MATHEMATICAL MODELLING AND SIMULATION OF MOBILITY OF HEAVY METALS IN SOIL CONTAMINATED WITH SEWAGE SLUDGE

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NOVEMBER, 2005

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A RESEARCH PROJECT SUBMITTED TO THE
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DECLARATION

I, Bello Alhassan (99/8121EH) hereby declare that this research project, "Mathematical Modelling and Simulation of Mobility of Heavy Metals in Soil Contaminated with Sewage Sludge", carried out under the supervision of Engineer Abdulfatai Jimoh and presented in partial fulfilment of the requirement for the award of Bachelor of Engineering (B. Eng.) Degree in Chemical Engineering has not been presented for any degree elsewhere, to the best of my knowledge.

Bello Alhassan

5/12/05

Date

CERTIFICATION

This is to certify that this research project titled "Mathematical Modelling and Simulation of Mobility of Heavy Metals in Soil Contaminated with Sewage Sludge" was carried out by Bello Alhassan (99/8121EH) and submitted to the Department of Chemical Engineering, School of Engineering and Engineering Technology, Federal University of Technology, Minna, Niger State, in partial fulfilment of the requirement for the award of Bachelor of Engineering (B. Eng.) Degree in Chemical Engineering.

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5/12/05
Date

Dr. F. Aberuagba
(Head of Department)

Date

External Examiner

Date

DEDICATION

This project is dedicated to Almighty Allah. Then, to my caring mother.

ACKNOWLEDGEMENT

All thanks are due to Allah, he most gracious, the most merciful, for His enormous guidance and inspiration in enabling me to commence and completed this project.

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ABSTRACT

This project aim at developing a model equation that can predict the mobility of heavy metal in the soil contaminated with sewage sludge. The model was developed and represented by the expression below $C = e^{\frac{1}{\left(1+\frac{k_d \cdot \rho_b}{\theta}\right)} \cdot t} - e^{\frac{v_x}{D_L} \cdot x}$. The developed equation was then simulated using MathCAD 2000 professional software. The experimental and model results obtained from the simulation of the developed equation were compared numerically and graphically. It was observed that there are reasonable levels of agreement between the two results. The model revealed close fitting when compared with the experimental results. This is further substantiated through the result of the correlation coefficient analysis that was found to be unity for the experiment. Thus, the model developed can be considered as a good representation of the phenomenon of mobility of heavy metals in the soil.

TABLE OF CONTENT

Title page i
Declaration ii
Certification iii
Dedication iv
Acknowledgement v
Abstract vii
Table of contents viii
List of tables xi
List of figures xii
Nomenclature xiii

CHAPTER ONE

1.0 Introduction 1
1.1 Aims and objective 3
1.2 Scope of research 3
1.3 Justification 3

CHAPTER TWO

1.0 Literature review 4
1.1 Heavy metals 4
2.2 Environmental and health risks of heavy metals 5
2.3 Soil 8
2.4 Sources of contaminants 11
2.5 Movement of heavy metals through soil contaminated with sewage sludge 14
2.6 Fate of metals in the soil environment 18
2.7 Soil solution chemistry 20
2.8 Solid phase formation of metals in soils 22

2.9 Surface reactions 23

2.10 Anions in the soil environment 25

2.11 Soil properties affecting adsorption 26

2.12 Factors affecting adsorption and precipitation 27

2.13 Behaviour of specific metals in soils 39

2.14 Influence of soil properties on mobility 48

CHAPTER THREE

3.0 Methodology 51

3.1 Sources of sample 51

3.2 Preparation of sample 51

3.3 Apparatus and instruments 51

3.4 Reagents 52

3.5 Samples 52

3.6 Experimental procedure 52

CHAPTER FOUR

4.0 Modelling 61

4.1 Conceptualization of modelling 61

4.2 Principles of mathematical formulation 61

4.3 Simulation 62

4.4 Importance of mathematical modelling 63

4.5 Modelling of mobility of heavy metals in soil 64

CHAPTER FIVE

5.0 Results and discussion 70

5.1 Results 70

5.2 Discussion of results 84

CHAPTER SIX

6.0 Conclusion and recommendations 88
6.1 Conclusion 88
6.2 Recommendation 88
References 89
Appendix 94
Appendix A: Graph 94
Appendix B: Simulation Algorithms 99

LIST OF TABLES

Table 5.1: Experimental results for 100% soil 69

Table 5.2: Experimental results for 90% soil + 10% sewage 70

Table 5.3: Experimental results for 80% soil + 20% sewage 71

Table 5.3: Experimental results for 80% soil + 20% sewage 72

Table 5.4: Experimental results for 50% soil + 50% sewage 73

Table 5.5: Experimental results for 100% sewage 74

Table 5.6: Simulated results for 100% soil 75

Table 5.7: Simulated results for 90% soil + 10% sewage 76

Table 5.8: Simulated results for 80% soil + 20% sewage 77

Table 5.9: Simulated results for 50% soil + 50% sewage 78

Table 5.10: Simulated results for 100% sewage 79

Table 5.11: Experimental and simulated results for 100% soil 80

Table 5.12: Experimental and simulated results for 90% soil + 10% sewage 81

Table 5.13: Experimental and simulated results for 80% soil + 20% sewage 82

Table 5.14: Experimental and simulated results for 50% soil + 50% sewage 83

Table 5.15: Experimental and simulated results for 100% sewage 84

LIST OF FIGURES

Fig. 2.1: Principal controls on free trace metal concentrations in soils solution (Mattigod, et al., 1981). 19

Figure 2.2: Relative mobility of cations through soil. (From Korte, Skopp, Fuller, Niebla, and Alesii, 1976). 26

Figure 2.3: Relative mobility of anions through soil. (From Korte, Skopp, Fuller, Niebla, and Alesii, 1976) 27

Figure 2.4: Effect of soil pH level on maximum Pb, Cu, Zn, and Ni retention by Dekalb and Hagerstown A and B horizons. Ni1 and Ni2 refer to two apparent sorption maxima. (Harter, 1983). 32

Figure 2.5: Selenite adsorption envelope for five alluvial soils. The intitial total selenite concentration was approximately 2 mmol kg-1 (Neal, et al., 1987a). 32

Figure 2.6: Adsorption of Cu [50 mmol m-3 (50 mM)] by Na-montmorillonite in the presence and absence of water soluble extract of sewage sludge (WSE). GEOCHEM simulations were constructed employing the "mixture model" (Baham and Sposito, 1986). 34

Figure 3.1: Experimental set up of the experiment 53

Figure 3.2: Particle size distribution for silica sand used in column experiments 54

Fig. 4.1: A visual description of the natural system being modelled 64

Fig. A1: Mobility pattern of heavy metal in soil for 100% soil 94

Fig. A2: Mobility pattern of heavy metal in soil for 100% soil 95

Fig. A3: Mobility pattern of heavy metal in soil for 100% soil 96

Fig. A4: Mobility pattern of heavy metal in soil for 100% soil 97

Fig. A5: Mobility pattern of heavy metal in soil for 100% soil 98

NOMENCLATURE

α_L	Dynamic dispersivity along length of column
C	Concentration of solute
C_0	Initial concentration of solute
C`	Mass of solute sorbed per dry unit weight of soil
D_L	Hydrodynamic dispersion coefficient along
D`	Diffusion coefficient
De	Effective diffusion coefficient
k_d	Distribution coefficient
R	Retardation factor
T	Time
v_x	Pore velocity along flow path
V	Volume
W	Weight
X	direction along column length (flow direction)
ρ_b	Soil density
θ	Moisture content of soil (simply porosity for saturated conditions)

CHAPTER ONE

1.0 INTRODUCTION

In process industries such as: fertilizer breweries, refineries, paper mills, textiles, chemical and petrochemicals, water could be used as coolant, process water, and raw material solvent. e t c. in the process of usage, industry water become polluted and contaminated with various substances. It comes in contact with and this givers rise to waste water. It consist of water with variety of potentially harmful substance which are the sources of environmental pollution (Odigure, 1998).Sewage sludge is therefore, a by – product of purification of waste water. This process of waste water treatment produces treated water that can be discharged back into the local bodies of water and sewage sludge. The resulting sewage sludge has significant organic mater content and contained macro and micró nutrient that are essential for plant growing. Swage sludge can also contain contaminant such as heavy metals, organic contaminant and pathogen. These heavy metals which may include cranium, lead, arsenic etc are metallic element with relatively high atomic weight that can contaminate ground water, surface water, food etc. and have the potential to be toxic and relatively low concentration metal (Kennish, 1992). All heavy metal exist in waste water in colloidal, particulate and dissolve phases, although dissolve concentration (kennish, 1992). The colloidal and particulate may be found in hydrozide, oxide, silicate or substance: or absorbed to clay, silica or organic mater (Connell et al; 1984).

Heavy metals released from sewage sludge are distribution throughout the soil system, while remaining in the soil solution as iron and organic and inorganic complexes are mobile for uptake by plants (Hooda et al, 1997). This mobility and availability depends on several factor including soil texture and PH (Nouri, 1980 and Alloway 1995). Mobile forms of metals release from sludge, which are not taken up by plant root, may move down the profile and reach the water table. This pollution of ground water may affect surface water and possibly portable water supplies. Changes can occur in chemical form and mobility of metal in the leachate, such as complexities of chalation which are usually the result of variation in PH or reduction-oxidation (Sims and Patrick, 1978). In situation where a concentration of heavy metal iron exist in leacheat, the PH is probably low and sorptive/precipitation of these iron will be achieved by increasing the PH (Brallier at al, 1996). Evidence for the high degree of retention of certain heavy metals in the top soil includes studies conducted in connection with the application of sewage sludge in agricultural soil (Keefer and Singh, 1986; Alloway and Jackson, 1991). Several worker have already investigated the mobility of heavy metal in the soil amended with sewage sludge and concluded that only relatively small amount of metal were available for transpory in he soil water immediately after sludge application (Slide and Kardos 1977).

Giordano and Mortvedt 1976) show that under excessive leaching condition, movement of heavy metal in soil is somewhat greater from inorganic than from complexed sources found in sewage sludge. However, little or nothing had been done as regard to modeling of the process of mobility of heavy metals in the soil after the application of sewage sludge. This research work, therefore aimed at developing a mathematical model equation that shows the mobility of heavy metals in the soil amended with sewage sludge.

Mathematically modeling is the general characterization of a process or concept in mathematical terms, thus enabling the relatively simple manipulation of variables to be accomplished in other to determine how these processes or concept would behave in different situation. (Payne 1982).

1.1 AIMS AND OBJECTIVE

The aim of this research project is to develop and simulate a mathematical model equation for the mobility of heavy metals in the soil amended with sewage sludge. This aim can be achieved through the realization of the following objectives;

i. Collection of data showing the concentration of heavy metals at different percentage of sewage sludge amended to the soil with respect to distance and time.

ii. Development of mathematical model equations for the mobility of heavy metals in the soil amended with different percentage of sewage sludge.

iii. Simulation of the model equation using a computer software programme, MathCAD 2000 professional.

iv. Compare the simulated result with the experimental data.

1.4 SCOPE OF RESEARCH

This research work will be limited to the development of mathematical model equation for the mobility of heavy metals in the soil amended with sewage sludge and the validity of the model will be verified using computer software programme, MathCAD 2000 professional. Research is restricted to be available experimental data.

1.5 JUSTIFICATION

It is unfortunate, that experimental approach for the mobility of heavy metals in the soil contaminated with sewage sludge will be time an energy consuming or probably not feasible because of lack of equipment. This research work bear the task to develop the mathematical model predicting the mobility of heavy metals in the soil as a function of time and distance.

CHAPTER TWO

3.0 LITERATURE REVIEW

3.1 Heavy Metals

The term heavy metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations. Examples of heavy metals include mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), thallium (Tl), and lead (Pb) (Chang, et al. 1989).

Heavy metals are natural components of the Earth's crust. They cannot be degraded or destroyed. To a small extent they enter our bodies via food, drinking water and air. As trace elements, some heavy metals (e.g. copper, selenium, zinc) are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning. Heavy metal poisoning could result, for instance, from drinking-water contamination (e.g. lead pipes), high ambient air concentrations near emission sources, or intake via the food chain (Chang, et al. 1989).

Heavy metals are dangerous because they tend to bioaccumulate. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted.

Heavy metals can enter a water supply by industrial and consumer waste, or even from acidic rain breaking down soils and releasing heavy metals into streams, lakes, rivers, and groundwater (Chang, et al. 1989).

2.2 Environmental and Health Risks of Heavy Metals

2.2.1 Effects of antimony on the environment

Antimony is a metal used in the compound antimony trioxide, a flame retardant. It can also be found in batteries, pigments, and ceramics and glass. Exposure to high levels of antimony for short periods of time causes nausea, vomiting, and diarrhea. There is little information on the effects of long-term antimony exposure, but it is a suspected human carcinogen. Most antimony compounds do not bioaccumulate in aquatic life.

2.2.2 Effects of Cadmium on the environment

Cadmium derives its toxicological properties from its chemical similarity to zinc an essential micronutrient for plants, animals and humans. Cadmium is biopersistent and, once absorbed by an organism, remains resident for many years (over decades for humans) although it is eventually excreted (Dowdy, et al.,1998).

In humans, long-term exposure is associated with renal disfunction. High exposure can lead to obstructive lung disease and has been linked to lung cancer, although data concerning the latter are difficult to interpret due to compounding factors. Cadmium may also produce bone defects (osteomalacia, osteoporosis) in humans and animals. In addition, the metal can be linked to increased blood pressure and effects on the myocardium in animals, although most human data do not support these findings.

The average daily intake for humans is estimated as 0.15μg from air and 1μg from water. Smoking a packet of 20 cigarettes can lead to the inhalation of around 2-4μg of cadmium, but levels may vary widely.

2.2.3 Effects of chromium on the environment

Chromium is used in metal alloys and pigments for paints, cement, paper, rubber, and other materials. Low-level exposure can irritate the skin and cause ulceration. Long-term exposure can cause kidney and liver damage, and damage too circulatory and nerve tissue. Chromium often accumulates in aquatic life, adding to the danger of eating fish that may have been exposed to high levels of chromium (Elliot, 2001).

2.2.4 Effects of Copper on the environment

Copper is an essential substance to human life, but in high doses it can cause anemia, liver and kidney damage, and stomach and intestinal irritation. People with Wilson's disease are at greater risk for health effects from overexposure to copper. Copper normally occurs in drinking water from copper pipes, as well as from additives designed to control algal growth.

2.2.5 Effects of lead on the environment

In humans exposure to lead can result in a wide range of biological effects depending on the level and duration of exposure. Various effects occur over a broad range of doses, with the developing foetus and infant being more sensitive than the adult. High levels of exposure may result in toxic biochemical effects in humans which in turn cause problems in the synthesis of haemoglobin, effects on the kidneys, gastrointestinal tract, joints and reproductive system, and acute or chronic damage to the nervous system (Elliot, 2001).

Lead poisoning, which is so severe as to cause evident illness, is now very rare indeed. At intermediate concentrations, however, there is persuasive evidence that lead can have small, subtle, subclinical effects, particularly on neuropsychological developments in children. Some studies suggest that there may be a loss of up to 2 IQ points for a rise in blood leadlevels from 10 to 20μg/dl in young children.

Average daily lead intake for adults in the UK is estimated at 1.6μg from air. 20μg from drinking water and 28μg from food. Although most people receive the bulk of their lead intake from food, in specific populations other sources may be more important, such as water in areas with lead piping and plumbosolvent water, air near point of source emissions, soil, dust, paint flakes in old houses or contaminated land. Lead in the air contributes to lead levels in food through deposition of dust and rain containing the metal, on crops and the soil. However, dietary lead exposure is well below the provisional tolerable weekly intake recommended by the UN Food and Agriculture Organisation and the World Health Organisation.

2.2.6 Effects of mercury on the environment

Mercury is a toxic substance which has no known function in human biochemistry or physiology and does not occur naturally in living organisms. Inorganic mercury poisoning is associated with tremors, gingivitis and/or minor psychological changes, together with spontaneous abortion and congenital malformation.

Monomethylmercury causes damage to the brain and the central nervous system, while foetal and postnatal exposure have given rise to abortion, congenital malformation and development changes in young children.

2.2.7 Effects of nickel on the environment

Small amounts of Nickel are needed by the human body to produce red blood cells, however, in excessive amounts, can become mildly toxic. Short-term overexposure to nickel is not known to cause any health problems, but long-term exposure can cause decreased body weight, heart and liver damage, and skin irritation. The EPA does not currently regulate nickel levels in drinking water. Nickel can accumulate in aquatic life, but its presence is not magnified along food chains (Elliot, 2001).

2.2.8 Effects of selenium on the environment

Selenium is needed by humans and other animals in small amounts, but in larger amounts can cause damage to the nervous system, fatigue, and irritability. Selenium accumulates in living tissue, causing high selenium content in fish and other organisms, and causing greater health problems in human over a lifetime of overexposure. These health problems include hair and fingernail loss, damage to kidney and liver tissue, damage to circulatory tissue, and more severe damage to the nervous system (Elliot, 2001).

2.3 Soil

Soil is what you find under your feet. Think of soil as a thin living skin that covers the land. It goes down into the ground just a short way. Even the most fertile topsoil is only a foot or so deep. Soil is more than rock particles. It includes all the living things and the materials they make or change (Kuo, 1999).

Let's take an elevator ride from the surface to the bedrock below. We'll pass several distinct layers, or horizons, as we go. Together, these layers form the soil profile. Going down!

Plants grow and animals live here. A thick cover of plants can keep the soil cool and keep it from drying out. Decomposers recycle dead plants and animals into humus.

Plants grow and animals live on top of the soil. This is sometimes called the organic layer. A thick cover of plants can keep the soil cool and keep it from drying out. Decomposers recycle dead plants and animals into humus.

This is a mix of mineral particles and some humus near the top. Subsoil is very low in organic matter compared to the topsoil. This is the layer where most of the soil's nutrients are found. Deep plant roots come here looking for water. Clays and minerals released up above often stick here as water drains down.

This horizon can be very deep. There's no organic matter here at all. We're out of reach of all living and dead organisms down here. It's all rock particles, full of minerals.

The entire soil profile used to look like this all the way to the surface. Physical weathering broke the parent material up into small pieces. Don't be fooled! This layer may contain rock particles that are different from the bedrock below. A river or a glacier might have brought it from somewhere else.

We finally found solid rock! The bedrock formed before the soil above it. It will wait here until erosion or an earthquake exposes it to the surface. Then some of it will be weathered to become the next batch of parent material. The soil-making process will start all over again (Kuo, 1999).

2.3.1 Soil pH

pH is a measure of how acidic or basic things are and is measured using a pH scale between 0 to 14, with acidic things having a pH between 0-7 and basic things having a pH from 7 to 14. For instance, lemon juice and battery acid are acidic and fall in the 0-7 range, whereas seawater and bleach are basic (also called "alkaline") and fall in the 7-14 pH range. Pure water is neutral, or 7 on the pH scale (Kuo, 1999).

2.3.1.1 The Importance of Soil pH

The pH of soil or more precisely the pH of the soil solution is very important because soil solution carries in it nutrients such as Nitrogen (N), Potassium (K), and Phosphorus (P) that plants need in specific amounts to grow, thrive, and fight off diseases.

If the pH of the soil solution is increased above 5.5, Nitrogen (in the form of nitrate) is made available to plants. Phosphorus, on the other hand, is available to plants when soil pH is between 6.0 and 7.0.

Certain bacteria help plants obtain N by converting atmospheric Nitrogen into a form of N that plants can use. These bacteria live in root nodules of legumes (like alfalfa and soybeans) and function best when the pH of the plant they live in is growing in soil within an acceptable pH range.

For instance, alfalfa grows best in soils having a pH of 6.2 - 7.8, while soybean grows best in soils with a pH between 6.0 and 7.0. Peanuts grow best in soils that have a pH of 5.3 to 6.6. Many other crops, vegetables, flowers and shrubs, trees, weeds and fruit are pH dependent and rely on the soil solution to obtain nutrients.

If the soil solution is too acidic plants cannot utilize N, P, K and other nutrients they need. In acidic soils, plants are more likely to take up toxic metals and some plants eventually die of toxicity (poisoning).

Herbicides, pesticides, fungicides and other chemicals are used on and around plants to fight off plant diseases and get rid of bugs that feed on plants and kill plants. Knowing whether the soil pH is acidic or basic is important because if the soil is too acidic the applied pesticides, herbicides, and fungicides will not be absorbed (held in the soil) and they will end up in garden water and rain water runoff, where they eventually become pollutants in our streams, rivers, lakes, and ground water (Kuo, 1999).

2.4 Sources of Contaminants

Surface water and groundwater may be contaminated with metals from wastewater discharges or by direct contact with metals-contaminated soils, sludge, mining wastes, and debris. Metal-bearing solids at contaminated sites can originate from a wide variety of sources in the form of airborne emissions, process solid wastes,. sludges or spills. The contaminant sources influence the heterogeneity of contaminated sites on a macroscopic and microscopic scale. Variations in contaminant concentration and matrix influence the risks associated with metal contamination and treatment options (Cynthia, et al., 1997).

2.4.1 Airborne Sources

Airborne sources of metals include stack or duct emissions of air, gas, or vapor streams, and fugitive emissions such as dust from storage areas or waste piles. Metals from airborne sources are generally released as particulates contained in the gas stream. Some metals such as arsenic, cadmium, and lead can also volatilize during high-temperature processing. These metals will convert to oxides and condense as fine particulates unless a reducing atmosphere is maintained. (Smith et al., 1995) Stack emissions can be distributed over a wide area by natural air currents until dry and/or wet precipitation mechanisms remove them from the gas stream. Fugitive emissions are often distributed over a much smaller area because emissions are made near the ground. In general, contaminant concentrations are lower in fugitive emissions compared to stack emissions. The type and concentration of metals emitted from both types of sources will depend on site-specific conditions (Cynthia, et al., 1997).

2.4.2 Process Solid Wastes

Process solid wastes can result from a variety of industrial processes. These metal-bearing solid wastes are disposed above ground in waste piles or below ground or under cover in landfills. Examples of process solid wastes include slags, fly ash, mold sands, abrasive wastes, ion exchange resins, spent catalysts, spent activated carbon, and refractory bricks (Zimmerman and Coles, 1992). The composition of the process waste influences the density, porosity, and leaches resistance of the waste and must be considered in evaluating the contaminated matrix. Because waste piles are above ground, they are exposed to weathering which can disperse the waste pile to the surrounding soil, water and air and can result in generation of leachate which infiltrates into the subsurface environment. The ability of landfills to contain process solid wastes varies due to the range of available landfill designs. Uncontained landfills can release contaminants into infiltrating surface water or groundwater or via wind and surface erosion (Cynthia, et al., 1997).

2.4.3 Sludges

The composition of sludges depends on the original waste stream and the process from which it was derived. Sludges resulting from a uniform wastestream, such as wastewater treatment sludges, are typically more homogeneous and have more uniform matrix characteristics. Sludge pits, on the other hand, often contain a mixture of wastes that have been aged and weathered, causing a variety of reactions to occur. Sludge pits often require some form of pretreatment before wastes can be treated or recycled (Smith et al., 1995).

2.4.4 Soils

Soil consists of a mixture of weathered minerals and varying amounts of organic matter. Soils can be contaminated as a result of spills or direct contact with contaminated waste streams such as airborne emissions, process solid wastes, sludges, or leachate from waste materials. The solubility of metals in soil is influenced by the chemistry of the soil and groundwater (Evans, 1989). Factors such as pH, Eh, ion exchange capacity, and complexation/chelation with organic matter directly affect metal solubility.

2.4.5 Direct Ground-Water Contamination

Groundwater can be contaminated with metals directly by infiltration of leachate from land disposal of solid wastes, liquid sewage or sewage sludge, leachate from mine tailings and other mining wastes, deep-well disposal of liquid wastes, seepage from industrial waste lagoons, or from other spills and leaks from industrial metal processing facilities (e.g., steel plants, plating shops, etc.). A variety of reactions may occur which influence the speciation and mobility of metal contaminants including acid/base, precipitation/dissolution, oxidation/reduction, sorption or ion exchange. Precipitation, sorption, and ion exchange reactions can retard the movement of metals in groundwater. The rate and extent of these reactions will depend on factors such as pH, Eh, complexation with other dissolved constituents, sorption and ion exchange capacity of the geological materials, and organic matter content. Ground-water flow characteristics also influence the transport of metal contaminants.

2.5 Movement of Heavy Metals through Soil Ammended with Sewage Sludge

The application of sewage sludge to land is, in principle, an effective disposal method. Not only does it provide a solution to the sludge disposal problem, but it can prove to be beneficial to agricultural productivity (Chang et al. 1978). The presence of heavy metals, such as Cd, Zn, Cu, Ni, Cr and Pb, is the most critical long-term hazard when applying sludge to land (Logan and Chaney 1983). Short-term benefits from sludge nutrients may then be negated by long-term deleterious effects on crop yield and quality, or, in the case of Cd, direct human toxicity. While it has generally been assumed that these metals are immobile in managed agricultural soils (McBride 1995), factors that enhance mobility could result in more plant uptake or leaching of the metals to the groundwater. These factors include the properties of the metals in question, the quantity and typeof soil binding sites, pH, the concentration of complexing anions (organic and inorganic), and competing cations in soil solution (Tyler and McBride1982). Metals can bind to soil through the processes of ion exchange and chemisorption. Oxides of Fe, Al, and Mncan provide chemisorption sites for metals. Soil organic matter also plays a key role in complexing and retaining metals. McLaren and Crawford (1973) showed how Cuwas strongly bound to the soil organic matter. Layersilicate minerals provide exchange sites for cations, and a few chemisorption sites at crystal edges. Kuo et al.(1985) showed that Cd retention was greater in fine-textured soils with high cation exchange capacity (CEC)compared to coarse-textured soils with lower CEC. McBride et al. (1981) showed that Cd retention was most closely related to the exchangeable base content of the soil. Many metals at high soil contamination levels will form precipitates with oxides, hydroxides and carbonates (Jenne 1968), especially at higher soil pH. Organic matter, both soluble and insoluble, forms complexes with metals by exchange and chemisorption reactions. Metals bond with carboxyl, phenol, alcohol,carbonyl and methoxyl functional groups. When two or more functional groups bind with a single metal ion, the resulting five or six member chelation ring holds the metal very strongly (Snoeyink and Jenkins 1980).Chelation is pH dependent, because at low pH the metals must compete with H ions for coordination sites on the functional groups. This experiment examined the mobility of four metals: Cd, Zn, Cu and Pb. Of these, Cu and Pb form stronger complexes with surfaces and soluble organics than do Cd and Zn. This tends to make them less mobile in soils, but also provides a greater opportunity for facilitated transport by soluble organics (if present).Numerous studies (Elliott et al. 1986; Tyler and McBride1982) have shown the relative mobility of these elements in soil is typically Cd>Zn>Cu>Pb. Knowledge of the movement of these metals is primarily based on homogenized soil column studies, and under these conditions none of these metals is considered to be mobile (especially when applied via sewage sludge)except perhaps in very acid or coarse-textured soils. A laboratory study (Gerritse et al. 1982) showed that the relative velocity of these metals was about 0.01 to 0.1%of the velocity at which water moved through soil, even for a sandy loam soil with a CEC of only 0.16 cmol kg .-1Studies performed by Emmerich et al. (1982) and Giordano and Mortvedt (1976) further confirmed the immobility of these metals in conventionally-homogenized laboratory soil columns. Although the sludge-applied metals were taken up by plants, they did not leach through the soil below the depth of incorporation. Other studies done on field sludge application sites have concluded that metals are strongly bound in the top soil, since little or no metals accumulate in the soil below the depth of incorporation (Chang et al. 1984; Williams et al. 1987). However, when doing a mass balance of the metals at these sites, Williams et al.(1987), and several other researchers, could not account for all the metals that had been applied. McGrath and Lane (1989) found that 68% of the metals applied to the field site they were studying could not be accounted for. They blamed most of this loss on lateral movement of soil due to mechanical cultivation or erosion. Dowdy etal. (1991) claimed that some metal extraction methods used did not fully recover the metals from the interior of soil minerals or strong sorption sites. While this could cause metal balances to be inaccurate, this is an unlikely explanation because of the vigorous soil digestion methods used in most studies. They also mentioned the possibility that metals are transported to lower depths in the soil through cracks and macro pores in a process they call non-matrix water flow, more generally known as preferential flow. Preferential flow has been shown to greatly increase the mobility and velocity of solute movement to the groundwater (Steenhuis et al. 1995). Various forms of preferential flow exist. In homogeneous sandy soils, preferential flow is caused by instability at the wetting front (Glass et al., 1989) or by sloping textural interfaces (Kung, 1990). In finer soils, structural cracks, wormholes, plant root channels and other high conductivity paths form the network for preferential flow. Water added to the soil can rapidly flow through this preferential network, bypassing most of the soil matrix. In contrast, conventional laboratory leaching studies have generally considered soil to be a homogeneous mixture (and, by experimental design, force it to be the case) where infiltrating water will travel through the entire soil matrix. The possibility that water and solutes can bypass much of the soil matrix via preferential flow paths has therefore been ignored. It has been demonstrated that preferentially-transported pesticides can rapidly reach groundwater, despite conventional model predictions to the contrary (Steenhuis, et al. 1994). It is therefore conceivable that preferential transport could also increase metal movement. Another factor that could enhance metal mobility is transport of metals incorporated in soluble metal-organic complexes. While metal-organic complexation generally leads to decreased mobility, metal-organic complexes can become soluble at pH's above 7 (McBride 1994). Also, as the organic matter in soil decomposes, it could release soluble metal organic complexes. This was demonstrated by Lund et al. (1976). Metal movement below sludge disposal ponds was correlated with soil chemical oxygen demand, suggesting that the metals were transported through the soil as metal-organic complexes. Van Erp and van Lune (1991) in a 14 year study of sludge-amended soil found that concentrations of Cd and Zn in the leachate decreased over time while Cu and Pb concentrations increased. This was attributed to the fact that Pb and Cu are strongly bound to organic matter and would be slowly-released over time as the organic matter of the sludge decomposed. Cd and Z nare not as strongly bound to organic matter and therefore would not be as greatly affected by sludge decomposition. This slow release of metals is a potential "time bomb" effect that sludges have because of their high organic matter content (McBride 1995).The literature shows that metals movement through soil is still not well understood. The roles of preferential flow paths and soluble organic matter are especially unclear. The objective of this study was to examine the effects (separately and in combination) of preferential flow paths and soluble organics on the mobilities of Cd,Zn, Cu and Pb through soil columns. To do this we carried out an experiment wherein metals in solution (in water or in an organic solution) were applied to both conventional and undisturbed soil columns. Leachates were monitored to determine metal transport. The extent of preferential water flow was characterized with chloride tracer.

Contamination of soil and water with hazardous metals– such as cadmium, copper, lead, and nickel – is a national environmental concern. Excessive amounts of metals accumulating in soils can be toxic to humans, animals, and plants. Natural soil concentrations of nickel are normally less than 50 parts per mil-lion (ppm), but they have increased overtime. This increase may be due to activities at industries like tanneries and smelters. Also, the disposal of sewage sludge may increase nickel concentrations in soils to more than 2,500 ppm – levels that are potentially toxic to humans, animals, and plants. Predicting the movement of environ-mental contaminants requires an under-standing of how metals are retained on the surface of soil particles. Metal retention (or sorption) on the surface of soil particles decreases the ability of a contaminant to move through soil and water.

2.6 Fate of Metals in the Soil Environment

In soil, metals are found in one or more of several "pools" of the soil, as described by Shuman (1991):

1. dissolved in the soil solution;
2. occupying exchange sites on inorganic soil constituents;
3. specifically adsorbed on inorganic soil constituents;
4. associated with insoluble soil organic matter;
5. precipitated as pure or mixed solids;
6. present in the structure of secondary minerals; and/or
7. present in the structure of primary minerals.

In situations where metals have been introduced into the environment through human activities, metals are associated with the first five pools. Native metals may be associated with any of the pools depending on the geological history of the area. The aqueous fraction, and those fractions in equilibrium with this fraction, i.e., the exchange fraction, are of primary importance when considering the migration potential of metals associated with soils.

Multiphase equilibria must be considered when defining metal behavior in soils (Figure 2.2). Metals in the soil solution are subject to mass transfer out of the system by leaching to ground water, plant uptake, or volatilization, a potentially important mechanism for Hg, Se, and As. At the same time metals participate in chemical reactions with the soil solid phase. The concentration of metals in the soil solution, at any given time, is governed by a number of interrelated processes, including inorganic and organic complexation, oxidation-reduction reactions, precipitation/dissolution reactions, and adsorption/desorption reactions. The ability to predict the concentration of a given metal in the soil solution depends on the accuracy with which the multiphase equilibria can be determined or calculated.

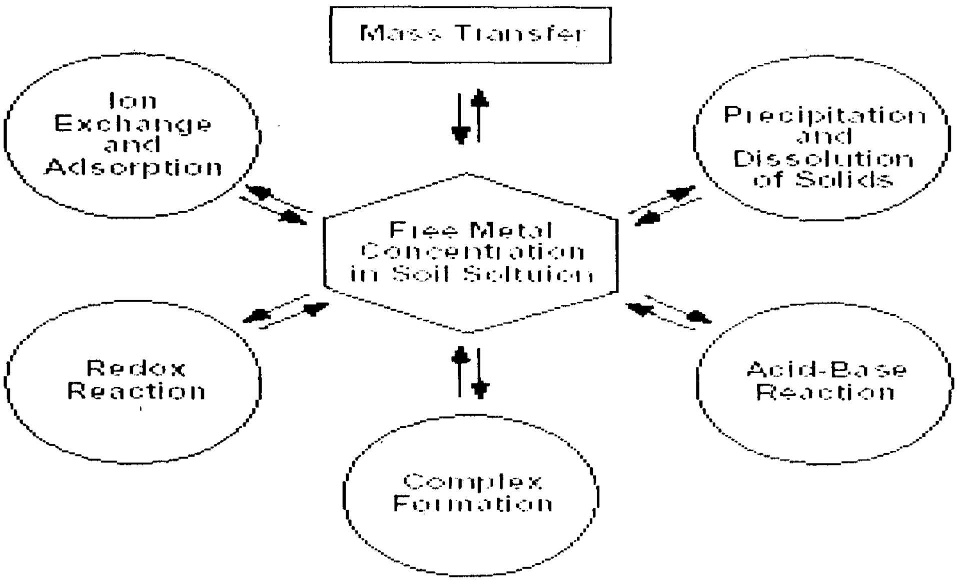

Fig. 2.1: Principal controls on free trace metal concentrations in soils solution (Mattigod, et al., 1981).

Most studies of the behavior of metals in soils have been carried out under equilibrium conditions. Equilibrium data indicate which reactions are likely to occur under prescribed conditions, but do not indicate the time period involved. The kinetic aspect of oxidation/reduction, precipitation/dissolution, and adsorption/desorption reactions involving metals in soil matrix suffers from a lack of published data. Thus the kinetic component, which in many cases is critical to predict the behavior of metals in soils, cannot be assessed easily. Without the kinetic component, the current accepted approach is to assume that local equilibrium occurs in the soil profile. Equilibrium thermodynamic data can then be applied not only to predict which precipitation/dissolution, adsorption/desorption, and/or oxidation/reduction reactions are likely to occur under a given set of conditions, but also to estimate the solution composition, i.e., metal concentration in solution, at equilibrium. This approach relies heavily on the accuracy of thermodynamic data that can be found in the literature.

2.7 Soil Solution Chemistry

Metals exist in the soil solution as either free (uncomplexed) metal ions (e.g., Cd^{2+}, Zn^{2+}, Cr^{3+}), in various soluble complexes with inorganic or organic ligands (e.g., $CdSO_4$ $ZnCl^{+}$, $CdCl^{3-}$), or associated with mobile inorganic and organic colloidal material. A complex is defined as an unit in which a central metal ion is bonded by a number of associated atoms or molecules in a defined geometric pattern, e.g $ZnSO_4$, $CdHCO^{3+}$, $Cr(OH)^{4-}$. The associated atoms or molecules are termed ligands. In the above examples, SO_4^{2-}, HCO^{3-}, and OH^{-} are ligand. The total concentration of a metal, MeT, in the soil solution is the sum of the free ion concentration $[Me^{z+}]$, the concentration of soluble organic and inorganic metal complexes, and the concentration of metals associated with mobile colloidal material.

Metals will form soluble complexes with inorganic and organic ligands. Common inorganic ligands are SO_4^{2-}, C^{1-}. OH^{-}, PO_4^{3-}, NO^{3-} and CO_3^{2-}. Soil organic ligands include low molecular weight aliphatic, aromatic, and amino acids and soluble constituents of fulvic acids. Formation constants for various metal complexes are available in the literature. Organic complexation of metals in soil is not as well defined as inorganic complexation because of the difficultly of identifying the large number of organic ligands that may be present in soils. Most of the metal-organic complex species identified in the literature were generated from metal interaction with fulvic acids extracted from sewage sludges (Baham, et al.,1978). The soluble metal organic complexes that may form in other waste systems, however, have not been identified.

The presence of complex species in the soil solution can significantly affect the transport of metals through the soil matrix relative to the free metal ion. With complexation, the resulting metal species may be positively or negatively charged or be electrically neutral (e.g., $CdCl^{3+}$, $CdCl^{-}$, $CdCl_2$).

Atomic absorption spectrophotometers (AA) and inductively coupled plasma emission spectrometers (ICP) are commonly used to determine the metal concentration in soil solutions. Both techniques measure the total metal concentration in the solution without distinguishing metal speciation or oxidation state. Free metal, complexed metal ion concentrations and concentration of metals in different oxidation states can be determined using ion selective electrodes, polarography, colorimetric procedures, gas chromatography-AA, and high performance liquid chromatography-AA (see Kramer and Allen, 1988). While these specific methods are necessary for accurate measurements of metal speciation and oxidation state, these methods are not routinely performed by commercial laboratories nor are these procedure standard EPA methods.

Formation constants are known for many metal complexes. There is, however, only limited information for metal-organic complexes, including formation constants for many naturally occurring ligands and those in waste disposal systems. The required input data for these models include: the concentration of the metal of interest, the inorganic and organic ligands, and the major cations and other metal ions, and pH. In specific cases the redox potential and pCO_2 also may be required. Output consists of an estimation of the concentration of free metals and complexed metals at equilibrium for the specified conditions.

Many predictive methods, based on solution and solid phase chemistry, do not adequately describe transport of metals under field conditions. Solution chemistry considers the interaction between dissolved species, dissolved being defined as substances that will pass a 0.45μm filter. However, in addition to dissolved metal complexes, metals also may associate with mobile colloidal particles. Colloidal size particles are particles with a diameter ranging from 0.01 and 10μm (Sposito, 1989). Gschwend and Reynolds (1987) reported that colloidal particles of intermediate diameter, 0.1μm to 1μm, were the most mobile particles in a sandy medium. Colloidal particles include iron and manganese oxides, clay minerals, and organic matter. These surfaces have a high capacity for metal sorption. Puls et al. (1991) reported a 21 times increase in arsenate transport in the presence of colloidal material compared with dissolved arsenate. This increased transport of contaminants associated with mobile colloidal material has been termed facilitated transport.

2.8 Solid Phase Formation of Metals in Soils

Metals may precipitate to form a three dimensional solid phase in soils. These precipitates may be pure solids (e.g., $CdCO_3$, $Pb(OH)_2$, ZnS_2) or mixed solids (e.g., (FexCr1-x)$(OH)_3$, $Ba(CrO_4,SO_4)$). Mixed solids are formed when various elements co-precipitate. There are several types of coprecipitation, inclusion, adsorption and solid solution formation, distinguished by the type of association between the trace element and the host mineral (Sposito, 1989). Solid solution formation occurs when the trace metal is compatible with the element of the host mineral and thus can uniformly replace the host element throughout the mineral. An example of solid solution formation is the substitution of Cd for Ca in calcium carbonate. Cadmium and Ca have almost identical ionic radii so that Cd can readily substitute of Ca in this carbonate mineral. Mechanisms of retention, whether surface adsorption, surface precipitation, co-precipitation, and pure solid formation are often difficult to distinguish experimentally.

Retention involves a progression of these processes. The term sorption is used when the actual mechanism of metal removal from the soil solution is not known. Stability diagrams are used as a convenient technique for illustrating how the solubility of metal compounds varies with soil pH and with metal concentration (or activity). The diagrams also allow some prediction of which solid phase regulates metal activity in the soil solution. Methods for constructing such diagrams is given in Sposito (1989) and Lindsay (1979). Santillan-Medrano and Jurinak (1975) used stability diagrams for predicting the formation of precipitates of Pb and Cd in a calcareous soil. Solution activity of Cd is consistently higher than that for Pb indicating that Cd may be more mobile in the environment. Lead phosphate compounds at lower pH and a mixed Pb compound at pH>7.5 could be the solid phases regulating Pb in solution. The authors concluded that cadmium solution activity is regulated by the formation of $CdCO_3$ and $Cd(PO_4)_2$ or a mixed Cd solid at pH<7.5. At higher pH, the system is undersaturated with respect to the Cd compounds considered.

The formation of a solid phase may not be an important mechanism compared to adsorption in native soils because of the low concentration of trace metals in these systems (Lindsay, 1979). Precipitation reactions may be of much greater importance in waste systems where the concentration of metals may be exceedingly high. McBride (1980)

2.9 Surface Reactions

Adsorption is defined as the accumulation of ions at the interface between a solid phase and an aqueous phase. Adsorption differs from precipitation in that the metal does not form a new three dimensional solid phase but is instead associated with the surfaces of existing soil particles. The soil matrix often includes organic matter, clay minerals, iron and manganese oxides and hydroxides, carbonates, and amorphous aluminosilicates. Soil organic matter consists of 1) living organisms, 2) soluble biochemicals (amino acids, proteins, carbohydrates, organic acids, polysaccharides, lignin, etc.), and insoluble humic substances. The biochemicals and humic substances provide sites (acid functional groups, such as such as carboxylic, phenolics, alcoholic, enolic-OH and amino groups) for metal sorption. A discussion of the nature of soil organic matter and its role in the retention of metals in soil is given by Stevenson (1991) and Stevenson and Fitch (1990). The biochemicals form water soluble complexes with metals, increasing metal mobility, as discussed in a previous section. The humic substances consist of insoluble polymers of aliphatic and aromatic substances produced through microbial action.

Humic substances contain a highly complex mixture of functional groups. Binding of metals to organic matter involves a continuum of reactive sites, ranging from weak forces of attraction to formation of strong chemical bonds. Soil organic matter can be the main source of soil cation exchange capacity, contributing >200meq/100 g of organic matter in surface mineral soils. Organic matter content, however, decreases with depth, so that the mineral constituents of soil will become a more important surface for sorption as the organic matter content of the soil diminishes. There have been numerous studies of the adsorptive properties of clay minerals, in particular montmorillonite and kaolinite, and iron and manganese oxides. Jenne (1968) concluded that Fe and Mn oxides are the principal soil surface that control the mobility of metals in soils and natural water. In arid soils, carbonate minerals may immobilize metals by providing an adsorbing and nucleating surface (Santillan, et al., 1975).

2.10 Anions in the Soil Environment

Common anionic contaminants of concern include arsenic (AsO_4^{3-} and AsO^{2-})selenium (SeO_3^{2-} and SeO_4^{2-}), and chromium in one of its oxidation states ($CrO4^{2-}$). Soil particles, though predominantly negatively charged, also may carry some positive charges. The oxide surfaces, notably iron, manganese, and aluminum oxides, carbonate surfaces, and insoluble organic matter can generate a significant number of positive charges as the pH decreases. The edges of clay minerals also carry pH dependent charge. These edge sites may be important sites of retention of anions at pHs below the point of zero charge (PZC).

Clay minerals, oxides, and organic matter exert a strong preference for some anions in comparison to other anions, indicating the existence of chemical bonds between the surface and the specific anion. Phosphate has been the most extensively studied anion that exhibits this specific adsorption (inner sphere complex) phenomenon. Selenite (SeO_3^{2-}) and arsenate (AsO_4^{3-}) are adsorbed to oxides and soils through specific binding mechanisms (Rajan, 1979; Neal, et al., 1987b). Selenite (SeO_4^{2-}) and hexavalent chromium are only weakly bound to soil surfaces and are thus easily displaced by other anions. Balistrieri and Chao (1987) found the sequence of adsorption of anions onto iron oxide to be: phosphate = silicate = arsenate > bicarbonate/carbonate > citrate = selenite > molybdate > oxalate > fluoride = selenate > sulfate.

The adsorption capacity for anions is, however, small relative to cation adsorption capacity of soils.

2.11 Soil Properties Affecting Adsorption

The adsorption capacity (both exchange and specific adsorption) of a soil is determined by the number and kind of sites available. Adsorption of metal cations has been correlated with such soil properties as pH, redox potential, clay, soil organic matter, Fe and Mn oxides, and calcium carbonate content. Anion adsorption has been correlated with Fe and Mn oxide content, pH, and redox potential. Adsorption processes are affected by these various soil factors, by the form of the metal added to the soil, and by the solvent introduced along with the metal. The results of these interactions may increase or decrease the movement of metals in the soil water.

Korte et al. (1976) qualitatively ranked the relative mobilities of 11 metals added to 10 soils to simulate movement of metals under an anaerobic landfill situation. The leachate used was generated in a septic tank, preserved under carbon dioxide and adjusted to pH of 5. Of the cationic metals studied lead and copper were the least mobile and mercury(II) was the most mobile (Figure 2.4). The heavier textured soils with higher pHs (Molokai, Nicholson, Mohaveca and Fanno) were effective in attenuating the metals, while sandy soils and/ or soils with low pH did not retain the metals effectively. For the anionic metals, clay soils containing oxides with low pH were relatively effective in retaining the anions (Figure 2.4). As with the cationic metals, the light textured soils were the least effective in retaining the anions. Chromium (VI) was the most mobile of the metals studied. Griffin and Shimp (1978) found the relative mobility of nine metals through montmorillonite and kaolinite to be: Cr(VI) > Se > As(III) > As(V) > Cd > Zn > Pb > Cu > Cr(III).

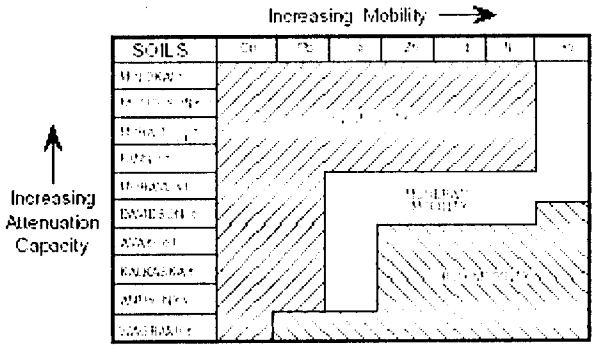

Figure 2.2: Relative mobility of cations through soil. (From Korte, Skopp, Fuller, Niebla, and Alesii, 1976).

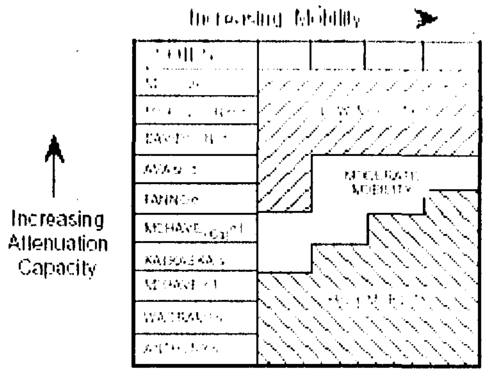

Figure 2.3: Relative mobility of anions through soil. (From Korte, Skopp, Fuller, Niebla, and Alesii, 1976)

2.12 Factors Affecting Adsorption and Precipitation

2.12.1 Reactions

Although the principles affecting sorption and precipitation are similar for cationic and anionic metals, for clarity, the following section will concentrate on a general discussion of factors affecting the behavior of cationic metals in soils. Factors affecting anion adsorption and precipitation will be discussed for each individual metal anion in a later section.

2.12.2 Effect of competing cations

For specific adsorption sites, trace cationic metals are preferentially adsorbed over the major cations (Na, Ca, Mg) and trace anionic metals are preferentially adsorbed over major anions (SO^{4-}, NO^{3-}, soluble ionized organic acids). However, when the specific adsorption sites become saturated, exchange reactions dominate and competition for these sites with soil major ions becomes important. Cavallaro and McBride (1978) found that adsorption of Cu and Cd decreased in the presence of 0.01M $CaCl_2$. They attributed this decrease to competition with Ca for adsorption sites. Cadmium adsorption was more affected by the presence of Ca than Cu. The mobility of Cd may be greatly increased due to such competition. Likewise, Harter

(1979) indicated the Ca in solution had a greater effect on Pb adsorption than on Cu. In another study, Harter (1992) added Cu, Ni and Co to calcium saturated soils. The presence of Ca, a common ion in soils with pH>5.6, did not affect Cu sorption but did limit the sorption of Co and Ni. The author emphasized the importance of these results in that standard management practice for metal contaminated soils is to raise the pH to 7, often using a Ca buffered system. The addition of Ca, as low as 0.01M Ca, may increase the mobility of some metals by competing for sorption sites.

Trace metals also will compete with each other for adsorption sites. Although there have been several studies on the relative adsorption affinities of trace metals by soils and soil constituents, these studies have compared how much of each metal, added to the soils as individual components, was adsorbed and not whether the adsorption of one metal will interfere with that of another. Few studies have looked directly at the competitive adsorption of metals. Kuo and Baker (1980) reported that the presence of Cu interfered with the adsorption of Zn and Cd. Adsorbed Cu was not significantly affected by added Zn but the presence of Cu, at concentrations as low as 15 μg/L, completely prevented Zn adsorption in one soil with a low cation exchange capacity (Kurdi and Doner, 1983). In contrast, McBride and Blasiak (1979) found that Cu was ineffective in competing for Zn adsorption sites over a pH range of 5-7. The inability of Cu to block Zn adsorption in this study was taken as evidence that Zn and Cu were preferentially adsorbed at different sites.

Simultaneous addition of Cd and Zn to Mn oxide lowered the adsorption of both metals (Zasoski and Burau, 1988). The presence of other cations, whether major or trace metals, can significantly effect the mobility of the metal of interest. Use of data from the literature, generation of laboratory data, or use of computer models that do not reflect the complex mixture of metals specific to a site may not be useful to understand or accurately predict metal mobility.

2.12.3 Effect of complex formation

Metal cations form complexes with inorganic and organic ligands. The resulting association has a lower positive charge than the free metal ion, and may be uncharged or carry a net negative charge. For example, the association of cadmium with chloride results in the following series of charged and uncharged cadmium species: Cd2+, $CdCl^+$, $CdCl_2$, $CdCl^{3-}$. Benjamin and Leckie (1982) stated that the interaction between metal ions and complexing ligands may result in either a complex that is weakly adsorbed to the soil surface or in a complex that is more strongly adsorbed relative to the free metal ion. In general, the decrease in positive charge on the complexed metal reduces adsorption to a negatively charged surface. One noted exception is the preferential adsorption of hydrolyzed metals ($MeOH^+$) versus the free bivalent metal (James and Healy, 1972). The actual effect of complex formation on sorption depends on the properties of the metal of interest, the type and amount of ligands present, soil surface properties, soil solution composition, pH and redox conditions, as is illustrated by the follow research results.

In the presence of the inorganic ligands Cl^- and SO_4^{2-}, the adsorption of Cd on soil and soil constituents was inhibited (O'Connor, et al., 1984; Hirsch et al., 1989; Egozy, 1980; Garcia-Miragaya and Page, 1976; Benjamin and Leckie, 1982) due to the formation of cadmium complexes that were not strongly adsorbed by the soils. Using much higher concentrations of salt than normally encountered in soil solutions (0.1 to 0.5M NaCl), Doner (1978) concluded that the increased mobility of Ni, Cu, and Cd through a soil column was due to complex formation of the metals with Cl^-. The mobility of Cd increased more than that of Ni and Cu, Ni being the least mobile. These observed mobilities are in the same order as that of the stability constants of the chloride complexes of these metals. Within normal concentration of electrolytes in soil solution, Elrashidi and O'Connor (1982) found no measurable change in Zn adsorption by alkaline soils due to complex formation of Zn with Cl^-, NO_3^{2-}, or SO_4^{2-} ions.

Under these conditions (anion concentration of 0.1M), anion complex formation did not compete with the highly selective adsorption sites for Zn. Shuman (1986), using acid soils, observed a decreased adsorption of Zn in the presence of Cl at the concentration of CaCl2 used by Elrashidi and O'Connor (1982) but no effect at lower concentrations. McBride (1985), using aluminum oxide, and Cavallaro (1982), using clays, found that high levels of phosphate suppressed adsorption of Cu and Zn. Phosphate did not form strong complexes with Cu or Zn but it was strongly adsorbed to soil surfaces thus physically blocking the specific adsorption sites of Cu and Zn.

Other researchers (Kuo 1984), using lower concentrations of added phosphate, demonstrated enhanced adsorption of Zn and Cd on oxide surfaces. At the concentration of phosphate used in these studies, the adsorption of phosphate onto the oxide surfaces increased the negative charge on the oxide surface, thus enhancing adsorption of the metal cations.

Complex formation between metals and organic ligands affects metal adsorption and hence mobility. The extent of complexation between a metal and soluble organic matter depends on the competition between the metal-binding surface sites and the soluble organic ligand for the metal. Metals that readily form stable complexes with soluble organic matter are likely to be mobile in soils. Overcash and Pal (1979) reported that the order of metal-organic complex stabilities, for the system they studied, was Hg > Cu > Ni > Pb > Co > Zn > Cd. Khan et al. (1982) showed that the mobility of metals through soil followed the order: Cu > Ni > Pb > Ag >Cd. The high mobility of Cu and Ni was attributed to their high complexing nature with soluble soil organic matter. Amrhein, et al. (1992) also showed the increased mobility of Cu, Ni, and Pb in the presence of dissolved organic matter. In this study, the Cd leached from the columns was not associated with dissolved organic carbon but was associated with Cl or acetate anions. Metals, such as Cd and Zn, that do not form highly stable complexes with organic matter are not as greatly affected by the presence of dissolved organic matter in the soil solution as metals that do form stable complexes, such as Cu, Pb, or Hg. Dunnivant et al. (1992) and Neal and Sposito (1986), however, demonstrated that dissolved organic matter does reduce Cd sorption due to complexation formation under their experimental conditions.

In systems where the organic ligand adsorbs to the soil surface, metal adsorption may be enhanced by the complexation of the metal to the surface-adsorbed ligand. Haas and Horowitz (1986) found that, in some cases, the presence of organic matter enhanced Cd adsorption by kaolinite. They interpreted these findings to suggest that the presence of an adsorbed layer of organic matter on the clay surface served as a site for Cd retention. Davis and Leckie (1978) found Cu adsorption to iron oxide increased in the presence of glutamic acid and 2,3 pyrazinendicarboxylic acid (2,3 PDCA) but decreased in the presence of picolinic acid. Picolinic acid complexed Cu and the resulting complex was not adsorbed by the oxide surface. The glutamic acid and 2,3 PDCA were adsorbed to the oxide surface, then complexed the added Cu. Using natural organic matter, Davis (1984) demonstrated the adsorption of Cu but not Cd to an organic coated aluminum oxide. The effect of complexation formation on sorption is dependent on the type and amount of metal present, the type and amount of ligands present, soil surface properties, soil solution composition, pH and redox. The presence of complexing ligands may increase metal retention or greatly increase metal mobility. Use of literature or laboratory data that do not include the presence of complexing ligands, both organic and inorganic, present at the particular site of interest, may lead to significant overestimation or underestimation of metal mobility.

2.12.4 Effect of pH

The pH, either directly or indirectly, affects several mechanisms of metal retention by soils. Figure 2.6 shows the impact of soil pH on the adsorption of Pb, Ni, Zn, and Cu by two soils adjusted to various pHs ranging from approximately 4.3 to 8.3 (Harter, 1983). As is true for all cationic metals, adsorption increased with pH. The author, however, points out that the retention of the metals did not significantly increase until the pH was greater than 7.

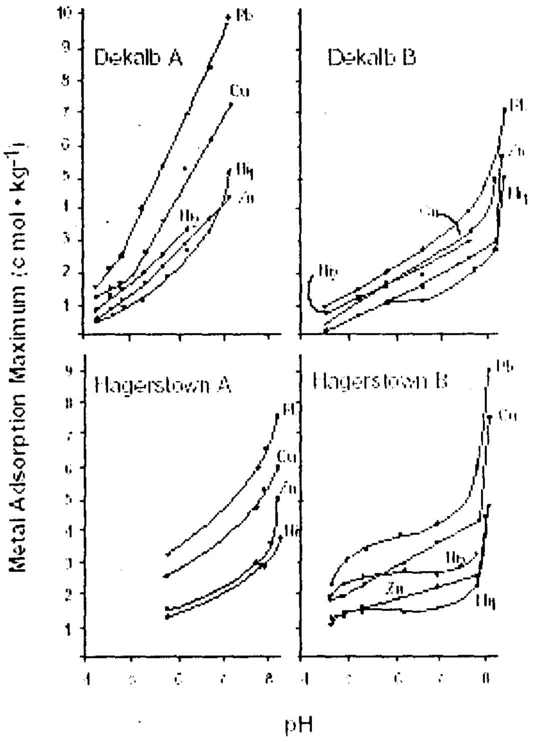

Figure 2.4: Effect of soil pH level on maximum Pb, Cu, Zn, and Ni retention by Dekalb and Hagerstown A and B horizons. Ni1 and Ni2 refer to two apparent sorption maxima. (Harter, 1983).

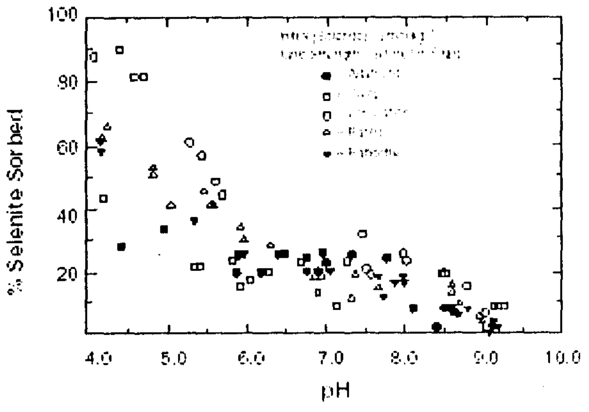

Figure 2.5: Selenite adsorption envelope for five alluvial soils. The intitial total selenite concentration was approximately 2 mmol kg-1 (Neal, et al., 1987a).

Figure 2.75illustrates the adsorption of selenite, SeO_3^{2-}, on five soils adjusted to various pHs. As is true with all oxyanions, i.e., arsenic, selenium and hexavalent chromium, sorption decreases with pH. The pH dependence of adsorption reactions of cationic metals is due, in part, to the preferential adsorption of the hydrolyzed metal species in comparison to the free metal ion (McBride, 1977; McLauren and Crawford, 1973; Davis and Leckie, 1978; Farrah and Pickering, 1976a,b; James and Healy, 1972; McBride, 1982; Cavallaro and McBride, 1980; Harter, 1983). The proportion of hydrolyzed metal species increases with pH.

Cavallaro and McBride (1980) found that copper adsorption by soils showed a stronger pH dependence than Cd. This finding is consistent with the hypothesis that hydrolysis of Cu at pH 6 increases its retention by soil, while cadmium does not hydrolyze until pH 8. Zinc was shown to be retained in an exchangeable form at low pH in four Fe and Mn oxide dominated soils but became nonexchangeable as the pH was increased above 5.5 (Stahl and James, 1991). The researchers attributed this change in mechanism of sorption as being due to the hydrolysis of Zn and the adsorption of the hydrolysis species by the oxide surfaces. Many adsorption sites in soils are pH dependent, i.e., Fe and Mn oxides, organic matter, carbonates, and the edges of clay minerals. As the pH decreases, the number of negative sites for cation adsorption diminishes while the number of sites for anion adsorption increases. Also as the pH becomes more acidic, metal cations also face competition for available permanent charged sites by Al^{3+} and H^+.

All trace metal hydroxide, oxide, carbonate, and phosphate precipitates form only under alkaline conditions (Lindsay, 1979). The dissolution of these metal precipitates is strongly dependent on the pH of the system. Jenne (1968) stated that hydrous oxides of Fe and Mn play a principal role in the retention of metals in soils. Solubility of Fe and Mn oxides is also pH-related. Below pH 6, the oxides of Fe and Mn dissolve, releasing adsorbed metal ions to solution (Essen and El Bassam, 1981).

Work by McBride and Blasiak (1979) showed increased retention of Zn with increasing pH, as is usual for metal cations. When the pH was increased above 7.5, however, the solution concentration of Zn increased. This phenomena has been observed in other studies when acid soils were adjusted to pH>7 (Kuo and Baker, 1980) and it has been attributed to the solubilization of organic complexing ligands which effectively compete with the soil surfaces for the metal cation.

Most functional groups of complexing ligands are weak acids thus the stability of the metal complex is pH-dependent with little association in acid media. The degree of association increases with pH. Baham and Sposito (1986) and Inskeep and Baham (1983) demonstrated that the adsorption of Cu to montmorillonite, in the presence of water soluble ligands extracted from sludges and various other organic materials, decreased with increasing pH. This behavior is the opposite of the typical relationship between metal adsorption and pH.

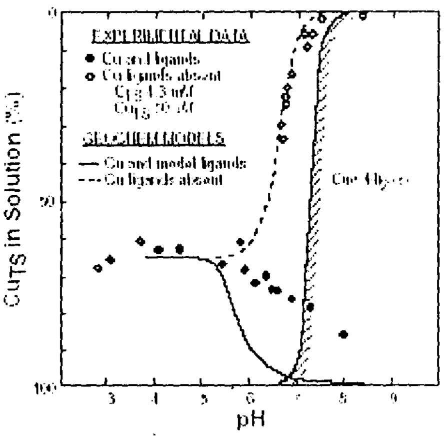

Figure 2.6: Adsorption of Cu [50 mmol m-3 (50 mM)] by Na-montmorillonite in the presence and absence of water soluble extract of sewage sludge (WSE). GEOCHEM simulations were constructed employing the "mixture model" (Baham and Sposito, 1986).

Figure 2.8, taken from Baham and Sposito (1986), illustrates that nearly 100% of the Cu added to the clay in the absence of the organic ligands was removed from solution at pH>7. In the presence of the organic ligands, the maximum amount of Cu removed from solution was at pH^{3}5.5. As the pH was increased above 5.5, adsorption of Cu decreased. The explanation for this phenomena is that at low pH, H$^+$ competes with the Cu for complexation with the organic matter. As the pH increases, more of the Cu can be complexed with the organic matter and less is therefore adsorbed by the clay. This phenomena has important implications with regards to the practice of liming acid soils to raise the pH increasing metal retention. In soils with significant levels of dissolved organic matter, increasing soil pH may actually mobilize metal due to complex formation.

The pH of the soil system is a very important parameter, directly influencing sorption/desorption, precipitation/ dissolution, complex formation, and oxidation-reduction reactions. In general, maximum retention of cationic metals occurs at pH>7 and maximum retention of anionic metals occurs at pH<7. Because of the complexity of the soil-waste system, with its myriad of surface types and solution composition, such a generalization may not hold true. For example, cationic metal mobility has been observed to increase with increasing pH due to the formation of metal complexes with dissolved organic matter.

2.12.5 Effect of oxidation-reduction

Almost half of the metals under consideration have more than one oxidation state in the soil environment and are directly affected by changes in the oxidation-reduction (redox) potential of the soil. The redox potential of a soil system is the measure of the electrochemical potential or availability of electrons within a system. A chemical reaction in which an electron transfer takes place is called an oxidation-reduction process. Metals or elements which gain electrons and lose in valence are undergoing reduction, while those losing electrons and gaining in valence are becoming oxidized. A measure of the redox potential (electron availability) indicates whether the metals are in an oxidize or reduced state. In soils, reducing conditions are brought about by the absence of oxygen (anaerobic). This is caused by the oxygen being utilized or consumed at a greater rate that it can be transported into the soil system. This can be caused by water-logged soils or soils contaminated with oxygen consuming compounds. The consumption could either be chemical or biological. The biological consumption of oxygen is the results of microbes utilizing the organic contaminant which have entered the soil system. Oxidizing conditions (aerobic) are normally found in well-drained soils as well as soils that have not been subjected to contamination by spills or leaks.

The degree of oxidation or reduction is indicated by the redox potential measurement. The four general ranges of redox conditions as suggested by Patrick and Mahapatra (1968) which may be encountered in soils are at pH 7, oxidized soils > +400 millivolts (mv); moderately reduced soils, from +400 to +100 mv; reduced soils, from +100 to -100 mv; highly reduced soils, -100 to -300 mv. The redox state of a soil, usually is closely related to the microbial activity and the type of substrate available to the organisms.

2.12.6 Effect of co-waste

Most soil-metal interaction studies have been performed using a specific, well characterized background solution, such as an inorganic salt solution (0.01M $CaCl_2$, Na_2SO_4, etc.) or a water soluble extraction of organic matter (leaf litter, sewage sludges, etc.). These studies, as reported above, have led to an understanding of the effects that metal type, metal concentration, solution composition, and soil surface type have on the retention of metals by soils. The behavior of metals associated with various industrial or mining wastes in soil systems has not been extensively studied, however. In such wastes the metal concentration may be much greater than used in studies of native metals and metals associated with the controlled application of fertilizers and sewage sludges, and may be associated with a myriad of inorganic and organic chemicals that have not been characterized but may have a great effect on predicting metal mobility.

The retention of Cd, Cu, and Zn by two calcareous soils using a water extract of an acidic milling waste as the background solution (pH=4.0, dominant major cation was Ca and anion was sulfate) was studied by Dudley et al. (1988, 1991). The presence of carbonate minerals is known to effectively immobilize Cd and Cu by providing an adsorbing or nucleating surface and by buffering pH (Santillan-Medrano and Jurinak, 1975; Cavallaro and McBride, 1978; McBride and Bouldin, 1984). For the soil with a lower carbonate content (0.2% $CaCO_3$), the sorption of Cd and Zn was slow to reach equilibrium (114 hours) due to the complex set of reactions that occurred when the soil (pH 8.6) and acid milling extract (pH 4.0) were combined. The dissolution of carbonates in the acid medium controlled the rate and extent of Cd and Zn sorption. The authors concluded that Cd and Zn were retained by an exchange mechanism only after the pH of the system reached equilibrium (pH 5.5), allowing time for significant transport of these metals. Copper sorption was independent of calcite dissolution. The soil with the higher carbonate content (30%) showed a significant drop in pH (pH 9.1 to 6.6) with the addition of the acid leachate but had sufficient carbonates to buffer the system and sorbed all three metals.

Kotuby-Amacher and Gambrell (1988) studied the retention of Cd and Pb on subsurface soils using a synthetic municipal waste leachate and a synthetic acid metal waste leachate, compared with $Ca(NO_3)_2$ as the background solution.

Sorption of the two metals was diminished in the presence of both synthetic leachates. The presence of competing cations and complexing organic and inorganic ligands in the synthetic wastes decreased the retention of Cd and Pb by the soils. Boyle and Fuller (1987) used soil columns packed with five different soils to evaluate the mobility of Zn in the presence of simulated municipal solid waste leachate with various amounts of total organic carbon (TOC) and total soluble salts (TSS). Zinc transport was enhanced in the presence of higher TOC and TSS. Soil properties considered important for retaining Zn in this study were surface area, CEC, and percent clay content. The authors, however, concluded that the leachate composition was more important than soil properties for determining the mobility of Zn.

Puls et al. (1991) studied the sorption of Pb and Cd on kaolinite in the presence of three organic acids, 2,4-dinitrophenol, p-hydroxybenzoic acid, and o-toluic acid. The acids were selected based on their frequent occurance at hazardous waste sites and their persistence in soils. Sorption of Pb decreased in the presence of all the acids due to the formation of 1:2 metal-organic complex resulting in an uncharged form of Pb. Sorption of Cd decreased in the presence of two of the acids but increased in the presence of 2,4-dinitrophenol. The authors attributed the increase in sorption as being due to either direct sorption of the acid to the clay with the subsequent sorption of Cd or to the enhanced sorption of the 1:1 complex formed between Cd and the acid. Sheets and Fuller (1986) studied the transport of Cd through soil columns with 0 to 100% ethylene glycol or 2-propanol as the leaching solution. Soils sorbed less Cd from the ethylene glycol solutions than when the columns were leached with water. The 2-propanol increased sorption in one of the soils tested. The effect on Cd sorption was attributed to the change in soil permeability and surface characterization due to the presence of the solvents.

Metal mobility in soil-waste systems is determined by the type and quantity of soil surfaces present, the concentration of metal of interest, the concentration and type of competing ions and complexing ligands, both organic and inorganic, pH, and redox status. Generalization can only serve as rough guides of the expected behavior of metals in such systems.

2.13 Behavior of Specific Metals in Soils

2.13.1 Copper

Copper is retained in soils through exchange and specific adsorption mechanisms. At concentrations typically found in native soils, Cu precipitates are unstable. This may not be the case in waste-soil systems and precipitation may be an important mechanism of retention. Cavallaro and McBride (1978) suggested that a clay mineral exchange phase may serve as a sink for Cu in noncalcareous soils. In calcareous soils, specific adsorption of Cu onto CaCO3 surfaces may control Cu concentration in solution (Cavallaro and McBride, 1978; Dudley, et al., 1988; Dudley et al., 1991; McBride and Bouldin, 1984). Cu is adsorbed to a greater extent by soils and soil constituents than the other metals studied, with the exception of Pb. Copper, however, has a high affinity for soluble organic ligands and the formation of these complexes may greatly increase Cu mobility in soils.

2.13.2 Zinc

Zinc is readily adsorbed by clay minerals, carbonates, or hydrous oxides. Hickey and Kittrick (1984), Kuo et al. (1983), and Tessier et al. (1980) found that the greatest percent of the total Zn in polluted soils and sediments was associated with Fe and Mn oxides. Precipitation is not a major mechanism of retention of Zn in soils because of the relatively high solubility of Zn compounds. Precipitation may become a more important mechanism of Zn retention in soil-waste systems. As with all cationic metals, Zn adsorption increases with pH.

Zinc hydrolysizes at pH>7.7 and these hydrolyzed species are strongly adsorbed to soil surfaces. Zinc forms complexes with inorganic and organic ligands that will affect its adsorption reactions with the soil surface.

2.13.3 Cadmium

Cadmium may be adsorbed by clay minerals, carbonates or hydrous oxides of iron and manganese or may be precipitated as cadmium carbonate, hydroxide, and phosphate. Evidence suggests that adsorption mechanisms may be the primary source of Cd removal from soils (Dudley et al., 1988, 1991). In soils and sediments polluted with metal wastes, the greatest percentage of the total Cd was associated with the exchangeable fraction (Hickey and Kittrick, 1984; Tessier et al., 1980; Kuo et al., 1983). Cadmium concentrations have been shown to be limited by $CdCO_3$ in neutral and alkaline soils (Santillan-Medrano and Jurinak, 1975). As with all cationic metals, the chemistry of Cd in the soil environment is, to a great extent, controlled by pH. Under acidic conditions Cd solubility increases and very little adsorption of Cd by soil colloids, hydrous oxides, and organic matter takes place. At pH values greater than 6, cadmium is adsorbed by the soil solid phase or is precipitated, and the solution concentrations of cadmium are greatly reduced. Cadmium forms soluble complexes with inorganic and organic ligands, in particular Cl-.The formation of these complexes will increase Cd mobility in soils.

2.13.4 Lead

Soluble lead added to the soil reacts with clays, phosphates, sulfates, carbonates, hydroxides, and organic matter such that Pb solubility is greatly reduced.

At pH values above 6, lead is either adsorbed on clay surfaces or forms lead carbonate. Pb is retained by soils and soil constituents to the greatest extent under the conditions of these studies. Most studies with Pb, however, have been performed in well defined, simple matrices, i.e., 0.01M $CaCl_2$. Puls et al. (1991), and Kotuby-Amacher and Gambrell (1988) have demonstrated decrease sorption of Pb in the presence of complexing ligands and competing cations. Lead has a strong affinity for organic ligands and the formation of such complexes may greatly increase the mobility of Pb in soil.

2.13.5 Nickel

Nickel does not form insoluble precipitates in unpolluted soils and retention for Ni is, therefore, exclusively through adsorption mechanisms. Nickel will adsorb to clays, iron and manganese oxides, and organic matter and is thus removed from the soil solution. The formation of complexes of Ni with both inorganic and organic ligands will increase Ni mobility in soils.

2.13.6 Silver

Published data concerning the interaction of silver with soil are rare. As a cation it will participate in adsorption and precipitation reactions. Silver is very strongly adsorbed by clay and organic matter and precipitates of silver, AgCl, Ag_2SO_4 and $AgCO_3$, are highly insoluble (Lindsay, 1979). Silver is highly immobile in the soil environment.

2.13.7 Mercury

The distribution of mercury species in soils, elemental mercury (Hg), mercurous ions (Hg_2^{2+}) and mercuric ions (Hg^{2+}), is dependent on soil pH and redox potential. Both the mercurous and mercuric mercury cations are adsorbed by clay minerals, oxides, and organic matter. Adsorption is pH dependent, increasing with increasing pH. Mercurous and mercuric mercury are also immobilized by forming various precipitates. Mercurous mercury precipitates with chloride, phosphate, carbonate, and hydroxide. At concentrations of Hg commonly found in soil, only the phosphate precipitate is stable. In alkaline soils, mercuric mercury will precipitate with carbonate and hydroxide to form a stable solid phase. At lower pH and high chloride concentration, HgCl2 is formed. Divalent mercury also will form complexes with soluble organic matter, chlorides, and hydroxides that may contribute to its mobility (Kinniburgh and Jackson, 1978).

Under mildly reducing conditions, both organically bound mercury and inorganic mercury compounds may be degraded to the elemental form of mercury, Hg. Elemental mercury can readily be converted to methyl or ethyl mercury by biotic and abiotic processes (Roger, 1976, 1977). These are the most toxic forms of mercury. Both methyl and ethyl mercury are volatile and soluble in water. Griffin and Shimp (1978) estimated that the removal of Hg from a leachate was not due to adsorption by clays, but was due to volatilization and/or precipitation. This removal of mercury increased with pH.

Rogers (1979) also found large amounts of mercury volatilized from soils. Amounts of mercury volatilized appeared to be affected by the solubility of the mercury compounds added to soil. Volatilization was also found to be inversely related to soil adsorption capacity.

2.13.8 Arsenic

In the soil environment arsenic exists as either arsenate, As(V) (AsO_4^{3-}), or as arsenite, As(III) (AsO^{2-}). Arsenite is the more toxic form of arsenic. The behavior of arsenate in soil is analogous to that of phosphate, because of their chemical similarity. Like phosphate, arsenate forms insoluble precipitates with iron, aluminum, and calcium. Iron in soils is most effective in controlling arsenate's mobility. Arsenite compounds are reported to be 4-10 times more soluble than arsenate compounds.

Griffin and Shimp (1978), in a study of arsenate adsorption by kaolinite and montmorillonite, found maximum adsorption of As(V) to occur at pH 5. Adsorption of arsenate by aluminum and iron oxides has shown an adsorption maximum at pH 3-4 followed by a gradual decrease in adsorption with increasing pH (Hingston et al., 1971; Anderson et al., 1976). The mechanism of adsorption has been ascribed to inner sphere complexation (specific adsorption), which is the same mechanism controlling the adsorption of phosphate by oxide surfaces (Hingston et al., 1971; Anderson et al., 1976; Anderson and Malotky, 1979). The adsorption of arsenite, As(III), is also strongly pHdependent.

Griffin and Shimp (1978) observed an increase in sorption of As (III) by kaolinite and montmorillonite over a pH range of 3-9. Pierce and Moore (1980) found the maximum adsorption of As(III) by iron oxide occurred at pH 7. Elkhatib et al. (1984b) found adsorption of As(III) to be rapid and irreversible on ten soils. They determined, in this study and another study (Elkhatib et al., 1984a), that Fe oxide, redox, and pH were the most important properties in controlling arsenite adsorption by these soils.

Both pH and the redox are important in assessing the fate of arsenic in soil. At high redox levels, As(V) predominates and arsenic mobility is low. As the pH increases or the redox decreases As (III) predominates. The reduced form of arsenic is more subject to leaching because of its high solubility. The reduction kinetics are, however, slow. Formation of As (III) also may lead to the volatilization of arsine (AsH3) and methylarsines from soils (Woolson 1977a). Under soil conditions of high organic matter, warm temperatures, adequate moisture, and other conditions conducive to microbial activity, the reaction sequence is driven towards methylation and volatilization (Woolson 1977a). Woolson's (1977b) study showed that only 1 to 2 percent of the sodium arsenate applied at a rate of 10 ppm was volatilized in 160 days. The loss of organic arsenical compounds from the soil was far greater than for the inorganic source of arsenic. Arsenite, As(III), can be oxidized to As(V). Manganese oxides are the primary electron acceptor in this oxidation (Oscarson et al., 1983).

2.13.9 Selenium

The behavior of selenium in soils has received great attention in recent years. Studies were stimulated by the high incidence of deformity and mortality of waterfowl at the Kesterson National Wildlife Refuge in California that resulted from the input of agricultural drainage water from the western San Joaquin Valley that was high in Se. Such studies have led to a better understanding of the distribution and movement of Se in soils and ground water. Selenium exists in the soil environment in four oxidation states: selenide (Se2-), elemental selenium (Seo), selenite (SeO_3^{2-}), and selenate (SeO_4^{2-}). The concentration and form of Se in soil is governed by pH, redox, and soil composition.

Selenate, Se(VI), is the predominant form of selenium in calcareous soils and selenite, Se(IV), is the predominant form in acid soil. Selenite, Se (IV) binds to sesquioxides, especially to Fe oxides. Balistriera and Chao (1987) found the removal of selenite by iron oxide to increase with decreasing pH. This study not only demonstrates the effect of pH on selenite adsorption but also the effect of concentration. The decrease in the percentage of selenite adsorbed with increasing concentration of selenite at a given pH indicated multiple sites of selenite retention.

At the two lower concentrations, high energy specific adsorption sites were available As the concentration of selenite was increased these sites became saturated and the lower energy sites were utilized. Griffin and Shimp (1978) found maximum adsorption of selenite on montmorillonite and kaolinite to occur at pH 2-3. Neal et al. (1987a) used five soils from the San Joaquin Valley and found that selenite adsorption by the soils decreased with increasing pH in the range of 4-9. Selenite adsorption to oxides and soils occurs through an inner sphere complexation (specific adsorption) mechanism (Rajan, 1979; Neal et al., 1987b).

Under reduced conditions, selenium is converted to the elemental form. This conversion can provide an effective mechanism for attenuation since mobile selenate occurs only under well aerated, alkaline conditions.

Organic forms of selenium are analogous to those of sulfur, including seleno amino acids and their derivatives. Like sulfur, selenium undergoes biomethlyation forming volatile methyl selenides.

2.13.10 Chromium

Chromium exists in two possible oxidation states in soils: the trivalent chromium, Cr(III) and the hexavalent chromium, Cr(VI). Forms of Cr(VI) in soils are as chromate ion, $HCrO^{4-}$ predominant at pH<6.5, or CrO_4^{2-}, predominant at pH 6.5, and as dichromate, $Cr_2O_7^{2-}$ predominant at higher concentrations (>10mM) and at pH 2-6. The dichromate ions pose a greater health hazard than chromate ions. Both Cr(VI) ions are more toxic than Cr(III) ions. Reviews of the processes that control the fate of chromium in soil and the effect these processes have on remediation are given in Bartlett (1991) and Palmer and Wittbrodt (1991).

Because of the anionic nature of Cr(VI), its association with soil surfaces is limited to positively charged exchange sites, the number of which decreases with increasing soil pH. Iron and aluminum oxide surfaces will adsorb CrO_4^{2-} at acidic and neutral pH (Davis and Leckie, 1980; Zachara et al., 1987;

Ainsworth et al., 1989). Stollenwerk and Grove (1985) concluded that the adsorption of Cr(VI) by ground-water alluvium was due to the iron oxides and hydroxides coating the alluvial particles. The adsorbed Cr(VI) was, however, easily desorbed with the input of uncontaminated ground water, indicating nonspecific adsorption of Cr(VI). The presence of chloride and nitrate had little effect on Cr(VI) adsorption, whereas sulfate and phosphate inhibited adsorption (Stollenwerk and Grove, 1985). Zachara et al. (1987) and Zachara et al. (1989) found SO_4^{2-} and dissolved inorganic carbon inhibited Cr(VI) adsorption by amorphous iron oxyhydroxide and subsurface soils. The presence of sulfate, however, enhanced Cr(VI) adsorption to kaolinite (Zachara et al., 1988). Rai et al. (1988) suggested that $BaCrO_4$ may form in soils at chromium contaminated waste sites. No other precipitates of hexavalent compounds of chromium have been observed in a pH range of 1.0 to 9.0 (Griffin and Shimp, 1978). Hexavalent chromium is highly mobile in soils.

In a study of the relative mobilities of 11 different trace metals for a wide range of soils, Korte et al. (1976) found that clay soil, containing free iron and manganese oxides, significantly retarded Cr(VI) migration (see Figure 2.4). Hexavalent chromium was found to be the only metal studied that was highly mobile in alkaline soils. The parameters that correlated with Cr(VI) immobilization in the soils were free iron oxides, total manganese, and soil pH, whereas the soil properties, cation exchange capacity, surface area, and percent clay had no significant influence on Cr(VI) mobility.

Rai et al. (1987) reported that Cr(III) forms hydroxy complexes in natural water, including $Cr(OH)^{2+}$, $Cr(OH)^{2+}$, $Cr(OH)_3$ o, and $Cr(OH)^{4-}$. Trivalent chromium is readily adsorbed by soils. In a study of the relative mobility of metals in soils at pH 5, Cr(III) was found to be the least mobile (Griffin and Shimp, 1978). Hydroxy species of Cr(III) precipitate at pH 4.5 and complete precipitation of the hydroxy species occurs at pH 5.5.

Hexavalent chromium can be reduced to Cr(III) under normal soil pH and redox conditions. Soil organic matter has been identified as the electron donor in this reaction (Bartlett and Kimble, 1976; Bloomfield and Pruden, 1980). The reduction reaction in the presence of organic matter proceeds at a slow rate at environmental pH and temperatures (Bartlett and Kimble, 1976; James and Bartlett, 1983a,b,c). Bartlett (1991) reported that in natural soils the reduction reaction may be extremely slow, requiring years. The rate of this reduction reaction, however, increases with decreasing soil pH (Cary et al., 1977; Bloomfield and Pruden, 1980). Soil organic matter is probably the principal reducing agent in surface soils. In subsurface soils, where organic matter occurs in low concentration, Fe(II) containing minerals reduce Cr(VI) (Eary and Raï, 1991). Eary and Rai (1991), however, observed that this reaction only occurred in the subsurface soil with a pH<5.

The reduction of Cr(VI) occurred in all four subsurface soils tested by decreasing the pH to 2.5. Bartlett and James (1979), however, demonstrated that under conditions prevalent in some soils, Cr(III) can be oxidized. The presence of oxidized Mn, which serves as an electron acceptor, was determined as an important factor in this reaction. Industrial use of chromium also includes organic complexed Cr(III). Chromium (III) complexed with soluble organic ligands will remain in the soil solution (James and Bartlett, 1983a). In addition to decreased Cr(III) adsorption, added organic matter also may facilitate oxidation of Cr(III) to Cr(VI).

2.14 Influence of Soil Properties on Mobility

Chemical and physical properties of the contaminated matrix influence the mobility of metals in soils and groundwater. Contamination exists in three forms in the soil matrix: solubilized contaminants in the soil moisture, adsorbed contaminants on soil surfaces, and contaminants fixed chemically as solid compounds. The chemical and physical properties of the soil will influence the form of the metal contaminant, its mobility, and the technology selected for remediation (Gerber et al., 1991).

2.14.1 Chemical Properties

The presence of inorganic anions (carbonate, phosphate, sulfide) in the soil water can influence the soil's ability to fix metals chemically. These anions can form relatively insoluble complexes with metal ions and cause metals to desorb and/or precipitate in their presence. Soil pH values generally range between 4.0 and 8.5 with buffering by Al at low pH and by $CaCO_3$ at high pH (Wild, 1988). Metal cations are most mobile under acidic conditions while anions tend to sorb to oxide minerals in this pH range (Dzombak and Morel, 1987).

At high pH, cations precipitate or adsorb to mineral surfaces and metal anions are mobilized. The presence of hydrous metal oxides of Fe, Al, Mn can strongly influence metal concentrations because these minerals can remove cations and anions from solution by ion exchange, specific adsorption and surface precipitation (Ellis and Fogg, 1985; Dzombak and Morel, 1987). As noted in the previous section, sorption of metal cations onto hydrous oxides generally increases sharply with pH and is most significant at pH values above the neutral range, while sorption of metal anions is greatest at low pH and decreases as pH is increased. Cation exchange capacity (CEC) refers to the concentration of readily exchangeable cations on a mineral surface and is often used to indicate the affinity of soils for uptake of cations such as metals. Anion exchange capacity (AEC) indicates the affinity of soils for uptake of anions, and is usually significantly lower than the CEC of the soil. In (Sposito, 1989). The presence of natural organic matter (NOM) has been shown to influence the sorption of metal ions to mineral surfaces. NOM has been observed to enhance sorption of Cu2+ at low pH, and suppress Cu2+ sorption at high pH (Tipping et al., 1983; Davis, 1984).

2.14.2 Physical Properties

Particle size distribution can influence the level of metal contamination in a soil. Fine

particles (<100 :m) are more reactive and have a higher surface area than coarser material. As a result, the fine fraction of a soil often contains the majority of contamination. The distribution of particle sizes with which a metal contaminant is associated can determine the effectiveness of a number of metal remediation technologies, e.g., soil washing (Dzombak et al., 1994).

Soil moisture influences the chemistry of contaminated soil. The amount of dissolved minerals, pH and redox potential of the soil water depends on the soil moisture content. Soil structure describes the size, shape, arrangement and degree of development of soils into structural units. Soil structure can influence contaminant mobility by limiting the degree of contact between groundwater and contaminants.

The physical and chemical form of the metal contaminant in soil or water strongly influences the selection of the appropriate remediation treatment approach. Information about the physical characteristics of the site and the type and level of contamination at the site must be obtained to enable accurate assessment of site contamination and remedial alternatives.

The importance of adequate, well-planned site characterization to selection of an appropriate cost-effective remediation approach has been discussed many times (e.g., CII, 1995) but cannot be overemphasized. The contamination in the groundwater and soil should be characterized to establish the type, amount, and distribution of contaminants
across different media.

Once the site has been characterized, the desired level of each contaminant in soil and groundwater must be determined. This is done by comparison of observed contaminant concentrations with soil and ground-water quality standards for a particular regulatory domain, or by performance of a site-specific risk assessment. Remediation goals for metals may be set as desired concentrations in groundwater, as total metal concentration in soil, as leachable metal in soil, or as some combination of these.

CHAPTER THREE

3.0 METHODOLOGY

The methodology of this project intends to study the mobility of heavy metals in soil contaminated with sewage sludge.

3.1 Sources of sample

The soil and sludge were collected in London in 1990.

3.2 Preparation of sample

The soil and sludge were collected and prepared in London in 1990. Duplicate 250 grams samples of air dried sewage sludge/soil mixtures comprising 100, 90, 80, 50 and 0 per cent soil were placed in sintered glass membrane filter funnels and kept at the field capacity moisture by regular watering with deionized water. Soil solution was extracted by placing the funnel in a suction flask linked to a vacuum line. The first early extraction produced very little filtrate so an improved standardized procedure was adapted in which 40 ml of deionized water was slowly added to the mixtures. 30 minutes before vacuum filtration. This filtrate was more realistically a "saturation extract" than a representative sample of soil solution. After filtration the pH values of the filtrates were determined and subsamples were taken to dryness with concentrated nitric acid to destroy any soluble organic molecules prior to chemical analysis. For comparative purposes, small subsamples of the sludge/soil mixtures, taken at the beginning and end of the experiment, were extracted with water and the metal concentrations determined in the extract (McLaren and Crawford, 1973). Twelve saturations extracts were obtained over a period of eight months.

3.3 Apparatus and Instruments

(i) Heavy metals (cadmim, lead and nickel)

(ii) Soil sample
(iii) Column (of soil)
(iv) Denver Instruments (mass measuring instruments)
(v) Plastic valve
(vi) pH/ion meter
(vii) Temperature probe
(viii) Vacuum filter
(ix) Funnel

3.4 Reagents

(i) 1M HCl
(ii) 0.01M $NaNO_3$
(iii) 0.01 M KNO_3
(iv) rainwater
(v) KNO_3
(vi) 1M HNO_3

3.5 Samples

(i) Soil
(ii) Sewage sludge

3.6 Experimental Procedure

This experimental analysis is based on the sample of soil + sewage taken at different locations for the study of mobility of heavy metals in soils contaminated with sewage.

3.6.1 Experimental determination of mobility of heavy metals in soils amended with sewage

An aqueous phase solution was pumped through a column of soil. Over time, the solution is collected at the outlet and is analyzed. Also, column solids are removed and the sorbed metal is quantified as a function of column depth. Periodic measurements are taken at the influent and sampling reservoirs during the experiment to monitor pH, ionic strength, and flowrate (Vince DeCapio, 2003).

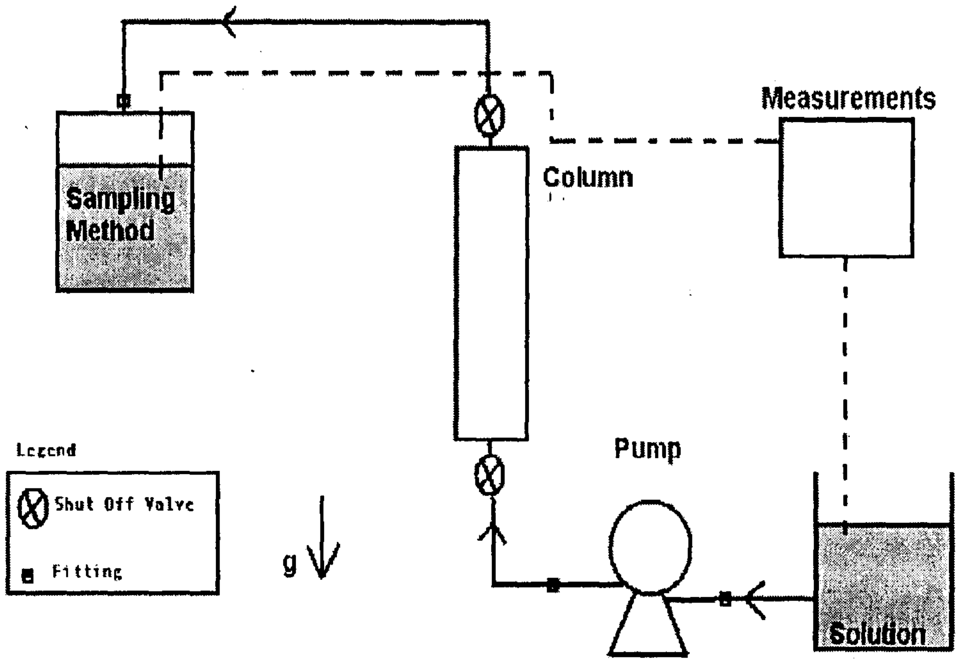

Figure 3.1: Experimental set up of the experiment

3.6.2 Analysis of soil properties

Silica sand was used for the soil column experiments. Specifically, grade manufactured by the U.S. Silica company was used. A particle size distribution based upon the data provided by the manufacturer is shown 3.2.

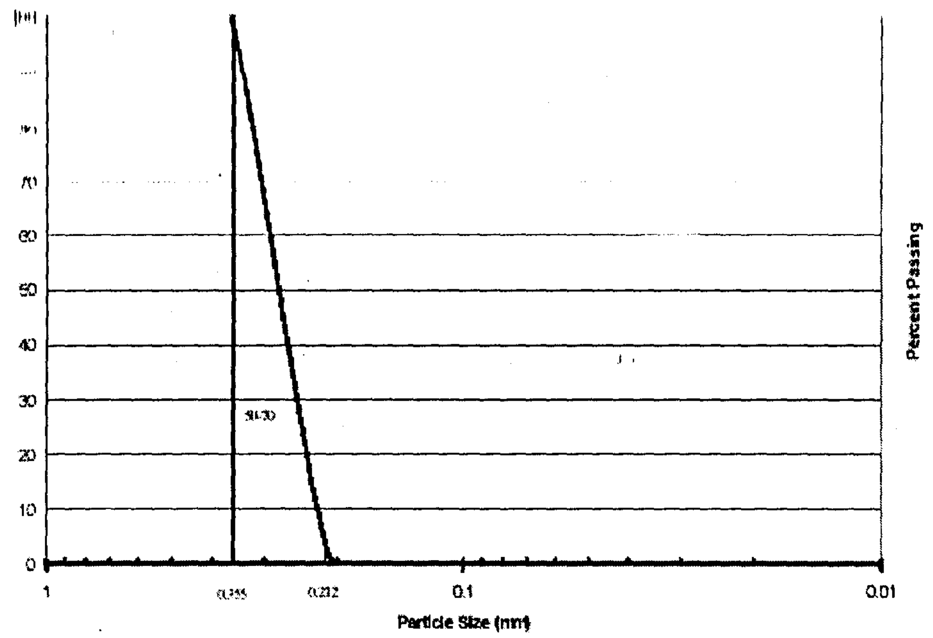

Figure 3.2: Particle size distribution for silica sand used in column experiments.

The 50-70 (sieve number) material is indicated between the two vertical lines connecting between the plot and the x-axis.

As can be seen from Figure 3.2, a significant amount of the sand is indeed 50-70 (sieve) material. In fact, 95.4% of the material is retained on the #70 sieve. Small percentages were retained on the 50 and 100 sieve. Therefore, most of the material is between 0.355 mm and 0.212 mm in diameter. According to the product MSDS, the soil is 99.2 to 99.9% SiO_2. The specific gravity of the sand is 2.65 (Vince DeCapio, 2003).

3.6.3 Determination of porosity and classification

The porosity of the soil in the columns was determined by filling the columns with soil and measuring their combined mass using the Denver Instruments APX 4001 scale with an accuracy of 0.1 grams. The columns were then filled with water. The mass of the columns filled with soil and water was then determined (Vince DeCapio, 2003).

A porosity of 0.388 was determined for this packed column. Typical values of porosity according to Das are 0.444 for loose uniform sand and 0.393 for loose angular-grained silty sand (Vince DeCapio, 2003).

3.6.4 Acid washing of sand

Washed silica sand samples used during experiments were soaked in 1M HCl for 24 hours. Goethite coated sand was acid washed before the coating process. Goethite Coating Sand Silica sand was coated with goethite by mixing 0.01M $NaNO_3$, goethite, and acid washed sand in a 1L container. The container was shaken for 24 hours to ensure efficient coating. Loose goethite particles were then removed through shaking a settling (coated sand settles faster than loose goethite particles). Columns For the tracer experiments conducted and sorption experiments (SE) I-III, Kontes fibreglass columns with two caps (one screw on, one permanent) 22 cm in length and 2.5 cm in diameter were used. For SE IV-V, Kontes Chromaflex 420830 glass columns 15 cm in length and 2.5 cm in diameter were used. The later columns had o-rings, plastic ferrule fittings for each end of the column, and both capped ends were removable (Vince DeCapio, 2003).

3.6.5 Experimental determination of flowrate

To determine the flowrate that would be used for the column experiment, local meteorological data was obtained for the St. Louis area. It was intended to use natural rainfall rates because of an attempt to create natural conditions in the lab. This data showed that typical rainfalls were in the order of 0.25 in/hr for a normal storm and 2.00 in/hr for a record storm (National Weather Service). In order to translate these rainfall rates to velocities through the soil, the hydraulic conductivity of the soil was used. Considering the column experiments would be conducted at saturated conditions, the saturated value of conductivity was used (Vince DeCapio, 2003).

Typical values of hydraulic conductivity at saturated conditions were presented by Tchobanoglous and Schroeder. These values were used to estimate a conductivity of 5 x 10^{-4} (fine sand) for the soil used in this experiment. Bouwer showed that the velocity of the water infiltrating through the soil from the surface cannot exceed the hydraulic conductivity of the soil. Therefore, the following was used to find the infiltration velocity in the soil: saturated filtration saturated rain rain iltration saturated rain (Vince DeCapio, 2003).

3.6.6 Experimental determination of metals sorption on silica sand columns

In this manner, the velocity of water through the soil could be calculated for record rainfall events (the typical rainfall value was not examined because of time constraints). Knowing the area of the column sample, the flowrate through the soil could then be determined. For the heavy rainfall event, the flowrate was found to be 7 x 10^{-9} m^3/s (0.0070 mL/s). Knowing the porosity, this translated to a pore velocity of 0.21 cm/min. This translated to a pore volume and residence time 44mL and 105 minutes for the columns of SE I-III and tracer experiments. The columns of SEIV-V had a pore volume of 30 mL and a residence time of 71minutes (Vince DeCapio, 2003).

The flowrate was delivered to the columns with a Cole Parmer MasterflexL/S Model 7519-10 peristaltic pump with cartridge 7519-75. The pump was calibrated at different dial gage settings to ensure the proper flowrate. During the experiments, the flowrate ranged between 0.0068 and 0.0073 mL/(desired 0.0070 mL/s). Cole Parmer Teflon tubing 0.031" ID and 0.015" wall thickness was used for tubing running from the outlet to the sampling reservoir. Cole Parmer Tygon tubing 0.0625" ID and

0.031" wall thickness was used from the influent reservoir to the pump and then from the pump to the column inlet.

Plastic valves and fittings were used to connect the tubing to the inlet and outlet. All influents pumped into the column were prepared using A. C. S. certified Fisher Chemicals. All pipetting was conducted with Eppendorf Research pipettes with plastic tips ranging from 10-100 μL to 500-5000 μL. For the tracer experiment, 0.01 M KNO_3 and 0.01 M $NaNO_3$ were prepared from 1M stock solutions and pumped through the column. For the sorption experiments, a synthetic rainwater containing metals was prepared. The synthetic rainwater was obtained from that presented by (Morel and Hering). The rainwater contained 10uM $Ca(NO_3)_2$, 10 μM $Pb(NO_3)_2$, and 10 μM $NaNO_3$. The metals was not observed but was just selected to match that observed for Na and Ca. The columns were pre-pumped with a 60 □M KNO_3 solution. This concentration was selected to match the ionic strength of the synthetic rainwater. For each experiment, KNO_3 was prepared and pumped through the columns in order to saturate the column. The ionic strength of the KNO_3 was matched with the synthetic rainwater so that any rapid changes that may cause goethite coated to the sand to be dislodged (typical during rapid changes in ionic strength) to occur during the saturation and not during the experiment (Vince DeCapio, 2003).

3.6.7 Measurements of pH and temperature

Measurements were taken periodically during both the tracer and sorption experiments. These samples were taken at both the influent and effluent reservoirs. Ionic strength was monitored with a Fisher Scientific Traceable Digital Conductivity Meter. The pH and temperature were measured with the Fisher Scientific Accumet Research AR 25 Dual Channel pH/ion Meter. Flowrate was measured by collecting the effluent solution in a pre-weighed container and weighing the container after effluent filling. The density of water was assumed for the conversion of weight to volume. The flowrate ranged between 0.0068 mL/s and 0.0073 mL/s. The pH of all influents during the experiments was

Metals Sorption on Goethite Coated Silica Sand Columns between 5.5 and 5.7. The temperature varied between 19 and 22 degrees Celsius. The conductivity of the influent potassium nitrate ranged between 10 s/cm and 12 s/cm, and the conductivity of the influent synthetic rainwater (SR) ranged between 8 us/cm and 15 s/cm (Vince DeCapio, 2003).

Sample Collection Effluent concentration samples were collected with a Spectra/Chrom CF-1 Fraction Collector. Tubing was connected from the outlet of the column to the fraction collector and samples were collected in Fisher Brand 5mL plastic tubes during each experiment. This allowed for continuous sampling of effluent during an experiment. The sampling time was 5 minutes for the tracer experiment and 10 or 11 minutes for the sorption experiments. The five minutes samples collected about 2.2 mL of effluent. These samples were diluted with a solution of 2% trace metal grade HNO_3 in order to have enough samples for elemental analysis. Samples collected for 10 or 11 minutes gave about 4.3 mL of effluent. These samples were acidified with 450μL of Lab Chem1M HNO_3 to preserve the metals in the sample. Samples were stored at room temperature in the plastic tubes until element analysis could be conducted (Vince DeCapio, 2003).

3.6.8 Extraction of the metals from the soil

Following each sorption experiment, the sand used in the columns was removed in sections. For SE I-III, sections of soil were removed in ~2 cm sections using clean metal spatulas, and for SE IV-V, ~1 cm sections of soil were removed.

The separate samples of soil were then placed in Aluminum drying pans and placed in the Fisher Scientific Isotemp Oven at 110-120 degrees Celsius for 24 hours. After drying, the soil was weighed using the Denver Instruments APX 4001 scale. Then, 1 g samples of soil were placed in 50 mL Fisher Brand plastic tubes. 40 mL of 2% HNO_3 was then pipetted into the plastic tube. The tubes were then placed on the New Brunswick Scientific Classic

Series C1 Platform Shaker for 2 hours. 10 mL of the sample was then used for ICP analysis. If the sand sample contained goethite, the 10 mL was syringe filtered to prevent any solids from being analyzed. This extraction procedure would show how much metals were sorbed onto the surface of soil particles during the sorption experiments.

To determine how much goethite was on the soil particles, a Citrate-Dithionite-Bicarbonate (CDB) procedure was used. This involved drying soil as described above and then subjecting the 1g of soil to a solution containing 0.3 M Sodium Dithionite, 0.3M Sodium Citrate, and 0.2 M Sodium Bicarbonate (Yanase et al., Clark et al., and Tessier et al.) The samples were then shaken for 1 hour. The samples were allowed to set overnight at room temperature until the soil returned to its natural color (no longer golden yellow but white). A sample of 10mL was then analyzed with ICP for iron. Uncoated samples of washed and unwashed silica sand were also analyzed for iron to determine the background iron levels (Vince DeCapio, 2003).

3.6.9 Determination of iron content of the soil

From the results of SE I-V it was necessary to determine how iron is playing a role in the sorption process. Therefore, samples of unwashed silica sand and samples of goethite coated silica sand were analyzed for iron.

Metals Sorption on Goethite Coated Silica Sand Columns found that goethite coated silica sand contains 2 mg of iron per gram of sand whereas unwashed silica sand has 0.05 mg of iron per gram of sand (Vince DeCapio, 2003).

3.6.10 Elemental analysis of metals present in the soil

Effluent solution samples collected were analyzed for lead, sodium, and iron depending upon the experiment. This was done using the Varian Liberty II Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) instrument. Standards were made in the laboratory of 0.05, 0.1, 0.5, 1, and 5 ppm from A.C.S. Fisher Chemicals. The calibration was conducted using a weighted fit on the standard deviation of intensity (Vince DeCapio, 2003).

CHAPTER FOUR

4.0 MODELLING

4.1 Conceptualization of Modelling

Mathematical modelling is the general characterization of a process or concept in mathematical terms, thus enabling the relatively simple manipulation of variables to be accomplished in order to determine how these processes or concept would behave in different situations. It attempts to describe the functional relationship of the variables and parameters by a set of equations and thus, showing more clearly the cause and effect relationships of the variables (Paynes, 2002).

Mathematical modelling is versatile and is widely used in practice. It is a recognised and valuable adjunct and usually a precursor of computer simulation. In developing a mathematical model, you need to determine the mathematical expression that will relate what is known to what you intend to determine. In developing a mathematical system that models the system when values are input into the model, it will act upon this input and produce an output. The major goal is to have this output to be of reasonable approximation of the corresponding response or output of the actual system. Many mathematical models that are difficult or tedious to solve by normal hand calculations can be solved efficiently with the computer. However, the solution will only be as good as the mathematical model (Paynes, 2002).

4.2 Principles of Mathematical Formulation

The principles involved in the formulation of mathematical models are as stated below:

1. Basis: The basis for the mathematical models are the fundamental physical and chemical laws, such as the law of mass, energy and momentum conservation

stated in their time derivative forms. Others include parameters such as mass transfer coefficient, diffusivity constant, reaction rates which are either obtained experimentally or from process operating data (Luyben, 1990).

2. Assumptions: There is need to make simplifying but realistic assumptions about the system while modelling. The outcome of the model is dependent on the assumptions as they impose limitation on the model (Luyben, 1990).

3. Mathematical consistency of model: Care must be taken not to under-specify or over-specify the number of variables or equations describing the system because in order to obtain a solution, the numbers of variables must equal the number of equations, that is, the degree of freedom of the system must be zero (Luyben, 1990).

4. Solution of the model equation: Available solution techniques and tools must be kept in mind in developing the model as one that contains unknown and immeasurable parameters is unsolvable and amount to a waste of time and energy. In the search for a method of solution, possible approximations for the defining equations, boundary and initial conditions and acceptable final solutions are considered (Luyben, 1990).

5. Verifications: The need to prove the validity of a model is an important part of mathematical modelling. Because of the complex nature of verifying the models, it is often neglected. However, one way of achieving this objective is by comparing average experimental result for similar operating conditions with the computed results (Luyben, 1990).

4.3 Simulation

Simulation of a system as the operation of a model, which is a representation of the system, the model being amenable to manipulations which would be impossible, too expensive or impractical to perform on the system it portrays (Paynes, 2002).

Simulation is used for two principal reasons:

i. To give greater understanding and insight into the behaviour of the physical system and the principles upon which its design is based.

ii. To provide a convenient, inexpensive and time saving means of gaining this understanding and insight under a variety of operating conditions.

4.3.1 Computer simulation

Computer simulation however means the running of a special program on a suitable type of computer which generates time response of the model that imitates the behaviour of the process being studied. There are two types of simulation methods, namely, analogue and digital simulation. However, digital simulation is more frequently used because of the enhanced capabilities and operational speed of modern electronic computers which are used in executing computer algorithm of the models (Paynes, 2002).

Modelling and simulation can be carried out with the aid of the computer using some powerful software packages like Excel, Polymath, MathCAD, SPSS and so on. In this work, a mathematical modelling was performed using Excel, MathCAD, and Polymath.

4.4 Importance of Mathematical Modelling

It is quite often the case that we have to design the control system for a chemical process before the process is being constructed. In such a case, we cannot rely on the experimental procedures and we need a different representation of the chemical process in order to study its dynamic behaviour. This representation is usually a set of mathematical equation whose solution yields the dynamics or static behaviour of the chemical process we examine.

Mathematical modelling and simulation can result in considerable saving of both time and money. When it is impractical to experiment with the real system, mathematical modelling and simulation can be used to explore the effect of changes on a system. It can also result in an increase in the fundamental knowledge about a system since it usually involves a considerable analysis of the system.

4.5 Modelling of Mobility of Heavy Metals in Soil

4.5.1 Diagram

The diagram describing the mobility of the heavy metal through the soil is as shown in Figure 4.1 below.

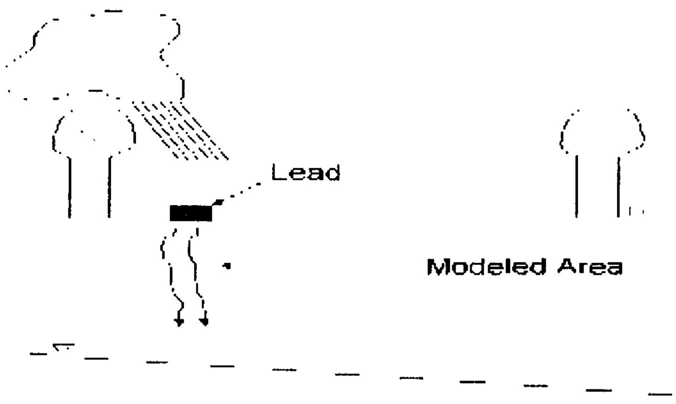

Fig. 4.1: A visual description of the natural system being modelled

4.5.2 Assumptions

The assumptions involved in this modelling of the mobility of heavy metals in the soil are thus:

1) Porous medium is homogeneous, isotropic, and saturated
2) There is no dispersion in the directions transverse to the flow direction

4.5.3 Modelling of the system

The equation that describes the flow of heavy metals material through soil is shown in equation 1 as (Vince DeCapio, 2003)

$$\frac{d}{dt}C = D_L \cdot \frac{d^2}{dx^2}C - v_x \cdot \frac{d}{dx}C - \frac{\rho_b}{\theta} \cdot \frac{d}{dt}(C'') \qquad (1)$$

This equation contains a term for dispersion, advection, and sorption (Vince DeCapio, 2003).

Knowing that

$$C'' = k_d \cdot C \qquad (2)$$

Equation (1) can then be written as

$$\frac{d}{dt}C = D_L \cdot \frac{d^2}{dx^2}C - v_x \cdot \frac{d}{dx}C - \frac{\rho_b}{\theta} \cdot \frac{d}{dt}\left(k_d \cdot C\right) \qquad (3)$$

Since k_d is a constant,

$$\frac{d}{dt}C = D_L \cdot \frac{d^2}{dx^2}C - v_x \cdot \frac{d}{dx}C - \frac{k_d \cdot \rho_b}{\theta} \cdot \frac{d}{dt}C \qquad (4)$$

Rearranging,

$$\frac{d}{dt}C + \frac{k_d \cdot \rho_b}{\theta} \cdot \frac{d}{dt}C = D_L \cdot \frac{d^2}{dx^2}C - v_x \cdot \frac{d}{dx}C \qquad (5)$$

and, rearranging further gives,

$$\frac{d}{dt}C\left(1 + \frac{k_d \cdot \rho_b}{\theta}\right) = D_L \cdot \frac{d^2}{dx^2}C - v_x \cdot \frac{d}{dx}C \qquad (6)$$

that is,

$$\left(1 + \frac{k_d \cdot \rho_b}{\theta}\right) \cdot \frac{d}{dt}C = D_L \cdot \frac{d^2}{dx^2}C - v_x \cdot \frac{d}{dx}C \qquad (7)$$

Let

$$R = \left(1 + \frac{k_d \cdot \rho_b}{\theta}\right) \qquad (8)$$

Equation can be written as

$$R \cdot \frac{d}{dt} C = D_L \cdot \frac{d^2}{dx^2} C - v_x \cdot \frac{d}{dx} C \tag{9}$$

The equation is the same as

$$D_L \cdot \frac{d^2}{dx^2} C - v_x \cdot \frac{d}{dx} C = R \cdot \frac{d}{dt} C \tag{10}$$

This is a second order differential equation which can be solved using any of the methods of solving second order differential equations. In order to solve the equation above, the left hand side is equated to zero as

$$D_L \cdot \frac{d^2}{dx^2} C - v_x \cdot \frac{d}{dx} C = 0 \tag{11}$$

assuming that,

$$m = \frac{d}{dt} C \tag{12}$$

(13)

Equation (12) can be written as

$$D_L \cdot m^2 - v_x \cdot m = 0$$

(14)

$$m \cdot \left(D_L \cdot m - v_x\right) = 0$$

$$m = 0$$

or

$$\left(D_L \cdot m - v_x\right) = 0$$

$$D_L \cdot m = v_x \tag{15}$$

$$m = \frac{v_x}{D_L} \tag{16}$$

In other words,

$$m_1 = 0$$

$$m_2 = \frac{v_x}{D_L}$$

The complementary function which is given as

$$C = A \cdot e^{m_1 \cdot x} + B \cdot e^{m_2 \cdot x} \qquad (17)$$

can, therefore, be written as

$$C = A \cdot e^{0 \cdot x} + B \cdot e^{\frac{v_x}{D_L} \cdot x} \qquad (18)$$

$$C = A + B \cdot e^{\frac{v_x}{D_L} \cdot x} \qquad (19)$$

The particular integral is given as

$$\frac{1}{C} \cdot dC = \frac{1}{R} \cdot dt \qquad (20)$$

$$\ln(C) = \frac{1}{R} t \qquad (21)$$

$$C = e^{\frac{1}{R} t} \qquad (22)$$

The general solution is the sum of the complementary function and the particular function as

"General solution" = "Complementary function + particular integ

$$C = A + B \cdot e^{\frac{v_x}{D_L} \cdot x} + e^{\frac{1}{R} \cdot t} \qquad (23)$$

Boundary conditions:

At t = 0 x = 0 C = 0

That is,

$$0 = A + B \cdot e^{\frac{v_x}{D_L} \cdot (0)} + e^{\frac{1}{R} \cdot (0)} \qquad (24)$$

$$0 = A + B \cdot e^{0} + e^{0}$$

$$0 = A + B \cdot 1 + 1$$

$$0 = A + B + 1$$

$$A = -B - 1$$

Also,

At $t = \infty$ $x = \infty$ $C = 0$

$$0 = A + B \cdot e^{\frac{v_x}{D_L} \cdot (\infty)} + e^{\frac{1}{R} \cdot (\infty)} \tag{25}$$

$$0 = A + B \cdot 0 + 0$$

$$0 = A + 0 + 0$$

$$A = 0$$

This means that from

$$A = -B - 1$$

$$0 = -B - 1$$

$$B = -1$$

Equation (23) can thus be written as

$$C = 0 + (-1) \cdot e^{\frac{v_x}{D_L} \cdot x} + e^{\frac{1}{R} \cdot t} \tag{26}$$

$$C = -1 \cdot e^{\frac{v_x}{D_L} \cdot x} + e^{\frac{1}{R} \cdot t} \tag{27}$$

$$C = e^{\frac{1}{R} \cdot t} - e^{\frac{v_x}{D_L} \cdot x} \tag{28}$$

Finally, substituting the value of R yields

$$C = e^{\frac{1}{\left(1 + \frac{k_d \cdot \rho_b}{\theta}\right)} \cdot t} - e^{\frac{v_x}{D_L} \cdot x} \tag{29}$$

Equation (29) is, therefore, the model equation for the mobility of heavy metals in soils amended with sewage sludge.

CHAPTER FIVE

5.0 RESULTS AND DISCUSSION

5.1 Results

5.1.1 Experimental Results

The results obtained from the experimental analysis are as shown in Table 5.1 – 5.5.

Table 5.1: Experimental results for 100% soil

	Concentrations (kmol/m^3)		
Time	Cadmium	Lead	Nickel
0	0.0070	0.1700	0.1000
5 hrs	0.0080	0.1300	0.0900
1 day	0.0090	0.1200	0.0900
4 days	0.0100	0.0900	0.0800
11 days	0.0080	0.0400	0.0700
18 days	0.0040	0.0400	0.0600
25 days	0.0020	0.0300	0.0400
1.5 months	0.0015	0.0280	0.0500
2 months	0.0010	0.0230	0.0400
3 months	0.0010	0.0200	0.0300
6 months	0.0010	0.0150	0.2400
8 months	0.0010	0.0110	0.0150

Table 5.2: Experimental results for 90% soil + 10% sewage

	Concentrations (kmol/m^3)		
Time	Cadmium	Lead	Nickel
0	0.1200	0.2500	1.3500
5 hrs	0.1000	0.1400	1.1500
1 day	0.0500	0.1200	0.4700
4 days	0.0500	0.0900	0.3700
11 days	0.0270	0.0500	0.2400
18 days	0.0200	0.0300	0.2200
25 days	0.0130	0.0200	0.1900
1.5 months	0.0120	0.0190	0.1700
2 months	0.0090	0.0180	0.1500
3 months	0.0070	0.0190	0.1400
6 months	0.0060	0.0150	0.1200
8 months	0.0040	0.0150	0.1400

Table 5.3: Experimental results for 80% soil + 20% sewage

	Concentrations (kmol/m^3)		
Time	Cadmium	Lead	Nickel
0	0.1300	0.2000	3.0000
5 hrs	0.1000	0.1600	2.1000
1 day	0.0600	0.1200	1.2500
4 days	0.0500	0.1000	0.9700
11 days	0.0500	0.0900	0.6900
18 days	0.0400	0.0800	0.5300
25 days	0.0200	0.0470	0.3900
1.5 months	0.1500	0.0300	0.2900
2 months	0.0130	0.0260	0.3000
3 months	0.0100	0.0220	0.2800
6 months	0.0110	0.0320	0.2400
8 months	0.0100	0.0300	0.2600

Table 5.4: Experimental results for 50% soil + 50% sewage

	Concentrations (kmol/m^3)		
Time	Cadmium	Lead	Nickel
0	0.1600	0.2400	11.0000
5 hrs	0.1200	0.2000	6.6000
1 day	0.1000	0.1600	4.1000
4 days	0.0800	0.1200	2.4300
11 days	0.0500	0.1100	2.4200
18 days	0.0250	0.1000	1.9800
25 days	0.0200	0.0600	1.7900
1.5 months	0.0190	0.0550	1.6000
2 months	0.0180	0.0400	1.2900
3 months	0.0170	0.0380	1.2300
6 months	0.0150	0.0400	0.8000
8 months	0.0100	0.0350	0.6300

Table 5.5: Experimental results for 100% sewage

	Concentrations (kmol/m^3)		
Time	Cadmium	Lead	Nickel
0	0.3700	0.4400	20.0000
5 hrs	0.3600	0.4000	14.0000
1 day	0.2300	0.3900	10.0000
4 days	0.1800	0.3500	9.3000
11 days	0.1600	0.3000	8.9000
18 days	0.0800	0.2000	7.0000
25 days	0.0500	0.1200	5.3000
1.5 months	0.0300	0.1100	3.8000
2 months	0.0250	0.0800	3.0000
3 months	0.0200	0.0500	2.1000
6 months	0.0180	0.0400	1.4000
8 months	0.0080	0.0400	1.0000

5.1.2 Simulated Results

The results obtained after the simulation of the model equation developed are as shown in Table 5.6 – 5.10.

Table 5.6: Simulated results for 100% soil

	Concentrations (kmol/m^3)		
Time	Cadmium	Lead	Nickel
0	0.0068	0.1699	0.1001
5 hrs	0.0079	0.1310	0.0970
1 day	0.0087	0.1201	0.0881
4 days	0.0090	0.0880	0.0801
11 days	0.0078	0.0392	0.0690
18 days	0.0038	0.0394	0.0600
25 days	0.0021	0.0300	0.0390
1.5 months	0.0016	0.0276	0.0501
2 months	0.0010	0.0240	0.0401
3 months	0.0010	0.0189	0.0298
6 months	0.0010	0.0148	0.2399
8 months	0.0010	0.0109	0.0149

Table 5.7: Simulated results for 90% soil + 10% sewage

	Concentrations (kmol/m^3)		
Time	Cadmium	Lead	Nickel
0	0.1201	0.2489	1.3490
5 hrs	0.0991	0.1397	1.1501
1 day	0.0499	0.1200	0.4698
4 days	0.0501	0.0910	0.3701
11 days	0.0271	0.0498	0.2400
18 days	0.0189	0.0299	0.2199
25 days	0.0130	0.0199	0.1900
1.5 months	0.0121	0.0189	0.1701
2 months	0.0091	0.0179	0.1501
3 months	0.0069	0.0191	0.1388
6 months	0.0057	0.0149	0.1199
8 months	0.0038	0.0149	0.1401

Table 5.8: Simulated results for 80% soil + 20% sewage

	Concentrations (kmol/m^3)		
Time	Cadmium	Lead	Nickel
0	0.1299	0.2000	2.9999
5 hrs	0.0999	0.1589	2.0998
1 day	0.0601	0.1201	1.2501
4 days	0.0490	0.1000	0.9800
11 days	0.0501	0.0920	0.7000
18 days	0.0398	0.0794	0.5299
25 days	0.0199	0.0469	0.4000
1.5 months	0.1489	0.0301	0.2901
2 months	0.0129	0.0259	0.2999
3 months	0.0099	0.0221	0.2801
6 months	0.0111	0.0319	0.2399
8 months	0.0101	0.0300	0.2594

Table 5.9: Simulated results for 50% soil + 50% sewage

	Concentrations (kmol/m^3)		
Time	Cadmium	Lead	Nickel
0	0.1601	0.2401	11.0001
5 hrs	0.1199	0.1999	6.6001
1 day	0.1000	0.1595	4.1001
4 days	0.0798	0.1201	2.4299
11 days	0.0501	0.1102	2.4200
18 days	0.0252	0.1001	1.9805
25 days	0.0203	0.0596	1.7896
1.5 months	0.0191	0.0549	1.5999
2 months	0.0179	0.0398	1.2901
3 months	0.0169	0.0378	1.2299
6 months	0.0150	0.0401	0.7999
8 months	0.0101	0.0349	0.6301

Table 5.10: Simulated results for 100% sewage

	Concentrations (kmol/m^3)		
Time	Cadmium	Lead	Nickel
0	0.3699	0.4399	19.9998
5 hrs	0.3600	0.4001	14.0001
1 day	0.2299	0.3901	10.0001
4 days	0.1801	0.3499	9.3000
11 days	0.1601	0.3001	8.9000
18 days	0.0799	0.1999	6.9999
25 days	0.0497	0.1190	5.2997
1.5 months	0.0295	0.1097	3.8000
2 months	0.0248	0.0798	2.9999
3 months	0.0202	0.0501	2.0998
6 months	0.0179	0.0401	1.4001
8 months	0.0081	0.0398	1.0000

5.1.3 Experimental and simulated results

The comparisons of experimental and simulated results are as shown in Table 5.11 – 5.15.

Table 5.11: Experimental and simulated results for 100% soil

	Cadmium (kmol/m^3)			Lead (kmol/m^3)			Nickel(kmol/m^3)		
Time	Exp	Sim	%Error	Exp	Sim	%Error	Exp	Sim	%Error
0	0.01	0.01	2.86	0.17	0.17	0.06	0.10	0.10	-0.10
5 hrs	0.01	0.01	1.25	0.13	0.13	-0.77	0.09	0.10	-7.78
1 day	0.01	0.01	3.33	0.12	0.12	-0.08	0.09	0.09	2.11
4 days	0.01	0.01	10.00	0.09	0.09	2.22	0.08	0.08	-0.13
11 days	0.01	0.01	2.50	0.04	0.04	2.00	0.07	0.07	1.43
18 days	0.00	0.00	5.00	0.04	0.04	1.50	0.06	0.06	0.00
25 days	0.00	0.00	-5.00	0.03	0.03	0.00	0.04	0.04	2.50
1.5 months	0.00	0.00	-6.67	0.03	0.03	1.43	0.05	0.05	-0.20
2 months	0.00	0.00	0.00	0.02	0.02	-4.35	0.04	0.04	-0.25
3 months	0.00	0.00	0.00	0.02	0.02	5.50	0.03	0.03	0.67
6 months	0.00	0.00	0.00	0.02	0.01	1.33	0.24	0.24	0.04
8 months	0.00	0.00	0.00	0.01	0.01	0.91	0.02	0.01	0.67

Table 5.12: Experimental and simulated results for 90% soil + 10% sewage

	Cadmium (kmol/m^3)			Lead (kmol/m^3)			Nickel(kmol/m^3)		
Time	Exp	Sim	%Error	Exp	Sim	%Error	Exp	Sim	%Error
0	0.12	0.12	-0.08	0.25	0.25	0.44	1.35	1.35	0.07
5 hrs	0.10	0.10	0.90	0.14	0.14	0.21	1.15	1.15	-0.01
1 day	0.05	0.05	0.20	0.12	0.12	0.00	0.47	0.47	0.04
4 days	0.05	0.05	-0.20	0.09	0.09	-1.11	0.37	0.37	-0.03
11 days	0.03	0.03	-0.37	0.05	0.05	0.40	0.24	0.24	0.00
18 days	0.02	0.02	5.50	0.03	0.03	0.33	0.22	0.22	0.05
25 days	0.01	0.01	0.00	0.02	0.02	0.50	0.19	0.19	0.00
1.5 months	0.01	0.01	-0.83	0.02	0.02	0.53	0.17	0.17	-0.06
2 months	0.01	0.01	-1.11	0.02	0.02	0.56	0.15	0.15	-0.07
3 months	0.01	0.01	1.43	0.02	0.02	-0.53	0.14	0.14	0.86
6 months	0.01	0.01	5.00	0.02	0.01	0.67	0.12	0.12	0.08
8 months	0.00	0.00	5.00	0.02	0.01	0.67	0.14	0.14	-0.07

Table 5.13: Experimental and simulated results for 80% soil + 20% sewage

	Cadmium (kmol/m^3)			Lead (kmol/m^3)			Nickel(kmol/m^3)		
Time	Exp	Sim	%Error	Exp	Sim	%Error	Exp	Sim	%Error
0	0.13	0.13	0.08	0.20	0.20	0.00	3.00	3.00	0.00
5 hrs	0.10	0.10	0.10	0.16	0.16	0.69	2.10	2.10	0.01
1 day	0.06	0.06	-0.17	0.12	0.12	-0.08	1.25	1.25	-0.01
4 days	0.05	0.05	2.00	0.10	0.10	0.00	0.97	0.98	-1.03
11 days	0.05	0.05	-0.20	0.09	0.09	-2.22	0.69	0.70	-1.45
18 days	0.04	0.04	0.50	0.08	0.08	0.75	0.53	0.53	0.02
25 days	0.02	0.02	0.50	0.05	0.05	0.21	0.39	0.40	-2.56
1.5 months	0.15	0.15	0.73	0.03	0.03	-0.33	0.29	0.29	-0.03
2 months	0.01	0.01	0.77	0.03	0.03	0.38	0.30	0.30	0.03
3 months	0.01	0.01	1.00	0.02	0.02	-0.45	0.28	0.28	-0.04
6 months	0.01	0.01	-0.91	0.03	0.03	0.31	0.24	0.24	0.04
8 months	0.01	0.01	-1.00	0.03	0.03	0.00	0.26	0.26	0.23

Table 5.14: Experimental and simulated results for 50% soil + 50% sewage

	Cadmium (kmol/m^3)			Lead (kmol/m^3)			Nickel(kmol/m^3)		
Time	Exp	Sim	%Error	Exp	Sim	%Error	Exp	Sim	%Error
0	0.16	0.16	-0.06	0.24	0.24	-0.04	11.00	11.00	0.00
5 hrs	0.12	0.12	0.08	0.20	0.20	0.05	6.60	6.60	0.00
1 day	0.10	0.10	0.00	0.16	0.16	0.31	4.10	4.10	0.00
4 days	0.08	0.08	0.25	0.12	0.12	-0.08	2.43	2.43	0.00
11 days	0.05	0.05	-0.20	0.11	0.11	-0.18	2.42	2.42	0.00
18 days	0.03	0.03	-0.80	0.10	0.10	-0.10	1.98	1.98	-0.03
25 days	0.02	0.02	-1.50	0.06	0.06	0.67	1.79	1.79	0.02
1.5 months	0.02	0.02	-0.53	0.06	0.05	0.18	1.60	1.60	0.01
2 months	0.02	0.02	0.56	0.04	0.04	0.50	1.29	1.29	-0.01
3 months	0.02	0.02	0.59	0.04	0.04	0.53	1.23	1.23	0.01
6 months	0.02	0.02	0.00	0.04	0.04	-0.25	0.80	0.80	0.01
8 months	0.01	0.01	-1.00	0.04	0.03	0.29	0.63	0.63	-0.02

Table 5.15: Experimental and simulated results for 100% sewage

	Cadmium (kmol/m^3)			Lead (kmol/m^3)			Nickel(kmol/m^3)		
Time	Exp	Sim	%Error	Exp	Sim	%Error	Exp	Sim	%Error
0	0.37	0.37	0.03	0.44	0.44	0.02	20.00	20.00	0.00
5 hrs	0.36	0.36	0.00	0.40	0.40	-0.02	14.00	14.00	0.00
1 day	0.23	0.23	0.04	0.39	0.39	-0.03	10.00	10.00	0.00
4 days	0.18	0.18	-0.06	0.35	0.35	0.03	9.30	9.30	0.00
11 days	0.16	0.16	-0.06	0.30	0.30	-0.03	8.90	8.90	0.00
18 days	0.08	0.08	0.13	0.20	0.20	0.05	7.00	7.00	0.00
25 days	0.05	0.05	0.60	0.12	0.12	0.83	5.30	5.30	0.01
1.5 months	0.03	0.03	1.67	0.11	0.11	0.27	3.80	3.80	0.00
2 months	0.03	0.02	0.80	0.08	0.08	0.25	3.00	3.00	0.00
3 months	0.02	0.02	-1.00	0.05	0.05	-0.20	2.10	2.10	0.01
6 months	0.02	0.02	0.56	0.04	0.04	-0.25	1.40	1.40	-0.01
8 months	0.01	0.01	-1.25	0.04	0.04	0.50	1.00	1.00	0.00

5.2 Discussion of Results

The activities of man has gotten to a level at which their effects are global in nature. The atmosphere, land and sea as well as animal and plant are being clearly disturbed. It is obvious that the concentrations of heavy metals in the soil have increased during the last century as a result of domestic sewage sludge being dumped on the soil for disposal. Considering the serious deteriorations of the basic characteristics of the environment, especially the soil, as a result of harmful pollutant released into it (soil), it has become necessary to seriously consider environmental management as a priority project if improved quality of life to be guaranteed.

The experimental results of this project are as shown in Tables 5.1 to 5.5. The experimental results show the presence of heavy metals in the soil as time increased from 0 to 8 months for different concentrations of sewage in the soil. For instance, the concentrations of cadmium, lead and nickel for ordinary soil (100% soil) at the initial time were found to be 0.007, 0.17 and 0.1 mg/m^3 respectively. As time increased to 5 hours, that is, after five hours, the concentration of cadmium had increased to 0.008 mg/m^3 while that of lead and nickel had decreased to 0.131 and 0.09 mg/m^3 respectively.

In Table 5.2, the concentrations of heavy metals present in the soil when the sewage percentage was 10% in the soil are shown. The results revealed that the concentrations of heavy metals present in the soil at this percentage of 10% sewage in the soil were higher than that of the 0% sewage. For instance, the concentrations of cadmium, lead and nickel were found, at the 10% sewage in the soil, to be 0.12, 0.25 and 1.35 mg/m^3 respectively. This shows that the more the percentage of sewage in any soil, the higher the concentration of heavy metals in that soil.

The trend of the concentration shows that the concentrations first increased and later decreased as the time increased. For instance, when the time was 5 hours, for soil with 20% sewage, the concentrations of cadmium, lead and nickel were found to be 0.10, 0.16, 2.1 mg/m^3 respectively while the concentrations when the time increased to 1 day (24 hours) were found to decrease to 0.06, 0.12 and 1.25 mg/m^3 respectively for cadmium, lead and nickel present in the soil. Further, in some cases, for instance, in the table for 90% soil, when the time increased again, the concentration which decreased before then increased. The same trend was observed in the simulated results.

The trend of the variation in concentration with respect to time and distance actually confirmed the mobility of heavy metals in the soil.

The comparisons between the experimental and simulated results are shown in Tables 5.11 to 5.15. The observations from the results showed there are good agreements between the experimental and simulated concentrations of heavy metals in the soil. For instance, for the 50% sewage soil, when the experimental concentration of cadmium was 0.12 mg/m^3 at the end of 5 hours, the simulated concentration was 0.1199 mg/m^3. At the same time of 5 hours when the experimental concentrations of lead and nickel were 0.2 and 6.6 mg/m^3, the simulated concentrations were found to be 0.1999 and 6.6001 mg/m^3 respectively.

The trend of the concentration shows that the concentrations first increased and later decreased as the time increased.

The mobility pattern of the heavy metals in the soil revealed that the heavy metals were moving slowly in the soil as shown by the slow change in the concentrations of the heavy metals in the soil as time increased. Besides, the pattern of movement, as depicted by Graph A1 – A5 shown in appendix A, zigzag pattern of movement substantiate this.

The agreement between the experimental and simulated concentrations of heavy metals in the soil can also be confirmed by calculating the value of correlation coefficient on the two results (experimental and simulated). From the calculations, it was obtained that the correlation coefficient for the 0% sewage model was 0.9983 while that of the 10% sewage was 0.9999. Moreover, the correlation coefficients for 20% and 50% sewage sludge were calculated to be unity (1.0000). Finally, the vale obtained for the correlation coefficient of the last one, which is 100% sludge, was also 1.0000.

Bearing in mind the aim of this project, to model an equation for the prediction of mobility of heavy metals amended with sewage sludge, it can be concluded that, looking at the results obtained, equation predicting the mobility of cadmium, lead and nickel in soil has been modeled and, within the range of experimental error, the equation represent of phenomenon of mobility of the metals in the soil very well because the correlation coefficients obtained from the calculations were between 0.9983 and 1.0000.

CHAPTER SIX

6.0 CONCLUSION AND RECOMMENDATIONS

6.1 CONCLUSION

CONCLUSION

The model equation developed for the mobility of heavy metals in the soil contaminated with sewage sludge is given as $C = e^{\frac{1}{\left(1+\frac{k_d \cdot \rho_b}{\theta}\right)} \cdot t} - e^{\frac{v_x}{D_L} \cdot x}$. The analysis of the result shows that there is a very good level of agreement between the experimental and simulated results obtained. This can also be confirmed by the statistical analysis of the result through the correlation coefficient found to be 0.9983, 0.9999, and 1.000 for 100% soil, 90% soil and 50% soil respectively

In conclusion, the model developed can be considered to be a good representation of the phenomenon of mobility of metals in the soil.

6.2 RECOMMENDATION

- MathCAD 2000 professional was used for the simulation of the model developed in this project; it is recommended that another software or program should be used to simulate the model.
- Other properties like the pH should be considered one of the factors affecting the mobility of heavy metals in the soil contaminated with sewage sludge.

REFERENCES

1) Vince DeCapio (2003); Lead Sorption on Goethite Coated Silica Sand Columns, Environmental Engineering Science, Washington, USA, Pp. 3-13.
2) Yanase, N., Nightingale, T., Payne, T., and Duerden, P. "Uranium Distribution in Mineral Phases of Rock by Sequential Extraction Procedure." Radiochimica Acta. Vol. 52/53. Pg. 387-393. 1991.
3) McLaren R. G. and P. V. Crawford (1973); Studies of Copper, The Fractionation of Copper in Soils, Journal of Soil Science, 24: 172-181.
4) Nouri J. (1980); Heavy Metals in Sewage Sludge, Soils Amended with Sludge and Their Uptake by Crop Plants, Ph. D. Thesis, University of London.
5) Luyben W. L. (1990), Processing Modelling, Simulation and Control for Chemical Engineers, Lehigh University International Edition, Singapore, Pg. 15-88.
6) Paynes James A. (1982), Introduction to Simulation, McGraw Hill, New York,.

1) Hemond, Harold F. and Fechner-Levy, Elizabeth J. Chemical Fate and Transport in the Environment 2nd Edition. Academic Press. San Diego, CA. 2000.
2) Chang, A.C., J.E. Warneke, A.L. Page, and L.J. Lund. 1989. Accumulation of heavy metals in sewage sludge-treated soils. J. Environ. Qual. 13:87-91.
3) Dowdy, R.H., J.J. Latterell, T.D. Hinesly, R.B. Grussman, and D.L. Sullivan. 1991. Trace metal movement in an Aeric Ochraqualf following 14 years of annual sludge applications. J. Environ. Qual. 20:119-123.
4) Ainsworth, C. C., D. C. Girvin, J. M. Zachara and S. C. Smith. 1989. Chromate adsorption on goethite: effects of aluminum substitution. Soil Sci. Soc. Am. J. 53:411-418.

5) Elliott, H.A., M.R. Liberati, and C.P. Huang. 2001. Competitive adsorbtion of heavy metals by soils. J. Environ. Qual. 15:214-219.

6) Kuo, S., E.J. Jellum, and A.S. Baker. 1999. Effects of soil type, liming, and sludge application on zinc and cadmium availability to swiss chard. Soil Sci. 122:350-359.

7) Cynthia R. Evanko, Ph. D. and David A. Dzombak, Ph. D., P.E. (1997); Ground-Water Remediation Technologies Analysis Center, Pittsburgh.

8) Smith, L.A., Means, J.L., Chen, A., Alleman, B., Chapman, C.C., Tixier, J.S., Jr., Brauning, S.E., Gavaskar, A.R., and Royer, M.D. (1995), Remedial Options for Metals-Contaminated Sites, Lewis Publishers, Boca Raton, FL.

9) Evans, L.J. (1989), "Chemistry of Metal Retention by Soils, Environ. Sci. Tech., 23: 1046-1056.

10) Chang, A.C., J.E. Warneke, A.L. Page, and L.J. Lund. 1984. Accumulation of heavy metals in sewage sludge-treated soils. J. Environ. Qual. 13:87-91.

11) Logan, T.J., and R.L. Chaney. 1983. Metals. In: Utilization of municipal wastewater and sludge on land. A.L. Page et al., eds. Univ. of California, Riverside, CA. pp. 235-326.

12) McBride, M.B., L.D. Tyler, and D.A. Hovde. 1981. Cadmium adsorption by soils and uptake by plants as affected by soil chemical properties. Soil Sci. Soc. Am. J. 45:739-744.

13) McBride, M.B., L.D. Tyler, and D.A. Hovde. 1981. Cadmium adsorption by soils and uptake by plants as affected by soil chemical properties. Soil Sci. Soc. Am. J. 45:739-744.

14) McLaren, R. G. and D. V. Crawford. 1973. Studies on soil copper: II. the specific adsorption of copper by soils. J. Soil Sci. 24:443-452.

15)Kuo, S., E.J. Jellum, and A.S. Baker. 1985. Effects of soil type, liming, and sludge application on zinc and cadmium availability to swiss chard. Soil Sci. 122:350-359.

16)Jenne, E. A. 1968. Control of Mn, Fe, Co, Ni, Cu, and Zn concentrations in soils and water-the dominant role of hydrous manganese and iron oxides. Adv. in Chem. 7:337-387.

17)Snoeyink, V.L., and D. Jenkins. 1980. Water chemistry. John Wiley and Sons, New York.

18)Elliott, H. A., M. R. Liberati and C. P. Huang. 1986. Competitive adsorption of heavy metals by soils. J. Environ. Qual. 15:214-219.

19)Steenhuis, T.S., C.J. Ritsema, L.W. Dekker, and J.-Y. Parlange. 1994. Fast and early appearance of solutes in groundwater by rapid and far-reaching flows, pp. 2a:184-203 in (J.D. Etchevers B., ed.) Transactions, 15th International World Congress of Soil Science (July 10-16, 1994, Acupulco, Mexico). International Soil

20)Science Society.

21)Glass, R.J., G.H. Oosting, and T.S. Steenhuis. 1989. Preferential solute transport in layered homogenous soils as a consequence of wetting front instability. Journal of Hydrology 110:87-105.

22)Lund, L.J., A.L. Page, and C.O. Nelson. 1976. Movement of heavy metals below sewage disposal ponds. J. Environ. Qual. 5:330-334.

23)Van Lune, P. 1991. Long-term heavy-metal leaching from soils, sewage sludge and soil/sewage sludge mixtures. In: Treatment and use of sewage sludge and liquid agricultural wastes. P.L. Hermite, ed. Elsevier Science Pub. Co., New York. pp. 122-127.

24)Shuman, L. M. 1991. Chemical forms of micronutrients in soils. In J. J. Mortvedt (ed.). Micronutrients in agriculture. Soil Soc. Soc. Amer. Book Series #4. Soil Sci. Soc. Amer., Inc., Madison, WI.

25)Mattigod, S. V., G. Sposito, and A. L. Page. 1981. Factors affecting the solubilities of trace metals in soils. In D. E. Baker (Ed.). Chemistry in the soil environment. ASA Special Publication No 40. Amer. Soc. Agronomy, Madison, WI. McBride, M. B. 1977. Copper (II) interaction with kaolinite factors controlling adsorption. Clays Clay Miner. 26:101-106.

26)Baham, J., N. B. Ball and G. Sposito. 1978. Gel filtration studies of trace metal-fulvic acid solutions extracted from sewage sludge. J. Environ. Qual. 7:181-188.

27)Gschwend, P. M. and M. D. Reynolds. 1987. Monodisperse ferrous phosphate colloids in an anoxic groundwater plume. J. of Contaminant Hydrol. 1:309-327.

28)Puls, R. W., R. M. Powell, D. Clark, and C. J. Eldred. 1991. Effect of pH, solid/solution ratio, ionic strength, and organic acids on Pb and Cd sorption on kaolinite. Water, Air, and Soil Pollution 57-58:423-430.

29)Sposito, G. 1979. Derivation of the Langmuir equation for ion exchange reactions in soils. Soil Sci. Soc. Am. J. 43:197-198.

30)Sposito, G. 1989. The chemistry of soils. Oxford University Press. New York.

31)Sposito, G., F. T. Bingham, S. S. Yadav and C. A. Inwye. 1982. Trace metal complexation by fulvic acid extracted from sewage sludge. II. development of chemical models. Soil Sci. Soc. Am. J. 46:51-56.

32)Lindsay, W. L. 1979. Chemical equilibria in soils. John Wiley and Sons. New York.

33)Stevenson, F. J. and A. Fitch. 1986. Chemistry of complexation of metal ions with soil solution organics. In P. M. Huang and M. Schnitzer (eds.). Interactions of soil

34)minerals with natural organics and microbes. Soil Sci Soc. Special Publ. No 17, Soil Sci Soc. Amer., Madison, WI.

35)Jenne, E.A. 1968. Controls on Mn, Fe, Co, Ni, Cu, and Zn concentration in soils and water: The significant role of hydrous Mn, and Fe oxides. In: Trace inorganics in water. Adv. In Chem. Ser. 73. R.F. Gould, ed. Am. Chem. Soc., Washington, DC. pp. 337-387.

36)Stevenson, F. J. 1991. Organic matter-micronutrient reaction sin soil. In J. J. Mortvedt (ed.). Micronutrients in agriculture. Soil Soc. Soc. Amer. Book Series #4. Soil Sci. Soc. Amer., Inc., Madison, WI.

37)Silviera, D. J. and L. E. Sommers. 1977. Extractability of copper, zinc, cadmium, and lead in soils incubated with sewage sludge. J. Environ. Qual. 6:47-52.

38)Hendrickson, L. L. and R. B. Corey. 1981. Effect of equilibrium metal concentration on apparent selectivity coefficients of soil complexes. Soil Sci. 131:163-171.

39)O'Connor, G. A., R. S. Bowman, M. A. Elrashidi, and R. Keren. 1983. Solute retention and mobility in New Mexico soils: I. characterization of solute retention reactions. Agric. Exper. Station Bulletin #701. New Mexico State University, Las Cruces, NM.

APPENDIX

APPENDIX A: GRAPHS

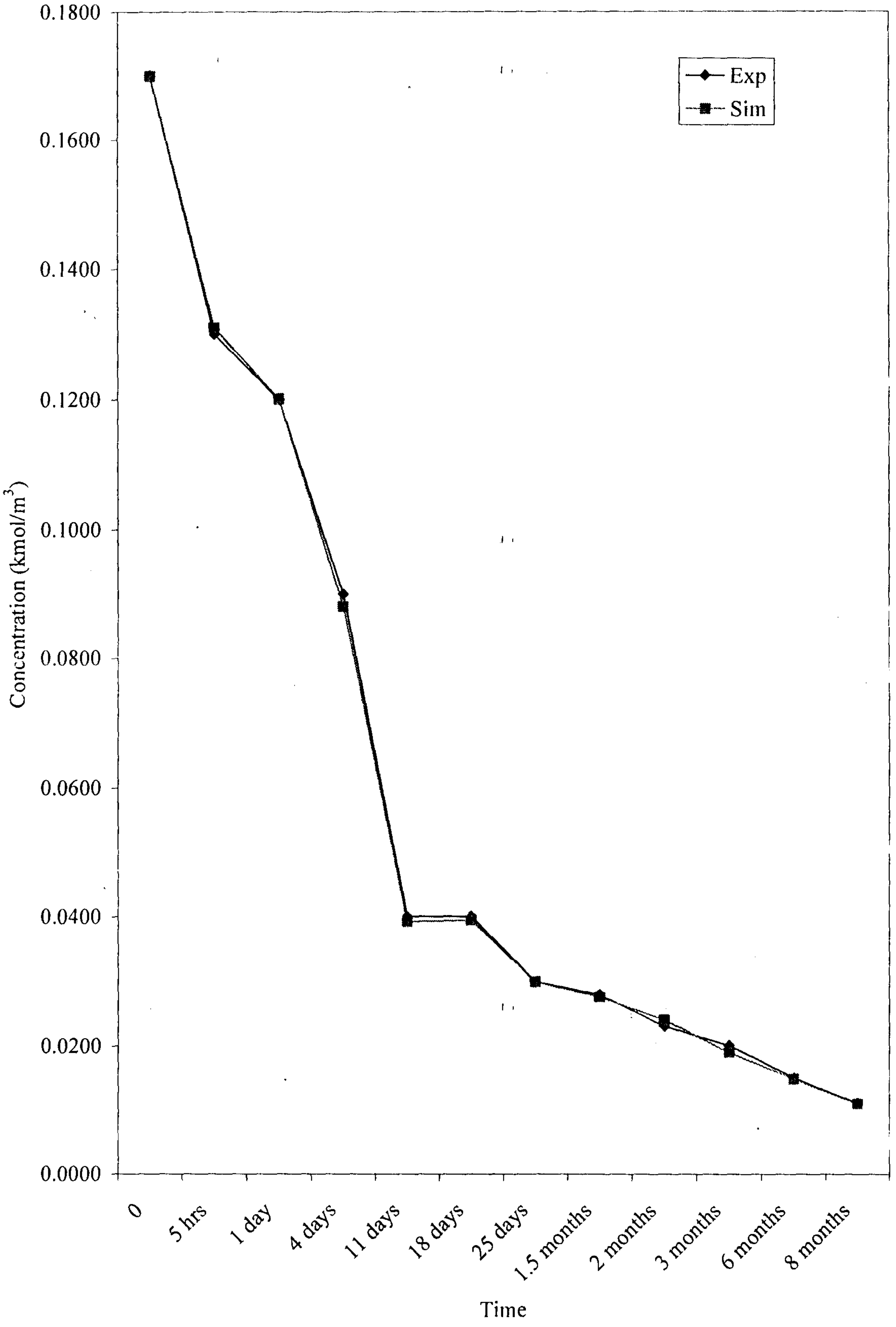

Fig. A1: Mobility pattern of heavy metals in soil for 100% soil

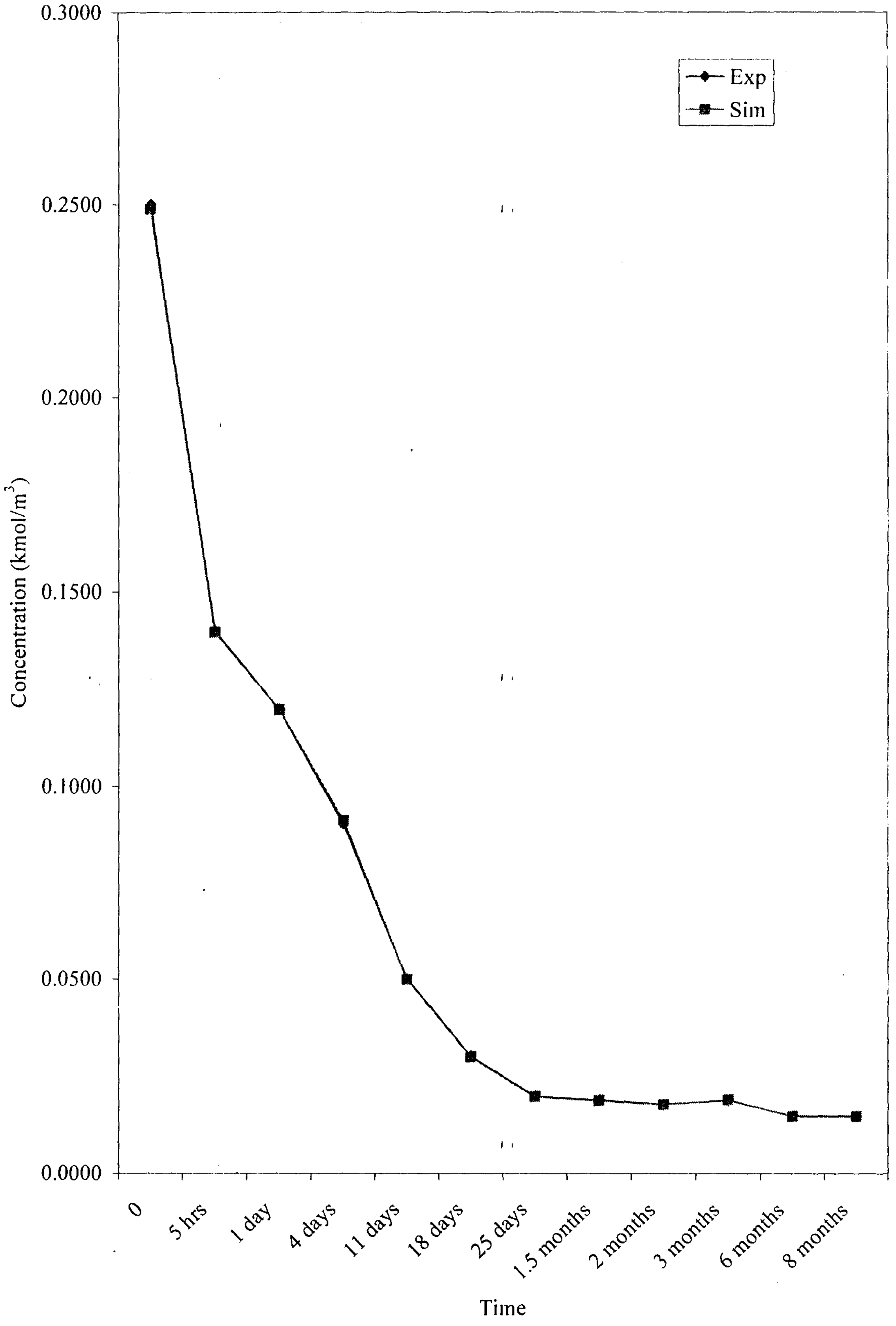

Fig. A2: Mobility pattern of heavy metals in soil for 90% soil

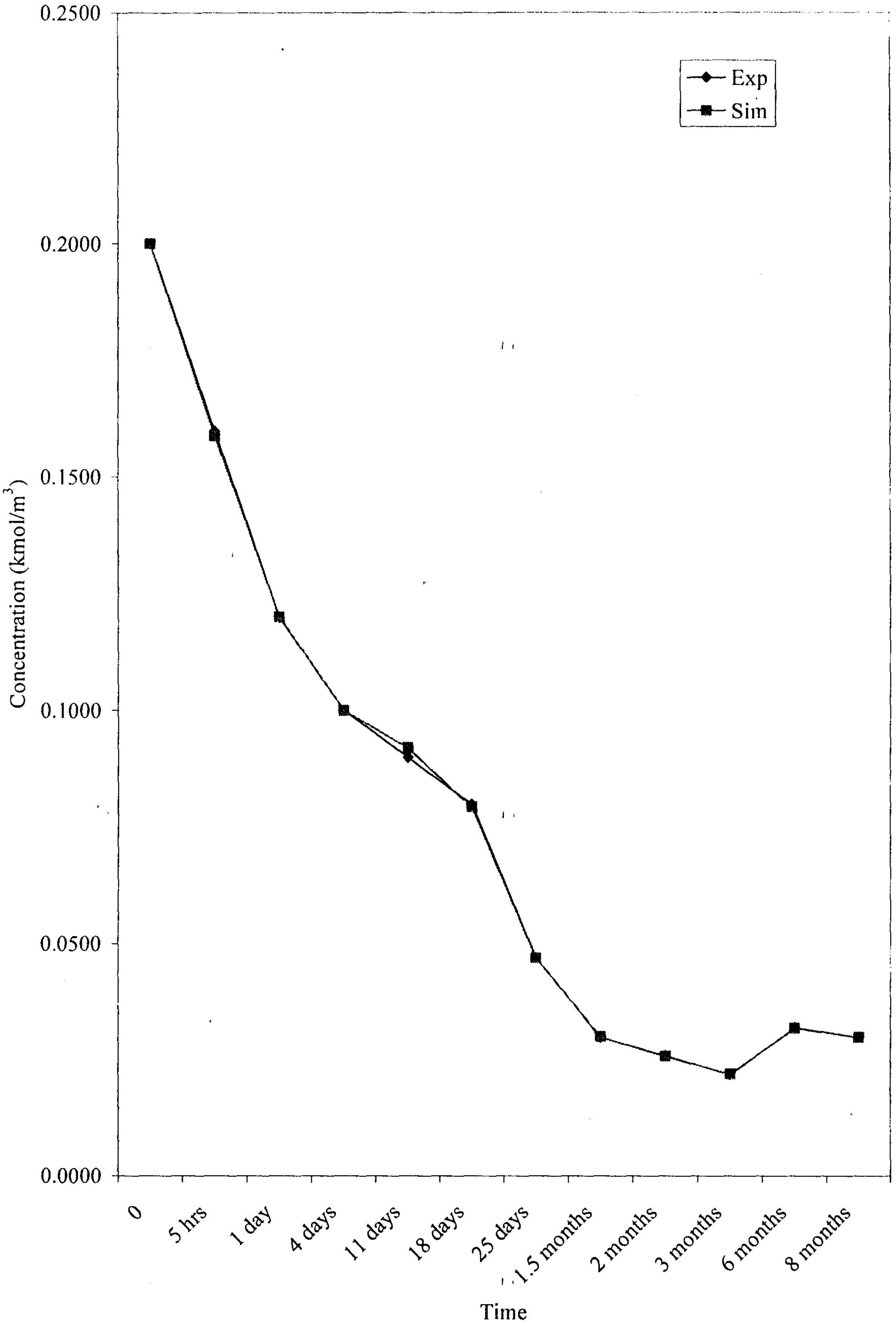

Fig. A3: Mobility pattern of heavy metals in soil for 80% soil

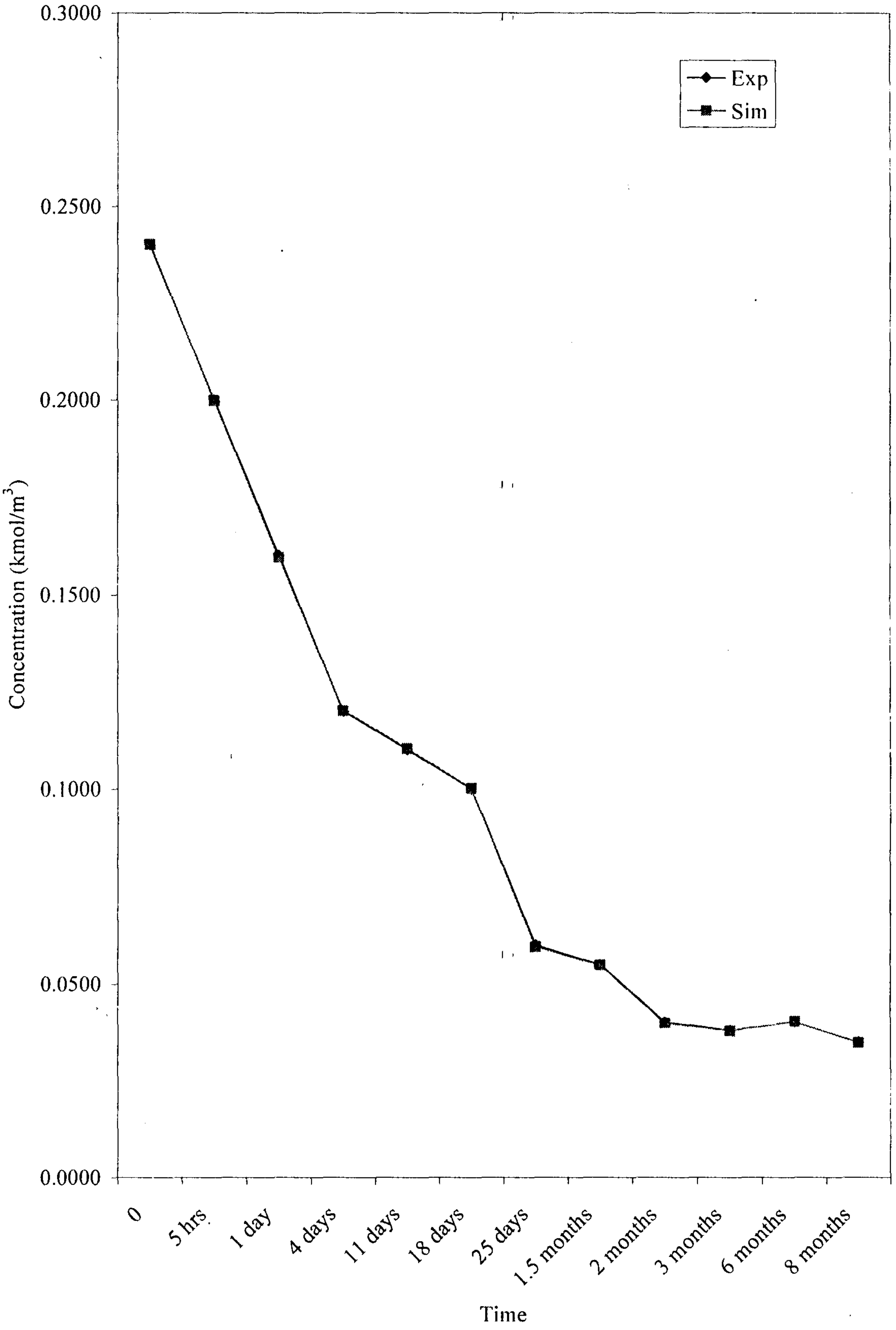

Fig. A4: Mobility pattern of heavy metals in soil for 50% soil

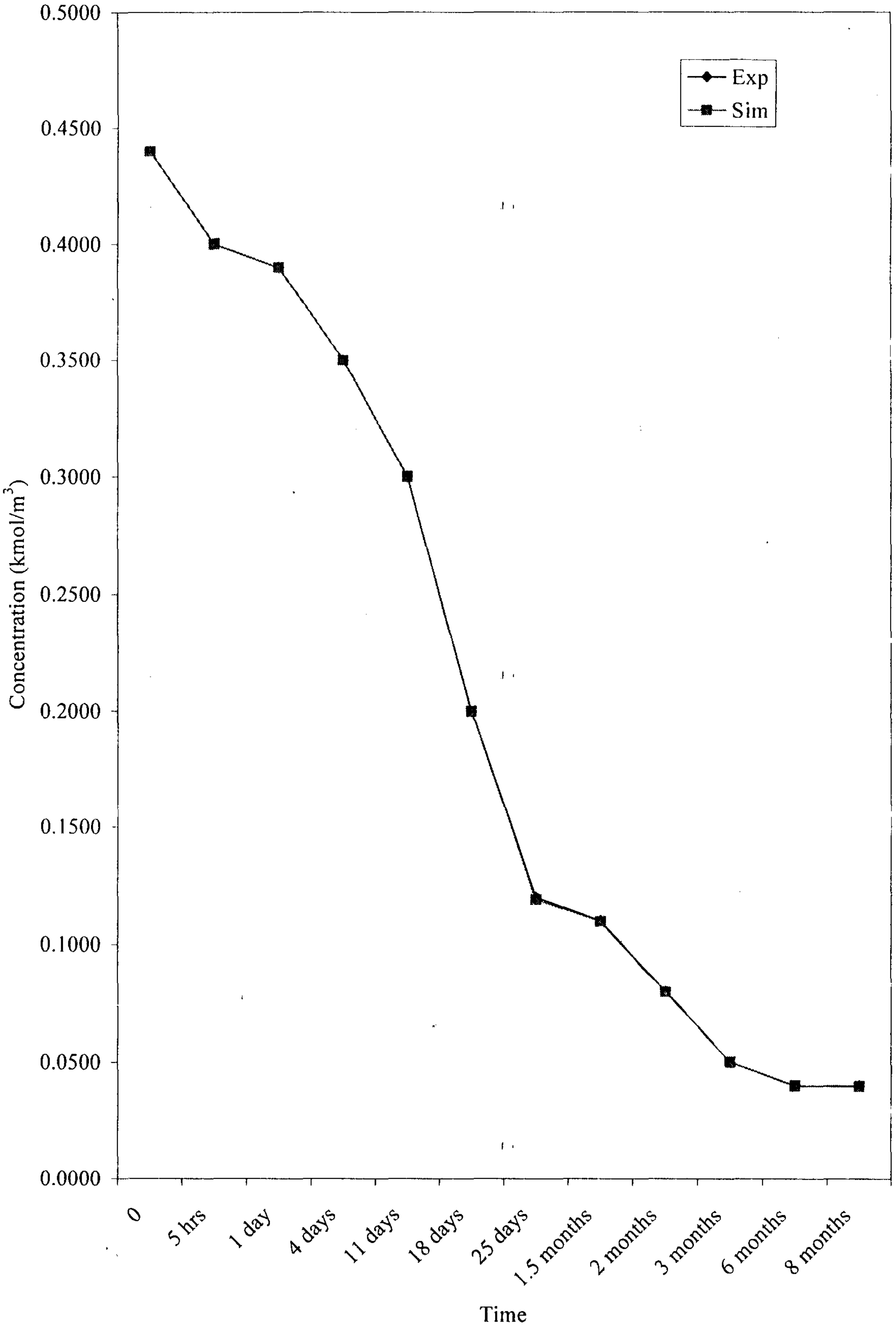

Fig. A5: Mobility pattern of heavy metals in soil for 100% sewage

APPENDIX B: SIMULATION ALGORITHMS

SIMULATION ALGORITHM FOR 100% SOIL

Given that,

$Cd := 112.41$ $\qquad \alpha_L := 5$

$Pb := 207.21$ $\qquad v := 15$

$Ni := 58.69$ $\qquad D_e := 0$

$fr := 1$

$K_d := 0.2$

$\rho_b := 2250$

$\theta := 0.15$

$v_x := 15$

$$t := \begin{pmatrix} 0 \\ 5 \cdot hrs \\ 1 \cdot day \\ 4 days \\ 11 days \\ 18 \cdot days \\ 25 \cdot days \\ 1.5 \cdot months \\ 2 \cdot months \\ 3 \cdot months \\ 6 \cdot months \\ 8 \cdot months \end{pmatrix} \qquad x := \begin{pmatrix} 0 \\ 0.5 \\ 1.0 \\ 1.5 \\ 2.0 \\ 2.5 \\ 3.0 \\ 3.5 \\ 4.0 \\ 4.5 \\ 5.0 \\ 5.5 \end{pmatrix}$$

$D_{LCd} := D_e + \alpha_L \cdot v + \mathrm{erf}(Cd)$

$D_{LPb} := D_e + \alpha_L \cdot v + \mathrm{erf}(Pb)$

$D_{LNi} := D_e + \alpha_L \cdot v + \mathrm{erf}(Ni)$

$$t := \frac{t}{hr}$$

$$C_{Cd} := \overrightarrow{\left| e^{\frac{1}{\left(1+\frac{K_d \cdot \rho_b}{\theta}\right)} \cdot t} - e^{\frac{v_x}{D_{LCd}} \cdot x} \right|}$$

$$C_{Pb} := \overrightarrow{\left| e^{\frac{1}{\left(1+\frac{K_d \cdot \rho_b}{\theta}\right)} \cdot t} - e^{\frac{v_x}{D_{LPb}} \cdot x} \right|}$$

$$C_{Ni} := \overrightarrow{\left| e^{\frac{1}{\left(1+\frac{K_d \cdot \rho_b}{\theta}\right)} \cdot t} - e^{\frac{v_x}{D_{LNi}} \cdot x} \right|}$$

Simulated results:

$$C_{Cds} = \begin{pmatrix} 0.0068 \\ 0.0079 \\ 0.0087 \\ 0.0090 \\ 0.0078 \\ 0.0038 \\ 0.0021 \\ 0.0016 \\ 0.0010 \\ 0.0010 \\ 0.0010 \\ 0.0010 \end{pmatrix} \qquad C_{Pbs} = \begin{pmatrix} 0.1699 \\ 0.1310 \\ 0.1201 \\ 0.0880 \\ 0.0392 \\ 0.0394 \\ 0.0300 \\ 0.0276 \\ 0.0240 \\ 0.0189 \\ 0.0148 \\ 0.0109 \end{pmatrix} \qquad C_{Nis} = \begin{pmatrix} 0.1001 \\ 0.0970 \\ 0.0881 \\ 0.0801 \\ 0.0690 \\ 0.0600 \\ 0.0390 \\ 0.0501 \\ 0.0401 \\ 0.0298 \\ 0.2399 \\ 0.0149 \end{pmatrix}$$

Experimental results:

$$C_{Cde} := \begin{pmatrix} 0.007 \\ 0.008 \\ 0.009 \\ 0.01 \\ 0.008 \\ 0.004 \\ 0.002 \\ 0.0015 \\ 0.001 \\ 0.001 \\ 0.001 \\ 0.001 \end{pmatrix} \qquad C_{Pbe} := \begin{pmatrix} 0.17 \\ 0.13 \\ 0.12 \\ 0.09 \\ 0.04 \\ 0.04 \\ 0.03 \\ 0.028 \\ 0.023 \\ 0.02 \\ 0.015 \\ 0.011 \end{pmatrix} \qquad C_{Nie} := \begin{pmatrix} 0.1 \\ 0.09 \\ 0.09 \\ 0.08 \\ 0.07 \\ 0.06 \\ 0.04 \\ 0.05 \\ 0.04 \\ 0.03 \\ 0.24 \\ 0.015 \end{pmatrix}$$

Correlation coefficient:

$$\operatorname{corr}\left(C_{Cde}, C_{Cds}\right) = 0.9983$$

$$\operatorname{corr}\left(C_{Pbe}, C_{Pbs}\right) = 0.9999$$

$$\operatorname{corr}\left(C_{Nie}, C_{Nis}\right) = 0.9993$$

Errors:

$$E_{Cd} := C_{Cde} - C_{Cds} \qquad E_{Pb} := C_{Pbe} - C_{Pbs} \qquad E_{Ni} := C_{Nie} - C_{Nis}$$

$$E_{Cd} = \begin{pmatrix} 0.0002 \\ 0.0001 \\ 0.0003 \\ 0.0010 \\ 0.0002 \\ 0.0002 \\ -0.0001 \\ -0.0001 \\ 0.0000 \\ -0.0000 \\ 0.0000 \\ 0.0000 \end{pmatrix} \qquad E_{Pb} = \begin{pmatrix} 0.0001 \\ -0.0010 \\ -0.0001 \\ 0.0020 \\ 0.0008 \\ 0.0006 \\ -0.0000 \\ 0.0004 \\ -0.0010 \\ 0.0011 \\ 0.0002 \\ 0.0001 \end{pmatrix} \qquad E_{Ni} = \begin{pmatrix} -0.0001 \\ -0.0070 \\ 0.0019 \\ -0.0001 \\ 0.0010 \\ -0.0000 \\ 0.0010 \\ -0.0001 \\ -0.0001 \\ 0.0002 \\ 0.0001 \\ 0.0001 \end{pmatrix}$$

Percentage errors:

$$P_{ECd} := \overrightarrow{\left(\frac{E_{Cd}}{C_{Cde}} \cdot 100\right)} \qquad P_{EPb} := \overrightarrow{\left(\frac{E_{Pb}}{C_{Pbe}} \cdot 100\right)} \qquad P_{ENi} := \overrightarrow{\left(\frac{E_{Ni}}{C_{Nie}} \cdot 100\right)}$$

$$P_{ECd} = \begin{pmatrix} 2.8571 \\ 1.1842 \\ 3.2749 \\ 9.9474 \\ 2.4342 \\ 4.8684 \\ -5.2632 \\ -7.0175 \\ 4.4737 \\ -0.5263 \\ 1.4737 \\ 2.4737 \end{pmatrix} \qquad P_{EPb} = \begin{pmatrix} 0.0588 \\ -0.7733 \\ -0.0877 \\ 2.2164 \\ 1.9868 \\ 1.4868 \\ -0.0175 \\ 1.4098 \\ -4.3707 \\ 5.4737 \\ 1.2982 \\ 0.8612 \end{pmatrix} \qquad P_{ENi} = \begin{pmatrix} -0.1000 \\ -7.7836 \\ 2.1053 \\ -0.1316 \\ 1.4211 \\ -0.0088 \\ 2.4868 \\ -0.2105 \\ -0.2632 \\ 0.6491 \\ 0.0395 \\ 0.6316 \end{pmatrix}$$

SIMULATION ALGORITHM FOR 90% SOIL + 10% SLUDGE

Given that,

$Cd := 112.41$

$Pb := 207.21$

$Ni := 58.69$

$fr := 0.1$

$K_d := 0.2$

$\rho_b := 2250$

$\theta := 0.15$

$v_x := 15$

$\alpha_L := 5$

$v := 15$

$D_e := 0$

$$t := \begin{pmatrix} 0 \\ 5 \cdot hrs \\ 1 \cdot day \\ 4days \\ 11days \\ 18 \cdot days \\ 25 \cdot days \\ 1.5 \cdot months \\ 2 \cdot months \\ 3 \cdot months \\ 6 \cdot months \\ 8 \cdot months \end{pmatrix} \qquad x := \begin{pmatrix} 0 \\ 0.5 \\ 1.0 \\ 1.5 \\ 2.0 \\ 2.5 \\ 3.0 \\ 3.5 \\ 4.0 \\ 4.5 \\ 5.0 \\ 5.5 \end{pmatrix}$$

$$D_{LCd} := D_e + \alpha_L \cdot v + \mathrm{erf}(Cd)$$

$$D_{LPb} := D_e + \alpha_L \cdot v + \mathrm{erf}(Pb)$$

$$D_{LNi} := D_e + \alpha_L \cdot v + \mathrm{erf}(Ni)$$

$$t := \frac{t}{hr}$$

$$C_{Cd} := \overrightarrow{\left| e^{\frac{1}{\left(1+\frac{K_d \cdot \rho_b}{\theta}\right)} \cdot t} - e^{\frac{v_x}{D_{LCd}} \cdot x} \right|}$$

$$C_{Pb} := \overrightarrow{\left| e^{\frac{1}{\left(1+\frac{K_d \cdot \rho_b}{\theta}\right)} \cdot t} - e^{\frac{v_x}{D_{LPb}} \cdot x} \right|}$$

$$C_{Ni} := \overrightarrow{\left| e^{\frac{1}{\left(1+\frac{K_d \cdot \rho_b}{\theta}\right)} \cdot t} - e^{\frac{v_x}{D_{LNi}} \cdot x} \right|}$$

Simulated results:

$$C_{Cds} = \begin{pmatrix} 0.1201 \\ 0.0991 \\ 0.0499 \\ 0.0501 \\ 0.0271 \\ 0.0189 \\ 0.0130 \\ 0.0121 \\ 0.0091 \\ 0.0069 \\ 0.0057 \\ 0.0038 \end{pmatrix} \qquad C_{Pbs} = \begin{pmatrix} 0.2489 \\ 0.1397 \\ 0.1200 \\ 0.0910 \\ 0.0498 \\ 0.0299 \\ 0.0199 \\ 0.0189 \\ 0.0179 \\ 0.0191 \\ 0.0149 \\ 0.0149 \end{pmatrix} \qquad C_{Nis} = \begin{pmatrix} 1.3490 \\ 1.1501 \\ 0.4698 \\ 0.3701 \\ 0.2400 \\ 0.2199 \\ 0.1900 \\ 0.1701 \\ 0.1501 \\ 0.1388 \\ 0.1199 \\ 0.1401 \end{pmatrix}$$

Experimental results:

$$C_{Cde} := \begin{pmatrix} 0.1200 \\ 0.1000 \\ 0.0500 \\ 0.0500 \\ 0.0270 \\ 0.0200 \\ 0.0130 \\ 0.0120 \\ 0.0090 \\ 0.0070 \\ 0.0060 \\ 0.0040 \end{pmatrix} \qquad C_{Pbe} := \begin{pmatrix} 0.2500 \\ 0.1400 \\ 0.1200 \\ 0.0900 \\ 0.0500 \\ 0.0300 \\ 0.0200 \\ 0.0190 \\ 0.0180 \\ 0.0190 \\ 0.0150 \\ 0.0150 \end{pmatrix} \qquad C_{Nie} := \begin{pmatrix} 1.3500 \\ 1.1500 \\ 0.4700 \\ 0.3700 \\ 0.2400 \\ 0.2200 \\ 0.1900 \\ 0.1700 \\ 0.1500 \\ 0.1400 \\ 0.1200 \\ 0.1400 \end{pmatrix}$$

Correlation coefficient: $\mathrm{corr}\left(C_{Cde}, C_{Cds}\right) = 0.9999$

Errors:

$$E_{Cd} := C_{Cde} - C_{Cds} \qquad E_{Pb} := C_{Pbe} - C_{Pbs} \qquad E_{Ni} := C_{Nie} - C_{Nis}$$

$$E_{Cd} = \begin{pmatrix} -0.0001 \\ 0.0009 \\ 0.0001 \\ -0.0001 \\ -0.0001 \\ 0.0011 \\ -0.0000 \\ -0.0001 \\ -0.0001 \\ 0.0001 \\ 0.0003 \\ 0.0002 \end{pmatrix} \qquad E_{Pb} = \begin{pmatrix} 0.0011 \\ 0.0003 \\ -0.0000 \\ -0.0010 \\ 0.0002 \\ 0.0001 \\ 0.0001 \\ 0.0001 \\ 0.0001 \\ -0.0001 \\ 0.0001 \\ 0.0001 \end{pmatrix} \qquad E_{Ni} = \begin{pmatrix} 0.0010 \\ -0.0001 \\ 0.0002 \\ -0.0001 \\ -0.0000 \\ 0.0001 \\ -0.0000 \\ -0.0001 \\ -0.0001 \\ 0.0012 \\ 0.0001 \\ -0.0001 \end{pmatrix}$$

Percentage errors:

$$P_{ECd} := \overrightarrow{\left(\frac{E_{Cd}}{C_{Cde}} \cdot 100\right)} \qquad P_{EPb} := \overrightarrow{\left(\frac{E_{Pb}}{C_{Pbe}} \cdot 100\right)} \qquad P_{ENi} := \overrightarrow{\left(\frac{E_{Ni}}{C_{Nie}} \cdot 100\right)}$$

$$P_{ECd} = \begin{pmatrix} -0.0833 \\ 0.8947 \\ 0.1895 \\ -0.2105 \\ -0.3899 \\ 5.4737 \\ -0.0405 \\ -0.8772 \\ -1.1696 \\ 1.3534 \\ 4.9123 \\ 4.8684 \end{pmatrix} \qquad P_{EPb} = \begin{pmatrix} 0.4400 \\ 0.2105 \\ -0.0044 \\ -1.1170 \\ 0.3895 \\ 0.3158 \\ 0.4737 \\ 0.4986 \\ 0.5263 \\ -0.5540 \\ 0.6316 \\ 0.6316 \end{pmatrix} \qquad P_{ENi} = \begin{pmatrix} 0.0741 \\ -0.0092 \\ 0.0414 \\ -0.0284 \\ -0.0022 \\ 0.0431 \\ -0.0028 \\ -0.0619 \\ -0.0702 \\ 0.8534 \\ 0.0789 \\ -0.0752 \end{pmatrix}$$

SIMULATION ALGORITHM FOR 80% SOIL + 20% SLUDGE

Given that,

$Cd := 112.41$ $\alpha_L := 5$

$Pb := 207.21$ $v := 15$

$Ni := 58.69$ $D_e := 0$

$fr := 0.2$

$K_d := 0.2$

$\rho_b := 2250$

$\theta := 0.15$

$v_x := 15$

$$t := \begin{pmatrix} 0 \\ 5 \cdot hrs \\ 1 \cdot day \\ 4 days \\ 11 days \\ 18 \cdot days \\ 25 \cdot days \\ 1.5 \cdot months \\ 2 \cdot months \\ 3 \cdot months \\ 6 \cdot months \\ 8 \cdot months \end{pmatrix} \qquad x := \begin{pmatrix} 0 \\ 0.5 \\ 1.0 \\ 1.5 \\ 2.0 \\ 2.5 \\ 3.0 \\ 3.5 \\ 4.0 \\ 4.5 \\ 5.0 \\ 5.5 \end{pmatrix}$$

$D_{LCd} := D_e + \alpha_L \cdot v + \mathrm{erf}(Cd)$

$D_{LPb} := D_e + \alpha_L \cdot v + \mathrm{erf}(Pb)$

$D_{LNi} := D_e + \alpha_L \cdot v + \mathrm{erf}(Ni)$

$t := \frac{t}{hr}$

$$C_{Cd} := \overrightarrow{\left| e^{\frac{1}{\left(1+\frac{K_d \cdot \rho_b}{\theta}\right)} \cdot t} - e^{\frac{v_x}{D_{LCd}} \cdot x} \right|}$$

$$C_{Pb} := \overrightarrow{\left| e^{\frac{1}{\left(1+\frac{K_d \cdot \rho_b}{\theta}\right)} \cdot t} - e^{\frac{v_x}{D_{LPb}} \cdot x} \right|}$$

$$C_{Ni} := \overrightarrow{\left| e^{\frac{1}{\left(1+\frac{K_d \cdot \rho_b}{\theta}\right)} \cdot t} - e^{\frac{v_x}{D_{LNi}} \cdot x} \right|}$$

Simulated results:

$$C_{Cds} = \begin{pmatrix} 0.1299 \\ 0.0999 \\ 0.0601 \\ 0.0490 \\ 0.0501 \\ 0.0398 \\ 0.0199 \\ 0.1489 \\ 0.0129 \\ 0.0099 \\ 0.0111 \\ 0.0101 \end{pmatrix} \quad C_{Pbs} = \begin{pmatrix} 0.2000 \\ 0.1589 \\ 0.1201 \\ 0.1000 \\ 0.0920 \\ 0.0794 \\ 0.0469 \\ 0.0301 \\ 0.0259 \\ 0.0221 \\ 0.0319 \\ 0.0300 \end{pmatrix} \quad C_{Nis} = \begin{pmatrix} 2.9999 \\ 2.0998 \\ 1.2501 \\ 0.9800 \\ 0.7000 \\ 0.5299 \\ 0.4000 \\ 0.2901 \\ 0.2999 \\ 0.2801 \\ 0.2399 \\ 0.2594 \end{pmatrix}$$

Experimental results:

$$C_{Cde} := \begin{pmatrix} 0.1300 \\ 0.1000 \\ 0.0600 \\ 0.0500 \\ 0.0500 \\ 0.0400 \\ 0.0200 \\ 0.1500 \\ 0.0130 \\ 0.0100 \\ 0.0110 \\ 0.0100 \end{pmatrix} \quad C_{Pbe} := \begin{pmatrix} 0.2000 \\ 0.1600 \\ 0.1200 \\ 0.1000 \\ 0.0900 \\ 0.0800 \\ 0.0470 \\ 0.0300 \\ 0.0260 \\ 0.0220 \\ 0.0320 \\ 0.0300 \end{pmatrix} \quad C_{Nie} := \begin{pmatrix} 3.0000 \\ 2.1000 \\ 1.2500 \\ 0.9700 \\ 0.6900 \\ 0.5300 \\ 0.3900 \\ 0.2900 \\ 0.3000 \\ 0.2800 \\ 0.2400 \\ 0.2600 \end{pmatrix}$$

Correlation coefficient: $\mathrm{corr}\left(C_{Cde}, C_{Cds}\right) = 1.0000$

Errors:

$E_{Cd} := C_{Cde} - C_{Cds}$ $\qquad$ $E_{Pb} := C_{Pbe} - C_{Pbs}$ $\qquad$ $E_{Ni} := C_{Nie} - C_{Nis}$

$$E_{Cd} = \begin{pmatrix} 0.0001 \\ 0.0001 \\ -0.0001 \\ 0.0010 \\ -0.0001 \\ 0.0002 \\ 0.0001 \\ 0.0011 \\ 0.0001 \\ 0.0001 \\ -0.0001 \\ -0.0001 \end{pmatrix} \qquad E_{Pb} = \begin{pmatrix} 0.0000 \\ 0.0011 \\ -0.0001 \\ -0.0000 \\ -0.0020 \\ 0.0006 \\ 0.0001 \\ -0.0001 \\ 0.0001 \\ -0.0001 \\ 0.0001 \\ -0.0000 \end{pmatrix} \qquad E_{Ni} = \begin{pmatrix} 0.0001 \\ 0.0002 \\ -0.0001 \\ -0.0100 \\ -0.0100 \\ 0.0001 \\ -0.0100 \\ -0.0001 \\ 0.0001 \\ -0.0001 \\ 0.0001 \\ 0.0006 \end{pmatrix}$$

Percentage errors:

$P_{ECd} := \overrightarrow{\left(\frac{E_{Cd}}{C_{Cde}} \cdot 100\right)}$ $\qquad$ $P_{EPb} := \overrightarrow{\left(\frac{E_{Pb}}{C_{Pbe}} \cdot 100\right)}$ $\qquad$ $P_{ENi} := \overrightarrow{\left(\frac{E_{Ni}}{C_{Nie}} \cdot 100\right)}$

$$P_{ECd} = \begin{pmatrix} 0.0769 \\ 0.0947 \\ -0.1754 \\ 1.9895 \\ -0.2105 \\ 0.4868 \\ 0.4737 \\ 0.7298 \\ 0.7287 \\ 0.9474 \\ -0.9569 \\ -1.0526 \end{pmatrix} \qquad P_{EPb} = \begin{pmatrix} 0.0000 \\ 0.6842 \\ -0.0877 \\ -0.0053 \\ -2.2281 \\ 0.7434 \\ 0.2016 \\ -0.3509 \\ 0.3644 \\ -0.4785 \\ 0.2961 \\ -0.0175 \end{pmatrix} \qquad P_{ENi} = \begin{pmatrix} 0.0033 \\ 0.0093 \\ -0.0084 \\ -1.0315 \\ -1.4500 \\ 0.0179 \\ -2.5655 \\ -0.0363 \\ 0.0316 \\ -0.0376 \\ 0.0395 \\ 0.2287 \end{pmatrix}$$

SIMULATION ALGORITHM FOR 50% SOIL + 50% SLUDGE

Given that,

$Cd := 112.41$

$Pb := 207.21$

$Ni := 58.69$

$fr := 0.5$

$K_d := 0.2$

$\rho_b := 2250$

$\theta := 0.15$

$v_x := 15$

$\alpha_L := 5$

$v := 15$

$D_e := 0$

$$t := \begin{pmatrix} 0 \\ 5 \cdot hrs \\ 1 \cdot day \\ 4 days \\ 11 days \\ 18 \cdot days \\ 25 \cdot days \\ 1.5 \cdot months \\ 2 \cdot months \\ 3 \cdot months \\ 6 \cdot months \\ 8 \cdot months \end{pmatrix} \qquad x := \begin{pmatrix} 0 \\ 0.5 \\ 1.0 \\ 1.5 \\ 2.0 \\ 2.5 \\ 3.0 \\ 3.5 \\ 4.0 \\ 4.5 \\ 5.0 \\ 5.5 \end{pmatrix}$$

$D_{LCd} := D_e + \alpha_L \cdot v + erf(Cd)$

$D_{LPb} := D_e + \alpha_L \cdot v + erf(Pb)$

$D_{LNi} := D_e + \alpha_L \cdot v + erf(Ni)$

$$t := \frac{t}{hr}$$

$$C_{Cd} := \overrightarrow{\left| e^{\frac{1}{\left(1+\frac{K_d \cdot \rho_b}{\theta}\right)} \cdot t} - e^{\frac{v_x}{D_{LCd}} \cdot x} \right|}$$

$$C_{Pb} := \overrightarrow{\left| e^{\frac{1}{\left(1+\frac{K_d \cdot \rho_b}{\theta}\right)} \cdot t} - e^{\frac{v_x}{D_{LPb}} \cdot x} \right|}$$

$$C_{Ni} := \overrightarrow{\left| e^{\frac{1}{\left(1+\frac{K_d \cdot \rho_b}{\theta}\right)} \cdot t} - e^{\frac{v_x}{D_{LNi}} \cdot x} \right|}$$

Simulated results:

$$C_{Cds} = \begin{pmatrix} 0.1601 \\ 0.1199 \\ 0.1000 \\ 0.0798 \\ 0.0501 \\ 0.0252 \\ 0.0203 \\ 0.0191 \\ 0.0179 \\ 0.0169 \\ 0.0150 \\ 0.0101 \end{pmatrix} \quad C_{Pbs} = \begin{pmatrix} 0.2401 \\ 0.1999 \\ 0.1595 \\ 0.1201 \\ 0.1102 \\ 0.1001 \\ 0.0596 \\ 0.0549 \\ 0.0398 \\ 0.0378 \\ 0.0401 \\ 0.0349 \end{pmatrix} \quad C_{Nis} = \begin{pmatrix} 11.0001 \\ 6.6001 \\ 4.1001 \\ 2.4299 \\ 2.4200 \\ 1.9805 \\ 1.7896 \\ 1.5999 \\ 1.2901 \\ 1.2299 \\ 0.7999 \\ 0.6301 \end{pmatrix}$$

Experimental results:

$$C_{Cde} := \begin{pmatrix} 0.1600 \\ 0.1200 \\ 0.1000 \\ 0.0800 \\ 0.0500 \\ 0.0250 \\ 0.0200 \\ 0.0190 \\ 0.0180 \\ 0.0170 \\ 0.0150 \\ 0.0100 \end{pmatrix} \quad C_{Pbe} := \begin{pmatrix} 0.2400 \\ 0.2000 \\ 0.1600 \\ 0.1200 \\ 0.1100 \\ 0.1000 \\ 0.0600 \\ 0.0550 \\ 0.0400 \\ 0.0380 \\ 0.0400 \\ 0.0350 \end{pmatrix} \quad C_{Nie} := \begin{pmatrix} 11.0000 \\ 6.6000 \\ 4.1000 \\ 2.4300 \\ 2.4200 \\ 1.9800 \\ 1.7900 \\ 1.6000 \\ 1.2900 \\ 1.2300 \\ 0.8000 \\ 0.6300 \end{pmatrix}$$

Correlation coefficient: $\mathrm{corr}\left(C_{Cde}, C_{Cds}\right) = 1.0000$

Errors:

$$E_{Cd} := C_{Cde} - C_{Cds} \qquad E_{Pb} := C_{Pbe} - C_{Pbs} \qquad E_{Ni} := C_{Nie} - C_{Nis}$$

$$E_{Cd} = \begin{pmatrix} -0.0001 \\ 0.0001 \\ -0.0000 \\ 0.0002 \\ -0.0001 \\ -0.0002 \\ -0.0003 \\ -0.0001 \\ 0.0001 \\ 0.0001 \\ -0.0000 \\ -0.0001 \end{pmatrix} \qquad E_{Pb} = \begin{pmatrix} -0.0001 \\ 0.0001 \\ 0.0005 \\ -0.0001 \\ -0.0002 \\ -0.0001 \\ 0.0004 \\ 0.0001 \\ 0.0002 \\ 0.0002 \\ -0.0001 \\ 0.0001 \end{pmatrix} \qquad E_{Ni} = \begin{pmatrix} -0.0001 \\ -0.0001 \\ -0.0001 \\ 0.0001 \\ -0.0000 \\ -0.0005 \\ 0.0004 \\ 0.0001 \\ -0.0001 \\ 0.0001 \\ 0.0001 \\ -0.0001 \end{pmatrix}$$

Percentage errors:

$$P_{ECd} := \overrightarrow{\left(\frac{E_{Cd}}{C_{Cde}} \cdot 100\right)} \qquad P_{EPb} := \overrightarrow{\left(\frac{E_{Pb}}{C_{Pbe}} \cdot 100\right)} \qquad P_{ENi} := \overrightarrow{\left(\frac{E_{Ni}}{C_{Nie}} \cdot 100\right)}$$

$$P_{ECd} = \begin{pmatrix} -0.0625 \\ 0.0789 \\ -0.0053 \\ 0.2434 \\ -0.2105 \\ -0.8211 \\ -1.5263 \\ -0.5540 \\ 0.5263 \\ 0.5573 \\ -0.0351 \\ -1.0526 \end{pmatrix} \qquad P_{EPb} = \begin{pmatrix} -0.0417 \\ 0.0474 \\ 0.3092 \\ -0.0877 \\ -0.1866 \\ -0.1053 \\ 0.6579 \\ 0.1722 \\ 0.4868 \\ 0.5125 \\ -0.2632 \\ 0.2707 \end{pmatrix} \qquad P_{ENi} = \begin{pmatrix} -0.0009 \\ -0.0016 \\ -0.0026 \\ 0.0039 \\ -0.0002 \\ -0.0255 \\ 0.0221 \\ 0.0059 \\ -0.0082 \\ 0.0077 \\ 0.0118 \\ -0.0167 \end{pmatrix}$$

SIMULATION ALGORITHM FOR 100% SLUDGE

Given that,

$Cd := 112.41$ $\alpha_L := 5$

$Pb := 207.21$

$v := 15$

$Ni := 58.69$

$D_e := 0$

$fr := 0$

$K_d := 0.2$

$\rho_b := 2250$

$\theta := 0.15$

$v_x := 15$

$$t := \begin{pmatrix} 0 \\ 5 \cdot hrs \\ 1 \cdot day \\ 4days \\ 11days \\ 18 \cdot days \\ 25 \cdot days \\ 1.5 \cdot months \\ 2 \cdot months \\ 3 \cdot months \\ 6 \cdot months \\ 8 \cdot months \end{pmatrix} \qquad x := \begin{pmatrix} 0 \\ 0.5 \\ 1.0 \\ 1.5 \\ 2.0 \\ 2.5 \\ 3.0 \\ 3.5 \\ 4.0 \\ 4.5 \\ 5.0 \\ 5.5 \end{pmatrix}$$

$$D_{LCd} := D_e + \alpha_L \cdot v + \mathrm{erf}(Cd)$$

$$D_{LPb} := D_e + \alpha_L \cdot v + \mathrm{erf}(Pb)$$

$$D_{LNi} := D_e + \alpha_L \cdot v + \mathrm{erf}(Ni)$$

$$t := \frac{t}{hr}$$

$$C_{Cd} := \overrightarrow{\left| e^{\frac{1}{\left(1+\frac{K_d \cdot \rho_b}{\theta}\right)} \cdot t} - e^{\frac{v_x}{D_{LCd}} \cdot x} \right|}$$

$$C_{Pb} := \overrightarrow{\left| e^{\frac{1}{\left(1+\frac{K_d \cdot \rho_b}{\theta}\right)} \cdot t} - e^{\frac{v_x}{D_{LPb}} \cdot x} \right|}$$

$$C_{Ni} := \overrightarrow{\left| e^{\frac{1}{\left(1+\frac{K_d \cdot \rho_b}{\theta}\right)} \cdot t} - e^{\frac{v_x}{D_{LNi}} \cdot x} \right|}$$

Simulated results:

$$C_{Cds} = \begin{pmatrix} 0.3699 \\ 0.3600 \\ 0.2299 \\ 0.1801 \\ 0.1601 \\ 0.0799 \\ 0.0497 \\ 0.0295 \\ 0.0248 \\ 0.0202 \\ 0.0179 \\ 0.0081 \end{pmatrix} \quad C_{Pbs} = \begin{pmatrix} 0.4399 \\ 0.4001 \\ 0.3901 \\ 0.3499 \\ 0.3001 \\ 0.1999 \\ 0.1190 \\ 0.1097 \\ 0.0798 \\ 0.0501 \\ 0.0401 \\ 0.0398 \end{pmatrix} \quad C_{Nis} = \begin{pmatrix} 19.9998 \\ 14.0001 \\ 10.0001 \\ 9.3000 \\ 8.9000 \\ 6.9999 \\ 5.2997 \\ 3.8000 \\ 2.9999 \\ 2.0998 \\ 1.4001 \\ 1.0000 \end{pmatrix}$$

Experimental results:

$$C_{Cde} := \begin{pmatrix} 0.3700 \\ 0.3600 \\ 0.2300 \\ 0.1800 \\ 0.1600 \\ 0.0800 \\ 0.0500 \\ 0.0300 \\ 0.0250 \\ 0.0200 \\ 0.0180 \\ 0.0080 \end{pmatrix} \quad C_{Pbe} := \begin{pmatrix} 0.4400 \\ 0.4000 \\ 0.3900 \\ 0.3500 \\ 0.3000 \\ 0.2000 \\ 0.1200 \\ 0.1100 \\ 0.0800 \\ 0.0500 \\ 0.0400 \\ 0.0400 \end{pmatrix} \quad C_{Nie} := \begin{pmatrix} 20.0000 \\ 14.0000 \\ 10.0000 \\ 9.3000 \\ 8.9000 \\ 7.0000 \\ 5.3000 \\ 3.8000 \\ 3.0000 \\ 2.1000 \\ 1.4000 \\ 1.0000 \end{pmatrix}$$

Correlation coefficient: $\operatorname{corr}\left(C_{Cde}, C_{Cds}\right) = 1.0000$

Errors:

$$E_{Cd} := C_{Cde} - C_{Cds} \qquad E_{Pb} := C_{Pbe} - C_{Pbs} \qquad E_{Ni} := C_{Nie} - C_{Nis}$$

$$E_{Cd} = \begin{pmatrix} 0.0001 \\ -0.0000 \\ 0.0001 \\ -0.0001 \\ -0.0001 \\ 0.0001 \\ 0.0003 \\ 0.0005 \\ 0.0002 \\ -0.0002 \\ 0.0001 \\ -0.0001 \end{pmatrix} \qquad E_{Pb} = \begin{pmatrix} 0.0001 \\ -0.0001 \\ -0.0001 \\ 0.0001 \\ -0.0001 \\ 0.0001 \\ 0.0010 \\ 0.0003 \\ 0.0002 \\ -0.0001 \\ -0.0001 \\ 0.0002 \end{pmatrix} \qquad E_{Ni} = \begin{pmatrix} 0.0002 \\ -0.0001 \\ -0.0001 \\ -0.0000 \\ -0.0000 \\ 0.0001 \\ 0.0003 \\ -0.0000 \\ 0.0001 \\ 0.0002 \\ -0.0001 \\ -0.0000 \end{pmatrix}$$

Percentage errors:

$$P_{ECd} := \overrightarrow{\left(\frac{E_{Cd}}{C_{Cde}} \cdot 100\right)} \qquad P_{EPb} := \overrightarrow{\left(\frac{E_{Pb}}{C_{Pbe}} \cdot 100\right)} \qquad P_{ENi} := \overrightarrow{\left(\frac{E_{Ni}}{C_{Nie}} \cdot 100\right)}$$

$$P_{ECd} = \begin{pmatrix} 0.0270 \\ -0.0015 \\ 0.0412 \\ -0.0585 \\ -0.0658 \\ 0.1184 \\ 0.5895 \\ 1.6491 \\ 0.7789 \\ -1.0263 \\ 0.5263 \\ -1.3158 \end{pmatrix} \qquad P_{EPb} = \begin{pmatrix} 0.0227 \\ -0.0263 \\ -0.0270 \\ 0.0271 \\ -0.0351 \\ 0.0474 \\ 0.8289 \\ 0.2679 \\ 0.2434 \\ -0.2105 \\ -0.2632 \\ 0.4868 \end{pmatrix} \qquad P_{ENi} = \begin{pmatrix} 0.0010 \\ -0.0008 \\ -0.0011 \\ -0.0001 \\ -0.0001 \\ 0.0014 \\ 0.0056 \\ -0.0001 \\ 0.0032 \\ 0.0093 \\ -0.0075 \\ -0.0005 \end{pmatrix}$$