

**SORPTION OF COPPER, ZINC AND NICKEL BY SELECTED SOILS**

**by**

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**SORPTION OF COPPER, ZINC AND NICKEL BY SELECTED SOILS**

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## ABSTRACT

The objective of this study was to interpret the interaction of copper, zinc and nickel with soils of varying composition.

Soils were taken from different regions. Soil 1 was from Marmara region, soil 2 and soil 3 were from Mediterranean region. The soil samples were artificially polluted by copper, zinc and nickel with different concentrations and V/m ratios (where V stands for the solution volume added on the soil and m for the weight of soil taken) for 48 hours. The time 48 hours was determined as the equilibrium time of the interaction between metal ions and soils. The soils artificially contaminated with varying concentrations were then subjected to shaking and centrifuging. The amount of remaining copper, zinc and nickel in solution were determined by Atomic Absorption Spectrometry.

The adsorption-desorption behavior of copper, zinc and nickel were evaluated in mono and competitive multi metal systems with Freundlich isotherm equation; and related sorption constants were calculated from the isotherms. Thus, it was observed that in mono metal system more copper was adsorbed and desorbed than other metals on the soil with higher pH and CEC, namely soil1. In multi metal system, Ni was the metal which adsorbed-desorbed the most on soils 2 and 3. Adsorption-desorption intensity was calculated for multimetal systems. The findings derived from isotherms were in consistence with the adsorption-desorption intensity results.

## ÖZET

Bu çalışmanın amacı bakır, çinko ve nikelin değişik kompozisyonlara sahip topraklarla olan etkileşimini yorumlamaktır.

Topraklar, farklı bölgelerden alınmıştır. Birinci toprak Marmara bölgesinden, ikinci ve üçüncü topraklar Akdeniz bölgesinden alınmıştır. Topraklar, değişik derişimlerde ve değişik V/m oranlarında bakır, çinko ve nikel ile 48 saat süreyle yapay olarak kirletilmiştir (V toprağın üzerine konulan çözelti hacmini, m kullanılan toprağın ağırlığını ifade eder). 48 saat, önceden yapılan deneylerle metaller ile toprağın dengeye gelmesi için gerekli zaman olarak belirlenmiştir. Değişik derişimler ile yapay olarak kirletilen toprak mekanik çalkalayıcıda 48 saat süre ile etkileşime sokulmuş, ardından santrifüj edilmiştir. Atomik absorpsiyon spektrofotometresi kullanılarak çözeltide kalan metal miktarı belirlenmiştir.

Bakır, çinko ve nikelin tekli ve karşılaştırmalı çoklu sistemde iken toprağa bağlanma davranışları adsorpsiyon izotermi ile değerlendirilmiştir. Toprakların deneysel sorpsiyon sonuçları Freundlich izoterm eşitliğine yerleştirilerek, çeşitli sorpsiyon sabitleri hesaplanmıştır. Tekli sistemde, pH'sı ve katyon değiştirme kapasitesi en yüksek olan 1 numaralı toprakta en fazla bakırın adsorplandığı ve desorplandığı görülmüştür. Çoklu sistemde ise, 2 ve 3 numaralı topraklarda en fazla nikel adsorplanmış ve desorplanmıştır. Çoklu sistemde metallerin toprağa bağlanma yoğunlukları hesaplanmıştır. İzotermilerden elde edilen bulgular, metallerin bağlanma yoğunluklarının hesaplanmasından elde edilen sonuçlar ile desteklenmiştir.

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## LIST OF SYMBOLS/ABBREVIATIONS

$C_i$	Initial concentration
$C_e$	Concentration of adsorbate in solution at equilibrium
$C_s$	Amount of adsorbate adsorbed per unit mass of soil
$K_f$	Adsorption Capacity
$n$	Adsorption Intensity
$K_{fd}$	Desorption Capacity
$n_d$	Desorption Intensity
$V/m$	Volume/mass ratio
AAS	Atomic Absorption Spectrophotometer
OMC	Organic Matter Content
OC	Organic Carbon Content
CEC	Cation Exchange Capacity

## 1. INTRODUCTION

Soil is one of the key elements for all terrestrial ecosystems. It provides the nutrient-bearing environment for plant life and is of essential importance for the degradation and transfer of biomass. Soil is a very complex heterogeneous medium, which consists of solid phases (the soil matrix) containing minerals and organic matter and fluid phases (the soil water and soil air), which interact with each other and ions entering the soil system (Bradl, 2004).

Trace elements are considered to be one of the main sources of pollution in the environment, since they have a significant effect on its ecological quality (Tüzen, 2003). Trace elements are defined as elements that are present at low concentrations (mg/kg or less) in most soils, plants, and living organisms (Phipps, 2005). Trace elements that have been extensively studied in the last decade include copper (Cu), zinc (Zn), iron (Fe), manganese (Mn), molybdenum (Mo), boron (B), cobalt (Co), nickel (Ni), lead (Pb), cadmium (Cd), chromium (Cr), arsenic (As), and selenium (Se). Cu, Zn, Fe, Mn, Mo, and B are essential for the normal growth of plants, Cu, Zn, Fe, Mn, Mo, Co and Se are essential for the growth and health of animals and human beings, and Cu, Zn, Pb and Cd are the most environmentally concerning elements that have been often reported to cause contamination of soil, water, and food chains (He et al., 2005).

Human activity leads to increasing levels of heavy metal contamination in the environment. Heavy metals owing to atmospheric and industrial pollution accumulate in the soil and influence the ecosystem nearby (Tüzen, 2003). Growing concern about the quality of the natural environment has stimulated increasing interest in the occurrence and behavior of the heavy metals in soils and water (Srivastava et al., 2005). Heavy metal ions are the most toxic inorganic pollutants which occur in soils and can be of natural or anthropogenic origin. Some of them are toxic even if their concentration is very low and their toxicities increase with accumulation in water and soils (Bradl, 2004).



Accumulation of trace elements, especially heavy metals, in the soil has potential to restrict the soil's function, cause toxicity to plants, and contaminate the food chain. In recent years, it has also been found that heavy metals from point and non-point sources impair water systems, causing lesions and/or deformation in fish (Henry et al., 2004).

Only a small portion of trace elements in soil is bioavailable. The mobility and availability of trace elements are controlled by many chemical and biochemical processes such as precipitation–dissolution, adsorption–desorption, complexation-dissociation, and oxidation–reduction. Not all the processes are equally important for each element, but all these processes are affected by soil pH and biological processes. Therefore, it is crucial to understand some major reactions in soils that control the release of a specific trace element in the soil and the environment in order to overcome problems related to deficiency and contamination of these elements (He et al., 2005).

Adsorption is a major process responsible for accumulation of heavy metals. Therefore, the study of adsorption processes is of utmost importance for the understanding of how heavy metals are transferred from a liquid mobile phase to the surface of a solid phase. The most important parameters controlling heavy metal adsorption and their distribution between soil and water are soil type, metal speciation, metal concentration, soil pH, solid:solution mass ratio, and contact time. In general, greater metal retention and lower solubility occurs at high soil pH (Bradl, 2004).

In this thesis, adsorption-desorption behavior of Cu, Zn and Ni on three different soils having separate physicochemical properties which were obtained from various depths were examined. Competitive adsorption-desorption behavior of these heavy metals were analysed. In order to make a comparison between the results, initially, soils were characterised. Preliminary adsorption experiment was performed so as to determine equilibrium time for heavy metal adsorption of soils. Finally, adsorption–desorption behavior of the heavy metals were evaluated with Freundlich Isotherms.

## 2. THEORETICAL BACKGROUND

### 2.1. Soil

#### 2.1.1. Definition of Soil

Soil may be defined as material of variable depth with a substantial solids content at the Earth's surface which is undergoing change as a consequence of chemical, physical and biological processes. Thus, towards the bottom of a deep soil pit, material that was not changing with time would be classified as parent material, but not as soil (Cresser et al., 1993).

Soils are complex materials, reflecting the variability of the parent rock material and organic residues from which they form. Nevertheless, their elemental composition, particle size, and mineralogy can be related more or less systematically to the nature of parent material and the degree to which this material has been altered by weathering (McBride, 1994).

Soil essentially consists of three phases, a solid phase, a solution phase and a gas phase. The solid phase usually includes an intimate mixture of mineral material, originating from rock, sediment or till, and organic material arising as a consequence of biological activity. It interacts continuously with the solution phase, which originates from precipitation infiltrating the soil or from rising water or water moving laterally. The chemical composition of the soil solution depends upon the physicochemical characteristics of the soil solids, precipitation solute composition, biological activity within the soil matrix, and to some extent upon contact time (Cresser et al., 1993). It contains both organic stemming from breakdown (or decay) of the soil organic matter and inorganic components.  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$  are some ions of liquid phase (Bolt and Bruggenwert, 1978). The gas phase, or soil atmosphere, composition depends upon biological activity also. It may be greatly enriched in carbon dioxide compared to normal

above-ground air as a consequences of microbial and root respiration, and relatively depletion in oxygen. Under certain conditions, it may contain significant amounts of gases such as nitrous oxide or ammonia, and even hydrogen sulphide and ethlene (Cresser et al., 1993). Figure 2.1 represents the four major components of soils where OM refers to organic matter content of soils.

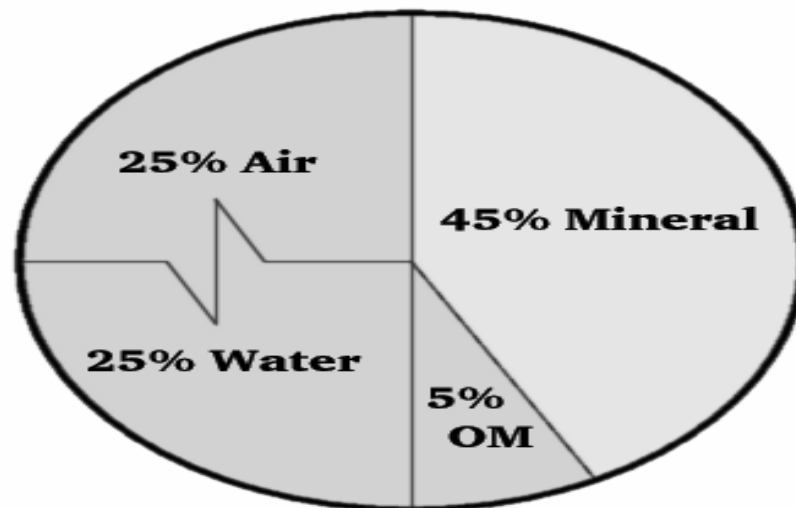


Figure 2.1. Composition of typical topsoil (Buckman and Brady, 1960).

### 2.1.2. Rock Weathering and Soil Formation

Weathering of rocks is one of the most important of all geologic processes. It provides the material from which sedimentary rocks are formed and produces soil, without which both plant and animal life on earth would be impossible. Rock fragments produced by weathering are removed by erosion. Weathering may be either mechanical (or physical) or chemical.

2.1.2.1. Mechanical Weathering Mechanical weathering takes place when rock is reduced to smaller fragments without any chemical change taking place. Rock weathering is very dependent on the type of rock and on time. It may be caused by any or all of the following factors acting for significant periods of time.

*Climate effects (including both temperature and rainfall)* These are probably the principal factors involved in rock disintegration. Daily temperature fluctuations may not be too

important, but freeze-thaw cycles over a long period of time cause rock fatigue even in milder climates. Severe temperature producing local freezing of short duration may be significant, since water in rock pores will increase in volume approximately 9 % at 0 °C and will exert tremendous pressures. As the freezing pressure will tend to extrude ice from the pores and reduce the expansion pressures, local effects will be greater when the temperature drops below 0 °C. In fact, some believe that temperature effects are one of the most significant mechanical agents in the weathering process (Bowles, 1984).

Exfoliation Exfoliation in geology is a weathering process, mainly caused in arid areas by differential heating and cooling of rock surfaces. Rocks underlying thick soil strata are under large compressive forces. Surface stress adjustments accompanying regional uplift, coupled with erosion from surface water runoff reducing the overburden stresses, cause the outer rock shell to separate (or spall) from the main rock.

Erosion by wind and rain Erosion is displacement of solids (soil, mud, rock and other particles) by the agents of ocean currents, wind, water, or ice by downward or down-slope movement in response to gravity or by living organisms. Flowing water carrying tiny particles of in suspension can erode or abrade the most solid of rock.

Abrasion Strictly, abrasion is the wear caused when two hard materials undergo relative movement while in contact.

Organic activity Cracking forces exerted by growing plants and roots in voids and crevasses of rocks can force fragments apart.

2.1.2.2. Chemical Weathering Chemical weathering involves alteration of the rock minerals into new compounds. It may include the following processes.

Oxidation A chemical reaction may take place when rocks are in contact with rainwater. Reaction may yield hydrated iron oxides, carbonates, and sulfates. If these reactions result in an increased volume, there will be a subsequent disintegration of the rocks.

Solution Certain rocks are partially or completely dissolved in rainwater, especially if the rainwater contains appreciable carbon dioxide in the form of weak carbonic acid or has a  $\text{pH} < 7$ .

Leaching Water reacting with the cementing material of sedimentary rocks may cause the particles to loosen, with the smaller particles and cementing agents carried away either to deeper strata or as surface runoff. Cementing agents carried to deeper strata by percolating rainwater may be a factor in future formation of new sedimentary rocks. In areas of little rainfall, water vapor may carry the cementing agents such as sulfates, carbonates, etc., to the ground surface, creating a salt crust which may make the soil unfit to support plant life.

Hydrolysis (formation of  $\text{H}^+$  ions)  $\text{H}^+$  ion from the water forces the  $\text{K}^+$  ion out of the feldspar. The  $\text{H}^+$  ion then combines with the aluminum silicate to form the clay mineral. A plant root in the soil may attract local soil-water and become surrounded by an excess of  $\text{H}^+$  ions, which initiates the hydrolysis process as seen in eq.2.1.

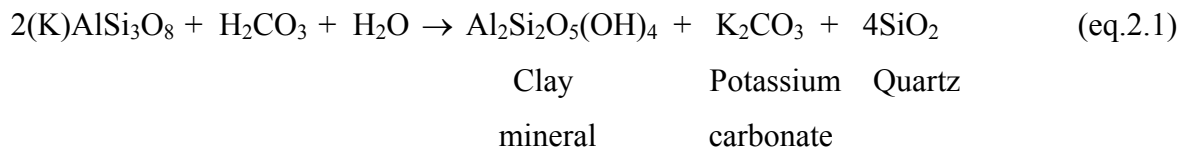


Figure 2.2 represents all the soil forming processes mentioned above (Bowles, 1984).

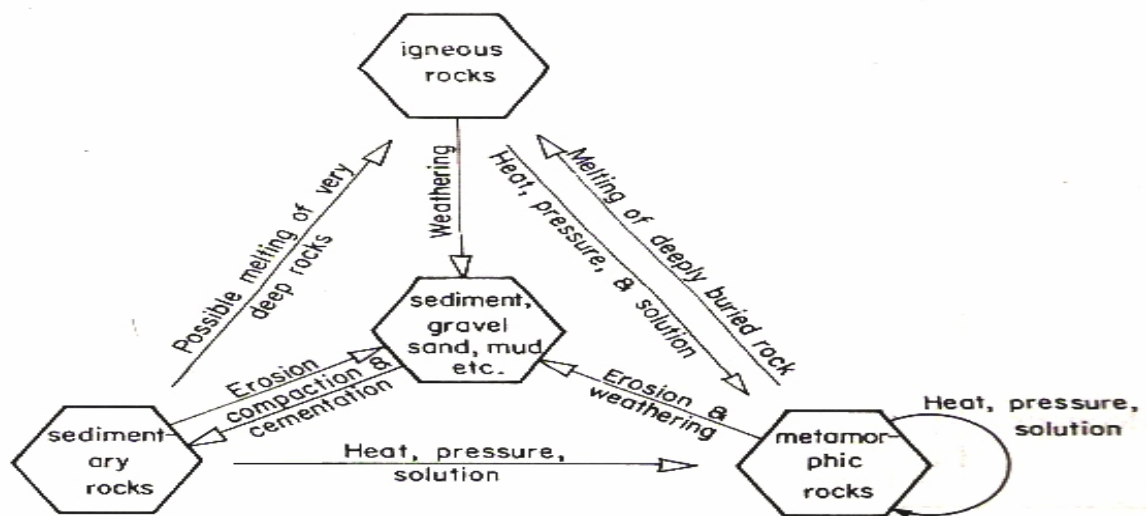


Figure 2.2. The rock-soil cycle (Bowles, 1984)

### 2.1.3. Soil Horizons

Soil is differentiated into layers that are approximately parallel to the land surface and several layers may evolve simultaneously over a period of time. The layers in a soil are genetically related; however, the layers differ from each other in their physical, chemical, and biological properties. In soil terminology, the layers are called horizons.

Horizonation (formation of soil horizons) results from the differential gains, losses, transformations, and translocations that occur over time within various parts of a vertical section of the parent material (Foth, 1990). For the analytical chemist, three soil horizonation conditions exist. High-rainfall areas typically have tree or tall grass vegetation and extensive horizon development. Low-rainfall and desert vegetation with little horizon development. Areas with rainfall between these extremes will have variable vegetation and horizonation. It is not possible to draw sharp boundaries between these areas because local conditions such as frequency, time of year, and intensity of the rainfall will dramatically affect the climate in transition areas (Conklin, 2005). Examples of the major kinds of changes that occur to produce horizons are:

- (1) Addition of organic matter from plant growth, mainly to the top soil.
- (2) Transformation represented by the weathering of rocks and minerals and the decomposition of organic matter.
- (3) Loss of soluble components by water moving downward through soil carrying out soluble salts.
- (4) Translocation represented by the movement of suspended mineral and organic particles from the topsoil to the subsoil (Foth, 1990).

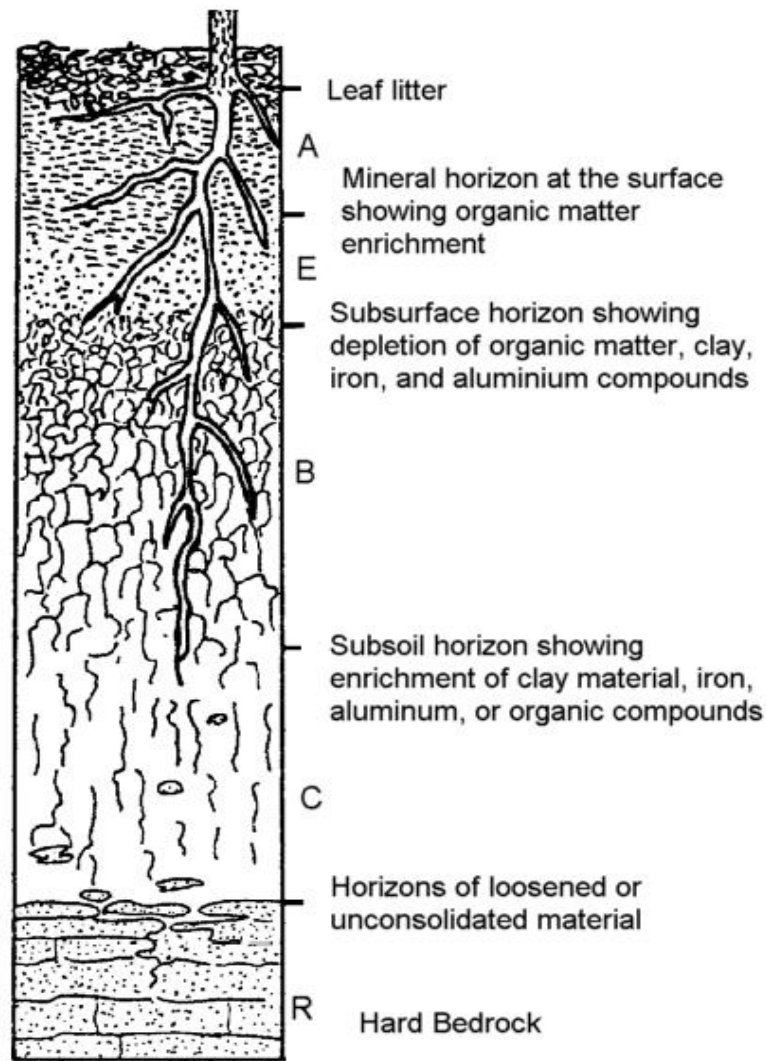


Figure 2.3. Hypothetical Soil Horizons Profile

A hypothetical soil profile, showing the various horizons, which might be possible in a highly developed soil, is presenting in Figure 2.3. In general;

A horizon is top zone consisting of topsoil and organic matter, and in humid areas, highly leached materials; in arid areas it may be rich in various water-soluble salts remaining as water vapor from the lower depths evaporates; it generally is highly weathered, dark-colored material including various shades of blacks and browns of a few centimeters to 1 or 2 m thick and grading into E horizon (Bowles, 1984).

E horizon is the downward translocation of colloids from the A horizon may result in the concentration of sand and silt-sized particles (particles larger than clay size) of quartz and other resistant minerals in the upper part of many soils. In soils with thin A

horizons, a light-colored horizon may develop at the boundary of the A and B horizons, called E horizon (Foth, 1990).

B horizon is underlying the E horizon and containing considerable leached materials (water-soluble salts such as carbonates, sulfates, and chlorides) and clay minerals; this zone may be on the order of 0.5 to several meters thick and grades into the C horizon.

C horizon is the transitional zone of freshly weathered parent material (rock); it may consist of considerable rock fragments or may be absent or of very shallow depth and grades into R horizon.

R horizon is parent or bed rock (Bowles, 1984).

#### **2.1.4. Soil Texture**

The physical and chemical weathering of rocks and minerals results in a wide range in size of particles from stones, to gravel, sand, silt, and to very small clay particles. The particles-size distribution determines the soil's coarseness or fineness, or soil's texture. Specifically, texture is the relative proportions of sand, silt, and clay in a soil.

Since a soil separate rarely makes up the soil, they are grouped on the basis of proportion to create the soil textural classes. Simply when the percentage of clay, silt and sand is known the soil class can be determined by the use of textural triangle representing Figure 2.4 (Foth, 1990).



Table 2.1. Some characteristics of soil separates (Foth, 1990)

Separate	Diameter, mm <sup>a</sup>	Diameter, mm <sup>b</sup>	Number of Particles per Gram	Surface Area in 1 Gram, cm <sup>2</sup>
Very coarse sand	2.00-1.00	-	90	11
Coarse sand	1.00-0.50	2.00-0.20	720	23
Medium sand	0.50-0.25	-	5700	45
Fine sand	0.25-0.10	0.20-0.02	46.000	91
Very fine sand	0.10-0.05	-	722000	227
Silt	0.05-0.002	0.02-0.002	5776000	454
Clay	Below 0.002	Below 0.002	90260853000	8000000 <sup>c</sup>

<sup>a</sup> United States Department of Agricultural System.

<sup>b</sup> International Soil Science Society System.

<sup>c</sup> The surface area of platy-shaped montmorillonite clay particles determined by the glycol retention method by Sor and Kemper. (See Soil Science Society of America Proceedings, Vol. 23, pp. 106, 1959). The number of particles per gram and surface area of silt and the other separates are based on the assumption that particles are spheres and the largest particle size permissible for the separate.

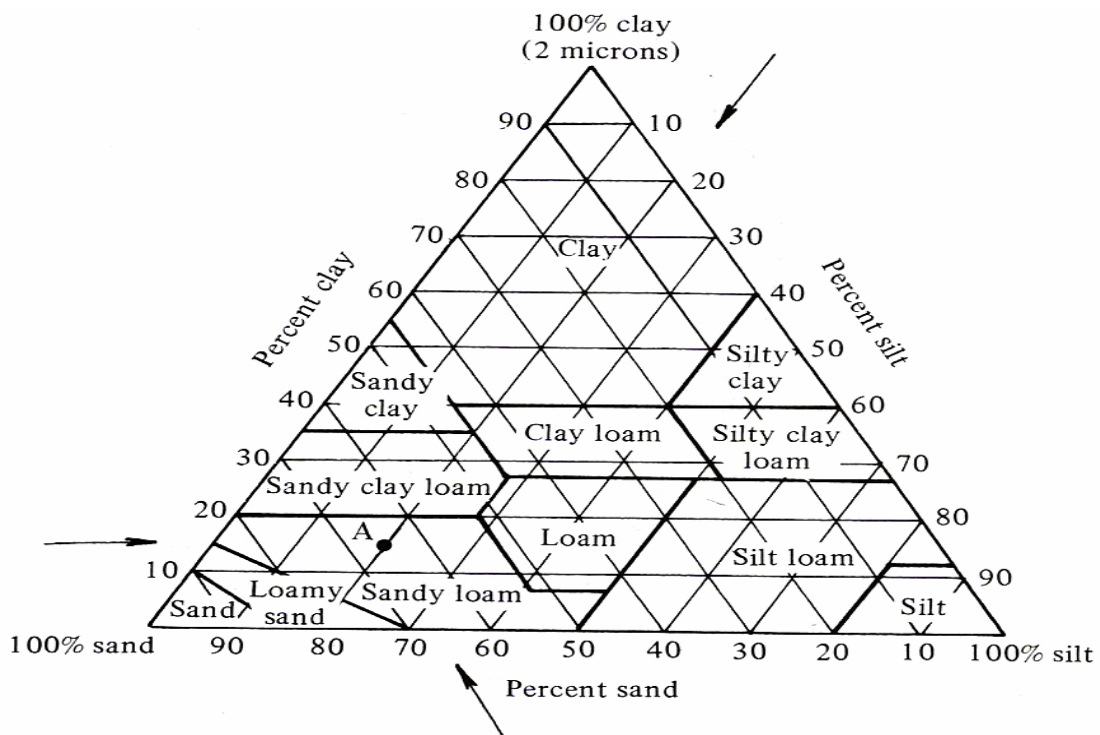


Figure 2.4. The textural triangle and limits of sand, silt and clay (Foth, 1990).

### **2.1.5. Soil pH**

The pH of a soil is one of the most important properties involved in plant growth. There are many soil pH relationships, including those of ion exchange capacity and nutrient availability. For example, solubility of iron compounds decrease with increasing pH, resulting, in many instances, is observed in iron deficiency for plant growth.

Parent materials have a wide ranging mineralogical composition and pH, and young soils inherit these properties from the parent material. Throughout the world there are parent materials and soils that contain several percent or more of calcium carbonate; they are calcareous. The hydrolysis of calcium carbonate produces  $\text{OH}^-$ , which contributes to alkalinity in soils.

The development of soil acidity requires the removal of the carbonates by leaching. When acidity develops, the weathering of primary minerals is greatly increased, causing an increase in the release of cations-calcium, magnesium, potassium and sodium. Leaching of these cations in humid regions, however, eventually results in the development of soil acidity (Foth, 1990).

### **2.1.6. Soil Organic Matter**

Soil organic matter (OM) represents an accumulation of partially decayed and partially resynthesized plant and animal residues. Such material is in an active state of decay, being subject to attack by soil microorganisms. Consequently, it is a rather transitory soil constituent and must be renewed constantly by the addition of higher plant residues.

The OM content of a soil is small-only about 3 to 5 % by weight in the case of a representative mineral topsoil. Its influence on soil properties and consequently on plant growth, however, is far greater than this low content would lead one to believe. In the first place, OM functions as a granulator of mineral particles, being largely responsible for the loose, friable condition of productive soils. Also, organic matter is a major soil source of two important mineral elements, phosphorus and sulphur, and essentially the sole source of

nitrogen. Through its effect on the physical condition of soils, OM also tends to increase the amounts of water a soil can hold and the proportion of this water that is available for plant growth. Last, OM is the main source of energy for soil microorganisms (Buckman and Brady, 1960).

The soil OM may be considered to consist of two general groups: (1) original tissue and its partially decomposed equivalents; and (2) the humus. Humus, also known as humic substances, is produced at the end of the humification process, which involves the complex reaction of various decomposition products to produce large, complex molecular chains, or polymers. The number of molecules involved in this process, as well as the number of ways in which they combine is most unlimited (Ellis and Mellor, 1995). Formation of humic substance can be seen in Figure 2.5.

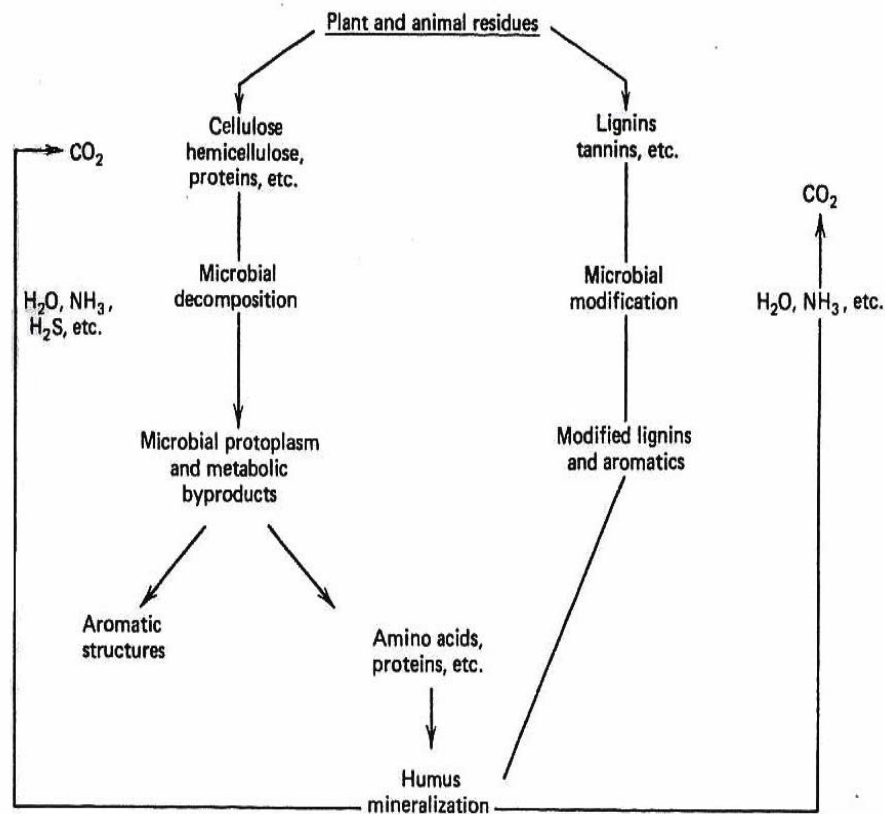


Figure 2.5. Organic matter decomposition and formation of humic substances (Bohn et al., 2001)

### 2.1.7. Soil Cation Exchange (Retention) Capacity

Probably the most important and distinctive property of soils is that they can retain ions and release them slowly to the soil solution and to plants. The retention prevents concentrations that are too high and too low. Soils give up other ions,  $H^+$  or  $OH^-$  and  $HCO_3^-$ , in equal amounts to those retained. When trace ions are removed from the soil solution, ion exchange to the soil solutions often unnoticed. The retention of organic and nonorganic substances usually results in their degradation by soil microbes and conversion to  $CO_2$  and water (Bohn et al., 2001).

Cation exchange capacity (CEC) of soils is the sum of positive (+) charges of the adsorbed cations that the mineral fraction (clays etc.) and organic fraction (humic substances) of soil can adsorb at a specific pH (Foth, 1990). The CEC of clays dependent on surface area, which is different for each clay type.

Soil organic matter usually have a large surface area and thus exhibit high CEC, many times higher than various clay minerals. The high CEC of OM is not only due to its relatively high surface area but also related to the presence of various functional groups. The pH of soil highly influences both the CEC of organic matter and clay minerals. Generally, the CEC of soils increases with increasing soil pH (Evangelou, 1998).

Cation retention by soils can be roughly divided into the weaker electrostatic interaction of soil particles with the alkali and alkaline earth cations and the soil's stronger chemical bonding with trivalent and transition metal cations.

Relatively weak (electrostatic) attraction-alkali and alkaline earth cations (mainly Ca, Mg, K, and Na);

- Nonspecific, depends mostly on the concentration ratios on the solid vs. the soil solution and on the ion charge ratio. Some clay minerals prefer one ion over others.
- Reactions are fast and reversible; time scale is seconds and minutes.

- Amount of retention depends on soil's cation exchange capacity, the negative charge of the soil particles.
- Largely due to aluminosilicate clay minerals plus soil OM.  
  
Strong (chemical bonding) attraction- H, Al, Be, Ti, transition metal, and heavy metal cations;
- Specific, that is, the strength of attraction depends mostly on the cation's water solubility and the amount of that cation on the surfaces of soil particles.
- Reaction time is rapid at first, but continues at ever-slower rates for a long period.
- Amount retention depends on soil pH rather than on the charge properties of soil clays.
- Aluminosilicates are less important, Fe and Mn oxides are more important, in this retention than in electrostatic cation retention.
- OM increases the range of sorptivity, possibly by adding soft Lewis base character (Bohn, 2001).

## 2.2. Pollution of Soil

Soil pollution could be typified very briefly as the malfunctioning of soil as an environmental component following its contamination with certain compounds particularly as a result of human activities. This is particularly the case when it is attempted-in view of presumed undesirability of soil pollution-to specify limits as to permissible and non-permissible human interference with soil. Such limits are the necessary prerequisites of any legislative action undertaken for protective purposes.

The reason for the above lack of clarity is all too obvious. In order to establish present or predict future malfunctioning of soil, one would have to know precisely how soil functions as an environmental component, both for “natural” and “man-made” conditions. In addition it would be required to extrapolate this knowledge to all those situations involving the presence of contaminants in order to see whether these could possibly interfere, and if so at what levels. Further dissection of the problem then shows that the functioning of soil as an environmental component is manifold-granted that its role as a support for the growth of plants is a major one while the term contaminants is often ill-defined as many compounds which are present regularly in particular soils and are even necessary in small amounts, may become inhibitive beyond certain limits. Finally the phrase resulting from human activities, though inferring a possibility of terminating such activities if adversely affecting the functioning of soil, does not necessarily point to the desirability of stopping these, as many human activities were designed to enhance the functioning of soil in certain aspects, though admittedly they could lead to undesirable effects in others (Bolt and Bruggenwert, 1978).

Only a small portion of trace elements in soil is bioavailable. The mobility and availability of trace elements are controlled by many chemical and biochemical processes such as precipitation–dissolution, adsorption–desorption, complexation-dissociation, and oxidation–reduction. Not all the processes are equally important for each element, but all these processes are affected by soil pH and biological processes. Therefore, it is crucial to understand some major reactions in soils that control the release of a specific trace element

in the soil and the environment in order to overcome problems related to deficiency and contamination of these elements (He et al., 2005).

### **2.2.1. Recognition and Prediction of Soil Pollution**

Much in contrast to the other two main environmental components, viz. air and water, pollution of soil is not easily measured in terms of a chemical composition. A pure soil is undefinable. The handling of potential pollution problems in soil must be based on the prediction of likely or possible impairment of the functioning of soil. In practice this implies in the first place knowledge of the composition of the influx. Next the fate of the compounds present in the influx when passing through the soil system be predicted. Thus the central theme of soil pollution phenomena is knowledge of transport and accumulation processes in soils, particularly of hazardous compounds. In this respect it is evident that accumulation and mobility are greatly governed by interactions of the compound of interest with the soil solid phase and in specific cases by its degradability. Such interactions can in a preliminary way be enumerated as:

- Positive adsorption as induced by electrostatic attraction between charged compounds and oppositely charged soil constituents.
- Electrostatic repulsion when electric charge of compound and soil constituent is of same sign. This is usually the case with certain anions and the predominantly negative charge on e.g. clay minerals.
- Chemisorption. This interaction mechanism can often hardly be distinguished from electrostatic positive adsorption except for the value of the adsorption energy. This is usually considerably higher in case of chemisorption. Moreover, and actually as one of the consequences of this high adsorption energy, chemisorption is usually characterized by a very limited exchangeability with other compounds.
- Precipitation and dissolution reactions. They may play a predominant role in governing the mobility of certain compounds like heavy metals and phosphorus.

- Decomposition and turnover reaction. Many compounds, when present in soil, are subjected to reaction as (photo) chemical degradation, microbial degradation, or a combination of these. The persistence in soil, air or water, as governed by the degradability of the compound, is one of the main factors with respect to possibly hazardous effects on the environment.

The above interaction mechanisms may either occur separately or in combination with each other, either successively, simultaneously or even altering.

Certain criteria in soil pollution evaluation are to be derived from the required standards of drainage water reaching the groundwater stream; these in turn may depend on the geographic location with respect to water harvesting for consumptive use and/or the vicinity of open water (Bolt and Bruggenwert, 1978).



### 2.3. Heavy Metals

Heavy metals have a density greater than  $3 \text{ g/cm}^3$ . They are found in nature as elements such as gold or as metal sulfides (e.g.,  $\text{CuS}_2$ ,  $\text{PbS}_2$ , and  $\text{FeS}$ ) or as metal oxides (e.g.,  $\text{MnO}_2$ ,  $\text{Cr}_2\text{O}_3$ , and  $\text{Fe}_2\text{O}_3$ ). Heavy metals are widely used industries and also serve as micronutrients to microorganisms and higher plants (Evangelou, 1998). Essential micronutrients for animals and plants can be seen in Table 2.2.

Table 2.2. Metals having essential functions (E) for plants or animals. A question mark after the letter E indicates that it has not been unequivocally established whether the metal is essential or not (Notter, 1993).

	<b>Al</b>	<b>B</b>	<b>Co</b>	<b>Cr</b>	<b>Cu</b>	<b>Fe</b>	<b>Mn</b>	<b>Mo</b>	<b>Ni</b>	<b>Se</b>	<b>V</b>	<b>Zn</b>
Plants, algae	E?	E	E?	-	E	E	E	E	-	-	E	E
Animals	-	-	E	E	E	E	E	E?	E?	E	E	E

Soil minerals bearing trace elements serve as reservoirs for the elements, releasing them slowly into the soil solution as weathering of the minerals continues. If a trace element is also micronutrient, then the rate of mineral weathering becomes a critical factor in soil fertility. For example, the ability of soils to provide copper to plants depends on the rate at which this element is transformed from a solid phase to a soluble chemical form. Soil chemical and physical properties like pH, redox potential, and water content will affect the rate of this transformation and thus control Cu solubility. In a similar manner, the weathering rate of soil solids containing cadmium as a trace element will determine in part the potential hazard of this toxic element to plants (Sposito, 1989). Figure 2.6 represents dynamic interactive processes governing solubility, availability, and mobility of elements in soils.

Heavy metal-contaminated soils is a common phrase. The real issue is whether soil components affect groundwater composition or can be taken up by plants and soil fauna.

Mixed adequately with soil, metal ions quickly react with the soil and are adsorbed/precipitated and tend to revert to their native states, and native availability in soils.

All of the essential microelements and most, if not all, of the trace elements are toxic at soil concentrations much above normal. Naturally occurring high concentrations of toxic elements are rare in soils, except for widespread  $\text{Al}^{3+}$  phytotoxicity in acid soils. Soil contamination by toxic elements generally is a result of human activities. Anthropogenic pollutant elements and their important oxidation states that have received attention include, in order of atomic number rather than importance: Be (II), F (-I), Cr (III –VI), Ni (II–III), Zn (II), As (III–V), Cd (II), Hg (0–I–II), and Pb (II – IV) (Bohn et al., 2001).

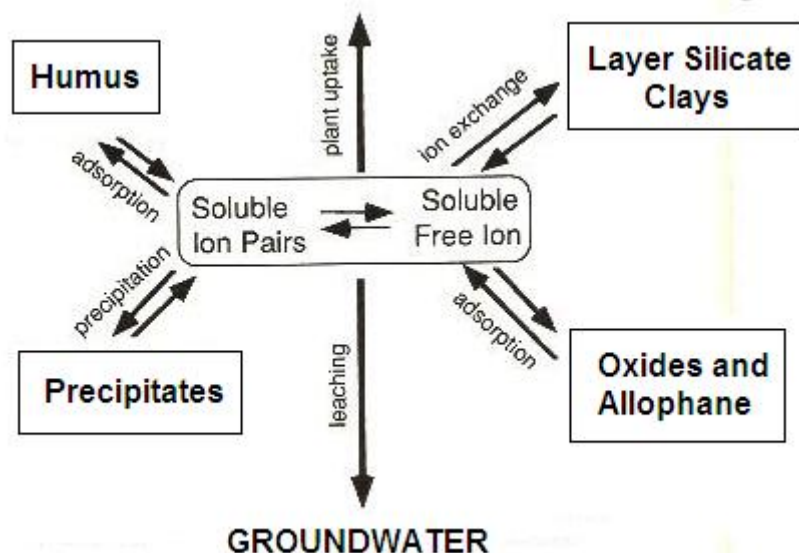


Figure 2.6. Dynamic interactive processes governing solubility, availability, and mobility of elements in soils (McBride, 1994).

Trace elements in agroecosystems The normal abundance of an element in earth material is commonly referred to by the geochemist as background, and for any particular element this value, or range of values is likely to vary according to the nature of the materials. Trace elements in soil are derived from parent materials and anthropogenic inputs. In remote or mountain areas where impacts of human activity are relatively small, trace elements in soil are mainly inherited from parent materials, whereas in urban areas or

agricultural land with a long history of crop production, the concentrations of trace elements in soil can be higher than those found in the parent materials (He et al., 2005).

Anthropogenic inputs Inputs of trace elements through human activities have been increased since the last century. Both industrial and agricultural operations contribute to the elevation of trace metals in soil. The smelter-related industries often act as point sources of metals, which enter agroecosystems by dry and wet deposit or use of industrial byproducts. Use of metal-containing substances in agriculture has significantly increased to sustain crop production. Application of trace elements such as Cu, Zn, Fe, Mn, and B that are essential to plant growth is now common practice for correcting deficiencies in these elements. Many chemicals including fungicides, pesticides, and herbicides contain Cu, Zn, Fe, Mn, and As. Some trace metals such as Cd and Pb enter the soil as impurities of fertilizers.

Fertilizers, manures, and chemicals Most fertilizers contain trace amounts of trace elements. Phosphorus (P) fertilizers such as triple superphosphates and calcium/magnesium phosphate contain varying concentrations of Cd, depending on the source of phosphate rock. Some P fertilizers can have Cd concentrations >450 mg/kg and they are banned for use in agriculture in an increasing number of countries. These fertilizers are important sources of trace elements for crops growing in soils subject to severe deficiency in these elements, such as sandy soils, peaty soil, and calcareous soils. Organic materials such as farm manures, biosolids or composts contain higher concentrations of trace elements than most agricultural soils. Use of biosolids and composts has been reported to increase total amounts of Cu, Zn, Pb, Cd, Fe, and Mn in the soils. Some biosolids can contain high concentrations of metals, with median values of Cu, Zn, Ni, Pb, Cd, and Cr of 463, 725, 29, 106, 7, and 40 mg/kg, respectively. Repeated use of biosolids/composts has been reported to contaminate the soils. Both US EPA and European countries have established maximum limits of heavy metal concentrations for use of biosolids in agriculture, although the standards differ among different countries.

Irrigation The input of metals through irrigation varies markedly from location to location. Non-contaminated fresh and salt water contains extremely low concentrations of heavy metals. Domestic and industrial wastewaters, however, often contain heavy metals in

significantly higher concentrations than natural waters. Repeated use of wastewaters, that have not been treated to filter heavy metals, may well contribute to the accumulation of these metals in the soil.

Dry and wet deposits Dry and wet deposits contribute variable amounts of metals to the soil, depending on the nature and distance of point sources. Emissions from large industrial sources, including iron and steel industry, primary and secondary base metal smelters, base metal refineries, and base metal foundries often have great impact on metal accumulation in the soil. Concentrations of Cu and Ni in the soil were reported to exponentially increase with a decrease in distance from the source. There is also considerable emission of metals from municipal sources such as electric generating stations and incinerators. Emission from automobiles that use Pb-enriched gasoline has caused a significant increase in the Pb concentration in the soils along old highways. More work is needed to quantify these sources.

Other point sources Mining activities have been reported to cause heavy metal contamination to the soil in a localized area. Metalliferous mine spoils result from disposal of metal rich over burden and excavation wastes. The polluted soil can contain heavy metal concentrations of 100–1000 times greater than their background. Some plants that eventually adapt to the contaminated soil may develop super-accumulating traits for the metals. Tailings of acid ores may produce high concentrations of metals and low pH leachates shortly after their exposure to the air. The leachate can quickly destroy soil biota and damage crops it reaches. Coal mine spoils often have this problem and cause severe pollution to the local soils

Outputs of trace elements from agroecosystems Outputs of trace elements from agroecosystems include crop harvest, losses by leaching, surface runoff, and gaseous emission. Crop harvest accounts for a big proportion of the output of trace elements, although the precise amounts of metal removal vary greatly with the type of soil, crop variety, and climate conditions. For most fine texture soil, leaching of trace elements is limited because of the strong binding of these elements with soil colloids, whereas for sandy soils, especially under acidic conditions, leaching can be an important output. Surface runoff losses of trace elements are often associated with transport of particulates

that contain adsorbed trace elements and organic-metal complexes. Relatively few studies have been conducted to quantify surface runoff losses of trace elements. Gaseous losses are important only for Se, As, and Hg. Some volatile organic Se and As compounds are formed in plants and emitted from plant leaves. Leaf emission has been reported to be an important pathway of Se output. Hg can be converted into methyl-Hg through microbial activity and emitted from the soil (He et al., 2005).

### **2.3.1. Copper**

Copper is a reddish metal that occurs naturally in rock, soil, water, sediment, and, at low levels air. Its average concentration in the earth's crust is about 50 parts copper per million parts soil (ppm). Copper also occurs naturally in all plants and animals. It is an essential element for all known living organisms including humans and other animals at low levels of intake. At much higher levels, toxic effects can occur. The term copper in this profile not only refers to copper metal, but also to compounds of copper that may be in the environment (Agency for Toxic Substance and Disease Registry, 2004).

Copper occurs in solids and solutions almost exclusively as the divalent cation  $\text{Cu}^{+2}$ . However, reduction of  $\text{Cu}^{2+}$  (cuprous) to  $\text{Cu}^{3+}$  (cupric) and  $\text{Cu}^0$  (metallic copper) is possible under reducing conditions, especially if halide or sulfide ions (soft bases) are present to stabilize  $\text{Cu}^+$  (a soft acid). Copper is classified as a chalcophile, owing to its tendency to associate with sulfide in very insoluble minerals,  $\text{Cu}_2\text{S}$  and  $\text{CuS}$ . In reduced soils, then, copper has very low mobility. Most of the colloidal material of soils (oxides of Mn, Al, and Fe, silicate clays, humus) adsorb  $\text{Cu}^{2+}$  strongly, and increasingly so as the pH is raised (McBride, 1994).

2.3.1.1. Environmental Fate of Copper Copper can enter the environment through releases from the mining of copper and other metals, and from factories that make or use copper metal or copper compounds. Copper can also enter the environment through waste dumps, domestic waste water, combustion of fossil fuels and wastes, wood production, phosphate fertilizer production, and natural sources (for example, wind-blown dust, from native soils, volcanoes, decaying vegetation, forest fires, and sea-spray). Therefore, copper is

widespread in the environment. Copper is often found near mines, smelters, industrial settings, landfills, and waste disposal sites.

When copper is released into soil, it can become strongly attached to the organic material and other components (e.g., clay, sand, etc.) in the top layers of soil and may not move very far when it is released. When copper and copper compounds are released into water, the copper that dissolves can be carried in surface waters either in the form of copper compounds or as free copper or, more likely, copper bound to particles suspended in the water. Even though copper binds strongly to suspended particles and sediments, there is evidence to suggest that some water-soluble copper compounds do enter groundwater. Copper that enters water eventually collects in the sediments of rivers, lakes, and estuaries. Copper is carried on particles emitted from smelters and ore processing plants, and is then carried back to earth through gravity or in rain or snow. Copper is also carried into the air on wind-blown metallurgical dust (Agency for Toxic Substance and Disease Registry, 2004).

An estimated 97% of copper released from all sources into the environment is primarily released to land. When considering the environmental fate of a metal, it is not always possible to clearly separate the processes related to the transport and partitioning of a metal, its compounds, and complexes from those related to transformation and degradation of these metal species. Because of analytical limitations, investigators do not often identify the form of a metal present in the environment. A change in the transport or partitioning of a metal may result from the transformation of the metal from one form to another. For example, complexation of a metal with small organic compounds may result in enhanced mobility, while formation of a less-soluble sulfide would decrease its mobility in water or soil. Adsorption may be the result of strong bonds being formed (transformation) as well as weak ones. Characterizing weak and strong adsorption is dependent on the analytical method that is used and care should be exercised when comparing results from different studies (Agency for Toxic Substance and Disease Registry, 2004).

Copper is released to the atmosphere in the form of particulate matter or adsorbed to particulate matter. It is removed by gravitational settling (bulk deposition), dry

deposition (inertial impaction characterized by a deposition velocity), in-cloud scavenging (attachment of particles by droplets within clouds), and washout (collision and capture of particles by falling raindrops below clouds). The removal rate and distance traveled from the source will depend on a number of factors, including source characteristics, particle size, turbulence, and wind velocity.

Much of the copper discharged into waterways is in particulate matter and settles out. In the water column and in sediments, copper adsorbs to organic matter, hydrous iron and manganese oxides, and clay. In the water column, a significant fraction of the copper is adsorbed within the first hour of introduction, and in most cases, equilibrium is obtained within 24 hours.

Copper's movement in soil is determined by a host of physical and chemical interactions of copper with the soil components. In general, copper will adsorb to OM, carbonate minerals, clay minerals, or hydrous iron and manganese oxides. Sandy soils with low pH have the greatest potential for leaching. In most temperate soils, the pH, organic matter, concentrations of metal oxyhydroxides and ionic strength of the soil solutions are the key factors affecting adsorption. The ionic strength and pH of the soil solution affect the surface charge of soils and thereby influence ionic interaction. Soil microorganisms also affect the absorption of copper in soils due to the uptake and assimilation of the metal by these microorganisms. However, it is not known how the rate of uptake and absorption capacity of the microorganisms for copper compares with the binding capacity and affinities of copper by organic matter in soils, such as humic and fulvic acids. When the amount of organic matter is low, the mineral content or Fe, Mn, and Al oxides become important in determining the adsorption of copper.

Total copper concentrations were high in the upper soil horizons and low in the lower horizons. Copper showed a pronounced solubility only in the oxidizing environment. In the reducing environment, solubility was low, possibly due to the formation of sulfides (Agency for Toxic Substance and Disease Registry, 2004).

### 2.3.2. Nickel

Pure nickel is a hard, silvery-white metal, which has properties that make it very desirable for combining with other metals to form mixtures called alloys. Some of the metals that nickel can be alloyed with are iron, copper, chromium, and zinc (Agency for Toxic Substance and Disease Registry, 2005).

The +2 oxidation state is the only stable form of nickel in soil environments. The  $\text{Ni}^{2+}$  cation is almost as electronegative as  $\text{Cu}^{2+}$ ; this fact and its electronic structure favor the formation of complexes with organic matter that are comparable in stability to those of  $\text{Cu}^{2+}$ . Bioaccumulation of Ni in humus is pronounced, and like  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  favors bonding to softer organic ligands containing nitrogen and sulfur. As the smallest of the divalent transition metal cations,  $\text{Ni}^{2+}$  fits easily into octahedral sites, co-precipitating readily into Mn and Fe oxides in soils. Chemisorption on oxides, noncrystalline aluminosilicates, and layer silicate clays is favorable above pH 6, but lower pH favors exchangeable and soluble  $\text{Ni}^{2+}$ . Because solubility decreases markedly at higher pH, mobility of Ni, rated as medium in acid soils, becomes very low in neutral to alkaline soils. Under reducing conditions,  $\text{Ni}^{2+}$  is incorporated into sulfides that restrict mobility to very low levels.

High OM levels in Ni - rich soils can solubilize  $\text{Ni}^{2+}$  as organic complexes, at least at higher pH. Nickel is a strongly phytotoxic element, being several times more toxic than copper. Like copper, it occurs commonly in industrial wastes and sewage sludges at appreciable levels, and may reach levels toxic to plants in waste-treated soils (McBride, 1994).

Nickel combined with other elements occurs naturally in the earth's crust. It is found in all soil, and is also emitted from volcanoes. Nickel is the 24<sup>th</sup> most abundant element. In the environment, it is primarily found combined with oxygen or sulfur as oxides or sulfides. Nickel is also found in meteorites and on the ocean floor in lumps of minerals called sea floor nodules. The earth's core is composed of 6 % nickel. Nickel is released into the atmosphere during nickel mining and by industries that make or use nickel, nickel alloys, or nickel compounds. These industries also might discharge nickel in



waste water. Nickel is also released into the atmosphere by oil-burning power plants, coal-burning power plants, and trash incinerators.

**2.3.2.1. Environmental Fate of Nickel** Nickel is released to the atmosphere by wind-blown dust, volcanoes, combustion of fuel oil, municipal incineration, and industries involved in nickel refining, steel production, and other nickel alloy production. The form of nickel emitted to the atmosphere is dependent upon the source. Complex nickel oxides, nickel sulfate, and metallic nickel are associated with combustion, incineration, and smelting and refining processes. Ambient air concentrations of nickel range between 7 and 12 ng/m<sup>3</sup>, mainly in the form of aerosols and can be as high as 150 ng/m<sup>3</sup> near point sources.

Nickel may be released to the environment from the stacks of large furnaces used to make alloys or from power plants and trash incinerators. The nickel that comes out of the stacks of power plants attaches to small particles of dust that settle to the ground or are taken out of the air in rain or snow. It usually takes many days for nickel to be removed from the air. If the nickel is attached to very small particles, it can take more than a month to settle out of the air.

Nickel can also be released in industrial waste water. A lot of nickel released into the environment ends up in soil or sediment where it strongly attaches to particles containing iron or manganese.

Under acidic conditions, nickel is more mobile in soil and might seep into groundwater. Nickel does not appear to concentrate in fish. Studies show that some plants can take up and accumulate nickel. However, it has been shown that nickel does not accumulate in small animals living on land that has been treated with nickel-containing sludge (Agency for Toxic Substance and Disease Registry, 2005).

### **2.3.3. Zinc**

Zinc is one of the most common elements in the Earth's crust. Zinc is found in the air, soil, and water and is present in all foods. In its pure elemental (or metallic) form, zinc

is a bluish-white, shiny metal. Powdered zinc is explosive and may burst into flames if stored in damp places. Metallic zinc has many uses in industry. A common use for zinc is to coat steel and iron as well as other metals to prevent rust and corrosion. Metallic zinc is mixed with other metals to form alloys such as brass and bronze. Metallic zinc is also used to make dry cell batteries.

Zinc can also combine with other elements, such as chlorine, oxygen, and sulfur, to form zinc compounds. Zinc compounds that may be found at hazardous waste sites are zinc chloride, zinc oxide, zinc sulfate, and zinc sulfide. Most zinc ore found naturally in the environment is in the form of zinc sulfide.

2.3.3.1. Environmental Fate of Zinc Zinc enters the air, water, and soil as a result of both natural processes and human activities. Most zinc enters the environment as the result of mining, purifying of zinc, lead, and cadmium ores, steel production, coal burning, and burning of wastes. These activities can increase zinc levels in the atmosphere. Waste streams from zinc and other metal manufacturing and zinc chemical industries, domestic waste water, and run-off from soil containing zinc can discharge zinc into waterways. The level of zinc in soil increases mainly from disposal of zinc wastes from metal manufacturing industries and coal ash from electric utilities. Sludge and fertilizer also contribute to increased levels of zinc in the soil. In air, zinc is present mostly as fine dust particles. This dust eventually settles over land and water. Rain and snow aid in removing zinc from air. Most of the zinc in lakes or rivers settles on the bottom. However, a small amount may remain either dissolved in water or as fine suspended particles. The level of dissolved zinc in water may increase as the acidity of water increases. Fish can collect zinc in their bodies from the water they swim in and from the food they eat. Most of the zinc in soil is bound to the soil and does not dissolve in water. However, depending on the type of soil, some zinc may reach groundwater, and contamination of groundwater has occurred from hazardous waste sites. Zinc may be taken up by animals eating soil or drinking water containing zinc. Zinc is also a trace mineral nutrient and as such, small amounts of zinc are needed in all animals.

Zinc occurs in the environment mainly in the +2 oxidation state. Sorption is the dominant reaction, resulting in the enrichment of zinc in suspended and bed sediments.

Zinc in aerobic waters is partitioned into sediments through sorption onto hydrous iron and manganese oxides, clay minerals, and organic material. The efficiency of these materials in removing zinc from solution varies according to their concentrations, pH, redox potential, salinity, nature and concentrations of complexing ligands, cation exchange capacity, and the concentration of zinc. Precipitation of soluble zinc compounds appears to be significant only under reducing conditions in highly polluted water.

In water, zinc dissolves in acids to form hydrated  $\text{Zn}^{+2}$  cations and in strong bases to form zincate anions, which are hydroxo complexes, e.g.,  $(\text{Zn}[\text{OH}]_3)^-$ ,  $(\text{Zn}[\text{OH}]_4)^{2-}$ , and  $(\text{Zn}[\text{OH}]_4[\text{H}_2\text{O}]_2)^{2-}$ . In most waters, zinc exists primarily as the hydrated form of the divalent cation. However, the metal often forms complexes with a variety of organic and inorganic ligands.

Zinc can occur in both suspended and dissolved forms in surface water. Dissolved zinc may occur as the free (hydrated) zinc ion or as dissolved complexes and compounds with varying degrees of stability.

The transport of zinc in the aquatic environment is controlled by anion species. In natural waters, complexing agents, such as humic acid, can bind zinc. The stability of zinc complexes depends on the pH of the water and the nature of the complex. Therefore, as the pH of the water decreases, the concentration of zinc ions in the water phase increases at the same rate as that of the release of zinc from the sediment. Zinc tends to sorb more readily at a high pH ( $\text{pH} > 7$ ) than at a low pH. Desorption of zinc from sediments occurs as salinity increases, apparently because of displacement of the adsorbed zinc ions by alkali and alkaline earth cations, which are abundant in brackish and saline waters.

In the atmosphere, zinc exists primarily in an oxidized form bound to aerosols, with the size of zinc particulates determined by the source of zinc emission. A major proportion of zinc released from industrial processes is adsorbed on particulates that are small enough to be in the respirable range. Wind-blown dust transports zinc bound to soil particulates into the atmosphere. The particulates may also contain other materials.

Zinc-bearing particles in the atmosphere are transported to soil and water by wet deposition (rain and snow) and dry deposition (gravitational settling and deposition on water and soil surfaces). Five zinc-bearing particles were identified in decreasing order of concentration in the aerosol, were zinc sulfide (ZnS), ferrous zinc ( $\text{Fe}_x\text{Zn}_y$ ), zinc phosphides ( $\text{Zn}_3\text{P}_2$ ), zinc chloride ( $\text{ZnCl}_2$ ), and metallic zinc (Zn). The presence of zinc sulfide in an area adjacent to mining and smelting activities was not unanticipated, but no conclusion regarding the speciation of zinc in the atmosphere could be drawn from this investigation. However, the relative concentration of zinc ions in rainwater from a rural area was approximately 10 times higher than in airborne particulates. This finding suggests that zinc sulfide in the atmosphere is oxidized to a more water-soluble form, zinc sulfate.

The redox status of the soil may shift zinc partitioning. Reductive dissolution of iron and manganese (hydr) oxides under suboxic conditions release zinc into the aqueous phase; the persistence of suboxic conditions may then lead to a repartitioning of zinc into sulfide and carbonate solids. In dry oxidized soils, zinc was associated with (hydr)oxide phases, while in flooded systems, zinc was associated with sulfides and carbonates. Reversible change occurred with flooding from dry soil. However, a small fraction of zinc became recalcitrant with (hydr) oxides fraction. Zinc sorbs strongly onto soil particulates. Little water-soluble and exchangeable heavy metals were found in soil irrigated with raw waste water. Although considerable amounts of metals were added to the soil in soluble and exchangeable forms during waste-water irrigation, they were converted into the less chemically active forms (i.e., organically bonded and inorganic precipitates).

Zinc accumulation in soil resulting from waste disposal occurred primarily as inorganic precipitates. The mobility of zinc in soil depends on the solubility of the speciated forms of the element and on soil properties such as cation exchange capacity, pH, redox potential, and chemical species present in soil; under anaerobic conditions, zinc sulfide is the controlling species.

Zinc undergoes reactions in sediment and soil involving precipitation/dissolution, complexation/dissociation, and adsorption/desorption. These reactions are controlled by the pH, redox potential, the concentration of zinc ions and other ions in the soil pore water, the number and type of adsorption sites associated with the solid phase, and the organic

ligands present that are capable of forming complexes with zinc. In acidic sediments and soils, more zinc is available in ionic forms, and cation exchange processes influence its fate. Depending on the nature and concentrations of other mobile metals in sediments and soils, competition for the binding sites probably occurs. In the absence of suitable binding sites, zinc may be mobilized. In alkaline soils, the chemistry of zinc is dominated by interactions with organic ligands.

As an element, zinc does not degrade in the environment. Degradation of an element is a nuclear process by definition, and stable elements, such as zinc, typically undergo such processes only at insignificant rates in the environment. Zinc can change from one form to another, sometimes reversibly, in numerous chemical reactions that can proceed under a wide range of common environmental conditions.

Generally, at lower pH values, zinc remains as the free ion. The free ion ( $Zn^{+2}$ ) tends to be adsorbed and transported by suspended solids in unpolluted waters. In polluted waters in which the concentration of zinc is high, removal of zinc by precipitation of the hydroxide is possible, particularly when the pH is  $>8$ . In anaerobic environments and in the presence of sulfide ions, precipitation of zinc sulfide limits the mobility of zinc. The relative mobility of zinc in soil is determined by the same factors that affect its transport in aquatic systems (i.e., solubility of the compound, pH, and salinity) (Agency for Toxic Substance and Disease Registry, 2005).

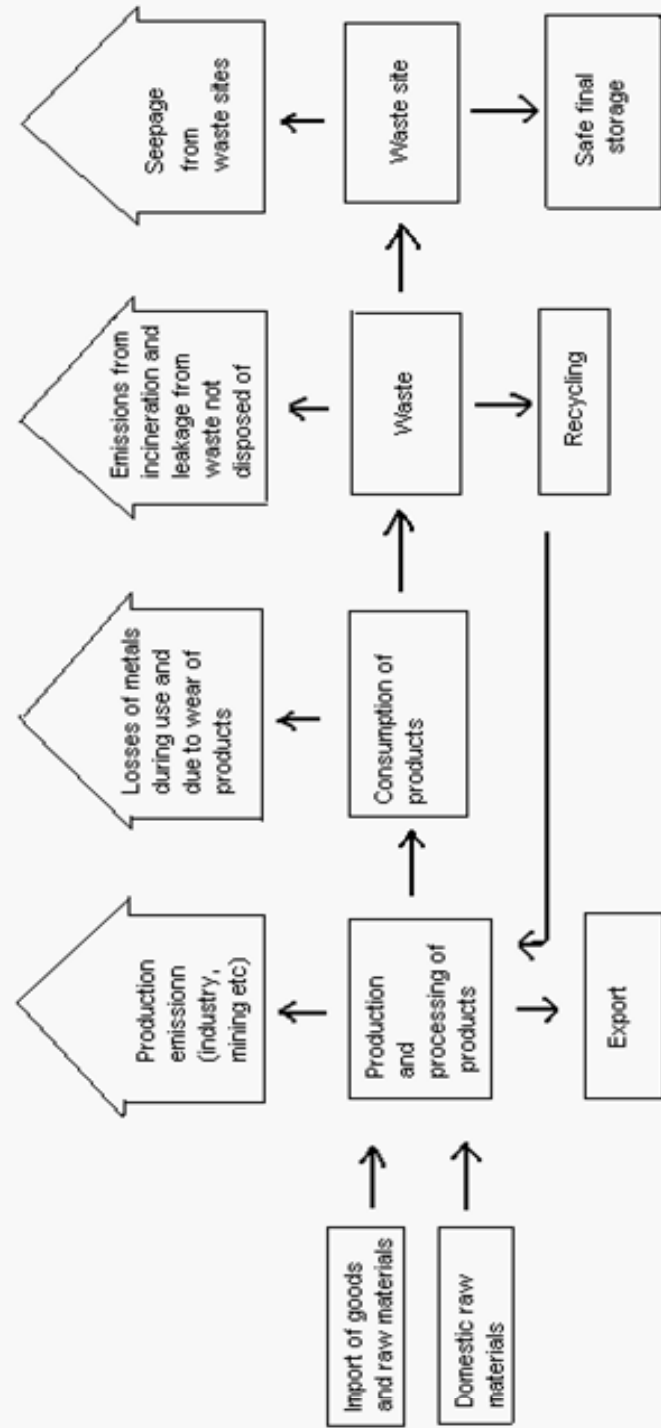


Figure 2.7. Schematic diagram of the input and output of metals in society and emissions entering the environment (Notter, 1993).

## 2.4. Adsorption

### 2.4.1. Adsorption Process in General

Adsorption can be defined as the accumulation of a substance or material at an interface between the solid surface and the bathing solution. Adsorption can include the removal of solute (a substance dissolved in a solvent) molecules from the solution, solvent (continuous phase of a solution, in which the solute is dissolved) from the solid surface, and attachment of the solute molecule to the surface. Adsorption does not include surface precipitation or polymerization processes. Adsorption, surface precipitation, and polymerization are all examples of sorption, a general term that is used when the retention mechanisms at a surface is unknown (Stumm, 1992).

It would be useful before proceeding any further to define a number of terms to retention (adsorption/sorption) of ions and molecules in soils. Some of the principal terms and properties associated with adsorption are defined in Table 2.4. The term adsorption is universally understood to mean the enrichment of one or more of the components in the region between two bulk phases (i.e. the interfacial layer). In the present context, one of these phases is necessarily a solid and the other a fluid (i.e. gas or liquid). With certain systems (e.g. some metals exposed to hydrogen, oxygen or water), the adsorption process is accompanied by absorption, i.e. the penetration of the fluid into solid phase. As already indicated, one may then use the term sorption (and the related terms sorbent, sorptive and sorbate).

The terms adsorption and desorption are often used to indicate the direction from which the equilibrium states have been approached. Adsorption hysteresis arises when the amount of adsorbed is not brought to the same level by the adsorption and desorption approach to a given 'equilibrium' pressure or bulk concentration. The relation, at constant pressure, or concentration, is known as the adsorption isotherm (Rouquerol et al., 1999).

Table 2.3. Definitions:adsorption (Rouquerol et al., 1999).

Term	Definition
Adsorption	Enrichment of one or more components in an interfacial layer
Adsorbate	Substance in the adsorbed state
Adsorptive <sup>a</sup>	Adsorbable substance in the fluid phase
Adsorbent	Solid material on which adsorption occurs
Chemisorption	Adsorption involving chemical bonding
Physisorption	Adsorption without chemical bonding
Monolayer capacity	either Chemisorbed amount required to occupy all surface sites or Physisorbed amount required to cover surface
Surface coverage	Ratio of amount of adsorbed substance to monolayer capacity

<sup>a</sup> Translated into French as “adsorbable ”

Adsorption is one of the most important chemical processes in soils. It determines the quantity of plant nutrients, metals, pesticides, and other organic chemicals that are retained on soil surfaces and therefore is one of the primary processes that affects transport of nutrients and contaminants in soils. Adsorption also affects the electrostatic properties, e.g., coagulation and settling, of suspended particles and colloids (Stumm, 1992).

Both physical and chemical forces are involved in adsorption of solutes from solution. Physical forces include van der Waals Forces (e.g., partitioning) and electrostatic outer-sphere complexes (e.g., ion exchange). Chemical forces result from short-range interactions that include inner-sphere complexation that involves a ligand exchange mechanism, covalent bonding, and hydrogen bonding (Stumm and Morgan, 1981).

**2.4.1.1. Surface Functional Groups** Surface functional groups in soil play a significant role in adsorption processes. A surface functional group is a chemically reactive molecular unit bound into the structure of a solid at its periphery such that the reactive components of the unit can be bathed by a fluid (Sposito, 1989). Surface functional groups can be organic (e.g., carboxyl, carbonyl, phenolic) or inorganic molecular units. The major inorganic surface functional groups in soils are the siloxane tetrahedral layer of a phyllosilicate and hydroxyl groups that are associated with the edges of inorganic minerals such as kaolinite,



amorphous materials, and metal oxides, oxyhydroxides, and hydroxides. A cross section of the surface layer of a metal oxide is shown in Figure 2.8. In Figure 2.8a the surface is unhydrated and has metal ions that are Lewis bases and that have a reduced coordination number. The oxide anions are Lewis bases. In Figure 2.8b, the surface metal ions coordinate to H<sub>2</sub>O molecules forming a Lewis acid site, and then a dissociative chemisorption (chemical bonding to the surface) leads to a hydroxylated surface (Figure 2.8c) with surface OH groups (Stumm, 1987, 1992).

The surface functional groups can be protonated or deprotonated by adsorption of H<sup>+</sup> and OH<sup>-</sup>, respectively as shown below;



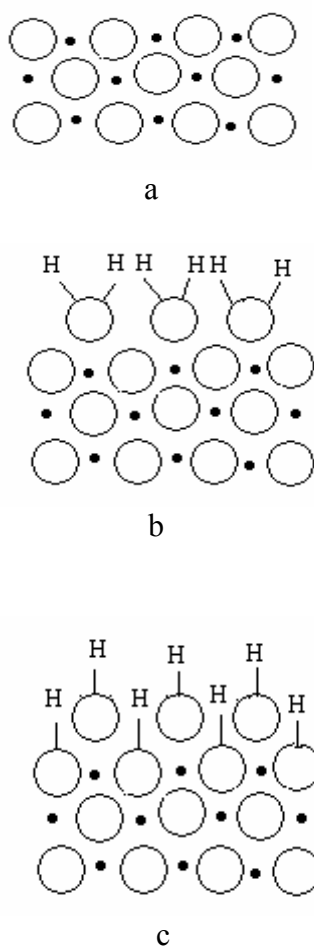


Figure 2.8. Cross section of the surface layer of a metal oxide. (•) Metal ions, (O) oxide ions. (a) The metal ions in the surface layer have a reduced coordination number and exhibit Lewis acidity. (b) In the presence of water, the surface metal ions may coordinate H<sub>2</sub>O molecules. (c) Dissociative chemisorption leads to a hydroxylated surface (Schindler, 1981).

2.4.1.2. Surface Complexes When the interaction of a surface functional group with an ion or molecule present in the soil solution creates a stable molecular entity, it is called surface complex. The overall reaction is referred to as surface complexation. There are two types of surface complexes that can form, outer-sphere and inner-sphere. Figure 2.9 shows outer- and inner-sphere complexes on an oxide surface (Sparks, 1995).

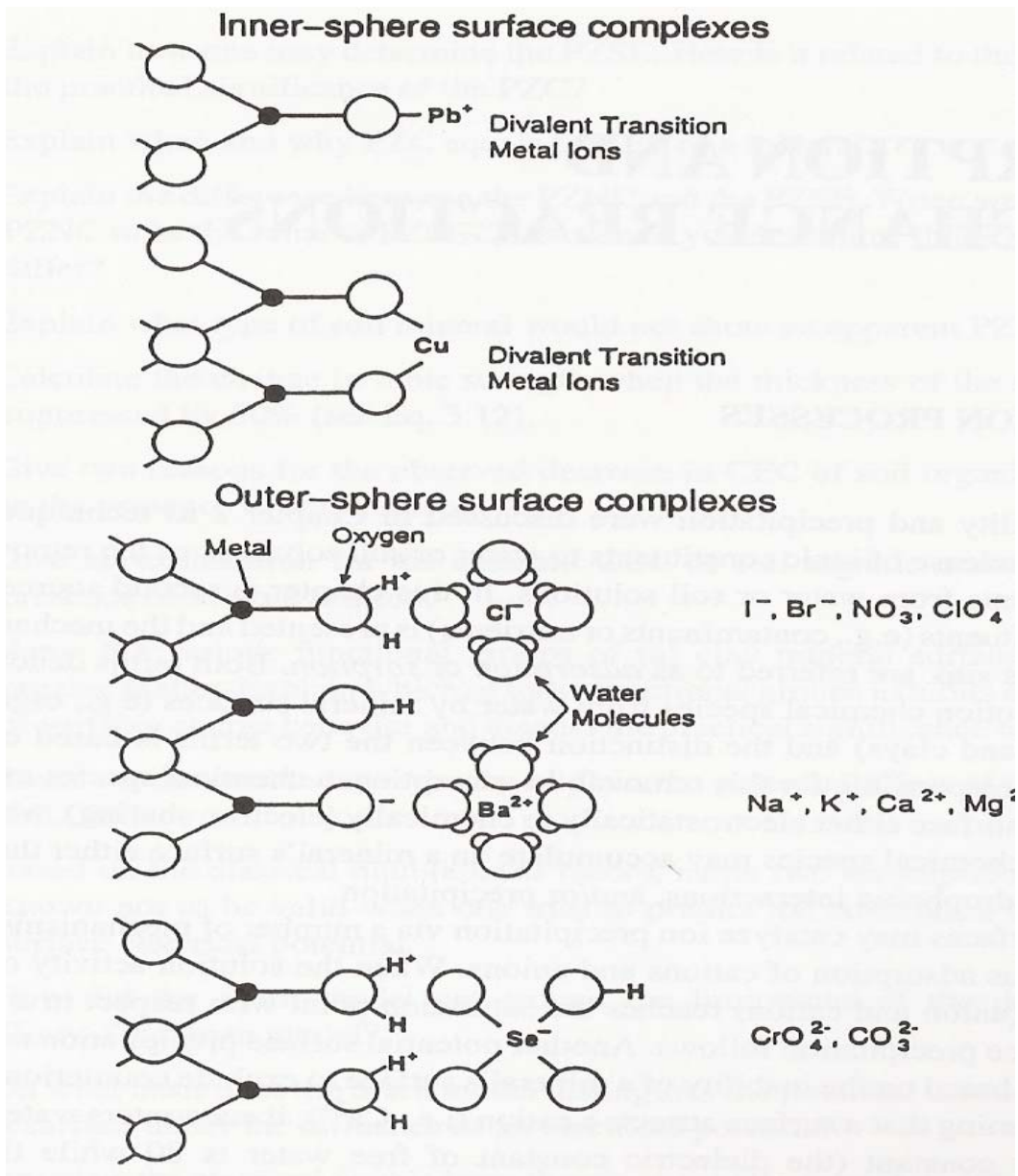


Figure 2.9. Schematic demonstrating inner- and outer sphere complexes between inorganic ions and hydroxyl groups of an oxide surface (Evangelou, 1998).

If a water molecule is present between the surface functional group and the bound ion or molecule, the surface complex is termed outer-sphere (Sposito, 1989). Outer-sphere complexation is usually a rapid process that is reversible, and adsorption via this mechanism is affected by ionic strength of the aqueous phase. Adsorption by outer-sphere complexation occurs only on surfaces that are of opposite charge to the adsorbate (Sparks, 1995).

If there is not a water molecule present between the ion or molecule and the surface functional group to which it is bound this is an inner-sphere complex. Inner-sphere complexation is usually slower than outer-sphere complexation; it is often not reversible and adsorption by this mechanism is weakly affected by the ionic strength of the aqueous phase. Inner-sphere complexation can increase, reduce, neutralize, or reverse the charge on the sorptive regardless of the original charge. Adsorption of ions via inner-sphere complexation can occur on a surface regardless of the surface charge. It is important to remember that outer- and inner-sphere complexation can, and often do, occur simultaneously (Sparks, 1995).

#### **2.4.2. Factors Affecting Adsorption**

Depending upon the properties of the adsorbate, adsorbent and solution adsorption is influenced by some factors.

2.4.2.1. Surface Area Adsorption is a surface phenomenon, the extent of adsorption is proportional to specific surface area. Specific surface area can be defined as that portion of the total surface area that is available for adsorption. Thus the amount of adsorption accomplished per unit weight of a solid adsorbent is greater the more finely divided and the more porous the solid (Weber, 1972). Particle sizes (Karickhoff et al., 1979) and particle volumes/surface diameters (Garbani and Lion, 1986) have been found to affect sorption capacities.

2.4.2.2. Nature of the Adsorbate The solubility of the solute is a factor controlling adsorption equilibria. There is an inverse relationship between the extent of the adsorption of a solute and its solubility in the solvent. As the solubility increases, the solute-solvent bond gets stronger, resulting in the extent of adsorption. In an aqueous solution, the more hydrophilic the solute, the less adsorption on adsorbent occurs. Another important parameter on adsorption is the polarity of adsorbent. In this case, the solute is strongly adsorbed from a non polar solvent. In most of the cases, water solubility is expected to increase due to increasing polarity, therefore a decrease in adsorption is expected to due to increasing polarity. Adsorbate dissociation is also important on sorption. The ionization of most weak acids and bases depends on the pH of the solution. Since the compounds are

simple in structure, adsorption for the charged species is at minimum and at maximum for the neutral species. When the compounds become more complex, the ionization effect becomes less (Nalçacioglu, 2003).

2.4.2.3. Temperature The effect of temperature on adsorption is ultimately linked to the thermodynamics of the adsorption process. Ionic or polar solutes probably shows temperature dependency. Adsorption reactions are normally exothermic. With decreasing temperature the extent of adsorption generally increases. Small variations in temperature do not alter the adsorption process to a significant extent (Weber, 1972).

2.4.2.4. pH The pH of the solution can control solubilization or agglomeration and therefore subsequent sedimentation of the metal species. The pH affects the bonding of metals to particulates because hydrogen ions influence adsorption and ion exchange by competing for active sites, modifying the sites, or changing the degree of proteolysis of the sorbing material. Generally, the adsorption of inorganic cations increases with increasing pH. (Bayat, 2002). As the pH increases, the surface charges and attractive forces become enlarged and metal ions will sorb on adsorbent more.

2.4.2.5. Ionic Strength The ionic strength of the solution may have several direct and indirect effects on adsorption data. The extent of these effects depend on the magnitude of the ionic strength and the concentration, composition, and charge of the ionic constituents. Ionic strength may have an effect on adsorption data in two ways:

- (a) by changing solute activity
- (b) by changing the thickness (and therefore properties) of the diffuse electrical double layers associated with colloidal particles.

As the ionic strength of the solution increases, because of the shielding effect of neighbouring ions the activity of most solutes show a decreasing tendency. But, a threshold ionic strength, some ionic constituents activities reverse themselves and steadily increase, finally exceed the original concentration activities (EPA, 1992).

2.4.2.6. Effect of Microbial Activities Degradation of organics within the waste by microbial action can cause the increase of acidity in the solution which causes the drop in pH and adsorption capacity of metals from the solution on solid waste. Sodium azide

( $\text{NaN}_3$ ) can be used in waste-solution mixture to suppress any microbial degradation (Hwang et al., 2002).

### 2.4.3. Adsorption Isotherms

An adsorption isotherm or curve is a graphic representation showing the amount of solute adsorbed by an adsorbing surface as a function of the equilibrium concentration of the solute. A sorption isotherm describes the relationship between the dissolved concentration of a given chemical species (adsorbate) in units of micrograms per liter ( $\mu\text{g/L}$ ), milligrams per liter ( $\text{mg/L}$ ), microequivalents per liter ( $\mu\text{equiv/L}$ ), or millimoles per liter ( $\text{mmol/L}$ ), and the sorbed quantity of the same species by the solid phase (adsorbent) in units of adsorbate per unit mass of adsorbent (solid) (e.g.  $\mu\text{g/kg}$ ,  $\text{mg/kg}$ ,  $\mu\text{eq/kg}$ , or  $\text{mmol/kg}$ ) at equilibrium under constant pressure and temperature. Sorption isotherms have been classified into four types, depending on their general shape (Fig. 2.10) (Myers, 1999).

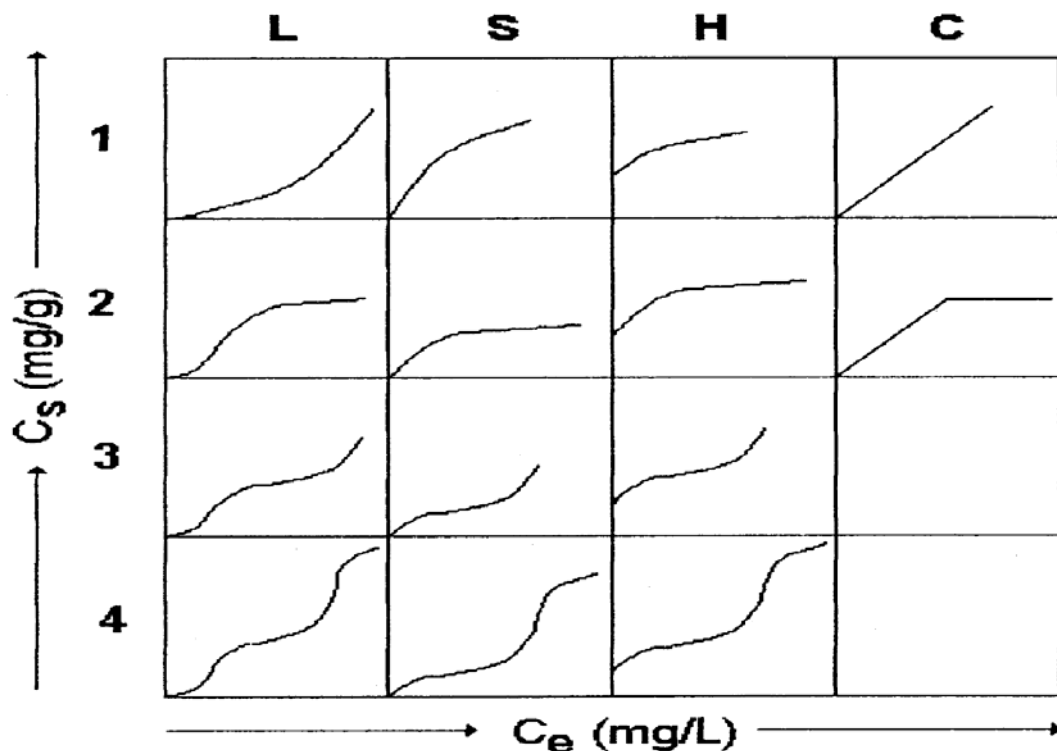


Figure 2.10. Classification of adsorption isotherms (Myers, 1999).

- L-type isotherm is characterized by an initial slope that does not increase with the concentration of adsorptive in the soil solution. This type of isotherm is the resultant effect of a high relative affinity of the soil particles for the adsorbate at low surface coverage

coupled with a decreasing amount of adsorbing surface remaining as the surface excess of the adsorbate increases (Sposito, 1998). As a result, L-type describes high-affinity adsorption between the adsorbate and adsorbent and usually indicates chemisorption (Evangelou, 1998).

- S-type isotherm is characterized by an initially small slope that increases with adsorptive concentration. This behavior suggests that the affinity of the soil particles for the adsorbate is less than that of the aqueous solution for the adsorptive (Sposito, 1998). This type of isotherm indicates that at low concentrations the surface has low affinity for the adsorptive which increases at higher concentrations (Sparks, 1995).

- C-type isotherm is characterized by an initial slope that remains independent of adsorptive concentration until the maximum possible adsorption is achieved (Sposito, 1998). The C-type isotherm is indicative of a partitioning mechanism whereby adsorptive ions or molecules are distributed or partitioned between the interfacial phase and bulk solution phase without any specific bonding between the adsorbent and adsorbate (Sparks, 1995).

- H-type isotherm is an extreme version of the L-type isotherm. Its characteristics large initial slope (in comparison with the L-type isotherm) suggests a very high relative affinity of the soil for an adsorbate. This condition is usually produced either by inner-sphere surface complexation or by significant van der Waals interactions in the adsorption process (Sposito, 1998).

Two major techniques commonly used to model soil adsorption or sorption equilibrium processes are (1) the Freundlich approach and (2) the Langmuir approach. Both involve adsorption or sorption isotherms.

2.4.3.1. Freundlich Equilibrium Approach The Freundlich or van Bemmelen equation is probably the oldest, most widely used adsorption equation, named after H. Freundlich (EPA, 1992). The Freundlich isotherm is originally of an empirical nature without a theoretical foundation, but later was interpreted as sorption to heterogeneous surfaces or surfaces supporting sites of varied affinities. It is assumed that sites having stronger binding are occupied first and that as the degree of site occupation increases the binding

strength decreases (Davis et al., 2003). The Freundlich isotherm has the general formula form:

$$q_A = K_F C_e^{1/n} \quad (\text{eq. 2.4})$$

where  $q_A$  is the amount of solute adsorbed per unit weight of solid adsorbent,  $K_F$  is the sorption capacity,  $n$  is the adsorption intensity and  $C_e$  is the equilibrium concentration of metal in solution.  $K_F$  can be determined from the intercept and  $1/n$  from the slope of its linear form which is obtained when  $\text{Log } q_A$  is plotted against  $\log C_e$ ;

$$\text{Log } q_A = \log K_F + 1/n \log C_e \quad (\text{eq. 2.5})$$

2.4.3.2. Langmuir Equilibrium Approach Langmuir derived the first isotherm model based on the assumption that only monolayer coverage on adsorbent surface and the heat of adsorption is independent of surface coverage, in 1918. This model contains very important assumptions, these are (Langmuir, 1918):

1. All molecules are adsorbed on definite sites of the adsorbent surface.
2. Each site can be occupied by only one molecule.
3. Equal adsorption energy in all sites.
4. There is no interaction between neighbouring adsorbed molecules.
5. Equilibrium is reached when the rate of adsorption of molecules onto surface is the same as the rate of desorption of molecules from the surface.
6. The rate at which adsorption proceeds is proportional to the driving force, which is the difference between the amount adsorbed at a particular concentration and the amount that can be adsorbed at that concentration.

The most commonly used expression of the Langmuir equation for solid-liquid systems can be generalized as ;

$$q_A = K_L M C_e / (1 + K_L C_e) \quad (\text{eq. 2.6})$$



where  $q_A$  is again the amount of solute adsorbed per unit weight of solid adsorbent,  $K_L$  is a term related to the binding energy of sorption and  $M$  is the adsorption maximum.  $K_L$  can be determined from the intercept and  $M$  from the slope of its traditional linear Langmuir form when  $C_e/q_A$  is plotted against  $C_e$ ;

$$C_e/q_A = 1 / K_L M + C_e / M \quad (\text{eq. 2.7})$$

However, all data in this work were examined using the Freundlich approach.

## 2.5 Desorption

While most studies in environmental soil chemistry have focused on the adsorption or sorption of ions and molecules on soils, the desorption process is also extremely important. This is particularly true for soils that are already contaminated. To predict the fate and mobility of contaminants in such soils and to develop sound and cost-effective remediation strategies, information on desorption is required. For example, if it is found that the contaminant is strongly bound to the soil and little if any desorption occurs, or if the desorption process is extremely slow, movement into groundwater may not be a problem. However, depending on the use of the soils, the persistence of the contaminant in the soil may present a problem for homosite construction or crop production. On the other hand, if desorption is effected easily, the contaminant could become mobile and contaminate water supplies. However, its ease of desorption could be an advantage in using remediation techniques such as leaching to decontaminate the soil (Sparks, 1995).

It is often observed that desorption is a more difficult process than adsorption and that not all of the adsorbate is desorbed, i.e., the reactions appear to be irreversible. Such apparent irreversibility is commonly referred to as hysteresis or nonsingularity. Thus, in such cases, the adsorption and desorption isotherms corresponding to the forward and backward reactions would not coincide (Verburg and Baveye, 1994). Such hysteresis is quite common with soil-pesticide interactions. There are a number of reasons that hysteresis may be observed, including artifacts related to experimental conditions such as failure to attain an adsorption equilibrium and chemical and microbial transformations that occur during particular experiment.

However, it appears that true hysteresis can occur, and that is dramatically affected by the type of adsorbent, especially humic substances, and time over which the adsorption process has occurred (Sparks, 1995).

## **3. MATERIALS AND METHODS**

### **3.1. Materials**

#### **3.1.1. Soil Samples**

Three soils were used in this study, one was from Bahcesehir ( 0-20 cm) , Istanbul in Marmara Region. It was collected from an area away from residential settlements. In this work, Bahçeşehir soil was referred to as Soil 1. The second and third samples were from Isparta from different locations and depths 0-20 cm and 20-60 cm, respectively. These were called as Soil 2 and 3, respectively.

#### **3.1.2. Copper**

Copper standard solution of 1000 mg/L concentration was purchased from Merck. For the experiments stock solutions (100 mg/L-250 mg/L) were prepared daily from the standard solution.

#### **3.1.3. Zinc**

Zinc standard solution of 1000 mg/L concentration was purchased from Merck. For the experiments stock solutions (100 mg/L-300 mg/L) were prepared daily from the standard solution.

#### **3.1.4. Nickel**

Nickel standard solution of 1000 mg/L concentration was purchased from Merck. For the experiments stock nickel solutions (150 mg/L) were prepared daily.

### **3.1.5. Calcium Nitrate ( $\text{CaN}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$ )**

$\text{CaN}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$  solution (0.01 M) was used in the adsorption experiment as background electrolyte supplied from Merck.

### **3.1.6. Barium Chloride ( $\text{BaCl}_2$ )**

$\text{BaCl}_2$  solution (0.1 mol/L and 0.0025 mol/L) was used in the cation exchange capacity analysis of soils, it was supplied from Merck.

### **3.1.7. Magnesium Sulfate ( $\text{MgSO}_4$ )**

$\text{MgSO}_4$  solution (0.0200 mol/L) was used in the cation exchange capacity analysis of soils, it was supplied from Merck.

### **3.1.8. Hydrochloric Acid (HCl)**

37 % HCl was used either in the cation exchange capacity analysis of soil or the determination of the initial heavy metal content of the soil by acid digestion method supplied from Merck. Besides, 0.1 M of HCl was prepared and used in the pH adjustment of the standard heavy metal solutions.

### **3.1.9. Acidified Lanthanum Solution (La)**

Acidified lanthanum solution (10 mg/L) was used in the cation exchange capacity analysis of soils purchased from Merck.

### **3.1.10. Hydrogen Peroxide ( $\text{H}_2\text{O}_2$ )**

30 %  $\text{H}_2\text{O}_2$  used in the initial heavy metal content determination of the soils by acid digestion method was supplied from Merck.

### **3.1.11. Nitric Acid (HNO<sub>3</sub>)**

65 % HNO<sub>3</sub> used in the initial heavy metal content determination of the soils by acid digestion method was supplied from Merck. Besides, 5 % of the HNO<sub>3</sub> solution was prepared for cleaning the glasswares.

### **3.1.12. Potassium Chloride (KCl)**

KCl (1 mol/L) was used in pH measurement of soils and it was supplied from Metrohm.

### **3.1.13. Calcium Chloride (CaCl<sub>2</sub>)**

CaCl<sub>2</sub> (0.01 mol/L) was used in pH measurement of soils and it was supplied from Merck.

### **3.1.14. Potassium Dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>)**

K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (1 N), which was used in the analysis of the organic matter content of the soils, was supplied from Merck.

### **3.1.15. Ferrous Ammonium Sulfate (Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O)**

Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.5 N) was used in the organic matter content analysis of soils supplied from Merck.

### **3.1.16. Phosphoric Acid (H<sub>3</sub>PO<sub>4</sub>)**

H<sub>3</sub>PO<sub>4</sub> was used in the determination of the soil organic matter content, it was supplied from Merck.

### 3.1.17. Diphenylamine Indicator ( $C_6H_5NHC_6H_5$ )

$C_6H_5NHC_6H_5$  indicator was prepared by using the diphenylamine in the analysis of the soil organic matter content supplied from Fischer Scientific Company.

### 3.1.18. Ammonium Fluoride ( $(NH_4)F$ )

$(NH_4)F$  was used in the soil organic matter determination, it was supplied from Merck.

### 3.1.19. Sulfuric Acid ( $H_2SO_4$ )

$H_2SO_4$  was used in the soil organic matter analysis and to stabilize the potassium dichromate solution. It was supplied from Tekkim Kimya Sanayi ve Ticaret Ltd.Sti.

### 3.1.20. Sodium Hydroxide ( $NaOH$ )

$NaOH$  (0.1 M) was used in the adsorption experiment so as to adjust the pH of the standard heavy metal solution.

### 3.1.21. Laboratory Equipment

WTW series Inolab pH/Cond 720 pH-meter : This pH – meter was used in order to adjust the pH of the standard solutions. The instrument was calibrated by using buffer solutions of pH 4.00 and 7.00.

Memmert Temperature Controlled Shaking Water Bath WB14 : This was used for the adsorption experiment to equilibrate the soil and the reactants.

Julabo Shaking Water Bath SW 22 : This was also used for the adsorption experiment to equilibrate the soil and the reactants.

AND GR-200 Analytical Balance: Balance was used for weighing certain amounts of soils and chemicals.

Benchtop Centrifuge Rotofix 32, HETTICH: Centrifuge was used to separate the soil from soil suspensions after the shaking period.

MSH Basic Yellow line hot plate and stirrer: It was used to digest the soil samples and stir the suspension.

Atomic Absorption Spectrophotometers (AAS):

(a) Perkin Elmer Analyst 300: It was used to determine the concentration of heavy metals in solutions.

(b) Varian SpectrAA 250 Plus : It was also used to determine the initial heavy metal content for each soil.

## **3.2. Experimental Procedures**

### **3.2.1. Methodology for Soil Analysis**

In order to specify the soil characteristics such as pH value, texture, soil OMC, organic carbon (OC), and CEC soil analyses were carried out. Initial heavy metal content of the soils were found out by acid digestion method using AAS.

### **3.2.2. pH Analysis**

The pH analysis of soils were carried out according to ISO 10390 standard test method. pH was measured separately in H<sub>2</sub>O, in aqueous 1 M KCl, and in aqueous 0.01 M CaCl<sub>2</sub> using 1:5 soil:solution mixture. A 10.0 g of air dried soil sample was weighed into a bottle and 50 mL of H<sub>2</sub>O, 1 M KCl, and 0.01 M CaCl<sub>2</sub> were added. The prepared soil suspension was mechanically shaken for 60±10 minutes at 130 rpm, and left for at least 1 hour. The electrode of the pH-meter was immersed into soil suspension and the measured values recorded as the equilibrium was reached.

### **3.2.3. Grain Size Analysis**

Particle size analysis was conducted to determine the relative proportions of different grain sizes that make up the soil. Therefore, mechanical analysis was carried out as outlined in ASTM D 422-63 (1990). It consists of a sieve analysis which measures the mass of soil retained on any sieve each having different mesh sizes. For the analysis, 300 g of the soils were weighed according to data given in Table 3.1 and passed through the sieves with numbers 4, 10, 20, 40, 60, 140, 200.



Table 3.1. Appropriate sample weights for different maximum particle sizes.

Maximum Particle Size	Minimum Sample Mass (g)
7.5 cm	6000
5 cm	4000
2.5 cm	200
1 cm	1000
Finer than No.4 sieve	200
Finer than No.10 sieve	100

### 3.2.4. Soil OMC

The OMC of the soil was determined according to standard method of Turkish Standard Institute (TSE) 8336 (1990) which is based on the Walkley-Black Method. For the analysis, 1.0 g of soil was weighed into a 500 mL erlenmeyer flask, to which 10 mL of 1 N potassium dichromate ( $K_2Cr_2O_7$ ) was added. A 20 ml of sulfuric acid solution was added and mixed by gentle rotation to disperse the soil in the solution, and let stand for 30 minutes. Solution was diluted to 200 mL with deionized water. 10 mL of phosphoric acid ( $H_3PO_4$ ), 0.2 g ammonium fluoride, and 10 drops of diphenylamine indicator ( $C_6H_5NHC_6H_5$ ) were added. Then, suspension was titrated with 0.5 N ferrous ammonium sulfate ( $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ ) (FAS) solution until the color changed from dull green to turbid blue. At this point, the titrating solution was added drop by drop until the end point was reached when as color shifted to a brilliant green. Assuming that 77 % of the organic matter was easily oxidizable, the carbon content was calculated as follows;

$$\% \text{ Organic carbon} = \frac{[(B - S) \times Nk \times 0.389]}{T} \quad (\text{eq. 3.1})$$

$B$  = mL of FAS used for blank

$S$  = mL of FAS used for sample

$Nk$  = Normality of FAS

$T$  = Weight of soil

Assuming that 58 % of organic matter consists of carbon, the organic matter content can be calculated as follows;

$$\% \text{ Organic matter} = 10 \left[ 1 - \left( \frac{S}{B} \right) \right] \times 0.67 \quad (\text{eq. 3.2})$$

$S$  = mL of FAS used while titrating the sample

$B$  = mL of FAS used while titrating the blank

OR

$$\% \text{ Organic matter} = \% \text{ Organic carbon} \times 1.724 \quad (\text{eq. 3.3})$$

### 3.2.5. CEC of Soil

The CEC analysis was carried out according to the international standard (ISO) ISO 11260:1994. For the analysis, 2.5 g of air dried soil (particle size < 2 mm) were transferred to a plastic erlenmeyer flask of about 100 mL capacity. The erlenmeyer flask and soil were weighed ( $m_1$ ). 30 mL of 0.1 mol/L  $\text{BaCl}_2$  were added to the soils and shaken for 1 hour. Then, they were centrifuged at 3000 rpm for 10 minutes. The supernatant liquid was transferred. Addition of 30 mL of 0.1 mol/L  $\text{BaCl}_2$ , shaking and centrifugation was repeated twice more. Then, 30 mL of 0.0025 mol/L  $\text{BaCl}_2$  solution was added to all the soil cakes and shaken overnight, centrifuged and the supernatant liquid decanted.

The flask with its contents and cover was weighed ( $m_2$ ). 30 mL of 0.020 mol/L  $\text{MgSO}_4$  solution was added to the soil cake and shaken overnight, centrifuged at 3000 rpm for 10 min. Supernatant solution was filtered. Blank was prepared by following the above procedure without addition of soil. 0.200 mL of the final filtrates of the soil samples and blanks were pipetted into individual 100 mL erlenmeyer flasks. 0.3 mL of the 0.1 mol/L  $\text{BaCl}_2$  solution was added. Finally, 10 mL of 10 mg/L acidified lanthanum solution was added to the each flasks, filled up to the mark with deionized water and mixed. The determination of the CEC of soils was performed by AAS (Perkin Elmer).

Calculation:

$$c_2 = \frac{c_1(30 + m_2 - m_1)}{30} \quad (\text{eq. 3.4})$$

where;

$c_2$  is the correct magnesium concentration in the sample, in milimoles per litre.

$c_1$  is the magnesium concentration in the sample, in milimoles per litre

$m_1$  is the mass of the centrifuged tube with air-dried soil, in grams

$m_2$  is the mass of the centrifuged tube with wet soil, in grams

CEC of the soils was calculated using the formula:

$$\text{CEC} = (cb_1 - c_2)3000/m \quad (\text{eq. 3.5})$$

where;

CEC is the cation exchange capacity of the soil, in centimoles positive charge per kilogram; (which is an absolute amount equivalent to the formerly used unit milielectrons per hundred grams)

$c_2$  is the correct magnesium concentration in the sample, in milimoles per litre.

$cb_1$  is the magnesium concentration in the blank, in milimoles per litre;

$m$  is the mass of the air-dried sample, in grams.

### 3.2.6. Acid Digestion Method for the Initial Heavy Metal Content in Soil

This method is a very strong acid digestion that will dissolve almost all elements that are environmentally available. The method was carried out as described in EPA 3050 B (1996). For the digestion of sample, 1 g of air dried soil was weighed into a 100 mL erlenmeyer flask. 10 mL of 1:1 HNO<sub>3</sub> was added and mixed, covered with a glass cover. Then, sample was heated to 95 °C ± 5 °C, refluxed for 10 to 15 minutes without boiling. Then, it was standing for a while to cool the sample. 5 mL of concentrated HNO<sub>3</sub> was added, the cover was replaced, and refluxed for 30 minutes. If brown fumes were generated, indicating oxidation of sample by HNO<sub>3</sub>, the step was repeated (addition of conc. HNO<sub>3</sub>) over and over until no brown fumes were given off by the sample indicating

the completion of reaction with  $\text{HNO}_3$ . Sample was heated at  $95^\circ\text{C}\pm 5^\circ\text{C}$  without boiling for 2 hours, and allowed to cool. 2 mL of deionized water and 3 mL of 30 %  $\text{H}_2\text{O}_2$  were added to the suspension. The flask was covered and put onto the heat and warmed a little bit to start the peroxide reaction. When the effervescence subsided the suspension was cooled. 1 mL of 30 %  $\text{H}_2\text{O}_2$  was added and warmed. Addition of 1 mL of 30 %  $\text{H}_2\text{O}_2$  was repeated until the effervescence was minimal or the general sample appearance was unchanged. Total addition of the  $\text{H}_2\text{O}_2$  must not exceed 10 mL. Then, sample was heated at  $95^\circ\text{C}\pm 5^\circ\text{C}$  without boiling for 2 hours, and allowed to cool again. 10 mL of HCl was added to the sample, after which it was refluxed at  $95^\circ\text{C}\pm 5^\circ\text{C}$  without boiling for 15 minutes, and allowed to cool. Then, suspension was filtered, collected, and analyzed by Varian AAS.

### 3.2.7. Adsorption Experiments

3.2.7.1. Preliminary Experiment The preliminary experiment was on the determination of the equilibrium time for soil. 20 mg/L of Cu solution was prepared from which 40 mL were added to plastic erlenmeyer flasks containing 2 g of air dried soil (<2mm) and placed in a mechanical shaker at 100 rpm and  $25^\circ\text{C}$  for 2, 4, 10, 24, 28, 34, 48, 52, and 72 hours. The pH of the solutions was determined before and after the shaking period to have an idea about the adsorption reaction between soil and heavy metal. Table 3.2. represents the soil-heavy metal interaction with time.

Table 3.2. Soil-heavy metal (Cu) interaction with time

<b>time (hour)</b>	<b>Concentration (mg/L)</b>
0	20
2	0.434
4	0.411
10	0.309
24	0.308
28	0.273
34	0.212
48	0.233
52	0.206
72	0.199

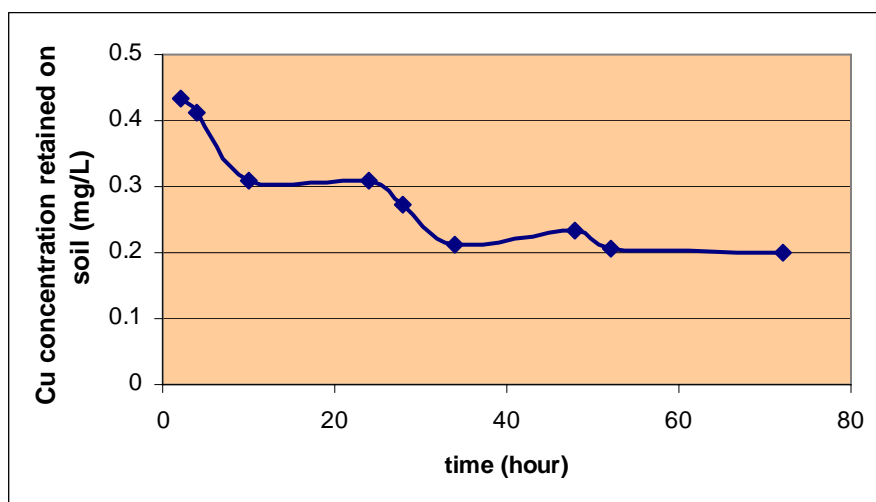


Figure 3.1. Determination of equilibrium time for soil.

According to Figure 3.1, equilibrium time is 48 hours. So, all the adsorption experiments were performed using this time period with different concentrations of three heavy metals.

**3.2.7.2. Adsorption Experiment** In order to determine the interaction between soil and metals, Cu, Zn and Ni, the following procedure was performed. The samples were prepared according to (V/m) ratio in which V represents the volume of heavy metal solution added to the soils with various concentrations (for Cu 20 mg/L, 50 mg/L, 75 mg/L, 100 mg/L, 150 mg/L, 200 mg/L; 50 mg/L, 100 mg/L, 150 mg/L, 200 mg/L, 250 mg/L and 300 mg/L for Zn and the concentrations for Ni are 15 mg/L, 30 mg/L, 45 mg/L, 60 mg/L, 75 mg/L, 90 mg/L) and m stands for the mass of the soil sample used. The standard solutions were used to prepare the stock solution (for Cu 100 mg/L and 250 mg/L, for Zn 200 mg/L and 300 mg/L, for Ni 150 mg/L) from which actual concentrations were prepared. The solutions were prepared by using the 0.01 M  $\text{Ca}(\text{NO}_3)_2$  as background electrolyte to minimize non-specific sorption of heavy metals due to ion exchange mechanisms (Carey et al. 1996) then added to plastic erlenmeyer flasks containing 2 g of air dried soil samples (< 2mm) at a soil:solution ratio 1:20 (Arias et al., 2005). pH values of the suspensions were recorded immediately after the solutions were added to the soil (before shaking period). Shaking was performed right after the pH measurement and continued for 48 hours at  $25 \pm 2^\circ\text{C}$ , 100 rpm. After the shaking period, pH of the suspensions were again recorded to see the difference, then centrifuged at  $1500 \times g$  for 10 minutes. Then, supernatants were filtered and acidified with concentrated  $\text{HNO}_3$  ( $\text{pH} < 2$ ),

and stored for AAS (Perkin Elmer). Competitive adsorption experiments were carried out as described above using the 1:1 ratio of heavy metals. All analysis were done in duplicate and the results represented the average of the two measurements.

### **3.2.8. Desorption Experiment**

Immediately after the adsorption experiment, desorption experiment was performed. For the analysis, 40 mL of heavy metal free 0.01 M  $\text{Ca}(\text{NO}_3)_2$  were added to the soil with the heavy metals and left to reach equilibrium for 48 hours. Then, suspensions were centrifuged, filtered, acidified, and stored as described above. Before and after the shaking period, pH of the solutions were recorded to see the difference. Competitive desorption experiments were performed as mentioned above.

## 4. RESULTS AND DISCUSSION

In this study, adsorption experiments were carried out to investigate soil behavior with respect to three different heavy metals: Cu, Zn, and Ni. The results were evaluated using isotherms and described by Freundlich adsorption models. Before starting the experiment, physicochemical properties and the equilibrium time of the soils were determined.

### 4.1. Soil Analysis

#### 4.1.1. pH Analysis

The pH of the soils was determined separately in water, in aqueous 1 M KCl, and in aqueous 0.01 M CaCl<sub>2</sub>. Soil pH is normally measured in soil-water slurry. However, sometimes the soluble salts may effect pH. In order to mask the effect of differential soluble salt concentrations in individual samples excess salt is provided in the slurry by using 0.01 M CaCl<sub>2</sub> and KCl solution instead of water (Özkaraova, 2001). According to the data given in the Table 4.1, for all soils the pH was higher for soil-water slurries than for soil-CaCl<sub>2</sub> and soil-KCl slurries. Soil 3 can be regarded as a neutral soil, whilst Soil 1 and Soil 2 as alkaline soils. The higher pH of Soil 1 is mainly due to its high CEC.

Table 4.1. pH values of the soil samples

	<b>Soil 1</b>	<b>Soil 2</b>	<b>Soil 3</b>
<b>pH in H<sub>2</sub>O</b>	8.12	8.04	7.17
<b>pH in KCl</b>	7.39	6.93	5.39
<b>pH in CaCl<sub>2</sub></b>	7.42	7.22	6.50

#### 4.1.2. Grain Size Analysis

In order to determine grain size distribution of soils mechanical analysis was carried out. The results of sieve analysis can be seen in the Table. 4.3. According to the data given in Table 4.2 all the soils had high sand percentages, with Soil 3 having the highest amount of sand.

Table 4.2. Soil texture percentages

<b>Soil texture</b>	<b>% Soil 1</b>	<b>% Soil 2</b>	<b>% Soil 3</b>
Gravel	25.99	17.30	13.66
Sand	72.55	78.70	87.74
Silt + clay	1.46	4.00	1.60

#### 4.1.3. Soil OMC

As outlined in section 3.2.4 OMC was determined and OMC and organic carbon (OC) content of soils can be seen in Table 4.3. Soil 2 and 3 can be considered as soils with relatively high OM, and Soil 1 as soil with moderate OMC. Generally, OM is present in higher amounts in fine-textured soils and in lower amounts in coarse-textured soils. Since they are all sandy soils, OMC could not be related to their textural properties. Thus, the variation in OMC might be related to the origin of soils (regional changes; Soil 2 and Soil 3 were from the same region, Soil 1 from a different region) or to the agricultural practices (Soil 2 was used for agricultural purposes), e.g. support with organic amendments or to the depths of the soils (Soil 1 and 2 were top soil, Soil 3 was sub soil).

Table 4.3. SOM and OC content of soils

<b>Soil</b>	<b>Soil organic matter (%)</b>	<b>Soil organic carbon (%)</b>
<b>Soil 1</b>	1.24	3.23
<b>Soil 2</b>	4.50	1.24
<b>Soil 3</b>	6.20	0.29



#### 4.1.4. CEC of Soil

The determination of CEC was carried out by saturating the soil sample with  $Mg^{2+}$ . When the saturation was completed, the amount of  $Mg^{2+}$  taken by the soil was determined by using AAS. To prepare the calibration curve for AAS, 0, 0.01, 0.02, 0.03, 0.04, and 0.05 mmol/L magnesium standard solutions were used and absorbances of these solutions were recorded (Table 4.5).

Duplicate analyses were performed and average values of CEC were determined to be 33.6 cmol+/kg, 23.8 cmol+/kg, and 22.3 cmol+/kg, for Soil 1, Soil 2 and Soil 3, respectively. The CEC of soils can be well related to their pH. Hence, the higher the pH value, the higher the CEC. This correlation can be explained by considering that pH is the main soil characteristic to influence the CEC of highly weathered soils and the dominant ionic forms in solution. (Tyler and McBride, 1982; King, 1988). CEC of soils were calculated using the formula as mentioned in section 3.2.5.

Table 4.4. Dry and wet weight of the tube and soils in grams.

Soil	Dry weight of tube and soil in grams ( $m_1$ )	Wet weight of tube and soil in grams ( $m_2$ )
Soil 1	24.68	26.73
Soil 2	24.75	26.32
Soil 3	24.59	26.38

Table 4.5. Absorbance values due to Mg content in calibration series

Mg concentration in mmol/L	0	0.01	0.02	0.03	0.04	0.05
Absorbance	0	0.052	0.105	0.151	0.202	0.243

The absorbance values of the standard solutions were plotted against their concentrations to prepare the calibration curve.

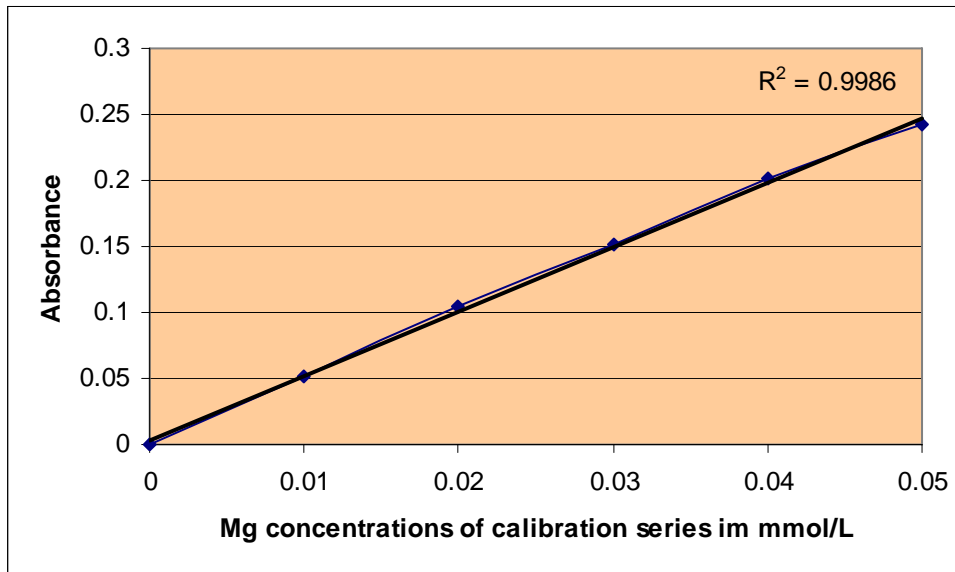


Figure 4.1. Absorbance vs. Mg concentration (mmol/L) calibration curve

Table 4.6. Mg concentrations in diluted samples and blanks

Samples	Mg concentrations (mmol/L)
Soil 1	0.015
Soil 2	0.023
Soil 3	0.024
Blank	0.044

According to formula which was previously mentioned in section 3.2.5, CEC of soils as follows.

Table 4.7. CEC of soils

Samples	CEC (cmol+/kg)
Soil 1	33.6
Soil 2	23.8
Soil 3	22.3

#### 4.1.5. Acid Digestion Method for the Initial Heavy Metal Content in Soil

The concentration of each heavy metal for each soil sample, determined by acid digestion method, is given in Table 4.8.

Table 4.8. Initial heavy metal content of soils

<b>Soil</b>	<b>Cu (mg/kg)</b>	<b>Zn (mg/kg)</b>	<b>Ni (mg/kg)</b>
<b>Soil 1</b>	0.45	3.93	1.47
<b>Soil 2</b>	1.61	5.65	1.39
<b>Soil 3</b>	0.67	6.75	1.39

Comparing the results in Table 4.8 with the maximum permissible limits for the pH range of the original soils used (Table 4.9), we can say that all three soils were free of heavy metals prior to the experiments.

Maximum permissible concentrations of potentially toxic elements (PTE) in soils after application of sewage sludge and maximum annual rates of addition are given in Table 4.9 (Department of the Environment, 1996).

Table 4.9. Maximum permissible limits of Cu, Zn and Ni in soils

<b>Soil pH values</b>	<b>Cu (mg/kg)</b>	<b>Ni (mg/kg)</b>	<b>Zn (mg/kg)</b>
<b>5.0-5.5</b>	80	50	200
<b>5.5-6.0</b>	100	60	200
<b>6.0-7.0</b>	135	75	200
<b>&gt;7.0</b>	200	110	300

## 4.2. Adsorption Experiments

Adsorption experiments were performed as described in the materials and methods section. According to data evaluation, equilibrium was reached in 48 hours.  $C_i$ ,  $C_e$  and  $C_s$  values for each soil are given in Tables 4.17-4.19.  $C_i$  is the initial heavy metal concentration,  $C_e$  is the concentration of heavy metals remaining in the aqueous solution after the metals are sorbed on the soils at equilibrium, and  $C_s$  is the content of the metals adsorbed per gram of soils.  $C_s$  was calculated from the difference between the initial  $C_i$  and the equilibrium  $C_e$  concentrations of the metals.  $C_e$  versus  $C_s$  plots are given in Figures 4.2-4.23. Examples to plots of  $\ln C_s$  versus  $\ln C_e$  are given in Appendix A.

### 4.2.1. Adsorption Behavior for Soil 1

4.2.1.1. Adsorption of Cu The adsorption experiment of Cu on soils were examined within a concentration range of 20-200 mg/L, considering the permissible limits in terms of soil pH, given in the Table 4.9.

In Soil 1, Cu experiments were performed within the three different Cu solutions: a) low range Cu concentrations (20-200 mg/L), b) high range Cu concentrations (300-800 mg/L) with low Cu solution pH (where  $\text{pH} < 1$ ), and c) high range Cu concentrations (300-800 mg/L) with high Cu solution pH (where  $6 < \text{pH} < 7$ ).

For low range adsorption, the value  $\ln C_e$  was negative, indicating most of the Cu initially added to the soil was adsorbed. Hence, low and high range Cu concentration experiments were carried out in order to make a precise conclusion about Cu. Copper adsorption was observed to decrease in the following order: high range Cu concentrations with high Cu solution  $\text{pH} >$  high range Cu concentrations with low Cu solution pH. As can be seen in Table 4.10,  $R^2$  values were 0.96 and 0.94,  $K_f$  values were 4359 and 89 in the same sequence. Low  $K_f$  values indicate that most of the metals remain in the solution and are available for transport, chemical processes, and plant uptake; on the other hand, high values of  $K_f$  reflect a large affinity of solid soil components for the metals (Li et al, 2007).

Table 4.10. Freundlich Adsorption Capacity ( $K_f$ ) and Intensity ( $n$ ) of Cu for Soil 1

Soil 1	$\ln K_f$	$K_f$	$n$	$R^2$
low range (pH<1)	8.03	3072	0.58	0.90
high range with low sol. pH (pH<1)	4.49	89	0.74	0.94
high range with high sol. pH (6<pH<7)	8.38	4359	0.25	0.96

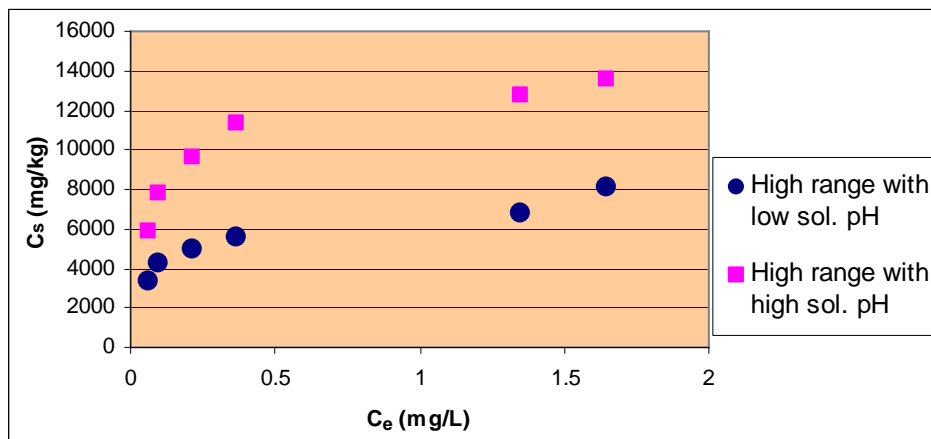


Figure 4.2. Linear Adsorption Isotherm of Cu (high range) on Soil 1

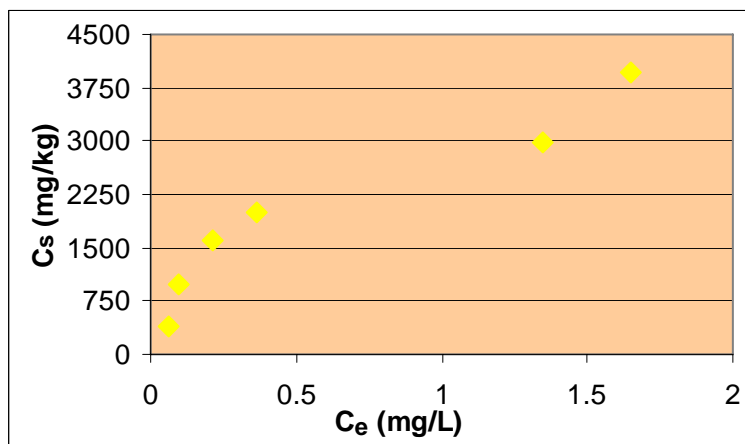


Figure 4.3. Linear Adsorption Isotherm of Cu (low range) on Soil 1

**4.2.1.2. Adsorption of Zn and Ni** The adsorption of Zn and Ni on Soil 1 were carried out within the concentration range of 50-250 mg/L and 15-90 mg/L, respectively, considering permissible limits in terms of soil pH.

Table 4.11. Freundlich Adsorption Capacity ( $K_f$ ) and Intensity ( $n$ ) of Zn and Ni on Soil 1

Soil 1	$\ln K_f$	$K_f$	$n$	$R^2$
Zn (pH<1)	6.14	464	0.35	0.97
Ni (pH<1)	5.73	308	0.43	0.99

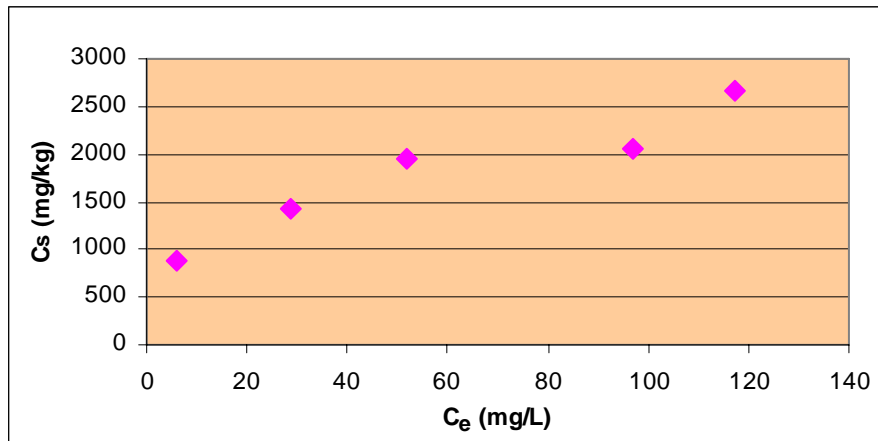


Figure 4.4. Linear Adsorption Isotherm of Zn for Soil 1

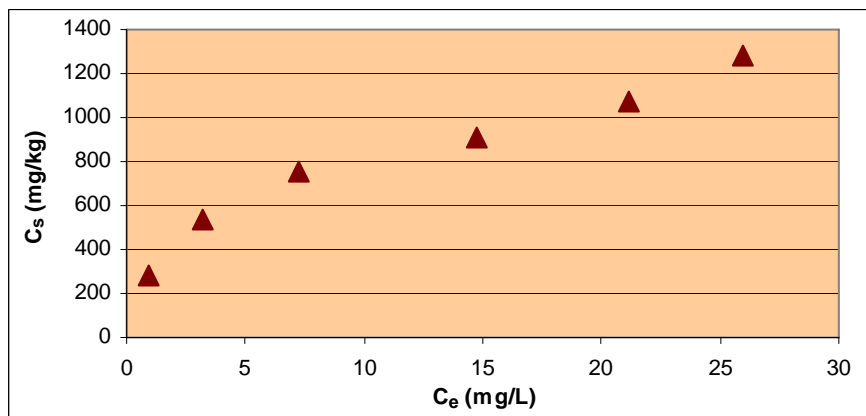


Figure 4.5. Linear Adsorption Isotherm of Ni for Soil 1

#### 4.2.2. Adsorption Behavior for Soil 2

4.2.2.1. Adsorption of Cu, Zn and Ni The adsorption experiments of metals on Soil 2 were performed as described for Soil 1. Only low range Cu concentrations were used in this part of the study.

Table 4.12. Freundlich Adsorption Capacity ( $K_f$ ) and Intensity ( $n$ ) for Cu, Zn and Ni on Soil 2

Soil 2	$\ln K_f$	$K_f$	$n$	$R^2$
Cu (pH<1)	6.46	639	0.17	0.96
Zn (pH<1)	3.07	22	0.69	0.94
Ni (pH<1)	3.47	32	0.50	0.96

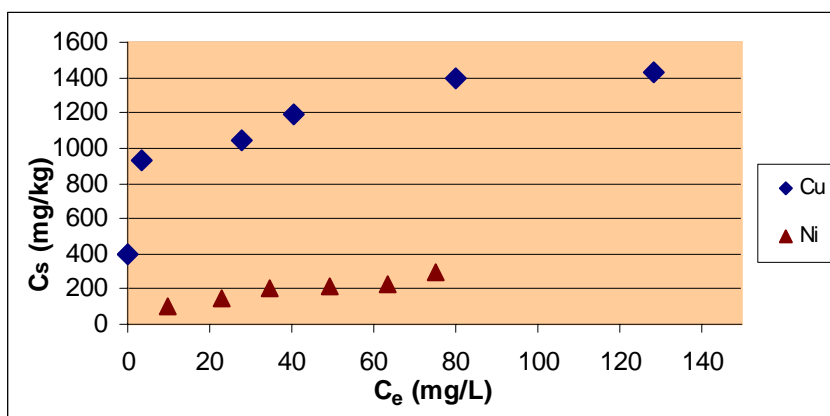


Figure 4.6. Linear Adsorption Isotherm of Cu and Ni for Soil 2

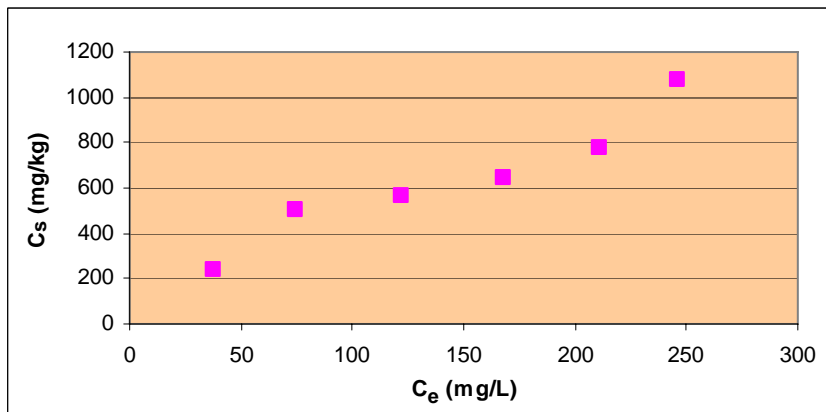


Figure 4.7. Linear Adsorption Isotherm of Zn for Soil 2

### 4.2.3. Adsorption Behavior for Soil 3

**4.2.3.1. Adsorption of Cu, Zn and Ni** The adsorption experiments of metals on Soil 2 were performed as described Soil 1. Only low range Cu concentrations were used in this part of the study.

Table 4.13. Freundlich Adsorption Capacity ( $K_f$ ) and Intensity ( $n$ ) for Cu, Zn and Ni on Soil 3

Soil 3	$\ln K_f$	$K_f$	$n$	$R^2$
Cu (pH<1)	5.30	200	0.40	1.00
Zn (pH<1)	4.15	63	0.28	0.90
Ni (pH<1)	4.00	55	0.33	0.97

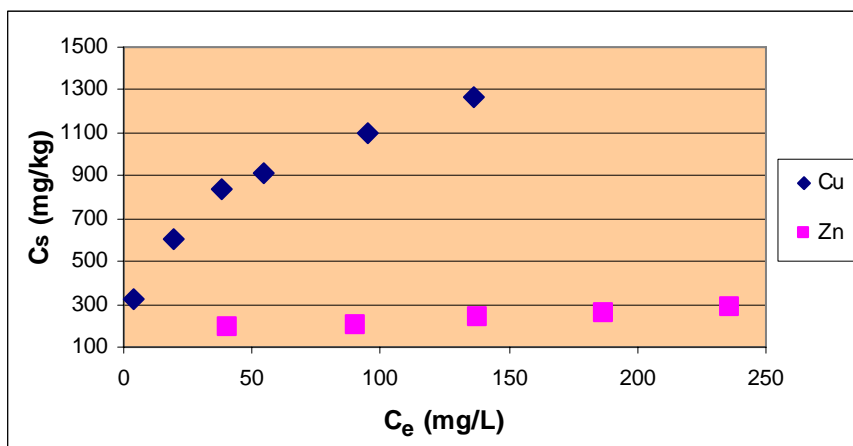


Figure 4.8. Linear Adsorption Isotherm of Cu and Zn for Soil 3

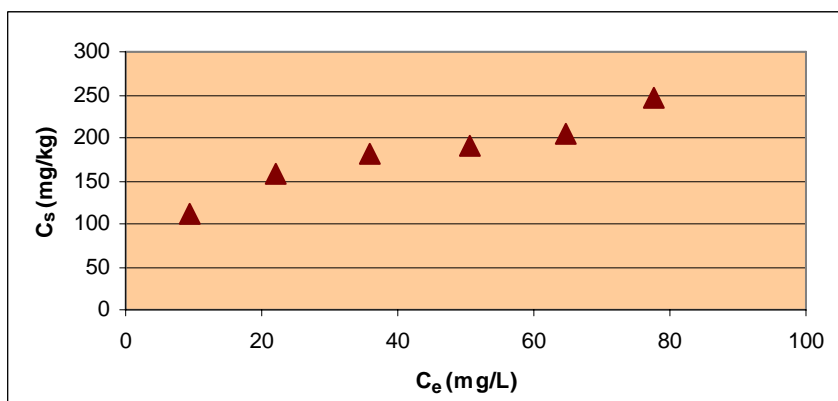


Figure 4.9. Linear Adsorption Isotherm of Ni for Soil 3



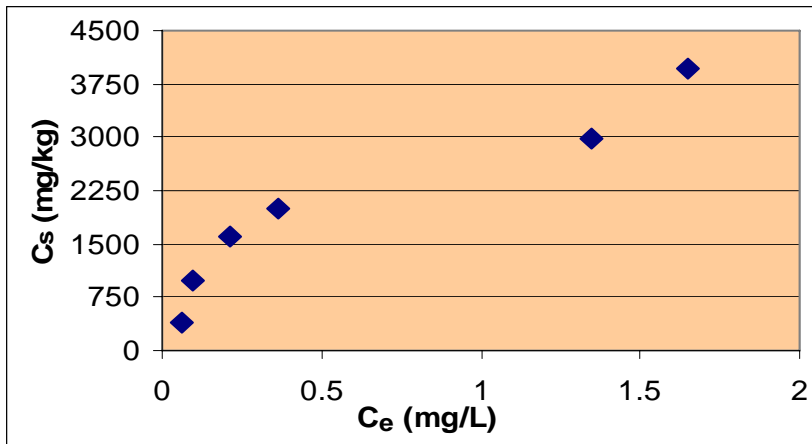


Figure 4.10. Linear Adsorption Isotherm of Cu for Soil 1

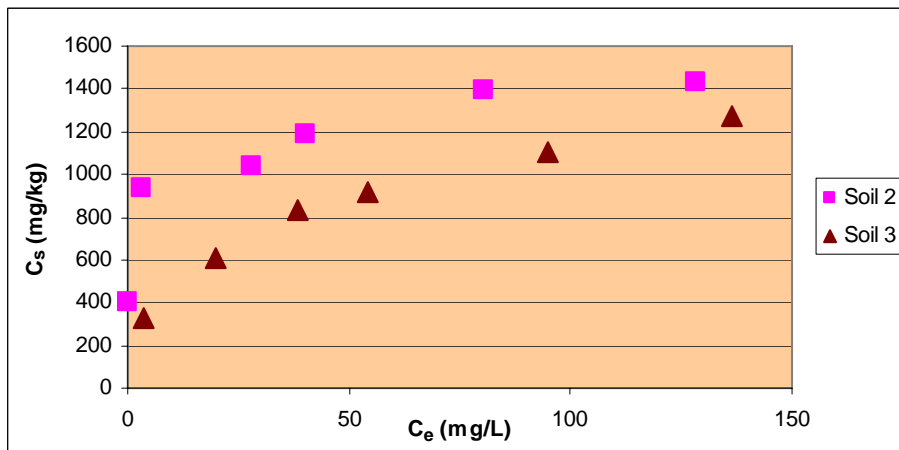


Figure 4.11. Linear Adsorption Isotherm of Cu for Soil 2, and 3

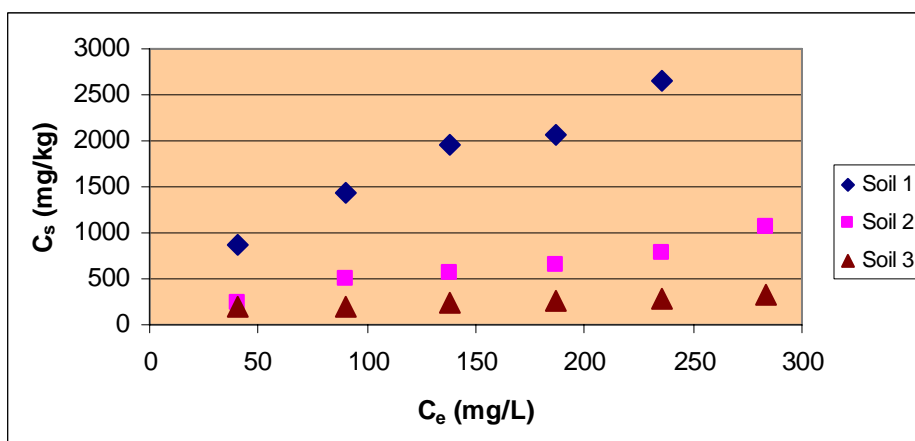


Figure 4.12. Linear Adsorption Isotherm of Zn for Soil 1, 2, and 3

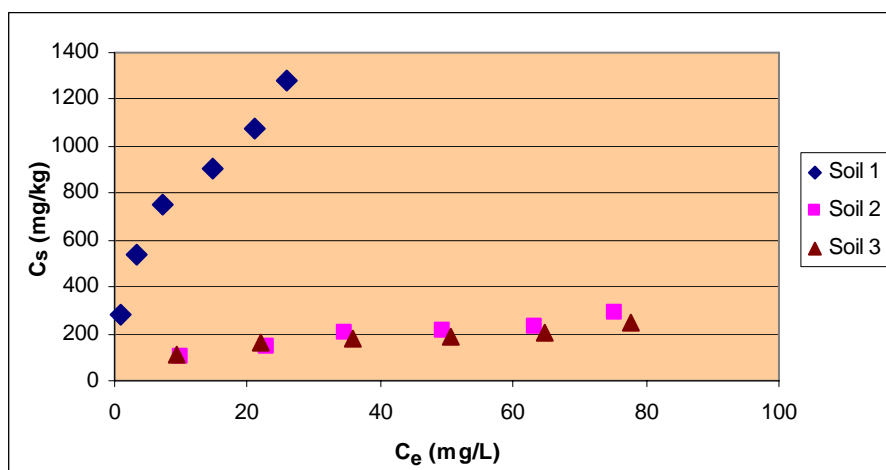


Figure 4.13. Linear Adsorption Isotherm of Ni for Soil 1, 2, and 3

Adsorption of each heavy metal, i.e. Cu, Zn, and Ni, on soils increased as their initial concentration increased. Adsorption capacity of these metals increased as the soil was changed in the order Soil 1, Soil 2, and Soil 3. This was not surprising since Soil 1 has the highest CEC (>30) and pH values (>8). This correlation can be explained by considering that pH is the main soil characteristic to influence the CEC of highly weathered soils and the dominant ionic forms in solution. The pH and CEC are, almost always, reported as soil characteristics to show good association to soil adsorption of elements (Tyler and McBride, 1982; King, 1988).

Among the heavy metals, Cu was adsorbed to higher extent than Zn and Ni in all the soils. In Soil 1, and 3 adsorption order were Cu>Zn>Ni while in Soil 2 Cu>Ni>Zn.  $K_f$  values for Cu were higher than others for all the soils, as expected, since it was more adsorbed. In this work, the Cu, Zn and Ni adsorption data were fitted satisfactorily by Freundlich model ( $R^2$  between 0.90- 1.00 for Cu, 0.90- 0.97 for Zn, 0.96-0.99 for Ni). The Freundlich equation is often useful for modeling adsorption onto solids with heterogeneous surfaces and has frequently proved superior to the Langmuir equation for adsorption of cations or anions on soils.

As already mentioned, adsorption of heavy metal ions on soils and soil constituents is influenced by a variety of parameters, the most important ones being pH, OMC, CEC, and soil composition. This work indicated that, there was no correlation between the OMC, grain size of the soils and metal adsorption, and this is in agreement with the literature (Harter, 1979, 1983). If these parameters were dominant, adsorption of metals would have

been the highest for Soil 3 because of the highest OMC being greater than 6. Besides, Leyva-Ramos et al. (2004) report that decreasing the grain size does not increase the adsorption capacity. This work designated the same result, although Soil 2 had the highest silt+clay content (%4), adsorption of metals was not high compared to Soil 1. However, It was revealed that, adsorption of metals was influenced by pH and CEC as Gürel, (2006) reported.

As mentioned before section 2.4.3, adsorption isotherms of soils can be classified according to their shapes. In Soil 1, Cu adsorption was consistent with S-type isotherm for all adsorption experiments. Both Zn and Ni adsorption experiment curves were H-type. In Soil 2, all three metals showed H-type. In Soil 3, Cu was S-type, whereas Zn and Ni were H-type. Figure 4.10 represents the S-type isotherm for low range Cu in Soil 1. This type of isotherm indicates that at low concentrations the surface has low affinity for the adsorptive which increases at higher concentrations (Sparks, 1995). Figure 4.9. represents the H-type isotherm for Ni in Soil 3. Its characteristics large initial slope (in comparison with the L-type isotherm) suggests a very high relative affinity of the soil for an adsorbate (Sposito, 1998).

#### 4.2.4. Competitive Adsorption Behavior for Soils

Competitive adsorption experiments in which all three metals were introduced into the soil together, were carried out as outlined in section 3.2.7.2.

Table 4.14. Freundlich Adsorption Capacity ( $K_f$ ) and Intensity ( $n$ ) for Cu, Zn and Ni in competition on Soil 1

Soil 1	$\ln K_f$	$K_f$	$n$	$R^2$
<b>Cu</b>	8.6	5452	0.5	0.97
<b>Zn</b>	7.5	1808	0.4	0.94
<b>Ni</b>	7.0	1097	0.3	0.92

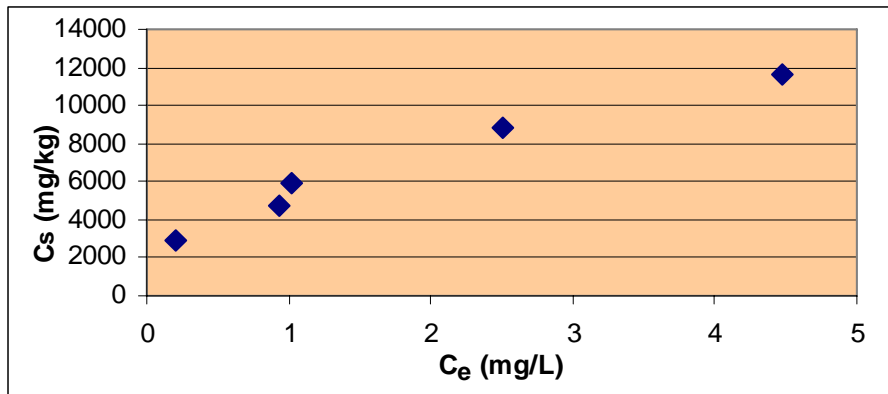


Figure 4.14. Competitive Adsorption Isotherm of Cu for Soil 1

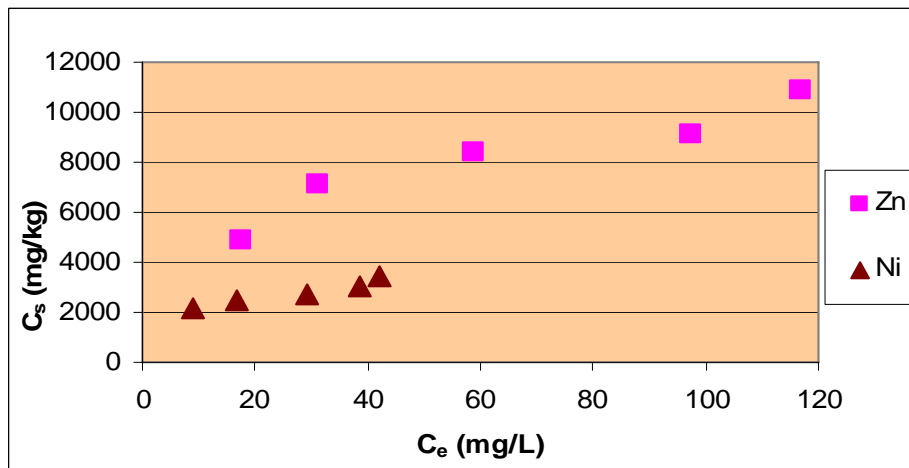


Figure 4.15. Competitive Adsorption Isotherms of Zn and Ni for Soil 1

Since the  $C_e$  scale of the Cu results were very different from the Zn and Ni results, Cu results were plotted separately on Figure 4.14.

Table 4.15. Freundlich Adsorption Capacity ( $K_f$ ) and Intensity ( $n$ ) for Cu, Zn and Ni in competition on Soil 2.

Soil 2	$\ln K_f$	$K_f$	$n$	$R^2$
Cu	6.90	992	0.40	0.96
Zn	4.76	117	0.72	0.92
Ni	3.40	30	1.40	0.93

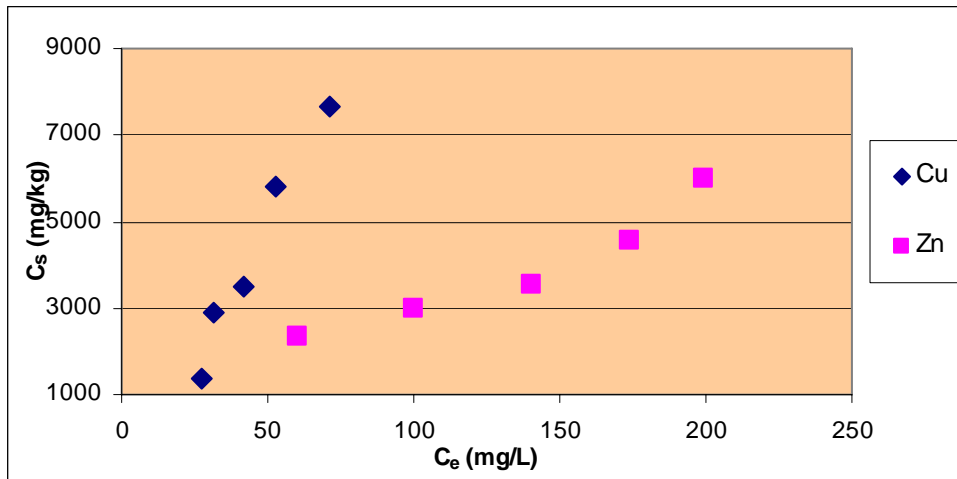


Figure 4.16. Competitive Adsorption Isotherms of Cu and Zn for Soil 2

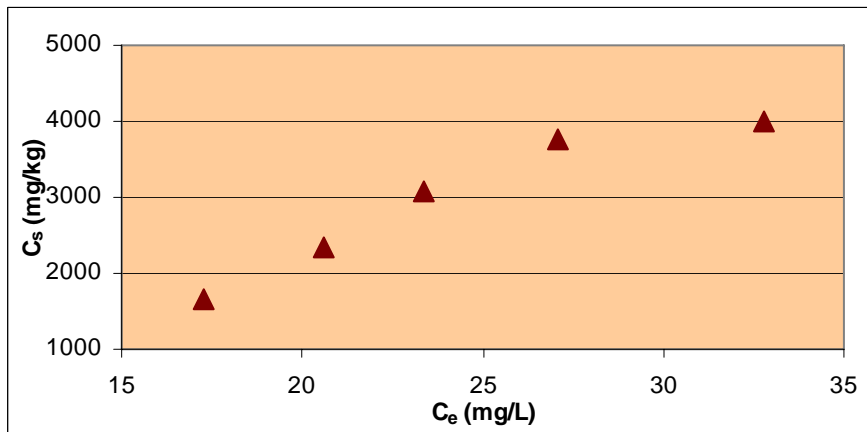


Figure 4.17. Competitive Adsorption Isotherms of Ni for Soil 2

Since the  $C_e$  scale of the Ni results were very different from the Cu and Zn results, Ni results were plotted separately on Figure 4.14.

Table 4.16. Freundlich Adsorption Capacity ( $K_f$ ) and Intensity ( $n$ ) for Cu, Zn and Ni in competition on Soil 3

Soil 3	$\ln K_f$	$K_f$	$n$	$R^2$
Cu	4.73	113	0.97	1.00
Zn	1.59	5	1.57	0.93
Ni	5.58	265	0.30	0.98

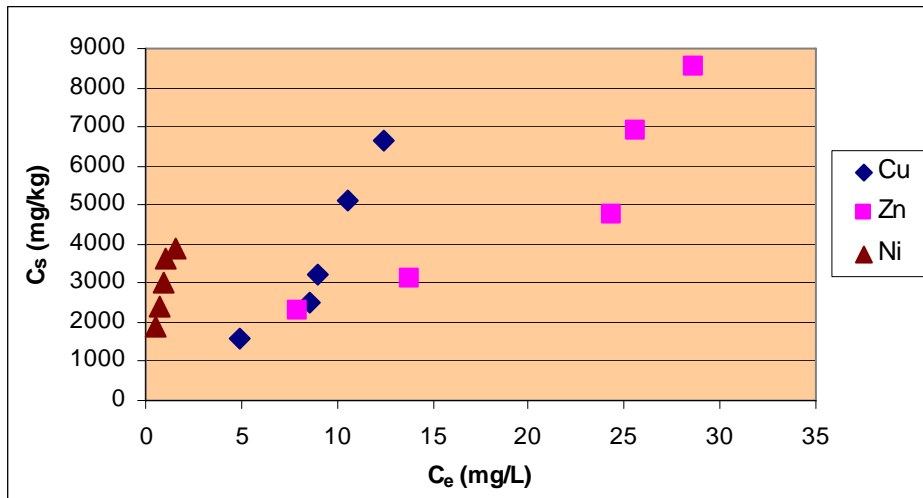


Figure 4.18. Competitive Adsorption Isotherms of Cu, Zn, and Ni for Soil 3

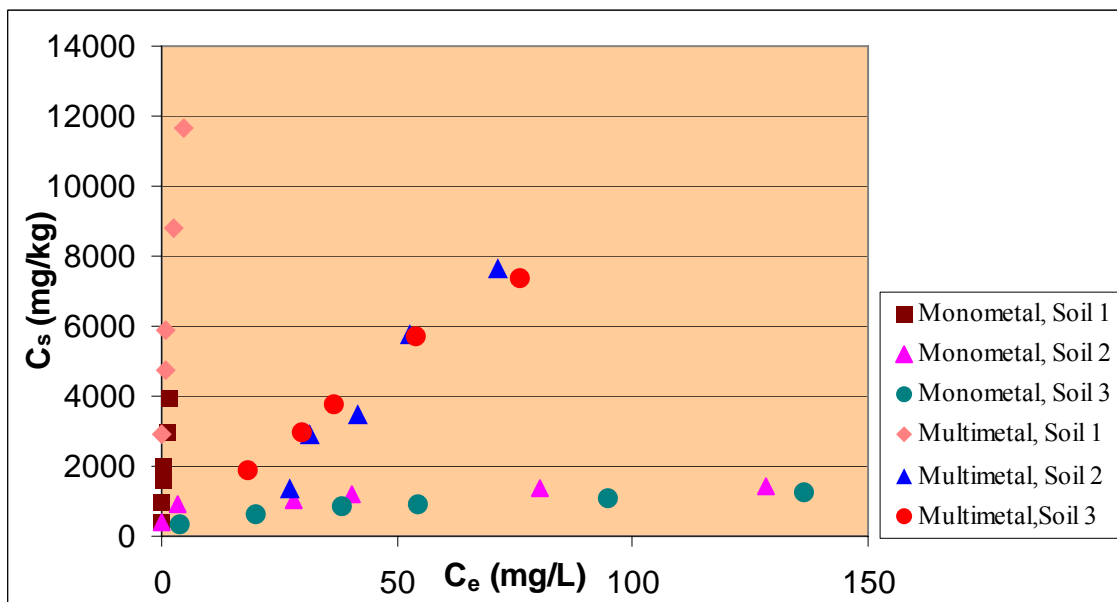


Figure 4.19. Monometal-competitive multimetal Linear Adsorption Isotherms for Cu for all Soils

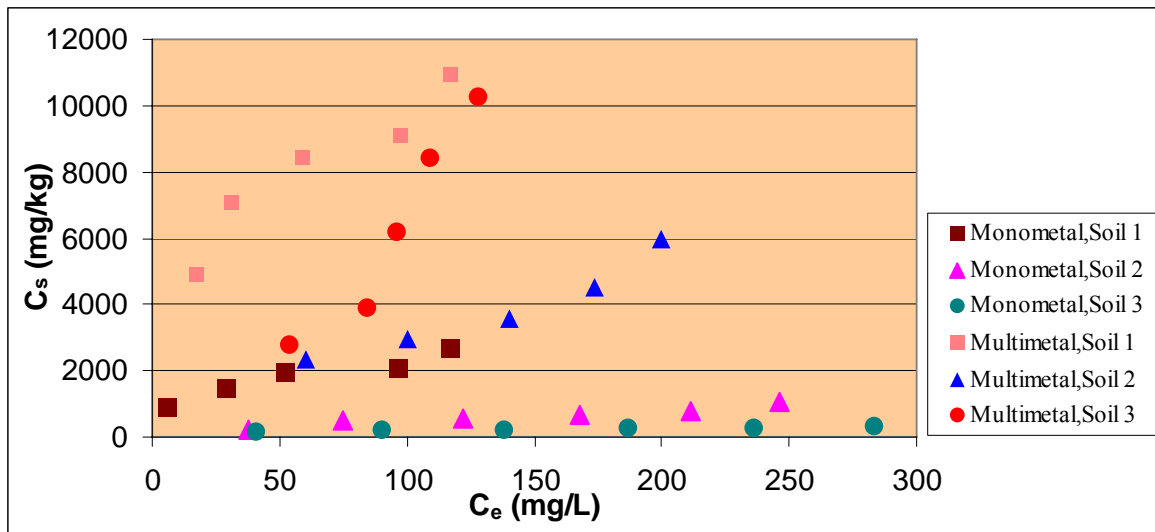


Figure 4.20. Monometal-competitive multimetal Linear Adsorption Isotherms of Zn for Soils

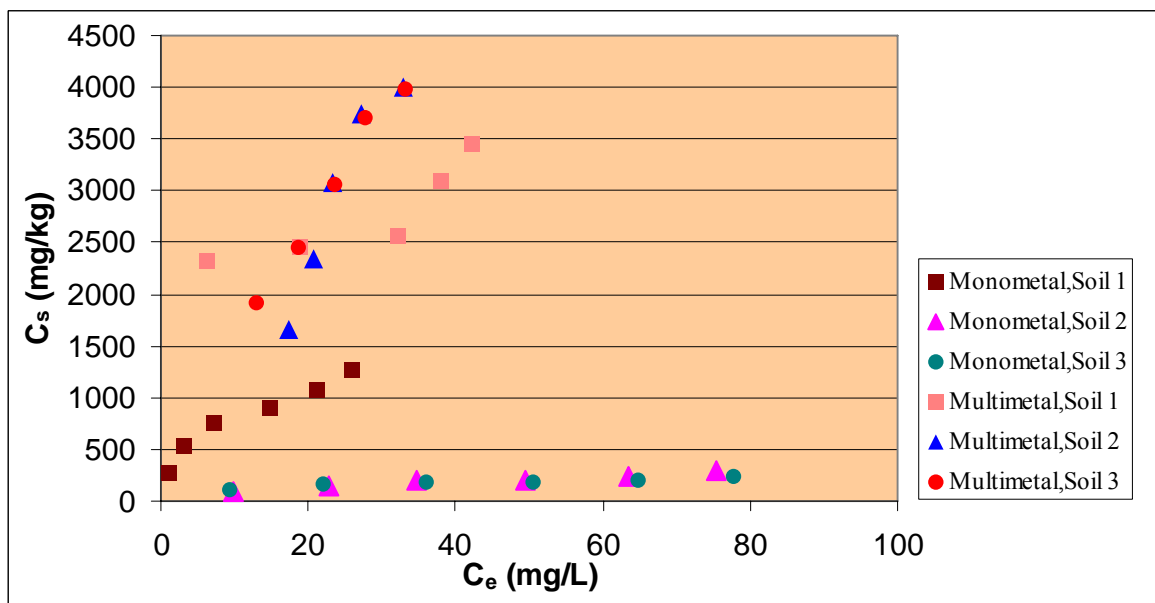


Figure 4.21. Monometal-competitive multimetal Linear Adsorption Isotherms of Ni for Soils

In the monometal adsorption experiments, adsorption of each heavy metal on soil increased as the initial metal concentration increased. In Soil 1, Cu was adsorbed more than Zn and Ni. In Soil 2 Ni and Cu were in competition with each other initially. As the concentrations increased, Cu was adsorbed more than Ni. This is because, the sorption intensity of heavy metals decreased with increasing original concentration treatment. When the original concentrations were at high levels, the sorbed amounts by the soil of the strong sorption metal group (Cu, Cr, and Pb) evidently increased. As a result, the sorption

intensity of 'strong sorption metals' increased. On the other hand, when the original metal concentrations in treatment solutions (ie. pollutant solutions) were at high levels, the sorbed amount of weak sorption metal group (Cd, Ni, and Zn) increased slightly. As a result, the sorption intensity of 'weak sorption metals' decreased (Li et al, 2007).

In Soil 1, 2 and 3, adsorption order was Cu>Zn>Ni in monometal system. However, this sequence was changed for Soil 3 in competitive multimetal system, but stayed same for Soil 1 and Soil 2. This might be because of charge forces, molecular size of the metals and chemical bonding. According to literature survey, in most of the cases adsorption order is Cu>Zn>Ni. However, Antoniadis et al. (2007) reported that, metal sorption can not solely be predicted by any given affinity sequence model. For instance, when metal adsorption is covalent, affinity sequence is Cd>Ni>Zn (Gomes et al., 2001). If metal adsorption was entirely electrostatic, that would predict a different sequence: Ni>Zn>Cd (Antoniadis et al., 2007). In our work, more Ni was adsorbed in competitive multimetal system in Soil 3. Cu was more adsorbed in competitive multimetal system in Soils 1 and 2. Adsorption of all the three heavy metal was increased in competitive multimetal system.

The Cu, Zn and Ni competitive adsorption data were fitted satisfactorily by Freundlich model. For instance,  $K_f$  value for Cu, were higher than others for the Soil 1 as expected since it was more adsorbed.  $R^2$  value was also higher than others,  $n$  values were in the reverse direction for heavy metals for Soil 1 in terms of adsorption. Fontes et al. (2003) reported that, competition among heavy metals is very strong in soils with lower capacity to hold metal cations in which more Ni and Zn are dislocated from the adsorption complex and substituted by Cu. In a field situation, this could impose a much higher risk of contamination of aquifers, creeks, groundwaters etc., through leaching of these heavy metals in the soil profile and also a much higher risk of making them available for plant uptake by plants.

If a comparison is made among the monometal and competitive multimetal systems in terms of adsorption of heavy metals, we can say that more Cu, Zn and Ni were adsorbed in competitive multielement system in Soil 1, where the more nickel was adsorbed in Soil 3.



In this work sorption intensity was also calculated. The sorption intensity is the ratio of the quantity adsorbed in the solid phase to the initial solution quantity (Xiong et al., 2005). This way the ability of soil to sorb different metals from the mixed solution was calculated for both metals and soils. The sorption intensity is calculated by taking the difference between the original treatment concentration of each metal and its supernatant concentration, then dividing the difference by the original treatment concentration, and then expressing this as a percentage. The  $C_i$  and  $C_e$  values can be seen in Tables 4.17-4.19.

Five sets of treatments were used in the competitive multimetal adsorption studies. The concentrations of each metal ions in the initial treatment solution is indicated in Table 4.17-19 in which Cu concentration in treatment 1 was 50 mg/L, Zn concentration was 100 mg/L, Ni concentration was 45 mg/L for all soils. In treatment 2, Cu concentration was 80 mg/L, Zn concentration was 150 mg/L, Ni concentration was 60 mg/L.

Table 4.17.  $C_i$ ,  $C_e$  and  $C_s$  values of Cu for Soils.

(Treatment)	Soil 1		Soil 2		Soil 3	
	$C_e$ (mg/L)	$C_s$ (mg/kg)	$C_e$ (mg/L)	$C_s$ (mg/kg)	$C_e$ (mg/L)	$C_s$ (mg/kg)
(1) 50	0.20	2933.80	27.38	1349.14	18.18	1897.73
(2) 80	0.94	4714.67	31.58	2887.60	29.80	2993.44
(3) 100	1.02	5902.21	41.47	3490.46	36.60	3780.56
(4) 150	2.50	8795.23	52.88	5791.59	53.88	5731.96
(5) 200	4.47	11659.45	71.50	7662.49	76.05	7391.17

Table 4.18.  $C_i$ ,  $C_e$  and  $C_s$  values of Zn for Soils.

(Treatment)	Soil 1		Soil 2		Soil 3	
	$C_e$ (mg/L)	$C_s$ (mg/kg)	$C_e$ (mg/L)	$C_s$ (mg/kg)	$C_e$ (mg/L)	$C_s$ (mg/kg)
(1) 100	17.50	4919.50	60.40	2361.36	53.40	2778.77
(2) 150	31.08	7091.53	100.00	2981.51	84.17	3925.58
(3) 200	58.80	8419.80	140.42	3552.77	96.04	6199.17
(4) 250	97.36	9101.79	173.75	4546.81	108.96	8410.55
(5) 300	116.98	10913.54	199.58	5988.07	127.92	10261.18

Table 4.19.  $C_i$ ,  $C_e$  and  $C_s$  values of Ni for Soils.

(Treatment)	Soil 1		Soil 2		Soil 3	
	$C_e$ (mg/L)	$C_s$ (mg/kg)	$C_e$ (mg/L)	$C_s$ (mg/kg)	$C_e$ (mg/L)	$C_s$ (mg/kg)
(1) 45	9.11	2139.95	17.29	1652.36	12.94	1911.90
(2) 60	16.85	2453.79	20.60	2349.43	18.73	2461.24
(3) 75	29.08	2738.22	23.38	3078.41	23.55	3067.98
(4) 90	38.54	3068.57	27.10	3750.75	27.70	3714.97
(5) 100	42.20	3446.63	32.80	4007.16	33.20	3983.42

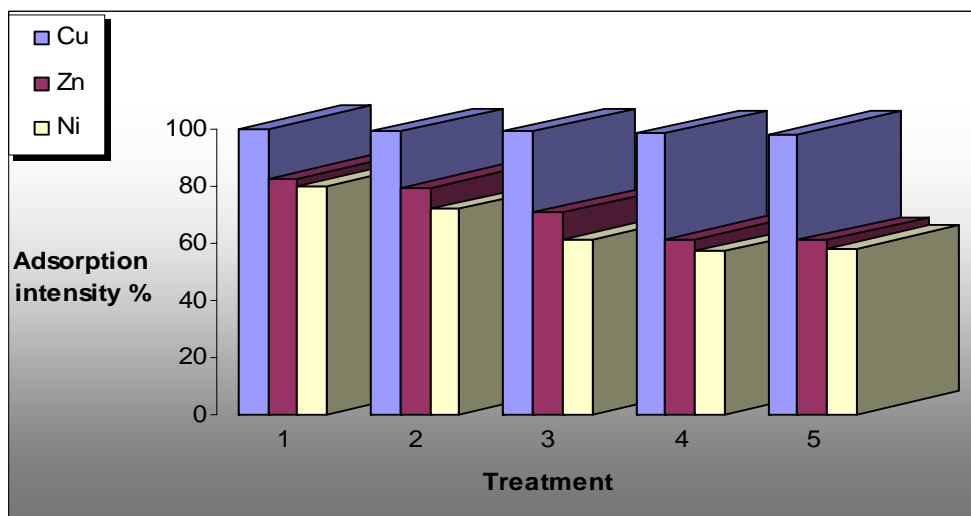


Figure 4.22. Adsorption intensity of heavy metals for Soil 1

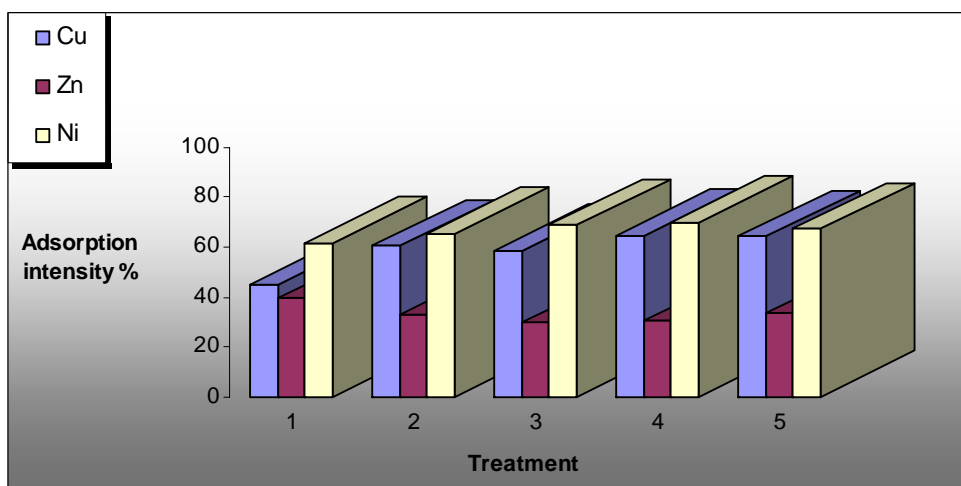


Figure 4.23. Adsorption intensity of heavy metals for Soil 2

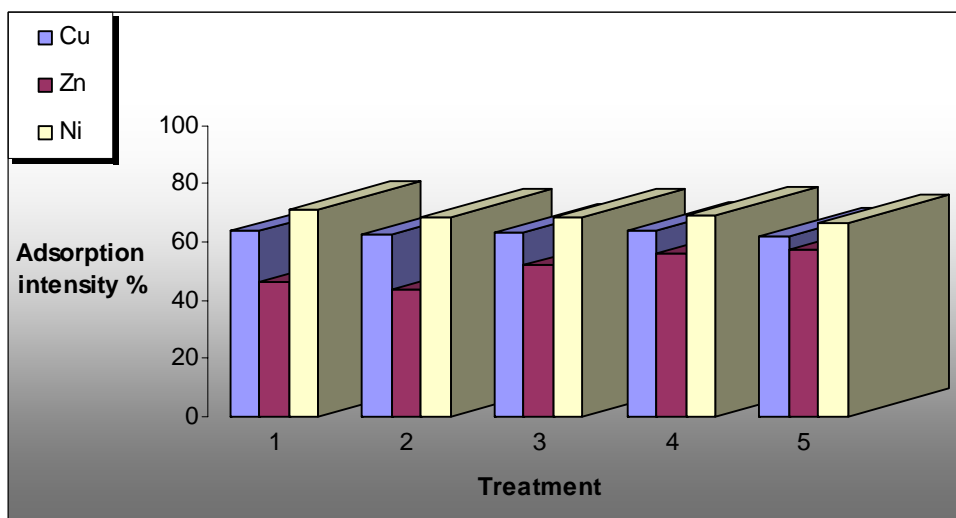


Figure 4.24. Adsorption intensity of heavy metals for Soil 3

As described above, Soil 1 showed the higher adsorption intensity of heavy metals, and Cu was adsorbed more than others. For Soil 2 and Soil 3, nickel adsorption was highest when the initial concentration were taken into account. As the concentrations Cu, Zn and Ni increased, adsorption intensities were decreased for Soil 1. For instance, in treatment 1, where Cu concentration was 50 mg/L, sorption intensity was 99.8 % for Soil 1. In treatment 5, where Cu concentration was 200 mg/L sorption intensity was 97.8 % for soil 1. For Ni, sorption intensity was 79.7 % for the concentration 45 mg/L in treatment 1, while sorption intensity was 57.8 % for the concentration of 90 mg/L in treatment 5 for the soil 1. This indicated that they were in competition at high concentrations as suggested in the literature. Thus, at low metal concentrations, effects of competition were not strong (Antoniadis et al., 2007). This seems to concur with the work of Saha et al. (2002) who found no evidence of metal competition (Cd, Zn and Pb) at low concentrations ( $5 \times 10^3$  times lower than the highest added concentration in Antoniadis et al. (2007) study in which highest metal concentration was 1000 mg/kg). At low added metal concentrations, metals are mainly adsorbed onto specific adsorption sites, while at higher metal inputs, soils lose some of their ability to bind heavy metals as adsorption sites overlap, becoming thus less specific for a particular metal. This, in turn, induces a reduction in metal sorption.

Although the sorption intensity of heavy metals decreased with increasing original concentration treatment, the total sorption amounts of heavy metals increased as shown in Tables 4.16-4.18. When the original concentrations were at higher levels, the sorbed

amounts by the soil of the strong sorption metal group (Cr, Cu and Pb) evidently increased, because the sorption intensity were still high. On the other hand when the original metal concentrations were at high levels, the sorbed amount of weak sorption metal group (Cd, Ni, and Zn) increased slightly, because their sorption intensity decreased (Li et al, 2007).

### 4.3 Desorption Experiments

Desorption experiments were performed as described in materials and methods section.  $C_i$ ,  $C_e$  and  $C_s$  values for the soils are given in Table 4.27-4.29.  $C_i$  is the initial heavy metal concentration,  $C_e$  is the concentration of heavy metals remaining in the aqueous solution after the metals are sorbed on the soils at equilibrium.  $C_s$  is the content of the metals adsorbed per gram of soils.  $C_s$  was calculated from the difference between the initial  $C_i$  and the equilibrium  $C_e$  concentrations of the metals.  $C_e$  versus  $C_s$  plots are given in Figures 4.25-4.45.

#### 4.3.1. Desorption Behavior for Soils

4.3.1.1. Desorption of Cu, Zn and Ni Desorption experiment were carried out immediately after the adsorption experiment were performed, as outlined before. 40 mL of heavy-metal-free 0.01 M  $\text{Ca}(\text{NO}_3)_2$  solution was added to the soil with heavy metals, and was left to reach the equilibrium for 48 hours.

Freundlich constants for desorption experiments (defined with subscript 'd' for desorption) are given in Tables 4.20-4.26.

Table 4.20. Freundlich Desorption Capacity ( $K_{fd}$ ) and Intensity ( $n_d$ ) of Cu for Soil 1

Soil 1	$\ln K_{fd}$	$K_{fd}$	$n_d$	$R^2$
low conc. range (pH<1)	10.57	38949	1.29	0.97
high conc. range with low sol. pH(pH<1)	5.15	172	0.71	0.91
high conc. range with high sol. pH (6<pH<7)	8.90	7332	0.51	0.93

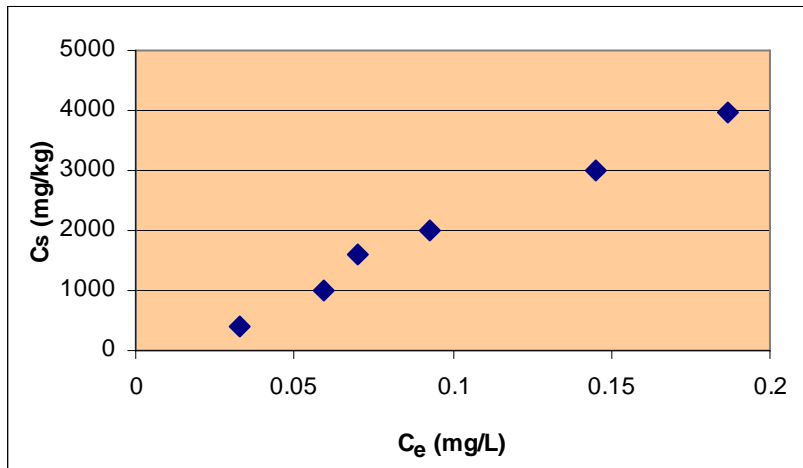


Figure 4.25. Linear Desorption Isotherm for Cu, low range for Soil 1

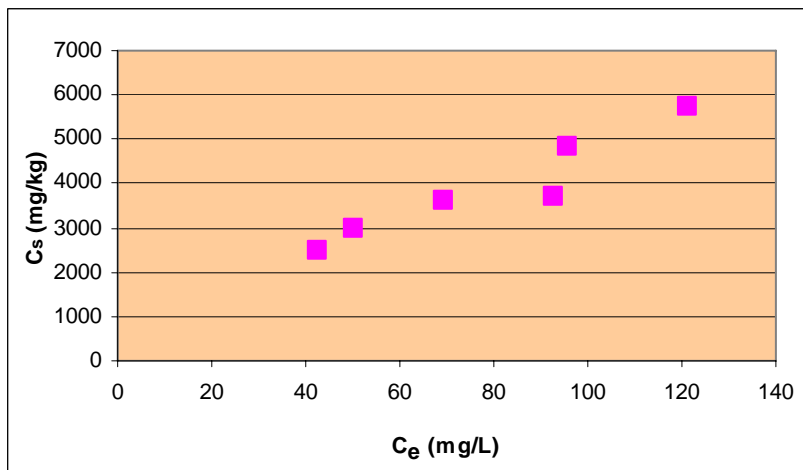


Figure 4.26. Linear Desorption Isotherm for Cu, high range with low solution pH for Soil 1

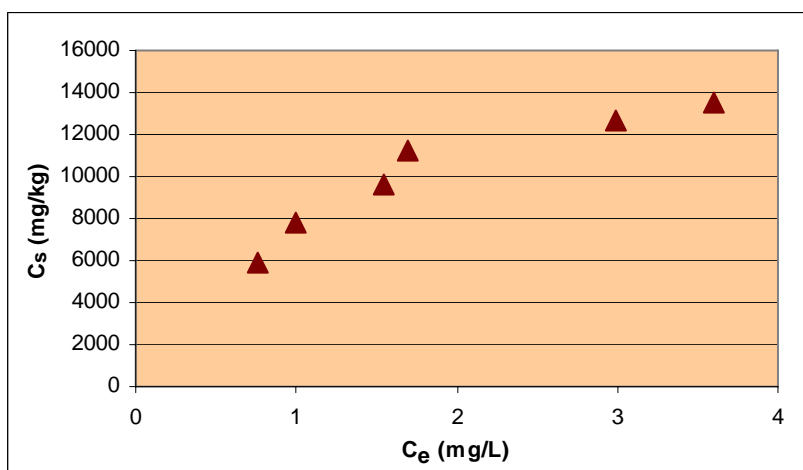


Figure 4.27. Linear Desorption Isotherm for Cu, high range with high solution pH for Soil 1

Table 4.21. Freundlich Desorption Capacity ( $K_{fd}$ ) and Intensity ( $n_d$ ) of Zn and Ni for Soil 1

Soil 1	$\ln K_{fd}$	$K_{fd}$	$n_d$	$R^2$
Zn (pH<1)	6.65	773	0.38	0.97
Ni (pH<1)	6.50	665	0.50	0.98

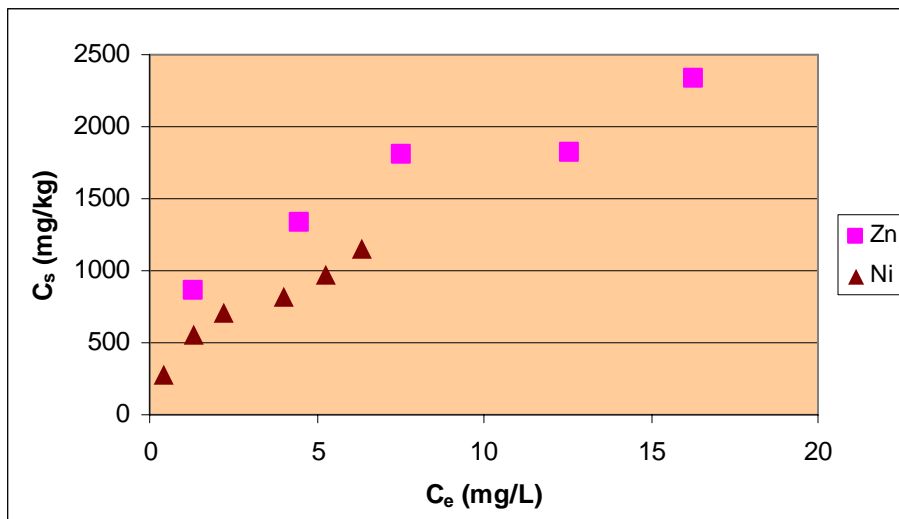


Figure 4.28. Linear Desorption Isotherm of Zn and Ni for Soil 1

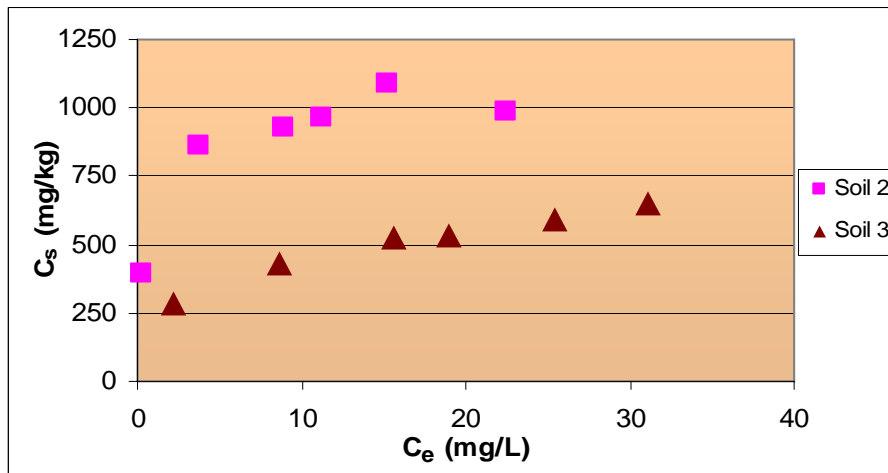


Figure 4.29. Linear Desorption Isotherm of Cu for Soil 2 and 3

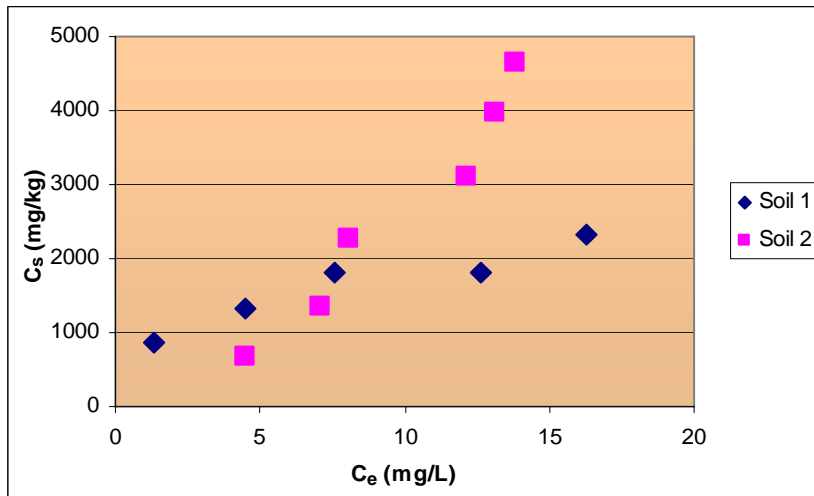


Figure 4.30. Linear Desorption Isotherm of Zn for Soil 1 and 2

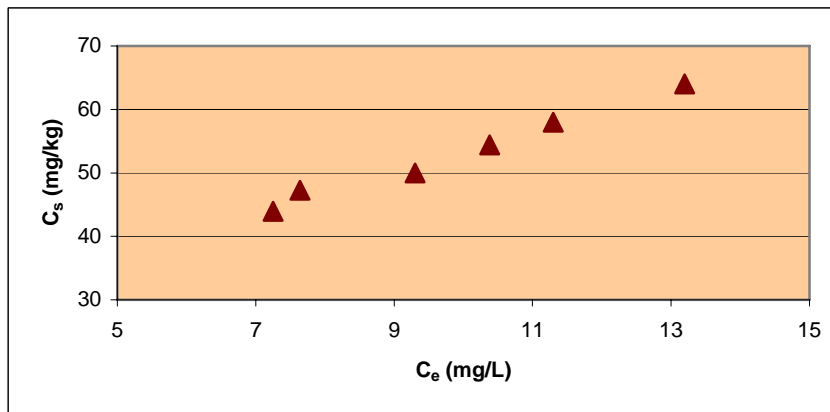


Figure 4.31. Linear Desorption Isotherm of Zn for Soil 3

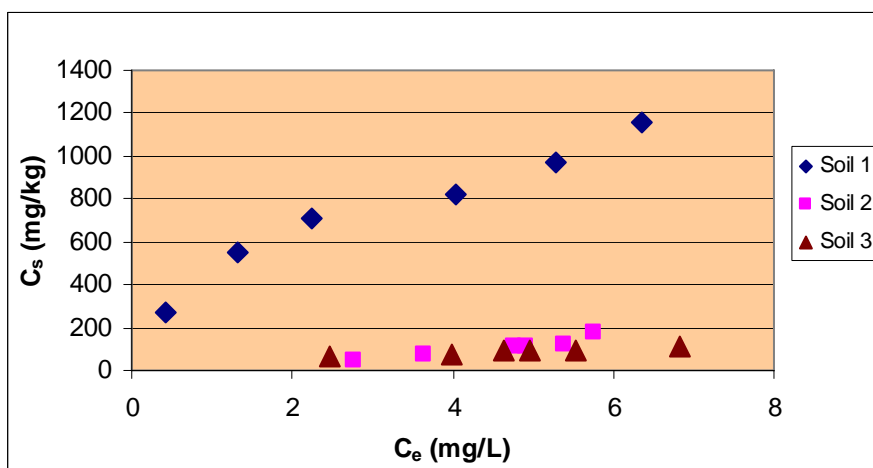


Figure 4.32. Linear Desorption Isotherm of Ni for Soils



Table 4.22. Freundlich Desorption Capacity ( $K_{fd}$ ) and Intensity ( $n_d$ ) of Cu, Zn and Ni for Soil 2

Soil 2	$\ln K_{fd}$	$K_{fd}$	$n_d$	$R^2$
Cu (pH<1)	6.33	561	0.22	0.94
Zn (pH<1)	4.11	61	1.63	0.97
Ni (pH<1)	2.08	8	1.69	0.97

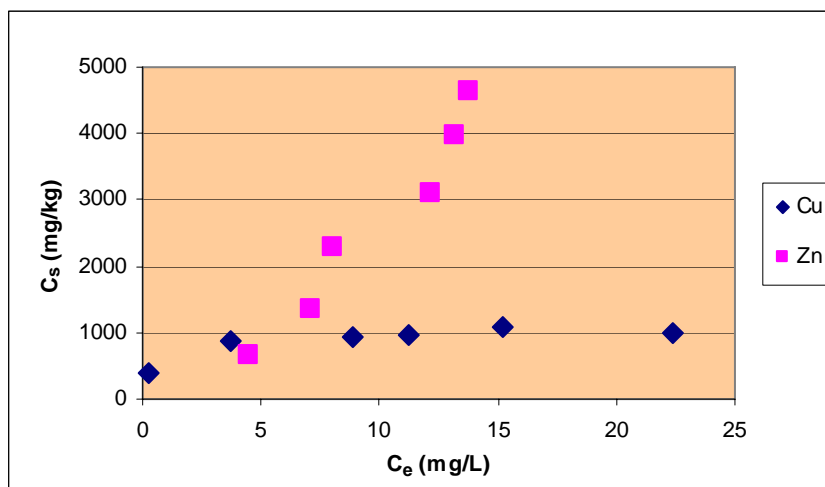


Figure 4.33. Linear Desorption Isotherm of Cu and Zn for Soil 2

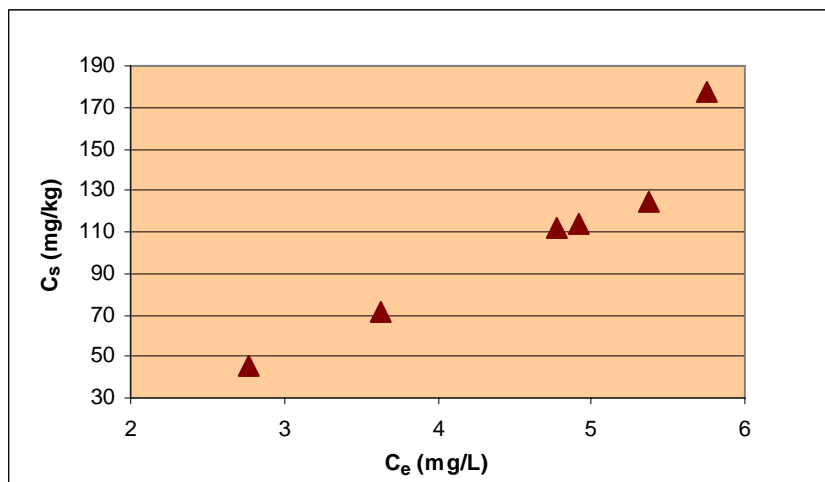


Figure 4.34. Linear Desorption Isotherm of Ni for Soil 2

Table 4.23. Freundlich Desorption Capacity ( $K_{fd}$ ) and Intensity ( $n_d$ ) of Cu, Zn and Ni for Soil 3

Soil 3	$\ln K_{fd}$	$K_{fd}$	$n_d$	$R^2$
Cu (pH<1)	5.41	224	0.30	0.99
Zn (pH<1)	2.62	14	0.59	0.97
Ni (pH<1)	3.66	39	0.53	0.98

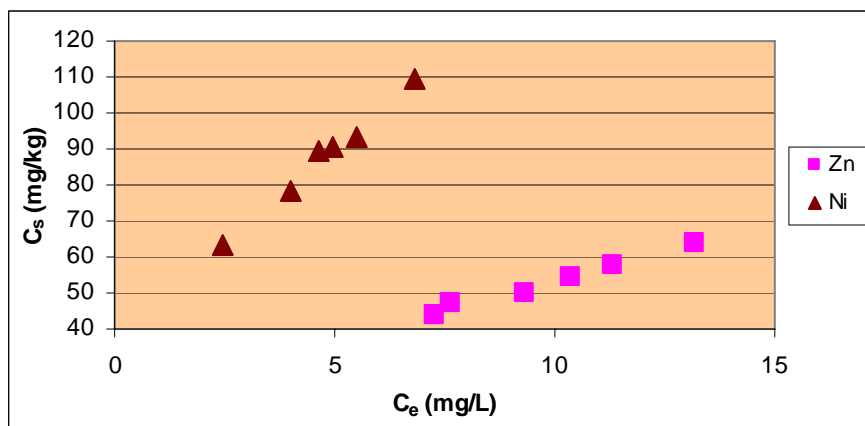


Figure 4.35. Linear Desorption Isotherm of Zn and Ni for Soil 3

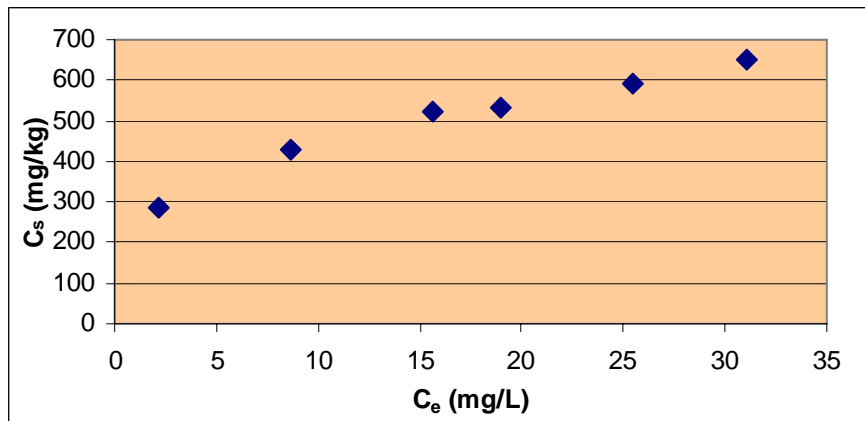


Figure 4.36. Linear Desorption Isotherm of Cu for Soil 3

Table 4.24. Freundlich Desorption Capacity ( $K_{fd}$ ) and Intensity ( $n_d$ ) of Cu, Zn and Ni in competition for Soil 1

Soil 1	$\ln K_{fd}$	$K_{fd}$	$n_d$	$R^2$
Cu (pH<1)	8.5	4915	1.90	0.90
Zn (pH<1)	7.4	1636	0.53	0.94
Ni (pH<1)	7.55	1901	0.74	0.94

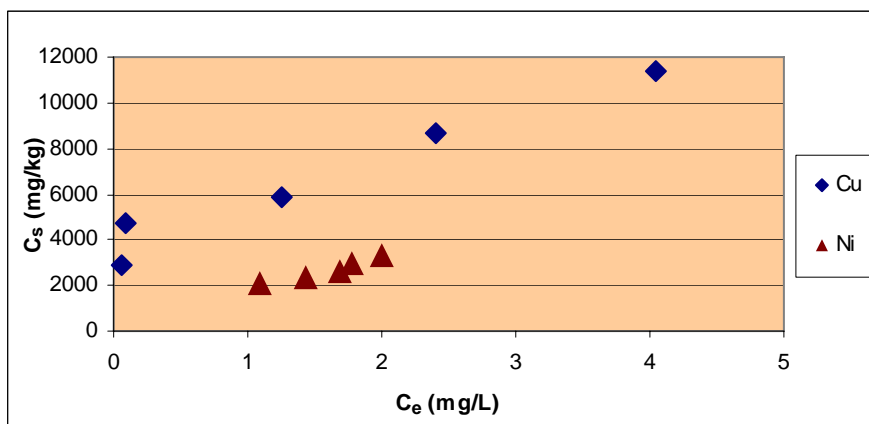


Figure 4.37. Competitive Desorption Isotherms of Cu and Ni for Soil 1

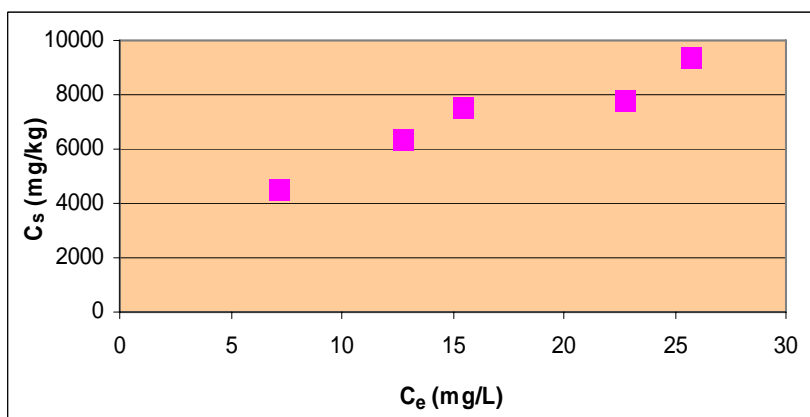


Figure 4.38. Competitive Desorption Isotherms of Zn for Soil 1

Since the  $C_e$  scale of the Zn results were very different from the Cu and Ni results, Zn results were plotted separately on Figure 4.38.

Table 4.25. Freundlich Desorption Capacity ( $K_{fd}$ ) and Intensity ( $n_d$ ) of Cu, Zn and Ni in competition for Soil 2

Soil 2	$\ln K_{fd}$	$K_{fd}$	$n_d$	$R^2$
Cu (pH<1)	7.69	2186	0.38	0.98
Zn (pH<1)	5.83	340	0.74	0.91
Ni (pH<1)	8.15	3463	0.95	0.90

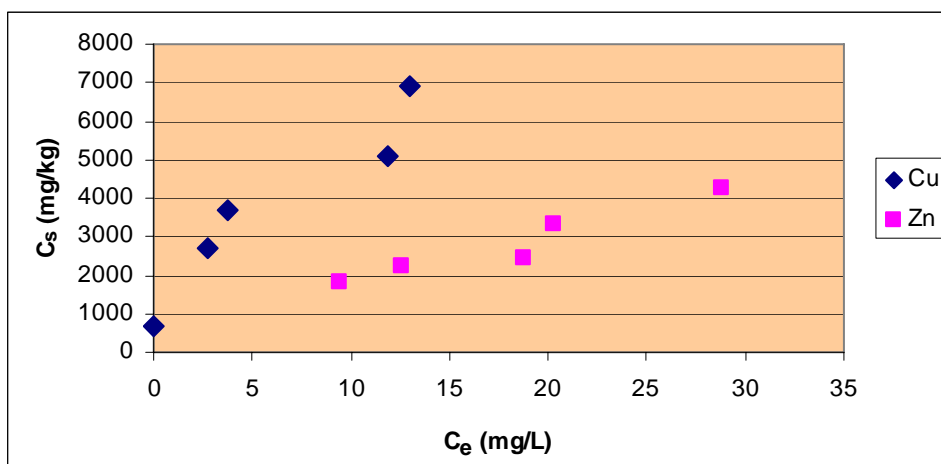


Figure 4.39. Competitive Desorption Isotherms of Cu and Zn for Soil 2

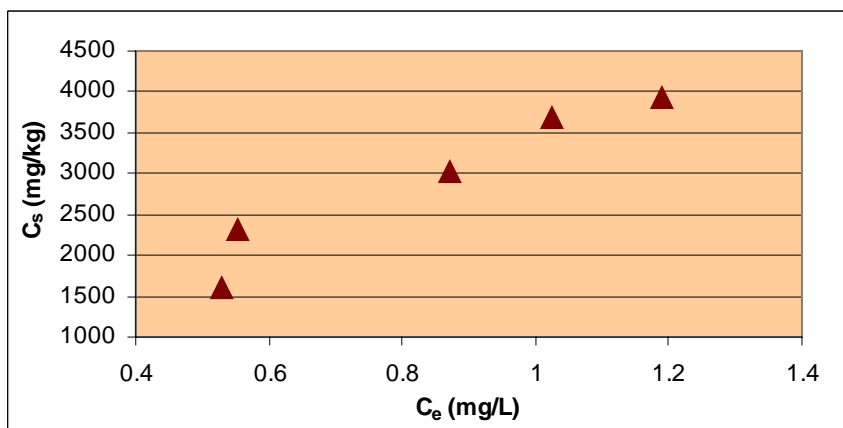


Figure 4.40. Competitive Desorption Isotherms of Ni for Soil 2

Since the  $C_e$  scale of the Ni results were very different from the Cu and Zn results, Ni results were plotted separately on Figure 4.40.

Table 4.26. Freundlich Desorption Capacity ( $K_{fd}$ ) and Intensity ( $n_d$ ) of Cu, Zn and Ni in competition for Soil 3

Soil 3	$\ln K_{fd}$	$K_{fd}$	$n_d$	$R^2$
Cu (pH<1)	4.79	120	1.54	0.90
Zn (pH<1)	5.68	293	0.94	0.90
Ni (pH<1)	8.04	3103	0.74	0.92

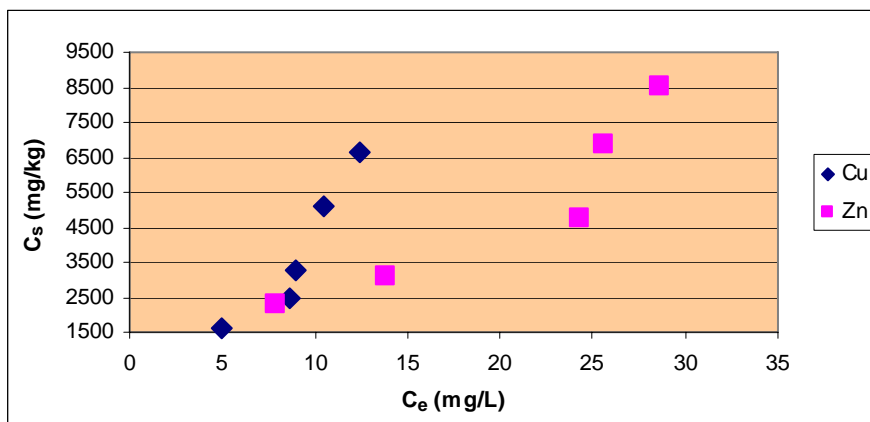


Figure 4.41. Competitive Desorption Isotherms of Cu and Zn for Soil 3

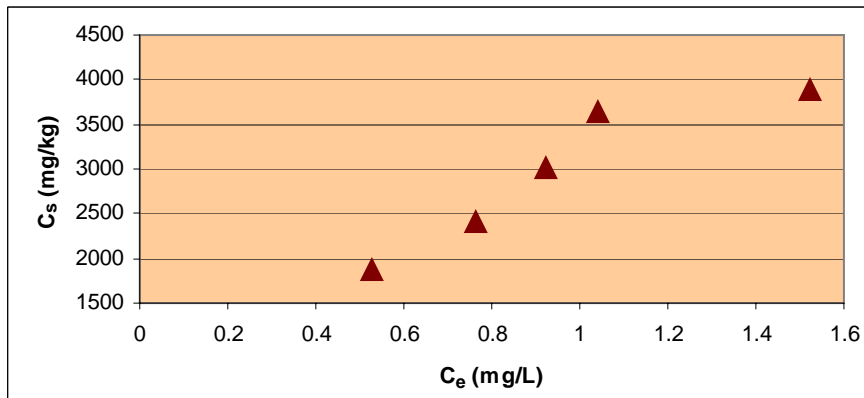


Figure 4.42. Competitive Desorption Isotherms of Ni for Soil 3

Since the  $C_e$  scale of the Ni results were very different from the Cu and Zn results, Ni results were plotted separately on Figure 4.42.

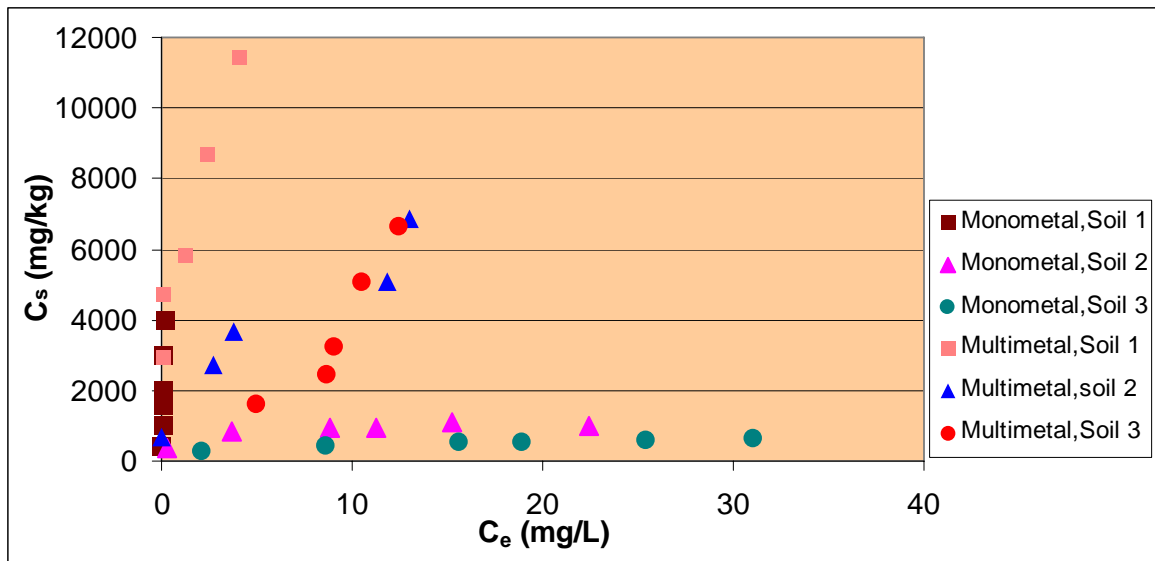


Figure 4.43. Mono-competitive multimetal Linear Desorption Isotherms of Cu for Soils

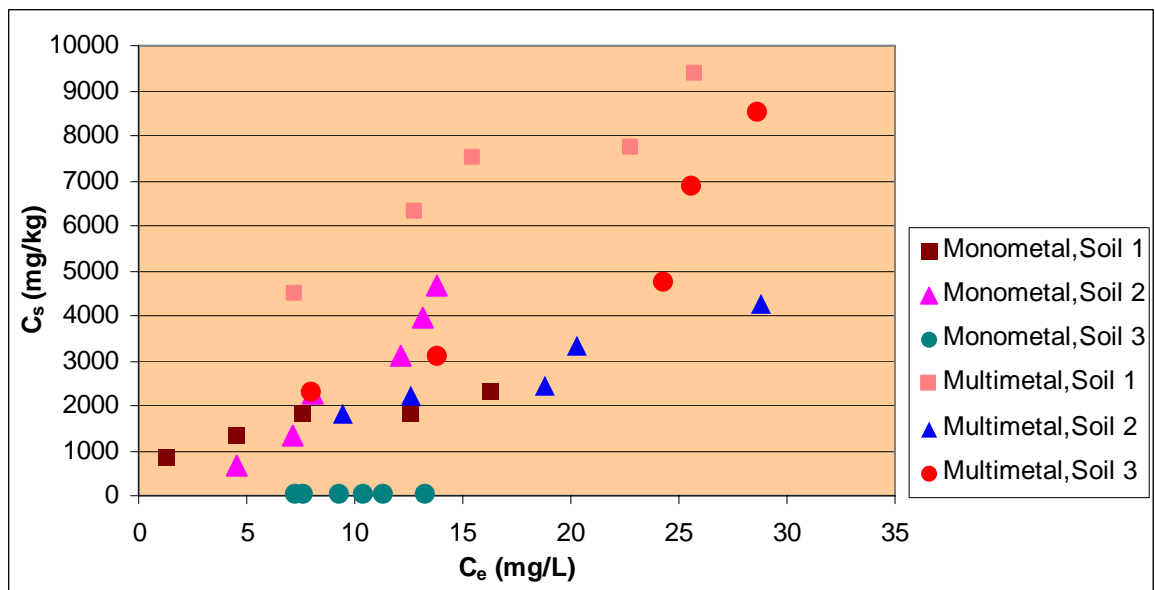


Figure 4.44. Mono-competitive multimetal Linear Desorption Isotherms of Zn for Soils

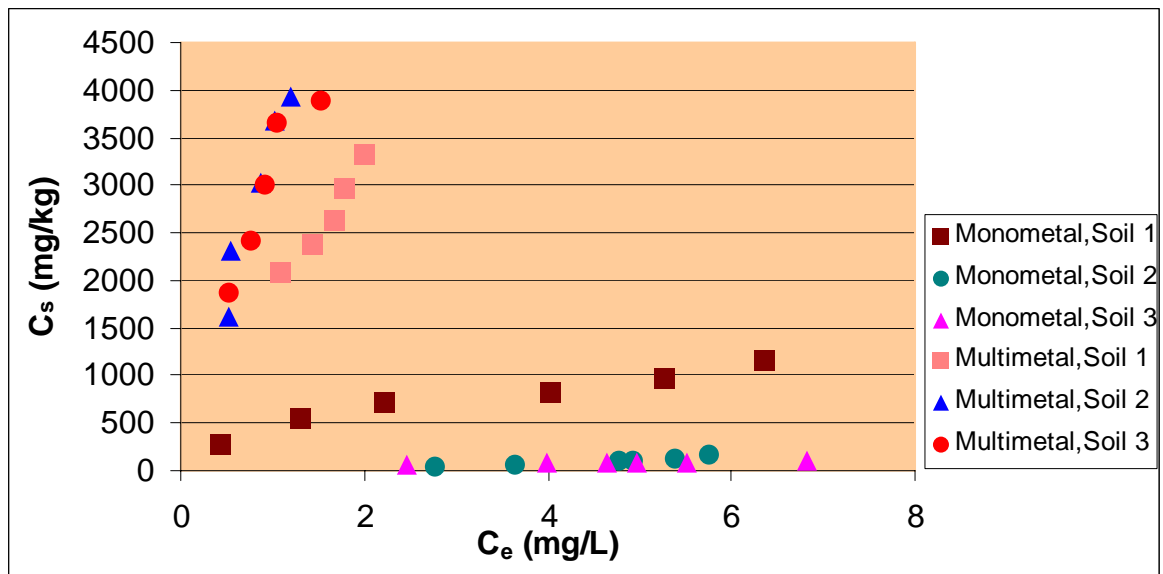


Figure 4.45. Mono-competitive multi metal Linear Desorption Isotherms of Ni for Soils

Five sets of treatments were used in the competitive multimetal desorption studies. The concentrations of each metal ions in the initial treatment solution is indicated in Table 4.27-29 in which Cu concentration in treatment 1 was 49.20 mg/L, Zn concentration was 82.5 mg/L, Ni concentration was 35.89 mg/L for Soil 1. In treatment 2, Cu concentration was 79.07 mg/L, Zn concentration was 118.93 mg/L, Ni concentration was 41.15 mg/L for Soil 1.

Table 4.27.  $C_i$ ,  $C_e$  and  $C_s$  values of Cu for Soils

Soil 1			Soil 2			Soil 3		
(Treatment)	$C_e$	$C_s$	(Treatment)	$C_e$	$C_s$	(Treatment)	$C_e$	$C_s$
$C_i$ (mg/L)	(mg/L)	(mg/kg)	$C_i$ (mg/L)	(mg/L)	(mg/kg)	$C_i$ (mg/L)	(mg/L)	(mg/kg)
(1)	0.06	2930.23	(1)	0.04	680.89	(1)	4.95	1602.56
(2)	0.09	4709.30	(2)	2.74	2724.36	(2)	8.60	2480.62
(3)	1.25	5827.67	(3)	3.75	3662.79	(3)	9.00	3243.89
(4)	2.40	8684.14	(4)	11.85	5084.97	(4)	10.50	5105.84
(5)	4.05	11417.95	(5)	13.00	6887.30	(5)	12.40	6651.76

Table 4.28.  $C_i$ ,  $C_e$  and  $C_s$  values of Zn for Soils

Soil 1			Soil 2			Soil 3		
(Treatment) $C_i$ (mg/L)	$C_e$ (mg/L)	$C_s$ (mg/kg)	(Treatment) $C_i$ (mg/L)	$C_e$ (mg/L)	$C_s$ (mg/kg)	(Treatment) $C_i$ (mg/L)	$C_e$ (mg/L)	$C_s$ (mg/kg)
(1) 82.5	7.20	4490.16	(1) 39.60	9.40	1800.83	(1) 46.60	7.90	2307.69
(2) 118.93	12.75	6331.25	(2) 50.00	12.60	2230.17	(2) 65.83	13.80	3102.68
(3) 141.20	15.48	7496.72	(3) 59.58	18.80	2431.72	(3) 103.96	24.30	4750.15
(4) 152.64	22.80	7742.40	(4) 76.25	20.32	3335.12	(4) 141.05	25.60	6884.02
(5) 183.02	25.75	9378.06	(5) 100.42	28.80	4270.72	(5) 172.08	28.65	8552.77

Table 4.29.  $C_i$ ,  $C_e$  and  $C_s$  values of Ni for Soils

Soil 1			Soil 2			Soil 3		
(Treatment) $C_i$ (mg/L)	$C_e$ (mg/L)	$C_s$ (mg/kg)	(Treatment) $C_i$ (mg/L)	$C_e$ (mg/L)	$C_s$ (mg/kg)	(Treatment) $C_i$ (mg/L)	$C_e$ (mg/L)	$C_s$ (mg/kg)
(1) 35.89	1.08	2075.31	(1) 27.71	0.53	1620.81	(1) 32.06	0.53	1880.44
(2) 41.15	1.44	2368.22	(2) 39.40	0.55	2316.52	(2) 41.28	0.77	2415.62
(3) 45.92	1.69	2637.57	(3) 51.63	0.87	3026.45	(3) 51.45	0.92	3012.88
(4) 51.46	1.78	2962.49	(4) 62.90	1.03	3689.56	(4) 62.30	1.04	3652.89
(5) 57.80	2.00	3327.37	(5) 67.20	1.19	3936.20	(5) 66.80	1.52	3892.61

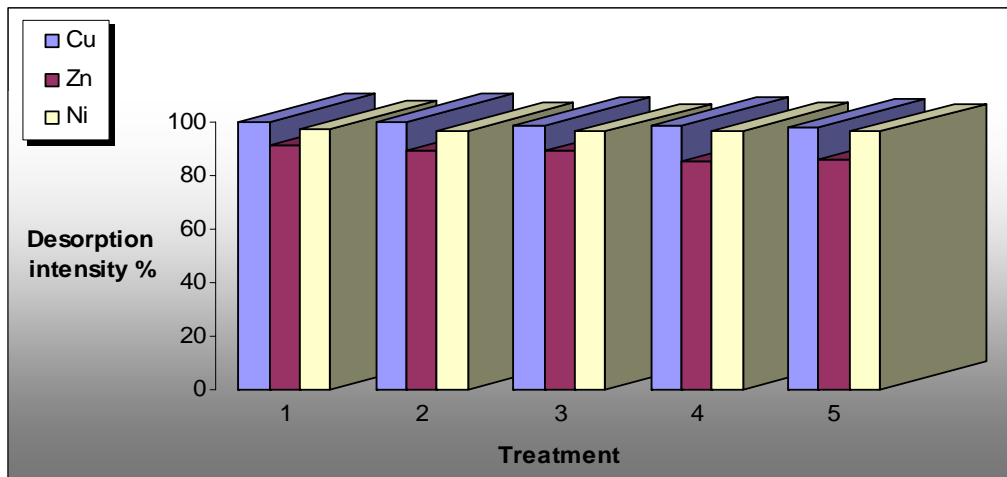


Figure 4.46. Desorption intensity of heavy metals %, for Soil 1



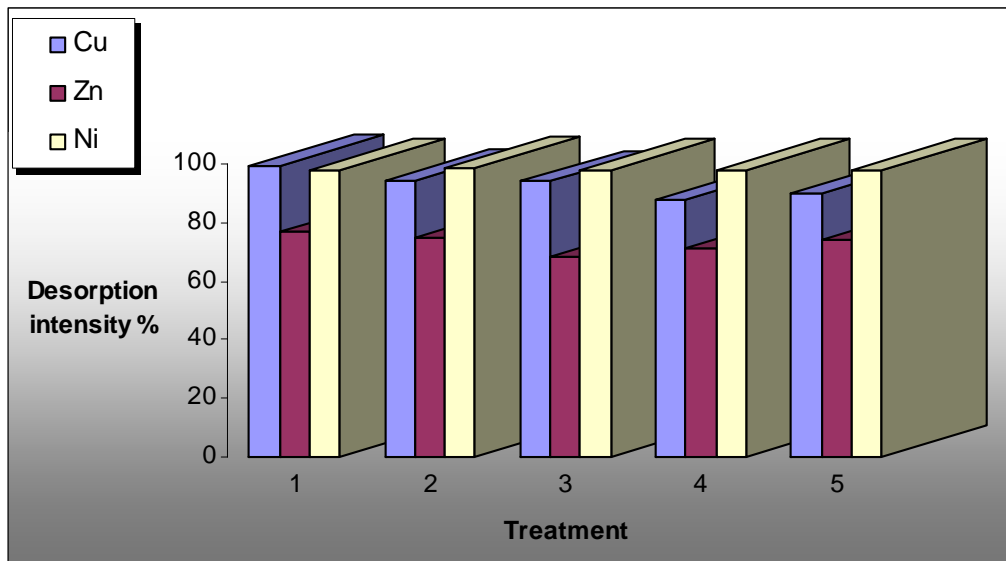


Figure 4.47. Desorption intensity of heavy metals %, for Soil 2

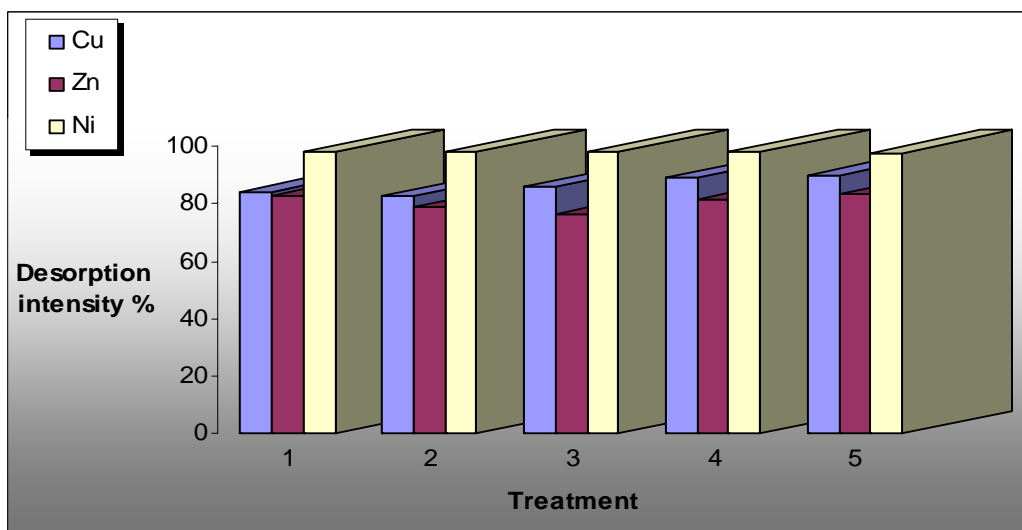


Figure 4.48. Desorption intensity of heavy metals %, for Soil 3

Desorption of the heavy metals were fitted to the Freundlich model. For Soil 1, high range Cu with high solution pH was desorbed more than others. Copper was desorbed more than Zn and Ni from Soil 1.  $K_{fd}$  values of the metals were supported the same observation,  $n_d$  values were in the reverse direction as in the adsorption of Soil 1. For Soil 2, desorption order was  $Cu > Zn > Ni$ , and for Soil 3, desorption order was  $Cu > Ni > Zn$ .

As mentioned before section 2.4.3 desorption isotherms of soils can be classified according to their shapes. In soil 1, Cu desorption was consistent with C-type isotherm for all adsorption experiments. Both Zn and Ni adsorption experiment curves were H-type. In Soil 2, Cu was L-type, whereas Zn and Ni were H-type. In Soil 3, all three metals showed C-type. Figure 4.38 represents the C-type isotherm for Cu in Soil 3.

In competitive multimetal systems, desorption order was Cu>Ni>Zn for Soil 1 but desorption order was Ni>Cu>Zn and Ni>Zn>Cu for Soil 2 and Soil 3, respectively. Desorption intensity of the heavy metals had the same order for Soil 1 and 2. As in the adsorption, increasing the metal concentration led to decrease in the desorption intensity. For instance, for Soil 1, desorption intensity was 91.3 % for Zn in treatment 1 where concentration was 82.5. Desorption intensity decreased (85.9 %) in treatment 5, where concentration was 183.0.

The  $K_f:K_{fd}$  ratio shows the hysteresis of the sorption-desorption processes. Tables 4.29-30 show the  $K_f:K_{fd}$  ratios for soils. According to the data given in the table,  $K_f:K_{fd}$  ratios of nickel for Soil 2 and of zinc Soil 3 were 4.0 and 4.6, respectively indicating the reversible bindings and a higher dependency of the sorption behavior on Soils. Similar strong and irreversible bindings among the adsorption-desorption was revealed for Soil 3 in competitive multielement system of Cu. These results were in agreement with the literature (Lair et al., 2006).

Table 4.30.  $K_f:K_{fd}$  ratio for Soil 1, 2 and 3 (monometal)

	<b>Metal</b>	<b><math>K_f</math></b>	<b><math>K_{fd}</math></b>	<b><math>K_f:K_{fd}</math></b>
<b>Soil 1</b>	<b>low range Cu (pH&lt;1)</b>	3072	38949	0.08
	<b>high range with low sol. pH Cu (pH&lt;1)</b>	89	172	0.52
	<b>high range with high sol. pH Cu (6&lt;pH&lt;7)</b>	4359	7332	0.59
	<b>Zn (pH&lt;1)</b>	464	773	0.60
	<b>Ni (pH&lt;1)</b>	308	665	0.46
<b>Soil 2</b>	<b>Cu (pH&lt;1)</b>	639	561	1.14
	<b>Zn (pH&lt;1)</b>	22	61	0.36
	<b>Ni (pH&lt;1)</b>	32	8	4.00
<b>Soil 3</b>	<b>Cu (pH&lt;1)</b>	200	224	0.89
	<b>Zn (pH&lt;1)</b>	63	14	4.50
	<b>Ni (pH&lt;1)</b>	55	39	1.41

Table 4.31.  $K_f:K_{fd}$  ratio for Soil 1, 2 and soil 3 (multimetals)

	<b>Metal</b>	<b><math>K_f</math></b>	<b><math>K_{fd}</math></b>	<b><math>K_f:K_{fd}</math></b>
<b>Soil 1</b>	<b>Cu (pH&lt;1)</b>	5452	4915	1.11
	<b>Zn (pH&lt;1)</b>	1808	1636	1.11
	<b>Ni (pH&lt;1)</b>	1097	1901	0.58
<b>Soil 2</b>	<b>Cu (pH&lt;1)</b>	992	2186	0.45
	<b>Zn (pH&lt;1)</b>	117	340	0.34
	<b>Ni (pH&lt;1)</b>	30	3463	0.008
<b>Soil 3</b>	<b>Cu (pH&lt;1)</b>	113	120	0.94
	<b>Zn (pH&lt;1)</b>	5	293	0.02
	<b>Ni (pH&lt;1)</b>	265	3103	0.09

## 5. CONCLUSION

1. In mono- and multimetal systems, Cu adsorption is greater than others; adsorption order was  $Cu \gg Zn \sim Ni$ , for Soil 1 and 2. Furthermore, adsorption capacity increased in multimetal systems. Soil 1 and 2, especially Soil 1, takes up all metals to a higher extent when all the metals are present in the polluting solution together. Thus, multimetal systems seem to show synergism in Soil 1 and 2. However, in multimetal system for Soil 3, adsorption order was  $Ni > Cu > Zn$ , since their  $K_f$  values were decreased compared to monometal systems, Cu and Zn can be said to be in competition.
2. Overall metal adsorption is greater in Soil 1. In literature, Brown et al. (1997) suggested a link between metal movement and the formation of fulvic acid-metal complexes, which can increase at elevated pH values. This might be the reason for the greater adsorption on Soil 1, but fulvic acid contents of soils were not determined. Lowest adsorption is in Soil 3. This can be explained by the fact that, Soil 1 and 2 were top soils (0-20 cm), whereas Soil 3 was sub soil (20-60 cm). This might be the reason for the difference on adsorption behavior of metals with respect to soils.
3. Increasing the concentration of the heavy metal in the polluting solution led to an increase in metal adsorption. Adsorption and desorption of metals onto soils were found to fit the Freundlich isotherm satisfactorily for both monometal and multimetal systems.
4. When the soil characteristics were taken into account, it was seen that silt and clay contents of the soils had no effect on the adsorption phenomena. The fact that, Soil 2 had silt and clay contents higher than the others (4%) made no significant difference in the adsorption of the metals. Although the OMC of Soil 1 was lowest, its OC content was the highest among the soils. If we assume that, all the dissolved

OC content in solution was fulvic acid, this might explain the higher metal adsorption capacity of Soil 1.

5. It seems that more than the silt+clay content and OMC, it is the pH of the solution that influences the adsorption characteristics. It is suggested in the literature that the higher the pH, the higher would be the CEC. Soil 1, with highest pH and highest CEC, has the highest adsorption capacity. As the soil pH is changed for Cu adsorption, and the pH of the solution is decreased, adsorption of Cu on Soil 1 is highly inhibited and  $K_f$  values go down by > 90 %.
6. In the multimetal systems, the order of adsorption was determined by both  $K_f$  values obtained from Freundlich treatment and by calculations of the sorption intensities.  $K_f$  results obtained for Soil 1 suggest that metal adsorption follows the order  $\text{Cu} > \text{Zn} > \text{Ni}$ . This is in good agreement with the sorption intensity values calculated. Hence, Cu, with the highest sorption intensity, proves to be a “strong sorption metal” on Soil 1. On the same soil, a decrease in the sorption intensities of both Zn and Ni indicate that these are “weaker sorption metals”. According to the sorption intensity results for Soils 2 and 3, the order is changed to  $\text{Ni} > \text{Cu} > \text{Zn}$ . This might be explained by the fact that adsorption might be “covalent” in Soil 1, whereas “electrostatic” in Soils 2 and 3.
7. The ratios of  $K_f:K_{fd}$  were calculated, for nickel for Soil 2 and for zinc for Soil 3 as 4.00 and 4.60, respectively, suggesting reversible bindings and a higher dependency of the sorption behavior on soils. The similar strong and irreversible bindings among the adsorption–desorption was revealed for Soil 3 in multielement system for Cu, for which  $K_f:K_{fd}$  was 0.94.
8. In the desorption experiments, the order of desorption was determined both by Freundlich treatment and by calculations of the desorption intensities. In both treatments, desorption results were in good agreement and followed  $\text{Cu} > \text{Ni} > \text{Zn}$  order for Soil 1.  $K_f$  results obtained for Soil 2 suggest that metal desorption follows the order  $\text{Ni} > \text{Cu} > \text{Zn}$ . This order was also obtained from the calculation of the desorption intensity values. However, for Soil 3, desorption order was not the same

when the results obtained from Freundlich treatment and from the calculation of desorption intensity values were compared. When a comparison was made among the  $C_i$  and the  $C_e$  of metals,  $C_i$  for all metals were almost the same ( $>30$  mg/L). The  $C_e$  values were higher for Zn ( $>7$  mg/L) and lower for Ni ( $<0.6$ ). Desorption intensity values were calculated. Low  $C_i$  value of Ni indicated that, soil could hold the metal adsorbed strongly. High  $C_i$  value of Zn demonstrated that, soil could release the metal adsorbed with more ease. Since the desorption intensity of Ni was the highest, and Zn desorption intensity was the lowest, this might explain why Ni is more tightly adsorbed than Zn. Under this condition, one could conclude the differences in metal desorption order gaining from the Freundlich treatment and from the calculation of desorption intensity values.

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## APPENDIX A

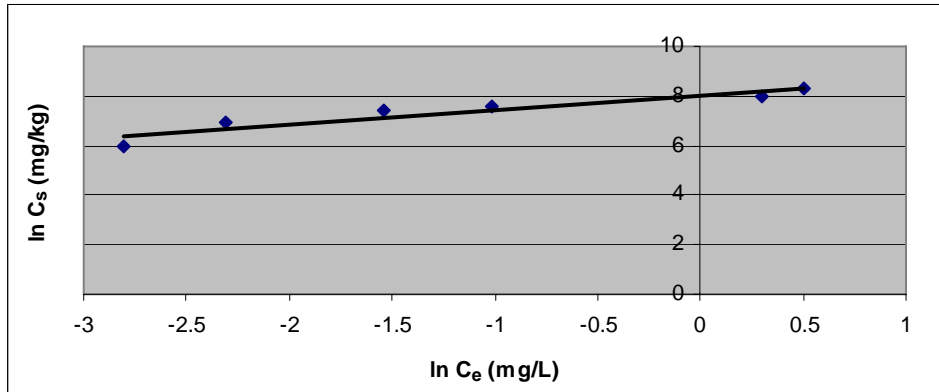


Figure A.1. Freundlich Adsorption Isotherm of Cu (low range) for soil 1

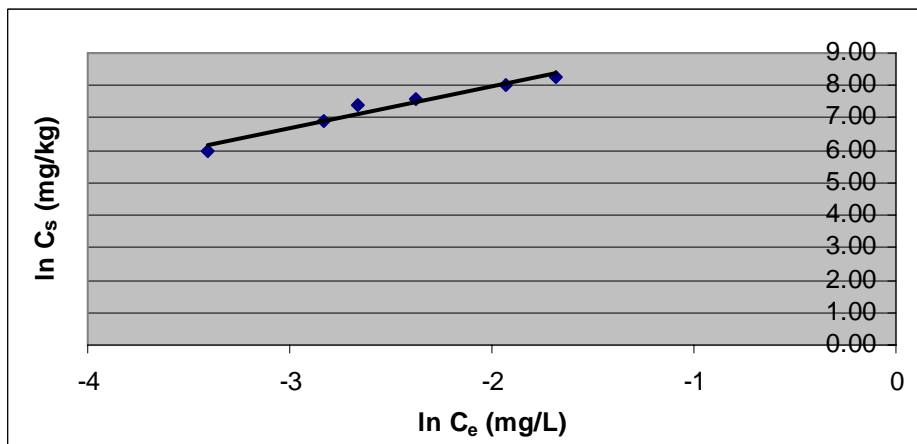


Figure A.2. Freundlich Desorption Isotherm of Cu (low range) for soil 1

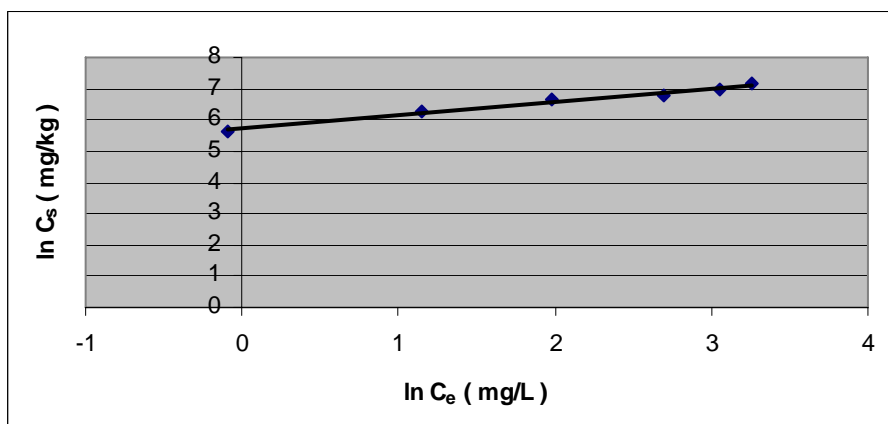


Figure A.3. Freundlich Adsorption Isotherm of Ni for soil 1

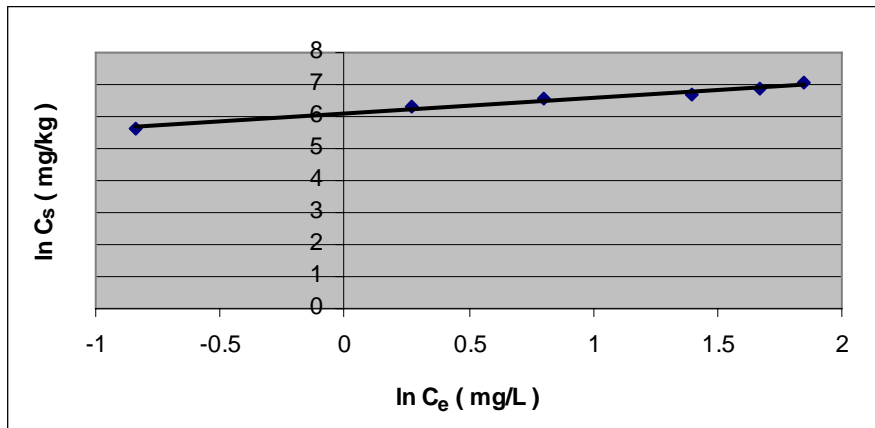


Figure A.4. Freundlich Desorption Isotherm of Ni for soil 1

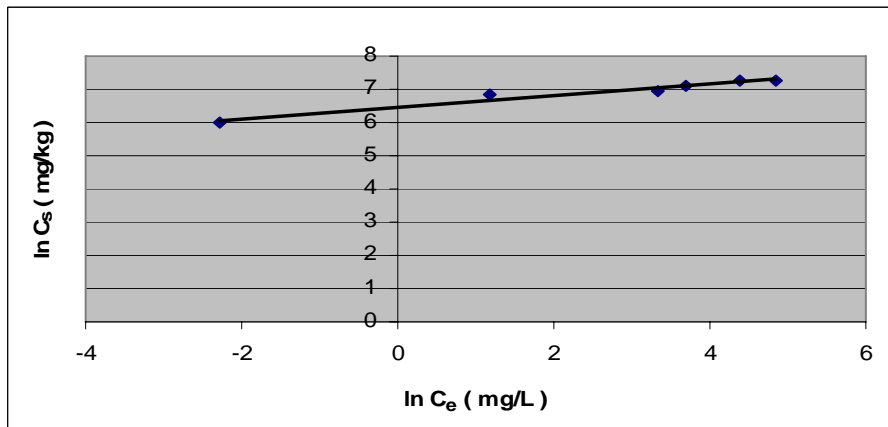


Figure A.5. Freundlich Adsorption Isotherm of Cu for soil 2

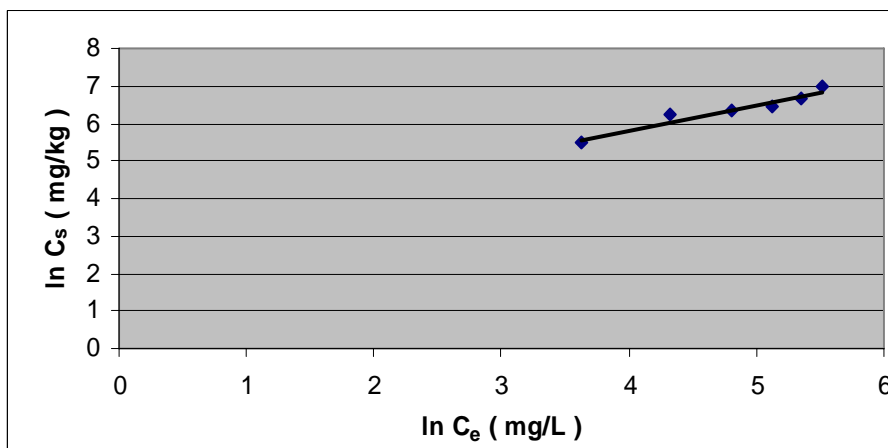


Figure A.6. Freundlich Adsorption Isotherm of Zn for soil 2

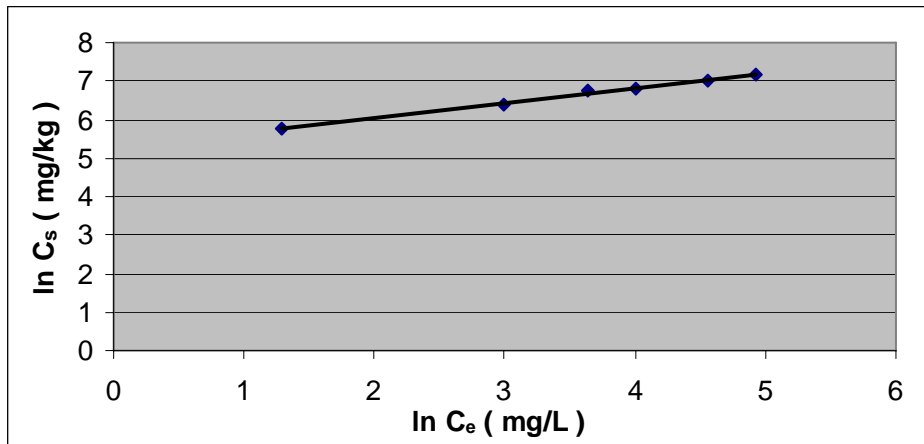


Figure A.7. Freundlich Adsorption Isotherm of Cu for soil 3

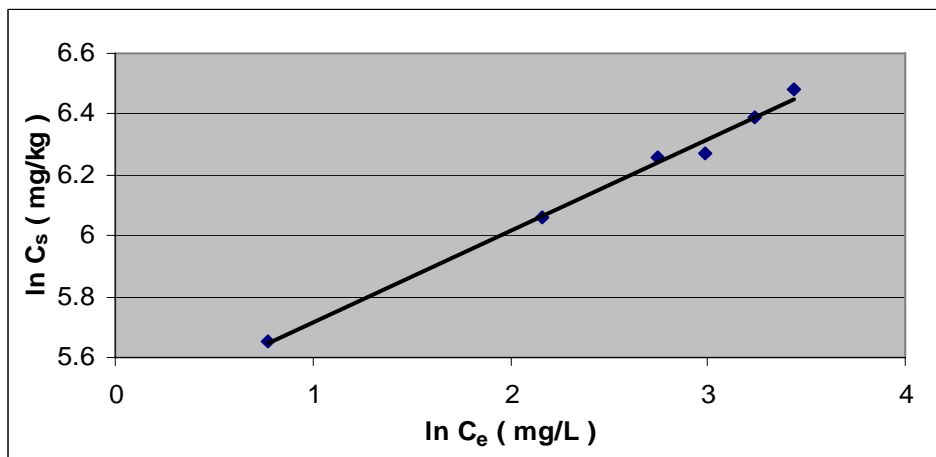


Figure A.8. Freundlich Desorption Isotherm of Cu for soil 3

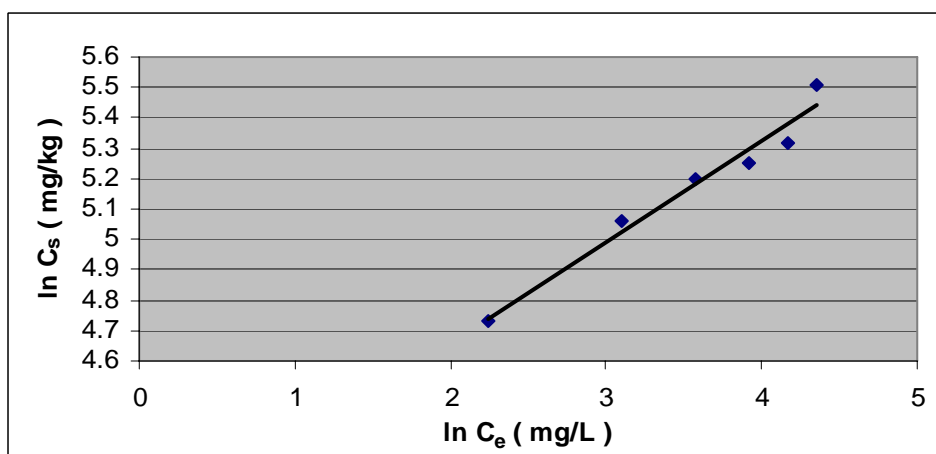


Figure A.9. Freundlich Adsorption Isotherm of Ni for soil 3



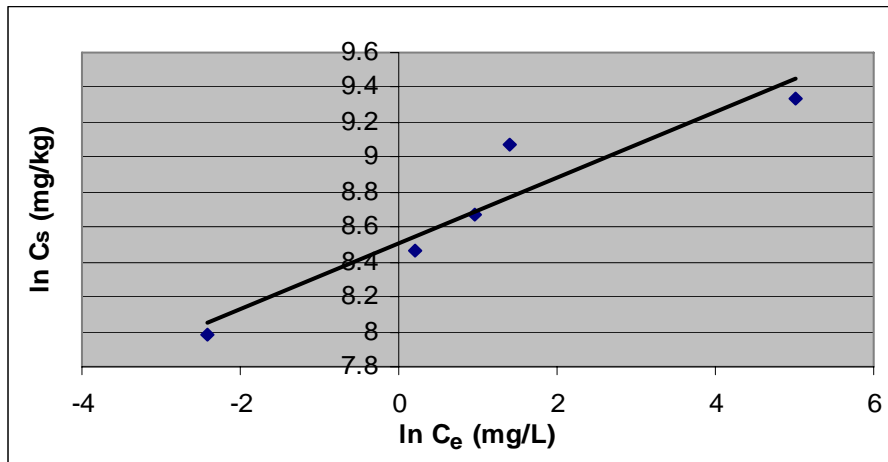


Figure A.10. Freundlich competitive multimetal Desorption Isotherm of Cu for soil 1

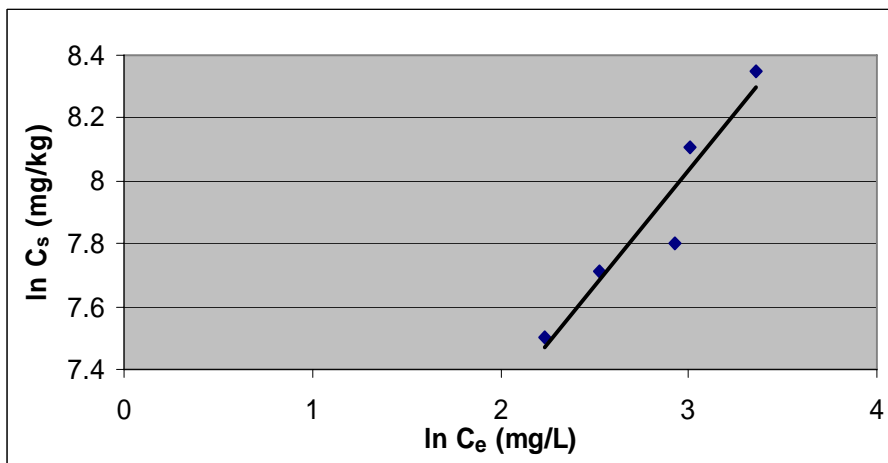


Figure A.11. Freundlich competitive multimetal Desorption Isotherm of Zn for soil 2

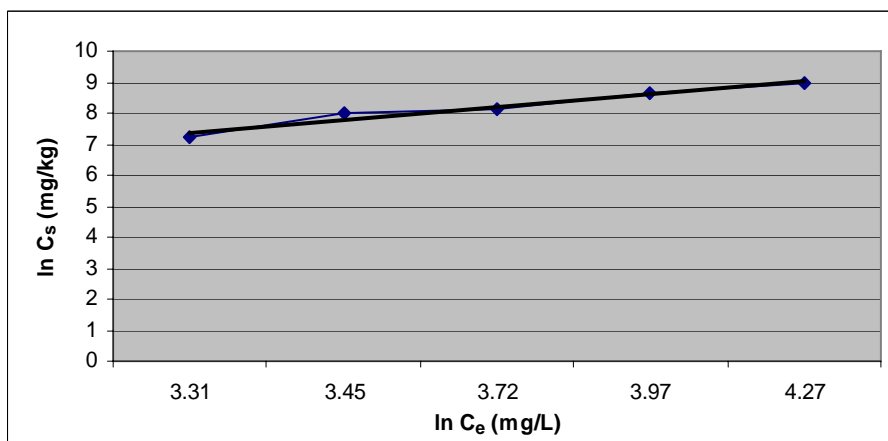


Figure A.12. Freundlich competitive multimetal Adsorption Isotherm of Cu for soil 2

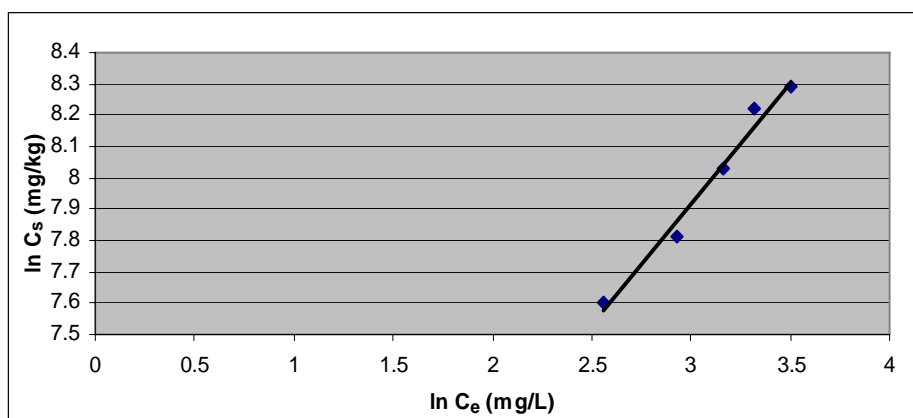


Figure A.13. Freundlich competitive multimetal Adsorption Isotherm of Ni for soil 3

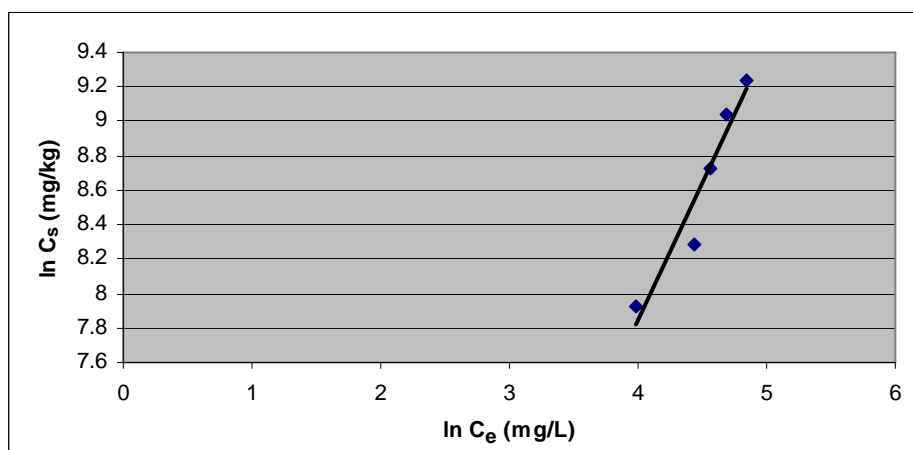


Figure A.14. Freundlich competitive multimetal Adsorption Isotherm of Zn for soil 3

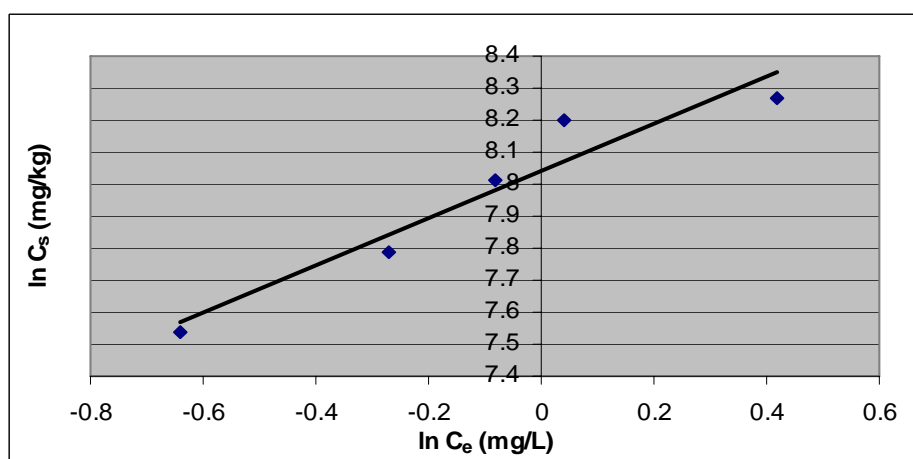


Figure A.15. Freundlich competitive multimetal Desorption Isotherm of Ni for soil 3