7.98	0.043	0.009	2
26	1	0-100	931.4	6296	154	152	79	0.91	7.26	0.078	0.599	6
26	1	100-200	894.7	5533	155	179	84	0.53	6.97	0.078	0.059	6
26	1	200-300	889.5	5584	122	180	90	0.33	7.08	0.078	0.041	4
26	1	300-400	1013.7	6076	89	188	92	0.33	7.37	0.080	0.035	4
26	1	400-500	1134.0	6543	81	184	83	0.29	7.48	0.078	0.038	4
26	2	0-100	428.4	6916	107	123	75	0.28	8.24	0.077	0.025	4
26	2	100-200	399.5	7276	107	116	66	0.19	8.34	0.071	0.021	4
26	2	200-300	401.9	7208	85	117	58	0.21	8.31	0.082	0.019	4
26	2	300-400	451.8	7087	65	116	69	0.23	8.17	0.190	0.023	4
26	2	400-500	452.1	6924	47	113	63	0.31	8.07	0.057	0.028	4
26	3	0-100	480.1	6528	133	127	63	0.67	8.06	0.069	0.060	6
26	3	100-200	418.4	6663	106	110	65	0.35	8.27	0.056	0.030	4
26	3	200-300	376.2	6492	78	120	67	0.26	8.40	0.056	0.022	4
26	3	300-400	388.8	7068	60	114	57	0.23	8.42	0.054	0.020	4
26	3	400-500	363.1	7189	71	115	68	0.14	8.48	0.056	0.014	4
27	1	0-100	409.08	846	466	60	83	0.88	6.93	0.148	0.08	26
27	1	100-200	370.57	456	319	55	51	0.75	5.27	0.23	0.061	28
27	1	200-300	373.11	636	330	100	47	0.62	5.09	0.25	0.042	26
27	1	300-400	395.69	555	263	102	43	0.64	5.07	0.317	0.029	24
27	2	0-100	569.05	450	436	90	54	0.9	6.04	0.152	0.091	28
27	2	100-200	702.76	411	355	75	68	0.79	4.81	0.216	0.063	26
27	2	200-300	684.56	505	406	106	63	0.69	4.94	0.294	0.035	22
28	1	0-100	3453.01	258	160	13	7	1.78	3.69	0.311	0.072	16
28	1	100-200	1705.05	239	108	13	4	0.54	3.96	0.187	0.027	22

28	1	200-300	1528.22	245	107	14	6	0.46	3.89	0.207	0.035	22
28	1	300-400	1413.13	265	95	16	3	0.38	3.9	0.209	0.027	22
28	1	400-500	1400.1	276	88	17	2	0.3	4.03	0.246	0.023	26
28	2	0-100	3534.27	303	152	27	4	1.93	4.05	0.442	0.103	16
28	2	100-200	3366.69	272	134	27	5	1.82	3.82	0.38	0.081	16
28	2	200-300	2453.47	328	138	28	1	0.81	4.26	0.416	0.038	14
28	3	0-100	3015.69	301	132	29	9	1.79	3.93	0.315	0.063	16
28	3	100-200	1959.73	234	90	29	12	0.64	3.85	0.181	0.036	22
28	3	200-300	4064.24	247	93	19	10	0.43	4.37	0.205	0.038	22
28	3	300-400	5636.36	326	97	26	9	0.34	4.87	0.204	0.029	22
28	3	400-500	4587.83	348	90	24	9	0.3	5.08	0.189	0.029	22
29	1	0-100	9457.13	1843	607	264	104	5.38	4.93	0.35	0.523	16
29	1	100-200	5743.87	1368	484	229	65	3.7	4.79	0.275	0.425	20
29	1	200-300	1489.94	537	212	100	53	0.94	4.3	0.209	0.076	28
29	1	300-400	1193.76	611	254	112	64	0.72	4.18	0.238	0.057	34
29	2	0-100	9605.29	1529	804	203	37	5.48	4.34	0.416	0.603	18
29	2	100-200	10453.41	1510	582	192	32	5.28	4.23	0.388	0.593	22
29	2	200-300	3534.62	1143	443	168	77	2.56	4.14	0.293	0.214	26
29	2	300-400	1929.96	943	343	151	53	0.98	4.8	0.276	0.09	36
29	2	400-500	1816.8	902	357	145	57	0.86	4.84	0.285	0.084	24
29	3	0-100	7194.45	1580	498	222	84	3.85	4.42	0.372	0.439	28
29	3	100-200	2054.39	1092	435	178	43	1.35	4.53	0.362	0.114	30
29	3	200-300	954.02	1076	452	167	34	1.11	5.46	0.31	0.081	36
29	3	300-400	481.81	975	407	166	41	0.82	6.13	0.31	0.062	38
30	1	0-100	1976.1	1379	641	386	95	2.23	4.27	0.379	0.286	26
30	1	100-200	1113.65	1619	589	469	123	1.32	4.56	0.218	0.117	0
30	1	200-300	551.83	1658	526	664	84	0.72	5.74	0.206	0.055	0
30	1	300-400	730.49	2262	498	1013	126	0.58	6.31	0.264	0.059	48
30	1	400-500	712.27	2161	472	1234	154	0.52	6.6	0.272	0.051	42
30	2	0-100	3180.29	2183	488	552	44	2.43	4.87	0.389	0.204	30
30	2	100-200	1190.2	3300	602	896	163	1.46	5.25	0.539	0.098	50
30	2	200-300	862.84	4195	719	1439	292	1.31	5.83	0.608	0.09	54
30	2	300-400	730.49	2262	498	1013	126	0.58	6.31	0.264	0.059	48
30	2	300-400	794.25	3784	608	1767	375	1.03	6.37	0.461	0.085	46
30	2	400-500	842.94	3524	544	2163	449	0.96	6.64	0.419	0.065	32
30	3	0-100	973.23	1602	352	525	24	1.05	5.83	0.192	0.074	28
30	3	100-200	593.17	1929	341	666	39	0.98	6.44	0.255	0.063	32
30	3	200-300	597.91	1872	310	878	90	0.95	6.69	0.32	0.049	38
30	3	300-400	638.13	2187	285	1133	196	0.75	6.87	0.277	0.065	42
30	3	400-500	606.04	1582	243	1008	181	0.63	6.83	0.239	0.078	32

31	1	0-100	8838.38	223	666	23	5	5.76	3.5	0.457	0.809	10
31	1	100-200	11423.75	532	401	36	15	6.31	3.49	0.899	0.958	10
31	1	200-300	11550.31	556	252	48	16	6.56	3.48	0.425	0.799	10
31	1	300-400	3405.86	397	70	55	7	1.55	4.02	0.1	0.148	12
31	1	400-500	2070.91	363	72	56	7	0.73	4.18	0.107	0.068	24
31	2	0-100	10161.35	341	970	33	14	9.56	3.3	0.975	1.035	8
31	2	100-200	14590.54	552	765	44	30	8.4	3.53	0.355	1.005	8
31	2	200-300	10600.86	706	516	48	27	4.54	4	0.125	0.456	10
31	2	300-400	3569.56	416	220	21	9	1.17	4.33	0.105	0.103	14
31	2	400-500	3074.69	537	229	28	16	1.22	4.24	0.064	0.096	14
31	3	0-100	1424.58	156	224	29	5	1.85	4.09	0.091	0.141	12
31	3	100-200	603.43	75	110	9	2	1.03	4	0.149	0.071	14
31	3	200-300	501.92	90	73	12	4	0.63	3.8	0.128	0.044	22
31	3	300-400	594.14	135	49	21	4	0.59	3.69	0.129	0.056	22
31	3	400-500	537.37	124	36	19	0	0.53	3.76	0.134	0.045	24
32	1	0-100	834.0	21125	437	757	190	0.71	7.64	2.213	0.117	31
32	1	100-200	931.4	21549	298	817	209	0.46	7.80	2.787	0.073	29
32	1	200-300	835.7	20195	256	922	314	0.52	7.92	1.914	0.077	31
32	1	300-400	696.4	6048	369	906	590	0.77	8.26	0.216	0.112	41
32	1	400-500	583.6	6034	306	1281	983	0.61	8.40	0.090	0.086	47
32	2	0-100	1503.7	7707	773	752	216	2.18	7.68	0.322	0.262	27
32	2	100-200	874.6	6702	784	742	240	1.08	7.98	0.180	0.142	33
32	2	200-300	875.6	6637	666	739	250	1.11	7.94	0.188	0.148	37
32	2	300-400	705.5	6143	476	808	305	0.67	8.09	0.161	0.098	47
32	2	400-500	675.4	6476	489	925	380	0.57	8.06	0.166	0.106	47
32	3	0-100	1306.0	9858	632	603	147	1.28	7.69	0.512	0.163	25
32	3	100-200	969.7	7122	615	522	152	1.20	7.86	0.168	0.164	29
32	3	200-300	738.4	7236	570	596	188	0.89	7.89	0.182	0.129	23
32	3	300-400	672.2	7934	488	748	252	0.72	7.87	0.166	0.110	41
32	3	400-500	669.9	7219	325	788	261	0.66	7.96	0.168	0.106	45
33	1	200-300	9159.7	3354	798	512	251	4.49	6.31	0.213	0.313	20
33	1	300-400	8161.7	3243	742	588	316	4.54	6.88	0.338	0.346	20
33	1	400-500	999.2	982	405	313	153	1.25	7.12	0.435	0.066	4
33	2	0-100	23197.8	3064	1115	481	324	11.52	4.90	0.211	1.204	6
33	2	100-200	5955.7	2656	610	475	346	2.56	6.78	0.194	0.168	16
33	2	200-300	4186.3	1902	650	614	642	2.44	7.24	0.429	0.158	8
33	3	0-100	21372.5	2410	1244	258	174	8.94	7.67	0.166	1.094	12
33	3	100-200	7858.4	996	501	175	118	3.42	8.52	0.227	0.320	14
33	3	200-300	2383.1	1561	373	235	120	2.18	6.61	0.071	0.118	6
34	1	0-100	2298.9	4566	24	117	48	0.82	7.86	0.055	0.134	4

34	1	100-200	904.0	4640	16	98	56	0.14	8.14	0.035	0.057	2
34	1	200-300	635.0	4625	14	96	48	0.06	8.51	0.038	0.011	2
34	1	300-400	626.4	4583	15	96	49	0.06	8.46	0.036	0.011	2
34	1	400-500	600.6	4598	14	101	56	0.06	8.43	0.036	0.010	4
34	2	0-100	2909.2	7362	23	141	83	1.11	7.67	0.050	0.149	4
34	2	100-200	1041.8	7552	13	110	88	0.21	7.94	0.044	0.030	4
34	2	200-300	1022.5	7749	16	116	81	0.10	8.06	0.032	0.018	2
34	2	300-400	1008.4	7658	13	112	86	0.05	8.26	0.042	0.012	4
34	2	400-500	667.4	7682	13	120	87	0.03	8.37	0.032	0.008	4
34	3	0-100	1865.4	8053	35	130	106	0.52	7.82	0.043	0.097	4
34	3	100-200	696.7	7882	26	117	87	0.06	7.98	0.036	0.012	4
34	3	200-300	628.5	7594	18	123	92	0.05	8.12	0.037	0.008	4
34	3	300-400	823.0	7610	22	123	86	0.19	7.91	0.035	0.021	4
34	3	400-500	66.1	7768	22	126	90	0.03	8.12	0.068	0.015	4
35	1	0-100	409.77	416	104	116	62	0.97	5.27	0.095	0.056	22
35	1	100-200	293.32	309	91	101	53	0.88	5.16	0.18	0.054	26
35	1	200-300	186.96	196	61	73	51	0.73	4.56	0.131	0.035	30
35	1	300-400	237.48	224	57	83	49	0.59	4.6	0.132	0.038	24
35	1	400-500	240.68	305	57	108	46	0.52	5.08	0.139	0.032	26
35	2	0-100	1188.98	1071	352	198	16	2.43	5.73	0.175	0.393	14
35	2	100-200	429.21	321	125	64	70	0.99	4.86	0.113	0.078	18
35	2	200-300	559	405	110	73	48	0.72	5.24	0.13	0.042	20
35	2	300-400	380.36	357	83	68	32	0.63	5.83	0.103	0.039	20
35	2	400-500	512.9	440	65	92	37	0.54	5.43	0.117	0.035	26
35	3	0-100	432.33	439	47	76	18	1.28	4.36	0.17	0.102	22
35	3	100-200	291.77	320	60	88	34	0.81	4.34	0.17	0.165	22
35	3	200-300	232.44	288	76	85	33	0.65	4.23	0.131	0.041	26
35	3	300-400	222.06	297	68	87	45	0.53	4.26	0.133	0.046	28
35	3	400-500	161.07	351	38	103	56	0.44	4.6	0.132	0.038	30
36	1	0-100	3727.79	1527	184	132	77	3.15	5.33	0.353	0.284	14
36	1	100-200	1522.2	811	117	75	39	1.1	5.11	0.139	0.072	16
36	1	200-300	508.91	598	71	70	34	0.5	5.34	0.132	0.039	22
36	1	300-400	337.95	556	72	65	32	0.41	5.56	0.134	0.032	22
36	1	400-500	5276.29	1849	103	98	67	3.55	4.8	0.502	0.344	18
36	2	0-100	3727.79	1527	184	132	77	3.15	5.33	0.353	0.284	14
36	2	100-200	2438.34	1141	87	86	48	2.05	4.64	0.272	0.15	24
36	2	200-300	917.64	773	80	63	34	0.82	4.67	0.155	0.063	22
36	2	300-400	421.66	740	76	65	29	0.61	4.86	0.147	0.039	22
36	2	400-500	208.95	575	73	62	28	0.46	4.87	0.146	0.043	26
36	3	0-100	2785.07	889	109	135	46	2.43	5.14	0.216	0.143	12

36	3	100-200	1917.73	656	102	67	37	2.04	5.46	0.22	0.164	14
36	3	200-300	320.93	329	71	32	19	0.62	5.7	0.134	0.067	18
36	3	300-400	231.03	354	87	33	24	0.54	5.84	0.12	0.055	22
36	3	400-500	170.96	457	112	36	26	0.47	5.67	0.119	0.043	24
37	1	0-100	4683.6	1064	614	316	157	2.71	4.70	0.109	0.300	2
37	1	100-200	4035.1	1104	400	238	83	1.84	5.59	0.091	0.162	8
37	1	200-300	1693.5	724	269	198	66	0.92	6.10	0.077	0.087	10
37	1	300-400	990.5	573	218	176	53	0.50	6.36	0.071	0.050	14
37	1	400-500	932.3	558	213	175	52	0.41	6.44	0.073	0.043	20
37	2	0-100	4611.0	713	559	242	136	1.43	4.73	0.080	0.152	22
37	2	100-200	3042.9	335	302	195	63	0.49	5.02	0.075	0.075	10
37	2	200-300	2649.4	296	302	177	64	0.46	4.44	0.076	0.066	12
37	2	300-400	2161.8	251	275	161	48	0.44	4.42	0.075	0.064	12
37	2	400-500	1679.2	249	298	169	64	0.39	4.36	0.072	0.065	12
37	3	0-100	2688.7	328	307	147	59	1.32	3.74	0.101	0.148	14
37	3	100-200	1638.2	289	244	122	57	0.55	4.30	0.075	0.066	8
37	3	200-300	1343.7	337	284	161	55	0.47	4.94	0.077	0.054	12
37	3	300-400	1261.0	349	313	179	56	0.45	5.31	0.076	0.053	20
37	3	400-500	950.6	320	286	174	65	0.33	5.70	0.074	0.042	20
38	1	0-100	571.02	818	127	279	96	2	6.18	0.293	0.103	22
38	1	100-200	412.61	571	73	314	38	1.06	6.6	0.258	0.048	24
38	1	200-300	460.05	528	73	325	35	0.83	6.67	0.291	0.038	28
38	1	300-400	476.39	486	58	308	2	0.61	6.96	0.268	0.031	30
38	1	400-500	390.47	580	48	314	33	0.48	7.24	0.205	0.025	8
38	2	0-100	10803.28	3183	1126	940	80	4.93	5.28	0.361	0.073	12
38	2	100-200	4051.82	1767	684	800	47	2.76	5.57	0.308	0.538	12
38	2	200-300	471.05	753	316	371	95	1.23	5.88	0.417	0.387	18
38	2	300-400	367.06	588	152	323	40	0.87	5.79	0.177	0.089	22
38	2	400-500	407.41	511	70	322	12	0.61	5.74	0.215	0.058	26
38	3	0-100	3924.61	1394	350	238	24	2.87	4.84	0.251	0.045	14
38	3	100-200	402.13	625	189	156	19	1.02	4.86	0.225	0.053	12
38	3	200-300	366.32	526	170	156	27	0.85	4.56	0.33	0.051	26
38	3	300-400	348.49	490	151	201	49	0.76	4.24	0.305	0.057	32
39	1	0-100	9455.36	3329	1093	1060	16	7.66	4.54	0.59	1.038	8
39	1	100-200	3201.99	1501	495	527	49	3.26	5.26	0.143	0.332	10
39	1	200-300	1574.7	854	332	340	33	1.66	4.6	0.139	0.168	10
39	1	300-400	642.47	488	214	164	19	0.75	4.48	0.122	0.066	14
39	1	400-500	478.48	433	215	99	11	0.56	4.6	0.133	0.048	22
39	2	0-100	8258.36	3475	1105	1231	81	7.28	4.52	0.414	0.897	10
39	2	100-200	1509.59	944	413	491	64	2.47	4.14	0.114	0.234	8

39	2	200-300	691	494	313	283	33	0.95	4.29	0.13	0.095	10
39	2	300-400	751.44	435	324	209	17	0.63	4.67	0.138	0.055	14
39	2	400-500	529.41	424	319	182	19	0.54	4.3	0.153	0.048	16
39	3	0-100	12638.87	4656	1187	1062	79	8.31	4.24	0.486	1.166	8
39	3	100-200	4359.24	2295	772	998	35	3.49	4.78	0.175	0.435	8
39	3	200-300	1098.88	759	464	462	57	1.37	4	0.107	0.177	14
39	3	300-400	424.64	478	339	282	28	0.62	3.94	0.239	0.073	12
39	3	400-500	326.66	511	332	247	31	0.53	3.87	0.104	0.066	12
40	1	0-100	605.4	254	103	62	42	0.15	5.64	0.083	0.014	8
40	1	100-200	297.7	253	80	68	56	0.92	5.76	0.086	0.068	10
40	1	200-300	313.4	207	72	60	44	0.54	5.34	0.071	0.036	12
40	1	300-400	446.8	263	85	70	67	0.61	5.60	0.060	0.050	10
40	1	400-500	329.2	254	81	66	50	0.52	5.89	0.081	0.047	10
40	2	0-100	147.4	157	69	49	71	0.25	4.46	0.069	0.023	10
40	2	100-200	178.8	168	65	49	65	0.40	4.33	0.076	0.026	10
40	2	200-300	167.4	198	88	67	69	0.59	4.36	0.087	0.037	10
40	2	300-400	142.2	206	79	66	60	0.54	4.52	0.081	0.033	10
40	2	400-500	146.7	169	67	59	38	0.44	4.73	0.077	0.025	10
40	3	0-100	7377.0	735	426	130	81	5.46	5.03	0.182	0.729	4
40	3	100-200	3319.8	372	188	86	61	3.23	4.96	0.087	0.341	6
40	3	200-300	205.2	158	44	56	24	0.50	4.67	0.069	0.037	6
40	3	300-400	139.6	148	45	54	36	0.43	4.47	0.064	0.028	8
40	3	400-500	138.8	165	58	57	38	0.37	4.57	0.076	0.025	8

site number	location at site	Depth	Cr	Co	Ni	Cu	Zn	Cd	Pb
1	1	0-100	15.4394	4.2808	30.5126	30.3148	73.4469	0.8536	22.5371
1	1	100-200	9.7272	2.7713	26.1683	28.0292	68.6449	0.0796	14.7310
1	1	200-300	14.3061	8.2607	25.3614	37.1169	117.3492	0.5905	18.9613
1	1	300-400	6.7222	7.3208	21.2180	32.7366	75.5514	0.6777	13.6247
1	2	0-100	9.8492	7.0596	119.8504	13.4910	30.8887	0.9316	5.2106
1	2	100-200	10.9251	18.5402	332.9858	13.9814	15.8575	0.9374	2.6362
1	2	200-300	11.8250	18.6228	336.4599	13.7475	7.2459	1.0884	0.7515
1	2	300-400	9.3645	18.5289	333.0842	12.3614	4.7657	1.2217	1.6220
1	2	400-500	10.7894	21.5069	389.6736	13.9388	6.0683	0.8007	0.9929
1	3	0-100	11.7788	16.4075	292.5805	29.5991	80.2741	1.1992	9.0094
1	3	100-200	11.5560	17.6056	318.0220	33.2140	78.3415	1.5600	11.0232
1	3	200-300	11.8908	17.2445	320.3876	23.5386	57.1683	1.2734	7.8844
1	3	300-400	15.3771	16.6556	287.0937	90.4290	346.7561	0.3088	46.2479
1	3	400-500	12.7343	14.0334	255.3570	38.2496	127.3348	0.2785	22.6078
2	1	0-100	183.6191	12.9585	82.1042	339.6455	711.4276	2.8501	117.4214
2	1	100-200	68.1066	9.7550	74.4097	63.4782	143.9006	0.4709	25.6969
2	1	200-300	12.0737	7.2391	71.4052	10.0808	18.3173	0.2956	5.1320
2	1	300-400	12.3053	8.2424	74.2369	8.9952	13.0611	0.1662	5.7046
2	1	400-500	46.7945	8.7224	81.5429	39.3795	86.4510	0.5084	18.7927
2	2	0-100	141.2984	13.9401	74.2746	175.8052	421.7668	2.1820	78.9562
2	2	100-200	123.7445	13.5403	72.1386	111.6025	244.1193	1.5718	49.0397
2	2	200-300	19.7588	5.8635	53.2118	18.6913	44.0065	0.7143	10.6141
2	2	300-400	9.8493	4.6670	46.7326	7.4581	13.9212	0.5118	5.5147
2	2	400-500	18.3371	5.8239	51.1247	14.8738	30.3876	0.5130	9.9834
2	3	0-100	116.6946	12.6733	60.3458	103.9523	241.8332	1.9342	47.7162
2	3	100-200	122.1474	13.0657	75.1060	132.4188	311.9928	2.1486	61.8463
2	3	200-300	103.6448	10.1270	54.7499	113.2442	275.4544	1.9878	62.5230
2	3	300-400	121.0046	15.9758	73.6716	207.1368	677.3304	1.5293	137.1437
2	3	400-500	13.7895	3.4944	41.8114	11.9676	45.6597	1.1475	10.7631
3	1	0-100	49.7988	10.4264	27.5942	71.7555	251.3738	2.0375	78.2250
3	1	100-200	43.9037	6.8042	30.3207	18.5350	77.5548	1.2652	9.3692
3	1	200-300	42.5535	5.6757	19.0405	15.4898	45.4798	1.3030	8.0877
3	1	300-400	37.4674	3.1731	13.1994	13.3378	31.1637	1.1518	8.0604
3	1	400-500	48.8303	4.8450	19.0742	17.7602	42.1002	1.1772	10.9053
3	2	0-100	42.2752	7.0066	31.6640	19.4802	62.2035	0.8625	11.3885
3	2	100-200	43.9649	7.2663	29.3557	19.7779	54.9867	1.1747	10.3952

3	2	200-300	40.2500	7.4175	38.7804	17.8460	46.5529	0.7857	8.4461
3	2	300-400	42.1703	7.5718	34.9979	17.2012	49.8149	1.0381	8.9370
3	2	400-500	43.7366	5.8698	27.3298	14.7079	36.7991	1.1137	6.7879
3	3	0-100	51.0289	5.8732	21.7588	18.9482	109.5965	1.5903	19.5327
3	3	100-200	42.1983	7.8424	40.4527	17.3434	84.8996	1.1158	8.0234
3	3	200-300	38.7433	6.6274	27.0946	16.4618	42.8493	0.9996	6.5399
3	3	300-400	44.1541	5.1124	20.5099	14.7152	38.4373	1.2768	6.9249
3	3	400-500	50.0392	5.6278	22.4430	17.7557	49.8556	0.7918	9.0874
4	1	0-100	8.8745	0.2905	9.3432	4.5838	9.9997	0.8725	2.8690
4	1	100-200	6.7542	0.1824	3.9531	3.7726	6.0964	0.9833	1.9528
4	1	200-300	4.4152	0.2836	5.9024	3.9644	5.8757	0.8127	1.5659
4	1	300-400	3.3845	0.2568	1.4074	2.0782	1.0652	0.8552	1.5785
4	1	400-500	7.8599	0.1812	5.0786	3.9014	7.4566	0.9495	2.4958
4	2	0-100	7.4814	0.3437	6.2846	4.3978	9.8556	0.7808	2.6348
4	2	100-200	34.6782	0.4240	13.2308	6.1536	5.1683	0.9722	2.1689
4	2	200-300	6.5392	0.1745	3.8589	3.5808	5.8219	0.7242	1.3045
4	2	300-400	6.0070	0.0887	3.7794	3.6474	5.7054	0.5499	1.9840
4	3	0-100	7.5837	0.3181	5.7472	5.8510	12.3260	0.9133	2.8922
4	3	100-200	10.1741	0.2376	5.4447	5.7900	4.7123	1.0336	1.8739
4	3	200-300	7.6100	0.2439	8.7456	3.7877	6.7969	0.9039	2.3767
4	3	300-400	5.5732	0.1417	3.2565	3.8946	4.4268	0.7777	2.0041
4	3	400-500	6.8896	0.1665	8.9776	4.0635	8.3794	1.0258	1.8139
5	1	0-100	26.5406	3.0794	9.6538	5.9491	25.2349	-0.1363	5.8413
5	1	100-200	25.2397	3.9358	9.0597	4.9018	16.8547	-0.2656	4.6335
5	1	200-300	20.5010	1.5113	5.7701	4.3000	5.9903	0.3414	3.2446
5	1	300-400	18.2631	1.0547	5.5524	3.8443	4.3510	0.2354	3.2981
5	1	400-500	22.1934	4.0117	8.5248	2.8473	7.5584	0.3068	4.7330
5	2	0-100	25.8254	3.2968	22.9892	43.4186	38.7386	-0.3490	6.2939
5	2	100-200	24.1850	4.4995	8.5734	4.2577	35.3459	-0.7035	4.5288
5	2	200-300	28.4808	4.4531	10.5467	4.4126	20.5514	-0.2869	5.9018
5	2	300-400	24.8988	4.1275	9.8418	3.1429	9.4240	0.2650	5.7363
5	2	400-500	25.6696	3.9091	8.2444	2.9476	7.1405	0.1593	4.9690
5	3	0-100	24.9186	3.8229	8.6216	3.3704	7.1009	0.1509	4.6416
5	3	100-200	26.0417	4.6717	9.3224	10.1671	8.0451	0.3413	4.9232
5	3	200-300	24.0537	3.6019	10.9771	2.9377	8.3444	-0.1596	5.1837
5	3	300-400	23.2769	3.6457	15.0363	2.4574	7.6419	0.1868	4.7398
5	3	400-500	21.1029	1.1574	6.6569	3.3038	6.9276	0.1188	3.2527

6	1	0-100	15.9060	4.6875	14.5820	12.7270	38.6950	0.5086	27.6030
6	1	100-200	12.8660	3.9062	16.3000	9.6608	29.5130	0.4402	25.1340
6	2	0-100	11.5110	3.0527	17.3560	6.8331	22.0310	0.3525	104.5600
6	2	100-200	20.0540	4.9320	14.3900	10.4730	34.9670	0.6529	54.0810
6	2	200-300	21.8310	4.0075	15.2760	11.9400	37.0460	0.6856	59.1660
6	3	0-100	53.2100	9.0167	3.4437	188.9800	528.5200	1.8369	296.6600
6	3	100-200	49.2890	6.8604	3.7300	106.6100	309.8900	0.9452	233.0800
7	1	0-100	154.1030	42.7687	101.7269	124.7874	430.5612	1.5821	51.9211
7	1	100-200	149.9858	43.4147	99.9360	62.8569	145.5569	1.1971	23.4338
7	1	200-300	145.1018	35.1648	93.4642	125.7391	57.3566	0.9172	7.7075
7	1	300-400	114.9821	24.6791	68.8128	41.3744	46.9863	0.9673	6.7457
7	2	0-100	171.9852	49.0229	108.0230	65.0639	105.7519	1.1679	27.4012
7	2	100-200	135.3938	58.6365	117.2997	54.6309	57.4105	0.9703	17.5123
7	3	0-100	173.3910	49.1016	109.8060	50.1459	95.9567	1.2887	9.0821
7	3	100-200	108.1355	40.9746	74.9654	31.7929	33.9549	0.9794	8.0886
7	3	200-300	102.0070	63.5793	108.0083	38.8212	22.8649	-1.1179	10.6986
8	1	0-100	90.3630	11.6950	8.6259	160.3600	110.6400	0.8003	42.9130
8	1	100-200	69.4000	13.1520	10.4270	139.0200	76.9570	0.5031	24.7950
8	1	200-300	60.9110	12.5320	10.7740	108.5200	50.4890	0.4882	13.9300
8	2	0-100	79.3530	7.7861	1.0603	261.9800	105.1200	0.7554	28.4050
8	2	100-200	48.6160	5.0027	2.4151	293.8100	108.9200	0.6475	16.7310
8	3	0-100	53.3670	4.2725	2.2663	121.5600	52.8580	0.5975	14.5300
8	3	100-200	119.0200	12.3770	22.9660	35.0030	65.2170	0.6369	18.3110
9	1	0-100	183.3700	24.1380	100.0000	70.9010	250.9300	0.5925	69.6340
9	1	100-200	160.9600	22.7770	73.4000	55.3080	93.8790	-0.0006	28.5940
9	1	200-300	175.7900	27.2610	86.3450	63.6770	91.0300	0.4572	36.1630
9	2	0-100	323.8900	12.0830	87.9150	171.4000	1119.0000	3.8334	90.3920
9	2	100-200	337.7100	14.7400	108.9000	203.2100	1254.2000	6.5018	116.7700
9	2	200-300	327.7900	14.9650	131.9400	153.1300	1100.3000	4.0959	93.0360
9	2	300-400	304.9700	14.3970	148.0700	91.3430	697.8200	2.9480	47.6020
9	2	400-500	291.8300	22.5530	166.4200	87.5200	771.8000	2.8465	51.6430
9	3	0-100	293.3000	22.2490	159.7900	164.0400	1102.6000	4.4719	83.1720
9	3	100-200	251.0500	18.7910	110.8200	114.3300	758.4000	1.8275	53.9590
9	3	200-300	260.7800	19.5140	157.1200	156.9600	1386.3000	3.8426	70.9990
10	1	0-100	141.6600	18.6470	62.7750	68.0000	76.7430	0.0942	26.8930
10	1	100-200	132.6200	21.6820	56.0270	62.5260	54.0320	0.2377	22.2870
10	1	200-300	129.0900	17.3500	48.4880	58.3270	46.5680	0.0363	13.9980

10	1	300-400	142.0000	20.0000	57.0760	61.8140	56.6880	0.0683	13.0190
10	1	400-500	140.1000	19.1190	59.7900	63.5790	49.5590	-0.3197	14.5240
10	2	100-200	131.1300	23.4600	50.5310	63.3720	58.8030	-0.0254	18.5940
10	2	200-300	188.2500	24.8910	75.0570	89.7290	77.8380	0.0517	27.8490
10	2	300-400	128.2600	17.4400	50.9760	59.0650	45.3710	0.2624	14.4830
10	2	0-100							
11	1	0-100	66.9330	7.1130	42.7020	22.2770	110.6400	-0.6197	7.5126
11	1	100-200	63.0830	7.8950	50.7950	18.1120	106.0500	-0.0311	10.8610
11	2	0-100	45.3220	4.9501	14.3270	14.3230	37.7060	-0.5455	4.3935
11	2	100-200	45.2690	5.5899	25.9110	15.6640	22.3980	-0.7123	5.4130
11	2	200-300	36.8310	5.3041	20.9040	14.5090	20.2920	-0.5655	5.5166
11	3	0-100	50.8520	6.1819	21.1610	19.7480	42.2910	-0.2597	7.1460
11	3	100-200	41.2780	5.6194	11.0130	18.3070	58.8870	-0.5908	5.9323
11	3	200-300	41.6500	5.0510	11.9560	10.5310	21.5660	-0.6175	3.8832
11	3	300-400	44.8370	5.6199	11.0100	13.9170	30.5110	-0.5218	7.4358
12	1	0-100	307.6700	37.9690	138.2100	23.4980	39.7310	-0.6734	9.5726
12	1	100-200	264.5300	28.0570	100.1300	14.5080	32.6340	-0.6835	4.2649
12	1	200-300	382.9600	39.5410	139.1400	20.7240	57.1800	-0.5868	9.2003
12	2	0-100	383.2000	31.7130	121.6400	18.5710	38.4880	-0.4210	7.0176
12	2	100-200	362.1900	27.4600	116.0800	18.8420	33.8870	-0.5073	6.9078
12	2	200-300	621.1400	39.2010	152.2400	24.2620	39.8230	-0.5942	9.1945
12	2	300-400	510.2500	34.6080	120.0400	18.6360	25.9870	-0.5987	8.9328
13	1	0-100	56.7011	7.3563	24.2743	39.2841	155.8354	0.2149	53.6019
13	1	100-200	26.1688	7.0821	25.3134	31.6748	104.6103	-0.0531	14.2561
13	1	200-300	21.3667	5.7312	9.0624	8.2030	20.4427	0.1448	8.7159
13	1	300-400	16.6718	4.8826	7.3732	5.0915	15.2403	-0.4106	6.4263
13	1	400-500	16.1148	5.0387	7.1137	4.5288	12.6115	-0.1601	7.0154
13	2	0-100	56.3430	7.3521	30.0171	67.7059	254.4536	0.3822	74.1749
13	2	100-200	52.3188	7.0671	19.6672	36.9112	112.3953	0.2130	33.7880
13	2	200-300	59.2805	7.7590	14.9313	9.9567	32.1594	0.1325	7.4788
13	2	300-400	60.8402	6.4387	11.8297	7.9132	24.9598	-0.3159	5.6014
13	2	400-500	60.9622	5.8328	11.9864	7.5546	24.3093	0.4618	7.7977
13	3	0-100	103.9848	5.4873	100.0823	249.5920	1032.6480	-0.0469	95.6814
13	3	100-200	50.6867	0.5933	13.7563	16.2910	89.7459	-1.1694	16.6210
13	3	200-300	66.1959	4.1230	15.1290	8.1362	42.4159	-0.0410	9.5649
13	3	300-400	58.2092	3.8304	11.5961	5.6959	36.3403	-0.0226	8.4614
13	3	400-500	60.9358	3.4873	13.3657	6.0470	41.5501	-0.0397	7.6641

14	1	0-100	176.2048	20.4776	105.6129	383.5691	1309.8010	4.7873	599.6211
14	1	100-200	89.5454	13.2796	45.3173	185.1587	519.4290	2.3442	240.5770
14	1	200-300	56.9653	12.2727	27.0767	64.2259	160.3461	0.7412	76.0057
14	1	300-400	75.3794	16.7512	37.0797	111.9032	276.6880	2.3974	135.6604
14	2	0-100	111.8661	25.5708	56.4212	45.4802	82.5960	0.5806	35.2698
14	2	100-200	108.6749	24.6463	53.1106	39.1429	65.0904	-0.4298	27.6624
14	2	200-300	109.3708	26.2540	50.3258	37.4488	75.6397	0.5269	20.9790
15	1	0-100	40.0130	2.5039	15.7360	17.1590	23.1580	0.4779	14.0240
15	1	100-200	36.9000	2.5374	15.6300	14.6680	13.8330	0.3995	8.9322
15	1	200-300	40.3420	2.0985	14.4860	9.8619	11.3480	0.4590	6.2930
15	1	300-400	36.1110	2.3058	11.5150	9.9453	15.4330	0.4323	7.1573
15	1	400-500	30.5550	2.2407	13.7370	8.6037	12.8190	0.5568	5.3632
15	2	0-100	120.1700	7.3442	27.5020	27.3230	83.0040	0.3445	45.0960
15	2	100-200	56.1680	5.4107	2.9923	21.5310	25.0710	0.3293	11.1620
15	2	200-300	33.9310	2.2894	11.8830	9.3698	16.1320	0.4247	6.4296
15	2	300-400	41.1680	3.8696	7.7026	13.6760	16.2490	0.4121	7.6621
15	2	400-500	36.5210	3.0274	7.7253	13.1530	14.3510	0.4574	7.4670
16	1	0-100	115.2161	9.7728	47.1044	1465.7120	197.3957	4.4307	805.1101
16	1	100-200	66.3734	13.9891	39.9030	1225.6910	192.0218	1.9933	249.0226
16	1	200-300	52.2832	16.5662	76.6733	1441.3210	534.4868	1.2182	144.1478
16	2	0-100	43.9019	7.0775	24.3731	615.7899	136.0127	2.4960	208.3760
16	2	100-200	23.9920	32.7321	126.2526	704.6785	833.7919	1.1296	40.5644
16	2	200-300	19.1442	13.2130	30.9606	186.7833	195.1965	0.3795	29.0070
16	3	0-100	48.2829	15.7823	68.1846	1131.5710	375.4058	1.8700	307.9789
16	3	100-200	22.1655	7.2470	61.6370	216.8335	301.0238	0.0678	22.2043
16	3	200-300	23.4981	13.4589	121.9578	795.9641	634.0702	0.6625	31.2988
17	1	0-100	19.9956	0.4668	9.7070	15.2177	42.9190	0.7248	3.6613
17	1	100-200	5.8641	0.2009	5.9598	4.6629	23.5115	1.1688	1.5123
17	1	200-300	3.5679	0.0146	3.7769	3.2840	5.3310	0.7868	0.8302
17	1	300-400	4.4602	0.0175	3.0080	3.3232	15.3889	0.9590	1.8756
17	1	400-500	5.9118	-0.0064	4.2884	3.4162	3.8662	1.1541	-0.0077
17	2	0-100	4.0657	0.0029	3.2723	3.1972	3.3847	0.8617	1.1707
17	2	100-200	4.1749	-0.0374	5.8837	3.2864	6.5252	1.0083	1.2170
17	2	200-300	3.7014	-0.0799	3.3560	2.7491	3.3447	0.9699	0.2025
17	2	300-400	3.8472	-0.0875	2.9895	2.7090	2.0244	0.9550	0.1360
17	2	400-500	5.7057	-0.0687	3.5117	2.7996	2.7932	1.2797	0.1158
17	3	0-100	5.0893	0.0160	7.7095	3.7179	0.9036	1.0508	0.2631

17	3	100-200	4.8293	0.0882	1.0509	3.1505	-0.8720	1.0283	0.3258
17	3	200-300	4.9012	0.0875	0.7460	1.5239	0.7085	1.2438	0.4501
17	3	300-400	4.6864	0.0025	0.8438	1.3714	0.4069	0.7552	0.4420
18	1	0-100	35.1178	2.7509	16.3084	73.5534	97.2585	0.8613	14.0577
18	1	100-200	28.5418	1.6973	14.9472	257.0854	271.4840	0.6301	38.0484
18	2	0-100	28.0156	4.0363	23.9673	81.8257	207.0022	0.6794	30.6761
18	2	100-200	32.7536	10.1365	41.3539	40.4661	122.8793	0.8919	10.5196
18	3	0-100	31.3834	5.7846	32.1896	69.3225	162.6570	1.3357	21.3013
18	3	100-200	23.9961	4.1176	23.1724	32.3136	74.4244	1.2224	10.4564
19	1	0-100	45.2369	4.7797	27.9591	23.4771	80.7966	1.5645	27.7976
19	1	100-200	53.6382	5.2197	22.3730	21.6425	73.2477	1.2652	16.1575
19	1	200-300	32.2702	2.5371	13.1454	10.3110	22.7163	1.1729	3.4660
19	1	300-400	33.3689	2.6208	13.3738	10.9286	30.5705	1.1757	4.7410
19	1	400-500	34.3077	3.1686	13.5969	10.2251	22.1806	0.7664	5.5386
19	2	0-100	44.0943	6.6966	21.3163	43.5319	181.8528	1.8653	126.8398
19	2	100-200	43.4436	4.4926	19.9423	19.6027	69.2361	1.4377	11.7664
19	2	200-300	34.5930	2.7562	14.2456	12.2140	28.8397	1.0502	4.0723
19	2	300-400	30.7375	2.3055	16.8126	9.2304	20.7503	0.9528	3.5783
19	2	400-500	31.9834	2.7118	11.1485	10.3650	22.1295	0.9974	3.6856
19	3	0-100	34.0962	3.0212	12.6881	12.0384	28.9964	0.9184	4.9524
19	3	100-200	39.5760	3.8427	17.1193	13.3132	37.7938	1.0976	5.0307
19	3	200-300	38.5159	3.8579	15.0039	11.9221	30.9763	0.9452	3.8696
19	3	300-400	44.0450	4.1591	19.7794	14.5142	36.8285	1.0810	4.5246
19	3	400-500	46.8698	4.3445	27.0919	15.1446	35.9934	1.0273	4.9261
20	1	0-100	414.0400	19.7890	89.9930	310.5700	246.5700	2.8468	62.1430
20	1	100-200	130.5200	15.3980	33.4110	85.8670	59.2620	0.9683	16.9260
20	1	200-300	108.7000	14.5430	21.8400	54.4580	37.9660	0.7696	12.5170
20	1	300-400	126.5300	18.9090	27.6860	58.1540	56.0000	0.7452	15.7020
20	1	400-500	129.3300	20.4640	31.3900	61.9250	120.6500	0.5424	23.2260
20	2	0-100	149.3400	20.7970	35.0650	50.9280	64.3670	1.8015	24.7050
20	2	100-200	111.3300	12.8490	20.8690	32.1960	35.8720	0.7867	12.8290
20	2	200-300	123.2500	13.5140	27.5930	37.3250	49.4170	0.5570	15.0590
20	2	300-400	119.9800	16.1500	16.5410	33.5660	43.7420	0.5352	11.8990
20	2	400-500	113.8100	10.7270	17.6130	35.4540	40.2280	0.6773	11.3280
20	3	0-100	186.3100	15.4350	36.1900	84.4200	96.1670	1.2965	38.0250
20	3	100-200	109.6800	13.3580	29.4020	143.0800	776.4800	1.1205	103.0800
20	3	200-300	84.5240	11.3770	10.6560	29.8080	41.3530	0.6776	11.5040

20	3	300-400	83.8150	11.0250	7.9057	25.9780	48.0480	0.6075	11.9740
20	3	400-500	83.0290	8.5693	5.7719	21.3330	27.5180	0.4665	10.0820
21	1	0-100	172.8300	52.1870	45.3460	90.8420	76.2050	0.8633	35.2890
21	1	100-200	104.2900	31.6650	19.9220	54.1330	36.7840	0.5719	19.2940
21	1	200-300	90.4200	25.7630	16.2460	50.0350	45.0480	0.4999	14.2580
21	1	300-400	94.3180	25.7640	18.5960	51.0240	33.6910	0.3822	12.9100
21	1	400-500	119.7200	33.7440	31.5220	65.4870	39.1220	0.5841	17.0700
21	2	0-100	112.2700	29.2170	17.6040	52.6870	57.6580	0.6073	20.0110
21	2	100-200	110.2900	30.8180	24.9770	55.8870	43.5460	0.4833	18.3960
21	2	200-300	120.7600	33.1810	35.4210	69.3060	50.9280	0.6366	18.9840
21	2	300-400	90.7230	23.5070	21.8170	49.6690	37.5780	0.6494	12.5330
21	2	400-500	102.0300	28.6620	24.4250	56.4560	36.3880	0.4436	14.6310
21	3	0-100	106.0500	37.0250	27.3430	68.9620	57.3660	0.5950	20.0840
21	3	100-200	117.5000	46.8330	31.9140	82.7720	58.3820	0.5840	24.1940
21	3	200-300	84.7820	32.1700	19.0970	60.2150	34.4380	0.4392	16.8900
21	3	300-400	100.2500	33.3720	27.2170	69.8600	43.3750	0.4836	15.4700
21	3	400-500	99.4370	30.7890	26.6980	67.7220	37.3650	0.5000	14.8820
22	1	0-100	86.2460	7.9662	6.2694	21.9530	30.6620	0.8189	12.2550
22	1	100-200	91.7460	15.9180	18.6220	17.1840	28.4320	0.4945	10.2510
22	1	200-300	91.2560	20.9600	13.9020	17.4170	19.7590	0.4434	11.0610
22	1	300-400	45.0800	8.2770	18.9880	18.6380	18.4650	0.5419	4.4020
22	2	0-100	61.6090	4.2731	2.6448	19.8040	19.8060	0.6444	9.1801
22	2	100-200	52.6160	3.0268	0.1893	15.7350	24.4140	0.4958	5.7870
22	2	200-300	54.2650	4.5677	5.6544	12.0130	27.5590	0.5014	6.6124
22	2	300-400	66.5310	3.5757	6.4108	13.9510	19.3130	0.5412	5.1690
22	2	400-500	64.9300	4.0326	6.6026	11.0280	14.9260	0.4619	5.7451
22	3	0-100	66.2210	4.0646	2.4092	20.1110	28.1910	0.4427	7.7966
22	3	100-200	60.4910	4.0214	5.4326	17.6170	24.5360	0.4809	7.9355
22	3	200-300	59.0630	7.5164	5.9749	14.7110	19.5480	0.5866	6.0278
22	3	300-400	62.7250	6.0258	2.5544	13.4540	12.6480	0.7582	5.1699
22	3	400-500	62.5340	5.2223	1.8941	14.5300	14.5720	0.5383	6.3643
23	1	0-100	55.4610	3.4683	-9.0572	11.4040	25.6050	0.3860	20.3070
23	1	100-200	63.8150	8.6718	-4.1988	13.5850	48.5860	0.4410	23.6030
23	1	200-300	31.7260	2.8909	-15.0310	4.9828	21.4100	0.4970	9.3869
23	1	300-400	37.9630	3.3768	-13.5580	6.5540	21.9680	0.4459	11.8280
23	1	400-500	58.2880	4.6703	-10.0170	10.3430	27.9070	0.4515	17.7370
23	2	0-100	39.3140	2.2985	-11.4490	9.2873	31.8400	0.5129	17.2190

23	2	100-200	63.7040	18.6410	-5.2203	11.8450	47.8800	0.4526	29.0140
23	2	200-300	70.2760	15.2270	2.5349	13.9800	81.4930	0.4177	27.6540
23	2	300-400	90.1520	16.9460	14.8110	19.1490	95.0240	0.5352	34.7860
23	2	400-500	74.2030	14.3630	-0.2777	14.4670	57.3560	0.4477	28.6920
23	3	400-500	102.3400	6.1873	14.9220	23.8440	100.8100	0.6355	35.9230
23	3	0-100	70.1010	4.6636	2.2098	21.7610	71.7600	0.5008	37.6980
23	3	100-200	90.6560	6.3678	12.0190	24.8070	72.3330	0.3980	39.4950
23	3	200-300	86.0500	5.3559	6.5271	21.7380	57.8870	0.4884	39.6420
23	3	300-400	74.8000	9.8570	9.9127	29.1000	66.5000	0.7844	25.9200
24	1	0-100	333.9900	24.1410	174.0400	311.3300	3746.6000	40.8400	117.1100
24	1	100-200	358.1600	32.1440	199.5600	318.5300	3626.1000	44.6920	116.9800
24	1	200-300	264.8100	37.3550	145.7800	224.1800	1995.8000	30.0670	79.6770
24	1	300-400	112.4500	51.1400	86.4920	97.2210	145.0800	0.9316	12.5970
24	1	400-500	108.9200	44.7460	106.0900	94.3000	76.3020	0.0949	10.5590
24	2	0-100	239.4600	25.5930	161.4000	167.6700	904.8200	14.5120	56.2780
24	2	100-200	201.5400	31.3380	108.6000	137.2600	826.0700	10.6540	46.1370
24	2	200-300	160.0500	47.6260	142.8000	78.2510	460.9800	3.9032	16.2190
24	2	300-400	148.6600	57.3990	143.2000	71.2130	410.1700	1.7704	12.2000
24	2	400-500	143.7000	51.0180	155.8400	70.2150	248.1200	0.1347	14.3430
24	3	0-100	246.3800	26.6670	134.6900	168.4500	1395.3000	17.9530	63.8290
24	3	100-200	196.8500	38.7990	128.8200	118.8400	939.3400	10.5140	40.2780
24	3	200-300	140.3600	58.4870	118.0600	64.9910	185.5400	0.8416	14.9170
24	3	300-400	147.3500	55.7260	111.3200	64.2160	107.9200	0.1775	16.1350
24	3	400-500	149.7800	53.3070	120.5400	70.0070	75.1440	-0.0691	15.6260
25	1	0-100	181.4969	13.9235	74.2051	254.5273	1115.5490	6.3194	367.0012
25	1	100-200	54.5659	1.3626	16.0748	53.1920	224.0691	2.8891	71.0082
25	1	200-300	6.1257	1.7095	4.2246	5.4668	16.4369	0.5485	8.9227
25	2	0-100	18.8846	2.6058	9.3706	30.0005	72.1177	0.4678	28.6717
25	2	100-200	12.5757	2.5608	7.0833	10.2705	40.2787	0.4943	18.8171
25	2	200-300	9.7549	1.7033	3.5961	4.4076	13.7824	0.3344	16.2924
25	2	300-400	31.6552	3.1291	8.6514	15.4598	46.4402	0.2178	47.4431
25	2	400-500	15.1718	2.9537	7.5517	4.5909	30.7659	0.3211	13.8401
25	3	0-100	58.8149	3.0009	10.4778	20.8404	80.9601	0.5055	37.1390
25	3	100-200	17.6916	1.5184	3.6783	0.6669	6.8606	0.6486	8.0337
25	3	200-300	11.0477	1.4804	2.9699	0.9654	5.7850	0.0549	6.9658
25	3	300-400	7.6640	1.4716	3.6825	2.0968	5.9112	0.2631	6.3846
25	3	400-500	7.1011	1.2553	3.3755	0.4046	7.0972	0.3570	4.7749

26	1	0-100	29.6718	3.8872	16.0302	8.1106	46.9103	0.2855	12.8875
26	1	100-200	28.2196	2.8748	12.5376	8.9277	88.0374	0.6142	9.4282
26	1	200-300	27.6874	2.6643	12.2576	5.7008	50.4545	-0.1186	5.8168
26	1	300-400	29.4518	2.8612	13.9759	5.1305	27.6796	0.5243	5.3526
26	1	400-500	30.6066	2.9811	13.9150	5.8337	16.7678	0.1703	5.5460
26	2	0-100	25.0627	3.4820	15.8287	2.4103	12.4103	0.2535	5.1505
26	2	100-200	25.3632	3.6688	17.5741	1.8210	9.7434	-0.4908	4.1479
26	2	200-300	25.0261	3.7697	21.4336	1.7888	11.4899	-0.3280	4.3188
26	2	300-400	23.8148	3.6036	24.1985	2.0342	9.5049	0.5332	5.3979
26	2	400-500	25.6355	3.4449	17.0347	2.3215	25.8855	0.0515	6.0614
26	3	0-100	27.8046	3.7047	13.8579	2.1525	11.8727	0.2652	4.3561
26	3	100-200	28.1346	3.6741	28.2482	2.0569	9.5422	0.5533	3.6343
26	3	200-300	23.7383	3.7500	23.9406	2.0250	8.8603	0.7312	5.2030
26	3	300-400	26.7192	4.1335	23.5044	2.2000	8.3419	0.0412	5.0054
26	3	400-500	26.0643	3.9956	21.8993	2.5200	9.0490	0.1151	3.6293
27	1	0-100	125.3400	27.6910	52.9360	38.1690	36.3720	-0.1409	21.2060
27	1	100-200	93.6640	32.5930	49.9620	34.1790	19.1310	0.1853	18.3410
27	1	200-300	129.3500	55.6280	64.6100	43.8170	27.7620	-0.6187	30.8510
27	1	300-400	168.4100	81.6360	100.4300	55.8620	35.2280	-0.2637	70.9670
27	2	0-100	114.2800	22.6790	52.7810	37.0120	46.7260	0.1521	18.4520
27	2	100-200	144.9900	69.8820	86.7110	47.8920	61.0430	-0.1453	43.3540
27	2	200-300	168.7400	86.5790	94.0870	52.4170	47.0750	0.0584	71.5420
28	1	0-100	198.7900	75.6770	56.1690	87.6050	246.5100	5.4284	87.1390
28	1	100-200	121.5300	21.9660	18.2200	24.2520	94.2180	1.0653	13.1010
28	1	200-300	138.4300	12.3780	22.7080	26.9590	96.1810	0.9345	11.3110
28	1	300-400	149.4700	31.1960	24.3190	27.8000	91.9540	0.9097	14.0610
28	1	400-500	144.2600	32.8820	29.4000	30.8110	95.2760	1.0015	14.6310
28	2	0-100	189.3400	66.8360	64.5080	73.0080	203.7100	3.4105	73.7650
28	2	100-200	205.3400	69.4140	71.6860	69.3450	221.0200	3.3796	72.5350
28	2	200-300	192.2900	44.3850	73.3370	43.7400	160.0000	0.9990	35.6200
28	3	0-100	246.5800	67.0560	92.3690	88.5940	240.3500	4.2161	88.8660
28	3	100-200	194.8600	24.6880	79.0200	35.8930	154.3200	0.9672	19.1100
28	3	200-300	221.3100	14.3790	117.7400	30.5520	329.2500	1.0777	13.3250
28	3	300-400	192.6400	16.4190	130.1100	25.7260	416.7400	0.4779	10.2170
28	3	400-500	182.8000	17.9620	163.0200	29.5690	401.8900	-0.4972	10.5580
29	1	300-400	116.3800	26.2670	41.8320	71.6720	113.9900	-0.0966	13.6130
29	1	0-100	372.0000	25.3710	62.4690	174.4700	698.5300	7.2402	361.2800

29	1	100-200	5.6271	26.1130	47.9630	93.8480	490.2200	6.8502	111.8700
29	1	200-300	135.4200	25.4710	51.7800	76.0130	150.8100	1.4963	49.7750
29	2	0-100	328.7500	27.9320	64.9350	190.1500	727.9400	8.8617	342.8700
29	2	100-200	425.0800	31.1880	82.1230	180.3000	727.3500	9.3125	496.6800
29	2	200-300	205.7600	28.0280	51.5620	117.4700	284.2700	3.7240	134.5600
29	2	300-400	117.3300	22.6150	42.7790	96.4190	149.3500	0.4821	14.9340
29	2	400-500	115.6300	23.6830	37.1920	96.8770	134.7800	-0.1356	12.8570
29	3	0-100	296.3500	32.8630	61.5450	171.9800	561.5700	6.9397	269.8200
29	3	100-200	122.6000	31.9220	49.2950	108.0200	162.2400	0.5777	35.7630
29	3	200-300	114.1100	29.1070	39.2000	95.5490	75.4440	-0.3822	13.4630
29	3	300-400	120.4700	26.8170	46.7480	104.3700	40.8130	-0.5937	10.5250
30	1	0-100	90.1500	7.5375	8.9219	32.6000	83.7830	0.6403	22.0520
30	1	100-200	40.9360	3.7843	7.5299	34.1640	33.8310	0.4326	8.1686
30	1	200-300	130.0400	12.3790	30.0130	27.9860	42.8360	0.4115	11.2410
30	1	300-400	144.3400	13.3470	39.5090	34.3410	70.1160	0.3996	13.1390
30	1	400-500	152.9200	14.1850	42.6500	42.9400	54.8170	0.3822	11.3400
30	2	0-100	122.8200	12.6640	22.0700	61.1640	205.0300	0.9387	63.9590
30	2	100-200	147.2200	17.8360	41.0790	35.0640	72.8810	0.5904	19.9350
30	2	200-300	137.0700	16.1190	39.3070	28.8520	42.1410	0.5832	12.5130
30	2	300-400	179.4800	19.4880	54.7250	35.9500	48.1250	0.6012	14.8580
30	2	400-500	152.3900	17.5680	43.6350	33.2500	45.4100	0.5007	14.4700
30	3	0-100	116.7400	11.3080	22.0310	28.9880	65.8130	0.6347	19.5920
30	3	100-200	97.0330	9.3180	15.4330	21.1400	32.7890	0.5358	9.9409
30	3	200-300	143.6200	12.1690	31.6910	27.9370	41.7330	0.4558	9.2390
30	3	300-400	148.4600	12.7130	35.4840	27.3890	36.3300	0.3531	9.8888
30	3	400-500	148.8900	13.5430	37.7080	28.9600	36.5730	0.4251	9.9002
31	1	0-100	457.1000	20.9110	91.1470	485.7300	517.0400	13.4100	374.1600
31	1	100-200	657.6200	25.7660	191.2700	594.5400	813.1400	17.5680	505.2100
31	1	200-300	495.1200	24.2010	118.0200	527.4200	692.6300	17.0720	398.4800
31	1	300-400	150.0000	12.3900	64.9110	235.7700	1248.8000	3.3591	198.2400
31	1	400-500	104.7100	8.9918	26.6070	78.0810	271.5200	1.5943	54.8410
31	2	0-100	589.3500	22.1000	76.9330	566.1400	481.7600	17.2820	479.6400
31	2	100-200	631.9300	32.8940	131.1100	629.9300	833.0200	20.6450	512.9100
31	2	200-300	333.3900	25.5460	107.5000	327.7500	775.5000	11.4780	295.3000
31	2	300-400	97.6400	12.4980	35.1660	110.6900	280.9200	2.9532	52.1660
31	2	400-500	158.1400	20.1230	88.9100	315.1500	1248.4000	4.6993	191.9000
31	3	0-100	107.2800	6.8218	14.7720	79.2710	105.0500	1.4772	58.8550

31	3	100-200	67.4110	4.0349	-0.4889	36.1630	62.8330	0.6330	22.2810
31	3	200-300	79.1580	4.3058	5.6089	39.7050	94.4750	0.4808	19.4650
31	3	300-400	86.8000	4.7986	8.1075	33.6550	43.7070	0.4814	13.6620
31	3	400-500	76.6990	3.8499	5.4390	29.9780	48.6610	0.6521	12.3690
32	1	0-100	44.2860	18.0556	103.0217	32.8227	115.9529	1.0052	22.2158
32	1	100-200	46.4167	16.0056	94.7758	29.2582	108.1575	1.2062	19.0537
32	1	200-300	46.1619	15.3386	95.1498	28.4527	103.5457	1.6028	17.3289
32	1	300-400	55.7039	15.2427	82.3819	31.4068	87.9585	1.5612	19.8649
32	1	400-500	49.6578	12.4252	46.2366	27.5863	74.0128	1.1797	16.4095
32	2	0-100	59.2902	14.7330	68.3944	37.4374	144.9366	1.2392	24.4660
32	2	100-200	61.8134	14.3995	74.3050	33.4138	94.4731	1.2135	19.7074
32	2	200-300	49.7601	12.1124	47.5435	31.8352	94.6922	0.8255	19.3344
32	2	300-400	47.7869	11.8481	46.3170	27.2114	73.2194	0.9380	15.4723
32	2	400-500	59.0482	17.9022	129.9313	31.6540	87.5787	1.0101	14.7196
32	3	0-100	54.1006	16.3456	72.7452	34.2754	144.5044	1.9785	26.9983
32	3	100-200	60.5479	14.3208	68.8116	31.4520	119.6353	1.5383	23.3353
32	3	200-300	62.8074	17.5852	110.8145	32.7043	95.8023	1.3641	19.3506
32	3	300-400	60.9289	18.4389	121.1887	33.2024	103.4477	1.1777	18.7637
32	3	400-500	55.6793	16.4750	116.2365	28.3225	82.1041	1.2632	15.4724
33	1	200-300	223.1711	113.2217	75.9001	167.3553	830.4201	2.2073	919.4335
33	1	300-400	250.4227	124.6477	78.0436	159.0263	812.9876	3.2854	993.2934
33	1	400-500	109.3550	37.8286	27.5030	48.0624	112.8695	0.8057	110.8292
33	2	0-100	305.5551	47.3074	55.7048	168.0017	947.7687	5.0302	282.0348
33	2	100-200	174.1896	72.3094	43.9805	86.5378	477.3625	1.9316	490.7899
33	2	200-300	173.4020	71.6038	44.0271	97.7985	441.3861	1.7670	508.2287
33	3	0-100	359.0103	41.0030	55.4425	176.0418	727.5508	2.8275	316.4386
33	3	100-200	172.1886	61.3076	39.0884	191.0644	420.5232	2.3413	473.4890
33	3	200-300	143.3616	74.0122	39.6505	69.1058	372.8606	1.2930	583.4938
34	1	0-100	37.0919	7.3455	95.3662	46.8711	234.2540	2.1984	27.9579
34	1	100-200	15.6217	7.3179	73.2223	13.1553	25.2583	0.6347	6.7414
34	1	200-300	13.2736	6.6394	61.0923	10.2515	20.7592	1.0972	4.9235
34	1	300-400	11.3988	5.4299	50.0431	27.9870	11.6870	0.4349	5.1674
34	1	400-500	7.6519	4.4234	61.8197	6.9971	8.7716	0.6207	4.3482
34	2	0-100	44.7030	6.1304	55.0437	121.2944	304.6108	1.2583	53.5854
34	2	100-200	17.1090	7.3905	72.3175	21.2805	53.1484	1.2033	11.2385
34	2	200-300	12.7573	7.5636	78.7661	12.5956	19.2388	0.8820	6.1867
34	2	300-400	9.7451	7.3360	78.8571	8.8717	11.0762	0.5045	4.6504

34	2	400-500	7.9099	6.8979	96.4822	8.5441	5.8346	0.4401	3.8575
34	3	0-100	17.9647	7.2632	71.2402	27.1589	68.9413	0.6331	14.2485
34	3	100-200	10.5388	6.2155	59.2339	4.9697	7.3294	0.2367	5.5733
34	3	200-300	9.6060	6.1973	58.7830	4.4489	7.5184	0.2401	4.3217
34	3	300-400	10.9753	6.2368	59.9659	6.9239	17.0642	0.2478	5.8902
34	3	400-500	8.7271	6.1951	79.0245	5.9167	3.8487	0.8030	2.1019
35	1	0-100	121.1700	7.4025	38.2710	21.2300	71.4000	-0.0676	16.9310
35	1	100-200	102.1000	7.4345	33.7020	16.6800	44.5600	-0.0095	15.1590
35	1	200-300	75.5430	7.0807	35.3420	15.7520	52.3270	-0.2037	8.9664
35	1	300-400	77.7130	8.1285	34.6530	18.5530	35.6610	-0.1251	10.8500
35	1	400-500	83.7090	7.7648	49.4770	19.5260	34.0800	0.0273	10.9230
35	2	0-100	210.3400	6.4039	33.2690	24.8900	112.5000	0.5943	26.5010
35	2	100-200	112.0300	7.6617	35.2700	19.4260	65.4560	0.2650	14.7640
35	2	200-300	68.5750	6.0207	36.0190	16.3050	93.9290	-0.0200	11.2450
35	2	300-400	71.9110	5.3586	32.1490	14.5700	38.5310	0.0388	7.5970
35	2	400-500	74.6950	5.8693	33.9380	17.9500	33.0030	-0.0485	8.3902
35	3	0-100	126.5700	10.0160	57.0420	28.3140	69.7000	-0.0991	18.0030
35	3	100-200	168.2900	5.9103	36.0400	18.9850	59.7520	0.2317	20.2820
35	3	200-300	100.0500	6.3311	33.3980	15.9370	40.5300	-0.2069	12.8380
35	3	300-400	82.5510	6.7220	37.7310	16.5340	35.3720	0.0736	10.7630
35	3	400-500	85.2940	8.0338	33.3580	17.9710	34.2170	-0.3008	10.2230
36	1	0-100	25.2510	1.6164	17.3450	117.4663	22.0190	0.4820	4.4365
36	1	100-200	135.6000	13.7610	4.1498	122.8900	296.5700	2.9661	66.9830
36	1	200-300	125.0900	19.7050	12.1160	80.5510	208.5300	1.0292	17.8690
36	1	300-400	114.9100	28.2490	10.4380	58.1560	136.5800	0.6675	15.4970
36	2	0-100	243.4200	40.0930	24.8250	293.0100	522.2600	5.7823	331.9800
36	2	100-200	214.3700	35.8500	18.4390	211.0100	293.3600	3.5287	180.6200
36	2	200-300	149.3800	24.4220	10.5220	134.5300	138.4400	1.7103	78.3640
36	2	300-400	122.3300	31.0450	11.3580	85.1110	121.9000	1.5354	27.0350
36	2	400-500	112.3200	32.3110	11.5140	50.2790	105.1900	1.1793	18.1830
36	3	0-100	175.5100	62.1920	18.9370	311.2000	680.6700	9.6281	222.5500
36	3	100-200	150.6400	23.9670	16.7340	237.1300	619.4100	7.0277	147.1700
36	3	200-300	75.8900	6.2662	3.9182	47.7750	178.7200	1.5514	13.1960
36	3	300-400	92.7940	4.8288	10.3470	39.7940	180.7600	1.3307	8.9788
36	3	400-500	110.0500	4.9795	11.9990	39.7580	158.4900	1.1526	11.3870
37	1	0-100	66.2109	9.0269	35.4348	43.9808	328.7585	1.5194	35.4198
37	1	100-200	69.9962	12.2265	46.7226	31.5698	209.5037	1.3939	25.2863

37	1	200-300	72.8823	12.9634	45.3646	22.8419	82.0688	0.8241	14.8998
37	1	300-400	82.9437	11.4248	42.0410	19.6336	53.2243	1.0268	16.2847
37	1	400-500	78.0764	11.2709	33.7650	16.6995	36.4452	1.2594	9.5361
37	2	0-100	72.8887	5.0553	29.8943	30.7231	183.8648	1.3808	23.4007
37	2	100-200	75.2233	4.3966	29.4664	17.9397	74.7997	0.9994	9.2937
37	2	200-300	85.4937	4.3459	32.5121	17.5401	58.1763	1.2335	9.9770
37	2	300-400	86.4933	4.0456	39.2478	17.1184	51.4178	1.2177	9.7986
37	2	400-500	87.8201	4.5525	40.4495	19.9142	59.6798	0.9950	10.2927
37	3	0-100	80.2899	5.1211	34.9333	29.1942	106.5969	1.0425	22.7547
37	3	100-200	79.6711	7.1645	28.7320	18.3543	68.2821	1.0035	11.0463
37	3	200-300	74.7769	7.0866	25.8764	17.9070	64.5545	0.9398	9.6965
37	3	300-400	78.8674	11.3310	41.9355	16.7652	74.8972	1.1470	9.4237
37	3	400-500	81.2567	12.3241	38.9142	16.6071	52.6402	0.9790	8.1455
38	1	0-100	72.1940	23.3040	53.9760	46.5070	53.3440	-0.1762	12.3660
38	1	100-200	64.0890	24.0090	42.3910	45.1020	33.8800	-0.2973	8.4498
38	1	200-300	61.3640	24.9130	41.6300	46.4130	31.0700	-0.7673	7.0883
38	1	300-400	63.6040	30.2880	39.5340	45.0010	29.9180	-0.6126	6.8265
38	1	400-500	54.5700	31.2590	34.0080	37.6210	23.9940	-0.5796	5.6263
38	2	0-100	256.2500	11.2320	56.9850	114.1100	640.2100	0.7112	82.4660
38	2	100-200	116.3500	10.7930	43.3520	56.3760	251.4900	0.1395	33.8530
38	2	200-300	54.7730	17.7060	39.2590	37.1580	50.9910	-0.1512	8.1079
38	2	300-400	52.6650	19.0380	41.7180	37.8340	36.8680	-0.3472	6.5623
38	2	400-500	56.9790	21.0290	38.7220	44.3280	32.7520	-0.7778	5.8268
38	3	0-100	121.7200	14.9470	53.1580	70.3060	265.5500	0.0893	37.8730
38	3	100-200	57.7840	28.6240	53.9600	49.1070	45.8690	-0.3153	7.7659
38	3	200-300	63.6190	19.0870	61.3400	53.4430	41.4750	-0.1510	7.8543
38	3	300-400	69.5730	15.2940	57.9200	57.0220	42.8720	-0.3261	9.8125
39	1	0-100	119.9000	9.4244	64.9030	418.5000	619.4300	3.5762	92.0400
39	1	100-200	94.4500	11.4190	38.7760	182.0200	239.0800	0.3914	47.8460
39	1	200-300	76.9570	12.1460	33.2580	110.6300	128.6400	-0.2470	33.0600
39	1	300-400	75.6160	11.0700	33.6670	48.3140	66.9600	-0.5634	13.3780
39	1	400-500	67.6160	15.2870	28.5430	27.1900	49.9580	-0.3938	10.5880
39	2	0-100	121.6100	11.6080	69.8430	425.6200	553.1100	3.0164	87.8800
39	2	100-200	95.7690	13.7650	55.6550	136.1000	161.1800	0.5511	46.0800
39	2	200-300	94.2740	13.0170	46.9540	49.5540	77.3880	-0.3903	14.2960
39	2	300-400	101.8600	22.0820	54.1430	32.2990	90.1140	-0.3774	8.9483
39	2	400-500	99.2370	27.1910	53.1720	29.7350	71.2120	-0.6594	10.5820

39	3	0-100	153.6400	9.8368	83.8040	573.4600	874.9400	2.4844	127.6000
39	3	100-200	109.6900	11.4930	55.8090	247.9400	318.5700	0.6651	59.6190
39	3	200-300	95.0250	9.4243	41.4540	104.5200	109.2900	-0.1631	24.4770
39	3	300-400	80.2800	6.9410	31.8360	41.9570	54.6090	-0.4835	10.4200
39	3	400-500	92.3820	7.9657	33.4200	40.5760	29.2680	-0.6253	11.7190
40	1	0-100	27.2906	4.2350	10.2803	10.6792	23.1403	0.6251	8.9235
40	1	100-200	28.1109	4.9698	14.8777	8.9937	18.5656	0.0020	7.8026
40	1	200-300	26.6500	5.4653	8.7777	10.3689	14.7030	0.1812	8.7570
40	1	300-400	27.1603	5.8551	9.3752	10.8930	18.6655	0.9072	8.6085
40	1	400-500	28.1456	4.8640	9.6501	10.9136	20.3444	0.0277	7.2044
40	2	0-100	20.7597	3.8129	20.9814	4.2460	6.5593	0.0132	7.6737
40	2	100-200	27.6992	5.6853	8.3936	6.6285	9.6136	0.0464	8.2174
40	2	200-300	24.4750	5.8485	8.4600	8.5657	12.8610	-0.0097	8.0941
40	2	300-400	25.3069	4.6218	11.9588	7.9493	10.5774	-0.4196	7.4799
40	2	400-500	22.7277	2.7846	14.6586	5.4128	6.5892	0.1842	4.7757
40	3	0-100	50.9558	4.1195	31.4329	69.8494	142.5209	-0.3059	12.9505
40	3	100-200	27.6269	3.0344	16.0485	30.1955	33.6088	1.3170	7.6484
40	3	200-300	17.5004	2.1738	9.9639	4.5188	7.9340	-0.0887	5.4553
40	3	300-400	17.8985	2.3346	5.4835	3.9744	8.0487	-0.2387	5.7751
40	3	400-500	16.1764	1.9546	4.4879	2.6473	9.0794	0.4116	4.8432

site number	location at site	Depth	Cr	Co	Ni	Cu	Zn	Cd	Pb
1	1	0-100	0.0565	0.5906	1.4958	6.0033	18.4038	0.0651	2.8749
1	1	100-200	0.0562	0.1237	1.4274	8.2558	23.0747	0.0760	3.6287
1	1	200-300	0.0427	0.1350	1.8184	9.3504	26.5506	0.0988	5.5475
1	1	300-400	0.0534	0.1489	1.6458	8.6201	22.9532	0.0985	3.7806
1	2	0-100	0.0402	0.1137	1.3310	2.5385	11.6134	0.0346	1.8032
1	2	100-200	0.0452	0.1337	2.0997	0.8255	4.2193	0.0300	1.0443
1	2	200-300	0.0344	0.1305	2.9194	0.3371	1.0215	0.0208	0.5465
1	2	300-400	0.0335	0.1194	2.2227	0.2103	0.6203	0.0120	0.4461
1	2	400-500	0.0338	0.1056	1.5317	0.1410	0.3308	0.0122	0.2513
1	3	0-100	0.0494	0.1396	3.7902	4.4188	13.5254	0.0460	1.7746
1	3	100-200	0.0349	0.1423	3.2504	5.8496	17.0557	0.0736	2.4604
1	3	200-300	0.0477	0.1132	1.8480	3.7008	11.6288	0.0415	1.4909
1	3	300-400	0.0372	0.1811	3.7110	10.6983	37.1135	0.2036	6.7777
1	3	400-500	0.0362	0.1226	1.3516	5.5213	20.8844	0.1077	3.8355
2	1	0-100	0.4269	1.5058	5.8715	28.3275	56.2626	0.7068	16.3093
2	1	100-200	0.1060	0.7497	2.6322	10.8565	23.0663	0.2197	4.3046
2	1	200-300	0.0627	0.2524	1.7905	3.2514	5.0864	0.0319	0.8084
2	1	300-400	0.0583	0.1913	1.8408	1.8078	2.5930	0.0390	0.5397
2	1	400-500	0.0955	0.6177	2.2677	6.8649	13.6976	0.0986	2.1617
2	2	0-100	0.2134	1.7822	4.9579	20.6692	45.0797	0.7482	12.4112
2	2	100-200	0.1815	1.4853	3.2420	13.7874	28.5162	0.3392	5.9857
2	2	200-300	0.0470	0.3658	2.0569	4.8899	10.2394	0.0563	1.6824
2	2	300-400	0.0412	0.2151	1.7427	1.9695	4.1249	0.0475	0.7903
2	2	400-500	0.0480	0.3478	2.3861	3.8301	10.4550	0.1946	2.4720
2	3	0-100	0.1100	1.2517	2.7926	13.3670	26.6065	0.2742	7.8925
2	3	100-200	0.0898	1.0268	2.0613	5.2093	37.6410	0.2163	8.0740
2	3	200-300	0.0860	1.1905	3.5707	14.8648	32.6726	0.3884	10.5163
2	3	300-400	0.1223	1.8658	3.4286	17.1956	45.3049	0.6203	15.4317
2	3	400-500	0.1612	0.2786	1.6732	3.2681	16.2858	0.1819	2.6842
3	1	0-100	0.1335	2.2941	4.5900	11.6865	43.8738	0.6359	12.4568
3	1	100-200	0.0296	0.9478	2.7716	2.4641	21.3274	0.1353	2.4700
3	1	200-300	0.0449	1.9131	2.4364	2.5635	5.2179	0.0334	3.3717
3	1	300-400	0.0439	1.6825	1.5656	2.2425	1.0069	0.0132	2.7632
3	1	400-500	0.0410	1.6973	1.7360	2.0737	1.0217	0.0130	2.8974
3	2	0-100	0.0316	0.3638	1.5442	2.3484	4.5783	0.0373	2.8160
3	2	100-200	0.0308	0.3572	1.7195	3.0862	3.9420	0.0244	3.0394

3	2	200-300	0.0295	0.2127	1.4239	1.6943	1.8761	0.0203	2.1166
3	2	300-400	0.0263	0.1757	1.1118	1.5107	1.9461	0.0144	1.8053
3	2	400-500	0.0321	1.1104	1.4248	1.3928	0.4916	0.0117	1.5882
3	3	0-100	0.0611	1.5399	2.3110	3.0653	21.6073	0.1394	3.8884
3	3	100-200	0.0293	0.4534	2.0335	1.4809	18.5402	0.1268	1.2836
3	3	200-300	0.0308	0.7329	1.8933	1.5704	3.5599	0.0251	1.8800
3	3	300-400	0.0437	1.6531	1.9629	1.9893	0.6809	0.0162	2.3787
3	3	400-500	0.0389	1.5026	1.5064	1.9079	0.4491	0.0127	2.2664
4	1	0-100	0.0610	0.0336	0.2655	0.6501	4.5977	0.0139	0.5967
4	1	100-200	0.0431	0.0280	0.9374	0.1945	1.6447	0.0049	0.1981
4	1	200-300	0.0472	0.0339	2.8688	0.1736	1.0914	0.0063	0.1375
4	1	300-400	0.0393	0.0216	0.2264	0.1243	0.7731	0.0038	0.1243
4	1	400-500	0.0421	0.0434	1.0355	0.1586	1.1794	0.0038	0.1414
4	2	0-100	0.0478	0.0448	0.5099	0.4903	3.8203	0.0142	0.9170
4	2	100-200	0.0491	0.0425	0.9742	0.1758	0.6512	0.0051	0.2783
4	2	200-300	0.0431	0.0323	0.2939	0.1267	0.4158	0.0040	0.2110
4	2	300-400	0.0539	0.0376	0.5023	0.1331	0.3230	0.0016	0.1247
4	3	0-100	0.0470	0.0518	0.8807	0.3029	1.4129	0.0073	0.4526
4	3	100-200	0.0553	0.0687	1.5319	0.3072	0.7283	0.0042	0.3485
4	3	200-300	0.0565	0.0532	0.4453	0.2668	0.6234	0.0052	0.2581
4	3	300-400	0.0580	0.0426	0.2107	0.2206	0.5090	0.0046	0.1825
4	3	400-500	0.0694	0.0438	0.5442	0.1965	0.3355	0.0017	0.1292
5	1	0-100	0.0751	0.2968	0.5783	1.5018	11.1821	0.0207	0.7616
5	1	100-200	0.0662	0.9836	0.5585	1.0463	5.5925	0.0167	0.8648
5	1	200-300	0.0541	1.3551	0.6725	0.5754	0.9482	0.0193	0.6980
5	1	300-400	0.0426	1.2720	0.8694	0.4393	0.3406	0.0178	0.8040
5	1	400-500	0.0580	1.4935	1.2170	0.3883	0.3640	0.0237	1.0272
5	2	0-100	0.0687	0.6927	0.5153	1.4460	16.3168	0.0266	1.0084
5	2	100-200	0.0588	1.4175	0.7259	0.8464	13.1745	0.0253	1.1073
5	2	200-300	0.0517	1.4670	0.8173	0.5437	6.7944	0.0233	0.9626
5	2	300-400	0.0359	1.2081	0.8017	0.2823	1.1791	0.0140	0.6383
5	2	400-500	0.0332	1.1664	0.7645	0.2740	0.3117	0.0143	0.6734
5	3	0-100	0.0514	0.8434	0.8743	0.5127	0.4935	0.0187	0.6083
5	3	100-200	0.0454	1.2268	1.2182	0.4378	0.4094	0.0168	0.8199
5	3	200-300	0.0354	1.3158	1.1957	0.2578	0.2625	0.0121	1.0109
5	3	300-400	0.0387	0.8507	0.7121	0.1543	0.1247	0.0081	0.4921
5	3	400-500	0.0389	0.8983	0.7544	0.1448	0.1100	0.0065	0.5719

6	1	0-100	-0.0427	1.2484	0.5810	3.6711	14.1360	0.0797	13.6710
6	1	100-200	-0.0228	0.5034	0.3312	2.7011	10.8770	0.0301	10.8450
6	2	0-100	0.0012	1.0267	0.4764	2.7001	3.8735	0.0304	13.5140
6	2	100-200	-0.0057	0.8965	0.5103	1.7516	5.3595	0.0151	18.7500
6	2	200-300	0.0454	0.3028	0.4655	2.9586	9.8868	0.0175	28.0180
6	3	0-100	0.0972	0.3557	0.5159	27.7620	120.8600	0.2188	33.1430
6	3	100-200	0.0872	0.1809	0.6987	41.6270	148.0100	0.3134	28.4400
7	1	0-100	0.1650	4.7326	9.0212	14.7685	63.4642	0.2775	11.3019
7	1	100-200	0.0881	4.4185	8.0777	7.1562	22.4744	0.0891	5.2691
7	1	200-300	0.0424	4.0553	7.4033	14.6909	6.9522	0.0212	1.9581
7	1	300-400	0.0439	4.4403	7.2073	6.1330	3.3692	0.0180	1.8054
7	2	0-100	0.1120	4.9544	7.4620	9.4381	24.1481	0.0768	11.1652
7	2	100-200	0.0509	4.6795	6.4121	5.5819	12.4301	0.0336	5.8309
7	3	0-100	0.0566	6.4377	8.6215	5.1145	15.0983	0.0508	2.7603
7	3	100-200	0.0405	4.9041	8.0762	3.0340	1.6953	0.0204	1.6529
7	3	200-300	0.0382	5.6850	9.2179	3.0409	0.8407	0.0179	1.3908
8	1	0-100	0.7050	2.1438	6.7928	63.0850	67.7930	0.2456	15.8770
8	1	100-200	0.3182	2.5950	5.4068	49.8740	28.9220	0.0874	8.0905
8	1	200-300	0.1389	3.3920	7.2462	36.1550	16.8500	0.0742	4.6969
8	2	0-100	0.4667	0.5466	3.9826	134.8800	66.4770	0.1606	7.8110
8	2	100-200	0.1408	0.3734	1.6690	150.7600	22.5540	0.1212	1.6239
8	3	0-100	0.2798	0.8056	2.6903	63.8760	28.2020	0.1234	4.3690
8	3	100-200	0.0142	0.0979	0.6944	23.0760	73.4340	1.1665	45.3040
9	1	0-100	0.0719	0.1888	0.9025	26.5910	76.0620	1.1990	37.7360
9	1	100-200	0.0608	0.7854	2.9601	6.1648	16.9090	0.1075	7.4252
9	1	200-300	0.0051	0.9789	3.4873	6.0340	15.6320	0.1473	8.5003
9	2	0-100	0.3713	1.1740	13.2110	86.8900	512.9000	0.6978	6.8705
9	2	100-200	0.5127	2.6258	33.4760	66.2060	510.4300	1.0758	9.1641
9	2	200-300	0.8499	2.8729	45.5120	62.5770	466.1300	0.9821	6.8836
9	2	300-400	0.1985	2.8805	43.5850	28.9770	336.4500	0.5973	4.4521
9	2	400-500	0.6927	7.3386	55.8750	28.7310	353.6300	0.6803	3.9998
9	3	0-100	0.1371	3.2758	40.9360	69.5560	517.8300	1.1239	13.9090
9	3	100-200	0.8381	2.2724	39.5540	73.5980	672.3300	1.4522	13.3580
9	3	200-300	0.2826	1.7634	30.7820	51.4060	394.3300	0.8755	11.6860
10	1	0-100	0.0465	15.0300	3.0649	14.4027	16.3466	0.7436	1.7170
10	1	100-200	0.0218	11.7830	1.8305	12.4670	15.6580	0.1459	5.6475
10	1	200-300	0.0345	11.0120	2.3850	12.5550	12.6500	0.1526	2.9186

10	1	300-400	0.0335	10.6380	3.6412	10.9430	12.4350	0.1211	2.6004
10	1	400-500	0.0766	9.5959	2.0713	11.1880	10.8250	0.1217	1.9299
10	2	0-100	0.0423	9.7228	1.2992	12.4600	10.9600	0.1236	5.7199
10	2	100-200	0.0290	9.0243	1.2874	11.9590	7.9858	0.0917	3.2603
10	2	200-300	0.0038	1.3486	4.6614	8.9141	6.9420	0.2607	2.6610
10	2	300-400	0.0039	0.1147	0.1164	0.2369	1.3982	0.0040	0.3623
11	1	0-100	0.1448	1.4421	1.1472	4.1830	10.2840	0.0226	2.1015
11	1	100-200	0.0239	0.0600	0.1153	0.1717	0.4568	0.0036	0.0501
11	2	0-100	0.2198	1.3487	1.0391	3.8248	8.4440	0.1007	2.2128
11	2	100-200	0.1813	1.2305	1.5525	3.9482	2.9113	0.0621	2.0797
11	2	200-300	0.1206	1.2720	1.5464	3.1743	1.6524	0.0138	1.5446
11	3	0-100	0.0994	0.4834	0.8171	5.4625	36.0640	0.0322	3.1914
11	3	100-200	0.2396	1.5484	1.0919	4.4973	13.8050	0.0326	2.2528
11	3	200-300	0.1559	1.2949	0.9103	2.5220	3.8679	0.0009	1.6440
11	3	300-400	0.1383	1.4122	0.8732	3.1399	5.8237	0.0029	1.6804
12	1	0-100	0.0396	1.4811	7.5798	3.8085	6.9426	0.0217	2.1707
12	1	100-200	0.1526	0.9285	3.8367	2.5191	3.2022	0.0234	1.2474
12	1	200-300	0.0286	1.2611	5.1626	3.3143	5.3391	0.0476	1.5243
12	2	0-100	0.0135	0.8438	3.9021	8.7266	3.3097	-0.0068	1.5982
12	2	100-200	0.1876	1.2990	4.4643	5.6320	2.3816	0.0217	2.0672
12	2	200-300	0.2391	1.9047	11.7190	2.6659	71.2540	0.0936	2.2506
12	2	300-400	0.1858	1.7768	9.6361	3.0093	34.2520	0.0651	1.4423
13	1	0-100	0.4713	1.8264	5.3521	8.4888	31.5030	0.1061	13.7289
13	1	100-200	0.2357	1.9029	7.7239	9.4785	30.3599	0.0755	6.2340
13	1	200-300	0.1087	0.6959	1.9161	2.1967	4.3906	0.0145	1.3928
13	1	300-400	0.1053	0.7309	1.3962	1.4934	2.4321	0.0160	1.2955
13	1	400-500	0.0884	0.6142	0.9530	1.0961	1.4923	0.0102	1.0708
13	2	0-100	0.2746	1.4653	6.4279	13.3476	52.5742	0.2619	23.4453
13	2	100-200	0.2590	1.8023	4.0129	9.0503	31.2128	0.1116	13.8113
13	2	200-300	0.0725	2.2765	2.2262	3.7312	10.0982	0.0264	2.0903
13	2	300-400	0.0483	1.6133	1.0465	1.9979	4.1196	0.0140	1.2319
13	2	400-500	0.0717	1.6213	1.1462	1.7579	3.1193	0.0155	1.2240
13	3	0-100	0.9527	1.5856	18.8153	29.2860	80.7966	0.5125	43.5510
13	3	100-200	0.2359	0.8641	4.5767	7.1196	30.8603	0.0485	9.8389
13	3	200-300	0.0933	0.5534	1.0975	2.3585	10.6044	0.0118	2.8533
13	3	300-400	0.0789	0.6148	0.7869	1.5664	10.5553	0.0116	1.6854
13	3	400-500	0.1124	0.4146	0.7726	1.0941	10.9687	0.0099	1.1724

14	1	0-100	0.2480	1.7613	7.1887	24.8502	81.6037	1.0179	38.2371
14	1	100-200	0.0634	1.1306	4.1453	17.6387	44.1260	0.3164	25.8144
14	1	200-300	0.0704	1.2368	3.0786	11.2472	27.7316	0.1675	17.5112
14	1	300-400	0.0929	3.0484	14.0241	28.8752	88.0328	0.3849	36.1598
14	2	0-100	0.0709	2.9762	2.9486	3.8649	8.0060	0.0396	4.0875
14	2	100-200	0.0706	3.2429	2.2858	2.3085	2.3333	0.0111	2.1567
14	2	200-300	0.0855	3.9536	3.7349	3.1511	4.5827	0.0226	3.7340
15	1	0-100	-0.0135	0.1603	0.1552	1.1901	5.1278	0.0231	2.5311
15	1	100-200	0.0116	0.1416	0.0688	0.3562	0.9839	0.0016	1.0249
15	1	200-300	0.0267	0.1983	0.0913	0.5271	1.2865	0.0006	1.4558
15	1	300-400	0.0264	0.1824	0.1793	0.9977	1.3774	0.0087	1.5200
15	1	400-500	-0.0019	0.2375	0.1491	0.7274	0.8114	0.0013	1.5584
15	2	0-100	0.1354	0.0930	0.3631	1.4370	3.6057	-0.0015	1.5169
15	2	100-200	0.0918	0.0732	0.2654	1.9469	1.8630	-0.0058	1.6584
15	2	200-300	0.0492	0.2013	0.4834	1.1506	2.8317	1.2813	3.3991
15	2	300-400	-0.0148	0.1988	0.0357	0.5701	1.5390	0.0211	1.3128
15	2	400-500	-0.0027	0.1239	0.0297	0.2688	0.3730	0.0045	1.0956
16	1	0-100	0.2640	0.7457	4.1445	12.5196	35.8027	0.3393	94.8206
16	1	100-200	0.3043	1.3989	5.9408	33.8969	42.3655	0.6485	57.3501
16	1	200-300	0.1224	3.6562	19.0710	22.2852	139.4274	0.3381	53.9985
16	2	0-100	0.2753	0.9598	4.8035	91.5547	31.2224	0.6683	53.1601
16	2	100-200	0.2010	6.9357	35.4006	69.1603	189.6550	0.4204	18.9753
16	2	200-300	0.1217	3.1494	7.5298	25.7030	38.5181	0.1388	11.5555
16	3	0-100	0.2051	4.2604	21.1361	6.5386	92.2809	0.4126	63.4791
16	3	100-200	0.0900	2.3913	11.5343	24.8321	48.5809	0.1534	9.3812
16	3	200-300	0.1137	5.2689	31.4622	45.6640	154.8781	0.6156	16.5131
17	1	0-100	0.7578	0.0881	2.2127	3.8563	19.5316	0.0488	1.9514
17	1	100-200	0.0776	0.0226	0.2644	0.6710	3.6179	0.0029	0.3480
17	1	200-300	0.0793	0.0161	0.2724	0.4458	3.0252	0.0006	0.2645
17	1	300-400	0.0579	0.0135	0.2337	0.3729	2.7139	-0.0013	0.2134
17	1	400-500	0.1024	0.0149	0.2667	0.4778	3.3869	0.0019	0.2412
17	2	0-100	0.0609	0.0172	0.6248	0.7389	8.4398	0.0145	0.3694
17	2	100-200	0.0499	0.0133	0.4074	0.5288	6.5633	0.0090	0.2420
17	2	200-300	0.0351	0.0090	0.2284	0.2948	3.9690	0.0012	0.1274
17	2	300-400	0.0468	0.0205	0.1804	3.1115	2.8286	0.0004	0.1414
17	2	400-500	0.0454	0.0106	0.1232	0.2411	1.7179	-0.0017	0.1132
17	3	0-100	0.0338	0.0115	1.0330	0.3903	0.5159	0.0010	0.1267

17	3	100-200	0.0311	0.0118	0.6472	0.2695	0.3230	0.0000	0.1016
17	3	200-300	0.0372	0.0113	0.5954	0.2490	0.3720	-0.0002	0.0947
17	3	300-400	0.0466	0.0111	0.4141	0.2258	0.2786	-0.0013	0.0938
18	1	0-100	0.1145	0.8047	1.9510	16.8318	28.7704	0.0500	5.3687
18	1	100-200	0.0392	1.2353	0.8399	1.8627	1.0504	0.0008	1.1891
18	2	0-100	0.0581	0.2508	1.4247	24.4910	35.5526	0.0735	7.2453
18	2	100-200	0.0413	0.1988	1.1852	5.2350	11.8763	0.0357	1.6712
18	3	0-100	0.0845	0.3822	1.4100	9.0806	27.4776	0.0996	6.2700
18	3	100-200	0.0628	0.6609	1.2605	6.3119	17.4644	0.0432	3.0572
19	1	0-100	0.1036	1.8632	4.9636	6.0463	23.1998	0.2478	14.0721
19	1	100-200	0.0647	1.4805	2.5456	3.4870	12.5507	0.0689	5.5684
19	1	200-300	0.0418	1.1659	1.7095	1.5462	1.6899	0.0183	1.2936
19	1	300-400	0.0436	1.2703	2.0009	1.7887	1.5373	0.0077	1.3862
19	1	400-500	0.0437	1.4554	1.3340	0.9267	0.4781	0.0007	1.2765
19	2	0-100	0.1784	2.3788	4.2035	10.2479	38.2000	0.5055	31.4227
19	2	100-200	0.0620	1.6000	3.2127	4.6345	15.1519	0.0990	7.2739
19	2	200-300	0.0423	1.2150	2.1106	2.1701	3.8030	0.0229	2.2830
19	2	300-400	0.0352	0.9044	0.9995	0.9394	0.9449	0.0048	1.3566
19	2	400-500	0.0397	1.0689	0.9360	0.7032	0.3279	-0.0009	1.0336
19	3	0-100	0.0606	1.1590	1.3431	2.5087	4.1102	0.0294	2.5720
19	3	100-200	0.0385	1.3132	1.4975	1.5584	1.0247	0.0105	1.7231
19	3	200-300	0.0391	1.5653	1.3589	1.4726	0.6097	0.0050	1.6166
19	3	300-400	0.0401	1.2162	0.9584	1.2387	0.5509	-0.0003	1.0470
19	3	400-500	0.1144	0.8283	2.0477	15.8113	27.0840	0.0557	5.5229
20	1	0-100	0.8993	3.1131	39.9880	197.8300	185.1300	1.3055	30.4300
20	1	100-200	0.4800	7.8854	23.1090	51.3950	26.9120	0.4572	6.0738
20	1	200-300	0.3689	10.2350	12.3270	26.2190	8.2712	0.2228	4.6382
20	1	300-400	0.0423	11.3840	8.4722	20.4940	7.5943	0.1682	9.4344
20	1	400-500	0.0064	14.5540	6.9485	13.0830	3.6562	0.1282	8.9557
20	2	0-100	0.3720	11.9080	25.9650	24.1800	36.5060	1.2117	15.9640
20	2	100-200	0.0463	7.5239	9.2582	8.9065	10.5020	0.3207	6.2574
20	2	200-300	0.0087	9.1264	6.3480	5.9337	5.0296	0.1595	5.0993
20	2	300-400	0.0183	11.2980	5.9409	4.9924	4.2180	0.0651	5.4434
20	2	400-500	-0.0078	6.3480	4.6737	3.9540	3.5229	0.0742	4.8089
20	3	0-100	1.0740	7.5827	22.7160	38.8410	40.7520	0.5312	23.5120
20	3	100-200	0.4395	8.4665	8.7680	19.3610	12.5140	0.3570	11.4210
20	3	200-300	0.0617	6.7476	4.9878	8.9344	5.8949	0.1990	4.5130

20	3	300-400	0.0751	6.6695	3.6528	6.1250	3.7405	0.1235	3.7805
20	3	400-500	0.0835	6.0364	2.8988	5.5874	2.9709	0.1199	5.0262
21	1	0-100	0.0443	14.1080	2.5560	8.8119	7.7921	0.0473	7.5482
21	1	100-200	0.0230	14.5220	2.7330	8.5529	3.5747	0.0678	6.4719
21	1	200-300	-0.0106	12.9930	1.7722	6.9413	0.2348	0.0142	3.7075
21	1	300-400	-0.0112	17.1830	1.8230	8.9898	1.0761	0.0110	4.9103
21	1	400-500	-0.0487	13.4400	1.3173	6.0916	0.2461	0.0103	3.1697
21	2	0-100	0.0084	14.9720	3.2160	9.0259	20.8490	0.0703	7.6596
21	2	100-200	-0.0308	12.4540	2.7611	7.6056	4.7663	0.0527	5.1840
21	2	200-300	-0.0359	14.9000	2.0170	7.6837	0.7805	0.0137	4.6166
21	2	300-400	-0.0268	17.1470	2.0339	8.4483	0.1939	0.0090	5.0147
21	2	400-500	-0.0182	12.1460	1.3965	5.5858	0.4592	0.0081	3.0045
21	3	0-100	0.0756	20.8620	4.5848	11.8480	7.4038	0.0533	5.0323
21	3	100-200	0.0531	22.4000	4.3138	12.3150	3.5727	0.0422	5.1066
21	3	200-300	-0.0563	11.8350	2.0524	8.0460	1.0486	0.0553	4.0716
21	3	300-400	-0.0528	12.6920	1.7890	7.6201	0.4172	0.0055	3.1640
21	3	400-500	-0.0509	12.1930	1.3441	6.0721	0.3478	0.0163	2.3108
22	1	0-100	0.2742	1.5216	3.9203	5.8427	10.7120	0.0559	2.5411
22	1	100-200	0.1166	7.4752	15.7810	3.2609	12.5730	0.0485	1.8919
22	1	200-300	0.0822	6.4038	11.8520	2.8052	3.1780	0.0423	2.5586
22	1	300-400	0.0759	11.1130	6.1439	2.2318	2.5038	0.0209	3.8007
22	2	0-100	0.1590	0.2458	2.9863	5.0900	4.5991	0.0204	2.0447
22	2	100-200	0.1149	0.4870	2.7803	2.1955	2.0865	0.0013	1.4408
22	2	200-300	0.0832	1.8833	6.3084	1.9660	3.7905	0.0173	1.8293
22	2	300-400	0.0801	0.4305	3.8656	1.4248	1.6395	0.0015	1.7175
22	2	400-500	0.0266	0.3077	1.7639	1.3834	0.9121	0.0037	1.7500
22	3	0-100	0.1312	0.7835	3.5377	4.3088	11.4980	0.0036	2.2325
22	3	100-200	0.1416	1.1912	6.5827	4.4321	9.5530	0.0044	1.9122
22	3	200-300	0.0788	4.0234	6.4633	2.6754	6.4714	0.0020	1.9969
22	3	300-400	-0.0127	2.8551	2.7075	1.6829	1.5728	0.0016	1.8769
22	3	400-500	-0.0165	1.5412	1.6058	1.1147	0.9807	0.0080	1.6779
23	1	0-100	0.1354	1.1162	1.0186	1.3107	1.1726	0.0143	4.3570
23	1	100-200	0.0962	5.5783	3.6585	3.6035	22.7860	0.0246	5.8834
23	1	200-300	0.0540	3.4231	1.8392	1.2761	17.3480	0.0265	5.4579
23	1	300-400	0.0368	2.6666	0.8281	0.9239	4.7740	0.0243	5.2881
23	1	400-500	0.1598	3.0921	1.0723	1.5090	2.0725	0.0026	3.1979
23	2	0-100	0.1161	0.2035	2.4503	2.3379	7.7739	0.0116	6.0062

23	2	100-200	0.0691	13.0520	1.1699	1.8615	5.0598	0.0218	6.7546
23	2	200-300	0.0436	9.3776	5.1530	2.9714	30.4480	0.0720	8.3824
23	2	300-400	0.0223	9.2075	7.6802	3.9283	24.7120	0.0092	9.2198
23	2	400-500	-0.0097	8.6113	2.3024	3.0646	2.0726	0.0128	12.2010
23	3	400-500	0.0684	0.8527	2.9257	3.9019	41.8720	0.0562	6.8178
23	3	0-100	0.2102	0.9343	6.3499	7.2721	32.9790	0.0793	7.6310
23	3	100-200	0.1602	0.4937	3.7814	4.4221	14.9620	0.0389	4.6247
23	3	200-300	0.2446	0.3766	2.8681	4.5139	11.4920	0.0517	6.0053
23	3	300-400	0.1259	0.3298	1.7490	3.0899	12.7840	0.0310	4.4901
24	1	0-100	0.0410	2.6270	28.1370	64.7940	870.5700	12.3330	8.3121
24	1	100-200	-0.0309	8.3618	2.8246	15.1530	35.6420	0.4896	1.7084
24	1	200-300	0.1133	0.1808	0.6476	0.7100	1.5746	1.3514	0.9134
24	1	300-400	0.0013	0.2914	0.1785	0.5563	3.5249	0.0444	0.0481
24	1	400-500	0.0833	0.1994	0.9892			1.2330	
24	2	0-100	0.2194	4.6726	16.3980	52.2710	459.4900	4.2817	4.4142
24	2	100-200	0.2866	10.5380	20.7400	44.2000	499.6400	4.5542	4.1042
24	2	200-300	0.1201	0.1808	0.6948	0.7100	1.5746	1.3937	0.9437
24	2	300-400	0.1201	0.1753	0.6712	0.7100	1.5746	1.3514	0.9134
24	2	400-500	0.0476	10.1110	4.2976	3.0113	51.5410	0.8107	0.9918
24	3	0-100	0.2830	3.9067	25.9920	60.2540	696.5200	6.0331	6.7120
24	3	100-200	0.1139	7.0113	13.6810	19.2800	263.2400	3.2995	3.3426
24	3	200-300	0.1201	0.1864	0.6712	0.7100	1.5223	1.3514	0.9437
24	3	300-400	-0.0068	33.5500	7.1948	9.3022	34.1180	0.2310	2.9654
24	3	400-500	0.1201	0.1808	0.6712	0.7100	1.5746	1.3514	0.9437
25	1	0-100	0.9387	2.6149	9.1752	18.0029	80.3910	2.1175	39.3722
25	1	100-200	0.8251	1.7020	6.3746	11.4587	52.2304	1.0256	25.2593
25	1	200-300	1.0888	0.6007	2.4686	4.2410	16.1219	0.1667	5.2263
25	2	0-100	0.6278	1.3587	5.4825	22.1375	65.1522	0.9706	17.4924
25	2	100-200	0.0966	1.0932	2.6984	13.1246	25.7733	0.2207	7.6082
25	2	200-300	0.6269	0.5455	1.3435	3.8646	13.7905	0.0996	15.7288
25	2	300-400	0.3830	0.9986	2.6598	5.2169	32.5572	0.0671	21.8004
25	2	400-500	0.2946	0.9112	2.3439	2.1079	24.0845	0.1040	8.3614
25	3	0-100	0.1794	0.2444	1.8052	5.4884	23.2443	0.3252	12.4066
25	3	100-200	0.2479	0.0732	0.4816	0.5562	3.1026	0.0320	3.1652
25	3	200-300	0.2608	0.0540	0.3180	0.3827	1.8769	0.0296	2.8636
25	3	300-400	0.2631	0.0465	0.2104	0.1008	0.5010	0.0097	1.8207
25	3	400-500	0.3368	0.0543	0.2706	0.3296	1.6707	0.0259	1.6010

26	1	0-100	0.0660	0.5672	1.4682	2.5182	18.7966	0.0675	6.4504
26	1	100-200	0.0694	0.1869	1.2621	1.8524	23.8654	0.0333	1.2451
26	1	200-300	0.0564	0.1548	1.3190	1.3974	20.0841	0.0451	0.7857
26	1	300-400	0.1436	0.5062	7.2434	0.7667	3.9245	-0.0360	0.2873
26	1	400-500	0.0634	0.1605	1.4236	1.4340	2.7364	0.0220	0.5014
26	2	0-100	0.0876	0.2541	1.3409	0.3765	0.8277	0.0120	0.3604
26	2	100-200	0.0876	0.2084	1.1681	0.1836	0.5784	0.0123	0.2044
26	2	200-300	0.0789	0.1617	1.2883	0.1992	0.5065	0.0143	0.2914
26	2	300-400	0.0544	0.2012	1.2222	0.1736	0.5847	0.0126	0.8992
26	2	400-500	0.0800	0.2172	1.3380	0.1777	0.5410	0.0322	0.3096
26	3	0-100	0.0548	0.2914	1.0658	0.2292	1.0523	0.0169	0.3302
26	3	100-200	0.0591	0.2012	1.2373	0.2989	0.5739	0.0189	0.2459
26	3	200-300	0.0766	0.2278	1.3675	0.2671	0.5296	0.0195	0.2148
26	3	300-400	0.0669	0.1802	1.1904	0.1538	0.2620	0.0081	0.1428
26	3	400-500	0.0740	0.1872	1.2798	0.2318	0.2321	0.0109	0.1413
27	1	0-100	-0.0168	10.6630	4.8585	6.8700	0.8605	0.0282	3.4038
27	1	100-200	-0.0065	16.9530	2.9749	6.7747	0.7818	0.0204	5.8193
27	1	200-300	0.1193	4.0541	2.4868	5.7180	6.4034	0.7080	4.0268
27	1	300-400	0.0203	20.8900	6.2416	8.3593	14.5930	0.0653	6.3277
27	2	0-100	0.1115	31.0770	7.7271	9.6737	13.9050	0.0429	7.7435
27	2	100-200	-0.0127	21.8470	6.2355	7.2026	9.9138	0.0591	7.9576
27	2	200-300	0.0415	0.4056	0.1730	0.2060	0.2926	0.0013	0.1151
28	1	0-100	0.4138	29.2900	26.7630	27.0980	122.6600	1.6707	17.2740
28	1	100-200	0.0930	25.9300	26.2700	8.9922	116.8100	0.6186	6.2540
28	1	200-300	0.0066	7.5925	15.1850	6.2117	84.3920	0.3083	4.3531
28	1	300-400	0.0228	28.7470	25.0080	6.0462	73.6190	0.2940	2.5078
28	1	400-500	0.1656	0.0837	0.2582	0.6858	1.8084	1.3465	0.9541
28	2	0-100	0.9547	24.7690	53.1540	31.2080	125.6500	1.3999	9.3020
28	2	100-200	0.7825	17.2760	58.4020	28.1340	141.7600	1.2304	6.9644
28	2	200-300	0.2794	21.8250	74.0950	9.8828	169.3100	0.4085	3.8988
28	3	0-100	0.7402	22.9990	29.0400	33.4630	108.9300	1.2799	8.8081
28	3	100-200	0.0361	14.3860	29.6540	8.6800	87.8200	0.8493	3.6586
28	3	200-300	-0.0240	8.7762	60.8710	6.4896	264.0800	1.1503	3.2803
28	3	300-400	-0.0406	12.5800	78.6300	5.4603	376.3500	0.6909	2.5754
28	3	400-500	-0.0423	12.2930	93.0360	5.1410	315.8700	0.1618	2.2497
29	1	0-100	1.9779	5.8281	18.8130	63.3500	379.9200	2.9589	39.2600
29	1	100-200	0.6502	8.9878	16.4590	51.5060	304.0200	2.8649	38.1090

29	1	200-300	0.1607	12.0740	6.1524	15.7830	86.0890	0.5886	7.6979
29	1	300-400	0.0377	11.8810	3.5061	12.5630	65.2190	0.3108	2.6915
29	2	0-100	0.6602	5.0392	21.4670	67.0200	446.2400	3.4816	30.3990
29	2	100-200	0.9783	5.2887	23.8880	56.0850	385.6600	3.4830	41.9500
29	2	200-300	0.3097	10.0090	14.4870	29.2590	203.1400	2.1856	15.5960
29	2	300-400	0.0397	10.0590	5.1616	19.2990	111.5400	0.6796	3.1721
29	2	400-500	0.0125	9.4508	3.1685	14.1770	79.7810	0.3893	2.2030
29	3	0-100	0.8419	6.6495	14.1710	39.5390	237.4600	2.1632	18.7520
29	3	100-200	0.0957	0.1710	0.6082	0.6291	1.4350	1.2386	0.8628
29	3	200-300	0.0474	5.9365	3.0125	11.0930	7.8887	0.0910	6.5850
29	3	300-400	-0.0013	9.5137	3.4258	7.5087	1.2409	0.0225	3.6694
30	1	0-100	0.4190	3.2563	6.2514	12.8660	30.4410	0.2804	15.1420
30	1	100-200	0.1553	6.0489	8.8350	9.3281	13.9900	0.1367	8.8787
30	1	200-300	0.1706	7.2840	13.6580	6.9719	2.6538	0.0382	3.7371
30	1	300-400	0.0513	6.4187	13.7340	9.5456	2.1056	0.0198	7.2827
30	1	400-500	0.0628	5.5577	12.3840	9.1684	1.9776	0.0275	7.4194
30	2	0-100	0.2698	5.6150	10.2560	25.9350	104.5600	0.3818	27.9360
30	2	100-200	0.0146	7.9617	15.5270	9.7818	14.2320	0.0751	10.6850
30	2	200-300	0.0189	7.6077	19.2340	7.5557	4.0477	0.0283	8.4426
30	2	300-400	-0.0146	5.8416	15.7540	6.8831	2.0991	0.0275	8.4314
30	2	400-500	0.0918	6.1237	16.6000	9.2086	2.8882	0.0136	9.1391
30	3	0-100	0.1401	5.1106	8.0901	7.0543	14.6800	0.1391	11.1850
30	3	100-200	-0.0040	6.8021	10.8260	6.2141	7.4609	0.1194	10.2710
30	3	200-300	0.0490	5.9626	9.4670	5.5116	1.5866	0.0306	5.5837
30	3	300-400	0.0095	5.7106	10.3370	5.3789	1.1196	-0.0041	4.9643
30	3	400-500	-0.0066	5.4219	12.1810	5.5876	1.4585	0.0071	5.6133
31	1	0-100	2.7483	2.3546	26.7410	123.9500	164.8700	2.5353	37.8770
31	1	100-200	2.8238	4.3710	45.1210	159.5200	238.8100	3.1630	33.7970
31	1	200-300	1.8806	4.5485	49.5000	173.2300	328.4900	4.3023	48.9760
31	1	300-400	0.6986	2.8507	22.9230	52.8430	194.0300	1.2157	25.2610
31	1	400-500	0.2781	1.9113	13.4930	24.3620	131.6300	0.6200	17.8120
31	2	0-100	3.1073	2.8748	26.9990	238.3700	203.5300	4.1906	73.5240
31	2	100-200	3.5836	5.8055	62.3370	236.6400	509.5400	5.9772	74.3460
31	2	200-300	1.3576	7.1701	61.0830	130.3800	579.0500	3.9707	47.9400
31	2	300-400	0.5210	4.5966	27.9980	58.1220	261.3300	1.6832	17.5220
31	2	400-500	0.5429	3.6863	20.2950	59.9320	158.5100	1.3266	17.1220
31	3	0-100	0.6284	1.1047	7.5271	25.2730	52.0320	0.3387	18.6320

31	3	100-200	0.3287	0.4517	2.3464	11.8350	18.2230	0.1147	8.7727
31	3	200-300	0.2518	0.3836	1.8140	9.2319	14.9090	0.0464	4.2529
31	3	300-400	0.1818	0.3926	2.0443	8.8174	16.0170	0.0578	5.0397
31	3	400-500	0.1900	0.4019	2.3148	9.4185	17.7580	0.1323	4.9113
32	1	0-100	0.0302	0.4444	2.1356	3.1469	2.8247	0.0470	2.1642
32	1	100-200	0.0337	0.2782	2.1243	1.8473	1.1678	0.0260	1.3727
32	1	200-300	0.0321	0.3513	2.3565	2.0628	1.1143	0.0326	1.5348
32	1	300-400	0.0348	0.3551	1.9959	2.1422	0.6548	0.0358	1.6667
32	1	400-500	0.0376	0.2052	1.6313	1.4338	0.2487	0.0232	1.1137
32	2	0-100	0.0339	0.3135	2.4481	4.4181	12.8799	0.0842	4.8665
32	2	100-200	0.0312	0.2382	1.6506	2.9683	2.6571	0.0455	1.8852
32	2	200-300	0.0341	0.2326	1.7159	2.3961	3.5840	0.0432	2.0123
32	2	300-400	0.0334	0.1954	1.6937	1.9050	1.1803	0.0219	1.2955
32	2	400-500	0.0281	0.2529	1.6113	1.9493	0.5706	0.0233	1.3156
32	3	0-100	0.0279	0.2563	2.1874	2.9889	8.6595	0.0687	3.8588
32	3	100-200	0.0296	0.2139	1.8552	3.3399	7.8402	0.0724	4.2336
32	3	200-300	0.0283	0.1782	1.4356	2.0362	1.4086	0.0313	1.6399
32	3	300-400	0.0388	0.2349	1.8401	1.5216	0.6392	0.0163	1.0943
32	3	400-500	0.0294	0.2472	1.9464	1.8552	0.5938	0.0194	1.3681
33	1	200-300	0.2467	2.6532	4.2420	14.8628	55.2437	0.4889	65.3172
33	1	300-400	0.1940	1.5961	3.2137	14.6240	54.1907	0.5009	73.7366
33	1	400-500	0.2295	4.2211	3.1725	11.3490	27.5240	0.2096	32.5885
33	2	0-100	0.5762	3.9666	6.7558	14.2700	65.9984	0.6241	21.9723
33	2	100-200	0.3227	3.3131	5.0396	14.5984	60.8348	0.5013	70.0278
33	2	200-300	0.2428	1.6463	1.8602	13.4527	53.0686	0.4482	68.0897
33	3	0-100	0.9478	3.1647	6.9870	17.2685	62.8629	0.5102	25.1353
33	3	100-200	0.4654	3.7476	3.8206	12.0231	39.9615	0.3575	37.8658
33	3	200-300	0.3506	4.2118	3.2958	10.2902	40.6084	0.2579	76.9979
34	1	0-100	0.1994	0.2156	2.1220	8.1464	23.1475	0.1091	3.6014
34	1	100-200	0.1149	0.1560	1.5211	3.5364	6.3909	0.0310	0.8401
34	1	200-300	0.0764	0.1263	1.3689	0.9635	0.9896	0.0116	0.1921
34	1	300-400	0.0648	0.1439	1.5371	0.9418	1.5577	0.0370	0.3331
34	1	400-500	0.0650	0.1497	1.6759	1.2924	2.1752	0.0119	0.4062
34	2	0-100	0.0818	0.1672	1.9497	11.2485	29.7781	0.1753	5.4822
34	2	100-200	0.0647	0.1247	1.3042	5.8577	12.4669	0.0407	2.0857
34	2	200-300	0.0547	0.1276	1.4033	2.9870	3.7933	0.0190	0.5623
34	2	300-400	0.0413	0.1434	1.6051	1.3418	2.4736	0.0156	0.3431

34	2	400-500	0.0391	0.1369	1.3795	1.1700	1.1485	0.0239	0.2576
34	3	0-100	0.1184	0.1520	1.6000	4.5967	16.2101	0.0687	1.9314
34	3	100-200	0.0386	0.1526	1.7109	0.5136	0.9824	0.0105	0.1879
34	3	200-300	0.0563	0.1469	1.4913	0.3715	0.7328	0.0201	0.1551
34	3	300-400	0.0488	0.1185	1.3043	1.3571	4.5006	0.0161	0.5381
34	3	400-500	0.0399	0.1647	1.8219	0.4175	0.8104	0.0135	0.1837
35	1	0-100	0.1441	3.2428	2.7684	5.6677	32.9210	0.0984	7.1018
35	1	100-200	0.4390	4.0756	4.1694	4.6253	27.0470	0.1315	6.0493
35	1	200-300	0.0423	4.1437	1.3067	2.7313	5.3558	0.0245	4.0242
35	1	300-400	0.0587	3.6763	1.9984	2.3927	6.3218	0.0313	3.6873
35	1	400-500	0.1525	3.6530	1.6043	3.7130	12.3840	0.0155	2.9517
35	2	0-100	0.1118	3.3261	5.6362	3.6395	41.3510	0.1005	6.4836
35	2	100-200	0.1017	2.4544	1.6250	3.1118	12.9180	0.0290	3.6783
35	2	200-300	0.0831	2.2250	0.9667	2.5539	3.6733	0.0181	2.6568
35	2	300-400	0.0261	0.0732	0.0928	0.1006	0.4842	0.0024	0.0658
35	2	400-500	0.0567	2.1394	0.8630	2.5419	3.8355	0.0005	1.9411
35	3	0-100	0.9702	2.4427	2.7817	5.8885	21.3900	0.0965	5.5452
35	3	100-200	0.1893	3.3954	2.4291	3.6552	13.1230	0.0500	5.2785
35	3	200-300	0.0687	2.8964	0.9645	2.8455	7.4984	0.0244	3.6602
35	3	300-400	0.0583	4.2659	0.9581	2.8317	4.2402	0.0167	3.3447
35	3	400-500	0.0434	3.2155	1.5286	2.4120	3.4600	0.0222	2.9799
36	1	0-100	0.6330	12.5390	11.6400	233.1200	591.2200	5.1571	112.1600
36	1	100-200	0.8667	8.2116	8.0372	87.6250	285.6300	1.7738	28.1970
36	1	200-300	0.1663	9.5915	5.7910	38.4340	172.1000	0.5089	8.4099
36	1	300-400	0.0182	16.0840	4.1323	18.8590	78.8720	0.2683	5.8065
36	2	0-100	0.3959	13.4070	11.4160	141.2400	266.9300	2.1034	71.3070
36	2	100-200	0.5940	10.0580	8.1970	113.5400	171.0900	1.4713	55.5940
36	2	200-300	0.4545	7.5448	4.5487	68.4190	76.7990	0.7187	28.2940
36	2	300-400	0.1152	19.5020	5.8509	46.3710	80.7960	0.7682	8.8391
36	2	400-500	0.0050	20.2230	4.0016	16.0890	69.7860	0.5018	4.7664
36	3	0-100	0.8322	43.3480	16.4610	248.7600	634.3100	6.4895	103.8700
36	3	100-200	0.6267	6.8078	7.5307	84.7700	276.0000	2.8699	39.4700
36	3	200-300	0.2323	3.3570	7.0986	36.0370	228.5200	1.2815	6.2690
36	3	300-400	0.0674	1.6422	7.4239	21.8870	211.9000	0.9854	4.0044
36	3	400-500	0.0229	1.1082	4.8825	13.8020	138.5300	0.5858	3.1614
37	1	0-100	0.2068	1.5271	6.1231	8.2105	53.2358	0.1445	6.2716
37	1	100-200	0.1960	2.3099	8.4179	7.1407	44.4507	0.1169	6.7797

37	1	200-300	0.1336	3.0450	7.6975	5.5346	23.9267	0.0681	6.0826
37	1	300-400	0.0739	2.9394	5.3721	3.2774	9.9182	0.0344	3.7245
37	1	400-500	0.0524	2.6678	3.5827	2.5773	3.9602	0.0133	2.8075
37	2	0-100	0.1690	1.0700	3.5316	6.3834	36.4646	0.0800	3.4873
37	2	100-200	0.1895	0.8418	3.2520	3.7158	18.2419	0.0218	1.7545
37	2	200-300	0.1825	0.6868	2.7358	3.0754	13.5330	0.0117	1.7405
37	2	300-400	0.1335	0.4850	2.1912	2.6008	8.8506	0.0061	1.4316
37	2	400-500	0.1354	0.4092	0.9074	2.4286	5.7516	0.0021	1.3516
37	3	0-100	0.1901	0.6194	2.9697	5.3799	24.3604	0.0470	2.8950
37	3	100-200	0.1159	1.5006	2.1461	3.4334	16.3230	0.0247	1.4769
37	3	200-300	0.1143	2.6266	2.7614	3.2407	18.6393	0.0417	1.7754
37	3	300-400	0.1043	2.4831	4.6326	3.3973	22.7435	0.0536	2.6721
37	3	400-500	0.0813	2.4735	5.3655	3.0294	15.2762	0.0204	3.2857
38	1	0-100	0.0494	10.8120	2.4541	9.9847	12.6410	0.0294	2.9923
38	1	100-200	-0.0296	11.0460	1.2563	7.1022	1.4927	0.0033	1.3844
38	1	200-300	0.0413	6.2274	1.0045	3.7582	1.1237	0.6990	1.1861
38	1	300-400	-0.0286	14.3450	0.9238	4.9676	0.4843	0.0037	1.1440
38	1	400-500	0.1201	0.1808	0.6712	0.7100	1.5746	1.3514	0.9437
38	2	0-100	0.7004	1.2156	7.6700	33.2690	299.3400	0.2838	10.9610
38	2	100-200	0.2002	1.4923	4.0884	17.9180	161.8100	0.1501	7.5242
38	2	200-300	0.0199	5.3807	1.1744	8.5704	14.4870	0.0242	2.4507
38	2	300-400	-0.0277	8.5927	0.5947	6.8211	2.6558	0.0046	1.4251
38	2	400-500	0.0242	10.1290	0.3967	7.1283	2.8197	0.0069	1.5148
38	3	0-100	-0.0054	4.4908	1.0866	7.9139	2.1335	0.0054	1.4245
38	3	100-200	0.0018	1.3814	0.6941	8.2318	2.0450	0.0127	1.6270
38	3	200-300	0.0752	4.9278	1.1536	7.4895	1.5942	-0.0056	1.3007
38	3	300-400	0.0447	1.3353	0.6898	8.1184	1.5588	-0.0074	1.3136
39	1	0-100	0.2428	0.6391	25.4280	197.4200	303.2100	1.3770	8.1403
39	1	100-200	0.2304	1.0890	10.6200	86.4670	138.3100	0.4580	5.9981
39	1	200-300	0.0958	2.3952	8.0919	62.4060	78.9150	0.2039	5.3593
39	1	300-400	0.0171	3.0083	4.0453	20.6640	34.9400	0.0856	2.7598
39	1	400-500	0.0066	7.0127	2.6171	7.6493	21.7930	0.0919	2.4034
39	2	0-100	0.0572	3.0189	5.0789	21.5910	36.2760	0.1655	2.3116
39	2	100-200	0.0210	9.9437	5.4881	8.2750	46.0850	0.1437	1.8327
39	2	200-300	0.0050	14.8880	5.3348	7.0741	28.4950	0.0610	1.9202
39	2	300-400	0.0797	9.5496	4.4760	6.4419	35.4360	0.1263	1.8226
39	2	400-500	0.0746	14.8680	4.2237	5.4004	20.2870	0.0635	2.0886

39	3	0-100	0.0541	0.8018	7.8284	53.6300	51.5140	0.1773	2.5808
39	3	100-200	0.0104	0.7376	3.7437	16.7350	15.5420	0.0289	1.3782
39	3	200-300	0.0552	0.0511	0.1502	0.9990	1.0990	0.0231	0.0478
39	3	300-400	0.0737	0.8017	3.1452	13.1280	11.1320	0.0299	1.3148
39	3	400-500	0.0206	0.8573	2.8616	10.2790	7.6444	0.0707	1.7921
40	1	0-100	0.1851	0.7157	1.4752	3.0523	10.1239	0.0247	1.8037
40	1	100-200	0.1243	0.7654	0.5876	2.3082	3.1874	0.0130	1.5285
40	1	200-300	0.1017	0.6329	0.3303	2.0234	1.2440	0.0101	1.2376
40	1	300-400	0.1287	1.0117	0.7456	3.3938	4.7722	0.0227	1.5670
40	1	400-500	0.1287	0.6821	0.8660	3.0012	5.2597	0.0251	1.7175
40	2	0-100	0.0898	1.0656	0.5320	1.4130	1.6764	0.0076	2.0392
40	2	100-200	0.0717	1.5159	1.0425	1.7446	1.1004	0.0126	2.3326
40	2	200-300	0.0324	1.6819	1.2771	2.1347	1.2110	0.0132	2.1158
40	2	300-400	0.0740	1.0514	1.3724	1.8660	0.5922	0.0061	1.8178
40	2	400-500	0.1352	0.3385	0.9053	1.0753	0.4684	0.0070	1.6696
40	3	0-100	0.1203	0.2723	3.3605	6.5401	28.7152	0.0903	0.9948
40	3	100-200	0.0941	0.1191	1.8495	4.7136	12.6818	0.0517	1.1033
40	3	200-300	0.0927	0.0633	0.2515	1.2826	1.6626	0.0070	1.0872
40	3	300-400	0.1335	0.0658	0.3312	1.2119	1.2710	0.0085	1.2113
40	3	400-500	0.1275	0.0503	0.2084	0.6942	1.1005	0.0129	0.9452

site number	location at site	Depth	Cr	Co	Ni	Cu	Zn	Cd	Pb
1	1	100-200	0.0168	0.0078	0.1156	0.2196	0.0821	-0.0033	0.0037
1	1	200-300	0.0235	0.0093	0.1278	0.4467	0.5155	-0.0053	0.0899
1	1	0-100	0.0781	0.0214	0.2609	1.2903	2.7956	0.0152	0.5172
1	1	100-200	0.0187	0.0111	0.1501	0.2413	0.1658	-0.0026	0.0078
1	2	200-300	0.0290	0.0109	0.1460	0.2151	0.5430	0.0012	0.1148
1	2	300-400	0.0159	0.0118	0.2563	0.0504	0.0163	-0.0010	0.0017
1	2	0-100	0.0180	0.0131	0.1517	0.0411	0.0120	-0.0015	0.0001
1	2	100-200	0.0154	0.0089	0.2862	0.0296	0.0264	-0.0082	-0.0028
1	2	200-300	0.0169	0.0106	0.1693	0.0340	-0.0031	-0.0051	-0.0038
1	3	300-400	0.0189	0.0157	0.2504	0.2745	0.1246	-0.0059	0.0084
1	3	400-500	1.9446	1.9436	20.6401	22.5438	9.1297	0.9570	0.3290
1	3	0-100	0.0189	0.0125	0.1807	0.1779	0.0981	0.0050	0.0030
1	3	100-200	0.0233	0.0177	0.2029	0.3672	0.3671	0.0006	0.0375
1	3	200-300	0.0196	0.0128	0.1602	0.1594	0.1834	0.0022	0.0094
2	1	0-100	0.0664	0.0762	0.6162	1.5627	0.4123	0.0167	0.0291
2	1	100-200	0.0403	0.0682	0.4311	0.7435	0.2190	0.0130	0.0047
2	1	200-300	0.0273	0.0540	0.8447	0.2296	0.0679	0.0097	-0.0048
2	1	300-400	0.0265	0.0492	0.3823	0.1299	0.0589	0.0128	-0.0028
2	1	400-500	0.0320	0.0634	0.4685	0.3237	0.1126	0.0111	-0.0034
2	2	0-100	0.0434	0.0779	0.5852	1.0662	0.1497	0.0115	0.0012
2	2	100-200	0.0568	0.0749	0.4605	0.5990	0.1629	0.0117	0.0090
2	2	200-300	0.0426	0.0535	0.3773	0.3493	0.1450	0.0104	0.0039
2	2	300-400	0.0338	0.0582	0.4652	0.1776	0.1088	0.0104	0.0034
2	2	400-500	0.0393	0.0610	0.5625	0.1549	0.0889	0.0135	-0.0030
2	3	0-100	0.0696	0.0900	0.6571	0.8475	0.1805	0.0118	0.0131
2	3	100-200	0.1435	0.0928	0.6976	0.8821	0.4949	0.0161	0.0706
2	3	200-300	0.0561	0.0963	0.3984	1.4850	2.1372	0.0513	0.1739
2	3	300-400	0.1438	0.0913	0.6047	0.9789	0.8638	0.0210	0.1255
2	3	400-500	0.0353	0.0458	0.3286	0.1138	0.2414	0.0183	0.0022
3	1	0-100	0.0155	0.0701	0.4448	0.3367	1.4173	0.0136	-0.0020
3	1	100-200	0.0135	0.0282	0.2881	0.0790	0.1496	0.0002	-0.0023
3	1	200-300	0.0124	0.0121	0.1690	0.0396	0.0582	0.0002	-0.0043
3	1	300-400	0.0098	0.0153	0.1835	0.0312	0.0864	-0.0084	-0.0040
3	1	400-500	0.0099	0.0156	0.1936	0.0369	-0.0077	-0.0098	-0.0013
3	2	0-100	0.0128	0.0219	0.2333	0.0844	0.0147	-0.0112	-0.0022

3	2	100-200	0.0136	0.0141	0.1931	0.0671	0.1250	-0.0033	-0.0026
3	2	200-300	0.0126	0.0272	0.2787	0.0613	0.0556	-0.0042	-0.0039
3	2	300-400	0.0113	0.0176	0.2141	0.0532	-0.0071	-0.0090	-0.0021
3	2	400-500	0.0136	0.0214	0.2103	0.0614	-0.0310	-0.0081	-0.0011
3	3	0-100	0.0142	0.0576	0.4196	0.1213	5.2814	0.0125	0.0221
3	3	100-200	0.0156	0.0228	0.2655	0.0608	0.1754	-0.0018	-0.0031
3	3	200-300	0.0139	0.0139	0.1939	0.0433	0.1352	-0.0049	-0.0044
3	3	300-400	0.0115	0.0089	0.1543	0.0260	0.0855	-0.0083	-0.0039
3	3	400-500	0.0107	0.0120	0.1209	0.0333	0.1186	-0.0063	-0.0038
4	1	0-100	0.0147	0.0090	0.1060	0.0628	0.6459	-0.0006	0.0032
4	1	100-200	0.0125	0.0045	0.0793	0.0381	0.2868	-0.0003	0.0013
4	1	200-300	0.0134	0.0018	0.0687	0.0328	0.2451	0.0010	-0.0003
4	1	300-400	0.0152	0.0051	0.6680	0.0315	0.2161	0.0037	0.0015
4	1	400-500	0.0187	-0.0005	0.0554	0.0384	0.2116	-0.0044	0.0073
4	2	0-100	0.0153	0.0216	0.1718	0.0922	0.2591	-0.0010	0.0185
4	2	100-200	0.0137	0.0095	0.1166	0.0484	0.1173	-0.0024	0.0005
4	2	200-300	0.0136	0.0087	0.1092	0.0534	0.1029	0.0031	0.0035
4	2	300-400	0.0159	0.0059	0.0939	0.0369	0.1318	0.0030	0.0013
4	3	400-500	0.0129	-0.0072	0.0141	0.0045	-0.0037	0.0045	0.0010
4	3	0-100	0.0146	0.0037	0.0787	0.0573	0.1332	-0.0033	0.0000
4	3	100-200	0.0150	0.0011	0.0747	0.0428	-0.0128	-0.0017	-0.0016
4	3	200-300	0.0136	0.0008	0.3626	0.0391	0.0257	0.0016	-0.0037
4	3	300-400	0.0153	-0.0014	0.0608	0.0390	0.0015	-0.0012	0.0028
4	1	400-500	0.0144	-0.0013	0.0589	0.0323	-0.0125	0.0018	-0.0019
5	1	300-400	0.0304	0.1307	0.3183	0.1595	4.3628	0.0215	0.0028
5	1	400-500	0.0269	0.1491	0.2478	0.0977	1.2910	0.0134	-0.0019
5	1	0-100	0.0242	0.1231	0.8297	0.1171	0.3750	0.0124	0.0013
5	1	100-200	0.0268	0.0753	0.3578	0.1091	0.1404	0.0111	0.0002
5	2	200-300	0.0237	0.0513	0.6747	0.0470	0.1302	0.0148	-0.0017
5	2	300-400	0.0275	0.1585	0.4133	0.1800	9.5735	0.0257	-0.0008
5	2	400-500	0.0315	0.0980	0.4672	0.0850	5.3760	0.0151	-0.0014
5	2	0-100	0.0285	0.0593	0.5335	0.0594	1.4323	0.0140	-0.0051
5	2	100-200	0.0254	0.0466	1.0733	0.0449	0.3500	0.0133	0.0002
5	3	200-300	0.0228	0.0396	0.3388	0.0407	0.1274	0.0115	-0.0056
5	3	300-400	0.0275	0.0369	0.1981	0.0415	0.0336	0.0084	-0.0017
5	3	400-500	0.0306	0.0326	0.1986	0.0336	0.0386	0.0087	-0.0037

5	3	0-100	0.0289	0.0312	0.1771	0.0345	0.0488	0.0099	-0.0044
5	3	100-200	0.0314	0.0321	0.1871	0.0383	0.0884	0.0093	-0.0048
5	1	200-300	0.0325	0.0322	0.2613	0.0314	0.0655	0.0082	-0.0026
6	1	0-100	0.0086	0.0422	0.1236	0.2269	0.3649	0.0243	0.0434
6	2	100-200	0.0292	0.0268	0.1273	0.1002	-0.0169	0.0254	-0.0203
6	2	0-100	0.0493	0.0584	0.1863	0.1434	-0.0435	0.0252	-0.0120
6	2	100-200	0.0236	0.0421	0.1579	0.0989	-0.0363	0.0235	-0.0066
6	3	200-300	0.0344	0.0347	0.1075	0.1220	0.0035	0.0215	0.0056
6	3	0-100	0.0660	0.0481	0.1912	1.1716	1.6492	0.0255	0.5888
6	1	100-200	0.0289	0.0595	0.2431	1.2788	0.7602	0.0238	0.2003
7	1	300-400	0.0357	0.2569	1.5462	0.8332	23.6620	0.0190	0.0175
7	1	400-500	0.0197	0.1140	3.6848	0.2035	13.7748	0.0300	0.0074
7	1	0-100	0.0190	0.0352	1.0214	0.3509	0.8676	0.0112	0.0021
7	2	100-200	0.0206	0.0379	0.7732	0.0937	0.1164	0.0073	0.0015
7	2	200-300	0.0169	0.8534	1.0174	0.1815	2.4599	0.0116	0.0011
7	3	300-400	0.0163	0.9444	1.6664	0.1389	2.6174	0.0074	0.0027
7	3	0-100	0.0178	0.0880	2.5147	0.1110	5.8115	0.0150	0.0030
7	3	100-200	0.0143	0.0134	0.1474	0.0612	0.0758	0.0062	-0.0009
7	1	200-300	0.0190	0.0074	0.1006	0.0627	0.0826	0.0181	0.0008
8	1	0-100	0.2002	0.6982	1.3955	2.5119	13.9710	0.0754	0.6993
8	1	100-200	-0.0010	1.2956	1.7313	1.0209	6.7798	0.0661	0.0146
8	2	200-300	-0.0254	1.3949	1.9527	0.4421	3.5256	0.0707	-0.0126
8	2	0-100	0.6004	0.3816	2.0506	10.5700	37.2340	0.1446	1.1127
8	3	100-200	0.1005	0.2913	1.1470	11.1740	15.6660	0.1351	0.1066
8	3	0-100	-0.0035	0.4634	1.1171	1.7966	12.6580	0.1006	0.0056
8	1	100-200	-0.0112	0.5928	1.1209	0.9692	8.1342	0.1133	0.0277
9	1	0-100	0.0439	0.0608	0.2881	0.3701	0.1892	0.0210	0.0503
9	1	100-200	0.0274	0.0407	0.2022	-0.1685	0.0654	0.0093	0.0063
9	2	200-300	0.3166	0.0732	0.3166	0.1840	0.2333	0.0276	0.1133
9	2	0-100	0.3346	1.0469	11.3120	348.2000	3.9436	0.4244	0.1998
9	2	100-200	0.3051	1.7006	25.7120	338.5400	4.3091	0.5802	0.1732
9	2	200-300	0.3706	1.6070	38.6990	378.4300	3.7721	0.5949	0.1290
9	2	300-400	0.2339	2.0321	42.3940	326.4200	2.1685	0.5517	0.1059
9	3	400-500	0.1246	2.0113	50.9420	328.5300	1.6033	0.5080	0.0367
9	3	0-100	0.5183	0.7428	14.6930	123.3000	2.4932	0.1340	0.4597
9	3	100-200	0.0358	0.1080	11.1680	85.1210	0.3588	0.0943	0.0135

9	1	200-300	0.1520	0.5210	15.6030	108.9800	1.0188	0.1693	0.1540
10	1	0-100	0.0159	1.2840	0.9014	11.4520	0.1761	0.1533	0.0242
10	1	100-200	0.0093	1.3780	1.4408	13.0420	0.4478	0.2641	0.0858
10	1	200-300	0.0055	0.7871	1.0658	11.4660	0.5560	0.2807	0.0435
10	1	300-400	0.0037	0.2506	1.4399	12.6910	0.8517	0.3203	0.0144
10	2	400-500	0.0193	0.1868	2.2519	12.6430	0.9076	0.2971	0.0108
10	2	0-100	0.0263	1.7402	1.3354	15.8110	0.3030	0.1467	0.0370
10	2	100-200	0.0110	1.1038	1.2294	12.0180	0.2964	0.2276	0.0359
10	2	200-300	0.0124	0.6328	0.8706	8.4487	0.4063	0.1991	0.0483
10	1	300-400	0.0181	0.4370	0.7691	6.7599	0.6263	0.2032	0.0185
11	1	0-100	-0.0066	0.2992	1.9575	0.1957	18.7360	0.0530	-0.0027
11	2	100-200	-0.0051	0.5974	2.9167	0.1830	14.2690	0.0665	0.0023
11	2	0-100	-0.0065	0.0307	0.1164	0.2111	0.2437	0.0176	0.0396
11	2	100-200	-0.0213	0.0388	0.1144	0.1910	0.1119	0.0205	0.0163
11	3	200-300	-0.0271	0.0457	0.1073	0.1142	0.0985	0.0211	-0.0014
11	3	0-100	-0.0094	0.0300	0.1149	0.1998	0.2860	0.0182	0.0176
11	3	100-200	-0.0057	0.0226	0.0947	0.1170	0.1658	0.0236	0.0119
11	3	200-300	0.0024	0.0209	0.0893	0.1383	0.1170	0.0220	0.0048
11	1	300-400	-0.0210	0.0214	0.0738	0.1672	0.1049	0.0272	0.0204
12	1	0-100	0.0125	0.0984	1.4383	0.0951	2.7056	0.0270	-0.0056
12	1	100-200	-0.0017	0.0967	0.8969	0.1266	0.7151	0.0289	-0.0045
12	2	200-300	-0.0057	0.0989	1.1926	0.1686	1.2509	0.0353	0.0013
12	2	0-100	-0.0042	0.1228	1.1309	0.2819	1.4411	0.0337	-0.0072
12	2	100-200	0.0055	0.0873	0.8203	0.2194	1.2169	0.0341	-0.0106
12	2	200-300	0.0167	0.0774	0.7464	0.1543	0.8737	0.0278	0.0010
12	1	300-400	0.0223	0.0685	0.6750	0.1352	0.7607	0.0240	-0.0006
13	1	0-100	0.0361	0.3131	2.8086	0.2288	16.8570	0.0209	0.0513
13	1	100-200	0.0390	0.0609	1.7822	0.1740	5.4453	0.0114	0.0208
13	1	200-300	0.0302	0.0390	0.2445	0.0535	0.1705	0.0092	-0.0035
13	1	300-400	0.0238	0.0392	0.5178	0.0418	0.1468	0.0056	-0.0059
13	2	400-500	0.0244	0.0393	0.2617	0.0408	0.0937	0.0083	-0.0027
13	2	0-100	0.0349	0.0553	0.6056	0.4927	0.7507	0.0162	0.0075
13	2	100-200	0.0286	0.0462	0.3443	0.2755	0.2092	0.0095	-0.0019
13	2	200-300	0.0328	0.0431	0.2655	0.1166	0.1605	0.0131	-0.0026
13	2	300-400	0.0319	0.0467	0.2191	0.0784	0.1241	0.0114	0.0000
13	3	400-500	0.0304	0.0421	0.3037	0.0582	0.1451	0.0099	-0.0004

13	3	0-100	0.0520	0.0732	3.2307	0.6679	26.8895	0.0173	0.0752
13	3	100-200	0.0503	0.0577	0.4646	0.1401	4.4652	0.0113	0.0495
13	3	200-300	0.0332	0.0632	0.9803	0.0865	3.0225	0.0110	0.0067
13	3	300-400	0.0364	0.0740	0.3876	0.0820	4.0527	0.0116	0.0060
13	1	400-500	0.0269	0.0724	2.4166	0.0774	5.9149	0.0144	0.0086
14	1	300-400	0.0301	0.1295	1.5470	0.4337	0.7497	0.0206	0.0046
14	1	400-500	0.0397	0.1222	1.4836	0.6142	0.3894	0.0191	0.0624
14	1	0-100	0.0310	0.1075	1.5427	0.3639	0.2500	0.0156	0.0287
14	2	100-200	0.0323	0.1276	1.4795	0.5170	0.4615	0.0224	0.0514
14	2	200-300	0.0271	0.6280	1.5612	0.0861	1.5079	0.0146	0.0107
14	2	300-400	0.0223	0.0352	0.9475	0.0423	0.1217	-0.0017	0.0441
14	1	0-100	0.0147	0.0552	0.3391	0.0587	0.0615	0.0018	-0.0002
15	1	0-100	0.0048	0.0833	0.1385	0.0852	0.9609	0.0271	-0.0097
15	1	100-200	0.0382	0.2309	0.1824	0.1986	0.5219	0.0251	0.1562
15	1	200-300	0.0093	0.2263	0.1852	0.0855	0.9793	0.0360	0.2466
15	1	300-400	0.0342	0.1036	0.2663	0.0774	1.0069	0.0281	0.1496
15	2	400-500	0.0156	0.1560	0.2180	0.1017	3.0014	0.0248	0.1447
15	2	0-100	0.0182	0.0830	0.2651	0.1823	2.3168	0.0277	0.0515
15	2	100-200	0.0513	0.0445	0.0705	0.1875	0.1804	0.0237	0.0789
15	2	200-300	0.0014	0.0383	0.0323	0.0500	-0.0105	0.0268	-0.0150
15	2	300-400	-0.0001	0.1624	0.0539	0.0483	-0.0469	0.0222	0.0080
15	1	400-500	0.0405	0.1802	0.0751	0.0563	0.0476	0.0249	0.0844
16	1	0-100	0.0776	0.9604	5.6122	38.7166	38.7336	0.0912	15.6187
16	1	100-200	0.0721	1.5172	7.9045	27.8184	43.9010	0.0970	8.9870
16	2	200-300	0.0318	0.3755	5.0707	17.8797	17.3434	0.0308	0.0870
16	2	0-100	0.0625	1.0298	5.9848	50.7051	32.8277	0.0597	10.8656
16	2	100-200	0.0374	0.3869	13.4823	11.2517	51.2595	0.0559	0.1103
16	3	200-300	0.0281	0.1004	1.6567	1.7420	7.9836	0.0158	0.0464
16	3	0-100	0.0577	1.6591	9.6321	32.4266	47.7562	0.1319	5.3950
16	3	100-200	0.0239	0.3382	12.5547	17.1749	62.0606	0.0934	0.0623
16	1	200-300	0.0216	0.0986	2.8053	2.1426	14.6388	0.0295	0.0169
17	1	0-100	0.0186	0.0004	0.1017	0.0529	1.5863	-0.0022	-0.0004
17	1	100-200	0.0130	-0.0015	0.3484	0.0130	0.3015	-0.0065	-0.0031
17	1	200-300	0.0130	-0.0032	0.0663	0.0217	0.5518	-0.0005	0.0010
17	1	300-400	0.0113	-0.0042	0.0677	0.0092	0.5117	-0.0076	0.0002
17	2	400-500	0.0148	-0.0043	0.0714	0.0143	0.5460	-0.0061	-0.0011

17	2	0-100	0.0121	-0.0048	0.0508	0.0145	0.7630	-0.0086	-0.0040
17	2	100-200	0.0121	-0.0021	0.0797	0.0187	1.5196	-0.0030	-0.0040
17	2	200-300	0.0109	-0.0045	0.0606	0.0148	0.9488	-0.0086	-0.0033
17	2	300-400	0.0104	-0.0030	0.0641	0.0146	0.6936	-0.0049	-0.0040
17	3	400-500	0.0132	-0.0037	0.0590	0.0186	0.4980	-0.0086	-0.0048
17	3	0-100	0.0102	-0.0040	0.1215	0.0244	0.0667	-0.0072	-0.0020
17	3	100-200	0.0117	-0.0037	0.0866	0.0194	0.0237	-0.0032	-0.0025
17	3	200-300	0.0128	-0.0039	0.0973	0.0301	0.0639	-0.0088	-0.0023
17	1	300-400	0.0128	-0.0041	0.0885	0.0163	0.1036	-0.0117	-0.0024
18	1	0-100	0.0119	0.0090	0.1370	0.6170	0.6208	-0.0025	-0.0038
18	1	100-200	0.0171	0.0232	0.2151	2.6719	0.5070	0.0009	0.0017
18	2	0-100	0.0169	0.1634	0.3039	1.0907	0.2918	0.0027	0.0258
18	2	100-200	0.0179	0.0267	0.2799	0.1578	0.0144	-0.0021	-0.0010
18	3	0-100	0.0115	0.0127	0.1314	0.2850	0.1232	-0.0031	-0.0026
18	3	100-200	0.0157	0.0087	0.1221	0.1460	0.1703	0.0004	-0.0016
19	1	0-100	0.0095	0.0222	0.0891	0.1275	0.1609	0.0035	0.0095
19	1	100-200	0.0103	0.0050	0.1090	0.0628	0.0211	0.0008	0.0026
19	1	200-300	0.0098	0.0019	0.0556	0.0407	-0.0139	-0.0038	-0.0017
19	1	300-400	0.0080	0.0000	0.0410	0.0349	-0.0240	-0.0050	-0.0026
19	1	400-500	0.0110	0.0049	0.0754	0.0387	-0.0183	-0.0059	-0.0004
19	2	0-100	0.0194	0.0426	0.2130	0.5546	1.2185	0.0127	0.1252
19	2	100-200	0.0094	0.0033	0.0748	0.1033	0.0191	-0.0019	-0.0016
19	2	200-300	0.0095	0.0014	0.0659	0.0448	-0.0151	-0.0045	-0.0033
19	2	300-400	0.0106	0.0030	0.1622	0.0356	-0.0114	-0.0039	-0.0017
19	2	400-500	0.0106	0.0007	0.0601	0.0233	-0.0242	-0.0043	-0.0035
19	3	0-100	0.0098	-0.0031	0.0290	0.0304	0.0011	-0.0050	-0.0042
19	3	100-200	0.0079	-0.0020	0.0470	0.0224	0.0065	-0.0088	-0.0026
19	3	200-300	0.0091	-0.0001	0.5361	0.0166	-0.0214	-0.0065	-0.0021
19	3	300-400	0.0094	0.0072	0.0944	0.0237	-0.0260	-0.0063	-0.0047
19	3	400-500	0.0166	0.0143	0.1326	0.0354	-0.0122	-0.0025	0.0052
20	1	0-100	0.1671	0.0594	0.9822	2.5425	0.8269	0.0396	0.0780
20	1	100-200	-0.0007	0.0383	0.2865	0.5938	0.1289	0.0311	-0.0163
20	1	200-300	0.0175	0.0677	0.3834	0.4904	1.0020	0.0410	0.0080
20	1	300-400	-0.0083	0.0422	0.2396	0.3254	0.3019	0.0374	-0.0048
20	1	400-500	-0.0062	0.0402	0.1422	0.1758	0.1869	0.0291	0.0517
20	2	0-100	0.0007	0.0449	0.8879	0.2489	0.5649	0.0491	-0.0127

20	2	100-200	-0.0004	0.0299	0.2015	0.2013	0.1786	0.0308	0.0096
20	2	200-300	-0.0147	0.0207	0.1038	0.1320	0.0802	0.0352	-0.0027
20	2	300-400	0.0083	0.0261	0.0835	0.1072	0.1253	0.0319	0.0041
20	2	400-500	-0.0167	0.0204	0.0783	0.0888	0.0529	0.0576	-0.0027
20	3	0-100	0.0657	0.0655	0.9314	0.4593	0.7196	0.0397	0.0143
20	3	100-200	-0.0111	0.0367	0.2675	0.2278	0.1993	0.0315	-0.0110
20	3	200-300	-0.0182	0.0287	0.1495	0.1716	0.0258	0.0352	-0.0040
20	3	300-400	-0.0114	0.0242	0.1209	0.1299	-0.0156	0.0324	-0.0139
20	3	400-500	-0.0121	0.0375	0.1128	0.1455	-0.0108	0.0347	0.0096
21	1	0-100	-0.0071	0.1198	0.7959	0.1067	2.9061	0.0532	-0.0086
21	1	100-200	-0.0020	0.0840	0.6163	0.0839	0.9157	0.0322	-0.0165
21	1	200-300	-0.0013	0.0534	0.3467	0.1092	0.0699	0.0270	-0.0204
21	1	300-400	0.0173	0.1220	0.4059	0.0943	0.6254	0.0267	-0.0138
21	1	400-500	0.0063	0.0316	0.1960	0.0691	0.0283	0.0237	-0.0209
21	2	0-100	0.0148	0.1273	1.8547	0.2493	13.4580	0.0439	-0.0032
21	2	100-200	0.0044	0.0727	0.7352	0.1045	1.8669	0.0314	-0.0213
21	2	200-300	0.0143	0.0611	0.5015	0.0506	0.2742	0.0232	-0.0209
21	2	300-400	0.0155	0.0414	0.2806	0.0845	0.0189	0.0214	-0.0168
21	2	400-500	0.0182	0.0577	0.2185	0.0809	0.0166	0.0226	-0.0207
21	3	0-100	0.0285	0.0595	0.7615	0.1184	1.3783	0.0310	-0.0160
21	3	100-200	0.0020	0.0722	0.5801	0.1008	0.5140	0.0308	-0.0225
21	3	200-300	-0.0072	0.0757	0.3797	0.0927	0.0289	0.0261	-0.0140
21	3	300-400	-0.0067	0.0299	0.1937	0.0602	0.0160	0.0229	-0.0156
21	3	400-500	-0.0023	0.0323	0.1763	0.0891	0.0350	0.0226	-0.0113
22	1	0-100	0.0366	1.0400	4.6776	0.4837	9.5543	0.0404	0.0699
22	1	100-200	0.0070	0.2315	10.5010	0.1134	6.6005	0.0304	-0.0200
22	1	200-300	0.0160	0.2334	3.4996	0.1340	2.0279	0.0354	-0.0077
22	1	300-400	-0.0057	0.1958	1.1325	0.0514	0.4944	0.0256	0.0006
22	2	0-100	-0.0035	0.1228	2.0202	0.2263	2.0854	0.0242	0.0049
22	2	100-200	0.0091	0.3289	2.7747	0.2706	2.2746	0.0349	0.0624
22	2	200-300	-0.0091	0.1780	5.9226	0.1526	2.6079	0.0535	0.0108
22	2	300-400	-0.0079	0.1437	3.6985	0.1203	1.1430	0.0305	0.0182
22	2	400-500	-0.0073	0.1679	1.5753	0.1207	0.4754	0.0292	0.1880
22	3	0-100	0.0172	0.4902	2.8633	0.2481	9.6590	0.0404	0.0702
22	3	100-200	0.0041	0.2863	5.2107	0.2716	7.1458	0.0290	0.0631
22	3	200-300	-0.0157	0.1110	4.5634	0.1499	4.4620	0.0269	0.0222

22	3	300-400	-0.0136	0.0835	1.6525	0.1180	1.0069	0.0289	0.0286
22	3	400-500	-0.0163	0.0306	0.9188	0.0411	0.5341	0.0277	0.0121
23	1	0-100	0.0065	0.2824	0.4463	0.0799	0.8160	0.1540	0.2535
23	1	100-200	-0.0146	0.3563	2.2348	0.1058	14.1080	0.1332	0.0340
23	1	200-300	-0.0097	0.0873	0.8564	0.0342	5.7129	0.0945	-0.0054
23	1	300-400	-0.0125	0.0513	0.4312	0.0478	1.3011	0.0850	-0.0015
23	1	400-500	0.0090	0.0403	0.3101	0.0439	0.3539	0.0811	-0.0060
23	2	0-100	0.0008	0.1437	1.0134	0.1022	4.4255	0.1019	0.1138
23	2	100-200	-0.0075	0.9689	0.8185	0.0987	3.2190	0.1252	0.1183
23	2	200-300	-0.0077	0.1669	2.8170	0.0803	15.3760	0.1129	0.0033
23	2	300-400	0.0027	0.0883	2.9721	0.0820	6.2764	0.0523	0.0071
23	2	400-500	0.0010	0.0280	0.2958	0.0649	0.2046	0.0403	0.0006
23	3	400-500	-0.0024	0.1409	1.3810	0.1849	12.2130	0.0861	0.0257
23	3	0-100	-0.0098	0.4732	2.1506	0.1461	9.1598	0.0568	0.0218
23	3	100-200	-0.0016	0.4133	2.1709	0.1578	7.2382	0.0912	0.0199
23	3	200-300	0.0044	0.3241	1.7258	0.1914	5.9170	0.1032	0.0350
23	3	300-400	-0.0003	0.2386	1.4330	0.2107	7.6262	0.1350	0.0775
24	1	0-100	0.4637	1.7768	11.7570	101.4700	2.0463	0.6554	0.2351
24	1	100-200	0.0659	0.3068	5.8670	34.3660	1.1134	0.3651	0.0426
24	1	200-300	0.0477	0.2311	2.9230	23.2320	0.4467	0.3158	0.0204
24	1	300-400	0.0112	0.2099	0.2419	0.4235	0.0314	0.0343	0.0034
24	1	400-500	0.0046	0.4017	0.1978	0.0657	-0.0010	0.0301	-0.0050
24	2	0-100	0.0297	3.6150	9.8330	360.8500	1.4249	1.8833	0.0395
24	2	100-200	0.0256	8.7097	13.3120	436.1400	1.3252	2.5544	0.0187
24	2	200-300	0.0177	18.9530	14.5890	332.2700	0.7264	2.1696	0.0266
24	2	300-400	0.0830	18.0600	15.5170	246.3900	0.6895	1.0211	0.1377
24	2	400-500	0.0102	2.6046	5.8729	77.8910	0.0234	0.2161	-0.0029
24	3	0-100	0.0189	2.1802	11.3980	245.2800	0.7509	0.9765	0.0007
24	3	100-200	0.0164	2.9686	10.9110	146.6900	0.3909	0.8558	0.0158
24	3	200-300	0.0131	4.1215	4.9090	42.2180	0.1115	0.2721	0.0073
24	3	300-400	0.0121	0.2724	3.2281	18.4610	0.0654	0.1692	0.0063
24	3	400-500	0.0155	0.0744	1.0895	3.4023	0.0444	0.0827	0.0115
25	1	0-100	0.2567	0.2507	1.1747	0.7567	3.7515	0.0409	0.3661
25	1	100-200	0.1748	0.1094	0.7755	0.4643	1.2084	0.0198	0.1750
25	1	200-300	0.0446	0.0780	0.4354	0.2011	0.3302	0.0108	0.0250
25	2	0-100	0.0427	0.2458	0.8605	0.1765	10.3071	0.0647	0.0700

25	2	100-200	0.0433	0.1793	0.3973	0.0863	5.0602	0.0181	0.0575
25	2	200-300	0.0351	0.0845	0.4179	0.0550	1.0943	0.0135	0.0505
25	2	300-400	0.0402	0.0795	0.5138	0.0646	0.9292	0.0098	0.0452
25	2	400-500	0.0308	0.0672	0.4458	0.0568	0.4396	0.0067	0.0063
25	3	0-100	0.0331	0.0550	0.3906	0.0722	0.1788	0.0077	0.0048
25	3	100-200	0.0359	0.0343	0.1555	0.0351	0.0308	0.0109	0.0043
25	3	200-300	0.0282	0.0302	0.1891	0.0295	0.0417	0.0093	0.0009
25	3	300-400	0.0309	0.0293	0.1172	0.0307	0.0245	0.0065	0.0025
25	3	400-500	0.0301	0.0319	0.3761	0.0386	0.0391	0.0102	0.0004
26	1	100-200	0.0449	0.0718	0.6048	0.3355	0.6915	0.0149	0.0243
26	1	200-300	0.0256	0.0457	0.3786	0.1213	0.2065	0.0076	-0.0030
26	1	0-100	0.0274	0.0495	0.3910	0.2797	0.3603	0.0134	0.0047
26	1	100-200	0.0227	0.0457	0.3977	0.1092	0.0572	0.0099	-0.0020
26	1	200-300	0.0618	0.0585	0.4683	0.2065	0.2537	0.0172	0.0245
26	2	300-400	0.0330	0.0495	0.4388	0.0861	0.0831	0.0090	0.0002
26	2	400-500	0.0689	0.0609	0.5376	0.0837	0.0916	0.0113	0.0069
26	2	0-100	0.0473	0.0516	0.4300	0.0770	0.0707	0.0090	-0.0024
26	2	100-200	0.0310	0.0517	0.4705	0.0664	0.0486	0.0141	-0.0016
26	2	200-300	0.0327	0.0517	0.4134	0.0674	0.0348	0.0153	0.0232
26	3	300-400	0.0298	0.0545	0.4579	0.0783	0.0356	0.0107	-0.0001
26	3	400-500	0.0289	0.0463	0.4053	0.0662	0.0618	0.0092	-0.0022
26	3	0-100	0.0298	0.0500	0.4615	0.0594	0.0262	0.0114	-0.0038
26	3	100-200	0.0301	0.0510	0.5257	0.0677	0.1023	0.0162	-0.0046
26	3	200-300	0.0268	0.0459	0.3713	0.0650	0.0557	0.0140	-0.0026
27	1	0-100	-0.0087	0.2553	0.2175	0.3300	0.7429	0.0191	0.1459
27	1	100-200	-0.0240	0.4205	1.1274	0.0968	0.6032	0.0671	0.0104
27	1	200-300	-0.0300	0.4406	2.3041	0.0986	0.5982	0.0803	0.0104
27	1	300-400	-0.0207	0.7235	1.3876	0.1082	0.5126	0.0846	0.0484
27	2	0-100	-0.0177	0.9428	0.6869	0.1512	1.1223	0.0372	0.0216
27	2	100-200	-0.0166	4.9271	3.1294	0.1741	7.0508	0.1259	0.0366
27	2	200-300	-0.0354	4.0138	3.3310	0.0908	3.6479	0.1053	0.0089
28	1	0-100	0.1128	4.8202	24.4970	2.2056	109.6500	1.2244	0.1956
28	1	100-200	0.0029	2.0883	18.4750	0.6395	90.5390	0.5611	0.0617
28	1	200-300	-0.0128	0.8764	13.8350	0.6587	72.8410	0.4192	0.0629
28	1	300-400	-0.0173	0.4440	11.9270	0.5442	59.1540	0.3142	0.0553
28	1	400-500	-0.0189	0.0792	11.2050	0.4728	52.2740	0.3130	0.0870

28	2	0-100	0.0789	0.9181	28.2390	1.1946	92.9930	0.8827	0.1189
28	2	100-200	0.1251	0.4403	31.8380	1.2104	102.0000	0.9276	0.2159
28	2	200-300	-0.0081	0.1865	38.5420	0.3655	93.4830	0.3085	0.0202
28	3	0-100	0.0448	4.9318	18.9960	1.6492	73.6660	0.9904	0.1045
28	3	100-200	-0.0128	1.0185	16.0300	0.5873	70.2630	0.8595	0.0380
28	3	200-300	-0.0283	0.2525	31.4790	0.1988	166.9000	0.8797	0.0036
28	3	300-400	-0.0211	0.1547	40.4170	0.1297	218.3900	0.5010	-0.0052
28	3	400-500	-0.0250	0.0981	51.6120	0.1121	206.2600	0.1638	-0.0080
29	1	300-400	-0.0149	1.4186	2.6128	1.3628	51.6810	0.4811	0.0519
29	1	0-100	0.0406	1.6875	3.9155	0.6138	57.3700	0.3328	0.1786
29	1	100-200	0.0562	1.6302	4.5549	0.5169	64.4960	0.4496	0.1054
29	1	200-300	0.0006	2.0863	4.4000	0.8060	71.0910	0.7061	0.0911
29	2	0-100	0.0752	1.8487	6.6593	0.7508	135.7700	0.6988	0.2757
29	2	100-200	0.0554	1.7422	8.4925	0.6108	151.6300	0.9669	0.1792
29	2	200-300	0.1528	0.4841	5.8301	0.5220	98.5560	0.8900	0.4804
29	2	300-400	-0.0151	0.4929	3.1870	0.7655	72.2000	0.5768	0.0261
29	2	400-500	-0.0270	0.5375	2.3492	0.8840	63.7710	0.4311	-0.0083
29	3	0-100	1.2397	0.4461	5.3708	1.4811	96.8290	0.5548	2.5572
29	3	100-200	-0.0011	0.0672	2.6936	0.2439	37.7490	0.1881	0.0448
29	3	200-300	-0.0228	0.0281	0.3349	0.0957	4.2096	0.0334	-0.0018
29	3	300-400	-0.0219	0.0213	0.0969	0.0565	0.6752	0.0229	-0.0098
30	1	0-100	0.0031	0.3696	2.3094	0.1861	7.3860	0.0983	0.0674
30	1	100-200	0.0006	0.1786	2.8529	0.1052	2.6669	0.0823	0.0271
30	1	200-300	-0.0171	0.0379	0.8852	0.0473	0.1484	0.0352	-0.0104
30	1	300-400	0.0469	0.0431	0.4406	0.1618	0.0648	0.0307	0.0398
30	1	400-500	-0.0013	0.0259	0.2256	0.0594	0.0034	0.0274	-0.0021
30	2	0-100	-0.0139	0.2301	1.1786	0.2334	7.1703	0.0545	0.0501
30	2	100-200	-0.0104	0.0368	0.8119	0.0501	0.3501	0.0341	-0.0092
30	2	200-300	-0.0077	0.0343	0.5362	0.1904	0.0221	0.0285	-0.0001
30	2	0-100	0.0035	0.0364	0.4045	0.1320	0.4096	0.0293	0.0585
30	2	100-200	-0.0123	0.0266	0.1944	0.0617	0.0088	0.0287	0.0097
30	3	200-300	-0.0121	0.0259	0.1867	0.0310	-0.0264	0.0285	-0.0144
30	3	300-400	0.0072	0.0263	0.2212	0.0702	-0.0417	0.0282	0.0200
30	3	400-500	-0.0105	0.0197	0.1836	0.0271	-0.0514	0.0331	-0.0035
31	3	0-100	0.4411	2.6978	27.1130	6.5802	136.8900	1.2501	0.4470
31	3	100-200	1.0442	4.4340	36.3770	257.7500	8.4359	1.9076	1.0110

31	1	200-300	0.3172	5.1021	44.6820	8.1521	247.6400	1.9306	0.4208
31	1	300-400	0.1391	2.7780	20.3680	2.8872	136.2800	0.6672	0.2060
31	1	400-500	0.0429	2.1637	14.7720	1.8807	101.3400	0.3958	0.1196
31	1	0-100	1.1447	3.3684	25.4850	17.5220	151.4000	1.8275	2.0922
31	1	100-200	0.5193	4.8808	40.5230	8.9404	281.6500	1.7887	0.6865
31	2	200-300	0.0984	4.2306	22.9750	3.0550	162.3500	0.8037	0.2501
31	2	300-400	0.0804	4.1613	22.1630	4.0629	113.1500	0.7402	0.1202
31	2	400-500	0.0919	1.0012	6.0801	1.2656	36.9410	0.2830	0.3342
31	2	0-100	0.1697	1.1449	6.8605	1.5952	36.3710	0.2971	0.4018
31	2	100-200	0.0781	0.6198	3.3187	1.7676	17.2240	0.2132	0.2440
31	3	200-300	0.0797	0.4927	2.4977	1.8913	12.9800	0.2223	0.1342
31	3	300-400	0.0738	0.5326	2.8268	1.7757	13.9350	0.2318	0.2029
31	3	400-500	0.0372	0.3843	2.0192	1.3278	13.0890	0.2375	0.3312
32	3	0-100	0.0142	0.0657	0.5554	0.1419	0.1008	0.0006	-0.0037
32	3	100-200	0.0157	0.1328	1.1426	0.2871	0.1813	0.0086	-0.0035
32	1	200-300	0.0162	0.0523	0.4169	0.1215	0.0342	0.0068	0.0023
32	1	300-400	0.0131	0.0272	0.2411	0.0777	0.1236	-0.0015	-0.0024
32	1	400-500	0.0136	0.0180	0.2557	0.0484	-0.0315	-0.0087	-0.0023
32	1	0-100	0.0149	0.0189	0.1985	0.0796	0.0461	0.0020	-0.0020
32	1	100-200	0.0217	0.0618	0.4648	0.2092	0.1801	0.0008	0.0081
32	2	200-300	0.0149	0.0319	0.2425	0.0874	0.1023	-0.0006	-0.0014
32	2	300-400	0.0137	0.0470	0.3652	0.1111	0.0452	-0.0015	-0.0042
32	2	400-500	0.0149	0.0234	0.2138	0.0547	0.1199	-0.0040	-0.0041
32	2	0-100	0.0891	0.0472	0.4188	0.1225	0.1519	0.0023	0.0014
32	2	100-200	0.0157	0.0500	0.4079	0.1341	0.0795	-0.0036	-0.0016
32	3	200-300	0.0157	0.0217	0.2143	0.0774	0.2255	-0.0026	-0.0007
32	3	300-400	0.0226	0.0603	0.4549	0.1590	0.0946	-0.0045	0.0061
32	3	400-500	0.0185	0.0639	0.6094	0.1478	0.1279	-0.0051	-0.0042
33	3	0-100	0.0203	0.0253	0.1120	0.6401	0.3661	0.0109	0.0060
33	3	100-200	0.0219	0.0256	0.0876	0.4895	0.1986	0.0082	0.0045
33	1	200-300	0.0670	0.0994	0.7410	0.3858	0.4250	0.0146	0.0943
33	1	300-400	0.0526	0.1154	1.1049	0.4265	0.2432	0.0186	0.0132
33	1	400-500	0.0299	0.0654	0.3113	0.1802	0.1778	0.0133	0.0185
33	2	0-100	0.1214	0.5087	2.5617	1.0208	16.0377	0.0626	0.0898
33	2	100-200	0.0407	0.0830	0.5963	0.2388	0.3230	0.0173	0.0182
33	2	200-300	0.0374	0.0586	0.6309	0.2175	0.2524	0.0179	0.0360

33	3	0-100	0.0217	0.0233	0.0619	0.0703	0.0133	0.0090	0.0000
33	3	100-200	0.0540	1.0098	1.8408	0.7373	27.3994	0.0836	0.3201
33	3	200-300	0.0434	0.0835	0.5300	0.1451	0.6342	0.0131	0.0622
34	1	0-100	0.0303	0.0506	0.3903	0.4421	0.1411	0.0109	0.1107
34	1	100-200	0.0289	0.0439	0.9425	0.2070	0.0829	0.0109	0.0017
34	1	200-300	0.0274	0.0473	0.8798	0.1261	0.0474	0.0113	-0.0030
34	1	300-400	0.0274	0.0455	0.3993	0.1145	0.0299	0.0148	-0.0025
34	1	400-500	0.0290	0.0491	0.3843	0.1298	0.0659	0.0110	-0.0020
34	2	0-100	0.0328	0.0551	0.6595	0.6074	0.1487	0.0118	-0.0003
34	2	100-200	0.0299	0.0474	0.3894	0.3072	0.0782	0.0121	-0.0020
34	2	200-300	0.0397	0.0482	0.3707	0.2985	0.1429	0.0114	0.0163
34	2	300-400	0.0302	0.0514	0.4600	0.1934	0.1455	0.0179	0.0009
34	2	400-500	0.0331	0.0517	0.8238	0.1813	0.0100	0.0108	-0.0044
34	3	0-100	0.0701	0.0612	0.6014	0.6535	0.8382	0.0096	0.0811
34	3	100-200	0.0444	0.0650	0.6858	0.1141	0.0658	0.0091	0.0016
34	3	200-300	0.0279	0.0497	0.5329	0.0953	0.0303	0.0127	-0.0028
34	3	300-400	0.0271	0.0490	0.3901	0.1810	0.0524	0.0122	-0.0034
34	3	400-500	0.0296	0.0458	0.5862	0.0839	0.0654	0.0107	-0.0026
35	1	0-100	0.0389	0.1350	1.0621	11.7790	0.0547	0.0900	0.0356
35	1	100-200	0.0385	0.1103	0.6865	6.5612	0.0317	0.0908	0.0439
35	1	200-300	0.0249	0.1339	0.3356	2.2268	0.0605	0.1604	0.1134
35	1	300-400	0.0308	0.1129	0.7344	3.3763	0.0595	0.1650	0.1240
35	1	400-500	0.0206	0.1006	0.9024	3.1682	0.0024	0.1349	0.0490
35	2	0-100	0.0655	0.1268	0.4939	3.0076	0.1154	0.0323	0.0056
35	2	100-200	0.0439	0.1329	1.9310	17.5400	0.0696	0.1228	0.0340
35	2	200-300	0.0301	0.0424	1.7295	22.1960	0.0114	0.0865	0.0167
35	2	300-400	0.0999	0.0659	0.3909	5.9398	0.0150	0.0702	0.0368
35	2	400-500	0.0203	0.1486	0.3692	1.4704	0.0002	0.0988	0.0252
35	3	0-100	0.1478	0.3615	1.8115	17.9690	0.1321	0.1591	0.0932
35	3	100-200	0.0438	0.3013	1.6068	12.2800	0.0531	0.1695	0.0973
35	3	200-300	0.0247	0.1416	0.7091	7.9390	0.0931	0.1763	0.1537
35	3	300-400	0.0242	0.1773	0.5464	4.0500	0.1001	0.1556	0.1341
35	3	400-500	0.0214	0.1124	0.7687	2.7509	0.0481	0.1456	0.1070
36	1	0-100	0.0585	5.0196	2.8262	2.6994	66.9660	0.4726	0.4643
36	1	100-200	0.0093	5.9320	4.0368	1.5599	98.5150	0.4362	0.0314
36	1	200-300	-0.0039	5.8762	3.2812	0.9496	58.7550	0.1556	-0.0059

36	1	300-400	-0.0149	2.6550	2.3431	0.4372	18.9300	0.0998	-0.0217
36	2	0-100	0.0564	2.3465	6.6398	2.4740	81.0290	0.4154	0.2399
36	2	100-200	0.1577	4.1011	4.7570	2.9528	67.6830	0.4838	0.6422
36	2	200-300	0.2309	5.8580	4.7129	2.9745	42.8240	0.3003	0.3117
36	2	300-400	-0.0030	4.0103	3.2356	1.0936	37.8760	0.3207	0.0032
36	2	400-500	-0.0168	5.0732	2.7679	0.2822	34.6990	0.2889	0.0079
36	3	0-100	0.0471	24.7780	6.6080	3.2401	112.5400	0.8718	0.1344
36	3	100-200	0.4444	8.7496	6.7756	5.0303	127.3100	0.7287	1.6052
36	3	200-300	0.0044	2.2316	4.1179	0.8735	85.4770	0.3855	0.0126
36	3	300-400	0.0023	1.2532	4.7187	0.5683	63.3990	0.2430	-0.0081
36	3	400-500	-0.0029	0.9168	3.2040	0.4028	46.4190	0.1800	-0.0187
37	1	0-100	0.0137	1.0671	2.4160	0.1552	29.4481	0.0102	0.0023
37	1	100-200	0.0191	0.1611	0.9575	0.0667	3.2261	0.0040	0.0126
37	1	200-300	0.0128	0.0097	0.3230	0.0327	0.5525	-0.0012	-0.0021
37	1	300-400	0.0133	0.0043	0.2995	0.0269	0.1219	-0.0045	-0.0039
37	1	400-500	0.0108	0.0088	0.2594	0.0297	0.0920	-0.0012	0.0042
37	2	0-100	0.0134	0.4206	1.1268	0.1404	15.7490	0.0062	-0.0004
37	2	100-200	0.0172	0.2191	0.5443	0.0799	3.4540	0.0007	0.0016
37	2	200-300	0.0303	0.2061	1.1481	0.1050	3.2027	0.0005	0.0102
37	2	300-400	0.0156	0.1287	0.3875	0.0869	1.7434	0.0044	0.0025
37	2	400-500	0.0280	0.1351	2.2842	0.1611	1.2105	0.0062	0.0127
37	3	0-100	0.0192	0.3061	1.2253	0.2692	15.7908	0.0121	0.0140
37	3	100-200	0.0147	0.7026	0.5793	0.0794	4.9440	0.0119	0.0060
37	3	200-300	0.0113	1.4550	0.6762	0.0589	4.9314	0.0096	0.0007
37	3	300-400	0.0098	1.4434	1.1335	0.0547	6.3386	0.0118	0.0013
37	3	400-500	0.0077	1.0045	1.4640	0.0439	1.3566	0.0023	-0.0005
38	1	0-100	-0.0244	0.1355	0.1319	0.0699	0.3924	0.0167	-0.0093
38	1	100-200	-0.0155	0.0599	0.0556	0.1146	0.1470	0.0104	0.0010
38	1	200-300	-0.0150	0.0294	0.0346	0.0475	0.1090	0.0093	-0.0030
38	1	300-400	-0.0182	0.0254	0.0372	0.0474	0.0767	0.0090	-0.0051
38	1	400-500	-0.0029	0.0340	0.0664	0.1021	0.1281	0.0089	0.0142
38	2	0-100	0.0419	0.1537	0.6750	0.8414	3.1569	0.0156	0.0215
38	2	100-200	0.0764	0.1009	0.3428	0.3944	2.3260	0.0150	0.0507
38	2	200-300	0.0070	0.0802	0.0434	0.3173	0.0266	0.0176	0.0240
38	2	300-400	0.0204	0.1195	0.1045	0.0142	0.0900	0.0188	0.0070
38	2	400-500	0.0116	0.1468	0.0487	-0.1451	0.0230	0.0297	0.0126

38	3	0-100	0.0403	0.1698	1.0083	16.4390	0.3626	0.0229	0.0005
38	3	100-200	0.0133	0.1375	0.5169	0.9368	0.1230	0.0558	0.0030
38	3	200-300	0.0141	0.3107	0.5434	0.5485	0.2147	0.0921	0.0160
38	3	300-400	0.0214	0.7066	0.4701	1.0029	0.4547	0.1529	0.0282
39	1	0-100	0.1998	0.2977	4.6224	4.7970	9.5503	0.1011	0.2919
39	1	100-200	0.0226	0.2449	1.3143	1.7672	2.1987	0.0291	0.0826
39	1	200-300	-0.0095	1.2682	2.9595	2.1935	14.8340	0.0947	0.0152
39	1	300-400	-0.0134	1.7771	2.2784	0.9918	13.2540	0.1174	0.0509
39	1	400-500	-0.0218	2.5692	1.7297	0.3387	9.0239	0.1120	-0.0082
39	2	0-100	0.0140	0.3371	5.1065	3.5425	8.4266	0.0921	0.0234
39	2	100-200	-0.0122	0.6319	3.6709	2.4481	22.0080	0.1547	0.0170
39	2	200-300	-0.0137	1.9345	2.7209	1.1382	16.4230	0.1766	0.0134
39	2	300-400	0.0023	3.7543	2.8406	0.4415	16.0030	0.1463	0.0806
39	2	400-500	-0.0184	2.0144	3.0158	0.3791	13.2700	0.1754	0.0057
39	3	0-100	0.2620	0.4571	6.9527	10.3480	13.7340	0.0848	0.4406
39	3	100-200	0.0384	0.4739	3.1001	5.1775	5.7053	0.0536	0.0409
39	3	200-300	0.0023	0.4183	4.2846	2.7100	22.2490	0.1512	0.0836
39	3	300-400	-0.0156	0.5231	2.7904	1.4501	8.8259	0.1558	0.0445
39	3	400-500	0.0000	0.7524	2.3603	1.2841	4.6181	0.1695	0.0155
40	1	300-400	0.0285	0.1354	1.4837	0.0970	3.6331	0.0180	0.0166
40	1	400-500	0.0268	0.0822	0.6730	0.0791	0.8256	0.0131	0.0090
40	1	0-100	0.0329	0.1486	0.5778	0.0925	0.5905	0.0138	0.0172
40	1	100-200	0.0291	0.0921	0.7775	0.0762	1.1670	0.0142	0.0024
40	1	200-300	0.0258	0.0610	0.2598	0.0603	0.8975	0.0159	-0.0004
40	2	300-400	0.0282	0.4395	0.4089	0.0648	0.7754	0.0127	0.0836
40	2	400-500	0.0258	0.4437	0.4090	0.0701	0.5095	0.0130	0.0806
40	2	0-100	0.0314	0.3568	1.1469	0.0713	0.6099	0.0111	0.0713
40	2	100-200	0.0298	0.1673	0.5959	0.0555	0.3095	0.0132	0.0658
40	2	200-300	0.0329	0.1217	0.5080	0.0456	0.2514	0.0100	0.0703
40	3	300-400	0.0509	0.1422	0.8281	0.1841	17.0921	0.0205	0.0090
40	3	400-500	0.0358	0.0796	0.6004	0.1336	5.8016	0.0111	0.0056
40	3	0-100	0.0298	0.0460	0.2255	0.1070	0.6625	0.0148	0.0474
40	3	100-200	0.0313	0.0430	0.2424	0.0853	0.5330	0.0127	0.0632
40	3	200-300	0.0497	0.0431	0.3151	0.0577	0.4977	0.0132	0.0630

Site number	pH(H2O)	NO3 mg/l	Na mg/l	K mg/l	Ca mg/l	Mg mg/l	Cl mg/l	SO4 mg/l	PO4 mg/l	EC mS/(me	Li ug/l	Be ug/l
6	6.35	11.97	8.47	0.84	9.14	3.72	4.38	5.08	0.00	12.00	3.71	7.16
20	6.95	9.09	7.21	0.97	2.82	2.02	12.72	1.45	0.00	7.00	2.45	3.32
21a	7.83	0.22	15.24	3.44	26.49	14.10	40.13	1.70	0.00	29.00	0.85	0.14
21b	7.74	1.42	53.10	2.10	141.90	123.50	611.60	186.70	0.00	164.00		
27	8.09	46.07	25.01	2.31	62.39	39.48	35.22	160.24	0.00	63.00		
28a	7.75	238.44	83.26	9.26	92.61	61.30	106.97	118.90	0.00	128.00	7.66	0.37
28b	7.66	410.20	85.70	8.90	123.10	70.60	92.90	122.10	0.00	133.00		
33a	8.45	699.78	295.40	3.20	431.70	102.10	174.40	304.34	0.00	232.00	0.50	1.16
33b	7.29	0.09	14.20	1.40	29.30	7.90	22.60	4.80	0.09	22.00	0.00	1.15
36	7.76	53.71	18.16	1.80	56.89	34.13	31.29	52.50	0.00	54.00		
35a	7.14	18.77	33.38	3.43	26.19	19.66	86.37	28.50	0.00	42.00	18.12	0.07
35b	7.28	611.83	126.50	9.60	85.70	67.40	148.60	156.90	0.00	148.00		

B ug/l	Ti ug/l	V ug/l	Cr ug/l	Mn ug/l	Co ug/l	Ni ug/l	Cu ug/l	Zn ug/l	As ug/l	Br ug/l	Se ug/l	Sr ug/l	Mo ug/l
59.303	52.447	19.55	3.4747	1.2993	1.8549	7.7368	7.6217	31.606	16.172	106.29	19.19	107.23	0.99803
63.16	10.69	11.477	0.17271	11.759	1.926	17.022	25.734	41.003	8.5563	52.675	12.374	10.841	0
130.19	167.96	5.88	13.04	170.96	8.27	10.28	32.26	16.83	0.24	240.73	3.62	206.67	1.18
286.34	302.48	12.88	13.18	610.27	6.62	10.96	34.17	26.72	0.00	375.19	5.35	139.33	0.47
0.00	43.74	2.61	0.00	147.83	2.45	5.50	5.37	21.65	0.19	120.00	7.89	58.38	2.63
0.00	323.52	7.24	1.13	345.06	4.86	19.27	10.28	22.00	5.28	2901.13	27.66	328.36	5.45
103.99	58.43	3.06	7.45	44.55	1.87	0.00	12.99	9.16	0.00	257.34	2.92	111.84	0.68

Pd ug/l	Cd ug/l	Sn ug/l	Sb ug/l	Te ug/l	I ug/l	Ba ug/l	W ug/l	Pt ug/l	Hg ug/l	Tl ug/l	Pb ug/l	Bi ug/l	U ug/l
	0.5557	1.0021	0.27392	0.85608	29.037	16.499	0.37151	0.32102	3.2771	0.17022	0	3.3576	1.6739
	0.30409	1.1019	0.12668	0.25132	65.473	15.724	0.30152	0.46991	2.9781	0.17078	0.15664	3.285	1.3601
0.16	0.29	0.29	5.86	0.10	<0.001	38.92	0.03	0.05	0.01	0.01	9.01	0.25	0.31
0.17	0.07	0.37	3.25	0.75	<0.001	20.96	0.15	0.08	0.00	0.04	2.50	0.07	0.34
0.00	3.44	0.00	2.66	1.46	13.76	71.53	1.72	2.43	1.05	0.68	17.53	1.95	3.98
0.00	2.92	0.00	2.75	1.95	409.64	94.27	1.84	2.69	1.17	0.73	9.03	1.99	6.24
0.00	0.00	0.32	4.49	0.22	<0.001	61.73	0.12	0.00	0.04	0.02	3.48	0.20	0.05

Appendix D

Results of Statistical Analyses

Regression Summary for Dependent Variable: DEPTH (wksta.sta)

R= .58246924 R^2= .33927041 Adjusted R^2= .28788033

F(7,90)=6.6019 p<.00000 Std.Error of estimate: 11.702

	BETA	St. Err. of BETA	B	St. Err. of B	t(90)	p-level
Intercpt			48.63821	21.34789	2.278361	0.025072
PH	-0.19398	0.097552	-2.4716	1.242962	-1.98847	0.049797
ORG_C_%	-1.04096	0.257486	-10.5884	2.619085	-4.0428	0.000111
S_TOTAL_	0.038979	0.148635	3.474104	13.24764	0.262243	0.793733
N_TOTAL_	0.494774	0.236685	43.22094	20.67559	2.090434	0.039399
CLAY_%	0.136338	0.177261	0.169539	0.220427	0.76914	0.443824
SAND_%	-0.08244	0.237038	-0.0673	0.193495	-0.3478	0.7288
SILT_%	0.040667	0.181842	0.066737	0.298416	0.223638	0.823546

Regression Summary for Dependent Variable: CR (wksta.sta)

R= .70134452 R^2= .49188414 Adjusted R^2= .45236401

F(7,90)=12.446 p<.00000 Std.Error of estimate: .07679

	BETA	St. Err. of BETA	B	St. Err. of B	t(90)	p-level
Intercpt			0.089268	0.140085	0.63724	0.525586
PH	-0.07555	0.085547	-0.0072	0.008156	-0.88319	0.379489
ORG_C_%	-0.0578	0.2258	-0.0044	0.017186	-0.25598	0.798551
S_TOTAL_	0.201062	0.130344	0.134095	0.086931	1.542544	0.12645
N_TOTAL_	0.575552	0.207558	0.376218	0.135673	2.772964	0.006752
CLAY_%	-0.19506	0.155447	-0.00182	0.001446	-1.25483	0.212789
SAND_%	-0.05527	0.207868	-0.00034	0.00127	-0.2659	0.790922
SILT_%	-0.02516	0.159464	-0.00031	0.001958	-0.15779	0.874976

Regression Summary for Dependent Variable: NI (wksta.sta)

R= .63687090 R^2= .40560455 Adjusted R^2= .35937379

F(7,90)=8.7735 p<.00000 Std.Error of estimate: 7.4509

	BETA	St. Err. of BETA	B	St. Err. of B	t(90)	p-level
Intercpt			10.30665	13.59247	0.758262	0.450275
PH	-0.29214	0.092526	-2.49875	0.79141	-3.15734	0.002167
ORG_C_%	-0.56095	0.244219	-3.83033	1.667605	-2.2969	0.023944
S_TOTAL_	0.679294	0.140977	40.64359	8.434941	4.81848	5.83E-06
N_TOTAL_	0.271539	0.22449	15.92347	13.16441	1.209585	0.229606
CLAY_%	-0.24928	0.168127	-0.20809	0.140349	-1.48266	0.141657
SAND_%	0.131602	0.224825	0.072116	0.123201	0.585353	0.559775
SILT_%	0.094058	0.172472	0.103619	0.190005	0.54535	0.586862

Regression Summary for Dependent Variable: ZN (wksta.sta)

R= .51871892 R^2= .26906931 Adjusted R^2= .21221915

F(7,90)=4.7330 p<.00015 Std.Error of estimate: 32.592

	BETA	St. Err. of BETA	B	St. Err. of B	t(90)	p-level
Intercpt			70.0221	59.45742	1.177685	0.242027
PH	-0.37126	0.102604	-12.5262	3.461857	-3.61834	0.000489
ORG_C_%	0.411861	0.270819	11.09359	7.294587	1.520797	0.131816
S_TOTAL_	-0.13814	0.156332	-32.6033	36.89688	-0.88363	0.379249
N_TOTAL_	0.053184	0.248941	12.30253	57.58494	0.213642	0.83131
CLAY_%	0.20968	0.18644	0.690455	0.613926	1.124654	0.263726
SAND_%	0.065869	0.249313	0.142383	0.538917	0.264202	0.792228
SILT_%	-0.19319	0.191258	-0.83954	0.831139	-1.01011	0.315149

Regression Summary for Dependent Variable: CU (wksta.sta)

R= .77661411 R^2= .60312947 Adjusted R^2= .57226176

F(7,90)=19.539 p<.00000 Std.Error of estimate: 40.449

	BETA	St. Err. of BETA	B	St. Err. of B	t(90)	p-level
Intercpt			-71.7538	73.79035	-0.9724	0.333457
PH	0.005756	0.075605	0.327118	4.296379	0.076138	0.939478
ORG_C_%	-0.50269	0.199557	-22.805	9.053035	-2.51905	0.013533

S_TOTAL_	0.799268	0.115195	317.7172	45.79132	6.938372	5.9E-10
N_TOTAL_	-0.13619	0.183435	-53.0608	71.46649	-0.74246	0.459744
CLAY_%	-0.45991	0.137381	-2.55069	0.761921	-3.34771	0.001191
SAND_%	0.12551	0.183709	0.456944	0.668829	0.6832	0.496235
SILT_%	0.580645	0.140931	4.249832	1.031495	4.120069	8.4E-05

Regression Summary for Dependent Variable: CD (wksta.sta)

R= .74044518 R^2= .54825907 Adjusted R^2= .51312367

F(7,90)=15.604 p<.00000 Std.Error of estimate: .21153

	BETA	St. Err. of BETA	B	St. Err. of B	t(90)	p-level
Intercpt			0.266398	0.385896	0.690336	0.491759
PH	-0.35344	0.080662	-0.09845	0.022468	-4.38168	3.18E-05
ORG_C_%	0.388163	0.212905	0.086316	0.047344	1.823171	0.071597
S_TOTAL_	0.233867	0.122901	0.455689	0.239471	1.902895	0.060251
N_TOTAL_	-0.1404	0.195706	-0.26813	0.373743	-0.71742	0.474973
CLAY_%	0.037688	0.14657	0.001025	0.003985	0.257131	0.797665
SAND_%	0.131395	0.195998	0.002345	0.003498	0.67039	0.504326
SILT_%	0.19287	0.150358	0.00692	0.005394	1.282739	0.202877

Regression Summary for Dependent Variable: PB (wksta.sta)

R= .64053444 R^2= .41028437 Adjusted R^2= .36441760

F(7,90)=8.9451 p<.00000 Std.Error of estimate: .14377

	BETA	St. Err. of BETA	B	St. Err. of B	t(90)	p-level
Intercpt			0.146942	0.262274	0.560262	0.576693
PH	-0.14066	0.092161	-0.02331	0.015271	-1.5262	0.130468
ORG_C_%	0.426854	0.243256	0.056463	0.032177	1.754755	0.082704
S_TOTAL_	-0.13648	0.140421	-0.15818	0.162756	-0.97191	0.3337
N_TOTAL_	0.312111	0.223604	0.354557	0.254014	1.395817	0.166204
CLAY_%	0.075953	0.167464	0.001228	0.002708	0.453548	0.651246
SAND_%	0.038084	0.223938	0.000404	0.002377	0.170063	0.865342
SILT_%	-0.14103	0.171792	-0.00301	0.003666	-0.82092	0.413859

Strongly Bound

Regression Summary for Dependent Variable: CD (strsta.sta)

R= .79263521 R^2= .62827057 Adjusted R^2= .59935829

F(7,90)=21.730 p<.00000 Std.Error of estimate: .55289

	BETA	St. Err. of BETA	B	St. Err. of B	t(90)	p-level
Intercpt			-0.77191	1.008619	-0.76531	0.446088
PH__H2O_	-0.02127	0.073171	-0.01707	0.058726	-0.29068	0.771963
ORG_C_%	1.50361	0.193132	0.96339	0.123743	7.785386	1.13E-11
S_TOTAL_	0.052695	0.111487	0.295839	0.625909	0.472656	0.637603
N_TOTAL_	-1.10993	0.17753	-6.10734	0.976855	-6.25204	1.33E-08
CLAY_%	-0.08686	0.132958	-0.0068	0.010414	-0.65326	0.515252
SAND_%	0.079237	0.177795	0.004074	0.009142	0.445667	0.656908
SILT_%	0.259044	0.136394	0.026778	0.014099	1.899229	0.060737

Regression Summary for Dependent Variable: DEPTH (strsta.sta)

R= .58246924 R^2= .33927041 Adjusted R^2= .28788033

F(7,90)=6.6019 p<.00000 Std.Error of estimate: 11.702

	BETA	St. Err. of BETA	B	St. Err. of B	t(90)	p-level
Intercpt			48.63821	21.34789	2.278361	0.025072
PH__H2O_	-0.19398	0.097552	-2.4716	1.242962	-1.98847	0.049797
ORG_C_%	-1.04096	0.257486	-10.5884	2.619085	-4.0428	0.000111
S_TOTAL_	0.038979	0.148635	3.474104	13.24764	0.262243	0.793733
N_TOTAL_	0.494774	0.236685	43.22094	20.67559	2.090434	0.039399
CLAY_%	0.136338	0.177261	0.169539	0.220427	0.76914	0.443824
SAND_%	-0.08244	0.237038	-0.0673	0.193495	-0.3478	0.7288
SILT_%	0.040667	0.181842	0.066737	0.298416	0.223638	0.823546

Regression Summary for Dependent Variable: CR (strsta.sta)

R= .62532409 R²= .39103022 Adjusted R²= .34366591

F(7,90)=8.2558 p<.00000 Std.Error of estimate: .23002

	BETA	St. Err. of BETA	B	St. Err. of B	t(90)	p-level
Intercpt			0.091171	0.419611	0.217276	0.828485
PH__H2O_	-0.08324	0.093653	-0.02171	0.024431	-0.8888	0.376478
ORG_C_%	0.460564	0.247195	0.095916	0.05148	1.863162	0.065701
S_TOTAL_	0.087344	0.142695	0.159388	0.260393	0.612106	0.542011
N_TOTAL_	0.225847	0.227225	0.403931	0.406396	0.993935	0.322919
CLAY_%	0.072506	0.170176	0.001846	0.004333	0.426066	0.671077
SAND_%	0.088088	0.227564	0.001472	0.003803	0.38709	0.699603
SILT_%	-0.24313	0.174574	-0.00817	0.005866	-1.39272	0.167136

Regression Summary for Dependent Variable: CO (strsta.sta)

R= .40872713 R²= .16705787 Adjusted R²= .10227348

F(7,90)=2.5787 p<.01807 Std.Error of estimate: 5.3929

	BETA	St. Err. of BETA	B	St. Err. of B	t(90)	p-level
Intercpt			4.921104	9.838155	0.500206	0.618151
PH__H2O_	-0.07134	0.10953	-0.37308	0.572818	-0.65131	0.516504
ORG_C_%	0.4569	0.289101	1.907567	1.207003	1.580417	0.11752
S_TOTAL_	0.321335	0.166885	11.75539	6.105163	1.925483	0.057326
N_TOTAL_	-0.60566	0.265746	-21.7161	9.528324	-2.27911	0.025025
CLAY_%	0.195404	0.199025	0.099736	0.101584	0.981807	0.328827
SAND_%	0.051665	0.266142	0.01731	0.089172	0.194124	0.846517
SILT_%	-0.27377	0.204169	-0.18441	0.137525	-1.34092	0.183322

Regression Summary for Dependent Variable: NI (strsta.sta)

R= .28445587 R²= .08091514 Adjusted R²= .00943076

F(7,90)=1.1319 p<.35041 Std.Error of estimate: 5.8224

	BETA	St. Err. of BETA	B	St. Err. of B	t(90)	p-level
Intercpt			10.40541	10.62168	0.979639	0.32989

PH__H2O_	0.024828	0.115054	0.133456	0.618438	0.215796	0.829635
ORG_C_%	0.241399	0.303682	1.035866	1.303131	0.794906	0.42876
S_TOTAL_	0.061871	0.175302	2.326341	6.591388	0.352936	0.724961
N_TOTAL_	-0.1378	0.279149	-5.07833	10.28718	-0.49366	0.622751
CLAY_%	-0.24598	0.209064	-0.12904	0.109674	-1.1766	0.242457
SAND_%	-0.26767	0.279566	-0.09218	0.096274	-0.95746	0.340902
SILT_%	0.00811	0.214467	0.005615	0.148478	0.037816	0.969918

Regression Summary for Dependent Variable: ZN (strsta.sta)

R= .79957294 R^2= .63931688 Adjusted R^2= .61126375

F(7,90)=22.790 p<.00000 Std.Error of estimate: 67.056

	BETA	St. Err. of BETA	B	St. Err. of B	t(90)	p-level
Intercpt			-124.816	122.3275	-1.02034	0.310303
PH__H2O_	0.044099	0.072076	4.357825	7.122415	0.611847	0.542182
ORG_C_%	0.529198	0.190241	41.7477	15.00786	2.781722	0.006587
S_TOTAL_	0.472607	0.109818	326.6894	75.91155	4.303554	4.26E-05
N_TOTAL_	-0.69781	0.174873	-472.761	118.4751	-3.99039	0.000134
CLAY_%	-0.46932	0.130968	-4.52622	1.26309	-3.58345	0.00055
SAND_%	0.107949	0.175134	0.683423	1.108766	0.616381	0.539199
SILT_%	0.573234	0.134352	7.295908	1.709984	4.266654	4.89E-05

Regression Summary for Dependent Variable: CU (strsta.sta)

R= .74228141 R^2= .55098169 Adjusted R^2= .51605805

F(7,90)=15.777 p<.00000 Std.Error of estimate: 46.620

	BETA	St. Err. of BETA	B	St. Err. of B	t(90)	p-level
Intercpt			67.50638	85.04778	0.793747	0.429431
PH__H2O_	-0.01737	0.080419	-1.06965	4.951833	-0.21601	0.829468
ORG_C_%	0.984555	0.212263	48.39762	10.43416	4.63838	1.19E-05
S_TOTAL_	-0.76618	0.12253	-330.015	52.77723	-6.25298	1.32E-08
N_TOTAL_	-0.02066	0.195115	-8.72176	82.36939	-0.10589	0.915908
CLAY_%	0.395525	0.146128	2.376915	0.878159	2.706703	0.00813

SAND_%	-0.07432	0.195406	-0.29317	0.770866	-0.38031	0.704611
SILT_%	-0.52579	0.149904	-4.1699	1.18886	-3.50748	0.000708

Regression Summary for Dependent Variable: CD (strsta.sta)

R= .79263521 R²= .62827057 Adjusted R²= .59935829

F(7,90)=21.730 p<.00000 Std.Error of estimate: .55289

	BETA	St. Err. of BETA	B	St. Err. of B	t(90)	p-level
Intercpt			-0.77191	1.008619	-0.76531	0.446088
PH__H2O_	-0.02127	0.073171	-0.01707	0.058726	-0.29068	0.771963
ORG_C_%	1.50361	0.193132	0.96339	0.123743	7.785386	1.13E-11
S_TOTAL_	0.052695	0.111487	0.295839	0.625909	0.472656	0.637603
N_TOTAL_	-1.10993	0.17753	-6.10734	0.976855	-6.25204	1.33E-08
CLAY_%	-0.08686	0.132958	-0.0068	0.010414	-0.65326	0.515252
SAND_%	0.079237	0.177795	0.004074	0.009142	0.445667	0.656908
SILT_%	0.259044	0.136394	0.026778	0.014099	1.899229	0.060737

Regression Summary for Dependent Variable: PB (strsta.sta)

R= .66009139 R²= .43572064 Adjusted R²= .39183224

F(7,90)=9.9279 p<.00000 Std.Error of estimate: 9.8174

	BETA	St. Err. of BETA	B	St. Err. of B	t(90)	p-level
Intercpt			-6.16602	17.90961	-0.34429	0.731435
PH__H2O_	0.120048	0.090151	1.38858	1.042771	1.331625	0.186346
ORG_C_%	1.429866	0.237952	13.20345	2.197256	6.009061	3.9E-08
S_TOTAL_	-0.11795	0.137359	-9.54356	11.11398	-0.8587	0.392788
N_TOTAL_	-0.75894	0.218729	-60.1855	17.34558	-3.46979	0.000802
CLAY_%	-0.02253	0.163813	-0.02543	0.184925	-0.13754	0.890914
SAND_%	0.06232	0.219055	0.046182	0.162331	0.284495	0.776684
SILT_%	-0.09813	0.168046	-0.14619	0.250354	-0.58392	0.560736