# EXPERIMENTAL STUDY OF HEAVY METALS DISTRIBUTION ATTENUATION AND MOBILITY IN TWO OKLAHOMA SOILS AMENDED WITH SEWAGE SLUDGE

By

KEFENI KEJELA

Master of Science
Tropical Agricultural Institute of
Krasnadar, Former Soviet Union
1982

Master of Science
University of East Anglia
Norwich, United Kingdom (England)
1988

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Thesis Approved:

Dee Ann Sanders

Thesis Advisor

Gregory G. Wilber

Hailin Zhang

Timothy J. Pettibone

Dean of the Graduate College

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# 1.0 INTRODUCTION

Sewage sludge contains significant amounts of plant nutrients that include nitrogen (0.5-10%), phosphorus (1-6%), sulfur (0.50-1.5%), calcium (1-20%), and magnesium (0.3-2%); and heavy metals such as copper, cadmium, lead, mercury, arsenic, nickel, cobalt, chromium, manganese, zinc, boron, cobalt, and molybdenum (Furr et al., 1988; Sommers, 1977).

Land application of sewage sludge represents the most common method of sludge management in the world in general and the United States in particular. Land application of sewage sludge has increased from 33 percent of all sewage sludge in 1982 to 59 percent in 1995 (Edgar, 1998). In some states, such as Colorado, Florida, and Washington, this percentage has passed 70 percent. One of the reasons for these increases is the comparative deregulation of land application of sewage sludge (Edgar, 1998).

The trend in land application of sewage sludge is likely to continue. Land application of sludge is projected to increase, and incineration, land filling and other alternative sludge disposal methods such as ocean dumping (banned in 1992) will decrease (Basta et al., 1992). Of the sewage sludge that is land applied, approximately 67 percent is applied on agricultural lands, three percent on forest lands, approximately nine percent on reclamation sites, and 12 percent is sold or given away in bags or containers for application to the land (Abby, 1999). Oklahoma is well above the national average (Basta et al., 1992a). State of Oklahoma regulations OAC 252-648-5-1 through OAC 252-648-

5-5 advocate beneficial use of sewage sludge through land application. Farmers and land managers in Oklahoma are interested in the value of biosolids (Turton, 1995).

Land application of sewage sludge containing heavy metals presents the potential for pollution. There is disagreement about whether current regulations are stringent enough, and whether today's sludges are clean enough to be confident that land application is a sustainable practice or at least an acceptable risk (McBride, 1995). Although the U.S. Environmental Protection Agency (EPA) asserts that application of sludges is a low risk and thus a low priority for their attention, there is always a concern in the application of sludge to areas where soils are acidic, sandy, and shallow depth, all of which tend to increase the movement of metals into ground water. Recent evidence suggests that losses of certain metals through leaching are not always negligible, so there may be removal of some fraction of the metals through ground water (Camobreco et al., 1996; Richards et al., 1997).

There are regulations that must be followed when applying sewage sludge to land. The EPA (40CFR 503.13) states that bulk sewage sludge sold or given away shall not be applied to the land if the concentration of any pollutant in the sewage sludge exceeds the ceiling concentration for the pollutant. The cumulative pollutant loading allowed under EPA Clean Water Act Part 503 sludge rules would result in contaminant levels approximately an order of magnitude higher than those allowed under rules in European countries (McGrath et al., 1994). EPA values used in considering the need for remediation of contaminated sites are significantly lower than the values that sludge application would allow (McGrath et. al., 1994). EPA values are based on an assessment of risks posed by soil ingestion (U. S. EPA, 1992, 1993a, 1993b). The allowable concentrations of metals in soil in other countries include both goals for soil quality and maximum levels allowed for contaminant accumulation. The Dutch intervention values were derived using a pathway risk analysis similar to that used for Part 503, yet the values they suggest for soil clean up of contaminated sites are sometimes lower than EPA regulations (McGrath et al., 1994).

Although the application of sewage sludge on agricultural land is beneficial to crops as a source of nutrients such as nitrogen and phosphorus, there is considerable concern for the amounts of heavy metals added as constituents of sludge. The concentrations of heavy metals such as chromium, copper, zinc, and nickel in sludge are much greater than those in agricultural soils (Berrow and Webber, 1987; Dudas and Pawluk, 1977). These elements pose potentially serious hazards to plants and to animals consuming these plants. Another concern regarding the land application of sludge is the increased metal loading in the food chain through the increased plant uptake of metals. Goldfarb (1999) states that the build up of heavy metals from land-applied biosolids might devalue the land in the future. A delicate balance must be sought between the needs for re-use or disposal of biosolids and the responsibility to protect public health and the environment. Pedogenic and geoenvironmental studies are used to evaluate the retention and mobility of heavy metals in different soils. The knowledge of how contaminants partition among the various geochemical phases allows for a better insight into the mechanisms of retention and release involved in the process of migration and decontamination (Goldfarb, 1999).

Existing data on baseline concentrations of heavy metals in Oklahoma soils are inadequate for determining allowable concentration for clean up of soils and for land application of sewage sludge (Holmgren et al., 1993). Very few studies have interpreted metal leaching process in different soil horizons (Karathanasis and Seta, 1996). While the technical literature contains many studies of contaminant migration through clayey soils having low hydraulic conductivity, considerably less attention has been given to other types of soils such as silt and sand (Yong et al., 1990). Studies of soils with low adsorption capacity and high infiltration rates (e.g., sand) have shown high amounts of heavy metals, which may affect ground water supplies.

Improving our knowledge of environmental damages resulting from soil pollution by heavy metals also requires a better characterization of the effects of soil physical and chemical properties on heavy metals movement and sorption (retention) on sludge amended soils, because the impact of heavy metal contamination of agricultural soils depends not only on types and amount of sewage sludge applied, but also on soil properties. The metal content of soils is quite variable depending on the soil type. Metals in soil are continuously interacting: forming precipitates (carbonates, hydroxides, and phosphates, etc.), interacting with soil organic matter, being sorbed by clay minerals, and being retained by hydrous oxides.

Conventionally, many researchers in the past several years have used 10-15 cm of topsoil to evaluate the impact of soil properties on land applied sewage sludge. The concept of judging soil retention and mobility based on only the top surface soil horizon (10-15cm), does not always provide enough information about the true nature of the pedogenic and geochemical processes in different soil series with different soil profile characteristics. No systematic research on mobility and retention of heavy metals has been conducted with well-characterized soil profiles and between soil series in Oklahoma Soils. This research is conducted based on the extended three soil horizons (0-20, 20-40, and 40-60cm) in order to investigate the relationship between soil properties and metal content, retention, and mobility. This research is, therefore, designed to examine an issue of great importance for long-term sustainability of our environment on land applied with sewage sludge. Laboratory scale soil column experiments were used to quantify heavy metal leaching for two widely different soils. Soils were treated with anaerobically digested sludge and sludge treated with lime and spiked with high concentrations of salts (nickel, chromium, and zinc), to conduct the leaching experiments. Laboratory scale columns were constructed and kept under constant hydraulic head for a period of 120 days to investigate the relationships between time of leaching and the amount of heavy metal leached.

The specific objectives of the study are: 1) To investigate soil physical and chemical characteristics, total heavy metals distributions and their fractionations in uncontaminated baseline soil horizons 2) To examine the effects of soil factors on heavy metals retention and mobility, and 3) To recommend future study necessary for better understanding of the behavior of metals (leaching and retention in soils after land application of sewage sludge under natural field conditions. It is assumed that sandy soils will leach heavy metals faster, while soils with high clay content will bind the metals more strongly than sandy soils. Application of lime increases soil pH and enhance metal accumulation on the top 20-40 cm soil depth.The purpose of this research is therefore, to study soil heavy metal interactions (mobility and attenuation), and to gain basic knowledge on the mechanisms of heavy metals retention/release by soil mineral colloids as affected by inorganic anions as a results of application of sewage sludge in the soil.

# 2.0 LITERATURE REVIEW

## 2.1 HISTORY OF LAND APPLICATION OF SEWAGE SLUDGE

Sludge is the solid material remaining after sewage treatment facilities purify wastewater from homes, businesses, and industries. In some communities, runoff from roads, lawns, and fields is also sent through the facility. In the thirty years since the U. S. Congress enacted the Clean Water Act, imposing minimum treatment requirements for municipal wastewater, the quantity of municipal sludge produced annually in the United States has almost doubled (Abby, 1999). Obtaining cleaner water from treatment facilities inevitably means producing more sludge. Whether the sludge is used or disposed of, it is important to avoid creating additional environmental problems and to keep costs down. In the past municipalities disposed of their sewage sludge in the least troublesome, most affordable ways possible: they sent barges of sludges to be dumped at sea, buried it in landfills or burned it in incinerators. However, communities are now reassessing their sludge management practices because of increasing landfill closure costs, more stringent environmental standards, and increased public concern about air, land and water (Metcalf and Eddy, 1991).

Treatment of municipal wastewater produces different types and volumes of sludge. Raw primary sludge is produced during the first phase of wastewater treatment. Primary treatment removes 40-50 percent of the solids in the water. They are removed by bar screens, grit chambers and primary sedimentation tanks. Primary sludge contains inorganic and organic material. Secondary sludge is generated after the wastewater travels through biological treatment unit and is allowed time to settle; it consists of microscopic material remaining after biological processes have removed dissolved organic matter. A third stage of wastewater treatment generates tertiary sludge by advanced processes such as chemical treatment and filtration.

Anaerobic sludge is generated by anaerobic digestion, a bacterial process that breaks down organic materials within waste in the absence of oxygen. Anaerobic digestion is among the oldest forms of biological wastewater treatment, and it can be traced from the 1850's. Standard rate digestion, sludge thickening, and supernatant formation are carried out simultaneously. Biological treatment in this process reduces the organic content and trace organic compounds. The removal of carbonaceous biological oxygen demand (BOD), coagulation of nonsettleable colloidal solids, and stabilization of organic matter are accomplished biologically using microorganisms (principally bacteria) that are used to convert the colloidal and dissolved carbonaceous organic matter into various gases.

There are several ways to dispose of sewage sludge; one increasingly popular method is land application. For centuries, land application of sludge has been practiced in many countries (U.S. EPA, 1993). Sludge can serve as a fertilizer and/or soil conditioner, reducing or eliminating commercial fertilizer use. Wastewater sludge contains necessary macronutrients for plants such as nitrogen, phosphorus, and potassium (Metcalf and Eddy, 1991). Sludge is applied on agricultural land as a soil amendment, applied on forestland, and used to reclaim strip mine lands, mine tailings, or other disturbed or marginal land for the growth of vegetation. Dedicated land disposal, the application of sludge to soils for the purpose of sludge disposal, has the highest sludge loadings of the various sludge application options. Agricultural application rates can range from 2-70metric tons/hectare in dry weight. Currently, land application is the most widely employed sludge use and disposal option for small to medium sized treatment plants in the U.S. (Metcalf and Eddy, 1991).

Federal and state regulations provide guidelines for municipal sludge treatment and disposal to ensure reasonable, but not risk free, protection of human health and environment. The regulatory development process takes years of scientific and technical analyses into consideration. A primary goal in managing sludge production should be to generate the best quality sludge possible. There are regulations that must be followed when applying sewage sludge to land. The U. S. Environmental Protection Agency (40 CFR 503.13) states that bulk sewage sludge sold or given away shall not be applied to the land if the concentration of any listed metal in the sewage sludge exceeds the ceiling concentration (Table 2.1).

Sewage sludge production in the European Economic Community exceeds 5.4 million metric tons of dry solids annually and is expected to increase substantially in the next decade (Matthews, 1996). Agricultural use of sewage sludge accounts for 44 percent of the sludge production in the United Kingdom (UK. Dept. of the Environment, 1985), and this dependence appears unlikely to decrease in the near future (Sterritte and Laster, 1990). In the United States, the virtual cessation of ocean dumping has most probably increased the agricultural use of sludge in excess of the 31 percent previously applied (Bausch, 1992).

**Table 2.1**

**Heavy metals contaminant standards in sludge**

| Country | Metal |  |  |
|---|---|---|---|
|  | Cr | Ni<br>ppm | Zn |
| European Community | 100-150 | 30-75 | 150-300 |
| France | 150 | 50 | 300 |
| German | 100 | 50 | 200 |
| Italy. | 150 | 50 | 300 |
| United Kingdom | 400 | 75 | 200 |
| Denmak | 30 | 15 | 100 |
| Finland | 200 | 60 | 150 |
| Norway | 100 | 30 | 150 |
| Sweden | 30 | 15 | 100 |
| United States | 150 | 210 | 1400 |

(Source: Harrison et al., 1999).

Most surface disposal of sewage sludge is subject to federal regulation (U.S. EPA, 1995) depending on whether the sewage sludge is disposed with or without household waste. Subpart C of Part 503 includes requirements including surface disposal site. A Part 503 Standard for surface disposal of sewage sludge includes pollutant limits, management practices, operational standards, and requirement for the frequency of monitoring, record keeping, and reporting.

## 2.2. REGULATIONS ON THE APPLICATION OF SEWAGE SLUDGE

Sewage sludges are a by-product of processes that clean wastewaters that are discharged into streams and estuaries. New treatment processes hold promise for significantly reducing or eliminating sludge production (Krogmann, 1998), but until they are widely adopted, managing sludges will be a necessity. There are currently limited options--

ocean dumping has been banned-- leaving landfilling, incineration, or application to the land.

There is a debate over whether recycling of sludges through land application as allowed under current regulations is protective enough, and whether it provides for a long term sustainable practice. People often ask if land application is "safe," but the question really is "is the risk acceptable?" People's acceptance of risk is subjective and depends in part on their values and beliefs, as well as their training and experience. For example, some people place faith in technological solutions and our ability to calculate impacts and risks. Others are more skeptical, believing that history shows that there have been numerous failures of technology resulting in unanticipated environmental and health damage. These are fairly fundamental differences in world view, leading some to favor precaution while others are willing to proceed until harm is shown to occur (Abby, 1999; Goldfarb, 1999).

There is also an interesting difference in the time scales over which people think. In the calculations performed for the risk assessment regarding land application of sludges, the EPA used a 100-year site life (U. S. EPA, 1993). This may seem a long time to Americans whose view of history is relatively short and who have been used to having huge land resources, making it easy to consider "moving on" to greener pasture if the need arises. However, current agricultural lands in the US are substantially the same ones people will be relying on for as long as humans continue to occupy the earth.

In contrast, in Europe the view of time and land is different since one can see lands that have been farmed for thousands of years. Vineyards that grew grapes for Roman wines are still growing grapes today, and lead used by Romans persists in the soil two millennia later (Krogmann et al., 1998). That makes the concept of sustainable practices much more salient in Europe. This is not to say that people have only one interest. The neighbor and environmentalist are also taxpayers concerned about economical sludge management. The generators and vendors depend on productive agriculture for a safe and economical food supply. But differences in the primary interest of different groups help to explain why intelligent, knowledgeable, concerned people can have very different views regarding land application (Citizen's Environmental Coalition and Scenic Hudson, 1996; Cornell Waste Management Institute, 1996; Cornell Waste Management Institute, 1997; Water Environment Federation, 1996). Thus, there is disagreement about whether current regulations are stringent enough and today's sludges are clean enough to give confidence that land application is a sustainable practice or at least an acceptable risk (McBride, 1995). While the U. S. EPA asserts that application of sludges is a low risk and thus a low priority for their attention, this seems to ignore the fact that sludges may end up spread over large areas where we grow our food, obtain our water, and where we live. It is a great concern for the application of the federal rules to Oklahoma and other parts of the country where some soils are shallow and have low pH, which tend to increase metal mobility, increasing the concern for ground water contamination (Holmgren et al., 1993).

The part 503 federal (U. S. EPA, 1993a) regulations also establish standards for nine heavy metal contaminants. The standards include "exceptional quality" (EQ) sludges that meet certain concentration limits for nine metals and for pathogens, and requirements for vector reduction. In regard to metal concentrations, sludges and sludge products which fail to meet one or more of those "EQ" pollutant concentrations but which fall below a higher ceiling concentration may be applied, but the applicator is directed to keep track of the total amount of each metal applied and cease application when a regulatory cumulative pollutant loading limit is reached. Sludge products which fail to meet one or more of the "EQ" pollutant concentrations but which fall below the ceiling concentration may still be distributed to homes or in bags so long as information on the acceptable annual pollutant-loading rate (APLR) is provided to the user.

The approach taken by the U. S. EPA to develop contaminant standards was to identify the various potential routes for exposure to sludge that is land applied and then to assess the risks posed by each of these exposure pathways. The risk associated with each pathway was calculated for each of the contaminants for which the assessment was performed using available data. The contaminant standard for that particular contaminant was the number generated by the pathway resulting in the lowest concentration that represented an acceptable risk according to the US EPA analysis. That pathway was called "the most limiting pathway" (U. S. EPA, 1993). Surprisingly to many, for most of the nine regulated heavy metal contaminants the pathway of a child directly ingesting sludge was deemed to be the most limiting path, generating the lowest acceptable level. Each pathway was assessed separately and independently and no attempt was made to look at the risk from exposure through several pathways simultaneously (U. S. EPA, 1995; U. S. EPA. 1996c) or the effects of more than one contaminant at a time. EPA uses risk assessment modeling. It is a modeling procedure, like all models, is a simplified simulation of real world conditions that relies on many assumptions and subjective judgments. Moreover, a model is only as good as the data from which it draws conclusions. The more complex the system being modeled, the more vulnerable the model and conclusions drawn from it are to errors resulting from the gaps between the model and reality. This is one reason why risk assessments generally fail to effectively evaluate impacts on ecosystems as a whole and do not address synergistic impacts. Because of the limitations inherent in a model, results should include an expression of their uncertainty (McBride, 1995).

Compared with different countries, U. S. EPA land application standards for unrestricted use (EQ) are significantly more lenient. In fact, EPA rules allow the application of sludges with metal concentrations up to the ceiling limits to be used in home gardens. Under the annual pollutant loading rate (APLR) approach (Table 2.2), EPA regulations allow bagged products to be distributed so long as a label states the maximum annual application rate. This policy has been criticized even by those otherwise relatively positive towards land application (National Research Council, 1996; Chaney et al., 1997). Since children ingesting sludge is the limiting pathway for many of the EQ contaminants, application of sludges potentially containing up to the far higher ceiling concentrations of pollutants around homes seems inadvisable.

The cumulative pollutant loading allowed under Part 503 would result in contaminant levels approximately an order of magnitude higher than those allowed under rules in European countries (McGrath et al., 1994). EPA numbers are based on an assessment of risks posed by soil ingestion (U. S. EPA, 1996). A site or soil background concentration is used when the risk-based number is lower than the background. The values for soil in other countries include both goals for soil quality and maximum levels allowed for contaminant accumulation.

These various soil levels are all far lower than those allowed under Part 503. The data gap, uncertainties, irreplaceable value of agricultural land, and persistence of contamination have led several European countries to adopt a different approach in which they strive to prevent the accumulation of metals above levels present in uncontaminated soils. They use a philosophy of "do no harm" to protect soil quality.

**Table 2.2**

**Metal limits and loading rates governing land application of sewage sludge in EPA regulations (40 CFR Part 503).**

| Metal | Ceiling con. mg/kg | Cumulative pollutant loading rates, kg/ha | Pollutant con*. mg/kg | Annual pollutant loading rates, kg/ha/365 days |
|---|---|---|---|---|
| Arsenic | 75 | 41 | 41 | 2.0 |
| Cadmium | 85 | 39 | 39 | 1.9 |
| Chromium | 3000 | 3000 | 1200 | 150 |
| Copper | 4300 | 1500 | 1500 | 75 |
| Lead | 840 | 300 | 300 | 15 |
| Mercury | 57 | 17 | 17 | 0.85 |
| Molybdenum | 75 | 18 | 18 | 0.90 |
| Nickel | 420 | 420 | 420 | 21 |
| Selenium | 100 | 100 | 36 | 5.0 |
| Zinc | 7500 | 2800 | 2800 | 140 |

(Source: U. S. EPA. 1993b), con* - Concentration, mg/kg

Their approach to achieving sustainability is to work towards limiting inputs to the soil so they do not exceed outputs, thus preventing accumulation of pollutants in the soil (McGrath, et al., 1994; Munters, 1997; and Witter, 1996). The "do no harm" philosophy of environmental management strives to limit the addition of contaminants to the levels that are present in uncontaminated soils while recognizing the inherent uncertainty involved in risk modeling. This "no net degradation" approach is precautionary – it permits land application of inorganic contaminants only to the extent to which there will be no accumulation above levels in uncontaminated agricultural soils (McGrath et al, 1994).

## 2.3. SLUDGE PROPERTIES

In order to assess the long-term risks from repeated application of sludge to land, it is appropriate to first consider the nature of heavy metals in the sludge itself. Anaerobic digester sludge is a complex mixture of particulate minerals and organic matter, bacterial residues and colloidal material both mineral and organic (MacNicol and Beckett, 1989). On leaving the digester, sludge undergoes rapid oxidation and changes in microbial activity. As a result, the chemical forms of heavy metals in sludge are a balance between solid precipitates, complexed and hydrated ions in solution, and the same ions held on organic materials, bacterial residues and on the surfaces and interstices of minerals (Fletcher and Beckett, 1987).

The principal metal forms in sludge are soluble (exchangeable forms), precipitated (carbonate forms), co precipitated, adsorbed and associated with biological residues (Lester, 1983). The distribution of metals between the specific forms varies widely according to the chemical properties of the individual metal and the characteristics of the sludge, which are functions of the physical and chemical properties imposed by the particular sludge treatment process. These include parameters such as oxidation-reduction potential, temperature, and concentration of ligands and complexing agents (Gould and Genetelli, 1978).

The organic carbon content can range from 6.5 to 48%, with median concentrations of 26.8 to 32.5%. This organic carbon consists of microbial and decomposition products. Wastewater sludges can also contain trace organic compounds such as PCB's, trichloroethylene, and DDT (Metcalf and Eddy, 1991).

## 2.4. SOURCES AND DISTRIBUTION OF METALS IN SEWAGE SLUDGE AND SOILS.

### *2.4.1 Sources and distribution of metals in sewage sludges.*

There are numerous sources of industrial effluents leading to heavy metal enrichment of wastewater sludges including electroplating, pulp and paper mills, petrochemicals, fertilizers, steel manufacturing, and motor vehicle emissions. Heavy metals can also come from storm water runoff, fat redering, bakery, ice cream, soft drinks, laundry and textile dyeing (Table 2.3). There is increasing awareness that urban runoff presents a serious problem of heavy metal contamination. A statistical summary of 12 U. S. cities (Bradford, 1997) revealed that urban storm water runoff is a major source of pollutants to surface waters. Pollutants such as street dust, dirt and various solids from car exhaust on paved areas can contaminate storm water runoff. Residential sources are often the major contributor of metals to wastewater treatment plants. Angino et al. (1974) found that detergents contain elevated concentrations of chromium and zinc. The major contributors of nickel to the wastewater are the electroplating industry, accounting for 62 percent, with the next highest contributor of nickel being residential, accounting for 25 percent.

**Table 2 .3**

**Metals in Industrial wastewater sludge**

| | Average concentration in μg/L | |
|---|---|---|
| Industries | Nickel | Zinc |
| Meat processing | 70 | 460 |
| Fat rendering | 280 | 3890 |
| Fish processing | 140 | 1590 |
| Bakery | 430 | 280 |
| Miscellaneous foods | 110 | 1100 |
| Brewery | 40 | 470 |
| Soft drinks/flavorings | 220 | 2990 |
| Ice cream | 740 | 1730 |
| Miscellaneous chemicals | 100 | 800 |
| Laundry | 100 | 1750 |
| Car wash | 190 | 920 |
| Textile dyeing | 250 | 050 |

(Klein and Becket, 1984)

### *2.4.2 Sources and Distribution of Heavy Metals in Soils*

#### 2.4.2.1 Zinc

Zinc is an essential trace element for humans, animals and higher plants. Total zinc content of soils is largely dependent on the composition of the parent rock material. In magmatic rocks, zinc seems to be quite uniformly distributed (Whitton and Wells, 1984). Mean zinc contents vary from 40 mg/kg in acid rocks (granite) to 100 mg/kg in basaltic rocks. In sedimentary rocks, the highest zinc contents are found in shale and clayey sediments (80-120 mg/kg. Sandstones, limestones and dolomites generally have lower contents, ranging from 10 to 30 mg/kg (Kabata-Pendias, 2000).

The total amount of zinc in soils is distributed over some more or less distinct fractions in the following five pools: (1) Adsorbed, chelated or complexed pool: Metals bound to organic ligands; (2) Water soluble pool: The fraction presents in soil solution; (3) Exchangeable pool: Ions bound the soil particles by electrical charges; (4) pool of clayey secondary minerals and insoluble metallic oxides; (5) pool of primary minerals (Table 2.4).

All these pools are mainly governed by the equilibrium constant of the corresponding reactions in which zinc is involved: precipitation and dissolution, complexation and decomplexation; adsorption and desorption (Loneragan, 1981). The most common and mobile zinc is believed to be in forms of free and complexed ions in soil solutions, but several other ionic species that occur as nonspecifically and specifically adsorbed cations can also be easily mobilized in soils (Kabata-Pendias, 1995). Abdul-Elfattah and Wada

(1981) found the highest selective adsorption of zinc by iron oxides and the lowest by montmorillonite.

**Table 2.4**

**Zinc content of surface soils (ppm)**

| Soil | Countries | Range | Mean |
|---|---|---|---|
| Sandy soils | Australia | 39-86 | N.D |
| | New Zealand | 14-146 | 42 |
| | Poland | 5-220 | 24 |
| | Romania | 25-188 | 61 |
| | U. S. | 5-164 | 40 |
| | Russia | 3.5-57 | 31 |
| | Germany | 40-76 | N.D |
| Silty soils | New Zealand | N.D | 61 |
| | Poland | 17-127 | 47 |
| | Romania | N.D | 73 |
| | U. S. | 20-109 | 58.5 |
| | Russia | 40-50 | 48 |
| | Germany | 58-100 | N.D. |
| Clay soils | Canada | 15-20 | 17 |
| | Great Britain | N.D | 70 |
| | New Zealand | 31-177 | 79 |
| | Poland | 13-362 | 67.5 |
| | Romania | 37-101 | 75 |
| | U. S. | 20-220 | 67 |
| | Russia | 9-77 | 35 |
| | Germany | 40-50 | N.D. |

Source: Kabata-Pendias, 1995, N. D.= No Data

Thus, clay minerals, hydrous oxides, and pH are likely to be the most important factors controlling zinc solubility in soils while organic complexing and precipitation of zinc as hydroxide, carbonate, and sulphide compounds appear to be of much less importance. Zinc can also enter some layer lattice silicate structures (e.g., montmorillonite, vermiculite and smectite clay minerals) and become very immobile. Soil organic matter is known to be capable of bonding zinc in stable forms; therefore, the zinc accumulation in organic soil horizons is observed (Lindsay, 1986). Zinc is considered to be readily soluble relative to the other heavy metals in soils. The zinc concentrations in soil solutions range from 4 to 270 μg/L (Kabata-Pendias, 1995), depending on the soil and the techniques used for obtaining the solution (Itoh et al., 1989).

The anthropogenic sources of zinc are mainly related to the ferric metal industry and to agricultural practices. Contamination with zinc has already brought zinc to an extremely high accumulation in topsoils. Additional problems related to zinc pollution are changes in the metal speciation. For examples, in soil (loamy sand, soil pH 6.1, organic matter, 1.25 percent) amended with zinc-enriched sewage sludge, an increase was observed of easily available zinc species from 3 percent to 21 percent; and weakly bound or exchangeable zinc species, from 21 percent to 35 percent of the total zinc content (Kabata-Pendias, 1995).

Calculating the first half-life of zinc in contaminated soils in lysimeters showed that zinc decrease was relatively rapid, and that soil containing 2210 ppm zinc will reduce zinc content by half during 70 to 80 years (Kitagishi and Yamane, 1981). These results, however, were reported for paddy soils with a long drainage period. Based on results of other experiments, the half-life of zinc as a pollutant in soil may be much longer. Soluble zinc organic complexes that occur particularly in municipal sewage sludge are very mobile in soils and, therefore, easily available to plants. Zinc contamination of soils may create an important environmental problem.

### 2.4.2.2 Chromium

Chromium has been used in alloy steels and chromium plating since about 1877. It is resistant to attacks by oxidation, which leads to its use in alloys that are resistant to corrosion. Chromium is produced from the ore chromate, which is a mixed oxide with the general formula $FeO\text{-}Cr_2O_3$, but also contains variable amount of magnesium and aluminum. Chromium is the seventh most abundant element in the crust rocks, with an average concentration of 100 mg/kg rock (Cary et al., 1977). Chromium is found in igneous rocks where it readily substitutes for iron. The soil chromium is inherited from parent rocks. Its higher concentration is in soil derived from magmatic and volcanic rocks, containing up to 3400 mg/kg of chromium. Soils derived from serpentines, in particular, are known to contain chromium from 0.2 to 0.4 percent. The total annual input of chromium into soil worldwide has been estimated to be 480-2300* $10^3$ tons (Bartlett et al., 1989). Sandy soils are usually poorest in chromium, and contain an average of 12 and 47 ppm. The grand mean chromium content is calculated to be 54 ppm for worldwide surface soils (Kabata- Pendias, 1995).

Chromium may exist in a number of oxidation states. Naturally occurring chromium compounds have principal valences of +3 (chromic) and +6 (chromate). These have sharply contrasting chemical properties: chromium (VI) exists as an anion. It is more readily extracted from soil and sediment particles and is considered the most toxic form. Chromate is in pH-dependent equilibrium with other forms of chromium (VI) such as $HCrO_4$ and dichromate $Cr_2O_7\ ^{2-}$, with $CrO^{2-}{}_4$ the predominant forms at pH greater than 6. Chromium (III), on the other hand, is much less mobile and adsorbs to particulates more strongly. The solubility of chromium (III) decreases above pH 4, and above pH 5.5, complete precipitation occurs (Griffin et al., 1987).

The behavior of soil chromium leaching has been extensively studied by Bartlet (1997). A broad review of chromium balance in the environment is studied by Mukherjee (1998). It has been shown that most of the soil chromium occurs as chromium (+3) and is within the mineral structures or forms of mixed chromium (+3) and iron (+3) oxides. Since chromium (III) is slightly mobile only in very acid media, and at pH 5.5 is almost completely precipitated, its compounds are considered to be very stable in soils. On the other hand, chromate ($CrO^2{}_4$) and chromic acid ($HcrO^2{}_4$) are forms of chromium VI that are very unstable in soil and are easily mobilized in both acid and alkaline soils (James et al., 1997).

The chromium content of surface soil is known to increase due to pollution from various sources, of which the main ones are several industrial wastes (electroplating sludges, chromium pigment and tannery wastes, leather manufacturing wastes) and municipal sewage sludges (Hemkes et al., 1980). Hemkes et al. (1980) reported a high chromium accumulation for surface horizons of sludged farmland, where the highest chromium levels ranged from 214 ppm to 727 ppm. Surface soil from the reclaimed land (1 meter deep layer above a chromium slag deposit) in Japan contains up to 4560 ppm chromium

VI (dry weight) due to the movement of this ion with capillary water (Izasaki et al., 1987). Izasaki et al. (1987) reported the movement of chromium pollutants to deeper layers of sandy soil, where it was detected in ground water at a depth of 2 to 3 meters (Table 2.5). Chaney et al. (1980) extensively discussed the chromium hazard in biological waste management and stated that the food chain is well protected from excess of chromium by the "soil-plant barrier."

**Table 2.5**

**Chromium content of surface soils of different countries**

| Soil | Country | Chromium, ppm Range |
|---|---|---|
| Sandy soils | Austria | 1.4-3.5 |
| | Canada | 2.6-34 |
| | Great Britain | 5-360 |
| | U. S. | 3-200 |
| | Belarus | 18-25 |
| Silty soils | Austria | 77-128 |
| | Chad | 180-300 |
| | New Zealand | 31-160[a] |
| | Poland | 21-38 |
| | U.S. | 10-100 |
| Clay soils | Austria | 23-24 |
| | Bulagaria | 107-122 |
| | Canada | 4-46 |
| | Poland | 35-81 |
| | U.S. | 20-200 |

Source: Kabata- Pendias, 2000; "a" soils derived from basalts and andesites

This statement, however, is not fully supported by the findings of Diez and Rosopulo (1986), who reported the ready availability of chromium from soils amended with sewage sludge. Solubility and toxicity characteristics of $Cr^{+3}$ and $Cr^{+6}$ in soil present a challenge for the establishment of maximum allowable concentration (MAC) which vary by regulatory agencies. The hazardous identification rule establishes the cumulative land application limit at 3000 kg chromium per hectare, based on data showing no effects on plants at this maximum level of chromium used in a field study (James et al., 1997).

### 2.4.2.3 Nickel

Nickel is a transition metal of Group VIII of the periodic table. Nickel can occur in a number of oxidation states, but only nickel (II) is stable over the wide range of pH and redox conditions found in the soil environment.

Nickel is extracted from sulfide and oxide ores, including lateritic oxides and penttandite. World production of nickel is approximately 800,000 metric tons/yr. The earth's crust has an average concentration of 75 ppm. The content of nickel in a soil depends very much on the nature of the parent materials. For example, soils formed from serpentine can contain 100-7000 ppm nickel ( Shacklette et al.,1984).

Research findings indicated that from 5000 to 22000 metric tons of nickel is added to soils each year as a result of disposal of sewage sludge globally (Adriano, 1998). Disposal of fly-ash on land is the largest single input of nickel in soils. The soil chemistry of nickel is simpler than that of chromium and is based on the nickel divalent metal ions (Berrow and Mitchell, 1980).

The great affinity of nickel for sulfur accounts for its frequent association with sulfur bodies. In terrestrial rocks, nickel occurs primarily in sulfides (millerites, NiS), arsenides (niccolite, NiAs), and antimonides (breithauptile, NiSb), and most of it is in ferromagnesians, replacing iron. Nickel is also associated with carbonates, phosphates, and silicates (Norrish, 1985).

Nickel is easily mobilized during weathering and then is coprecipitated mainly with manganese and iron oxides. However, unlike manganese and iron, nickel is relatively stable in aqueous solutions and is capable of migrating over a long distance. Organic matter reveals a strong ability to absorb nickel; therefore, this metal is likely to be concentrated in coal and oil. This concentration is apparently an effect of the precipitation of nickel as sulfides in sediments rich in organisms and under reducing conditions (Norrish, 1985). The solubility of the hydroxides of nickel together with other siderophylic elements, at different pH values gives some indication of the relative mobility of this element in different soils. Nickel is increasingly soluble at lower pH values.

In surface soil horizons, nickel appears to occur mainly in organically bound forms, a part of which may be easily soluble chelates (Bloomfield, 1980). However, Norrish (1985) stated that the fraction of soil nickel carried in the oxides of iron and manganese seems also to be the form most available for plants. Nickel distribution in soil profiles is related either to organic matter or to amorphous oxides and clay fractions, depending on soil types (Table 2.6). Concentration of nickel in natural solutions of surface horizons of different soils varies from 3 to 25 ppm (Anderson, 1983).

Information on the nickel ionic species in the soil solution is ruther limited, but the nickel species described by Garrels and Christ (1985) such as NiOH, $HNiO_2$ and $Ni(OH)_3$ are likely to occur when the nickel is not completely chelated. Generally, the solubility of soil nickel is inversely related to the soil pH. Nickel sorption on iron and manganese is especially pH dependent, probably because NiOH (nickel hydroxide) is preferentially sorbed, and also because the surface charge on sorbents is affected by pH (Boedek et al., 1988). Bloomfield (1980) stated that although organic matter is able to mobilize nickel from carbonates and oxides as well as to decrease nickel sorption on clays, the bonding of this metal to organic ligands could not be particularly strong. Nickel may be quite mobile in soils with high complexation ability (organic rich and polluted soils). Nickel content in surface soil is summarized in Table 2.7.

**Table 2.6**

**Nickel content of surface soils of the world**

| Soil types | Country | Range | Mean |
|---|---|---|---|
| Silty soils | Poland | 7- 70 | 19 |
| | U.S. | 5- 30 | 13 |
| | Austria | 13- 15 | N.D. |
| Clay soils | Burma | 27 -91 | 50 |
| | Canada | 3- 98 | 23 |
| | Poland | 10- 104 | 25 |
| | Romania | 24 -60 | 44 |
| | U.S. | 5- 50 | 21 |
| | Russia | N.D. | 24 |
| | New Zealand[a] | 9-110 | N.D. |

Source: Kabata- Pendias, 2000, [a] Soils derived from basalt and andesites, N.D.= No data

The nickel content in soils is highly dependent on the nickel content of parent rocks. However, the concentration of nickel in surface soils also reflects soil-forming processes and pollution. Soils throughout the world contain nickel within the broad range of from 0.2 to 450 ppm, while the range for soils of the U. S. is from less than 5 to 150 ppm

(Kabata-Pendias, 1995). The highest nickel contents are always in clay and loamy soils. The mean nickel content in surface soils from major agricultural production areas of the U. S. is 16.5 ppm, ranging from 0.7 to 269 ppm (Holmgren et al., 1993).

Nickel recently has become a serious pollutant that is released in the emission from metal processing operations and from the increasing application of sludges on agricultural lands (Mukherjee, 1998). Therefore, nickel cycling under anthropogenic impact is of environmental concern.

## 2.5. MECHANISMS OF MOVEMENT OF HEAVY METALS IN SOILS AND SEWAGE SLUDGES

### *2.5.1 Heavy Metal Distribution and Sorption Characteristics*

Some particles, such as clay minerals, have permanent overall negative surface charges. Compounds with a positive charge, such as metal ions, are thus more susceptible to adsorption to these particles than ions with a negative charge. Other particles such as iron and aluminum oxides and hydroxides as well, as organic macro molecules, possess functional groups that change with pH. Metal ions may become attached to these sites by chemical reaction, complexation, or electrical attraction. Not only do metal ions adsorb, but, inorganic and organic metal complexes can also undergo this process. Absorption is the process by which a compound in the solution attaches to the surface of the solid particle, then moves into the interior of the solid particle by diffusion into the interior space or lattice structure of the solid particle (Zachara et al., 1999). Desorption is the process by which sorbed species are released to the surrounding environment. Desorption from particle surface proceeds more readily than desorption from the interior of a particle. Extended research has shown that the sorption of heavy metals is highly pH-dependent. At a low pH value, metal ions must complete with protons for the available sorption sites, and more metal is found in solution. The sorption increases as pH increases, but can be affected by the formation of hydroxy-complexes and precipitation. Sorption is also affected by the composition of the surrounding environment, as the introduction of inorganic or organic ligands may reverse the process and lead to desorption. Metals also compete with each other and with other species for available sorption sites. Sorption of heavy metals in particular associates with the colloidal and organic fractions of a soil, that is, a soil that is high in clay particles, iron, aluminum, and manganese oxide or/and organic matter has high sorption capacities and thus good metal retaining properties.

Metal ions can also combine with an inorganic or organic compound or iron, i. e., a ligand, to form a soluble complex. Typical inorganic ligands in the upper profile of the soil system are hydroxides, nitrates, chlorides, sulfates, phosphates, and carbonates (White and Zelazny, 1986). Complexation may enhance the solubility of a specific heavy metal and reduce the fraction that precipitates or adsorbs. Complexation is often thought to increase the mobility of the heavy metals. There are four common methods of mobilizing metals that are sorbed to soil: change in acidity, complex formation, change in ionic strength, and change in oxidation/reduction potential. With most cationic metals, the potential for adsorption increases with increasing pH. In the presence of inorganic and organic ligands, metal cations form complexes. The formation of a complex occurs when an electron- rich atom in a molecule shares a pair of its electrons with a metal ion having an empty outer shell. These complexes often have a neutral, slight negative or a lower positive charge than the free metal ion itself. These complexes are not as strongly adsorbed to soil, allowing the metal ions to be removed easier (Zachara et al., 1999). Adsorption is affected by speciation of the elements in the soil solution and by pH, Eh, ionic strength, and composition of the soil solution, as well as by the clay and organic matter content of the soil (McLaren et al., 1981). Adsorption data for conditions in soils are indispensable for the proper modeling of the mobility of trace elements in soils (Christensen, 1981).

Generally, the distribution of heavy metals is primarily a function of mineral composition and amount of adsorption sites in each size fraction. The accumulation of metals in the clay fraction, according to Sholkovitzet al. (1980), was in agreement with the findings reported by several workers, which were attributed to the high surface area and the presence of clay minerals, organic matter, iron/manganese oxides and sulfides. Tyler (1981) found that maximum concentration in the clay and one of the sand fractions gives an indication that most of the metals are probably present in an adsorbed form on clay minerals present in the crystalline lattice of clay minerals. A simple balance of the heavy metals in the soil can be expressed as follows (Alloway, 1995):

$$Mtotal = (Mp + Ma + Mf + Mac + Mow + Mip) - (Mcr + Ml)$$

Where: "M" are heavy metals, "p" denotes parent material, "a" atmospheric deposition, "f" fertilizers sources, "ac" agrichemicals, ow" organic wastes, "ip" other inorganic pollutants, "cr" crop removal, and "l" losses by leaching, volatilization, etc.

The ecologically relevant fraction in the soil is the available or mobile pool of the heavy metals. The mobile metal fraction could pose a real danger either to growing organisms, e.g., plants roots, soil micro- and macro-organisms, or to ground and surface water (Gupta, 1993).

### *2.5.2 Leaching of Heavy Metals in Soils and Sludges*

Disposal of sewage sludge creates the potential for heavy metal concentration or accumulation in the environment. Land disposal of sewage sludge may result in leaching of heavy metals from the sludge and the soil into surface and groundwater (Adriano, 1998). The potential environmental risk from metal contamination associated with disposal of sewage sludge depends, in part, on the metal sorption characteristics of the soils that are a function of the soil physio-chemical properties. Herbert (1997) demonstrated that during the partitioning of metals between solid and liquid phases, components that partition to the solid phase more strongly exhibit low mobility in soils, while those that partition more strongly to the liquid phase have greater mobility of heavy metals and ultimately contaminate the surface and groundwater.

The leaching of heavy metals in soil depends on concentration, speciation and solubility (Ure, 1991). The solubility of heavy metals in soil is controlled by reactions with solid phases. Once sewage sludge is applied to soil, the heavy metal species undergo several possible fates including adsorption/desorption reactions, precipitation, dissolution reactions, plant uptake, and leaching through the soil profile (Sposito et al., 1981). Accumulation of heavy metals in surface soils has been reported from sewage sludge application (Sposito et al., 1984). Complexation of metals by organic ligands is one of the mechanisms controlling the availability and mobility of metals. Formation of soluble organo-metal complexes increases availability and mobility of heavy metals (Sposito et al., 1984). Therefore, organic matter may be an important factor influencing the retention of heavy metals by soils.

Heavy metal leaching in soils is a slow process (Dowdy and Volk, 1991). Long term (3-15 years) experiments have shown that downward displacement of heavy metals is in general limited to only a few centimeters below the depth of incorporation (Williams et al., 1984). However, Dowdy et al. (1991) found a significant enrichment of cadmium and zinc several decimeters below the depth of incorporation after 14 years of massive, annual sludge addition.

Investigations on the movement of metals in soils by a number of researchers have shown that most metals added to soils tend to remain in the surface (Miller et at. 1986). Boswell (1985) found very little zinc movement deeper than 15 cm in clay loam soil. Sidle et al. (1977) found that more than 93 percent of all heavy metals applied over two years were accumulated in the soil surface. Parker et al. (1978) reported that more 95 percent of cadmium, zinc, copper, and lead remained in the top 25 cm of the soil. Similar conclusions were reported by Williams et al. (1984) about the retention of metals on surface horizons.

The potential for heavy metals to leach out of sewage sludge was clearly demonstrated when Lagerwerff et al., (1976) leached a sludge from Baltimore with tap water and observed removal of 11, 2, and 36 percent of the cadmium, copper, and zinc, respectively, from the sludge. Lagerwerff et al., (1986) subjected the sludge to an artificial oxidation treatment with various concentrations of $H_2O_2$ and found that with increasing oxidation the metals became more water extractable. At disposal sites when large quantities of sewage sludges have been deposited, the potential for movement of metals into the soil is greatest. Lund et al. (1981) found enrichment of chromium, copper, and zinc to a depth of two meter underneath a sewage sludge drying bed that had been in use for more than 20 years. Elevated soil nickel and cadmium contents were detected to a depth of 3.5 meters. Kirkham (1975) has also observed movement of copper, cadmium, nickel, and zinc to 61 cm in soil below a sludge holding lagoon that had been used for three years.

Tinker (1981) reported the movement of cadmium, copper, chromium, nickel, and zinc to a depth of 30 to 45 cm in agricultural soil after application of 136 metric tons/acre total of sludge over a four-year period. Boswell (1985) reported zinc movement to a depth of 30 cm and cadmium, chromium, and copper to 15 cm after the application of 168 metric tons/ha sludges during a two-year study. Sidle and Kardos (1977) added 27 metric tons/ha of sewage sludge to a forest soil and after 17 months observed that 6.6, 0.3, and 3.2% of the applied cadmium copper, and zinc, respectively, had moved below 120 cm in the soil profile. In these agricultural situations where sewage sludges have been applied to soils and movement of metals measured, pH of the soils could have been a factor. Boswell (1985) applied a sewage sludge that had a pH of 5.6 to a soil that had been limed to a pH of 6.2. Emmirich et al. (1982) started with a soil pH of 5.6 that at the end of 2 years had dropped to 4.9. These lowered pH values could have increased the solubility of the metals and contributed to heavy metals leaching (Kabata-Pendias, 2000).

The studies conducted by Emmirich et al. (1982) seem to deviate from the study of Kabata-Pendias (2000). Emmrich et al. (1982) saw very little movement of metal with depth to 2-3 cm. Most investigators have shown movements of metals, even though the magnitude may have been small (Lund et al., 1976; Kirkham, 1975). Factors that may explain the absence of movement according to Emmirich et al. (1982), could be the sludge soil layer pH, or the time involved for movement to take place.

Lund et al. (1976) have shown that pH is a factor in controlling the leaching of heavy metals in soils under anaerobic conditions. The greatest reported depths of metal movement in soils have taken place over long periods of time (greater than 20 years) at a sludge disposal site (Lund et al.,1976, Kirkham, 1975). Neither Lund nor Kirkham reported pH values of the soils at the depths they sampled, therefore, the possible effect the pH could have had on the movement is unknown. In their studies, the soils were generally coarse textured. Given the long periods of time, high hydraulic loading, and soils that had large pores, the movement observed could have involved several commonly observed physical phenomena. Physical mechanisms of heavy metals movement could include colloidal precipitates and clay particles moving with the soil solution carrying the metals, or sludge moving through cracks in the soil created by repeated wetting and drying of cycles. Hem (1982) found that in the fine-textured soils, physical movement was less likely due to smaller pore sizes, destruction of soil structure and soil macropores because of reconstruction of the soil profiles, and repeated mixing of the sludge soil layers to prevent cracks. The time factor and hydraulic loading were also much smaller compare to similar studies. Hem (1982) investigated that an alkaline pH would induce a low solubility of heavy metals and probably played a role in the retention of the metals in the sludge-soil layers.

The research done by scientists and engineers in relation to heavy metals attenuation and mobility in different soils are encouraging. However, still unanswered questions need further research in the relationship between soil properties such as particle size distribution, organic matter, soil pH, CEC, clay mineralogy, aluminum and iron oxides, and heavy metal attenuation and mobility.

Movement of heavy metals through the top and subsoil horizon can gradually result in an increased content of heavy metals concentrations in the groundwater. Boyle and Fuller (1987) found that elevating the dissolved organic carbon enhanced zinc leaching through the soil horizon. Boyle and Fuller (1987) concluded that the mobility of chromium was enhanced by an increase in soil organic matter. Dowdy and Volk (1991) suggested that the movement of heavy metals in soils would occur in sandy, acidic soils, low in organic matter, subjected to heavy rainfall or irrigation. These conditions are similar to the soil conditions in the southeastern U.S., where Schirado et al. (1985) observed that zinc, cadmium, and nickel migrated from the cultivated soil layer into deeper layers in a silt loam soil due to high annual rainfall. However, some investigators reported that metal movements were low in soils treated with sludge (William et al., 1987; Dowdy et al., 1991). The low mobility of metals in sludge treated soils might be related to the retention of organic matter on the soil in the upper layers, because most of the heavy metals in organic wastes were associated with colloidal organic matter (Sposito et al., 1981; Sim and Kline, 1991).

### *2.5.3 Retention of heavy metals*

Metals in soil solution are continuously interacting: forming precipitates (carbonates, hydroxides, and phosphates, etc.), interacting with soil organic matter, being sorbed by clay minerals, and being retained by hydrous oxides. In general, the organic matter complexed with clay is more resistant to decomposition than "free" organic matter. The presence of acid functional groups in soil organic matter is responsible for metal retention through both exchange and chelation mechanisms (Sposito, 1981). Therefore, the metals retention capacity and cation exchange capacity (CEC) tend to increase as the clay, hydrous oxide, and organic matter contents increase. Because of these relations, the CEC has been used as an index of the metal retention capacity of a soil (Pierce et al., 1982).

EPA regulations in the past used soil CEC as a guide in setting limits upon cumulative heavy metals loading in the sludge application to sites used for crops (U. S. EPA, 1992). Soil permeability and texture (particle size distribution) provides guidance in determining the site drainage characteristics. It is important that a sludge application site be moderately permeable, and also not too impermeable to prevent excessive metal retention in soil profiles at hazardous level.

A sewage sludge that contains large quantities of heavy metals may contribute significantly to the build up of heavy metals in soils and subsequent accumulation in plants at low pH conditions. Fuller et al. (1986) in their study concluded that nickel, cadmium, zinc, and copper were found in the extracts of non-calcareous soil at hazardous levels, even at relatively low sludge loading rates. The concentrations of these metals in extracts of calcareous soil sludge mixtures were significantly lower. They suggested that in calcareous soils the addition of relatively large quantities of sludges is permissible. In non calcareous soils, substantially smaller amounts of sludge can be harmful if the sludge contains significant levels of heavy metals (McBride, 1995).

Heavy metals constitute only a small fraction of the sludge solids, usually, one percent dry weight; but the heavy metal contents of soils may be significantly raised through long-term land applications of sludges (Kirkham, 1975). Heavy metals added to soils may (i) be strongly adsorbed by clay minerals, hydrous iron and manganese oxides; (ii) form inorganic precipitates of hydroxide, carbonate, and sulfide; or (iii) be complexed by soil organic matter (Kinniburgh et al., 1986). Although heavy metals deposited in the soil may be slowly leached by electrolyte solutions, soils generally immobilize them readily (Williams et al., 1980). The buildup of heavy metals in the soil profile may constitute a hazard not only to plants, but also to consumers of the harvested crops (Chaney, 1983).

Chang et al. (1984) discovered that all deposited heavy metals concentrated in the surface layer. After six years of sludge application, more than 90 percent of the sludge- borne heavy metals remained in the soil layer where sludges were incorporated (0-15cm). Their experiments showed that there was slight but statistically significant ($p= 0.05$), increases occurred for all metals examined in the 15 to 75 cm soil depth.

## 3.0 MATERIALS AND METHODS

### 3.1 EXPERIMENTAL DESIGN

Two soil types, three soil horizons, three treatments and three replications were used for the design of this experiment as shown in Table 3.1

**Table 3.1**

**Experimental Designs**

| Soil type | Soil depth cm | Treatment | | |
|---|---|---|---|---|
| | | T1* 3 replicates | T2** 3 replicates | T3*** 3 replicates |
| Norge[1] | 0-20 | Soil and sludge | Soil, sludge, and lime | Soil, Sludge, and salt spikes[3] |
| | 20-40 | “ | “ | |
| “ | 40-60 | “ | “ | “ |
| Dougherty[2] | 0-20 | “ | “ | “ |
| “ | 20-40 | “ | “ | “ |
| “ | 40-60 | “ | “ | “ |

T1*= Soil and sludge; T2** = Soil, sludge and lime; T3*** = soil, sludge, and salt spikes, Norge[1] = Clay soil, Dougherty[2] = Sandy soil; Spikes[3] = chromium, nickel, and zinc chloride salts spiked with sludge. Treatment 1 (Soil and sludge serves as control since all treatments have the same amounts and volumes of soil and sludge).

#### *3.1.1 Treatment 1- soil and sludge*

In this treatment 18 g of digested sludge collected from Stillwater sewage sludge treatment plant was mixed into the top 20 cm soil depth (Norge and Dougherty soil series collected from Oklahoma State University Agronomic Research Stations –Stillwater) of each leaching column. Five pounds of soil were used in each column, where soils were packed incrementally following each soil horizon differentiation.

### *3.1.2 Treatment 2 – soil, sludge and lime*

In this treatment the soil was applied with sewage sludge and amended with lime. 18 g of digested sewage sludge was applied into the top 20 cm of soil column containing 5 pounds of soil from Norge clay and Dougherty sandy soil. The amount of lime required was based on the soil pH. No lime was amended above pH 6.5. The amount of lime amended ranged from 1-7000 pound/acre (0.82-6.11 g/horizon) with soil pH ranging from 5.5 to 6.5. As the soil pH increases, the amount of lime required (for both clay and sandy soils) decreases since the soil is approaching slightly acid to neutral, where the movement of metals is minimum and, therefore, addition of lime was not needed.

### *3.1.3 Treatment 3- Soil, Sludge and Spikes*

Nickel chloride ($NiCl_2$), zinc chloride ($ZnCl_2$), and chromium chloride ($CrCl_3$) were used as spiking materials. Chloride salts were selected by many researchers to undertake soil column leaching since their solubility is comparable to normal field metal leaching conditions. The amount of spiking materials required was calculated based on the allowable metal ceiling concentration set for each metal by EPA under subpart 503 of the Clean Water Act. The ceiling concentrations for the heavy metals under investigation are chromium 420 ppm, nickel 420 ppm and zinc 7500 ppm. It was anticipated that the final concentration of total metal (of each individual metal) would be equal to the ceiling concentration of each metal, where the total amount of metals in baseline soils is already included. So, the amount of spiking material required was equal to the metal ceiling concentration of each metal minus total metal content in baseline soil and sludge.

All treatments were allowed to leach through a constructed soil column of 75-cm length and 10 cm internal diameter to study the attenuation and movement mechanisms of heavy metals.

### Table 3.2

### Metals average value showing the amount of metals in soil, sludge and metal salt spikes

| Soil | Treatment | Metals, ppm | | |
|---|---|---|---|---|
| | | Chromium | Nickel | Zinc |
| Norge clay | **Soil and sludge (T1 &T2)** | | | |
| | In soil | 30.6 | 18.56 | 35.7 |
| | In sludge and lime | 62 | 29 | 917.6 |
| | **Soil, sludge, and spikes** | | | |
| | In spikes | 327.4 | 372.44 | 6546.67 |
| | Total amount required | 420 | 420 | 7500 |
| | Dougherty sandy soil | | | |
| | **Soil, sludge and lime (T1 &T2)** | | | |
| | In soil | 28 | 26 | 20.23 |
| | In sludge and lime | 62 | 29 | 917.6 |
| | **Soil, sludge and spikes (T3)** | | | |
| | in spikes | 330 | 365 | 65062.17 |
| | Total amount required | 420 | 420 | 7500 |

Total amount for each metal is equal to the ceiling concentrations used by U.S. EPA (U.S. EPA, 1993a).

## 3.2 LOCATION OF SAMPLING AREA

Two uncontaminated soil series were chosen for this study from different major land resource areas: the Oklahoma State University (OSU) Agronomy Research Station west of the OSU main campus, and the OSU Agronomy Research Station at Perkins. The soil series were selected based on agronomic and environmental importance and to provide a range of soil properties. The Norge soil series (clay soil) and Dougherty soil series (sandy soil) were selected for this study. Norge soils are fine, mixed, thermic, udic paleustolls of

Norge soil series (residuum shale); Dougherty soils are loamy, mixed, thermic arenic haplustalf (eolian sand)(Gray and Roozitalab, 1976).

The Norge soil series is located in section 16, T.19N. R2E, and the Dougherty soil series is located in section 36, T. 19N. R2E. Soil sampling sites were selected carefully to minimize the risk of anthropogenic contamination. Selected sites were far from any industrial stack emitter (fossil fuel, electric generator, and smelters) and were also far from highways and field boundaries. They were not in the vicinity of old buildings or construction sites, and samples were not collected from any field with a known history of sewage sludge application. However, small amounts of anthropogenic heavy metals from fertilizers, lime and pesticides may be present in these soils. The selection of the two soils was based on the known history of land use and presence of profile pits with initial background information.

## 3. 3 DATA COLLECTION

### *3.3.1 Field methods*

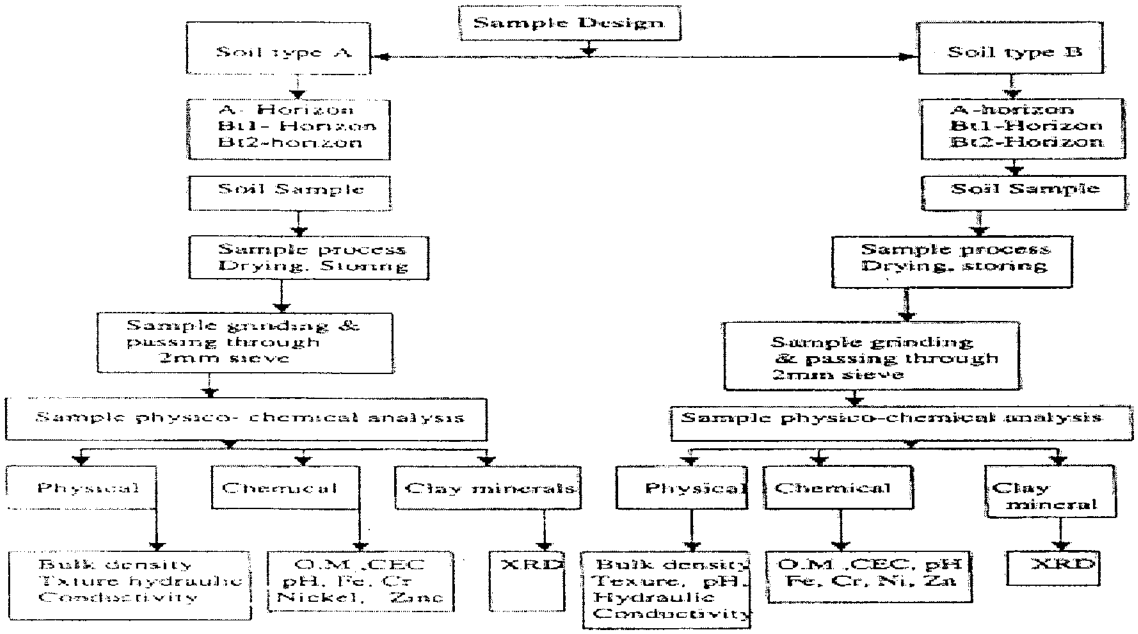
Two soils profiles representing two taxonomic soil series, Norge and Dougherty, (USDA, SCS, and Oklahoma Agricultural Experiment Station, 1979), were sampled. Soil samples were collected by horizon to a depth of 60 cm. Sampling was done in 20 cm increments from three horizons per each soil type (0-20 cm, 20-40 cm, and 40-60 cm) from pits excavated to parent material. The soil profile descriptions followed National Cooperative Soil Survey Guidelines (Soil Survey Division Staff, 1993).

### 3.3.1.1. Soil sampling

Conceptual process of data collection and analysis for this study is shown in figure 3.1 Five pound samples were collected from each horizon and placed in clean plastic bags and transported to the laboratory. Undisturbed samples were also collected with a core in a box that was driven carefully into the soil samples for bulk density measurement. Disturbed samples were collected with a shovel by cutting a v-shaped slice to a depth of 60 cm.

**Figure 3.1**

Flow chart illustrating conceptual process of data collection and analysis.



### 3.3.1.2 Sludge Sampling

Dried anaerobically digested sludge was collected from the Stillwater Wastewater Treatment Plant. In the laboratory, collected sludge samples were air-dried and ground to pass through a 2 mm sieve and stored in sealed polyethylene containers for chemical and physical analysis.

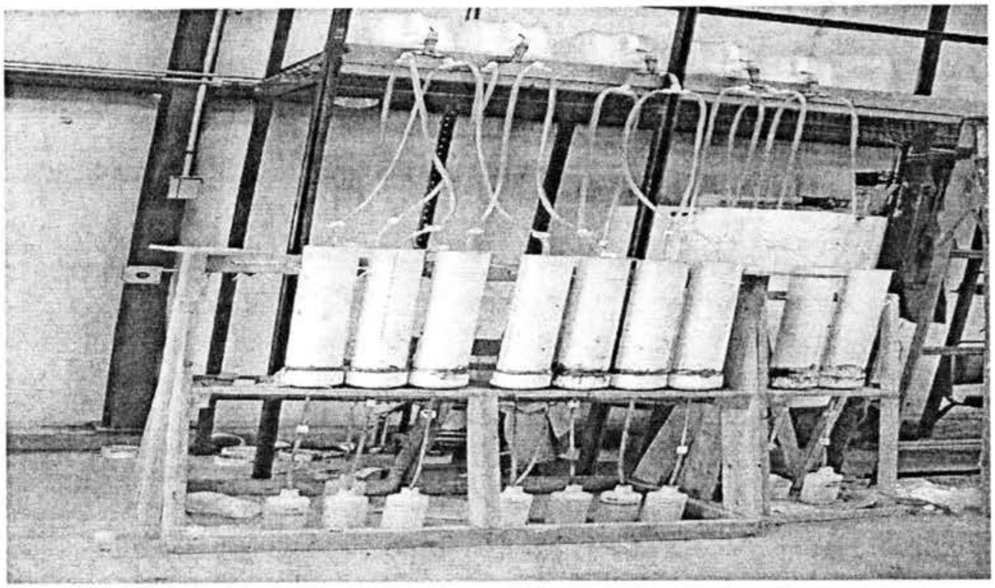
## 3.4 LABORATORY SOIL COLUMN LEACHING SYSTEM

A laboratory scale column testing system was designed and built in the Oklahoma Sate University, Civil and Environmental Engineering Laboratory to simulate a metal leaching process, as shown in Figure 3.2.

60 cm column length and 10 cm diameter on the rate of 20 tons/ hectare sewage sludge) of sewage sludge added to the topsoil up to 20 cm column depth. After each column was carefully packed, columns were eluted in order to saturate over night with $Ca(NO_3)_2$ salt solution to allow the constant water head in a steady condition. The columns were visually inspected for uniformity of packing and operated under saturation conditions and room temperature (22-25°C).

**Figure 3.2**

**Set up of Soil Column Leaching**



Eighteen soil columns were built with dimensions of 75 cm in length and 10 cm inside diameter. Soil occupied 60 cm, a constant water head occupied 10 cm, and sand occupied 5 cm at the bottom of the total 75 cm column length used for the study. A plastic mesh screen was placed at the bottom of soil with a cellulite filter over a plastic mesh screen. The filter was covered with a layer of filtering sands of different grades (#8, #16, and #50 arranged bottom to top, respectively) approximately 5 cm thick. Columns were packed following the soil horizons starting from below to the topsoil layer for an overall column profile depth of 60 cm. The soil was placed into the columns from the open top. Subsequently, columns were amended with 18.2 gm (calculated based on

Redistilled water was added as needed to maintain a 10 cm water head; and water was allowed to move through the soil profile under normal gravitational forces for the period of 120 days. Each column was set at a flow rate of 0.04 mm/hr to provide information on the mobility of metals after soils had interacted with the sludge.

At the end of leaching, effluents collected from each column during the period of 120 days were brought to the laboratory for heavy metal analysis. Columns were then dismantled, and the soils in each column were sectioned and sampled to facilitate complete analysis. Starting at the sludge soil interface (top 0-20 cm) and moving down the columns, horizons were sectioned into equal interval of 6 cm increments for the entire soil column length. Ten to twenty g soils were sampled from each sectioned horizon and analyzed for metals by sequential extraction methods and a complete mass balance system was used to calculate the amounts of metals extracted. The enrichment ratios of each metal was calculated by dividing the metal amount in each column by the metal in soil before sludge was amended to see the degree of metal movement against each treatment and soil type.

## 3.5 LABORATORY METHODS

### *3.5.1 Determination of soil properties*

Sample analyses were done on baseline soils, sewage sludge, contaminated soils (soil and sludge mixture), soils with sludge spiked with salts, and soils that were limed and treated with sludge. The amount of sludge required was based on the amount of nitrogen and phosphorus needed for maximum crop yield potential. The amount of sludge required for each column is calculated based on 20 metric ton/ha of sludge. The amount of lime required was based on soil acidity and ranges between 1-7000 pounds/acre. Lime was not amended above soil pH 6.5 since it approaches nearly neutrality and metals movement is insignificant. Particle size distribution for the two soils was determined by the pipette method for silt and clay. Soil pH was determined in a 1:2 soil and $0.01MCaCl_2$ slurry (McLean, 1982). Soil organic carbon was analyzed by combustion and a modified Mebius method described by Yeomans and Bremner (1988). The method of determining the organic carbon in the sample was with potassium dichromate. A known amount of potassium dichromate was added to the sample and mixed. The sample was then titrated with 0.5 N $FeSO_4$. Soil total nitrogen, nitrate nitrogen, and ammonium nitrogen were analyzed in the Oklahoma State University Soil and Forage Laboratory. Clay mineralogy was analyzed in the Geology Department Laboratory of Oklahoma State University. Clays were separated by sedimentation, and clay mineralogy was determined by an x-ray diffraction method (Jackson, 1979). The clay fraction of soil was separated using the method proposed by Jackson (1979). The clay then separated into fine clay and coarse clay using a Sharples high speed steam centrifuge (5000 rpm). X-ray examination of the clay fractions was completed using samples that had been treated as follows: (1) calcium saturated, (2) calcium saturated and ethylene glycol solvated, and (3) potassium saturated and heated to 550°C for four hours. These procedures attempted to identify the clay minerals present as follows: (1) identify all of the clay minerals which may be present, (2) differentiate expanding and non-expanding 2:1 clay minerals, and (3) differentiate between kaolinite and other minerals with similar diffraction characteristics. Iron oxides were determined by the citrate bicarbonate-dithionate (CBD) extraction developed by Jackson (1979). The total metals contents of the soil and sludge were determined using EPA Method 3050 using the nitric acid, hydrochloric acid and hydrogen peroxide digestion procedure.

### 3.5.2 *Determination of background metal concentration*

The metals analysis that was performed for this experiment was done using a Perkin-Elmer Model 100/300 Atomic Spectrophotometer (AAS). An air acetylene flame was used with a wavelength of 213.9 nm for zinc, 228 nm for chromium and wavelength of 412 nm for the determination of nickel. Metal standards for each metal were purchased from Fisher Scientific Co. (Pittsburgh, PA), at concentrations of 1000 ppm for each of the three metals, (zinc, chromium and nickel) being evaluated.

The initial baseline metals concentration for all soil samples collected from two soil types was determined using the EPA method 3050 outlined for acid digestion of soils with $HNO_3$, HCl and $H_2O$. For this study, one gram of soil was placed in 80 mL beaker along with 25 mL of reagent grade nitric acid (Fisher Scientific Co., Pittsburgh, PA). The solution was then stirred and placed on a hotplate and allowed to reflux for a period of three hours. Any losses of acid due to evaporation were replaced with an equivalent amount of nitric acid. After the samples were refluxed, they were removed from the hot plate and centrifuged at 3000 rpm for 15 minutes using an IEC Centra-7 centrifuge. The samples were then tested for zinc, nickel and chromium by Inductively Coupled Plasma Spectroscopy (ICP) at the Forage and Soil Testing Laboratory, Plant and Soil Science Department, Oklahoma State University.

The total heavy metal content was measured using EPA Method 3050 nitric acid hydrogen peroxide digestion procedure for both soil and sludge. For digestion of samples, a representative 1 g (dry weight) sample was digested with repeated additions of trace element grade nitric acid with redistilled water (RW). The digest was then brought to the volume of 100 ml. Reagent grade chemicals (con. Nitric acid and hydro chloric acid ) were used at all times. The digestion solutions were analyzed for chromium, nickel, and zinc. Standards were prepared using serial dilutions of Fisher Certified AAS standard metal solutions of 1000 ml.. The digestion solutions were analyzed for chromium, nickel, and zinc. Standards were prepared using serial dilutions of Fisher Certified AAS standard metal solutions of 1000 ml (Table 3.2). Two duplicate samples, triplicate blanks, and standard solutions were used in all tests. (All reagents conformed to the specifications of the Committee on Analytical Reagents of the American Chemical Society). Digestion was followed by analysis of the digest solution by atomic absorption spectrophotometer (AAS) Perkins Elmer model 100/300 and Ion Chromatography (ICP) in the Forage and Soil Laboratory of Oklahoma State University.

Redistilled (greater than 18 μmho /cm) water was used in the preparation of all solutions. All the glassware and plastic ware used for the digestion and metal analysis were acid soaked (ten percent $HNO_3$, and 10 percent HCl) and rinsed several times in deionized water. The digestion solutions were analyzed for chromium, nickel, and zinc. Standards were prepared using serial dilutions of Fisher Certified AAS standard metal solutions of 1000 ml.

**Table 3.2**

**Laboratory methods of sample analyses**

| Element | Equipment | Method |
|---|---|---|
| Total organic carbon | Digesters | EPA 9056 |
| Cation Exchange Capacity | ICP | EPA 9060 |
| Soil Texture | Pipette and cylinder | Wet method |
| Soil bulk density | Core samplers | Core sampling method |
| Soil | pH measurement | |
| EPA 9040B | | |
| **Metal** | | **Digestion and extraction** |
| Chromium | Atomic absorption (AA) | EPA 3050/7191/1311 |
| Nickel | Atomic absorption (AA) | EPA 3050/ 7521/1311 |
| Zinc | Atomic absorption (AA) | EPA 3050/ 7950/1311, |
| Clay mineralogy | Clay- diffraction | XRD |

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* Analysis Methods (SW**_ 846) and methods of soil analysis (SSS *** America, 1996). SW**- Solid Waste, and SSSA***; Soil Science Society of Ameica.

### *3.5.3 Heavy metals sequential extraction techniques*

The majority of the work done concerning metals in soils has focused primarily upon total metal concentrations. This suggests that all forms of a given metal have the same effect on the environment. It does not take into account the partitioning of the various forms in which the metal might exist when in the soil. A simple measure of total metal concentration does not take into account the availability or "mobility" the metal may have in soil. When it comes to determining the fractionation of metals in soils, there are essentially two approaches (Tessier et al., 1979). The first is a method designed to differentiate residual (the final product remained after extraction of metals in to extractable, carbonate, organic and oxide forms) and non-residual metals only. This technique uses only a single extraction and offers a rapid and relatively simple approach. The drawback of this technique is that the choice of extractant is often debatable, because one wants a reagent that would dissolve nonresidual forms of the metal without attacking the detritus (fractions other than residual) forms. The second approach is the use of sequential extractions. The use of multi-step sequential extractions provide more information as to the biological, physical and chemical availability, mobility and the partitioning of heavy metals within the soil.

Typically, a sequential extraction procedure involves five different steps designed to remove the metals from specific sites within the soil matrix. These steps are ordered such that the easiest fraction to remove (exchangeable cations) is removed first, and the extraction of the hardest fraction (residual) is performed last. The five main fractions that are usually investigated (Gibson and Farmer, 1986) include:

1. *Exchangeable fraction.* This fraction of the metals found in the soil is highly susceptible to changes in ionic strength.
2. *Fraction bound to carbonates.* This is the fraction of metals that are associated with the soils carbonates and are susceptible to changes in pH.
3. *Fraction bounds to iron oxides.* These oxides exist as nodules, concretions or as coatings on particles. They are excellent scavengers of trace metals, but are very unstable under anoxic conditions.
4. *Fraction bound to organic matter.* This fraction can be associated with the humic and fulvic acids found in the soil. Under certain oxidizing conditions found in natural waters the organic matter can be degraded, releasing soluble metals.
5. *Residual fraction.* This is the last fraction in which metals can be found. The metals found in the area are often in the crystalline structures of the primary and secondary minerals. The metals found in primary and secondary minerals are often are expected to leach within a reasonable time span under natural conditions.

These are the most common soil fractions examined (Tessiere et al., 1979). There are several methods presented in the literature that use various types of extracting agents to remove metals from the above mentioned fractions (Sposito et al., 1986; Shuman 1991, and Kou et al., 1983). Gibson and Farmer (1986), however, further divided the fraction bound to iron and manganese into two separate parts. The first part is classified as easily reducible. This targets the oxides and hydroxides of manganese, while the second fraction is called the moderately reducible fraction. This fraction targets the portion of the metals bound to the oxides and hydroxides of iron. Table 3.3 shows the analytical reagents that are used to remove the metals from each fraction without fractionating into reducible forms of metals.

## Table 3.3

## Sequential Extraction Reagents

| Authors | Exchangeable Fraction | Carbonate fraction | Oxide fraction | Organic fraction | Residual fraction |
|---|---|---|---|---|---|
| Tessier ct al. (1979) | 1M$CH_3COONa$ at pH= 8.2 | 1M$CH_3COONa$ +1M$H_3COONa$ at pH = 7.2 | 0.04M $NH_2OH.HCl$ | | HF- HCLO4 |
| Gibson and Farmer (1986) | 1M $CH_3COONH_4$ at pH = 7 | 1M $CH_3COONa$ at pH= 5 | 0.1M NH2OH in 25% $CH_3COOH$ | 30 % $H_2O_2$ + $0.0_2$M $HNO_3$ at 85 °C | Aqua regia HF + $HClO_4$ |

M= Mole; CH3COONa= Sodium acetate; $H_2O_2$ = Hydrogen peroxide; HF= Hydrogen floride; $HClO_4$= Hydrogen per chlorate; $CH_3COONH_4$ = Ammonium Acetate and NH2OH.HCl = Hydroxylaminehydrogen chloride

It shows two different sequential extraction methods that have been used on soils that are contaminated with zinc, chromium and nickel.

Chemical speciation of heavy metals in soil was determined by sequential extraction using the method developed by Gibson and Farmer (1986). Metals were speciated into (1) exchangeable, (2) carbonate, (3) oxide, (4) organic, and (5) residual fraction as follows:

Step1: Metals present on exchange sites

The exchangeable fraction was determined by extracting 1 g of soil with 20 ml of 0.5 M ammonium acetate in a centrifuge tube.

The mixture was placed on a reciprocal shaker for four hours, and then centrifuged 5000 rpm for 10 minutes. The supernatant was then decanted and saved for heavy metal analysis (Miller et al., 1986). The soil residue remaining in the centrifuge tube was saved for further extraction in step two.

Step 2: Metals bound to carbonate

The carbonate fraction was determined by extracting the residue in the centrifuge tube from step 1 with 20 ml of 1 M sodium acetate at pH 5. The soil was shaken for 5 h, centrifuged for ten minutes, and the supernatant decanted and saved for heavy metal determination (Gibson and Farmer, 1986). Shaker and centrifuge speeds were the same as step 1 throughout the sequential extraction procedure.

Step 3: Metals present in the reductive phase bound to iron oxides.

The oxide fraction was determined by extracting the residue in the centrifuge tube from step 2 with 15 ml of 0.04 M hydroxylamine hydrochloride in 25 percent acetic acid . The soil was shaken for 4 h at 90 ± 2°C in a hot water bath, centrifuged for 10 minutes, and the supernatant decanted for heavy metal analysis (Hickey and Kittrick, 1984). The residue was saved for further extraction in step four.

Step 4: Metals bound to organic matter (humic and fulvic acids).

The organic fraction was determined by shaking the residue from step 3 with 3 ml of 0.02 M $HNO_3$ and 5 ml of 30% $H_2O_2$ in a hot water bath at 85°C± 2°C. The final volume was then adjusted to 25 ml with 1 M ammonium acetate and in 0.6 percent $HNO_3$, shaken for 30 minutes without heating, centrifuged for 10 minutes, and the supernatant was decanted and kept for heavy metal analysis (Tessier et al., 1979).

Step 5: No soluble metals (residuals).

The residual for chromium, nickel and zinc was determined by difference between the soil total metal content and the sum of the above four chemical fractions. Total and sequentially extracted metal contents were calculated using the metals data from extracts analyzed in the laboratory and multiplied by dilution factors.

## 3.6 DATA ANALYSIS

Two statistical procedures were used to investigate differences in heavy metal content. Analysis of variance (ANOVA) was used to find differences in total metal content in different soil type. When differences were found, a comparison procedure was used to investigate differences in heavy metal content for each horizon between two different soil types.

# 4.0 RESULTS AND DISCUSSIONS

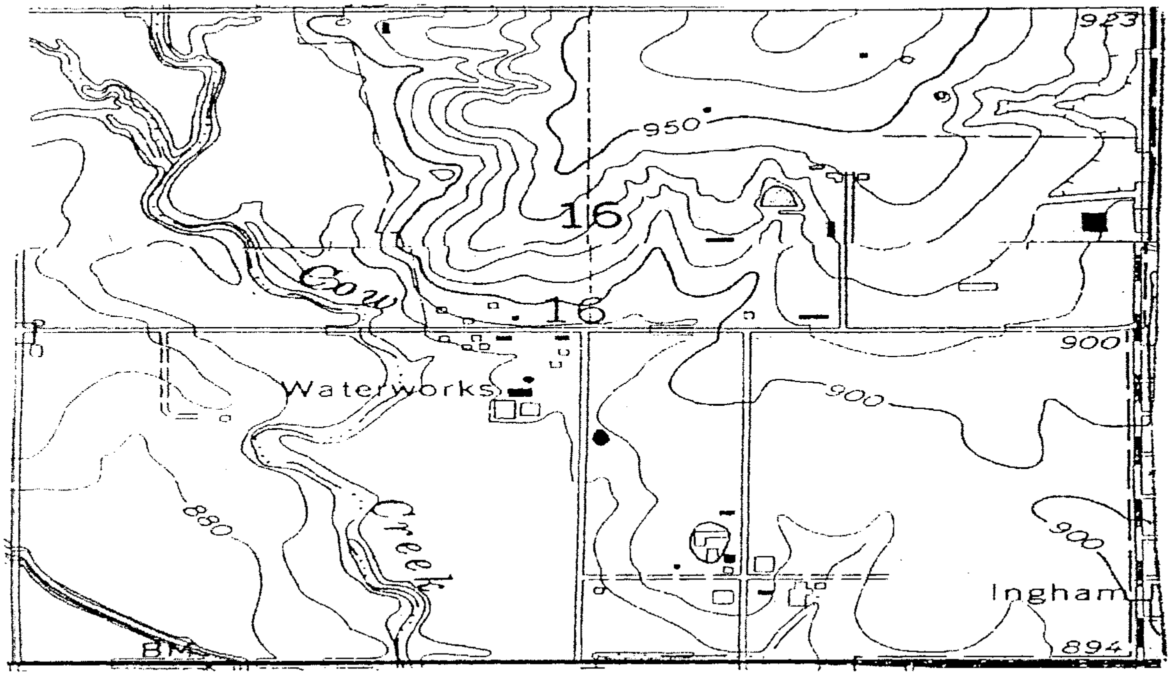
## 4.1 CHARACTERIZATION OF SOILS OF THE STUDY SITES

### *4.1.1 Norge soil series*

The Norge soil series is a member of the fine silty, mixed, thermic family of Udic Paleustolls. The pedon is located 900 feet above sea level northwest of the southeast corner of section 8, T. 19N, R.2E, 50 meters south east of water works as shown in Figure 4.1.

**Figure 4.1**

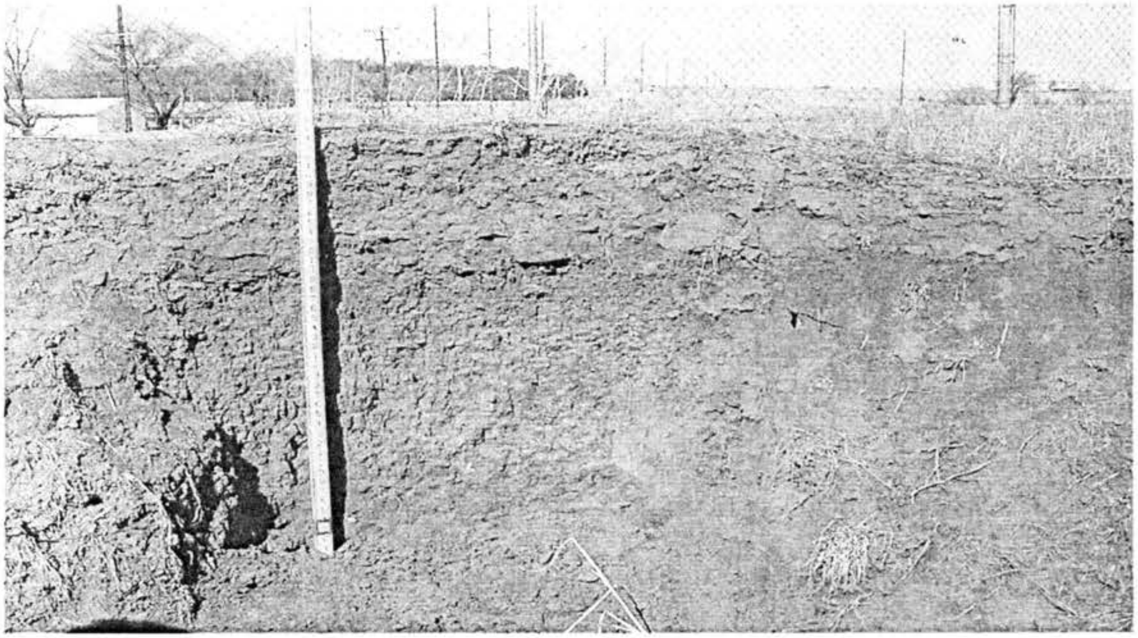
**Location of Norge clay loam soil series**



The site is located at the Oklahoma State University Agronomy Research Station, west of the main campus. It consists of very deep, moderately to slowly permeable upland soils that formed in loamy alluvium of pleistocene age. The soil has a mollic epipedon greater than 50 cm thick and has a fine control section. The soil is developed in material weathered from old loamy alluvium sediment underlying shales and sandstone (Gray and Roozitalab, 1979). The lower permeability of Norge soil very often causes ponding to occur on top surface of the soil (Gray and Roozitalab, 1979). A photograph of the Norge soil profile is shown in Figure 4.2.

**Figure 4.2**

**Soil profile of Norge clay soil (photo by Sanders, 2002)**



### 4.1.2.Dougherty soil series

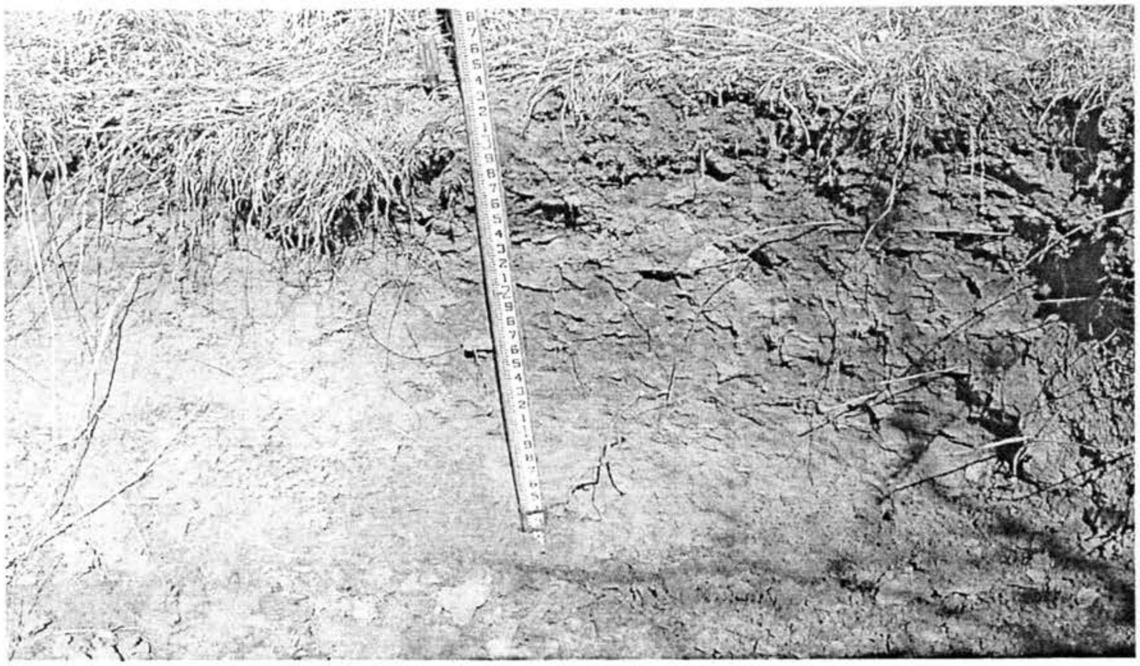
Organic carbon is known to have many ligand binding sites for cations, and for preferentially binding with heavy metals.

4.1.2 Dougherty Soil Series

The Dougherty soil series consists of fine-loamy, mixed, thermic, Udic Argiustolls developed on slopes ranging from zero to five percent. The sample site is located at the south-west corner of section 36, T. 18N, R2E at Oklahoma State University Agronomy Research Center, Perkins, Oklahoma. The soil is deep, well drained, and permeable, formed in thick deposits of Aeolian sand (Figure 4.3) underlying stratified shales and sandstones (Soil Survey of Payne country, Payne County Soil Survey, 1979).

**Figure 4.3**

**Soil profile of Dougherty sandy soil**



Dougherty soil has higher hydraulic conductivity and produces more leachate than Norge clay soil. Dougherty soil also had a lower soil pH compared to Norge soil, perhaps due to the presence of humic materials (Table 4.1).

## Table 4.1

## Physical and Chemical properties of soils and sludge

| | Soil type | | | | | | Sludge |
|---|---|---|---|---|---|---|---|
| Soil parameters | Norge clay | | | Dougherty sand | | | |
| Soil depth, cm | 0-20 | 20-40 | 40-60 | 0-20 | 20-40 | 40-60 | |
| Soil horizon | A | Bt1 | Bt2 | A | E | Bt | |
| Parent material | Alluvium | | | Aeolian sand | | | |
| Organic carbon, % | 0.867 | 0.65 | 0.51 | 0.77 | 0.43 | 0.31 | 19.22 |
| Organic matter, % | 1.49 | 1.12 | 0.86 | 1.26 | 0.75 | 0.42 | 33.21 |
| CEC, meq/100 g soil | 9.81 | 8.51 | 10.6 | 4.31 | 6.61 | 7.22 | N.D |
| Hydraulic conductivity | 1-4E | 1-E4 | N.D | 1-3E | N.D | N.D | N.D |
| pH | 6.02 | 6.23 | 6.103 | 5.31 | 5.21 | 5.52 | 6.41 |
| Bulk density, g/cm$^3$ | 1.47 | 1.52 | 1.57 | 1.42 | 1.62 | 1.62 | 0.91 |
| Sand, % | 37.55 | 40.45 | 38.43 | 71.25 | 60.41 | 52.22 | N.D |
| Silt, % | 35.32 | 36.31 | 30.93 | 21.52 | 24.01 | 28.41 | N.D |
| Clay, % | 27.05 | 23.11 | 30.43 | 6.72 | 15.41 | 19.02 | N.D |
| Textural class | L | CL | C | LFS | LFS | FSL | N.D |
| Total nitrogen % | 0.56 | 0.087 | N.D | 0.05 | 0.04 | 0 | 2.65 |
| N-NO$_3$ ppm | 2.12 | 2.82 | N.D | 0.71 | 0.31 | 0 | 111.71 |
| N-NH$_4$ ppm | 5.81 | 4.73 | N.D | 3.03 | 4.31 | 0 | 428.91 |
| Lime requirement, gm | 2.62 | 0.87 | 2.62 | 6.11 | 6.11 | 5.24 | N.D |
| Iron oxides | 1.53 | 1.67 | 1.82 | 1.2 | 1.43 | 1.49 | N.D. |

CEC- Cation exchange capacity of the soil; L- Loam; CL- Clay loam; C- Clay;

LFS- Loamy fine sand; FSL- fine sandy loam , N.D- No data

### *4.1.3 Clay Minerals*

Clay minerals are originated by inheritance from soil parent materials. Illites are formed on shales and clay bed (Gray and Roozitalab, 1976). Soils derived from alluvial sediment contain varying mixture of kaolinite, illite, and vermiculite. Most of the soils in central Oklahoma including soils of the study sites are originated mainly from shales, sandstone and aelolian sand of Permian age. Smectites and illites dominate the fine clay and kaolinites and quartz dominate coarse clay. During the study period investigation was made to determine the types of clay minerals prevailing in the study sites using x-ray defraction method. Smectite, and kaolinite are the dominant clay minerals followed by quartz and illites specially in Bt horizons (Table 4.2).

**Table 4.2**

**Types and percentage of clay minerals in Norge and Dougherty soils**

| Soil | Parent material | Horizon | Depth | Clay types and percent |
|---|---|---|---|---|
| Norge clay | Old Alluvium | A | 0-20 | $S_{47}I_8K_{35}\,Q_{10}$ |
| | | Bt1 | 20-40 | $S_{62}I_8\,K_{17}\,Q_{13}$ |
| | | Bt2 | 40-60 | $S_{66}\,I_5\,K_{16}Q_{13}$ |
| Dougherty Sand | Aeolian sand | A | 0-20 | $I_{16V2}\,K_{25}Q_{25}\,(S\text{-}V)_{32}$ |
| | | E | 20-40 | $I_{13}K_8\,Q_{11}(S\text{-}V)_{68}$ |
| | | Bt | 40-60 | $S_{70}I_3\,K_8\,Q_{19}$ |

S= Smectite; K=Kaolinite; Q=Quartz; I= Illite; and S-V= Smectite/vermiculite integrade. Numbers indicate percentage of each clay minerals in each soil horizon and depth. Bt1- Soil subhorizon with secondary caly where the clay content is less than the Bt2 horizon. Pedogenic process of clay translocation enriches the Bt2 horizon with clay. E-horizon is reffered to as "Albic horizon" where the content of clay and most soil nutrients are low compared to sub horizons of both Bt1 and Bt2. Quartz and other residual materials dominates the albic horizon. The content of iron oxides and clay increase after albic horizon.

## 4.2 TOTAL HEAVY METAL CONTENT IN BASELINE SOILS

Total heavy metal content results were summarized for the master horizon (A and B) and diagnostic horizons (Bt1, E, and Bt2). A comparison of total heavy metal content of surface soils in the present day study and previously published values is presented in Table 4.3. The range and distribution in total metal contents of the soils in this study are 25 to 33 mg kg$^{-1}$ chromium, 13.9 to 20.4 mg kg$^{-1}$ nickel, and 28.3 to 43.4 mg kg$^{-1}$ zinc for norge clay soils, and 26 to 31 mg kg$^{-1}$ chromium, 12 to 18 mg kg$^{-1}$ nickel, and 15.6 to

25.9 mg $kg^{-1}$ zinc for Dougherty sandy soils. The heavy metals contents of soils studied are with in the range reported by Ure and Berrow (1982) for world soils. Ure and Berrow (1982) summarized heavy metal results from studies of uncontaminated soils throughout the world up to 1982. The heavy metal contents from this study are also comparable to results reported from previous study (Table 4.3) of heavy metal content determine by various scientists across the world. There are minor differences exist between Holmgren's study and current study on metals content. Several possible explanations exist for the difference in heavy metals content between the two studies of Oklahoma soils. One possibility is that the geographical regions of Oklahoma soils sampled by Holmgren et al. (1993) and Tracy (1994) were different from this study. They sampled soils from the High Plains Region, from Interior Lowlands Region, from the Coastal Plain Region, and from the Ozark Plateau and Ouachita Mountain Region with significantly higher zinc content due to naturally high contents of zinc in soils and possible samples collected and analyzed from zinc smelters sites. Present sample sites have lower in chromium, nickel, and zinc contents than those sampled by Holmgren et al. (1993). Exact management histories of past study sample sites by Holmgren et al. (1993) were not known.

## Table 4.3

## Comparison of the present study with published data for the determination of heavy metals.

| Location | Mean total metal content, ppm | | |
|---|---|---|---|
| | Chromium | Nickel | Zinc |
| Oklahoma (Tracy, 1994) | 24.51 | 16.42 | 56.13 |
| Holmgren et al. (1993) | 31.22 | 11.11 | 21.03 |
| Present study: | | | |
| Norge clay soil | 28.3 | 16.8 | 35.7 |
| Dougherty sandy soil | 25.5 | 15.1 | 17.01 |
| Ohio (Logan and Miller, (1983) | 30.02 | 18.05 | 75.01 |
| Kentucky (Karathanssis and Seta, 1993) | 24.03 | 40.62 | 42.42 |
| Mississippi (Pettry and Seta, 1993) | 18.22 | 15.21 | 47.83 |
| California soil (Shacklett and Boenger, (1990) | 53.21 | 36.04 | 145.07 |
| USA soil (Shacklett, 1984) | 37.21 | 13.07 | 48.24 |
| Minnesota (Pierce et al. 1982) | 28.23 | 21.11 | 54.61 |
| (Sposito and Page, 1984) | 38.11 | 19.13 | 60.03 |
| English (McGrath, 1986) | 41.06 | 50.08 | 50.15 |
| Welsh (Davies and Paveley, 1985) | 23.07 | 212 | 85.13 |
| Swedish (Anderson, 1977) | 25.23 | 8.71 | 59.21 |
| World soils (Davies, 1992) 1999) | 50.09 | 25.22 | 90.04 |
| England (Bowen, 1977) Ure and Berrow (1982) | 31.23 | 33.72 | 59.81 |

(Source: Holmgren, 1993)

The metal contents of A horizon of the present study does not appear to have large anthropogenic additions because its metal content is similar or less than the B argillic horizons. The most suspect possibility for the differences in heavy metal contents between the two studies is the wet digestion procedure used. Holmgren et al. (1993) used pressurized wet digestion with $HNO_3$, $HClO_4$, and HF to dissolve heavy metals from soil samples. This method does dissolve heavy metal in primary and secondary minerals (Koon, 1984). In the resent study, EPA method 1311 was used to digest samples using $HNO_3$, HCl and $H_2O_2$. The combination of $HNO_3$, $HClO_4$ and HF method dissolves the soil sample and is considered a more complete digestion than $HNO_3$, HCl and $H_2O_2$ alone (Koon, 1984).

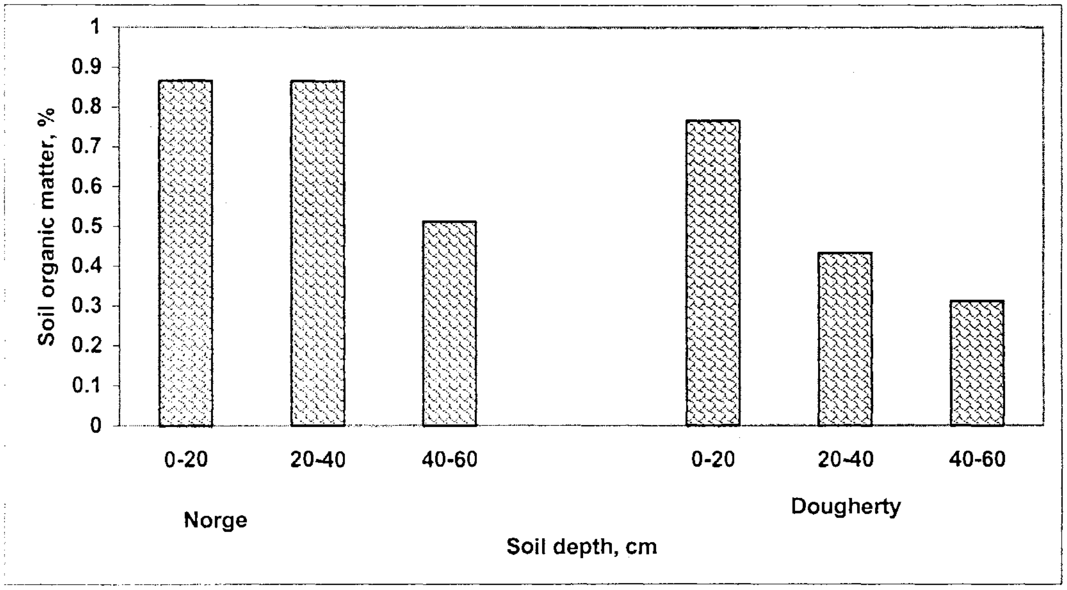
Study conducted buy Gibson and Farmer (1986) demonstrated that regardless of the differences in digestion procedures, heavy metals recoveries from different standard soil reference materials contain the same heavy metal that has been added as metal salts to soils or sediments. Non-occluded, adsorbed, and precipitated heavy metal would be recovered by both digestion procedures. Therefore, the discrepancy between the heavy metal contents of Oklahoma soils reported in two studies may be due to a combination of the above factors. However, the differences are not as such significant.

Distribution of heavy metals in both soils reflects pedogenic processes (Adriano, 1986). All three metals had accumulated in Bt1 and Bt2 horizons, but low metal concentrations between in E horizons were observed. Basically E-horizon is bleached horizon with very limited soil chemical properties, mainly dominated by qualtz and very low soil fertitilty. Most metals in Bt horizons were probably part of layer silicate or metal oxide structural components (Figure 4.6). A similar study conducted by Adriano (1986) showed that most heavy metals such as chromium, nickel and zinc have a strong affinity for noncrystalline aluminosilicate and oxyhydroxides of iron. Metal coprecipitation and immobilization by this material may play a significant role in its distribution in soils, especially in soils with Bt horizons where clay percentage increases down soil depth due to clay translocation (except E horizon where the clay percent is equal to less than the Bt or. This is consistent with the conclusion that clay strongly influences the behaviors of chemicals and water in Oklahoma soils (Holmgren et al., 1993).

Different soil formation processes apparently lead to different elemental distributions in soils. Metals tend to enrich in Bt horizons due to downward migration and accumulation in association with clay (Figure 4.5). Nickel distribution in the soil profiles is related either to organic matter or to amorphous oxides and clay (Kabata-Pendias, 1995). In surface horizons, nickel occurs mainly as organically bound forms, and in subsurface horizons, nickel is mobilized during weathering and is coprecipitated with iron oxides (Kabata-Pendias, 1995). Nickel concentrations for all soils increased with increased soil depth, reflecting an association with clay content, and/or parent material. The trends with Dougherty soil is slightly different due to low organic carbon and iron oxides. The carbon contents in the surface horizons of both soils range from 0.31 to 0.76% in sandy soils and from 0.51 to 0.87% in clay soil of the study site (Figure 4.4).

**Figure 4.4**

**Soil organic matter content in clay and sandy soils**



Possibly organic matter contents in clay soils are too low to concentrate nickel in surface horizons when soils have contrasting clay contents between horizons. Nickel concentration was correlated well to clay in both soils (Table 4.4).

The nickel concentration increases with increasing depth through all profiles except bleached horizon (E) where the clay content is low due to the presence of naturally residual materials such as quartz (Kabata, 1986). The change in nickel concentration as iron oxides and clay changes reinforces the idea that nickel content in a soil profile is dependent on the soil parent material with the presence of iron oxides in the soil horizons to occlude metals (Table 4.4).

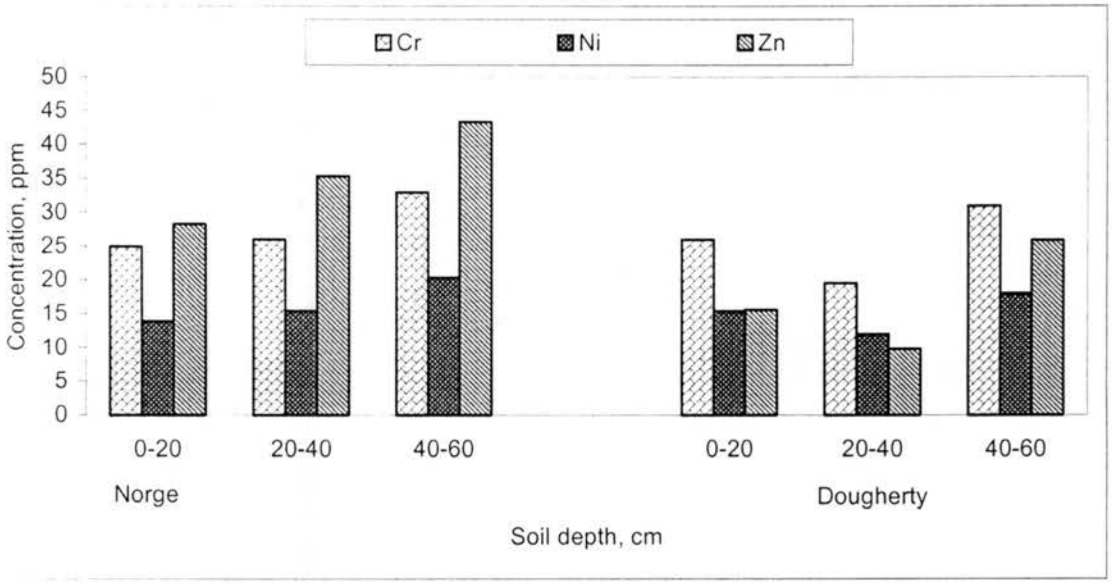
In the current study of theses two soils (sandy and clayey soils), chromium content ranged from 25 to 33 mg kg$^{-1}$. Total chromium concentration in the study soils was generally lower than those in U.S. and Oklahoma agricultural soils (Holmgren et al., 1993) as shown in Table 4.3. The low chromium concentration in the study soils could be explained by differences in soil parent materials, processes of soil formation, and geochemical properties of the soil. This was well elaborated by Sposito (1984).

The total distribution of chromium is shown in Figure 4.5. Concentration of chromium was higher in Norge soils than Dougherty soils, but there was no clear differences observed between the two soil series. Greater clay contents in Norge soil probably contributed to the differences in chromium metal concentration in parent materials of these two groups of soils.

Kabata-Pendias (2000) showed that sandy soil texture contributed to leaching of soluble and organically bound chromium from soils leaving only recalcitrant (e.g. large silicate) and structural or occluded forms (e.g. metal oxides). Additionally, organic matter contributes to soil CEC more significantly than soil clay contents, which may explain why total metal contents were poorly correlated with CEC (r=0.2). Low correlation between metal content and soil pH between these two sandy and clay soils was observed, possibly due to the relatively narrow soil pH differences (Sposito, 1986).

**Figure 4.5**

**Total heavy metals content in baseline clay and sandy soils**



Soils were digested by HNO3, H2O2 and HCl (EPA Method 1311) and analyzed by ICP (OSU forge and Soil test laboratory) from baseline soils of Norge clay and Dougherty sandy soils (without contamination).

The translocation of clay from the surface horizon to the subsurface argillic horizon is responsible for the large loss of metals in the surface horizon. Metal concentration increases with increasing soil depth as a pedogenic processes especially illuviation and leaching, influence metal distribution (Fuller et al.,1988).

Over time, some of these metals can be removed from the soil profile by translocation to groundwater. Removal of metals from the soil profile is evident by more developed, highly leached soils having the most loss (sandy soil) and the less leached soil having the least lose (clay soil) as enrichment ratios of the soil showed in Table 4.6.

Well-developed soils like the Norge series (soils containing argillic horizons, thick eluviated layers near the surface, and high organic matter concentration in the surface horizon) have relatively lower losses due to binding effect of soil organic matter. The heavy metals such as zinc could also be lost to plant uptake and subsequent removal by animal consumers, but this loss is probably relatively small compared to leaching loss of this metal from the upper 20 cm of soil. The distribution of heavy metals with particle size is a function of mineral composition and amount of adsorption sites in each size fraction (Esser et al., 1991).

Regression analysis of concentrations of trace elements against clay, organic matter, cation exchange capacity, and total concentrations of iron are shown in Table 4.4. The analysis confirmed CEC, iron oxide, and clay, content were strongly correlated with the concentrations of heavy metals in soils of the study sites, with the exception of nickel and CEC.

## Table 4.4

## Correlation coefficients between heavy metals and soil properties

| Metals | CEC | Clay | Iron | OM |
|---|---|---|---|---|
| Chromium | 0.9003 | 0.7334 | 0.9897 | -0.993044 |
| Nickel | -0.7046 | 0.8549 | 0.9354 | -0.5584 |
| Zinc | 0.94452 | 0.9959 | 0.8992 | 0.3381 |

CEC- Cation exchange capacity, OM- Organic matter

Actually, hydrous oxides of iron in soils were reported to be the most important compound in sorption of heavy metallic pollutants, and iron oxides exhibit diverse affinities to nickel and zinc (Fergusson, 1990).

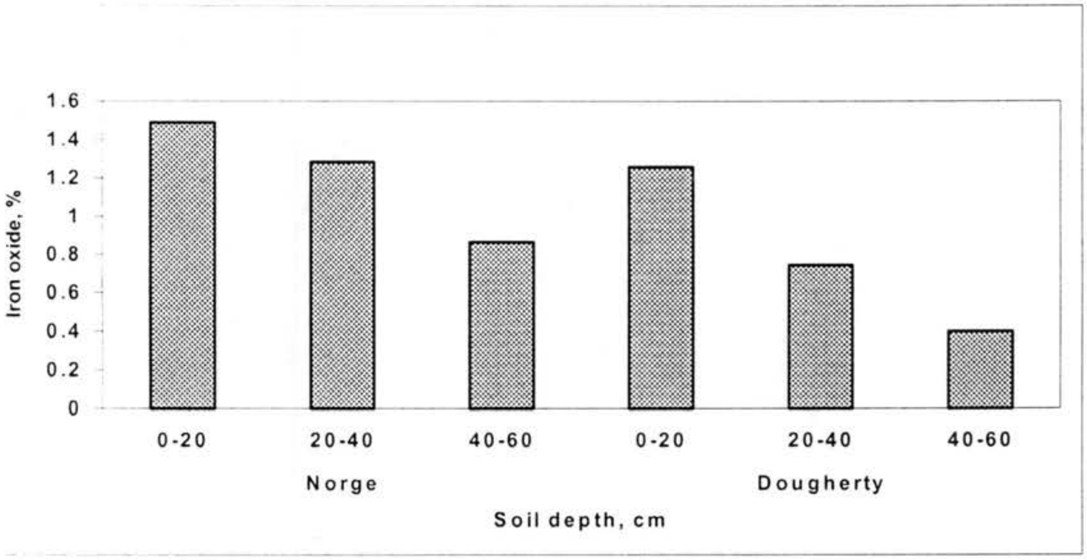
In addition, oxidation of chromium by iron oxides is likely to control the redox behavior of this element in soils (Kabata-Pendias and Pendias, 1992). In general, chromium closely resembles iron in ionic size and in geochemical properties. The association between chromium and iron may reflect the fact that most of the chromium in soils is present as chromic ($FeCr_2O_4$) or in other spinal structures, substituting for iron.

Distribution of heavy metals in different soil series also reflects pedogenic processes. Most metals in Bt horizons were probably part of layer silicate or metal oxide structural components, as supported by the high correlation coefficients of metal concentrations with clay content, but minimal correlation with CEC. Most heavy metals have a strong affinity for noncrystalline aluminosilicate and oxyhydroxides of iron (Adriano, 1986).

Metal coprecipitation and immobilization by clay material may play a significant role in its distribution in soils, especially in soils with Bt horizons. This is consistent with the conclusion that clay strongly influences the behaviors of chemicals and water in Oklahoma soils (Tracy, 1994). Different soil formation processes apparently lead to different elemental distributions in soils. Metals tend to enrich in Bt horizons due to downward migration and accumulation in association with clay. Chromium accumulates in Bt horizon along with organic matter.

Figure 4.6

**Iron oxide content of sandy and clay soils**



Dudka (1993) suggested that clay content was important in controlling the level and distribution of heavy metal concentrations in soils. A recent study conducted in south Florida demonstrated that chromium, cobalt, lead and mercury were generally not being cycled but were concentrated in the organic rich sediments (Gough, 1993). Cation exchange capacity showed significant positive correlation with zinc and chromium, but not nickel.

This result agrees with Holmgren et al. (1993), who reported that heavy metals show good correlation with both cation exchange capacity and organic carbon.

This is predictable since cation exchange capacity is correlated with clay-containing heavy metals and shows significant positive correlations with organic carbon and pH (Stevenson, 1982). All metals under study were highly correlated to iron oxide concentrations. This may occur because they may have similar ionic radii. Kabata-Pendias (1995) suggested that chromium and nickel were associated mostly with the clay in the soils.

## 4.3 DISTRIBUTION OF HEAVY METALS IN BASELINE SOIL FRACTIONS

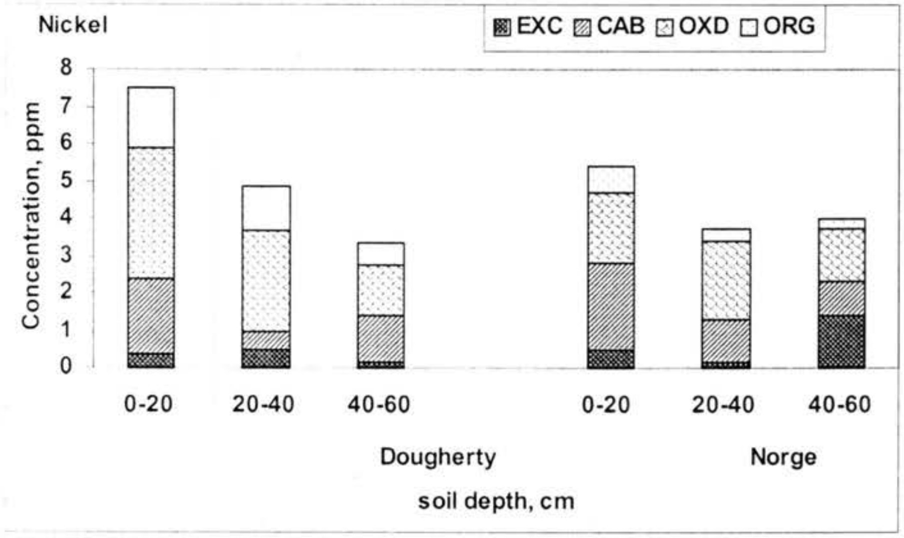
### *4.3.1 Nickel*

The percent of total nickel ranged from 0.73-3.24% in the exchangeable fraction, 3.18-14.38% in the carbonate fraction, 4.95-25.17% in the oxide fraction, 2.69-11.52% in the organic fraction in Norge clay soil. In Dougherty sandy soil, the content of nickel fractions varied from 1.83-6.29% in exchangeable fraction, 12.51-18.11% in carbonate fraction, 17.33- 33.32% in oxide fraction and 6.69-9.55% in organic fraction. In general, the oxide fraction contained the highest nickel. The organic and carbonate contained intermediate percentage, and the exchangeable fraction contained the smallest percentages of the total nickel.

The majority of the total nickel is in the sum of the oxide, organic, and residual fractions. Sposito (1982) also found that in sludge amended soils as well as baseline soils, the organic fraction was the largest next to residual fraction.

Figure 4.7

**Nickel fractionation in base line Norge clay and Dougherty sandy soils.**



EXC- Exchangeable form; CAB- Carbonate form; OXD- Oxide for; ORG- Organic for, and RES- Residual form

In polluted soils Hickey and Kittrick (1984) found approximately 50% of the nickel in the residual fraction and Soon and Bates (1982) found approximately 50% of the total nickel in the organic fraction of a soil collected near a nickel smelter sites.

Apparently, most nickel remains in the oxide and organic fractions in soils that are highly contaminated with nickel. Nickel was found to be the highest in the oxide fraction by many investigators (Emmerich et al., 1982; Sims and Kline, 1991; Shuman, 1991). The large proportion of nickel in the residual fraction might be because nickel has the highest crystal field stabilization energy of the common divalent metals, and thus has a high potential to be enriched in clay minerals (Bruemmer et al., 1988). The Fe oxide in soils has a high capacity to occlude nickel, and enrich it in this fraction (Uren, 1992).

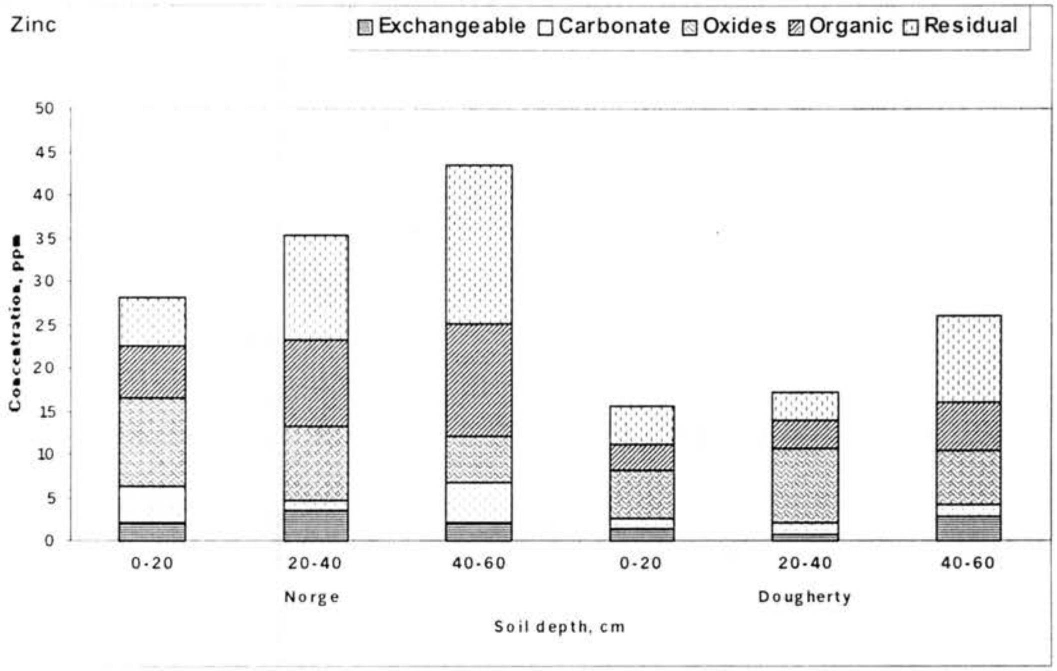
### *4.3.2. Zinc*

The distribution of zinc in the soils is shown in Figure 4.8. The total zinc content in the clay soil ranged from 28.3 ppm to 43.4 ppm, while in sandy soil, zinc concentration ranged from 9.8 ppm to 24.46 ppm.

The percentage of total zinc in the exchangeable fraction ranged from 5.07-9.88% in the baseline clay soils and 4.91-8.65% in sandy soils fraction. The percent of the total zinc in clay soil ranged from 3.24-14.84% in the carbonate fraction, 12.21-36.75% in the oxide fraction, and 21.21% in the organic fraction

**Figure 4. 8**

**Zinc metal fraction in Norge clay and Dougherty sandy soils**



EXC- Exchangeable form; CAB- Carbonate form; OXD- Oxide form, and ORG- Organic forms of metal fractions. Multi-sequential extraction method was used to partition metals. Ammonium acetate; Sodium acetate; Hydroxylammonium hydrogen chloride and hydrogen peroxides reagents were used to fractionate metals into exchangeable, carbonate, oxide and organic forms respectively.

In sandy soil, zinc content ranged from 4.91-8.65 % in the exchangeable fraction, 6.13-12.95% in the carbonate fraction, 25.35-46.93% in the oxide fraction, and 12.14-22.69% in the organic fraction. As the total zinc increased, the percent of the zinc in the sum of the oxide and organic fractions increased, ranging from 19.55 to 38.52% in the baseline soils. In baseline soils, Shuman (1991) found small amounts of zinc in the exchangeable fraction.

In contaminated soils, Koon et al., (1983) found an average of 8% of the total zinc in the exchangeable fraction. Kickey and Kittrick (1984) had similar results for the percentage of the total zinc in the exchangeable fraction (less than 14%). Hickey and Kittrick (1984) found a large percentage of the total zinc (28%) in the carbonate fraction in contaminated soils, and Sposito et al. (1982) found the carbonate fraction to have the largest percentage of the total zinc in sludge amended soils.

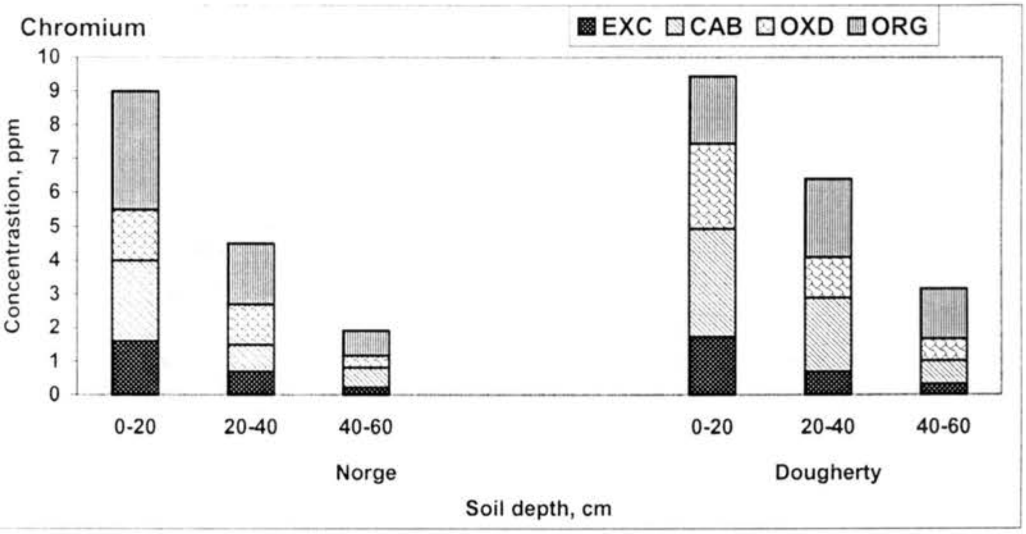
Other studies have shown that soils enriched in zinc have relatively large amounts of zinc metal in the oxide and organic fractions (McLean, 1982; Hickey and Kittrick, 1984; Gibson and Farmer, 1986; Koon, 1983; and Shuman, 1991). This is confirmed by the present study since most of the zinc fractions are found in the oxides and organic fractions.

### *4.3.3 Chromium*

Chromium distribution among the fractions in soils (Figure 4.9) showed organic fraction (0.75-3.5% in clay soils, and 1.5 to 2.3% in sandy soil), oxide fraction (0.35 to1.5% for

**Figure 4.9**

Chromium fractionation in clay and sandy baseline soils



**EXC**- Exchangeable form; **CAB**- Carbonate form; **OXD**- oxide form, and **ORG**- Organically bounded form and Metals were extracted by Multi- sequential extraction procedure using ammonium acetate; Sodium acetate; hydroxylammonium hydrogen chloride, and hydrogen peroxide for exchangeable, carbonate, oxide and organic fractions

clay soils, and 0.65 to2.5% in sandy soils), carbonate fraction (1.8 to 9.6% for clay soil and 3.2 to 12.31% for sandy soils, exchangeable fraction (0.22-1.6% for clay soil and 0.32-1.74% for sandy soil). Chromium tends to enrich in Bt horizons due to gradual downward migration and accumulation in association with clay. Total chromium in clay soil ranged from 25 ppm to 33 ppm, which is within the range of 10 to 40 ppm normally found in soils (Kabata- Pendias, 1992). Different soil formation processes apparently lead to different chromium distribution in soils.

## 4.4 MOVEMENT OF HEAVY METALS IN SEWAGE SLUDGE TREATED SOILS

### *4.4.1 Total Heavy Metal Contents before and after Sludge Application*

A controlled column study was conducted to evaluate the potential for chromium, nickel and zinc to move through three reconstructed soil profiles from surface applied sewage sludge. Anaerobically digested sewage sludge was mixed into the top 20 cm in air-dried form at a rate of 20 tons/ha. Eighteen soil columns were leached with redistilled water (RW) for the period of 120 days at 0.00408 mL/sec. The total concentrations of nickel, zinc and chromium in sludge soil layers are given in Figures 4.10, 4.11, and 4. 12 and Table 4.5. The greatest reported depths of metal movement in soils has taken place over long period of time (more than 20 years) by Kirkham (1975) was 120cm. Dougherty sandy soil with high sand percentage (71%), high hydraulic conductivity ($1*10^{-3}$cm/sec) and low organic matter (0.82%) contributed to high leaching rates as opposed to Norge clay soil with high clay percentage (30.4%) and high organic matter (1.49%) resulted in comparatively low metal movements.

Higher enrichment ratios of metals in sludge soil layer indicated that the leaching of metals was inevitable (Table 4.6). The heavy metals leached from Dougherty sandy soils might have involved several physical phenomena. Physical mechanisms of heavy metal movement could include colloidal precipitates and clay particles moving with the soil solution carrying heavy metals. This is indeed similar to the field conditions when, metals can move through cracks in the soil created by repeated wetting and drying cycles.

Figure 4. 10A

Total nickel leaching in Sandy and clay soils before and after sludge application

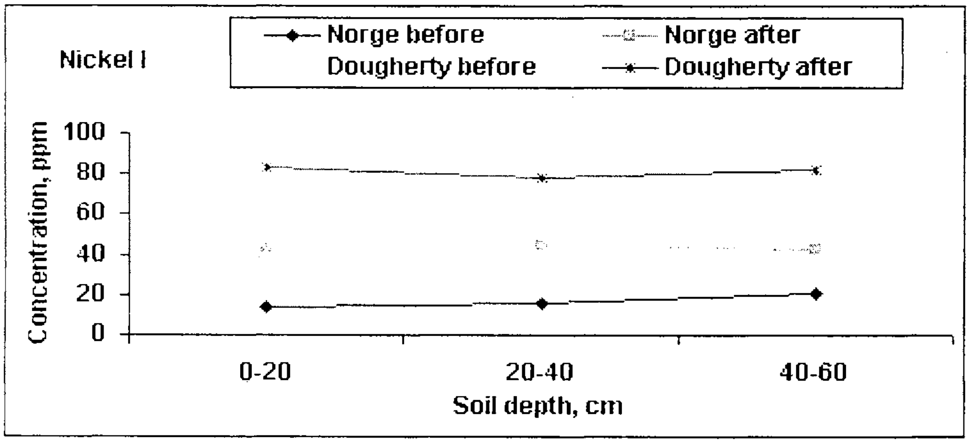


Figure 4.10B

Total nickel leaching in clay and sandy soils before and after sludge application and lime amendment

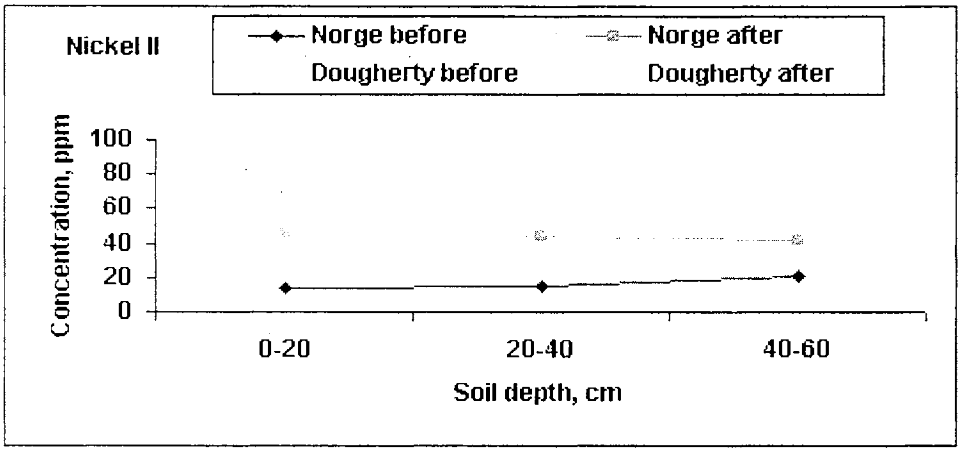


Figure.4.10C

Total nickel leaching in clay and sandy soil before and after sludge Application and metal salts spikes

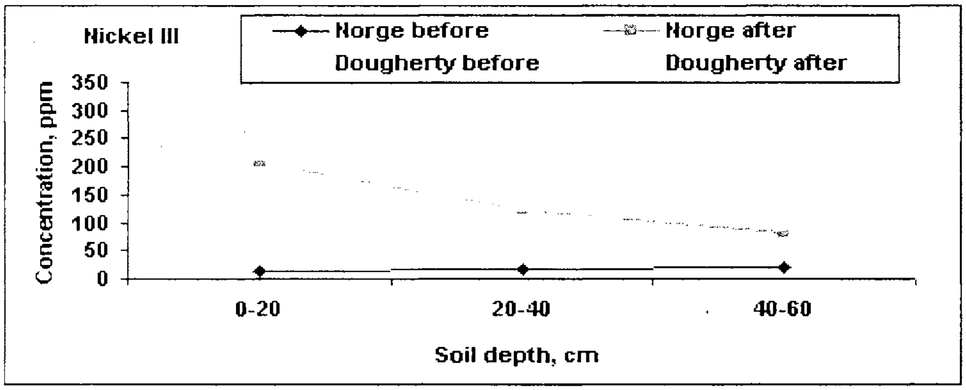


Figure 4.11A
Total zinc leaching in clay and sandy soils before and after sludge application

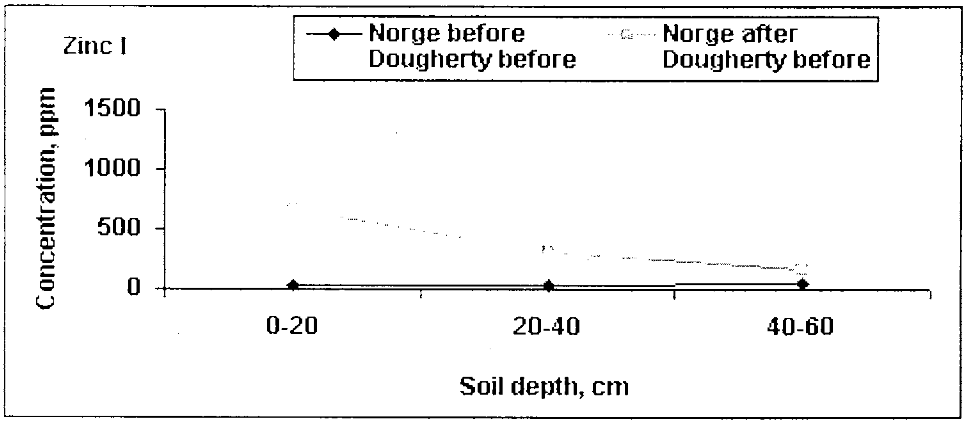


Figure 4.11B
Total zinc leaching in clay and sandy soils before and after sludge application and lime amendment

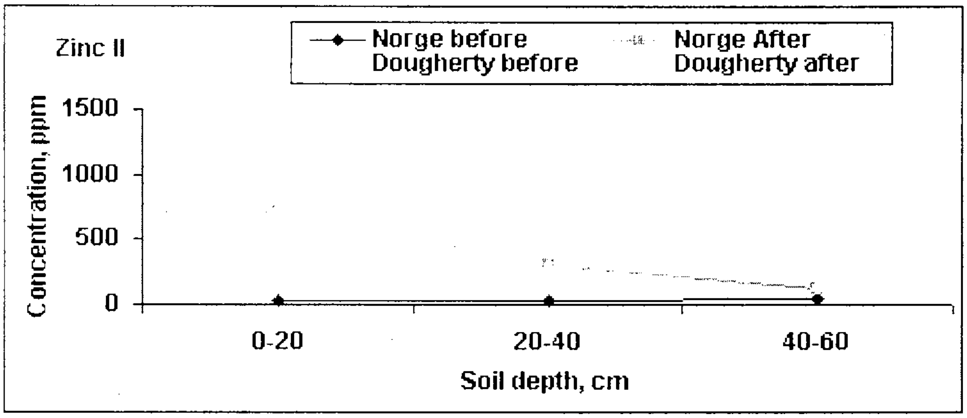


Figure 4.11C
Total zinc leaching in clay and sandy soils before and after sludge application and metal salts spikes

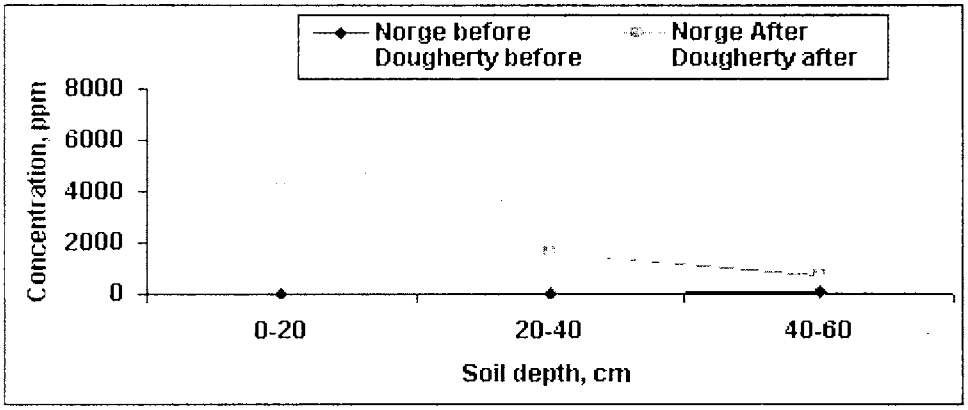


Figure 4.12A
Total chromium leaching in sandy and clay soils before and after sludge application

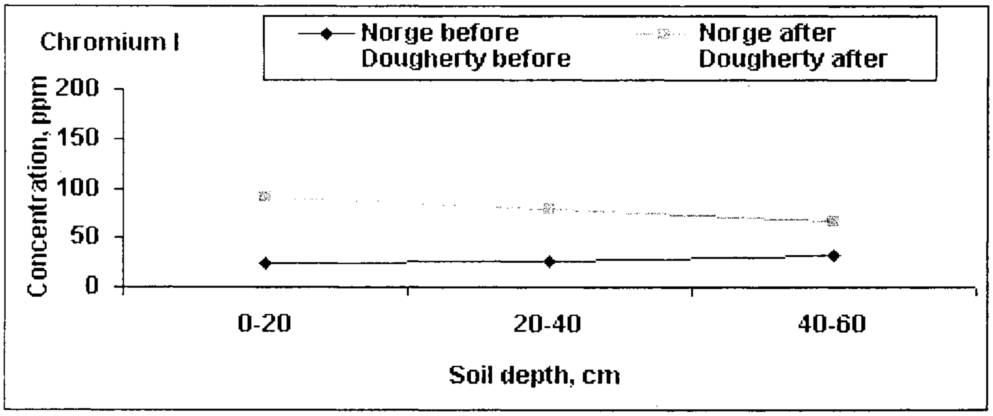


Figure 4.12B
Total chromium leaching in clay and sandy soil before and after
Sludge application and lime amendment

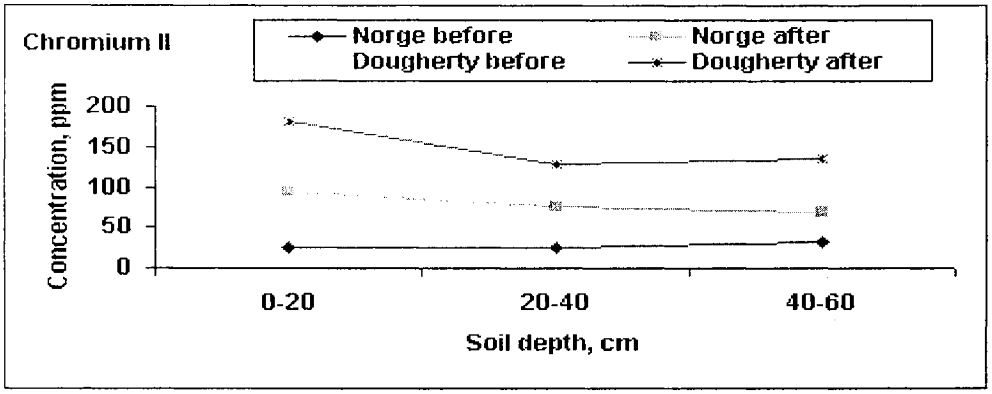
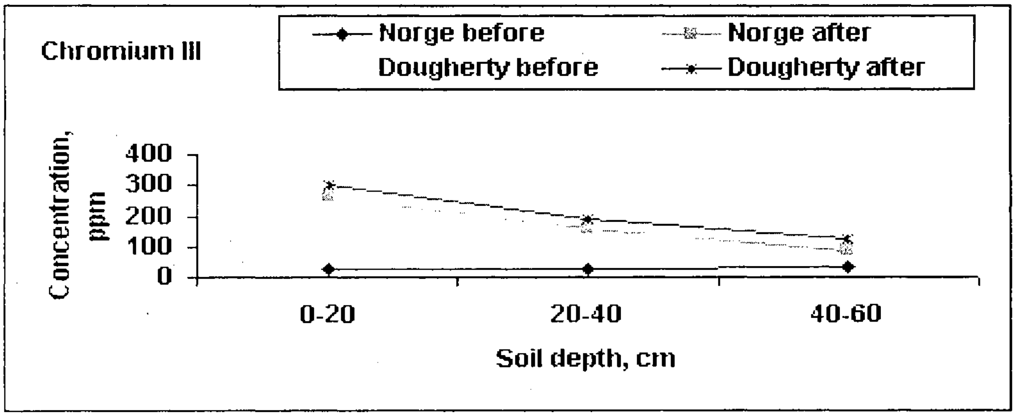


Figure 4.12C
Total chromium leaching in clay and sandy soils before and after sludge application and metal salts spikes



# Table 4.5

## Total metal distributions in different horizons of clay and sandy soils after column leaching

| Metal | Treatment | Total metal distribution in sludge amended clay and sandy soils, ppm | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 0-6 | 6-12 | 12-18 | 18-24 | 24-30 | 30-36 | 36-42 | 42-48 | 48-54 | 54-60 |
| Norge clay | | | | | | | | | | | |
| Chromium | T1 | 66.27 | 65.57 | 65.8 | 40.64 | 40.34 | 40.05 | 39.87 | 34.48 | 34.44 | 34.41 |
| | T2 | 69.48 | 68.8 | 68.28 | 37.86 | 37.68 | 37.42 | 37.18 | 35.96 | 35.87 | 35.68 |
| | T3 | 243.72 | 235.65 | 234.25 | 98.74 | 101.3 | 100.99 | 101.08 | 65 | 47.32 | 45.7 |
| Nickel | T1 | 29.48 | 28.96 | 28.67 | 21.87 | 23.14 | 21.58 | 20.89 | 22.32 | 22.198 | 22.134 |
| | T2 | 32.19 | 31.84 | 31.17 | 21.93 | 21.84 | 21.61 | 21.14 | 21.42 | 21.29 | 21.15 |
| | T3 | 194.72 | 193.42 | 194.97 | 90.44 | 88.96 | 87.21 | 53.84 | 62.52 | 60.54 | 60.44 |
| Zinc | T1 | 641.8 | 642.3 | 640.8 | 210.72 | 209.7 | 208.9 | 206.7 | 131.06 | 128.03 | 126.45 |
| | T2 | 696.54 | 696.2 | 694.91 | 213.75 | 205.08 | 199.26 | 187.22 | 88 | 85.51 | 82.69 |
| | T3 | 4139.4 | 4064.78 | 4057.64 | 1208.57 | 1205.41 | 1203.64 | 1201.53 | 689.59 | 669.98 | 659.01 |
| Dougherty sand | | | | | | | | | | | |
| Chromium | T1 | 57.3 | 54.9 | 53.3 | 28 | 26.4 | 25.3 | 24.7 | 33.2 | 33 | 32.7 |
| | T2 | 63.012 | 62.34 | 62.31 | 33.84 | 32.21 | 31.56 | 3'1.18 | 36.694 | 36.38 | 35.99 |
| | T3 | 210.02 | 209.18 | 209.66 | 121.46 | 116.8 | 116.5 | 113 | 81.93 | 75.9 | 70.7 |
| Nickel | T1 | 25.04 | 24.66 | 24.42 | 16.02 | 16.02 | 15.86 | 15.9 | 20.81 | 20.81 | 20.43 |
| | T2 | 33.44 | 32.55 | 32.11 | 18.44 | 18.27 | 17.83 | 17.78 | 19.69 | 19.57 | 19.53 |
| | T3 | 67.25 | 67.64 | 67.28 | 26.25 | 25.42 | 25.13 | 24.77 | 45.16 | 43.71 | 43.19 |
| Zinc | T1 | 542.77 | 540.6 | 537.28 | 217.23 | 216.85 | 217.4 | 217.6 | 113.762 | 112.69 | 112.07 |
| | T2 | 657.83 | 656.16 | 595.4 | 273.39 | 271.139 | 269.84 | 269.64 | 67.386 | 66.9 | 65.96 |
| | T3 | 3423.9 | 3421.79 | 3424.38 | 1715.84 | 1715.91 | 1710.53 | 1706.3 | 673.687 | 667.88 | 666.779 |

T1 and T2- Metal treatment contents are computed from metal contents in baseline soils and metal content from sludge applied put together

T3- treatment calculated from metal in baseline soils, from sludge applied and metal salts spikes (chromium, nickel and zinc chloride salts)designed to bring the metal content in the treatment equal to EPA standards heavy metal ceiling concentration for chromium,nickel and zinc in the study.

Top 0-20 cm soil depth is the soil/ sludge interface layer where sludge and metal salts spikes are applied to the soil and lime amendements were also mixed to the depth of 20 cm.

## Table 4.6

## Soil horizon Enrichment Ratios after soil column leaching with soils treated with sewage sludge, lime and spikes of metal salts spikes and lime.

| Metal | Treatment | | | |
|---|---|---|---|---|
| Soil depth, cm | | 0-20 cm | 20-40 cm | 40-60 cm |
| | | ER | ER | ER |
| Norge soil | | | | |
| Chromium | Treatment 1 | 3.49982 | 1.37935 | 1.28 |
| | Treatment 2 | 3.49358 | 1.51345 | 1.23 |
| | Treatment 3 | 16.85678 | 5.16235 | 1.59 |
| Nickel | Treatment 1 | 3.09012 | 1.25337 | 1.61 |
| | Treatment 2 | 3.09117 | 1.38879 | 1.38 |
| | Treatment 3 | 30.21671 | 5.66346 | 2.98 |
| Zinc | Treatment 1 | 33.42348 | 10.29312 | 4.54 |
| | Treatment 2 | 33.42091 | 10.36398 | 2.41 |
| | Treatment 3 | 300.00231 | 42.96043 | 15.51 |
| Dougherty soil | | | | |
| Chromium | Treatment1I | 3.38236 | 1.790034 | 0.790 |
| | Treatment 2 | 3.38871 | 1.94433 | 0.54 |
| | Treatment 3 | 16.15335 | 3.85468 | 0.61 |
| Nickel | Treatment1I | 2.88123 | 1.62238 | 0.61 |
| | Treatment 2 | 2.88092 | 1.76113 | 0.61 |
| | Treatment 3 | 27.27312 | 7.87298 | 0.41 |
| Zinc | Treatment 1 | 58.80157 | 37.68178 | 0.12 |
| | Treatment 2 | 58.09145 | 37.98034 | 0.14 |
| | Treatment 3 | 480.77316 | 182.91129 | 0.04 |

In the fine textured Norge soil used in the study, physical movement was less likely, due to smaller pore sizes, as well as the destruction of soil structure and soil micropores because of reconstruction of the soil profiles (formation of soil profile in soil column). An alkaline pH would induce a low solubility of heavy metals and probably played a role in the retention of the metals in the sludge soil layers (Hem, 1982).

Sludge added into the sludge soil layers seemed to have a buffering effect, regardless of the soil's original pH. The pH values for the soil sludge layers were all within the range of pH 6.7-7.4 at the end of the experiment. For this pH range, low solubility of the metals in the sludge soil layers would be expected as in the case of experimental treatment two where lime was amended to rise the level of soil pH higher and thus contributed low amount of metals leaching compared to soil treated only with sewage sludge. In some of the columns, there was a large pH change across the sludge soil layer. Starting at the sludge soil interface (soil layer), the pH of all soils decreased with depth in soil columns.

This decrease in soil pH was possibly due to the partial mineralization and nitrification of sludge added to soil containing nitrogen even though the period of full mineralization was not reached due to short life span of experiment (120 days).

The sludge contained 2.65% total nitrogen, 117ppm nitrate nitrogen and 5.8 ppm ammonium that through mineralization and nitrification processes produced $H^+$ ions, which could account for the decrease in soil pH. In clay soils, Iskandar (1988) observed a decrease in soil pH with high application of sludge, which attributed to the decrease of nitrification with subsequent movement of applied metals to the depth below soil/sludge interface. Therefore, the possibility exists that the metals in the sludge soil layer that did not move over the duration of this experiment could have become more mobile with increasing time. Comparison between chromium content in both soils before and after treatments showed reasonable difference in chromium concentration. The increased concentrations of chromium, nickel and zinc in soil profiles could account for the small percent of the recovered metals in the sludge soil layer. The unaccounted for metals in the sludge soil layer could be explained in at least two ways: First, the sludge soil layers were thoroughly mixed before samples were taken. After air drying each sample was crushed and mixed. The variability was probably due to the heterogeneous nature of sludge/soil mixture. The three replicated samples from each treatment helped reduce the variability in determining the total amount of metals in the sludge/ soil layers. However, the remaining variability could easily account for the deviation from a complete recovery. Among the heavy metals studied, chromium is found to be high in retention. Zinc and nickel were intermediate in retention and leaching (Table 4.7).

**Table 4.7**

**Retention and leaching of metals in soil/ sludge treated clay and sandy soils**

| Treatment | Metal | | | | | |
|---|---|---|---|---|---|---|
| | Cr | | Ni | | Zn | |
| | Leached % | Retained % | Leached % | Retained % | Leached % | Retained % |
| T IN | 3.74 | 94.39 | 10.58 | 85.15 | 4.3 | 88.73 |
| T IIN | 2.9 | 94.17 | 6.03 | 92.04 | 5.51 | 91.57 |
| T IIIN | 4.89 | 94.14 | 18.03 | 80.13 | 9.08 | 88.16 |
| T ID | 7.88 | 90.58 | 27.77 | 67.89 | 4.16 | 95.41 |
| T IID | 5.62 | 92.24 | 6.94 | 88.89 | 9.38 | 89.9 |
| T IIID | 12.97 | 85.78 | 25 | 74.04 | 11.81 | 87.89 |

TI-Sludge amended soil; TII- sludge amended and limed soil; and TIII- Sludge amended and spiked soil; N-Norge clay soil, and D- Dougherty sandy soil.

### *4.4.2 Multi-step Sequential Chemical Extraction of Heavy Metals in Sludge applied, Limed and Metal Salts Spiked Sandy and Clay Soils.*

Knowledge of the chemical forms of soluble heavy metals associated with particulates or colloids is essential for estimating mobility and chemical reactivity in soils and leachates. A sequential extraction procedure was used to fractionate chromium, nickel and zinc in sludge treated, limed, and metal salts spiked soils into designated forms of exchangeable (EXC), oxide (OXD), organically bound (ORG), carbonate (CAB) and residual (RES).

The applied sewage sludge and uncontaminated soil samples (baseline soil) were also sequentially extracted. The chemical forms of heavy metals found in the sludge soil layers at the termination of the leaching processes were compared with those initially present in natural condition in both sandy and clay soils. The results of sequential extraction of air-dried sewage sludge applied soils taken from different treatments expressed in concentration and percentages of chromium, nickel, and zinc for sandy and clay soils are given in Appendices A1.1, A1.2, and A1.3 for clay soil; A2.1, A2.2, and A2.3 for sandy soil. With the large percentages of metals in other than the most stable form, the possibility exists for the forms of the metals in the sludge to shift to more stable forms once incorporated into the soil. For all metals, in average greater than 30% of the total was in the residual form in the soils. This observation indicates that the metal were present in the baseline soils in a relatively stable form. A comparison of the sludge and soil percentages for the organically bound metals indicates that chromium has a high affinity for organic matter. The percentage of metals in exchangeable form was low in both soils with none being higher than 15%. The largest percentage of each of the metals in the columns was distributed among the organically bound, oxides, or residual forms depending on the type of metals.

#### 4.4.2.1. Nickel

Throughout the soil column the dominant forms of nickel was oxide. The nickel percentage indicated that there were substantial changes in forms. The changes were from the organically bound and carbonate forms to the oxide forms, with some of the metals coming from the exchangeable form in the sludge. The oxide fraction was by far the most important fraction for nickel. Norrish (1985) has indicated that silicates commonly occlude nickel during soil weathering. The iron- manganese oxide fraction was the next most important nickel-containing fraction. Jenne (1988) has suggested that adsorption by manganese oxides controls nickel levels in soils. Nickel distribution among the soil fractions with sewage sludge, limed sludge and spikes of metal salts sludge showed that more than 20% of the nickel resided in the oxide fraction with the order being OXD (16-30%)> ORG (7-15%) > CAB (5-14%) >EXC (2-4%). This order was consistent with the results by Hickey and Kittrick (1984). Nickel has been found to be the highest in the RES fraction and oxide fractions by many investigators (Emmerich et al., 1982; Sims and Kline, 1991; Shuman, 1991). The large proportion of nickel in the residual and oxide fractions might be because nickel has the highest crystal field stabilization energy of the common divalent metals, and thus has a high potential to be enriched in clay minerals. The iron and manganese oxides in soils have a high capacity to occlude nickel, and enrich it in this fraction. Ure and Berrow (1982) and Shuman (1991) found that iron oxides played a more important role than manganese oxides for the enrichment of nickel in fine textured soils.

Since nickel in soils resides predominantly in the oxides fractions, with the application of sewage sludge to the soil, most of the fractions showed a high capacity to retain nickel. The carbonate fraction displayed some ability to retain nickel, especially with application of sludge application. The results suggested that the nickel in the exchangeable fraction represented an intensity factor (movement factor), while the oxide, carbonate and organic fractions represented a capacity factor, which might be a pool of the potential source of nickel in soils. With more sludge amendment, the gradual high accumulation rates may cause contamination in the future.

The considerable losses of nickel from the organic A-horizon of sludge-applied soils may occur under conditions favoring the leaching of organic matter. Organic carbon plays a major role in the transport of metals during downward migration in soils and into groundwater. Organic matter may facilitate metal transport when it is dissolved under alkaline conditions. However, it may also enhance a soil's ability to sorb metals when present as solid phase. Soil column leaching test showed that concentrations of nickel metals in the column were significantly elevated in all soil horizons, especially the B horizon. Metal accumulation for an element in a given soil horizon was directly proportional to the soil's ability to retain metals. For nickel, the properties of the sludge seemed to dominate in the sludge/ soil layers, but below the sludge interfaces the soil properties seemed to dominate, as there was a change in the percentages across the interfaces (Figures 4.13 and 4.14).

Figure 4.13A

Nickel fractionations in clay soil before and after application of sludge

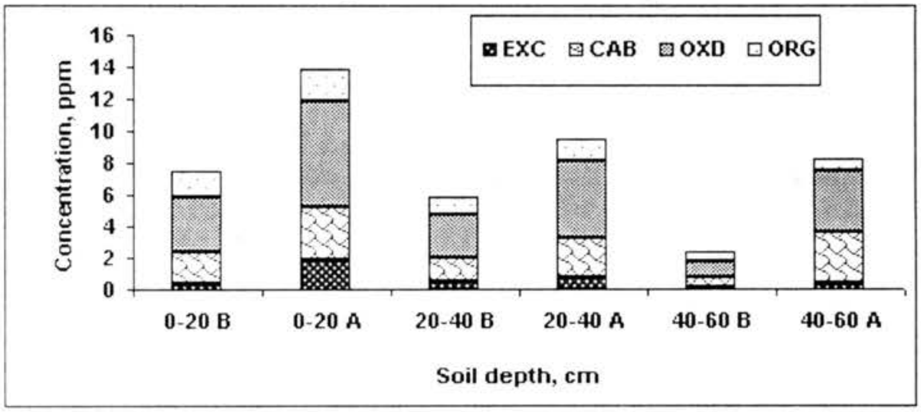


Figure 4.13B

Nickel fractionations in clay soil before and after application of sludge and lime

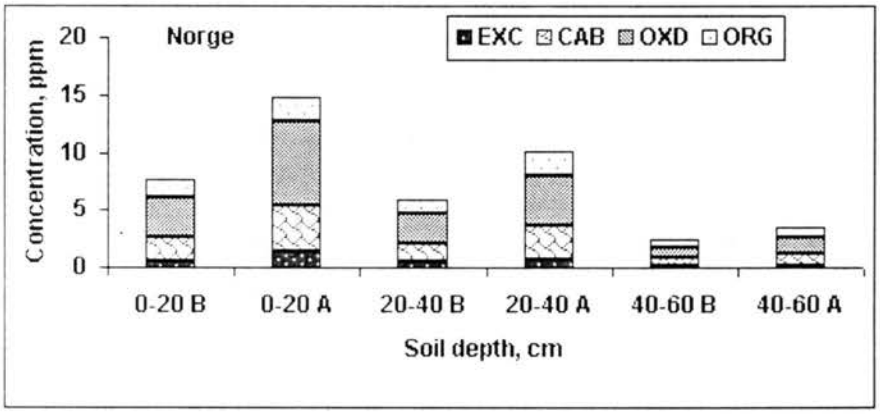


Figure 4.13C

Nickel fractionations in clay soil before and after sludge application and metal salts spikes

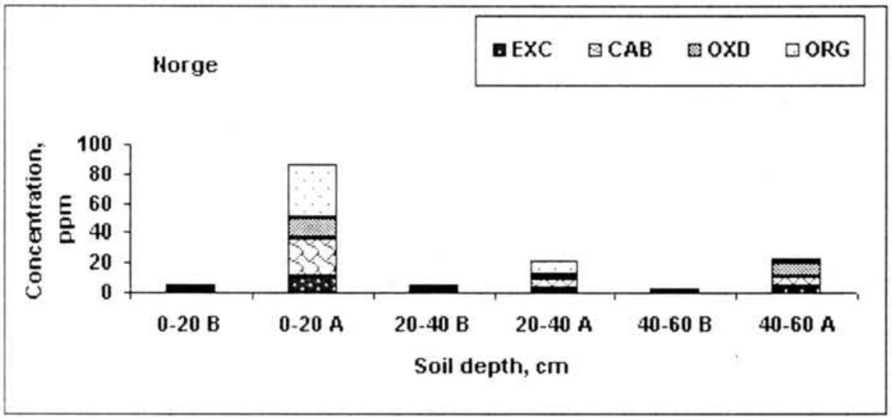


Figure 4. 14A

Nickel fractionations in sandy soil before and after

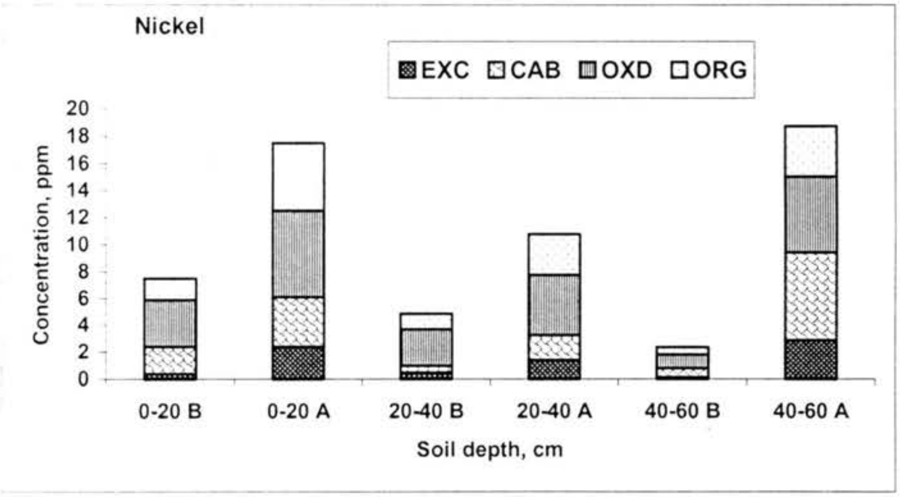


Figure 4.14B

Nickel fractionations in sandy soil before and after application of sludge and lime

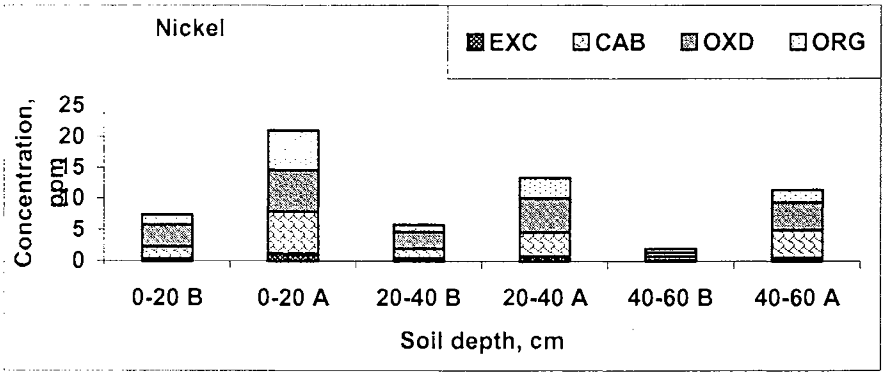
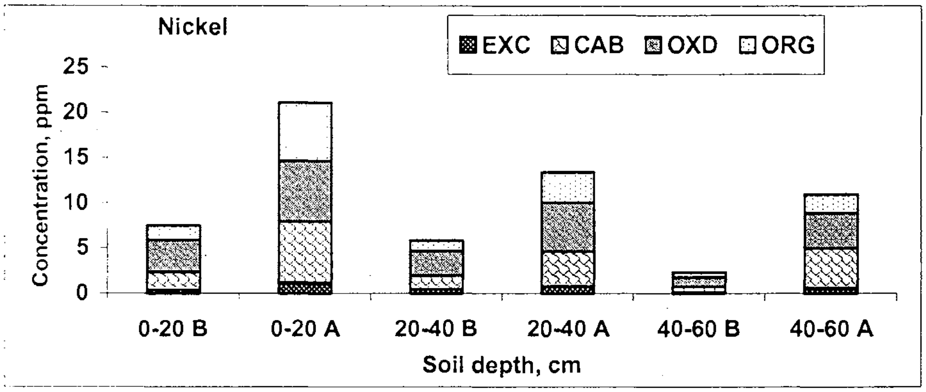


Figure 4. 14C

Nickel fractionations in sandy soil before and after application of sludge and metal salts spikes



#### 4.4.2.2 Zinc

The zinc fractions also showed a similar type of change with increases of zinc in the oxide and residual form. As more metals were added to the system, they were partitioned according to the existing equilibrium, and therefore the percentages of each form remained unchanged. This equilibrium was probably influenced by many factors, with pH being one of the most important ones. Changes of soil pH probably caused metals in solution to shift from organically complexed toward the free ionic form as exemplified by the changes of nickel in the soil profiles. The effect of pH on the equilibrium was likely different for each metal. The chemical properties of the sludge and soils were also expected to affect the equilibrium. The properties of the soil seemed to dominate for metal zinc, as there was no significant change in percentages across the sludge soil interface. Figures 4.15 and 4.16 show that the majority of zinc was associated with the oxide, which agrees with the observations of Hem (1982), Tessler et al. (1979), Harrison and Ure (1980), and Koon (1983). The organic fraction was the next most important fraction for zinc. Zinc contents of the exchangeable and organic fractions were appreciably high from the standpoint of potential mobility and bioavailability, even though they did not comprise a large percentage of the total. The carbonate fraction, however, was about equal importance, as the iron manganese oxides fraction in binding metals. It appears that large fractions of certain metals applied in the sludge amendment have redistributed and moved out of the soil surface by physical-chemical or biological processes and that there is potential for ground water and surface water contamination.

**Figure 4.15A**

**Zinc fractionation in clay soil before and after sludge application**

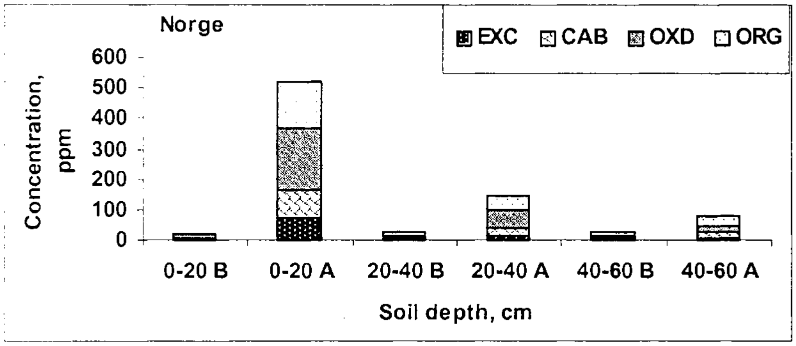


Figure 4.15B

Zinc fractionation in clay soil before and after application of sludge and lime

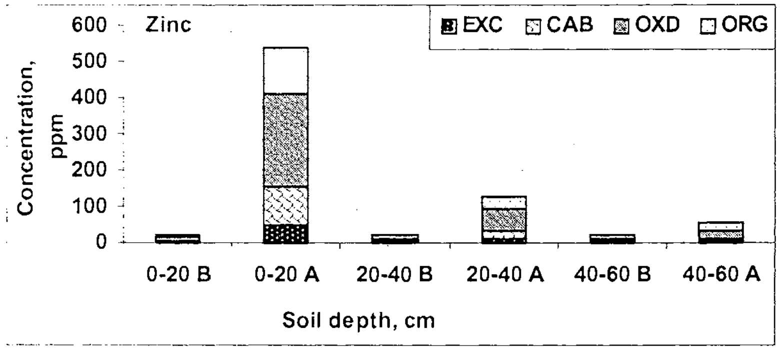


Figure 4.15C

Zinc fractionations in clay soil before and after application of sludge and spikes of metal salts

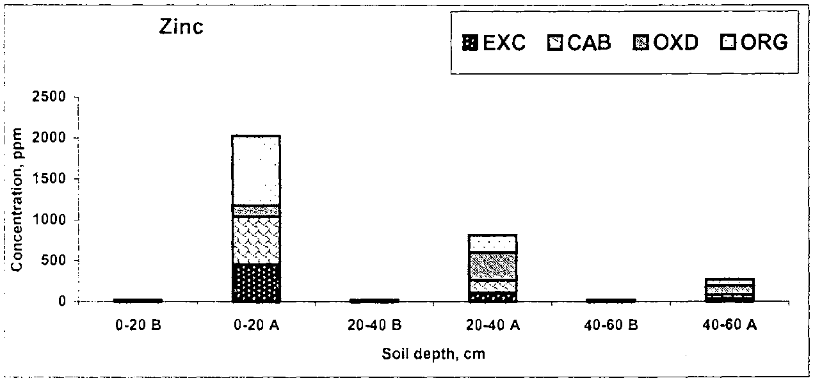


Figure 4.16A

Zinc fractionations in sandy soil before and after sludge application

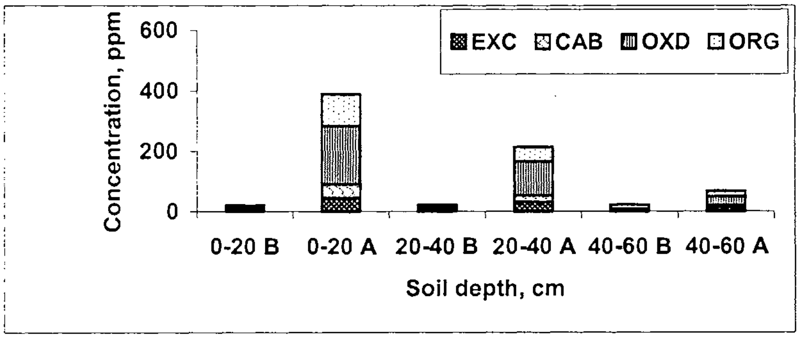


Figure 4.16B

Zinc fractionations in sandy soil before and after application of sludge and lime

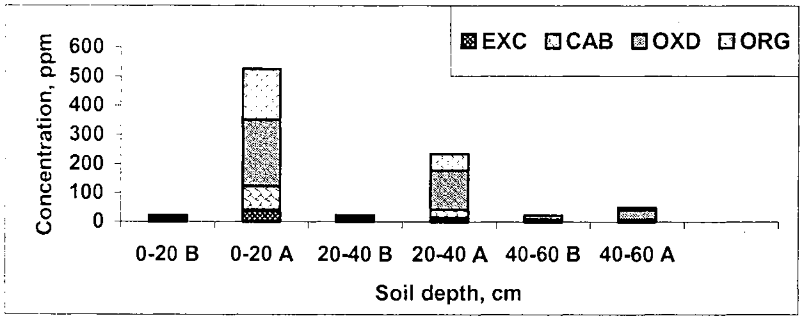
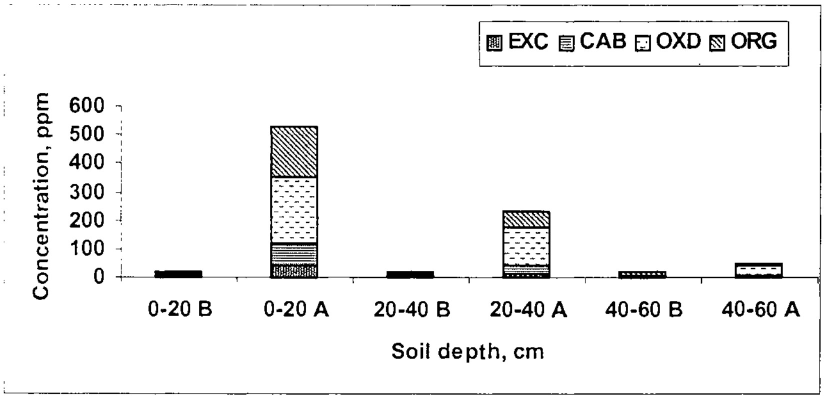


Figure 4.16C

Zinc fractionations in sandy soil before and after application of sludge and spikes of metal salts



Zinc contents of the exchangeable and organic fractions from both sandy and clay soils were appreciably high from the standpoint of mobility and bioavailability, even though they did not comprise a large percentage of the total. Comparison between zinc content in the base line soils and similar soils but treated with sewage sludge, lime and spikes of metal salts showed that soil A and B horizons were highly enriched by zinc after soil treated with sewage sludge.

### 4.4.2.3. Chromium

The majority of chromium has been found to be the highest in the organic fraction (Figure 4.17 and 4.18). Similar results were obtained by many other many investigators (Sim and Kline, 1991; Li and Shuman, 1996). This result has demonstrated that chromium was insignificantly mobilized by sludge application and spiking and was accumulated in A and B soil horizons.

Chromium was associated with organic and residual fractions. Chromium was the weakest adsorbed heavy metal ion among all the elements investigated, and there was weak relationship between chromium sorption and soil organic matter content. However, the concentration of chromium in sludge/soil layers for the 60 cm soil depth both in clay and sandy soils after leaching indicated that little but reasonable amount of metals has moved out of the sludge/soil layers.

**Figure 4.17A**

**Chromium fractionations in clay soil before and after sludge application**

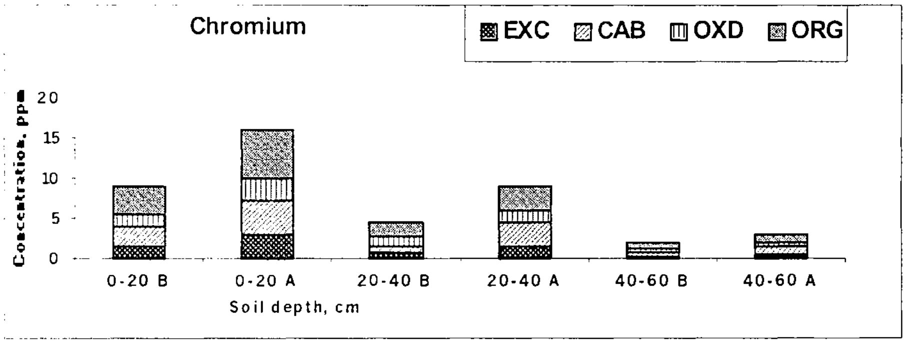


Figure 4.17B

Chromium fractionations in clay soil before and after application of sludge and lime

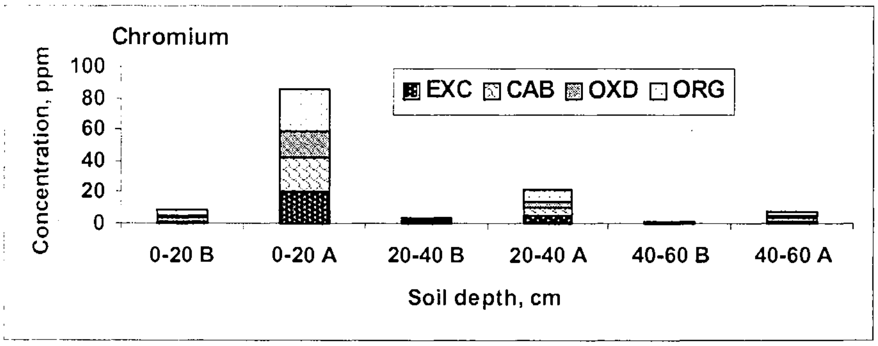


Figure 4.17C

Chromium fractionations in clay soil before and after application of sludge and spikes of metal salts

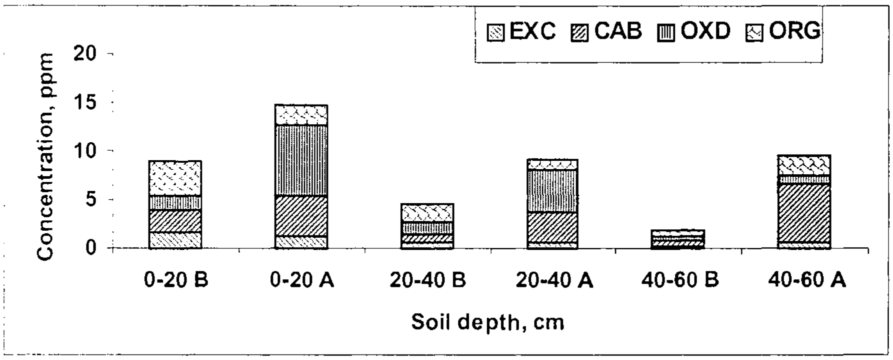


Figure 4.18A

Chromium fractionations in sandy soil before and after application of sludge

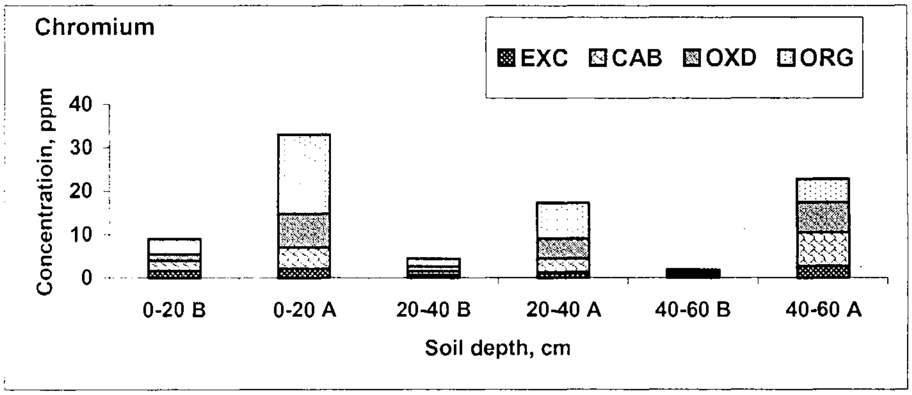


Figure 4.18B

Chromium fractionations in sandy soil before and after sludge application and lime

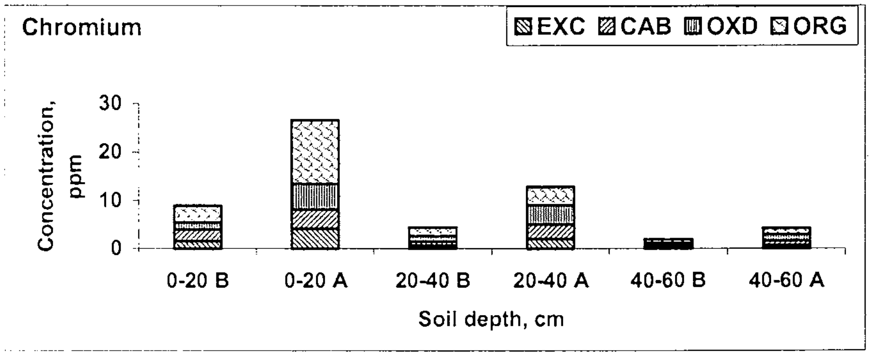
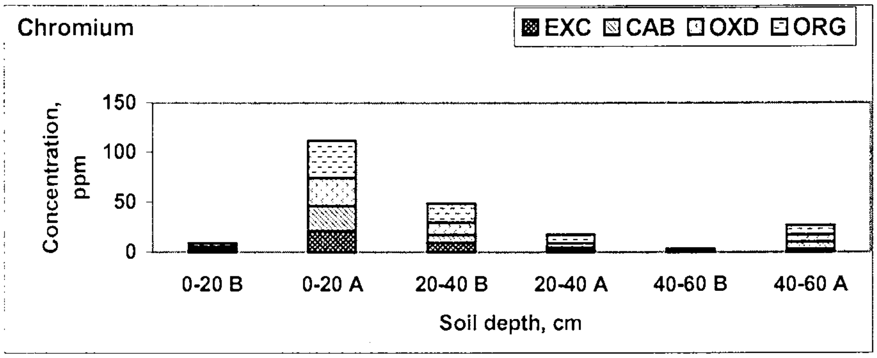


Figure 4.18C

Chromium fractionations in sandy soil before and after sludge application and metal salts spikes



# 5.0. CONCLUSIONS AND RECOMMENDATIONS

## 5.1 CONCLUSIONS

The present study demonstrated soil heavy metals interactions (mobility and attenuation), and provided basic knowledge on the mechanisms of heavy metals retention/release by soil mineral colloids as affected by inorganic anions as a result of application of sewage sludge in the soil. The study also identified areas which merit further investigation since land disposal of sewage sludge remains the major methods of waste management practices in different soil types.

### *5.1.1 Importance of soil properties on heavy metals concentration and distribution in soil horizons.*

1. The total average concentrations of three heavy metals in two Oklahoma soils, Dougherty sand and Norge clay were slightly lower than the average of USA and world soils. The upper limit of baseline concentrations for chromium, nickel, and zinc, however, corresponded well with those reported in the literature. Soil clay, iron oxide, soil pH, and organic matter showed the strongest relationship with concentrations of the studied metals in two different soil types. The study showed important interactions between soil types and heavy metals in different soil horizons.
2. The laboratory column leaching study clearly demonstrated that subsoils differing in physical and chemical properties possessed substantial differences in their ability to immobilize heavy metals. Sandy soils were much less effective in retaining metals than clay soils. Sub-soils are generally less effective in

immobilizing metals compared to surface soils with high organic matter content. The immobilizing capacity of metals increased with clay soil. The chemical properties of the sludge and soils were also affected the heavy metal equilibrium in soil horizon. The properties of soils (clay and iron oxide) seemed to dominate zinc, as there was no significant change in percentages across the sludge soil interface. For nickel and chromium, the properties of the sludge (organic matter content and soil pH) seemed dominate in the sludge soil layers, but below the sludge soil interface, the soil properties (mainly soil texture and iron oxide) dominated, as there was no change in the percentages across the interfaces.

3. The majority of zinc and nickel was associated with the oxide fraction, while chromium was associated with the organic and residual fractions. Chromium was the weakest adsorbed ion among all the elements investigated, and there was strong relationship between chromium sorption and soil organic matter content. In surface soil horizons, nickel appeared to occur mainly in organically bound forms. Nickel distribution in soil profiles was related to oxides of iron, and clay fractions. Nickel concentrations for sandy and clay soils were increased with increase soil depth, reflecting an association with iron oxides and clay content, or/and parent material with correlation coefficients of $r=0.93$ and $r=0.85$ for iron oxides and clay respectively. The residual fraction contained the largest percentage of the total nickel, the oxides and organic fractions contained intermediate percentages, and the carbonates and exchangeable fractions contained the smallest percentages of the total nickel. The large proportion of nickel in the residual fraction might be because nickel has the highest crystal field

stabilization energy of the common divalent metals, and thus has a high potential to be enriched in clay minerals. The iron and manganese oxides in soils have a high capacity to occlude nickel, and enrich it in this fraction.

### *5.1.2 Role of soil properties on heavy metals mobility and attentuation*

1. The laboratory column leaching study demonstrated substantial differences between sandy and clay soils in their ability to immobilize heavy metals. Sandy soils were much less effective in retaining metals than clay soils. Dougherty sandy soil with high sand percentage (71%), hydraulic conductivity ($1*10^{-3}$ cm/sec) and low organic matter (0.82%) contributed to high leaching rates as opposed to Norge clay soil with high clay percentage (23-30%) and high organic matter (1.49%)
2. The study showed that soils treated with lime retain or reduce the mobility of heavy metals compared to untreated soils.
3. Metal spiking demonstrated a very important aspect of metal partitioning. As more metals were added to the system, they were partitioned according to the existing equilibrium. This equilibrium was probably influenced by many factors, with pH being one of the most important ones. Changes of soil pH probably caused metals in solution to shift from organically complexed to the free ionic form. The effect of pH is substantially significant for metals in the organic form. The results of these studies clearly demonstrated that high amounts of heavy metals brought into the soils by application of sewage sludge or in the form of metal salts spikes are concentrated in the more mobile species when compared to

the relatively unpolluted background levels. Although the vertical metal concentration in the soil profiles failed to manifest substantial movement of most of the metals under investigation, it appears that large fractions of certain metals applied in the sludge amendment such as zinc and nickel as demonstrated by metal enrichment ratios have been distributed and moved out of the soil surface by physical and chemical processes, and that there is potential for ground water and surface water contamination.

4. Mobile organically complexed forms of metals could account for migration of heavy metals from the surface soils over 120 days of leaching periods. Although the concentration of most heavy metals was much higher in the surface 20 cm at the end of this study, this does not rule out the possibility of large cumulative losses by leaching from the surface soil over time, if there is little retention of the relatively non adsorptive metal organic complexes in the shallow subsoil.
5. The data from soil sequential extraction analysis, especially the distribution of heavy metals species, are useful for an estimation of mobility of metals in different environments.

## 5.2. RECOMMENDATIONS AND FUTURE STUDY

### *5.2.1 Recommendations*

There are a lot of questions that still need to be answered regarding land application of sewage sludge and heavy metals leaching and attenuation from scientific as well as regulatory points of view.

1. Land disposal remains one of the viable methods of waste management practices. An important task in waste disposal should be adequate evaluation of the confinement and the rate of movement of pollutant from the source of contamination in the soil. Also, precise information on the attenuation of pollutants is needed to establish a base for evaluating waste disposal systems.
2. The presence of buffer materials such as lime can be important in the retention of heavy metals even though it does not seem a sustainable practice to remediate the soil absolutely.
3. Faced with the difficult question of determining what levels of metals are harmful, one approach is to minimize any accumulation. This can be achieved by matching the metal inputs from sludge to soil with the small annual losses of metals due to crop removal, soil erosion, and leaching, so that metal concentrations do not exceed background levels.
4. Current 503 regulations are not based on sustainable agricultural practice. Even if these regulations are closely enforced, it may result in heavy metal loadings in the soil in the future. Sludge monitoring is costly, and more expensive the more we attempt to monitor. The danger is that the policy of allowing sludge on food producing land is cumulative. Since this is not a sustainable practice, we must find alternative methods of getting rid of sludge. The concern is we may continue to dispose sewage sludge on farm land until the toxicity is likely to occur.
5. The main problem with the application of sludges is that there is no general agreement concerning the maximum allowable concentrations of various metals in sewage sludge. Caution is appropriate for sewage sludge because heavy

metals, unlike any other pollutants, cannot degrade and therefore, can retain in soils virtually indefinitely. As a result, there is a little opportunity for natural recovery from the consequences of any error in judgment. Proper management of sewage sludge is necessary not only for our welfare, but also for the well being of future generation.

### *5.2.2. Future Study*

1. The increased use of sewage sludge as a fertilizer, combined with the idea that large fractions of sludge borne heavy metals cannot be accounted for several years after land application, indicates that more detailed study of potential mobility of these elements on undisturbed soils at field scale is needed.
2. Additional study should be conducted to insure good sampling of soil solution and better measurements of metal activities, if possible in situ measurements. Much of the previous work has focused on investigating only topsoils or sediments containing an appreciable amount of naturally occurring organic matter. Soil organic matter is known to be very effective in immobilizing most heavy metals. Subsoils contain much less organic matter and are the primary transport media if metals contamination of ground water is to occur. Research efforts should be directed toward processes regulating metal mobility in subsoils. An important factor that needs to be addressed in the future is the influence of subsoil redox potential on metal mobility. It is possible that the subsoil redox potential has substantial impact on metal retention and release.

3. If sludge must be applied on agricultural land, it is extremely important that site specific factors should be assessed in detail and adequately prior to determining whether a particular site can be used effectively for land application. These include: soil type, flooding susceptibility, slope gradient, length and aspect, depth to seasonal ground water table, permeability of the most restrictive soil layer, cropping patterns, vegetative cover, and soil organic matter content. Since many suitable sites will not be ideal, the planner must carefully consider such factors when choosing actual application sites and designing projects.
4. It is vitally important that where land application of sewage sludge is used, soils should be tested before application to determine soil acidity, nutrient requirements and metal concentrations, shallow water supply wells that are near and down-gradient of application, especially where excessive runoff is on shallow and extremely well drained coarse soils when percolation to ground water may be rapid.
5. The data presented in this research were obtained under saturated flow or waterlogged conditions. Data for modeling the attenuation or migration of heavy metals under unsaturated flow conditions in both sandy and clay soils should be developed. The model must be tested with multiple element combinations, element concentration, and field data from a wide variety of soils and climatic conditions.
6. As a limited number of soils were employed in this study, similar type of research should be conducted on more soils to check the results of this study and to collect data on effects of other soil parameters on migration rates.

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# APPENDICES

# APPENDIX A

# METAL FRACTIONS IN SLUDGE APPLIED, LIME AMENDED AND METAL SALTS SPIKED SOILS

# Appendix A1.1

## Chromium , Nickel, and Zinc fractionations in sludge amended clay soil

| Treatment | Soil depth | Metal fractionations in sludge amended clay soil | | | | | | | | | | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| cm | | Exchageable | | Carbonate | | Oxide | | Organic | | Residual | | |
| | | ppm | % | ppm | % | ppm | % | ppm | % | ppm | % | ppm |
| **Chromium** | **Chromium** | | | | | | | | | | | |
| SL1 | 0-6 | 2.949015 | 4.45 | 4.459971 | 6.7 | 2.776713 | 4.2 | 5.8185 | 8.78 | 50.74294 | 76.57 | 66.27 |
| SL2 | 6-12 | 2.911308 | 4.44 | 4.386633 | 6.7 | 2.767054 | 4.2 | 5.7767 | 8.81 | 50.26596 | 76.66 | 65.57 |
| SL3 | 12-18 | 2.95442 | 4.49 | 4.42834 | 6.7 | 2.77018 | 4.2 | 5.8036 | 8.82 | 50.50808 | 76.76 | 65.8 |
| SL4 | 18-24 | 1.80848 | 4.45 | 2.698496 | 6.6 | 1.70688 | 4.2 | 3.9624 | 9.75 | 50.50808 | 74.79 | 40.64 |
| SL5 | 24-30 | 1.27071 | 3.15 | 3.182826 | 7.9 | 1.65394 | 4.1 | 2.8399 | 7.04 | 50.50808 | 78.71 | 40.34 |
| SL6 | 30-36 | 1.325655 | 3.31 | 2.87559 | 7.2 | 1.926405 | 4.8 | 2.7274 | 6.81 | 50.50808 | 78.57 | 40.05 |
| SL7 | 36-42 | 1.31571 | 3.3 | 3.113847 | 7.8 | 1.523034 | 3.8 | 2.3683 | 5.94 | 50.50808 | 79.91 | 39.87 |
| SL8 | 42-48 | 0.93096 | 2.7 | 5.72368 | 17 | 1.32748 | 3.9 | 1.2792 | 3.71 | 50.50808 | 69.5 | 34.48 |
| SL9 | 48-54 | 0.692244 | 2.01 | 5.796252 | 17 | 1.391376 | 4 | 1.0608 | 3.08 | 50.50808 | 69.65 | 34.44 |
| SL10 | 54-60 | 0.55056 | 1.6 | 0.664113 | 1.9 | 1.345431 | 3.9 | 1.3179 | 3.83 | 50.50808 | 74.52 | 34.41 |
| | **Nickel** | | | | | | | | | | | |
| SL1 | 0-6 | 1.933888 | 6.56 | 3.52286 | 12 | 6.689012 | 23 | 2.1167 | 7.18 | 15.21758 | 51.62 | 29.48 |
| SL2 | 6-12 | 1.905568 | 6.58 | 3.44624 | 12 | 6.539168 | 23 | 2.0562 | 7.1 | 14.95205 | 51.63 | 28.96 |
| SL3 | 12-18 | 1.86355 | 6.5 | 3.113562 | 11 | 6.45075 | 23 | 2.047 | 7.14 | 13.61825 | 47.5 | 28.67 |
| SL4 | 18-24 | 1.367969 | 6.26 | 2.447253 | 11 | 5.071653 | 23 | 1.5812 | 7.23 | 11.36365 | 51.96 | 21.87 |
| SL5 | 24-30 | 0.770562 | 3.33 | 2.621762 | 11 | 5.245838 | 23 | 1.7748 | 7.67 | 12.81956 | 55.4 | 23.14 |
| SL6 | 30-36 | 0.494182 | 2.29 | 2.496806 | 12 | 4.624594 | 21 | 1.4178 | 6.57 | 12.66962 | 58.71 | 21.58 |
| SL7 | 36-42 | 0.442868 | 2.12 | 2.373104 | 11 | 4.443303 | 21 | 0.9233 | 4.42 | 12.52773 | 59.97 | 20.89 |
| SL8 | 42-48 | 0.575856 | 2.58 | 3.142656 | 14 | 4.167144 | 19 | 0.7991 | 3.58 | 13.70894 | 61.42 | 22.32 |
| SL9 | 48-54 | 0.388325 | 1.75 | 3.088848 | 14 | 3.763424 | 17 | 0.8721 | 3.93 | 13.99967 | 63.09 | 22.19 |
| SL10 | 54-60 | 0.336376 | 1.52 | 3.292944 | 15 | 3.644811 | 16 | 0.6019 | 2.72 | 14.28049 | 64.53 | 22.13 |
| | **Zinc** | | | | | | | | | | | |
| SL1 | 0-6 | 73.29356 | 11.42 | 93.3819 | 15 | 200.9476 | 31 | 155.89 | 24.29 | 122.4554 | 19.08 | 641.8 |
| SL2 | 6-12 | 73.54335 | 11.45 | 93.45465 | 15 | 198.9845 | 31 | 156.01 | 24.29 | 122.4866 | 19.07 | 642.3 |
| SL3 | 12-18 | 76.63968 | 11.96 | 93.30048 | 15 | 198.1354 | 31 | 149.31 | 23.3 | 124.6997 | 19.46 | 640.8 |
| SL4 | 18-24 | 19.91304 | 9.45 | 30.63869 | 15 | 73.47806 | 35 | 44.862 | 21.29 | 42.75509 | 20.29 | 210.72 |
| SL5 | 24-30 | 16.54533 | 7.89 | 25.98183 | 12 | 56.17863 | 27 | 43.743 | 20.86 | 67.18788 | 32.04 | 209.7 |
| SL6 | 30-36 | 14.53944 | 6.96 | 27.11522 | 13 | 52.80992 | 25 | 42.866 | 20.52 | 73.15678 | 35.02 | 208.9 |
| SL7 | 36-42 | 12.15396 | 5.88 | 20.19459 | 9.8 | 55.74699 | 27 | 43.366 | 20.98 | 78.44265 | 37.95 | 206.7 |
| SL8 | 42-48 | 6.61853 | 5.05 | 21.44142 | 16 | 23.8136 | 18 | 29.253 | 22.32 | 50.86439 | 38.81 | 131.06 |
| SL9 | 48-52 | 4.301808 | 3.36 | 22.27722 | 17 | 20.31836 | 16 | 28.653 | 22.38 | 53.61896 | 41.88 | 128.03 |
| SL10 | 52-60 | 3.89466 | 3.08 | 21.97701 | 17 | 16.77992 | 13 | 29.033 | 22.96 | 54.74021 | 43.29 | 126.45 |

Sl - Sludge amended clay soil

# Appendix-A1.2

## Chromium, nickel, and zinc fractionations in sludge amended and limed clay soil

| Treatment | Soil depth | Metal partition | | | | | | | | | | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Exchageable | | Carbonate | | Oxide | | Organic | | Residual | | |
| | cm | ppm | % | ppm | % | ppm | % | ppm | % | ppm | % | ppm |
| **Chromium fractionation in sludge amended and limed clay** | | | | | | | | | | | | |
| LM1 | 0-6 | 2.758356 | 3.97 | 4.606524 | 6.63 | 2.945952 | 4.24 | 8.108316 | 11.67 | 51.51942 | 74.15 | 69.48 |
| LM2 | 6-12 | 2.7176 | 3.95 | 4.56144 | 6.63 | 2.86896 | 4.17 | 8.04272 | 11.69 | 51.2216 | 74.45 | 68.8 |
| LM3 | 12-18 | 1.939152 | 2.84 | 4.520136 | 6.62 | 3.120396 | 4.57 | 7.968276 | 11.67 | 50.6979 | 74.25 | 68.28 |
| LM4 | 18-24 | 0.92757 | 2.45 | 2.547978 | 6.73 | 1.484112 | 3.92 | 4.130526 | 10.91 | 28.807674 | 76.09 | 37.86 |
| LM5 | 24-30 | 0.911856 | 2.42 | 2.890056 | 7.67 | 1.439376 | 3.82 | 3.726552 | 9.89 | 28.71216 | 76.2 | 37.68 |
| LM6 | 30-36 | 0.905564 | 2.42 | 2.851404 | 7.62 | 1.418218 | 3.79 | 3.266766 | 8.73 | 28.929402 | 77.31 | 37.42 |
| LM7 | 36-42 | 0.862576 | 2.32 | 3.212352 | 8.64 | 1.368224 | 3.68 | 2.966964 | 7.98 | 28.736422 | 77.29 | 37.18 |
| LM8 | 42-48 | 0.712008 | 1.98 | 5.8435 | 16.25 | 0.981708 | 2.73 | 2.4273 | 6.75 | 26.3407 | 73.25 | 35.96 |
| LM9 | 48-54 | 0.642073 | 1.79 | 5.864745 | 16.35 | 0.900337 | 2.51 | 2.130678 | 5.94 | 26.339341 | 73.43 | 35.87 |
| LM10 | 54-60 | 0.66008 | 1.85 | 6.015648 | 16.86 | 0.906272 | 2.54 | 1.769728 | 4.96 | 26.342544 | 73.83 | 35.68 |
| **Nickel fractionation in sludge amended and limed clay** | | | | | | | | | | | | |
| LM1 | 0-6 | 1.355199 | 4.21 | 4.187919 | 13.01 | 7.171932 | 22.28 | 2.336994 | 7.26 | 17.186241 | 53.39 | 32.19 |
| LM2 | 6-12 | 1.327728 | 4.17 | 4.158304 | 13.06 | 7.297728 | 22.92 | 2.298848 | 7.22 | 17.021664 | 53.46 | 31.84 |
| LM3 | 12-18 | 1.274853 | 4.09 | 4.064568 | 13.04 | 7.066239 | 22.67 | 1.948125 | 6.25 | 17.074926 | 54.78 | 31.17 |
| LM4 | 18-24 | 0.850884 | 3.88 | 2.820198 | 12.86 | 4.960566 | 22.62 | 1.502205 | 6.85 | 11.853165 | 54.05 | 21.93 |
| LM5 | 24-30 | 0.86268 | 3.95 | 2.972424 | 13.61 | 4.431336 | 20.29 | 1.358448 | 6.22 | 12.40512 | 56.8 | 21.84 |
| LM6 | 30-36 | 0.566182 | 2.62 | 3.146416 | 14.56 | 4.118866 | 19.06 | 0.695842 | 3.22 | 13.169134 | 60.94 | 21.61 |
| Lm7 | 36-42 | 0.579236 | 2.74 | 2.881382 | 13.63 | 3.96375 | 18.75 | 0.610946 | 2.89 | 13.187132 | 62.38 | 21.14 |
| Lm8 | 42-48 | 0.565488 | 2.64 | 3.4272 | 16 | 3.519306 | 16.43 | 0.563346 | 2.63 | 13.471038 | 62.89 | 21.42 |
| LM9 | 48-54 | 0.555669 | 2.61 | 3.57672 | 16.8 | 3.502205 | 16.45 | 1.143273 | 5.37 | 12.550455 | 58.95 | 21.29 |
| LM10 | 54-60 | 0.526635 | 2.49 | 3.52359 | 16.66 | 3.525705 | 16.67 | 1.118835 | 5.29 | 12.455235 | 58.89 | 21.15 |
| **Zinc fractionation in sludge amended and limed clay** | | | | | | | | | | | | |
| LM1 | 0-6 | 51.82258 | 7.44 | 101.2769 | 14.54 | 256.8143 | 36.87 | 132.6212 | 19.04 | 155.467728 | 22.32 | 696.54 |
| LM2 | 6-12 | 51.79728 | 7.44 | 101.1579 | 14.53 | 256.6889 | 36.87 | 126.9173 | 18.23 | 165.90446 | 23.83 | 696.2 |
| LM3 | 12-18 | 51.7708 | 7.45 | 101.1094 | 14.55 | 256.4218 | 36.9 | 128.2804 | 18.46 | 159.064899 | 22.89 | 694.91 |
| LM4 | 18-24 | 15.903 | 7.44 | 31.07925 | 14.54 | 79.06613 | 36.99 | 39.39413 | 18.43 | 48.756375 | 22.81 | 213.75 |
| LM5 | 24-30 | 14.43763 | 7.04 | 17.1857 | 8.38 | 72.20867 | 35.21 | 35.72494 | 17.42 | 67.225224 | 32.78 | 205.08 |
| LM6 | 30-36 | 13.66924 | 6.86 | 11.11871 | 5.58 | 52.20612 | 26.2 | 34.75094 | 17.44 | 87.514992 | 43.92 | 199.26 |
| LM7 | 36-42 | 10.95237 | 5.85 | 8.087904 | 4.32 | 47.19816 | 25.21 | 34.22382 | 18.28 | 87.80618 | 46.9 | 187.22 |
| LM8 | 42-48 | 4.4616 | 5.07 | 9.1432 | 10.39 | 18.7792 | 21.34 | 15.7432 | 17.89 | 40.392 | 45.9 | 88 |
| LM9 | 48-54 | 4.301153 | 5.03 | 8.901591 | 10.41 | 17.31578 | 20.25 | 14.38278 | 16.82 | 40.608699 | 47.49 | 85.51 |
| LM10 | 54-60 | 4.200652 | 5.08 | 8.59976 | 10.4 | 17.06722 | 20.64 | 12.37869 | 14.97 | 40.501562 | 48.98 | 82.69 |

LM- Lime treated clay soil

# Appendix- A1.3

## Chromium, nickel, and zinc fractions in sludge amended and metal salts spiked clay soil

| Treatment | Soil depth | Metal fractionation, ppm | | | | | | | | | | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| - | | Exchangeable | | Carbonate | | Oxide | | Organic | | Residual | | |
| | cm | ppm | % | ppm | % | ppm | % | ppm | % | ppm | % | ppm |
| **Chromium fractionations in sludge amended and metal salt spiked clay** | | | | | | | | | | | | |
| SPK1 | 0-6 | 20.61871 | 8.46 | 21.17927 | 8.69 | 17.52347 | 7.19 | 28.83208 | 11.83 | 156.4926 | 64.21 | 243.72 |
| SPK2 | 6-12 | 23.23509 | 9.86 | 20.54868 | 8.72 | 17.24958 | 7.32 | 27.8067 | 11.8 | 147.4226 | 62.56 | 235.65 |
| SPK3 | 12-18 | 18.5526 | 7.92 | 23.28445 | 9.94 | 13.23513 | 5.65 | 24.99448 | 10.67 | 154.4645 | 65.94 | 234.25 |
| SPK4 | 18-24 | 9.656772 | 9.78 | 8.629876 | 8.74 | 4.858008 | 4.92 | 9.706142 | 9.83 | 66.01756 | 66.86 | 98.74 |
| SPK5 | 24-30 | 9.6235 | 9.5 | 9.10687 | 8.99 | 4.90292 | 4.84 | 10.08948 | 9.96 | 67.80009 | 66.93 | 101.3 |
| SPK6 | 30-36 | 9.139595 | 9.05 | 10.31108 | 10.21 | 3.847719 | 3.81 | 9.987911 | 9.89 | 68.61261 | 67.94 | 100.99 |
| SPK7 | 36-42 | 8.612016 | 8.52 | 10.54264 | 10.43 | 2.57754 | 2.55 | 9.824976 | 9.72 | 69.6138 | 68.87 | 101.08 |
| SPK8 | 42-48 | 2.137885 | 6.38 | 3.853554 | 11.5 | 0.887993 | 2.65 | 2.22836 | 6.65 | 24.46169 | 73 | 33.50917 |
| SPk9 | 48-54 | 3.104192 | 6.56 | 5.593224 | 11.82 | 0.790244 | 1.67 | 3.260348 | 6.89 | 34.63824 | 73.2 | 47.32 |
| Spk10 | 54-60 | 2.70544 | 5.92 | 5.37889 | 11.77 | 0.74948 | 1.64 | 3.08475 | 6.75 | 33.78144 | 73.92 | 45.7 |
| **Nickel fractionations in sludge amended and metal salt spiked clay soil** | | | | | | | | | | | | |
| SPK1 | 0-6 | 10.9239 | 5.61 | 26.13169 | 13.42 | 13.14374 | 6.75 | 36.43249 | 18.71 | 108.4212 | 55.68 | 194.722 |
| SPK2 | 6-12 | 10.79284 | 5.58 | 25.02855 | 12.94 | 14.52584 | 7.51 | 36.05349 | 18.64 | 107.2707 | 55.46 | 193.42 |
| SPK3 | 12-18 | 10.89882 | 5.59 | 25.22912 | 12.94 | 12.79003 | 6.56 | 36.36191 | 18.65 | 109.8656 | 56.35 | 194.97 |
| SPK4 | 18-24 | 5.127948 | 5.67 | 9.306276 | 10.29 | 9.197748 | 10.17 | 13.58409 | 15.02 | 51.37896 | 56.81 | 90.44 |
| SPK5 | 24-30 | 7.001152 | 7.87 | 9.411968 | 10.58 | 9.38528 | 10.55 | 12.65901 | 14.23 | 51.24986 | 57.61 | 88.96 |
| SPK6 | 30-36 | 6.80238 | 7.8 | 9.104724 | 10.44 | 8.703558 | 9.98 | 11.52916 | 13.22 | 51.14867 | 58.65 | 87.21 |
| SPK7 | 36-42 | 3.348848 | 6.22 | 5.604744 | 10.41 | 9.701968 | 18.02 | 3.101184 | 5.76 | 32.23939 | 59.88 | 53.84 |
| SPK8 | 42-48 | 3.888744 | 6.22 | 7.433628 | 11.89 | 10.76594 | 17.22 | 3.194772 | 5.11 | 37.26817 | 59.61 | 62.52 |
| SPk9 | 48-54 | 3.698994 | 6.11 | 6.768372 | 11.18 | 9.704562 | 16.03 | 2.57295 | 4.25 | 38.01912 | 62.8 | 60.54 |
| Spk10 | 54-60 | 3.7775 | 6.25 | 6.545652 | 10.83 | 9.718752 | 16.08 | 1.970344 | 3.26 | 39.78765 | 65.83 | 60.44 |
| **Zinc fractionations in sludge amended and metal salt spiked clay soil** | | | | | | | | | | | | |
| SPK1 | 0-6 | 41.3936 | 12.45 | 601.8629 | 14.54 | 1361.022 | 32.88 | 845.6712 | 20.43 | 822.0769 | 19.86 | 4139.36 |
| SPK2 | 6-12 | 40.6478 | 11.46 | 585.7348 | 14.41 | 1419.015 | 34.91 | 789.7868 | 19.43 | 807.2653 | 19.86 | 4064.78 |
| SPK3 | 12-18 | 40.5764 | 9.44 | 589.9809 | 14.54 | 1335.369 | 32.91 | 910.5344 | 22.44 | 846.4237 | 20.86 | 4057.64 |
| SPK4 | 18-24 | 12.0857 | 9.45 | 166.1784 | 13.75 | 433.8766 | 35.9 | 238.9343 | 19.77 | 260.8094 | 21.58 | 1208.57 |
| SPK5 | 24-30 | 12.0541 | 8.86 | 149.4708 | 12.4 | 341.3721 | 28.32 | 198.4105 | 16.46 | 409.3572 | 33.96 | 1205.41 |
| SPK6 | 30-36 | 12.0364 | 8.87 | 128.7895 | 10.7 | 292.6049 | 24.31 | 222.3123 | 18.47 | 457.0221 | 37.97 | 1203.64 |
| SPK7 | 36-42 | 12.0153 | 6.87 | 112.3431 | 9.35 | 291.9718 | 24.3 | 246.9144 | 20.55 | 468.2362 | 38.97 | 1201.53 |
| SPK8 | 42-48 | 6.899 | 6.52 | 61.53908 | 8.92 | 148.8804 | 21.58 | 146.7417 | 21.27 | 288.7232 | 41.85 | 689.9 |
| SPk9 | 48-54 | 6.6998 | 5.27 | 54.26838 | 8.1 | 140.0928 | 20.91 | 142.5717 | 21.28 | 301.29 | 44.97 | 669.98 |
| Spk10 | 54-60 | 6.5901 | 5.37 | 50.94147 | 7.73 | 131.6702 | 19.98 | 144.1255 | 21.87 | 296.225 | 44.95 | 659.01 |

Sp- Metal salts spiked clay soil

# Appendix A2.1

# Chromium, nickel, and zinc partitions in sludge amended sandy soil

| Treatment | Soil depth | Metal fractionation, ppm | | | | | | | | | | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Exchangeable | | Carbonate | | Oxide | | Organic | | Residual | | |
| | cm | ppm | % | ppm | % | ppm | % | ppm | % | ppm | % | ppm |
| **Chromium fractionations in sludge amended sandy soil** | | | | | | | | | | | | |
| SL1 | 0-6 | 4.10268 | 7.16 | 4.0683 | 7.1 | 5.86752 | 10.24 | 14.65734 | 25.58 | 29.13132 | 50.84 | 57.3 |
| SL2 | 6-12 | 4.26573 | 7.77 | 4.0626 | 7.4 | 5.07825 | 9.25 | 13.5054 | 24.6 | 28.48212 | 51.88 | 54.9 |
| SL3 | 12-18 | 4.14674 | 7.78 | 3.96552 | 7.44 | 4.96223 | 9.31 | 11.23031 | 21.07 | 29.39495 | 55.15 | 53.3 |
| SL4 | 18-24 | 2.1784 | 7.78 | 2.072 | 7.4 | 2.8728 | 10.26 | 5.2164 | 18.63 | 15.6604 | 55.93 | 28 |
| SL5 | 24-30 | 1.80576 | 6.84 | 3.04392 | 11.53 | 3.67488 | 13.92 | 4.20288 | 15.92 | 13.92864 | 52.76 | 26.4 |
| SL6 | 30-36 | 2.23905 | 8.85 | 2.91962 | 11.54 | 4.78929 | 18.93 | 3.26876 | 12.92 | 12.08581 | 47.77 | 25.3 |
| SL7 | 36-42 | 2.21065 | 8.95 | 3.93718 | 15.94 | 4.67324 | 18.92 | 2.45024 | 9.92 | 11.60159 | 46.97 | 24.7 |
| SL8 | 42-48 | 2.1414 | 6.45 | 5.2788 | 15.9 | 5.75024 | 17.32 | 1.88244 | 5.67 | 18.47248 | 55.64 | 33.2 |
| SL9 | 48-54 | 1.8645 | 5.65 | 5.247 | 15.9 | 5.8806 | 17.82 | 1.8744 | 5.68 | 18.1335 | 54.95 | 33 |
| SL10 | 54-60 | 1.46169 | 4.47 | 4.54857 | 13.91 | 5.01291 | 15.33 | 1.8639 | 5.7 | 19.87833 | 60.79 | 32.7 |
| **Nicke partitions in sludge amended sandy soil** | | | | | | | | | | | | |
| SL1 | 0-6 | 2.438896 | 9.74 | 3.738472 | 14.93 | 6.502888 | 25.97 | 5.040552 | 20.13 | 7.316688 | 29.22 | 25.04 |
| SL2 | 6-12 | 2.401884 | 9.74 | 3.684204 | 14.94 | 6.404202 | 25.97 | 4.966524 | 20.14 | 7.205652 | 29.22 | 24.66 |
| SL3 | 12-18 | 2.38095 | 9.75 | 3.645906 | 14.93 | 6.341874 | 25.97 | 4.92063 | 20.15 | 7.135524 | 29.22 | 24.42 |
| SL4 | 18-24 | 1.560348 | 9.74 | 2.393388 | 14.94 | 4.160394 | 25.97 | 3.224826 | 20.13 | 4.681044 | 29.22 | 16.02 |
| SL5 | 24-30 | 1.34568 | 8.4 | 1.48185 | 9.25 | 4.807602 | 30.01 | 3.2841 | 20.5 | 5.111982 | 31.91 | 16.02 |
| SL6 | 30-36 | 1.14192 | 7.2 | 1.53049 | 9.65 | 4.854746 | 30.61 | 3.157726 | 19.91 | 5.17829 | 32.65 | 15.86 |
| SL7 | 36-42 | 1.60908 | 10.12 | 2.01135 | 12.65 | 4.23099 | 26.61 | 2.40249 | 15.11 | 5.66835 | 35.65 | 15.9 |
| SL8 | 42-48 | 5.2316 | 8.2 | 11.9306 | 18.7 | 10.5589 | 16.55 | 7.21578 | 11.31 | 29.04176 | 45.52 | 63.8 |
| SL9 | 48-54 | 1.683529 | 8.09 | 3.895632 | 18.72 | 3.444055 | 16.55 | 1.731392 | 8.32 | 10.09701 | 48.52 | 20.81 |
| Sl10 | 54-60 | 1.728378 | 8.46 | 3.814281 | 18.67 | 2.841813 | 13.91 | 2.128806 | 10.42 | 9.933066 | 48.62 | 20.43 |
| **Zinc fractionations in sludge amended sandy soil** | | | | | | | | | | | | |
| SL1 | 0-6 | 47.05816 | 8.67 | 45.3213 | 8.35 | 194.963 | 35.92 | 105.6773 | 19.47 | 151.4328 | 27.9 | 542.77 |
| SL2 | 6-12 | 46.7619 | 8.65 | 45.03198 | 8.33 | 193.6429 | 35.82 | 104.9845 | 19.42 | 150.6652 | 27.87 | 540.6 |
| SL3 | 12-18 | 46.47472 | 8.65 | 44.75542 | 8.33 | 192.4537 | 35.82 | 104.3398 | 19.42 | 149.7937 | 27.88 | 537.28 |
| SL4 | 18-24 | 29.66173 | 10.85 | 24.44017 | 8.94 | 98.03407 | 35.86 | 50.93069 | 18.63 | 70.80542 | 25.9 | 273.38 |
| SL5 | 24-30 | 34.35344 | 12.67 | 20.55241 | 7.58 | 117.1325 | 43.2 | 48.31715 | 17.82 | 51.27257 | 18.91 | 271.14 |
| SL6 | 30-36 | 34.18873 | 12.67 | 20.45387 | 7.58 | 116.5709 | 43.2 | 48.08549 | 17.82 | 51.02674 | 18.91 | 269.84 |
| SL7 | 36-42 | 34.18873 | 12.67 | 20.48086 | 7.59 | 116.5709 | 43.2 | 47.65374 | 17.66 | 51.02674 | 18.91 | 269.84 |
| SL8 | 42-48 | 16.33594 | 14.36 | 6.5412 | 5.75 | 26.48333 | 23.28 | 20.12414 | 17.69 | 44.27539 | 38.92 | 113.76 |
| SL9 | 48-54 | 15.05538 | 13.36 | 6.502213 | 5.77 | 30.29107 | 26.88 | 17.43314 | 15.47 | 43.45326 | 38.56 | 112.69 |
| SL10 | 54-60 | 13.89668 | 12.4 | 6.466439 | 5.77 | 31.25632 | 27.89 | 17.23637 | 15.38 | 43.21419 | 38.56 | 112.07 |

SL - Sludge amended soil and 1, 2, and 3… show soil depth series from 0-6 down soil profile

# Appendix A2.2

## Chromium, nickel, and zinc fractionations in sludge amended and limed sandy soil

| Treatment | Soil depth | Metal partition, ppm | | | | | | | | | | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Exchageable | | Carbonate | | Oxide | | Organic | | Residual | | |
| | cm | ppm | % | ppm | % | ppm | % | ppm | % | ppm | % | ppm |
| **Chromium fractionations in sludge amended and limed sandy soil** | | | | | | | | | | | | |
| LM1 | 0-6 | 2.148709 | 3.41 | 4.921237 | 7.81 | 7.725271 | 12.26 | 18.67046 | 29.63 | 29.56523 | 46.92 | 63.012 |
| LM2 | 6-12 | 2.125794 | 3.41 | 4.868754 | 7.81 | 7.642884 | 12.26 | 17.84794 | 28.63 | 29.87333 | 47.92 | 62.34 |
| LM3 | 12-18 | 2.124771 | 3.41 | 4.866411 | 7.81 | 8.262306 | 13.26 | 17.90166 | 28.73 | 29.23585 | 46.92 | 62.31 |
| LM4 | 18-24 | 1.153944 | 3.41 | 2.676744 | 7.91 | 4.724064 | 13.96 | 9.349992 | 27.63 | 16.21613 | 47.92 | 33.84 |
| LM5 | 24-30 | 1.330273 | 4.13 | 3.140475 | 9.75 | 4.483632 | 13.92 | 8.606512 | 26.72 | 14.74252 | 45.77 | 32.21 |
| LM6 | 30-36 | 1.429668 | 4.53 | 3.42426 | 10.85 | 4.708752 | 14.92 | 7.549152 | 23.92 | 14.44501 | 45.77 | 31.56 |
| LM7 | 36-42 | 1.412454 | 4.53 | 3.38303 | 10.85 | 4.652056 | 14.92 | 7.458256 | 23.92 | 14.27109 | 45.77 | 31.18 |
| LM8 | 42-48 | 4.78289 | 4.9 | 13.12855 | 13.45 | 12.02555 | 12.32 | 9.438887 | 9.67 | 59.1907 | 60.64 | 97.61 |
| LM9 | 48-54 | 1.798006 | 4.9 | 5.082119 | 13.85 | 4.373925 | 11.92 | 3.54831 | 9.67 | 22.25124 | 60.64 | 36.694 |
| LM10 | 54-60 | 1.735326 | 4.77 | 5.034992 | 13.84 | 4.696658 | 12.91 | 2.757604 | 7.58 | 22.16997 | 60.94 | 36.38 |
| **Nickel fractionations in sludge amended amended and limed sandy soil** | | | | | | | | | | | | |
| LM1 | 0-6 | 1.250656 | 3.74 | 6.998992 | 20.93 | 6.674624 | 19.96 | 6.731472 | 20.13 | 12.11197 | 36.22 | 10.8 |
| LM2 | 6-12 | 1.214115 | 3.73 | 6.48396 | 19.92 | 6.819225 | 20.95 | 6.545805 | 20.11 | 11.7831 | 36.2 | 9.3 |
| LM3 | 12-18 | 1.200914 | 3.74 | 6.720623 | 20.93 | 6.733467 | 20.97 | 5.84402 | 18.2 | 11.62703 | 36.21 | 8.8 |
| LM4 | 18-24 | 1.22298 | 3.74 | 6.84738 | 20.94 | 6.86046 | 20.98 | 5.9514 | 18.2 | 12.0336 | 36.8 | 8.6 |
| LM5 | 24-30 | 0.807672 | 4.38 | 2.902456 | 15.74 | 5.33838 | 28.95 | 2.511528 | 13.62 | 6.92422 | 37.55 | 7.7 |
| LM6 | 30-36 | 0.613352 | 3.44 | 2.813574 | 15.78 | 4.915731 | 27.57 | 2.262627 | 12.69 | 7.222933 | 40.51 | 6.5 |
| LM7 | 36-42 | 0.599186 | 3.37 | 2.796794 | 15.73 | 4.749038 | 26.71 | 2.594102 | 14.59 | 7.024878 | 39.51 | 6.9 |
| LM8 | 42-48 | 0.604483 | 3.07 | 4.205784 | 21.36 | 4.239257 | 21.53 | 2.366738 | 12.02 | 8.324932 | 42.28 | 6.5 |
| LM9 | 48-54 | 0.604713 | 3.09 | 4.40325 | 22.5 | 3.868989 | 19.77 | 2.011796 | 10.28 | 8.76736 | 44.8 | 6.4 |
| LM10 | 54-60 | 0.581994 | 2.98 | 4.64814 | 23.8 | 3.618909 | 18.53 | 1.767465 | 9.05 | 8.90568 | 45.6 | 6.8 |
| **Zinc fractionations in sludge amended and limed sandy soil** | | | | | | | | | | | | |
| LM1 | 0-6 | 43.7457 | 6.65 | 80.32104 | 12.21 | 235.5031 | 35.8 | 180.2454 | 27.4 | 115.3834 | 17.54 | 657.83 |
| LM2 | 6-12 | 43.63464 | 6.65 | 86.67874 | 13.21 | 234.9053 | 35.8 | 179.9191 | 27.42 | 115.0248 | 17.53 | 656.16 |
| LM3 | 12-18 | 39.5941 | 6.65 | 76.33028 | 12.82 | 213.7486 | 35.9 | 163.3182 | 27.43 | 104.4927 | 17.55 | 595.4 |
| LM4 | 18-24 | 14.46752 | 6.66 | 26.95824 | 12.41 | 79.94064 | 36.8 | 59.4993 | 27.39 | 38.10214 | 17.54 | 217.23 |
| LM5 | 24-30 | 10.43049 | 4.81 | 19.0828 | 8.8 | 106.9071 | 49.3 | 40.7678 | 18.8 | 41.6352 | 19.2 | 216.85 |
| LM6 | 30-36 | 10.17432 | 4.68 | 17.69636 | 8.14 | 109.5696 | 50.4 | 38.045 | 17.5 | 41.9582 | 19.3 | 217.4 |
| LM7 | 36-42 | 10.18368 | 4.68 | 19.34464 | 8.89 | 110.9542 | 50.99 | 32.57472 | 14.97 | 43.32416 | 19.91 | 217.6 |
| LM8 | 42-48 | 2.628054 | 3.9 | 6.576874 | 9.76 | 34.97333 | 51.9 | 7.978502 | 11.84 | 15.70094 | 23.3 | 67.386 |
| LM9 | 48-54 | 2.1408 | 3.2 | 6.54282 | 9.78 | 34.4535 | 51.5 | 7.6266 | 11.4 | 15.9222 | 23.8 | 66.9 |
| LM10 | 54-60 | 2.17668 | 3.3 | 7.0907 | 10.75 | 33.83748 | 51.3 | 7.45348 | 11.3 | 15.36868 | 23.3 | 65.96 |

LM- lime treated soil

# Appendix A2.3

## Chromium, nickel, and zinc fractionations in sludge amended and metal salts spiked sandy soil

| | | Metal partition | | | | | | | | | | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Treatment | Soil | Exchangeable | | Carbonate | | Oxide | | Organic | | Residual | | |
| | depth | ppm | % | ppm | % | ppm | % | ppm | % | ppm | % | ppm |
| **Chromium fractionations in sludge amended and metal salt spiked sandy soil** | | | | | | | | | | | | |
| SPK1 | 0-6 | 32.3636197 | 15.41 | 16.33932 | 7.78 | 19.37007 | 9.26 | 62.20704 | 29.62 | 96.43981 | 45.92 | 210.017 |
| SPK2 | 6-12 | 32.234638 | 15.41 | 16.2742 | 7.78 | 19.41452 | 9.26 | 61.95912 | 29.62 | 96.05546 | 45.92 | 209.18 |
| SPK3 | 12-18 | 32.329572 | 15.42 | 16.31155 | 7.78 | 11.2472 | 9.26 | 62.10129 | 29.62 | 96.27587 | 45.92 | 209.66 |
| SPK4 | 18-24 | 18.76557 | 15.45 | 9.449588 | 7.78 | 10.81568 | 9.26 | 35.97645 | 29.62 | 55.77443 | 45.92 | 121.46 |
| SPK5 | 24-30 | 20.48672 | 17.54 | 10.3368 | 8.85 | 19.1196 | 16.92 | 31.44256 | 26.92 | 35.93936 | 30.77 | 116.8 |
| SPK7 | 36-42 | 19.8202 | 17.54 | 10.0005 | 8.85 | 59.43319 | 16.92 | 30.4196 | 26.92 | 34.7701 | 30.77 | 113 |
| SPK8 | 42-48 | 10.56897 | 12.9 | 5.284485 | 6.45 | 7.83288 | 10.32 | 7.922631 | 9.67 | 49.69055 | 60.65 | 81.93 |
| SPk9 | 48-54 | 9.7911 | 12.9 | 4.89555 | 6.45 | 7.29624 | 10.32 | 7.34712 | 9.68 | 46.02576 | 60.64 | 75.9 |
| SPK10 | 54-60 | 9.1203 | 12.9 | 4.56015 | 6.45 | 6.089 | 10.32 | 6.84376 | 9.68 | 42.87248 | 60.64 | 70.7 |
| **Nickel fractionations in sludge amended and metal salt spiked sandy soil** | | | | | | | | | | | | |
| SPK1 | 0-6 | 13.27515 | 19.74 | 10.04715 | 14.94 | 17.47155 | 25.98 | 13.53743 | 20.13 | 19.65045 | 29.22 | 67.25 |
| SPK2 | 6-12 | 13.352136 | 19.74 | 10.10542 | 14.94 | 17.57287 | 25.98 | 13.61593 | 20.13 | 19.76441 | 29.22 | 67.64 |
| SPK3 | 12-18 | 13.281072 | 19.74 | 10.05163 | 14.94 | 17.47934 | 25.98 | 13.54346 | 20.13 | 19.65922 | 29.22 | 67.28 |
| SPK4 | 18-24 | 5.18175 | 19.74 | 3.92175 | 14.94 | 6.81975 | 25.98 | 5.284125 | 20.13 | 7.67025 | 29.22 | 26.25 |
| SPK5 | 24-30 | 3.0742 | 8.16 | 2.70723 | 10.65 | 7.781062 | 30.61 | 5.317864 | 20.92 | 8.29963 | 32.65 | 25.42 |
| SPK6 | 30-36 | 3.050608 | 8.16 | 2.910054 | 11.58 | 7.692293 | 30.61 | 5.257196 | 20.92 | 8.204945 | 32.65 | 25.13 |
| SPK7 | 36-42 | 3.0212 | 8.16 | 2.885705 | 11.65 | 7.582097 | 30.61 | 3.918614 | 15.82 | 8.087405 | 32.65 | 24.77 |
| SPK8 | 42-48 | 3.111524 | 6.89 | 8.449436 | 18.71 | 7.47398 | 16.55 | 5.559196 | 12.31 | 20.55683 | 45.52 | 45.16 |
| SPk9 | 48-54 | 3.011619 | 6.89 | 8.182512 | 18.72 | 7.234005 | 16.55 | 5.385072 | 12.32 | 19.89679 | 45.52 | 43.71 |
| SPK10 | 54-60 | 2.975791 | 6.89 | 8.085168 | 18.72 | 7.147945 | 16.55 | 5.321008 | 12.32 | 19.66009 | 45.52 | 43.19 |
| Zinc fractionations in sludge amended and metal salt spiked sandy soil | | | | | | | | | | | | |
| SPK1 | 0-6 | 467.022688 | 13.64 | 284.8701 | 8.32 | 1053.883 | 30.78 | 663.8981 | 19.39 | 953.5617 | 27.85 | 3423.92 |
| SPK2 | 6-12 | 398.296356 | 11.64 | 284.6929 | 8.32 | 1121.663 | 32.78 | 663.1429 | 19.38 | 952.9685 | 27.85 | 3421.79 |
| SPK3 | 12-18 | 364.354032 | 10.64 | 284.9084 | 8.32 | 1156.756 | 33.78 | 663.9873 | 19.39 | 953.6898 | 27.85 | 3424.38 |
| SPK4 | 18-24 | 148.248576 | 8.64 | 142.7579 | 8.32 | 606.5494 | 35.35 | 332.7014 | 19.39 | 495.0198 | 28.85 | 1715.84 |
| SPK5 | 24-30 | 80.132997 | 4.67 | 130.066 | 7.58 | 664.9151 | 38.75 | 319.5024 | 18.62 | 530.3878 | 30.91 | 1715.91 |
| SPK6 | 30-36 | 79.881751 | 4.67 | 129.6582 | 7.58 | 687.6331 | 40.2 | 318.5007 | 18.62 | 494.5142 | 28.91 | 1710.53 |
| SPK7 | 36-42 | 79.68421 | 4.67 | 129.3375 | 7.58 | 515.3026 | 30.2 | 310.5466 | 18.2 | 663.9213 | 38.91 | 1706.3 |
| SPK8 | 42-48 | 70.063448 | 10.4 | 38.87174 | 5.77 | 160.8765 | 23.88 | 103.6804 | 15.39 | 300.1949 | 44.56 | 673.687 |
| SPk9 | 48-54 | 69.45952 | 10.4 | 38.53668 | 5.77 | 160.2244 | 23.99 | 95.50684 | 14.3 | 304.2861 | 45.56 | 667.88 |
| SPK10 | 54-60 | 69.345016 | 10.4 | 38.47315 | 5.77 | 159.2935 | 23.89 | 75.94613 | 11.39 | 323.7879 | 48.56 | 666.779 |

SP- Metal salts spiked soil

# APPENDIX B

# CHROMIUM, NICKEL, AND ZINC FRACTIONS IN BASELINE SLUDGE APPLIED CLAY SOILS

# Appendix B
# Basa line metal fractions in sandy and clay soils

| Soil & Metal | Soil depth cm | EXC ppm | % | CAB ppm | % | OXD ppm | % | ORG ppm | % | RES ppm | % | Total ppm |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Norge | 0-20 | 1.6 | 6.4 | 2.4 | 9.6 | 1.5 | 6 | 3.5 | 14 | 16 | 64 | 25 |
| Cr | 20-40 | 0.7 | 6.4 | 0.8 | 3.076923 | 1.2 | 4.61538 | 1.8 | 6.923077 | 20.2 | 77.6923 | 26 |
|  | 40-60 | 0.22 | 2.69231 | 0.6 | 1.818182 | 0.35 | 1.06061 | 0.75 | 2.272727 | 22.4 | 67.8788 | 33 |
| Dougherty |  |  |  |  |  |  |  |  |  |  |  |  |
| Cr | 0-20 | 1.74 | 6.69231 | 3.2 | 12.30769 | 2.5 | 9.61538 | 2 | 7.692308 | 11.4 | 43.8462 | 26 |
|  | 20-40 | 0.7 | 3.57143 | 2.2 | 11.22449 | 1.2 | 6.12245 | 2.3 | 11.73469 | 1.6 | 8.16327 | 19.6 |
|  | 40-60 | 0.32 | 1.45653 | 0.7 | 3.186163 | 0.65 | 2.95858 | 1.5 | 6.827492 | 18.8 | 85.5712 | 21.97 |
| Norge |  |  |  |  |  |  |  |  |  |  |  |  |
| Nickel | 0-20 | 0.4 | 2.8777 | 2 | 14.38849 | 3.5 | 25.1799 | 1.6 | 11.51079 | 6.9 | 49.6403 | 13.9 |
|  | 20-40 | 0.5 | 3.24675 | 1.5 | 9.74026 | 2.7 | 17.5325 | 1.15 | 7.467532 | 7.8 | 50.6494 | 15.4 |
|  | 40-60 | 0.15 | 0.73529 | 0.65 | 3.186275 | 1.01 | 4.95098 | 0.55 | 2.696078 | 14.1 | 69.1176 | 20.4 |
| Dougherty |  |  |  |  |  |  |  |  |  |  |  |  |
| Nickel | 0-20 | 0.8 | 6.29921 | 2.3 | 18.11024 | 4 | 31.4961 | 1.1 | 8.661417 | 4.5 | 35.4331 | 12.7 |
|  | 20-40 | 0.5 | 4.16667 | 1.5 | 12.5 | 4 | 33.3333 | 0.8 | 6.666667 | 0.8 | 6.66667 | 12 |
|  | 40-60 | 0.33 | 1.83333 | 3.8 | 21.11111 | 3.12 | 17.3333 | 1.72 | 9.555556 | 6.54 | 36.3333 | 18 |
| Norge |  |  |  |  |  |  |  |  |  |  |  |  |
| Zinc | 0-20 | 2.1 | 7.42049 | 4.2 | 14.8401 | 10.4 | 36.749 | 6 | 21.2 | 5.6 | 19.788 | 28.3 |
|  | 20-40 | 3.5 | 9.88701 | 1.15 | 3.248588 | 8.6 | 24.2938 | 10.1 | 28.53107 | 12.05 | 34.0395 | 35.4 |
|  | 40-60 | 2.2 | 5.06912 | 2.5 | 5.760369 | 5.3 | 12.212 | 13.2 | 30.41475 | 18.2 | 41.9355 | 43.4 |
| Dougherty |  |  |  |  |  |  |  |  |  |  |  |  |
| Zinc | 0-20 | 1.35 | 8.6538 | 1.27 | 8.2051 | 5.49 | 35.8333 | 3.03 | 19.423 | 4.46 | 28.5897 | 15.6 |
|  | 20-40 | 0.8 | 8.16327 | 1.27 | 12.95918 | 4.6 | 46.9388 | 1.19 | 12.14286 | 1.94 | 19.7959 | 9.8 |
|  | 40-60 | 1.2 | 4.90597 | 1.5 | 6.132461 | 6.2 | 25.3475 | 5.55 | 22.69011 | 10.01 | 40.924 | 24.46 |

**EXC**-Exchangeable form; **CAB**-Carbonate form; **OXD**-Oxide form, **ORG**-Organic form, and **RES**-Residual forms of heavy metals

# APPENDIX C

# SOIL PROFILE CHARACTERIZATION

## Appendix C1

## Norge Series

The Norge series consists of very deep, well drained, moderately slowly permeable upland soils that formed in loamy alluvium of Pleistocene age. These nearly level to sloping soils are on broad flats and upper side slopes of upland terraces in the Central Rolling Red Prairies Slopes are 0 to 8 percent. Mean annual precipitation is 34 inches. Mean annual temperature is 61 degrees F. (Gray et al., 1979)

**Taxonomic class:** Fine-silty, mixed, active, thermic Udic Paleustolls

**Typical pedon:** Norge silt loam--cultivated. (Colors are for dry soil unless otherwise stated.)

**A**--0 to 20cm; dark brown (7.5YR 4/2) silt loam, dark brown (7.5YR 3/2) moist; moderate fine granular structure; slightly hard, friable; many fine roots; moderately acid; gradual smooth boundary. (15 to 24cm thick)

**Bt1**--20 to 40 cm; reddish brown (5YR 5/4) silty clay loam, reddish brown (5YR 4/4) moist; moderate fine subangular blocky structure; very hard, firm; common fine roots; nearly continuous clay films on faces of peds; moderately acid; gradual smooth boundary. (14 to 25 cm thick

**Bt2**--40 to 60 cm; red (2.5YR 5/6) silty clay loam, red (2.5YR 4/6) moist; moderate medium subangular blocky structure; very hard, firm; common fine roots; continuous clay films on faces of peds; slightly acid; gradual smooth boundary. (18 to 22s cm thick)

**Type location:** Payne County, Oklahoma State University Agronomy Research Station Main Campus,

**Range in characteristics:** Solum thickness is more than 60 cm. The mollic epipedon is less than 50cm thick. Depth to secondary carbonates is more than 60cm.

The A horizon has hue of 5YR to 10YR, value of 4 or 5, and chroma of 2 or 3. Texture is silt loam, loam, silty clay loam, or clay loam. Reaction ranges from moderately acid to neutral.

The Bt1 and Bt2 horizons have hue of 2.5YR or 5YR, value of 4 or 5, and chroma of 4 to 6. Texture is silty clay loam or clay loam. Reaction ranges from moderately acid to slightly alkaline.

Some pedons have a Bt4 horizon. Mottles may be present in shades of gray, yellow, or brown. Some pedons are coarsely mottled in this horizon. Texture is silty clay loam, clay loam or silty clay. Reaction ranges from slightly acid to slightly alkaline. Some pedons may have an accumulation of calcium carbonate (Btk horizon) in the lower 1/4 of the argillic.

**Geographic setting:** Norge soils are on nearly level to sloping broad flats and upper side slopes of upland terraces in the Central Rolling Red Prairies. Slopes are 0 to 8 percent. They formed in loamy alluvium of Pleistocene age.

Mean Annual Precipitation: 26 to 40 inches.

Mean Annual Temperature: 58 to 64 degrees F.

Thornthwaite Annual P-E indices: 44 to 64.

**Drainage and permeability:** Well drained; permeability is moderately slow; runoff is , very low on 1 to 3 percent slopes, low on 3 to 5 percent slopes and medium on 5 to 8 percent slopes.

**Use and vegetation:** Soils are mainly cultivated. Small grains, grain sorghums and alfalfa are the principal crops. Some areas are used for tame pasture or rangeland. Native vegetation consists of mid and tall grasses.

**Remarks:** Diagnostic horizons and features recognized in this pedon are:
Mollic epipedon - the zone from the surface of the soil to a depth of 50 (A horizon and BA horizon).
Argillic horizon - the zone from 120 cm to a depth of 60 (Bt horizons).

## Appendix C2

## Dougherty Soil Series

The Dougherty series consists of very deep, well drained, moderately permeable soils that formed in sandy and loamy sediments on terraces of Pleistocene age. These soils are on broad nearly level to moderately steep sandy reworked terraces in the Cross Timbers Slopes are dominantly 0 to 8.

**Taxonomic class:** Loamy, mixed, active, thermic Arenic Haplustalfs

**Typical pedon:** Dougherty loamy fine sand—Pasture land.

(Colors are for dry soil unless otherwise stated.)

**A1**--0 to 21 cm; grayish brown (10YR 5/2) loamy fine sand, dark grayish brown (10YR 4/2) moist; weak fine granular structure; soft, very friable; slightly acid; clear smooth boundary. (0 to 22 cm thick)

**E**--21 to 40 cm; very pale brown (10YR 7/3) loamy fine sand, brown (10YR 5/3) moist; single grained; soft, very friable; moderately acid; clear smooth boundary. (19 to 23 cm thick)

**Bt1**--40 to 60 cm; yellowish red (5YR 5/6) sandy clay loam, yellowish red (5YR 4/6) moist; moderate coarse prismatic structure parting to weak medium subangular blocky; very hard, friable; clay films on faces of peds and bridging between sand grains; moderately acid; diffuse smooth boundary. (17 to 25 cm thick)

**BC**--60 to 75 cm; yellowish red (5YR 5/6) fine sandy loam, yellowish red (5YR 4/6) moist; weak coarse prismatic structure; hard, friable; moderately acid; diffuse smooth boundary. (12 to 22 cm)

**Type location:** Payne County, Oklahoma; about 9 miles south of Stillwater on State Highway 33 at Oklahoma State University Agronomy Research Station, Perkins.

**Range in characteristics:** Thickness of solum cm ranges from 50 cm to more than 65cm. The thickness of the A and E horizons range from 20 to 40 cm.

The A1 horizon has hue of 7.5YR or 10YR, value of 4 to 7, and chroma of 2 to 4. The Ap or A1 horizon is loamy fine sand or fine sand. Reaction ranges from slightly acid to strongly acid.

The E horizon has hue of 7.5YR or 10YR, value of 5 to 8, and chroma of 2 to 4. It is loamy fine sand or fine sand. Reaction ranges from slightly acid to strongly acid.

The Bt horizons have hue of 2.5YR to 7.5YR, value of 4 to 7, and chroma of 4 to 8. The Bt horizon is fine sandy loam or sandy clay loam and the clay content ranges from 18 to 35 percent. Reaction ranges from slightly acid to strongly acid.

**Geographic setting:** Dougherty soils occur on nearly level to moderately steep terraces. They have developed in strongly acid through neutral sandy or loamy sediments. Slopes are dominantly between 0 to 8 percent. The climate is dry subhumid or moist subhumid. Mean Annual Precipitation: 30 to 38 inches. Mean Annual Temperature: 58 to 62 degrees F. Thornthwaite Annual P-E indices: 48 to 64 (Gray et al., 1979).

**Drainage and permeability:** Well drained; permeability is moderate; runoff is negligible on 0 to 1 percent slopes, very low on 1 to 3 percent slopes, low on 3 to 5 percent slopes and medium on 5 to 20 percent slopes (Payne County Soil Survey, 1974).

**Use and vegetation:** The sample are is used for astures. Native vegetation is mainly postoak, blackjack with considerable understory of little bluestem, big bluestem, and switchgrass.

**REMARKS.** Diagnostic horizons and features recognized in the pedon are:

Ochric epipedon - the zone from the surface of the soil to a depth of 18 cm (A horizon).

Albic horizon - the zone from 18 cm to a depth of 39 cm (E horizon).

Argillic horizon - the zone from 40 cm to a depth of 60 cm (Bt horizon).

# APPENDIX D

## SEWAGE SLUDGE GENERATION RATES

| Country | Amount (million tons dry Soilds/year | Disposal method (%)<br>Application to land | Land filling | Incineration | other |
|---|---|---|---|---|---|
| Austria | 320 | 13 | 56 | 31 | N.D. |
| Belgium | 75 | 3137 | 56 | 9 | 4 |
| Denmark | 130 | 5025 | 33 | 28 | 2 |
| France | 700 | 3 | 50 | N.D. | N.D. |
| Germany | 2500 | 28 | 63 | 12 | N.D. |
| Greece | 15 | 34 | 97 | N.D. | N.D. |
| Ireland | 24 | 81 | 18 | N.D. | 54 |
| Italy | 800 | 44 | 55 | 11 | N.D. |
| Luxembourg | 15 | 80 | 18 | N.D. | 1 |
| Holland | 282 | 10 | 53 | 3 | N.D. |
| Portugal | 200 | 45 | 13 | N.D. | 7 |
| Spain | 280 | 50 | 50 | 10 | 30 |
| Sweden | 180 | 55 | 55 | N.D. | N.D. |
| Switzerland | 215 | 30 | 30 | 20 | N.D. |
| United kingdom, 1991 | 1107 | 88 | 8 | 7 | 20 |
| United States | 6900 | 17 | 17 | 22 | 30 |

(Biosolids generation, use and disposal in the United States; U. S. EPA Agency, EPA530-R-99-009, Office of solid waste and Emergency Response: Washington,
DC, September, 1999).

N.D.=No data

# Appendix E

Heavy Metals contaminant standards

| Country | year | Metals, ppm | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | Cr | Ni | Zn | Cu | Cd | Hg | Pb |
| European community[a] | 1986 | 100-150 | 30-75 | 150-300 | 50-140 | 1-3 | 1-1.5 | 50-300 |
| France | 1988 | 150 | 50 | 300 | 100 | 2 | 1 | 100 |
| Gemany | 1992 | 100 | 50 | 200 | 60 | 1.5 | 1 | 100 |
| Italy | | 150 | 50 | 300 | 100 | 3 | | 100 |
| Spain | 1990 | 100 | 30 | 150 | 50 | 1 | 1 | 50 |
| The Nethelands [c] | | | | | | | | |
| Clean soil referane values | | 100 | 35 | 140 | 36 | 0.8 | 0.3 | 85 |
| Intervention values | | 380 | 210 | 720 | 190 | 12 | 10 | 530 |
| United kingdom[d] | 1989 | 400[a] | 75 | 200[e] | 135 | 3 | 1 | 300 |
| Denmark | 1990 | 30 | 15 | 100 | 40 | 0.5 | 0.5 | 40 |
| Finland | 1995 | 200 | 600 | 150 | 100 | 0.5 | 0.2 | 19 |
| Norway | | 100 | 30 | 150 | 50 | | 1 | 40 |
| Sweden | | 30 | 15 | 100 | 40 | 0.5 | 0.5 | 50 |
| United States[f] | 1993 | 1500 | 210 | 1400 | 720 | 20 | 8 | 1500 |

a Values are currently being revised

b Values are for soil pHs greater than6. At pH 5-6, the Cd and Zn limits are 1.0 and150 mg/kg respectively.

c Soil clean up levels which also apply to agricultural land amended with sewage sludge. Concentrations less tha the clean soil reference are considered clean soil.

d Values shown arefor soil pHs 6-7. Other values apply at pH 5-6 and greater than 7.

e Changed following Independent Scientific Committee recommendations.

f Calculated from maximum cumulative pollutant loading limits mixed into soil plow layer. Soil background concentrations are not taken into account.

# APPENDIX F

# HEAVY METALS DISTRIBUTION ANALYSIS IN NORGE CLAY AND DOUGHERTY SANDY SOILHORIZONS AFTER SLUDGE APPLICATION

# Appendix F1
# Chromium distribution analysis in norge clay and Dougherty sandy soil horizons after sludge application

**Soil depth, cm**

| Metal | Treatment | Statistical analysis | 0-6 | 6-12 | 12-18 | 18-24 | 24-30 | 30-36 | 36-42 | 42-48 | 48-54 | 54-60 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Norge clay soil** | | | | | | | | | | | | |
| Chromium | Soil and sludge | Mean | 66.68 | 65.67 | 65.3 | 39.8467 | 39.497 | 39.24 | 38.8767 | 35.353 | 34.93 | 34.753 |
| | (T1) | Stdvev | 0.854907 | 0.40628 | 0.37956 | 0.67967 | 0.6264 | 0.6152 | 0.74123 | 0.8196 | 0.47896 | 0.342 |
| | | Variance | 867.1367 | 851.994 | 843.041 | 307.157 | 302.47 | 298.659 | 291.274 | 239.02 | 237.547 | 236.92 |
| | Soil, sludge | Mean | 69.20333 | 68.43 | 67.56 | 37.29 | 36.7 | 36.5067 | 36.14 | 35.36 | 34.78 | 34.223 |
| | and lime | Stdvev | 0.257908 | 0.31281 | 0.44368 | 0.45602 | 0.6061 | 0.57063 | 0.64452 | 0.3756 | 0.72633 | 0.9061 |
| | (T2) | Variance | 792.2985 | 773.404 | 750.924 | 226.29 | 217.42 | 215.494 | 210.321 | 204.1 | 193.697 | 185.66 |
| | Soil, sludge | Mean | 244.2933 | 236.62 | 235.37 | 98.3367 | 100.64 | 100.047 | 99.7233 | 64.463 | 46.6 | 45.14 |
| | and metal spikes | Stdvev | 0.469491 | 0.7724 | 0.81584 | 0.70154 | 0.5601 | 0.68975 | 0.98341 | 0.4216 | 0.56149 | 0.5806 |
| | (T3) | Variance | 11890.18 | 11125.3 | 11003.6 | 1906.89 | 2003.3 | 1974.72 | 1950.64 | 820.4 | 424.145 | 397.36 |
| **Dougherty sandy soil** | | | | | | | | | | | | |
| | Soil and sludge | Mean | 66.99 | 65.62 | 64.81 | 39.66 | 39.477 | 55.5753 | 38.75 | 34.357 | 34.1433 | 34.24 |
| | (T1) | Stdvev | 0.662923 | 0.46267 | 0.85561 | 0.92477 | 0.6477 | 0.50933 | 0.88363 | 0.6873 | 0.66665 | 0.406 |
| | | Variance | 880.1858 | 849.256 | 818.582 | 300.725 | 301.85 | 606.648 | 287.358 | 227.08 | 224.471 | 229.07 |
| Chromium | | | | | | | | | | | | |
| | Soil, sludge | Mean | 63.66067 | 62.34 | 61.6467 | 33.9267 | 32.663 | 31.7567 | 31.1067 | 36.737 | 36.27 | 35.55 |
| | and lime | Stdvev | 0.469895 | 0.55522 | 0.60345 | 0.36445 | 0.713 | 0.67183 | 0.11813 | 0.7111 | 0.10985 | 0.5396 |
| | (T2) | Variance | 798.7803 | 763.703 | 27.3044 | 225.384 | 204.55 | 193.592 | 192.068 | 259.95 | 261.52 | 245.36 |
| | Soil, sludge | Mean | 210.0657 | 209.787 | 208.633 | 120.477 | 116.54 | 116.3 | 112.547 | 81.543 | 76.05 | 71.3 |
| | and metal spikes | Stdvev | 0.96408 | 0.52002 | 0.89448 | 0.70059 | 0.4182 | 0.48642 | 0.47542 | 0.5327 | 0.27068 | 1.5768 |
| | (T3) | Variance | 8745.392 | 8758.71 | 8631.69 | 2869.63 | 2697 | 2682.73 | 2512.16 | 1312.8 | 1148.56 | 974.13 |

# Appendix F2

## Nickel distribution analysis in soil horizons

| | | | Soil depth, cm | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Metal | Treatment | | 0-6 | 6-12 | 12-18 | 18-24 | 24-30 | 30-36 | 36-42 | 42-48 | 48-54 | 54-60 |
| **Norge clay soil** | | | | | | | | | | | | |
| Nickel | Soil and sludge | Mean | 31.70667 | 30.777 | 30.34 | 20.877 | 20.533 | 20.393 | 19.793 | 19.517 | 19.447 | 19.39 |
| | (T1) | Stdvev | 0.396008 | 0.8118 | 0.6736 | 0.7791 | 0.931 | 0.8708 | 0.9535 | 0.6398 | 0.598 | 0.5436 |
| | | Variance | 196.1891 | 180.07 | 176.36 | 6.4312 | 77.5 | 76.795 | 71.67 | 71.574 | 71.323 | 71.259 |
| | Soil, sludge | Mean | 66.68 | 65.67 | 65.3 | 39.847 | 39.497 | 39.24 | 38.877 | 35.353 | 34.93 | 34.753 |
| | and lime | Stdvev | 0.8549 | 0.4063 | 0.3796 | 0.6797 | 0.6264 | 0.6152 | 0.7412 | 0.8196 | 0.479 | 0.342 |
| | (T2) | Variance | 867.1367 | 851.99 | 843.04 | 307.16 | 302.47 | 298.66 | 291.27 | 239.02 | 237.55 | 236.92 |
| | Soil, sludge | Mean | 69.2033 | 68.43 | 67.56 | 37.29 | 36.7 | 36.507 | 36.14 | 35.36 | 34.78 | 34.223 |
| | and metal spikes | Stdvev | 0.25790 | 0.3128 | 0.4437 | 0.456 | 0.6061 | 0.5706 | 0.6445 | 0.3756 | 0.7263 | 0.9061 |
| | (T3) | Variance | 792.2985 | 773.4 | 750.92 | 226.29 | 217.42 | 215.49 | 210.32 | 204.1 | 193.7 | 185.66 |
| **Dougherty sandy soil** | | | | | | | | | | | | |
| | Soil and sludge | Mean | 25.3466 | 24.84 | 24.46 | 17.143 | 16.047 | 15.62 | 15.657 | 21.007 | 20.367 | 19.923 |
| | (T1) | Stdvev | 0.5582 | 0.9556 | 0.5478 | 0.9026 | 0.0759 | 0.2471 | 0.1778 | 0.2436 | 0.4557 | 0.3972 |
| | | Variance | 123.127 | 114.78 | 114.58 | 53.363 | 51.018 | 47.311 | 47.943 | 86.265 | 79.445 | 76.372 |
| Nickel | | | | | | | | | | | | |
| | Soil, sludge | Mean | 33.1333 | 32.29 | 31.57 | 18.523 | 17.763 | 17.3 | 17.327 | 18.987 | 18.587 | 18.507 |
| | and lime | Stdvev | 0.2414 | 0.4403 | 0.5472 | 0.7169 | 0.6608 | 0.7708 | 0.4188 | 0.5033 | 0.7016 | 0.9453 |
| | (T2) | Variance | 216.4192 | 203.03 | 192.71 | 63.8 | 58.827 | 55.088 | 57.307 | 68.517 | 64.344 | 62.35 |
| | Soil, sludge | Mean | 67.09333 | 67.227 | 66.593 | 26.46 | 25.323 | 25.123 | 24.447 | 45.183 | 43.247 | 43.003 |
| | and metal spikes | Stdvev | 0.395502 | 0.2951 | 0.6504 | 0.5236 | 0.2504 | 0.033 | 0.2414 | 0.5514 | 0.3839 | 0.2295 |
| | (T3) | Variance | 889.8374 | 896.03 | 870.01 | 134.74 | 125.78 | 125.91 | 117.22 | 398.63 | 367.55 | 365.96 |

# Appendix 3

## Zinc distribution analysis in soil horizon

| | | | Soil depth cm | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Metal | Treatment | Statistical analysis | 0-6 | 6-12 | 12-18 | 18-24 | 24-30 | 30-36 | 36-42 | 42-48 | 48-54 | 54-60 |
| **Norge clay soil** | | | | | | | | | | | | |
| | Soil and sludge | Mean | 642.337 | 641.97 | 640.73 | 210.91 | 209.44 | 208.38 | 207.36 | 130.06 | 128.7 | 125.78 |
| | (T1) | Stdvev | 0.40549 | 0.3459 | 0.606 | 0.2295 | 0.4396 | 0.6874 | 0.6307 | 0.8165 | 0.5825 | 0.7924 |
| | | Variance | 82415.3 | 82336 | 81953 | 8877 | 8736.4 | 8627.6 | 8548 | 3341.3 | 3283.1 | 3125 |
| Zinc | Soil, sludge | Mean | 697.523 | 696.78 | 695.03 | 213.94 | 206.13 | 165.71 | 187.43 | 89.263 | 86.193 | 82.27 |
| | and lime | Stdvev | 0.75332 | 0.4542 | 0.3737 | 0.2664 | 0.8635 | 46.929 | 0.8983 | 0.9706 | 0.8897 | 0.3956 |
| | (T2) | Variance | 97098.1 | 96973 | 96511 | 9131.6 | 8427.8 | 4473.4 | 6959.4 | 1559.8 | 1455.9 | 1340.8 |
| | Soil, sludge | Mean | 4140.57 | 4065.6 | 4060.5 | 1211.8 | 1205.6 | 1203.7 | 1200.3 | 691.91 | 671.72 | 672.73 |
| | and metal spikes | Stdvev | 0.93692 | 0.8865 | 0.7023 | 0.8464 | 0.815 | 0.7228 | 0.3827 | 0.7696 | 0.5641 | 0.6372 |
| | (T3) | Variance | 3427312 | 3E+06 | 3E+06 | 293274 | 290303 | 289414 | 287981 | 95535 | 90089 | 90343 |
| **Dougherty sandy soil** | | | | | | | | | | | | |
| | Soil and sludge | Mean | 542.65 | 540.61 | 536.52 | 217.23 | 216.12 | 217.62 | 216.72 | 113.3 | 111.93 | 111.57 |
| | (T1) | Stdvev | 0.84526 | 0.5552 | 0.7553 | 0.7308 | 0.5209 | 0.8187 | 0.7583 | 0.3894 | 0.5641 | 0.5028 |
| | | Variance | 58711 | 58331 | 57409 | 9374.5 | 9296.5 | 9400.8 | 0.5751 | 2550 | 2480.7 | 2467.2 |
| Zinc | Soil, sludge | Mean | 542.65 | 540.61 | 536.52 | 217.23 | 216.12 | 217.62 | 216.72 | 113.3 | 111.93 | 111.57 |
| | and lime | Stdvev | 0.84526 | 0.5552 | 0.7553 | 0.7308 | 0.5209 | 0.8187 | 0.7583 | 0.3894 | 0.5641 | 0.5028 |
| | (T2) | Variance | 58711 | 58331 | 57409 | 9374.5 | 9296.5 | 9400.8 | 0.5751 | 2550 | 2480.7 | 2467.2 |
| | Soil, sludge | Mean | 3422.8 | 3420.8 | 3424.4 | 1717.7 | 1716.7 | 1711.6 | 1706.8 | 673.43 | 667.88 | 665.63 |
| | and metal spikes | Stdvev | 0.8769 | 0.7757 | 0.5728 | 0.8861 | 0.6165 | 0.8055 | 0.991 | 0.889 | 0.8941 | 0.8256 |
| | (T3) | Variance | 2341908 | 2E+06 | 2E+06 | 589481 | 588966 | 585373 | 581955 | 90462 | 88976 | 88393 |

#2

# VITA

Kefeni Kejela

Candidate for the Degree of

Doctor of Philosophy

Thesis: EXPERIMENTAL STUDY OF HEAVY METALS DISTRIBUTION ATTENUATION AND MOBILITY IN TWO OKLAHOMA SOILS AMENDED WITH SEWAGE SLUDGE

Major Field: Environmental Science

Biographical:

Personal Data: Born in Ambo, Ethiopia, October 15, 1957, the son of Kejela Gutema. Married to Tsehay Alemu.

Education: Received Master of Science honors Degree in Agronomy specializing in soil science from Krasnodar Institute of Tropical Agriculture in spring 1982 (Former Soviet Union); Master of Science in Resource Assessment for Development Planning specializing in soil and water conservation from University of East Anglia, England in 1988, and completed requirement for the Doctor of philosophy degree at Oklahoma State University in May 2003.

Experience: Federal Senior Soil and Water Conservation Expert from 1988 until 1995, Coordinator of Swiss funded soil and water conservation research project under the Department of Natural Resources Development and Environmental Protection (Ethiopia), Editor of Ethiopian Soil Science Society between 1991-1993.

Professional Memberships: African Society of Soil Science, World Association of Soil and Water Conservation, American Society of Wetlands Scientists, Society of Environmental Science at Oklahoma State University, and United States National Registry of Environmental Professionals. Guest speaker on the Registry of Environmental professional's skill update workshop held in Texas, May 2001, Student employee of the month at Oklahoma State University in the year 2001.

Publications: Published 15 research and scientific papers on soil survey and natural resources conservation and development. As of October 2002 certified by National Registry of Environmental Professionals as Registered Environmental Professional.