

ADSORPTION AND HEAVY METAL PARTITIONING IN SOILS AND  
SEDIMENTS OF THE SALMON RIVER AREA  
BRITISH COLUMBIA

by

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## ABSTRACT

The role of soils in the adsorption and release of heavy metals and their interaction in soil systems has not been extensively investigated. The interface between soils and water systems and the effects of land use practices on heavy metal adsorption, partitioning and release is an area of inquiry that requires study. In this study, both empirical and mechanistic approaches were utilized for evaluating the fate and behaviour of the heavy metals cadmium, lead, copper and zinc in clay minerals, and soils and sediments of the Salmon River watershed.

Various extracting agents were chosen to study their effectiveness of heavy metal extraction following sample fortification. The extracting agent 0.05 M E.D.T.A. and a shaking period of two hours were selected as a good compromise for studying the distribution of heavy metals. Lead was retained to a greater extent than Cd, Cu and Zn and correlated with organic matter, and to a lesser extent with cation exchange capacity of the soils and sediments.

The physico-chemical approaches utilized for studying adsorption of Cd, Pb, Cu and Zn showed adsorption phenomena for the smectite group of minerals to be different than the 2:1 non-expanded type (illite) and the 1:1 clay mineral (kaolinite), when the data were incorporated into the Langmuir equation.

Irrespective of clay mineral type, adsorption conformed to the Freundlich equation at the pH values of 4, 5, 6 and 7 and over a concentration range of 0-3000 ppm.

Common among adsorption on clay minerals, soils and sediment was that heavy metal adsorption at low pH values was in excess of the corresponding cation-exchange capacity and adsorption increased with increasing pH. Adsorption mechanisms other than the monolayer type are suggested.

Conformity with the Langmuir equation for soil and sediment adsorption was found to vary with metal type, concentration range and pH. No differences in bonding energy of lead were observed among the soils at the same pH. Adsorption of Pb, Cd and Zn on soils and sediments at pH 5.0, were positively correlated with clay content, organic matter and cation exchange capacity; negative correlations by Pb and Cd were observed with oxalate extractable Fe and Al, but Zn was positively correlated. Adsorption by soils and sediments followed the Freundlich equation over the entire 0-3000 ppm concentration range. Competition studies showed adsorption of an equivalent mixture (1:1:1:1) of Cd, Pb, Cu and Zn on montmorillonite at pH 5 to follow the Langmuir equation. Adsorption from the same equivalent mixture on kaolinite and two soils of differing texture and organic matter content did not fit the Langmuir equation.



Comparative data from soils under different land use practices showed Pb and possibly Cd to be associated with traffic proximity. Analysis of the sediments indicated higher metal values in industrial, agricultural and near the mouth of the river than from upstream rural sites.

An extension of the physico-chemical approach to soils and sediments provides adsorption maxima that are of predictive value for the heavy metals studied. This approach is useful to evaluate the effect of land use practices on heavy metals.

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## INTRODUCTION

Rapid industrialization during the present century has created new environmental problems, faster than scientists have been able to develop technology to adequately minimize their impacts. One such problem is the interaction of "heavy metals" with the food chain and ultimately man.

The term "heavy metal" means different things according to the user's concept. Geochemists and biomedical researchers think of them as trace elements. To the geochemist and the geologist, they are regarded as trace elements because they are considered to be non-essential components of minerals comprising less than one per cent of the mineral. The biomedical researcher similarly looks upon these elements as trace because they are ordinarily present in animal or plant tissue in concentrations less than 1% of the organism. When essentiality of elements for normal plant growth is examined, one finds that some of the heavy metals do not participate in physiological reactions; instead, when they exceed critical levels, there is a harmful effect on growth and yield. Since soils and vegetation are important links in the food chain, it is imperative to fill in gaps in our knowledge about short-term and long-term effects of these metals.



The amounts of many of these elements responsible for acute intoxication are fairly well established. For example, the toxicology of cadmium has been recently reviewed. Poisoning caused by cadmium has been well exemplified in the Jintsu River Valley of Japan (Kobayashi, 1971). Similar reviews on the relation of heavy metals to health and disease have been extensively covered (Friberg, 1973; Page and Bingham, 1973; Lisk, 1972).

What are the factors which influence the extent of metal contamination? It would appear that levels vary with man's activity in a geographical region. Data as such are not available to reliably characterize relationships between heavy metals and their activities, in relation to topography, drainage, soil type and climate. Various monitoring programs have been undertaken to identify areas of metal contamination; these survey approaches have covered most of the facets of our physical environment (rocks, soils, water and atmosphere).

Knowledge pertaining to uptake and accumulation by plants are slowly accumulating (Lisk, 1972). There are tremendous variations in the uptake and tolerance of heavy metals among plant species, however more research effort is required before reliable conclusions can be drawn. In biomedical research, recent studies have revealed that highest priority is being given to the interactions between cadmium and zinc (and possibly copper) and their relationship to cardio-vascular disease (Hopps, 1974).

There are several sources by which cadmium and zinc can contaminate soils. They include mining and smelting operations, gasoline and fossil fuel combustion, biocides, industrial and sewage sludge application to agricultural and forested lands, and limestone and phosphate fertilizers.

A survey of the literature revealed that in Western Canada, and particularly in British Columbia, very few studies have been undertaken to elucidate the nature and extent of heavy metal contamination in soils and river sediments. It has been the purpose of this study to investigate further the fate and behaviour of heavy metals in the soil environment. The Lower Fraser Valley of British Columbia and within its boundaries, the Salmon River Watershed, is an important agricultural area. For the past decade, the watershed has been receiving heavy metal additions from several sources including agricultural, residential and more recently industrial wastes. The Salmon River is a tributary of the Fraser River and the watershed lies in the immediate vicinity of the estuaries and coastal waters. The metals Cd, Pb, Cu and Zn were selected because they have been suspected to create environmental problems in the province (Warren et al, 1971; John, 1972; Hall et al, 1975).

The overall objectives of the study were:

1. to evaluate the efficiency of several extractants on heavy metal recovery following sample fortification,
2. to characterize and evaluate the heavy metals in soils derived from different parent materials, and some surface sediments within the Salmon River Watershed,
3. to elucidate the effect of pH on the sorption capacities of clay minerals, soils and sediment for heavy metals over a concentration range of 0 to 3000 ppm, and
4. to determine sorption capacities of clay mineral and soils of differing parent materials, from an equivalent mixture of heavy metals.

Partitioning per se does not provide evidence concerning interactions between heavy metals and soils or soil components. In order to understand mechanisms, physico-chemical approaches are required. Such approaches have been just initiated, and, so far as British Columbia soils are concerned, only one author has been found in a survey of the literature (John, 1972b). Subsequently, the second objective was geared to gain insight into the mechanisms controlling the availability of these metals in the presence of pure inorganic soil components, namely the clay minerals: montmorillonite, vermiculite, illite and kaolinite. Individual adsorption studies between clay minerals and metals

were carried out; as well as competition studies between metal mixtures and minerals. The findings have permitted description and prediction of the patterns of adsorption over a wide concentration range and under varying pH conditions.

In order to evaluate the chemical behaviour of the heavy metals in natural systems compared to clay mineral systems similar studies were performed with three surface horizons of soils and a surface sediment.

The results of this investigation have been used to elaborate on metal retention characteristics. Causal relationships between sorption capacity and soil properties have also been examined.

The findings from the study should contribute to a better understanding of physico-chemical phenomena in natural systems. Most studies reported in the literature have dealt with low concentration ranges of the heavy metals (usually less than 250 ppm); this study has extended this range. It is the hope that further work in this line be pursued and that such understanding would help devise control measures to maintain desired levels so that water quality and biological activity are not affected. It should be emphasized that the data presented are in concentration units, and it will be readily recognized that inferences about mass fluxes depend on the assumption of continuity of processes in the soil.

## Heavy Metal Chemistry

### Zinc and Cadmium:

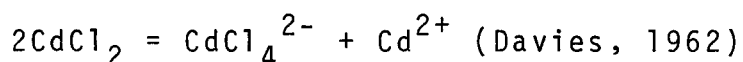
Zinc occurs as a mineral, but cadmium is a unique element in that no mines or ores are worked for its sole production. Zinc has a density of 7.14 at 20°C. Cadmium is usually found as impurities in zinc ores. It has a density of 8.69 at 20°C. Two other impurities associated with zinc ores are lead and iron. Lead does not enter into solid solution in zinc structures and therefore does not affect the physical properties of zinc. Cadmium and aluminum and to a lesser extent copper are the only elements which go into solid solution with zinc and decreases the malleability of zinc (Sneed and Brasted, 1955).

Zinc is used for the protection of iron against corrosion in bridges, automotive parts, machines, aircraft, etc. In moist air, it forms a hydrated oxycarbonate of the formulae  $5\text{ZnO} \cdot 2\text{CO}_2 \cdot 4\text{H}_2\text{O}$  and  $4\text{ZnO} \cdot \text{CO}_2 \cdot 4\text{H}_2\text{O}$ . Cadmium does not oxidize as readily as zinc, nor does it easily form an oxycarbonate on exposure to humid air. In their normal oxidation state, coordination numbers for the elements show close similarity (i.e. 2, 3, 4, 5 and 6), with six fold coordination occurring most frequently (Aylett, 1973).

Since cadmium is just above Co, Ni, Sn, Pb and  $\text{H}_2$ , but below Zn and Al in the electromotive series of elements, it can be precipitated from solution by the addition of Al or Zn dust.

These elements as described below differ from the alkali and alkaline earth elements in undergoing hydrolysis at lower pH values, and also differ in certain types of reactions (formation of inorganic complexes) that make them behave differently in the physical environment.

Both commercial zinc and cadmium dissolve in dilute acids. They are divalent in almost all their compounds. They form complex ions with ligands such as cyanide, ammonia, chloride, carbonate, hydroxide and many organic radicals. One particular feature of cadmium is the ability of cadmium salts to auto-complex:

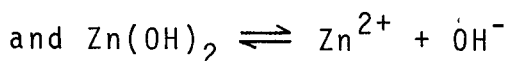
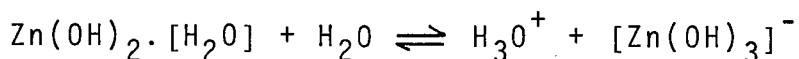
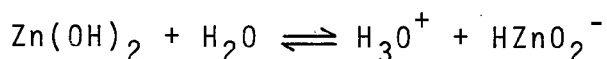


Zinc oxide is the most widely used zinc component and its solubility in water is 0.005g/litre at 25°C. Ammonium salts increase the solubility of zinc oxide. The co-valent character of the oxides is greater for cadmium than zinc, increases in accordance with this,  $\text{Cd}(\text{OH})_2$  is more basic than amphoteric  $\text{Zn}(\text{OH})_2$ . Zinc oxysalts change to zinc oxide in the presence of excess alkali, with the less stable and more soluble oxy-compounds such as the nitrates changing to zinc oxide at relatively low pH (Sneed and Brasted, 1955), whereas the more stable ones, such as the oxysulphate and oxycarbonate, require either higher pH or a longer period of time for the transformation.

Six forms of  $\text{Zn(OH)}_2$  have been described depending on concentration, pH and temperature. It appears that three of the forms of  $\text{Zn(OH)}_2$  have a characteristic x-ray pattern and a structure consisting of a double hexagonal layer of OH ions with Zn ions in the octahedral space analogous to brucite,  $\text{Mg(OH)}_2$  (Aylett, 1973; Sneed and Brasted, 1955).

Strong alkaline solutions (pH >9.5) react with zinc oxide or hydroxide to form zincates. Zincates although often written as  $\text{ZnO}_2^{2-}$ , are anions of hydroxo complexes with a general formula  $[\text{Zn}(\text{H}_2\text{O})_m(\text{OH})]^{2-n}$ . There is good evidence for the formation of various anionic hydroxo species such as  $[\text{Zn(OH)}_3]^-$  and  $[\text{Zn(OH)}_4]^{2-}$  in alkaline solution. Although other ions e.g. polynuclear  $[\text{Zn}_2(\text{OH})_3]^+$ ,  $[\text{Zn}_3(\text{OH})_3]^{3+}$  and six-coordinate  $[\text{Zn(OH)}_6]^{4-}$  have been proposed, the evidence for their existence is not strong (Aylett, 1973).

The equilibria of  $\text{Zn(OH)}_2$  indicates the ionization of the hydroxide both as an acid and a base:-



Various solid hydroxo complexes have been isolated from alkaline solutions: e.g.  $\text{NaZn(OH)}_3 \cdot 3\text{H}_2\text{O}$ ;  $\text{Na}_2\text{Zn(OH)}_4$  and

$\text{Na}_2 (\text{ZnOH})_4 \cdot 2\text{H}_2\text{O}$ . Reactions between  $\text{Zn}^{2+}$  and silicate ions lead to slimy precipitates of variable composition.

Cadmium salts hydrolyze less than the corresponding ones of zinc. Its hydroxide is a stronger base than  $\text{Zn}(\text{OH})_2$ . The following species have been found to exist in solution:  $\text{Cd}(\text{OH})^+$ ,  $\text{Cd}(\text{OH})_2$ ,  $\text{Cd}(\text{OH})_3^-$  and  $\text{Cd}(\text{OH})_4^{2-}$ . It is not well understood whether cadmium has amphoteric properties or can form polynuclear species like zinc. Cadmium complex ions have been reported by many researchers: e.g.  $\text{Cd}(\text{NH}_3(\text{OH}))_2$  (Danilov, 1971);  $\text{Cd}(\text{SO}_4)_2^{2-}$ ,  $\text{CdCl}(\text{SO})^-$  (Federov, 1971). With solutions of  $\text{CdCl}_2$ ,  $\text{NaOH}$  forms  $\text{Cd}(\text{OH})\text{Cl}$ ,  $\text{Cd}(\text{OH})_2$  and intermediate hydroxychlorides. Pure cadmium hydroxide begins to precipitate at pH 7.8. With a solution of cadmium nitrate,  $\text{NaOH}$  reacts to give  $\text{Cd}(\text{NO}_3)_2 \cdot 3\text{Cd}(\text{OH})_2$ .

### Copper

Copper has a density of 8.95 at 20°C. As simple monomers, copper is paramagnetic, as copper has one unpaired electron in the 4s orbital. The most common co-ordination number for Cu(I) is four; the majority of cuprous compounds are in tetrahedral co-ordination both in molecules or in polymeric structures. The usual co-ordination numbers adopted by Cu(II) are four, five and most commonly six.



The affinity of copper for oxygen is greater than that of zinc or cadmium. The cupric ion in aqueous solution is considered to be hydrated by six water molecules. The main species formed during the hydrolysis of the cupric ion are the hydroxyl bridged polynuclear ions  $\text{Cu}(\text{OH})_{2n-2}^{2+}$  not  $\text{Cu}(\text{OH})^+$  (Massey 1973). The solubility of copper hydroxide,  $\text{Cu}(\text{OH})_2$ , increases in the presence of  $\text{Na}(\text{OH})$  to give blue solutions of  $\text{Na}_2\text{CuO}_2$ . The structure of cupric hydroxide contains infinite chains of copper atoms linked by hydroxyl groups and the gel, therefore, retains large quantities of water. The product of the strong oxidation of cupric hydroxide may be perhaps  $\text{CuO.OH}$  (Massey, 1973). Inorganic complexes are well known. Aqueous  $\text{NH}_3$  dissolves  $\text{Cu}(\text{OH})_2$  to form  $\text{Cu}(\text{NH}_3)_4^{2+}$ . Complexes of cupric nitrate are  $\text{Cu}(\text{NO}_3)_4^{2-}$  and  $\text{Cu}_2\text{NO}_3(\text{OH})_3$  (Massey, 1973). A polymeric chain structure has been observed in the structures of  $\text{CuCl}_2$  and  $\text{CuBr}_2$ . Basic salts formed from the halogens are  $\text{Cu}(\text{OH})\text{F}$ ,  $\text{Cu}(\text{OH})\text{Cl}$ ,  $\text{Cu}_2(\text{OH})_3\text{Cl}$ ,  $\text{Cu}_2(\text{OH})\text{Br}$  and  $\text{Cu}_2(\text{OH})_3\text{I}$ . The chloride  $\text{Cu}_2(\text{OH})_3\text{Cl}$  is widely used as a biocide.

### Lead

Lead is one of the heavier elements with a density of 11.34. In moist air, it forms a thin surface film of oxycarbonate. It has a potential of 0.13V relative to the normal hydrogen electrode.

There appears to be one crystalline lead oxide-hydroxide ( $3\text{PbO}\cdot\text{H}_2\text{O}$ ).  $\text{Pb}_3(\text{OH})_4^{2+}$  and  $\text{Pb}_6(\text{OH})_6^{4+}$  are reported in partially hydrolyzed solutions of lead oxide. Alkaline solutions of lead contain a complex set of lead hydroxo cations, e.g.  $\text{Pb}(\text{OH})_3^-$ ,  $\text{Pb}(\text{OH})_6^{2-}$  (Abel, 1973); no evidence for  $\text{Pb}(\text{OH})_4^{2-}$  has been found.

The most common carboxylate of lead is lead acetate which is very soluble in water (1 g in 1.6 ml cold water); however, the solutions are only partially ionized at this concentration. Many other lead carboxylates are known such as formate, stearate, oxalate and tartrate.

Addition of  $\text{Na}(\text{OH})$  to  $\text{Pb}(\text{NO}_3)_2$  solution precipitates two basic nitrates:  $\text{Pb}(\text{NO}_3)_2\cdot\text{Pb}(\text{OH})_2$  and  $\text{Pb}(\text{NO}_3)_2\cdot 5\text{Pb}(\text{OH})_2$ ; there is no indication of precipitation of  $\text{Pb}(\text{OH})_2$  as such even at pH 2.0 (Abel, 1973). Organo-metallic nitrates of lead are well known, e.g.  $(\text{C}_2\text{H}_5)_2\text{PbNO}_3$  and  $\text{C}_6\text{H}_5\text{PbNO}_3$ ; equally well known are the organo lead oxides and hydroxides, e.g.  $\text{R}_2\text{Pb}(\text{OH})_2$ .

The following complex ions have been noted in perchlorate solutions:  $\text{Pb}_4(\text{OH})_4^{4+}$ ,  $\text{Pb}_2(\text{OH})^{3+}$ ,  $\text{Pb}_3(\text{OH})_4^{2+}$ ,  $\text{Pb}(\text{OH})^+$ ,  $\text{Pb}_6(\text{OH})_8^{4+}$  together with dissolved  $\text{PbO}_2$ ; however, the predominant ion is  $\text{Pb}_3(\text{OH})_4^{4+}$  (Abel, 1973).

### Summary

Some of the basic properties of the four elements are summarized below.

	<u>Oxidation state</u>	<u>Radius</u> A°	<u>Co-ordination No.</u>
Cd	2	1.15	6
	2	1.05	6
Zn	2	-	4
	1	1.05	2
Cu	2	0.97	4
	2	1.38	4
Pb	4	1.16	6

Since the soil is a complex mixture of various inorganic and organic constituents, the reactions of these elements in soils are more complex. In addition, soils in the field situation are dynamic constantly changing in boundary conditions; thus, laboratory analyses must be extrapolated with caution. For example partial pressures of carbon-dioxide and oxygen in soils are not the same as in laboratory studies; temperature in the temperate regions is on the average 10-18°C thus causing slow rates of reaction. An element that has precipitated in the soil may become irreversible with time and as it reorganizes, it becomes more regular with a lower specific surface and thus less reactive. Availability of an element in soil solution is controlled by the nature of the soil matrix, which is predominantly negatively charged; the mobility of elements such as Cd, Pb, Cu and Zn in soils is therefore regulated by the pH condition and retention characteristics of soils.

## PART I

### Selection of an Extractant and Partitioning of some Heavy Metals in the Salmon River Area

#### INTRODUCTION

Heavy metals are characterized by density greater than five. Those commonly encountered in soils are Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, and Zn.

These metals have been reported to affect biological activity. During the last decade, cadmium and lead have been in the forefront as those metals that directly or indirectly affect human health. The toxicology of cadmium (Friberg, 1973; Page and Bingham, 1973) and the impacts of lead in the environment (National Research Council, 1973) have been recently reviewed. Poisoning caused by cadmium have been well exemplified in the Jintsu River Valley of Japan (Kobayashi, 1971). Lagerweff (1972) following a review of lead problems in the environment, reported studies where and intake of 1000  $\mu\text{g}$  of soluble lead per day could cause adverse symptoms in humans in about eight years.

Preliminary surveys of cadmium, lead and zinc concentrations in whole blood samples of children living in urban areas have

been the subject of a recent study (Bogden, Singh and Joselow, 1974). Though copper and zinc are essential elements for the normal functioning of the plant, at high levels, they affect the food chain (National Academy of Sciences, 1974). Copper levels of 30 to 50 ppm have been reported to cause toxicity in citrus seedlings and pot studies (Rewther and Smith, 1953; Purves, 1972). A survey of the literature revealed that the uptake of cadmium from soils has been well demonstrated (Page, Bingham and Nelson, 1972; Haghiri, 1973; John, van Learhoven and Chuah, 1972; John, 1973; Lagerwerff, 1971; Jones, Hinesly and Ziegler, 1973). The uptake of lead is not as well understood as that of cadmium; however studies of lead absorption have been reported for some agricultural crops (Lagerwerff, 1971; Anon, 1974). Soil contamination by lead has been often related to industrial and urban centres, and road proximity (Chow, 1970; Lagerwerff and Specht, 1970, National Academy of Sciences, 1974). Samples between about 1.2 metres above curbside have shown lead in air at peak periods to be  $40 \mu\text{g Pb/m}^3$  in cities and  $6 \mu\text{g/m}^3$  near rural roads (Air Pollution Control Directorate, 1973).

Information about the effects of heavy metals on micro-organisms in soil is scanty; addition of 1000 ppm copper prevented nitrification in a sandy loam at pH 5-6.0 (Quraishi and Cornfield, 1972). Bhuyia and Cornfield (1973) injected

1000 ppm Cu, Zn and Pb and found from their studies that the amount of CO<sub>2</sub> released was reduced when compared to the control, and secondly straw mineralization rate decreased.

The physical environment is an interaction of the soil-plant-atmosphere system and uses the hydrological cycle to support and maintain its dynamic structure. Since man's activities affect the geochemical composition of inland and coastal waters; and, evidence is accumulating that heavy metals in waters and sediments (oceans, rivers and lakes) are affecting aquatic life-forms, the need for surveys according to land use and geographical region is relevant. Toxicity bioassays of heavy metals on selected fresh water invertebrates and the interaction of cadmium and zinc on the fresh water shrimp have been demonstrated (Northcote et al, 1975; Hall et al, 1975)

Based on the above, and the limited amount of information available in agricultural areas of Canada (John, 1971, 1972; MacClean and Longville, 1973; Chisolm, 1969) it was felt that a study on the partitioning of heavy metals in an agricultural watershed of the Lower Fraser Valley (Salmon River Watershed) would be an appropriate undertaking.

The objectives of this portion of the study, therefore, were:

1. to evaluate the efficiency of several extractants on heavy metal recovery sample fortification, and

2. to characterize and evaluate the heavy metals copper, lead, zinc and cadmium in soils derived from three parent materials, and some surface sediments within the Salmon River Watershed.

## MATERIALS AND METHODS

Soil samples of high and low organic matter content and low clay content derived from glacial till from the West coast of Vancouver Island were studied prior to selection of sampling sites in the Lower Mainland. For these preliminary assessments, the soils were selected because of their texture and range in organic matter content. They were part of a more comprehensive study (Lewis, 1974).

Following the preliminary studies, two Ap horizons from the Lower Mainland were selected to extend the findings to soils occurring in a different environmental setting. These were derived from two different parent materials, namely alluvium and outwash.

The materials in the remainder of the study were derived from three different parent materials within the Salmon River Watershed. They were representative of the soils found around the estuaries of the coastal waters of the Lower Mainland of British Columbia and the agricultural and rural areas of the Fraser Valley. The parent materials underlying these soils were floodplain alluvium, glacial outwash and glacial marine.

Two sampling sites were chosen from each parent material, a brief description of the sites is given in Table I.

Figure 1., illustrates the location of the study area. The sample sites were selected on the basis of their representativeness with regard to land use activities and soil conditions. It was understood that this approach would not yield statistically sound geographic extrapolation but would serve in achieving the objective of elucidating the retention characteristics of the soils for the heavy metals.

Five surface sediment samples were collected from the Salmon River. Sample  $S_1$  was collected in the stream bed of the alluvial geomorphic unit;  $S_2$  in the stream below the area of marine material drained by the river;  $S_3$  and  $S_6$  in the area of marine material. Sample  $S_7$  was collected in the area of glacial outwash. The land use in the vicinity of the sediment sites is described in Table (I).

Table I

Site Description

Sample Site	Parent Material	Land Use	Soil Classification
1	Alluvium	Golf Course	Gleysol
2	Alluvium	Crops	Gleysol
3	Glacial Outwash	Strawberry	Podzol
4	Glacial Outwash	Forest	Podzol
5	Marine Loam	Hay	Podzol
6	Marine Loam	Forest	Podzol



### Sediment Description\*

Sediment Number	Land Use Above site	Land Use Surrounding site
1	Industrial	Residential
2	Residential and agricultural	Residential and agricultural
3	-----"	-----"
6	Forest	Forest
7	Forest	Forest

\* As defined by Westwater Research Centre  
Vancouver. (Personal communications).

### Preparation of Materials

Samples were air-dried and ground to pass a 100 mesh stainless steel sieve. A stock solution of 200 ppm mixture of cadmium, lead, copper and zinc was prepared using analytical grade reagent and distilled-deionized water. The following extractants were used:-

5% $\text{CH}_3\text{COOH}$	1.0% $\text{CH}_3\text{COOH}$
0.1 $\text{N HCl}$	1.0 $\text{N HCl}$
0.05 $\text{M E.D.T.A.}$	1.0 $\text{N HNO}_3$

### Analytical Methods

#### Preliminary Procedure

In the preliminary study, 5 ml of the 200 ppm heavy metal mixture were added to 2.5 g samples of the Ah and Bgf horizons of the soils from Vancouver Island in a plastic centrifuge tube.

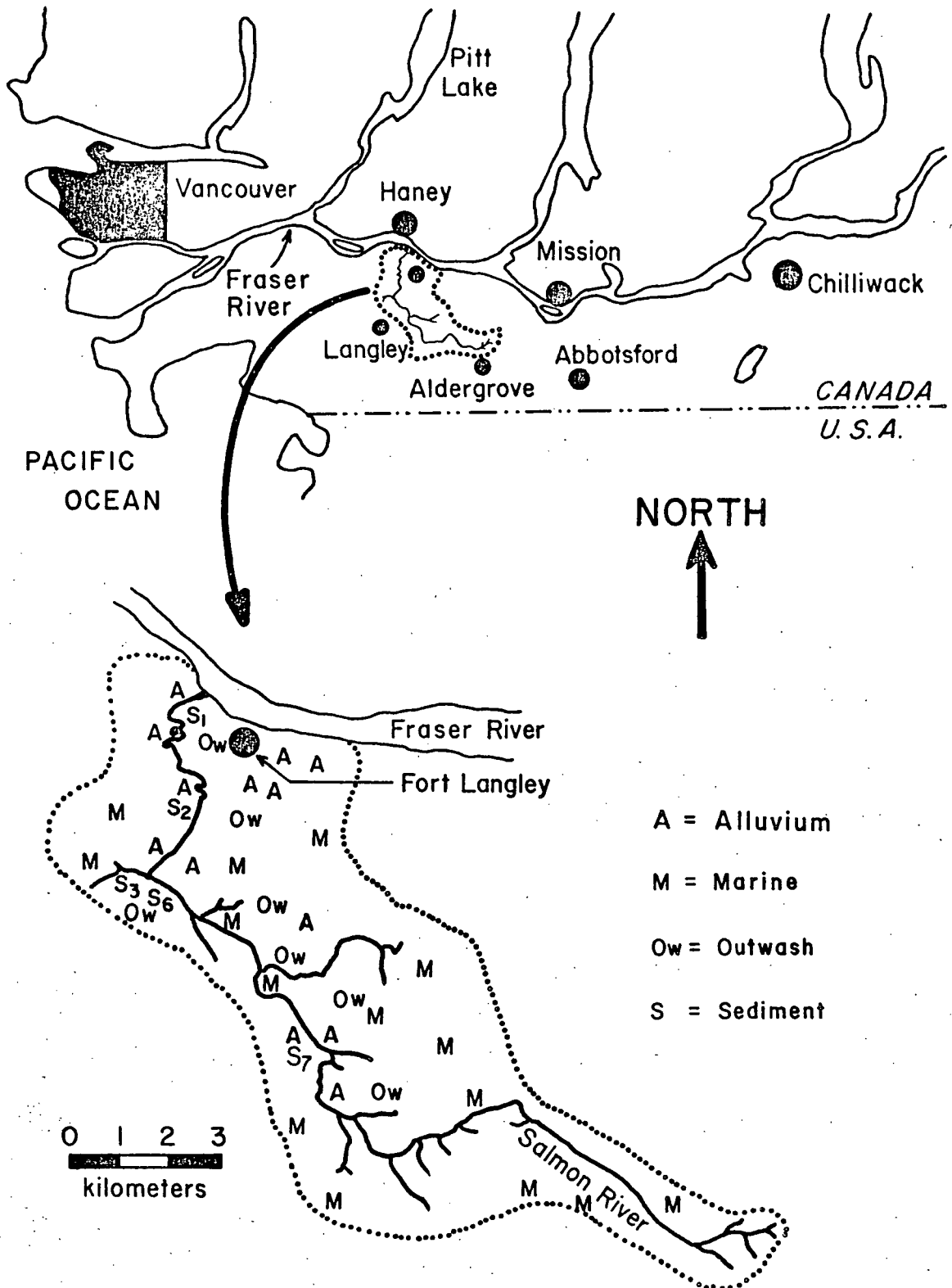


FIG. 1: LOCATION OF STUDY AREA AND SEDIMENT SAMPLING SITES (S<sub>1</sub> → S<sub>7</sub>). — SALMON RIVER, LOWER FRASER VALLEY, B.C.

Each sample was shaken for five minutes, allowed to stand overnight and centrifuged until the supernatant solution was clear. The supernatant solution was collected in a 100 ml volumetric flask; the centrifuge was washed with three 15 ml portions of deionized water and the washings were poured into the supernatant flask which was later brought to volume. The centrifugate was further washed with two 15 ml portions of isopropanol and the washings discarded. To triplicate samples of centrifugate, 25 ml portions of each extractant was added; (accordingly the ratio of soil to solution was 1:10). The contents were shaken for 6 hours on an end over end shaker and centrifuged until the supernatant liquid was clear. Aliquots of the supernatant liquid and the extractants were analyzed by atomic absorption spectrophotometry for cadmium, lead, copper and zinc using the Perkin Elmer Model 306 instrument.

#### Extraction Method

The preliminary procedure was modified as follows:-  
Triplicate samples of 2.5 g soil were fortified with 25 ml of 40 ppm mixture of cadmium, lead, copper and zinc and the pH adjusted to 4.0. The samples were left to stand for 48 hours, shaken for 30 minutes and centrifuged. Collection of the supernatant liquid and washing of the centrifugate followed the same procedure as described above. The extractants

used were 0.1 N HCl, 1.0 N HCl and 0.05 M E.D.T.A. The effects of two shaking periods (2 hours and 6 hours) were investigated.

The two-hour extraction method was further utilized to evaluate the extractants for soils derived from different parent materials.

#### Partitioning Study

The extractant selected for the partitioning study was 0.05 M E.D.T.A. Duplicate samples of 10.0 g of (<100 mesh) soil and sediment were shaken for two hours with 50 ml of 0.05 M E.D.T.A. in 100 ml plastic centrifuge tubes. The pH of all samples was measured prior to and following the shaking period. The solution was centrifuged until the supernatant liquid was clear and aliquot portions were analyzed by atomic absorption spectrophotometry for cadmium, lead, copper and zinc.

Analysis of variance was run on the data using the IBM 360 computer, and significant differences between means were determined by the Duncan's Multiple range test at the 5% significance level. Correlation analyses were also performed on the computer to study the relationship between extraction and soil properties.

## RESULTS AND DISCUSSION

Preliminary Study

## Copper

Table II summarizes the results obtained with the six reagents. Appendix I gives the readings in ppm of the heavy metals in the supernatant solutions and extracts. In the case of the surface horizon (Ah), Duncan Multiple Range test ( $\alpha = 0.05$ ) showed the efficiency of reagents to vary with the kind of heavy-metal. No significant differences were found between 5% and 10%  $\text{CH}_3\text{COOH}$ , between the mineral acids 0.1 N HCl, 1.0 N HCl, 1.0 N  $\text{HNO}_3$  and 0.05 M E.D.T.A., however, marked differences in recoveries were observed between 10% acetic acid and 1.0 N HCl, 0.1 N HCl and 0.05 M E.D.T.A.

Relationships observed between copper and extractants for the subsurface horizon Bgf (Table II) indicated that the trend regarding efficiency of extracts was similar to that observed for the surface horizon (Ah); however, higher recovery rates were obtained by the mineral acids. The greater recovery rate from subsurface samples may be attributed to reduced interaction of organic matter due to lower organic matter content. The complexing of copper by organic matter has been reported by several workers (Schnitzer and Khan, 1972; Rashid, 1973, Schnitzer, 1969). It is being claimed, that the effects of mineral acid extraction varies with the acid concentration; for example,

Table II\* Heavy metal recovery following sample fortification (six hours shaking) without pH adjustment.

	(a)* <u>High 0.M Soil (Ah)</u>				(b) <u>Low 0.M Soil (Bgf)</u>		
	<u>Cd</u>	<u>Pb</u>	<u>Cu</u>	<u>Zn</u>	<u>Cd</u>	<u>Pb</u>	<u>Cu</u>
	%				%		
5.0% CH <sub>3</sub> COOH	60.3	0.0	26.0	95.5	79.7	39.0	69.1
10.% CH <sub>3</sub> COOH	63.2	9.6	31.6	78.9	56.5	50.7	72.7
0.1 <u>N</u> HCl	73.6	36.8	58.0	99.9	99.9	98.0	91.9
1.0 <u>N</u> HCl	63.7	70.3	76.0	117.7	65.3	108.7	96.6
0.05 <u>M</u> E.D.T.A.	75.0	57.3	83.6	92.6	70.2	108.7	90.4
1.0 <u>N</u> HNO <sub>3</sub>	80.3	32.4	64.4	116.1	66.4	91.7	86.3

\* Duncan Multiple Range Test P(= 0.05).

copper extracted by 1.0 N HCl (Lagerwerff, 1971; Ennis and Brogan, 1961; Kline and Rust, 1966) extracts the slowly available forms. Copper extracted by 0.1 N HCl (Dollar and Keeney, 1971) extracts the immediate reservoir of exchangeable and readily plant available copper.

From the results obtained (Table II), it is evident that acetic acid is a poor extractant; similar observations have been reported (Bhuiya and Cornfield, 1974). Leeper (1972) suggested that the acetate ion has some complexing tendency which would make the reagent useful for determining the mobile reserves of heavy metals in soils. The results from this study and that of Bhuiya and Cornfield (1972) seem to provide contrary evidence in the case of copper. It would seem, therefore, that acetic acid, because of its very low dissociating ability, is not a good extractant; the amount extracted probably represented soluble and some easily exchangeable copper. McLaren and Crawford (1973) suggested that 2.5% acetic acid removed inorganically bound copper from soils.

## Lead

The results illustrated in Table II showed that there was a significant difference among the treatments; Duncan's Multiple Range Test showed differences to be significant between (a)

acetic and the mineral acids and EDTA, (b) 1.0 N HCl and 0.1 N HCl (c) 1.0 N HCl and 1.0 N HNO<sub>3</sub>. Data indicated that 1.0 N HCl was the most efficient reagent for extracting lead from surface horizons with high organic matter contents; however, no significant difference was found between 1.0 N HCl and 0.5 M EDTA extractions. As expected, good recovery was found with EDTA; in the case of 1.0 N HCl, the findings seem to support the contention maintained by Lagerwerff (1971), that, at this concentration it is a good extracting agent for lead; it would be appropriate to consider the corresponding release, in the form of ion-pairs or ion-complexes.

When the lead results from the surface horizon samples were compared with those obtained from the sub-surface horizon samples, it became apparent that irrespective of horizon type, EDTA and 1.0 N HCl were the most efficient extractants. These would then partly suggest that organic matter content does not interfere with the efficiency of extraction when considering 1.0 N HCl or EDTA. The high recovery rate by HNO<sub>3</sub> in the sub-surface horizon (91.7%) compared to a lower extraction in the surface horizon (32.4%) may be attributable in part to differences in organic matter content and texture. The findings contradict that reported by John (1971), who observed no effect on recovery with soils covering a wide range of organic matter and texture.



From this study, it can be inferred that organic matter has a very strong affinity for lead, and, once it is complexed cannot be easily exchanged by the hydrogen ion from nitric acid. The higher recovery from the sub-surface horizon, would, therefore seem to explain that in soils with low organic matter content, lead stays in an inorganically bound form by being either adsorbed to clay minerals, specifically sorbed to hydrous oxides or stay predominantly as  $Pb^{2+}$  in soil solution; or, more likely a combination of all these reactions. John (1971) assumed that applied lead was converted to lead compounds of  $Cl$ ,  $NO_3$ ,  $CO_3$ ,  $SO_4$  and that all these forms were extracted by  $HNO_3$ ; and, 1.0 N  $HNO_3$  proved to be a better extractant than 0.1 N  $HNO_3$ .

#### Cadmium

Irrespective of reagent type, recovery values for surface horizon samples ranged from 60.0% (acetic acid extraction) to 80.0% (mineral acid and EDTA extractions); in the case of sub-surface samples, they ranged from 65.0% (acetic acid extraction) to almost 100.0% (0.1 N  $HCl$  extraction). Duncan's Multiple Range Test ( $\alpha = 0.05$ ) showed no significant differences between treatments. It would appear that retention of cadmium in soils

differs from that of copper and lead, and, that even weak acids like acetic, (and possibly malic, oxalic etc.) seem to affect its distribution within a soil profile.

## Zinc

Values reported in Table II for the high organic matter soil showed high recoveries by all extracting agents, though in certain cases values greater than 100% have been noted; the latter may be due to contributions from native zinc and experimental error. Such findings should not jeopardize interpretation since only relative efficiency of extractants is being investigated. Sharpless et al. (1969) using 0.1 N HCl and neutral salts (1.0 N  $\text{CH}_3\text{COONH}_4$ ) observed high zinc recovery. This would support the suggestion that in soils, zinc does not behave like copper and lead but rather like cadmium.

Based upon this preliminary study, it was inferred that for the soils used, hydrochloric acid and ethylene diamine-tetra acetic acid appear to be better extractants than acetic and nitric acids for extracting a mixture of lead, copper, cadmium and zinc. Since further evaluation would provide added evidence for the selection of either hydrochloric or 0.05 M EDTA, it was felt desirable to use these two reagents for further work. They

were used to study the effect of different shaking periods on recovery rate and secondly to evaluate further their extracting efficiency on the same soils and two soils of the Salmon River watershed.

### Selection of Extractant

Data in Table III show the recovery rates for both HCl treatments (0.1 N HCl and 1.0 N HCl) and 0.05 M EDTA from the above-mentioned surface and sub-surface samples under two hour and six hour shaking periods. Appendix II and Appendix III summarize the original readings obtained in the supernatant liquid and extracts from both horizon samples.

It is apparent from the table that regardless of extractant type, and horizon type, no marked differences in recovery rates were found between the two hour and six hour shaking periods for any of the heavy metals. This was confirmed by analysis of variance which showed no significant differences at the five percent level. It would therefore appear that a two-hour shaking period is sufficient equilibration time for the extraction of these heavy metals from both surface and sub-surface soils used. Literature reviewed, revealed that a one hour shaking period has been most often used to extract metals such as copper, lead and zinc (Black, 1965; John, 1971; Tucker and Kurtz, 1955; Lagerwerff 1971).

Table III Heavy metal recovery from two soil samples following sample fortification with (two and six hours shaking) and pH adjustment.

		TWO HOURS SHAKING				SIX HOURS SHAKING			
		Cd	Pb	Cu	Zn	Cd	Pb	Cu	Zn
		%				%			
0.1 N HCl	Ah	45.1	49.8	60.2	100.7	69.7	43.4	65.7	142.2
	Bgf	82.0	87.6	79.4	182.2	66.8	78.4	72.8	166.6
1.0 N HCl	Ah	54.2	90.0	84.8	135.5	53.8	85.8	87.3	117.1
	Bgf	65.4	95.1	72.3	169.9	89.9	101.2	94.2	228.0
0.05 M E.D.T.A.	Ah	53.0	82.1	83.6	104.1	62.8	82.4	86.5	123.3
	Bgf	73.4	96.1	78.3	164.4	108.3	125.0	97.4	188.6

In order to evaluate this finding a bit further, analogous analytical results are presented in Table IV and Appendix III; two surface soils (Site I-Ap and Site III-Ap) of the Salmon River Watershed were used. The Site I-Ap was a clay loam with 21% O.M and the Site III-Ap a silt loam with 7% O.M. Some selected properties of these soils have been presented in Appendix IV and Appendices VI to VIII.

Variable results in cadmium recovery were noted between Site I-Ap and Site III-Ap, regardless of extractant. This made it difficult to assess whether differing organic matter content and parent material partly affected retention. Duncan's Multiple Range tests, showed that with both Site I-Ap and Site III-Ap samples, no significant differences was found between 0.1 N HCl and 1.0 N HCl treatments; but, there were significant differences between 0.1 N HCl and 0.05 M EDTA, and 1.0 N HCl and 0.05 M EDTA. Such consistent trends regardless of kind of parent material and organic matter content, favours the statement that EDTA is a more effective extractant for removing added cadmium from these soils.

The data collected for lead illustrated that 0.1 N HCl and 1.0 N HCl removed a greater percentage of added lead from Site III-Ap (low O.M. and clay) than Site I-Ap (high O.M. and clay); analogous results were obtained from the surface Ah and sub-

Table IV Heavy metal recovery following sample fortification, with (two hours shaking) and pH adjustment.

	Alluvium (Site-I Ap)				Glacial Outwash (Site III Ap)			
	Cd	Pb	Cu	Zn	Cd	Pb	Cu	Zn
	%				%			
0.1 <u>N</u> HCl	84.6	54.1	71.3	71.7	69.4	70.0	77.7	79.3
1.0 <u>N</u> HCl	85.3	73.5	92.5	68.1	68.1	80.9	92.0	90.8
0.05 <u>M</u> E.D.T.A.	113.0	115.4	115.3	114.7	89.8	103.5	91.6	97.0

surface (Bgf) samples used in the preliminary studies. It would, therefore, be reasonable to suggest that the efficiency of an extractant to extract added lead is partly a function of organic matter content and texture. Duncan's Multiple range test on the lead data from both samples (alluvial and outwash sites) showed significant differences between any two of the three treatments, with the EDTA extraction the most significant.

In the case of copper extracted from Site III-Ap, no significant difference between 1.0 N HCl and 0.05 M EDTA treatments was observed; however, significant differences, existed between 0.1 N HCl and 1.0 N HCl and between 0.1 N HCl and 0.05 M EDTA. Copper extracted from the alluvial horizon (Site I-Ap), showed differences between any two treatments (0.1 N HCl and 1.0 N HCl, 0.1 N HCl and 0.05 M EDTA, and 1.0 N HCl and 0.05 M EDTA) thus indicating EDTA to be the most effective extractant.

Differences in treatment means for zinc did not provide consistent recovery trends in both alluvial and outwash surface samples. With the alluvial horizon, significant difference was found between 1.0 N HCl and 0.05 M EDTA, 0.1 N HCl and 0.05 M EDTA, but no significant difference was noted between 0.1 N and 1.0 N HCl treatment means. Brown et al. (1971) reported from his studies on zinc that to properly characterize the zinc status in soils more than one extraction method may be required.

Discussions so far have illustrated that many parameters are involved in soil-heavy metal reactions. Because of the complexity of these reactions and the differing chemical properties of these transition metals, no conclusive statement can be made regarding a best extractant. The amount of metal present in an acid extract may be the sum of the readily soluble and exchangeable, slowly exchangeable and extractable, plus an amount which is released from the inner part of the inorganic and organic structures as it decomposes or is dissolved by the acid.

It can be inferred from this study that hydrochloric acid at the concentrations used (0.1 N HCl and 1.0 N HCl) and 0.05 M EDTA are fairly good extractants when the four metals are considered in a multi-component system. It is felt that EDTA (0.05 M) with a soil-solution ratio of 1:10 and an equilibration time of two hours is a good compromise and was selected as the means for removing the heavy metals without damaging the structural components of the soil. This selection is supported by the fact that the pH of equilibrated EDTA-soil solutions for all samples, ranged between 4.0 and 4.5; as expected, the samples with HCl as extractant had pH values of less than 1.0. It would be more likely to approach natural pH soil conditions with EDTA rather than with HCl.



### Correlation Studies

Examination of the factors affecting extraction was performed using correlation analysis. Simple correlations were run between percent recovery and some primary soil properties on the IBM Computer 360. For each treatment, data were drawn by combining recovery values for Site I-Ap and Site III-Ap. Because of the limited number of observations for the analyses and subsequently a limited degree of variation in the soil's data, very high correlations have been obtained. Since such analyses are only qualitative in nature, they should be interpreted with caution. Comparison of simple correlations for the treatments 0.1 N HCl, 1.0 N HCl and 0.05 M EDTA are given in Appendix X.

Correlations between the hydrochloric acid treatment and EDTA seem worthy of interpretation. Irrespective of hydrochloric acid normality, pyrophosphate-Al and oxalate-Al were positively correlated with percent lead recovered; and negatively correlated (-0.97) in the case of EDTA extraction. It was also observed for lead that when Pyrophosphate-Fe, Oxalate-Fe, organic matter and clay content were negatively correlated with percent recovery for the hydrochloric acid treatments, they were all positively correlated for the EDTA treatment. Such variation in correlation patterns would seem to suggest that the forms of lead extracted by mineral acid are different than that extracted by EDTA. John

(1971) found no correlation between lead extracted by  $\text{HNO}_3$  and organic matter but John (1972c) reported correlations with soil pH, extractable -Al (by  $\text{CH}_3\text{COONH}_4$ ) and total nickel. These results would therefore imply that in soils, organic acids analogous to EDTA would be able to extract lead associated with iron oxides, organic matter and clay, but would not be efficient in extracting lead in association with aluminum. It would also appear that the opposite would probably hold true for the forms of lead extracted by hydrochloric acid.

Different correlation trends were observed for copper, regardless of soil properties; percent recovery was loosely correlated (0.19) for the 1.0 N HCl treatment, but highly correlated (0.96) for the 0.1 N HCl and 0.05 M EDTA treatments. These findings would, therefore, substantiate the argument that varying the concentration of the extractant HCl, does have an effect on recovery of added copper. The high negative correlation (-0.96) found successively with organic matter and clay are as expected. Little copper was retained by the sample because of low organic matter and clay content. Strong positive correlations (0.99) with these two soil fractions for the EDTA treatment were in agreement with the postulate that EDTA extracts soluble, exchangeable and organically bound copper (McLaren and Crawford, 1973; Kishk et al. 1973). Similar correlation trends with pyrophosphate and ammonium oxalate were obtained for lead, copper,

zinc and cadmium extracted by EDTA; but, varied from metal to metal for the hydrochloric acid treatments.

The correlations obtained by the EDTA treatment for cadmium with clay and organic matter were noted to be similar to that obtained for zinc. When the mineral acid treatments were compared, high negative correlations ( $-0.89$ ) were obtained for zinc and strong positive correlations ( $+0.99$ ) for cadmium; similar trends were noted with pyrophosphate and ammonium-oxalate aluminum and iron. The high negative correlations for zinc would suggest that it is strongly held by organic matter and clay; and that, it would be difficult to extract it by HCl, but that EDTA is able to do so. Zinc retention by organic matter, clay and on cation exchange sites have been demonstrated (John, 1974; Dollar and Keeney, 1971; Brown *et al.*, 1971). However, Martens, Chesters and Peterson (1966) found that an increase in organic matter content with constant clay increased the amount of zinc extracted; this finding was supported by John (1972) who also noted extractable zinc in soil to increase with increased acidity, fine texture and higher organic carbon. Pietz, Adams and MacGregor (1970) also reported that the amount of soil zinc extracted by various buffers and dithizon is related to organic carbon and clay content thus inferring organic matter to be more important than clay in retaining zinc; and, that the ammonium ion was more effective in displacing zinc from organo-zinc complexes.

Opposite correlations for Zn and Cd (HCl treatments) lead to the suggestion that these two metals, though often associated in natural ores, may behave differently in the presence of a combination of mineral and organic components in the soil. But, data from EDTA treatments would lead to infer that similar kinds of retention occur by soil organic colloids for both zinc and cadmium, but not by the inorganic soil constituents.

### Heavy Metal Partitioning in Soils

The results of the partitioning of lead, copper, zinc and cadmium in the various parent materials of the Salmon River Watershed have been presented in Table V. Selected chemical and physical properties of the soils have been reported in Appendices IV, VI and VII; and the mineralogical composition of the less than two micron fraction in Appendix VIII.

### Alluvial Sites

Since the alluvial sites (Sites I - golf course and Site II - agricultural crops) have been under different land use practices, one would expect different distributions between soils; however, there were no marked differences in the intensity of contamination with depth between sites for any of the heavy metals. Both sites were in proximity to a road and have been under fertilization for the last decade.

Table V Distribution of selected heavy metals from six soils under different land use practices.

Parent Material	Horizon	Depth cm	Land Use	0.05 <u>M</u> E.D.T.A. Extractable.			
				Cd	Pb	Cu	Zn
				ppm			
Alluvium (Site I)	Ap	0-25	Golf	0.60	10.00	26.27	19.00
	Bg	25-40		0.30	2.00	19.50	12.95
	C	40 <sup>+</sup>		0.30	1.75	25.55	7.50
Alluvium (Site II)	Ap	0-20	Agricultural Crops	0.75	8.25	19.50	16.07
	Bg	20-40		0.27	1.00	20.00	4.35
	C	40 <sup>+</sup>		.22	0.50	15.15	6.50
Glacial Outwash (Site III)	Ap	0-12	Agricultural Crops	0.07	3.50	2.30	10.00
	B	12-90		0.22	1.75	2.12	9.12
	C	90 <sup>+</sup>		0.10	N.D	4.35	5.70
Glacial Outwash (Site IV)	A	0-10	Forest	0.30	7.00	2.87	7.22
	B	10-40		0.22	0.50	2.92	8.20
	C	40 <sup>+</sup>		0.32	2.00	5.00	6.97
Glacial Marine (Site V)	Ap	0-10	Hay	0.27	3.50	3.67	9.25
	B	10-70		0.20	1.50	2.87	6.85
	C	70 <sup>+</sup>		0.10	0.75	1.20	5.35
Glacial Marine (Site VI)	H	0-4	Forest	0.45	14.25	3.82	10.00
	Bf	4-75		0.30	2.25	1.50	5.20
	C	75 <sup>+</sup>		0.15	1.25	1.00	3.80

Values obtained in the top 25 cm were as follows:  
cadmium: 0.60 ppm and 0.75 ppm for Sites I and Sites II respectively; lead: 10.0 ppm (Site I) and 8.2 ppm (Site II); copper: 26.3 ppm (Site I) and 19.5 ppm (Site II); zinc: 19.0 ppm and 16.1 for Sites I and II, respectively. These data have illustrated that no marked differences existed between sites, which would seem to suggest that regardless of the type of agricultural management, and over a period of time, the same levels of heavy metals could prevail in soils derived from alluvial parent material. Accumulation of heavy metals in the surface horizon of agricultural soils has been reported previously (lead: Jones and Hatch, 1937; Presant and Tupper, 1965; John, 1971; Zinc: John, 1974; Walsh, 1972). Very little information is available in the literature on the partitioning of copper and cadmium in agricultural soils. As can be seen from Table V, there were twice as much cadmium and zinc, and, more than five times the amount of lead in the surface horizons of both sites compared to the sub-surface; however, the decrease in copper distribution with depth is not consistent.

Irrespective of site and horizon, both soils had vermiculite as the dominant clay mineral, followed by kaolinite, illite and chlorite with very little montmorillonite or interstratified minerals. These sites were fairly high, in organic matter (12-20%); cation exchange capacity ranged from 40-50 meq/100 g and the soils were high in clay content ( $\cong 35\%$ ).

It, therefore, appears that the various soil constituents, singly or in combination, reduce the movement of lead through the soil to a greater extent than zinc, cadmium or copper. The limited mobility of lead in soils, has been demonstrated by leaching studies (Anon, 1974); it has been found that only a third of the lead retained in the soil could be displaced by calcium chloride. In the case of zinc, Walsh (1972) observed that very little downward movement was observed following application of high rates of zinc on crops grown on irrigated sandy soils; the zinc had moved only to a depth of 30 cm in the soil two and a half years after application.

The high values observed for copper in both sites can be the result of copper additions through biocide applications, or as impurities in fertilizers. Literature surveyed revealed that studies on copper in soils only with surface horizons or soil fractions have been examined; information is scanty regarding profile distribution under different land use practices and parent materials. In this study, distribution patterns through alluvial and outwash soils seem to indicate that copper is fairly uniformly distributed to a depth greater than 40 cm. Evidence for copper mobility has been previously demonstrated. Leeper (1972) claimed that all the mobile forms of the metal are in anionic forms associated with chelating agents such as citric acid. The ability of chelates (EDTA) to bind copper has been demonstrated (Norvell and Lindsay, 1969).

### Outwash Sites

Data for these sites are reported in Table V, and some of their chemical, physical and mineralogical properties in Appendices IV, VI, VII and VIII.

Though Site III has been under continuous strawberry production for the past twenty years, the values found for the heavy metals are much lower than that encountered for the alluvial sites. The same holds true for Site IV which is under virgin forest and only 100 meters away from Site III with a road lying between them.

The surface horizon for Site III had 0.07 ppm cadmium, 3.5 ppm lead, 2.3 ppm copper and 10.0 ppm zinc. Site IV (forest) had 0.30 ppm Cd, 7.00 ppm Pb, 2.87 ppm Cu and 9.25 ppm Zn. The lower ratios observed between the surface and sub-surface horizons in the alluvial parent material than in the outwash sites indicated that there is a difference in distribution with depth with differing parent materials. In the case of the forested site, the distribution of zinc was uniform to a depth of 40 cm and in the strawberry site to a depth of 90 cm. X-ray mineralogy of the less than 2 micron fraction showed chlorite and kaolinite to be predominant in the strawberry site and, vermiculite and chlorite in the virgin forest site.

These two sites were low in organic matter, clay and cation exchange capacity; despite these facts, lead was limited to the top 12 cm, indicating again that compared to the other heavy



metals, mobilization does not seem to take place to a significant extent; in fact, beyond a depth of 90 cm, no lead was detected. However, the findings for copper were different; more copper was present in the C horizon (90 cm depth) than in the surface horizons. The possible explanation for this phenomenon in Site III may be due to the low organic matter and clay content in the surface and therefore minimal retention; since both sites regardless of land use have high copper-values in the C horizon, an alternative explanation may be the inherent nature of the parent material.

The low cadmium value (0.07 ppm) at Site III-Ap (despite biocide and fertilizer application) is hard to explain when compared to that in Site IV-Ap (0.30 ppm). In general, it appears that in outwash soils, the mobility of cadmium resembles closely that of zinc. The higher value of lead in Site IV-Ap than Site III-Ap can be explained by the fact that the road was closer to it than Site III-Ap; this would support previous reports that automobile exhaust is a major contributor in contaminating soils with lead (Lagerweff, 1971; Chow, 1970; John, 1972C).

### Glacial Marine Sites

Results presented in Table V, showed some striking differences in lead levels between the two sites. Lead values for Site VI

(virgin forest) averaged 14.25 ppm compared to 3.50 ppm for Site V which was under timothy grass; (the same remark holds true for surface values found in the outwash sites). Since both samples were taken within 100 feet from the roadside, it would be reasonable to assume that land use practices affect lead concentration in surface soils. The lower values in the timothy grass site may be explained by lead removal through plant uptake and subsequent crop harvest, thus entering the food chain and having little time to accumulate in the surface.

In the case of Site VI, lead accumulation in the surface may be attributed to retention by the high organic matter content; once more a significant drop in lead level with depth was noted. Jones and Hatch (1937) reported no correlation between depth and lead content; such findings may have been valid at that time since air and soil pollution by industry was not as acute as it is today. In this study, virgin forest soils on both glacial marine and glacial outwash parent materials showed a sharp decrease in lead content with depth. This seems to support previous findings (Chisolm, 1972; Lagerweff, 1967; Chow, 1970; Lagerweff and Specht, 1970) that lead does accumulate in the surface, and, there is a relationship between road proximity and lead contamination. In view of the dominating effects of certain soil constituents on lead mobility, it would be reasonable therefore to infer that no

relationship exists between kind of parent material and lead contamination.

At 70 cm depths, cadmium values for both sites were reduced three-fold, thus indicating lesser mobility than in the outwash sites and almost the same amount as in the alluvial sites. According to Allaway (1968), values for cadmium in non-polluted soils ranged from 0.01 to 7 ppm. Practically no information is available on the levels of cadmium in soils derived from different parent materials.

Greater levels of cadmium in the surface of both Sites IV and Site VI than in Sites V and Site III, seem to indicate that road proximity and type of land use would be contributing factors; consequently the lower levels under cropping would probably mean cadmium removal through plant uptake and subsequently into the food chain.

Copper contents in the surface horizons of both glacial marine sites were of the same magnitude and decreased almost three-fold with depth. Copper distribution within parent materials did not vary as much as it did between parent materials, thus indicating that the fate and distribution of copper in soils is affected not only by major properties such as CEC, clay and O.M, but also by the nature of the parent material.

With zinc, inconsistent trends with depth, made it difficult to infer whether the nature of the parent material has an effect on zinc distribution within the profile. In both glacial marine sites, a general decrease with depth was observed with values ranging from 10.0 ppm in the surface to 3.8 ppm in the C horizon of the forest site; and 9.2 ppm in the Ap and 5.4 ppm in the C horizon of the timothy grass site.

In general, for all sites studied, it appears that the amount of zinc extracted from surface soils is twice that extracted from sub-surface samples, a fact which has also been observed by John (1974) in some soils of British Columbia.

#### Heavy Metals in Sediments

As stated, the impacts of heavy metal contamination, extends beyond the boundaries of terrestrial plants and soils. Streams receive materials from upstream, bank erosion and overland flow from the various soils within a watershed. Since not much is known about heavy metal accumulation in tributaries, a preliminary survey was conducted for identifying the level of contamination of sediments within the watershed.

Results of the sediment analyses, are given in Table VI. Appendices V, VI, VII and IX describe the physical, chemical and mineralogical properties of the sites. Site 7 is situated upstream and is surrounded by glacial outwash; Site 6 is also situated upstream. Both sites had lower cadmium (0.10 ppm) and lead (1.00 ppm) than the other sites; they also had lower organic

Table VI Heavy metal distribution in surface sediments of the Salmon  
River Watershed

Sediment sample	0.05 <u>M</u> E.D.T.A. Extractable			
	Cd	Pb	Cu	Zn
	ppm			
S <sub>1</sub>	0.40	8.00	11.75	5.80
S <sub>2</sub>	0.45	8.50	10.00	24.62
S <sub>3</sub>	0.27	5.00	5.37	12.25
S <sub>6</sub>	0.10	1.00	16.50	8.67
S <sub>7</sub>	0.10	N.D	2.45	10.32

matter contents (0.3% and 0.6% respectively) and CEC values (3.70 me/100 g and 4.11 me/100 g respectively). Since Sites 1, 2 and 3 are located downstream in areas of increased suburban activity, it would be reasonable to assume that for these reasons, higher values for some metals have been obtained. Cadmium values were four times higher and lead about eight times higher downstream than upstream; however, the same does not hold true for copper and zinc. Values for copper ranged between 2.4 ppm for Site 7 to 16.5 ppm for Site 6 with a downstream average of 10.0 ppm. In the case of zinc, the highest value was obtained downstream (24.62 ppm) compared to 8.7 ppm upstream.

It appears that cadmium and lead levels can be related to sediment properties; higher values in the sediments downstream may be explained by the higher cation exchange capacity (24.9 me/100 g) and OM (6.0%) of the downstream sediments than the upstream sediments which had on the average 0.45% OM and CEC of 3.9 me/100 g.

X-ray mineralogy (Appendix IX) of the less than two micron fraction of all sites, showed vermiculite as the dominant clay mineral, with montmorillonite and kaolinite in moderate amounts; primary minerals being quartz, feldspars and micas. Almost the same minerals were found in the soils and have been reported in Appendix VIII; similar findings have been reported by Lund, Kohnke and Paulet (1974) who found only small differences between com-

composition of soil clays of a watershed and that of sediment clay. Since regardless of location, the surface sediments had almost identical primary and secondary minerals, it would seem that the latter would not serve as indicators of heavy metal enrichment. An approach, therefore, for exploring causes of heavy metal enrichment would be to compare the levels found in the sediments to that in the surrounding parent materials.

Site 6 was sampled within the glacial marine parent material. Cadmium values were four times higher in the virgin forested soils than in the sediments, and more than ten times in the case of lead. As one approaches downstream areas (agricultural and residential areas), the levels of all four metals in the sediments as well as in the soils increased significantly.

Site I was sampled in alluvial parent material and was situated downstream near the estuary leading to the main stem of the Fraser River. The ratio of values for the elements in surface soil to sediment for cadmium was approximately 1.5, lead 1, copper 2 and zinc 3. These ratios were different than the ones recorded upstream. Literature surveyed in Canada (Oliver and Kinrade, 1972) revealed that lead in the sediments of the Ottawa River and its tributary the Rideau to be 26 ppb and 42 ppb, respectively. Data from both the literature and this study, lead to suggest that lead is probably transferred to sediments and migrates by adhering to them during sediment transport. The

mobility of copper and removal from stream water have been investigated; Krauskopf (1972) postulated that the distance copper can travel is limited to a great extent by its strong adsorption to many kinds of surfaces. It has also been suggested that copper can be transported in water for a few kilometers before being deposited; in solutions that are not acid and oxidizing, the movement of copper is much more limited.

This investigation has provided evidence about the effectiveness of certain reagents to extract added elements from agricultural and non-agricultural soils of British Columbia. In order to understand whether the elements are retained by similar mechanisms under varying conditions of pH and concentration range, physico-chemical methods must be utilized. The next chapter will consider possible mechanisms responsible for the retention of these elements to the inorganic constituents of soils, namely clay minerals.

## CONCLUSIONS

Preliminary studies conducted on the extraction of added copper, lead, zinc and cadmium from some soils of British Columbia, showed hydrochloric acid and EDTA to be better extractants than nitric and acetic acids.



However, in the case of cadmium, Duncan's Multiple Range test ( $\alpha = 0.05$ ) showed no significant differences among treatments, thus indicating that even weak acids can affect its distribution within a profile.

Irrespective of heavy metal, differences in organic matter and cation exchange capacity between surface and sub-surface samples showed significant differences in percent recovery.

When further evaluation of the extractants hydrochloric acid and EDTA were undertaken, it emerged from the experiments, that no significant difference existed between percent recovery and shaking periods of two and six hours.

A concentration of 0.05 M EDTA, soil-solution ratio of 1:10 and an equilibration time of two hours were good compromises selected as the best means for removing the heavy metals without damaging the structuralyorganic and inorganic soil constituents.

Values of heavy metals in alluvial sites were generally higher than in the glacial outwash and glacial marine sites. Lead, cadmium and zinc levels decreased with depth; however, copper distribution in the profiles stayed almost constant. Lead was retained to a greater extent than the other metals, and correlated strongly with organic matter and to a lesser extent with cation exchange capacity. Copper seemed to exhibit greater mobility than cadmium or zinc in all sites. X-ray

mineralogy of the less than two micron fraction showed all sites to contain vermiculite, kaolinite in moderate amounts, with chlorite, illite, montmorillonite, quartz and feldspars in minor amounts. The alluvial sites were generally higher in organic matter, clay content and cation exchange capacity than the outwash and glacial marine sites.

Comparative data from soils under different land use practices showed lead and possibly cadmium in soils to be associated with traffic proximity.

Analysis of surface sediments from the Salmon River indicated higher metal values in industrial, agricultural and near estuary sites than from upstream rural sites. Mineralogical composition of the less than two micron fraction of sediments, showed only very small differences between composition of soil clay and sediment clay within the watershed.

Heavy metal ratios of surface soil to surface sediments downstream were 1.5 for cadmium, 1.0 for lead, 2.0 for copper and 3.0 for zinc; these ratios are higher than that observed upstream, indicating that contamination is related to land management.

Cation exchange capacity, organic matter and clay content were higher in the downstream sediments. It would appear that heavy metals are transferred to sediments and migrate by adhering to them during sediment transport.

## PART II

### Heavy Metal Adsorption Isotherms for some Clay Minerals

#### INTRODUCTION

Heavy metals such as zinc, copper, cadmium and lead are at present the subject of intensive biological and biomedical investigations. Control measures are being devised by environmental agencies to maintain desired levels so that water quality and biological activity are not affected. Since solubility and mobility of heavy metals in soils are affected by structural and chemical properties of the latter, it is worth elucidating the nature of interactions between some of the soil constituents and certain heavy metals.

Heavy metal studies conducted with clay minerals have dealt with, (a) ion-exchange equilibria, (Bingham, Page and Sims, 1964; Bitell and Miller, 1974; Tiller and Hodgson, 1962; Hodgson et al., 1964; Kishk and Hassan, 1973); (b) the factors influencing lattice fixation (McBride and Mortland, 1974); (c) pH effect on zinc adsorption by montmorillonite, illite and kaolinite and their bonding mechanisms (Reddy and Perkins, 1974);

and (d) sorption in excess of cation-exchange capacity arising partly from metal hydrolysis (Menzel and Jackson, 1950; De Mumbrum and Jackson, 1956a, 1956b) and ion-pair formation (Santillan-Medrano, 1974). In the previous section, the effectiveness of certain reagents to extract added heavy metals from soils were investigated. The experimental work described in this phase of study dealt primarily with the adsorption of lead, cadmium, copper and zinc on selected clay minerals over a wide concentration range and pH conditions. The clay minerals selected below were chosen because of their predominance not only in the soils of the watershed, but as well in the soils of British Columbia. Literature surveyed indicated that most of the work had been undertaken in chloride, sulphate, hydroxyl and phosphate systems, but virtually none in nitrate systems. The nitrate ion can be important in the distribution and transport of heavy metal ions, particularly in areas of intense pollution; subsequently, it was felt appropriate to work at a high concentration range to attempt to simulate the limits of potential pollution.

The objectives of this investigation were to elucidate:-

1. The effect of pH on the sorption capacities of montmorillonite, vermiculite, illite and kaolinite for heavy metals over a concentration range of 0 to 3000 ppm; and

2. the sorption capacities of montomorillonite and kaolinite from an equivalent mixture of heavy metals at a fixed pH. Use was made of the Langmuir and Freundlich equations to allow quantification and further interpretation of data.

## MATERIALS AND METHODS

The Langmuir equation is usually expressed as follows:-

$$\frac{C}{x/m} = \frac{1}{K_1 K_2} + \frac{C}{K_2}$$

where  $C$  = equilibration concentration of adsorbate

$x/m$  = amount of adsorbate adsorbed per unit of adsorbent

$K_2$  = adsorption maximum

$K_1$  = a constant related to the bonding energy of the adsorbent for the adsorbate

This equation was originally derived by Langmuir to illustrate that gas-molecules are adsorbed to a solid surface as a monolayer with a constant and specific energy of adsorption; it has since been applied to study the adsorptive behaviour of ions to any solid surface (Reddy and Perkins, 1973; Shuman, 1975).

Linearity in a plot of  $\frac{C}{x/m}$  vs  $C$  implies that the adsorbent will adsorb only a given amount of the ion, and that this will be as a monolayer with a uniform bonding energy. A curved relationship can be interpreted to imply that the adsorbent will adsorb a small amount with constant and firm bond energy, a slightly greater amount less firmly and so on. In this study, the equation has allowed the determination of the adsorption maxima of lead, copper, cadmium and zinc by layer silicates. One limitation in using such an equation is, that, little information concerning the mechanisms of adsorption of the ions under study is obtained. Another disadvantage is that a satisfactory fit of the experimental points to the equation does not necessarily mean that the mechanism underlying the monolayer theory is fulfilled. However, an advantage is that an adsorption maximum can be predicted within a given original concentration range from laboratory measurements. Because scanty information is available regarding heavy metal adsorption, amassing of such categories of data would allow generalizations to be made which would be of predictive value, though the phenomena are not completely understood.

The Freundlich adsorption isotherm is expressed as follows:

$$y = ac^b$$

where  $y$  = amount of adsorbate taken up by unit weight of adsorbent

$c$  = equilibrium concentration in solution

$b, a$  = slope and intercept of the isotherm, respectively

Logarithmic transformation of the above equation and plotting of  $\log y$  against  $\log C$  (x-axis) would yield a straight line. The constants 'a' (intercept) and 'b' (slope) provide rough estimates of the adsorbent capacity and the intensity of adsorption, respectively (Adamson, 1967). Conformity of experimental data with the Freundlich equation would suggest that this process goes on indefinitely.

### Preparation of Materials

#### Clay minerals

The clay minerals\* used were:

- i. Montmorillonite No. 31 (Arizona)
- ii. Vermiculite (Africa)
- iii. Illite No. 35 (Fithian, Illinois)
- iv. Kaolinite No. 5 (Bath, South Carolina)

These minerals were selected because of their predominance in the inorganic fraction of the soils of British Columbia. Prior to sodium saturation of the clays, they were ground to pass a 60 mesh stainless steel sieve. To 25 g of clay mineral, 200 ml of 1.0 N  $\text{NaNO}_3$  were added (mineral:solution ratio of 1:8). The

\* Available from Ward's Scientific

contents were shaken for 15 minutes on an end over end shaker and centrifuged until the supernatant solution was clear. The supernatant liquid was discarded and this procedure was repeated three times. Removal of excess salts was completed with three separate washings of a 1:1 water-ethanol mixture followed by ethanol. The sodium-saturated samples were freeze-dried and stored in a desiccator.

#### Stock Solutions

Cadmium: The metal was left in dilute nitric acid for approximately one hour, rinsed three to four times with distilled deionized water to remove any excess acid prior to washing with acetone. To prepare 4 litres of 6000 ppm cadmium, 24.0006 g of the cleaned metal was dissolved in 30 ml of concentrated nitric acid, which was diluted before use.

Zinc: Analytical grade zinc was washed prior to use by the same procedure as described for cadmium. To prepare one litre of 6000 ppm Zn, 6.0009 g of the metal was dissolved in 12.0 ml of conc. nitric acid (diluted before use).

Copper: To prepare one litre of 6000 ppm Cu, 6.0003 g of freshly washed copper metal (analytical grade) was immediately weighed and dissolved in 12 ml of concentrated nitric acid (diluted before use).



Lead: To obtain a 6000 ppm Pb, 19.2004 g of  $\text{Pb}(\text{NO}_3)_2$  (analytical grade) was dissolved in two litres of distilled-deionized water to which a few drops of nitric acid were added.

#### Equivalent mixture of Cd, Pb, Cu and Zn

To obtain a 4-litre stock solution of 100 me/litre, 12.7080 g Cu, 22.4820 g Cd and 13.076 g Zn (all freshly cleaned) were taken and allowed to dissolve in nitric acid. Approximately 100 ml of concentrated nitric acid (diluted before use) were needed to dissolve the metals; it was necessary to warm the container from time to time. Prior to bringing to volume, 66,2460 g of  $\text{Pb}(\text{NO}_3)_2$  were added.

#### Analytical Method

Individual study: In all experiments, 0.2 g of Na-saturated clay mineral (adsorbent) was weighed into a 50 ml plastic centrifuge tube. Triplicate samples were shaken with 25 ml of the corresponding adsorbate and the pH adjusted as desired with NaOH or  $\text{HNO}_3$ . The samples were then equilibrated at  $25 \pm 0.2^\circ\text{C}$ , on a thermostatically controlled end over end shaker. An equilibration time of 18 to 20 hours was chosen as being adequate. This arbitrary decision was made based on the findings of previous workers; John (1972b) and McLaren (1973) used equilibration times of 16 hr and 24 hr

respectively for cadmium and copper isotherms. The samples were then centrifuged and aliquots of the supernatant liquid were diluted when required, for analysis by atomic adsorption spectrophotometry.

Cd, Pb, Cu and Zn were adsorbed on montmorillonite, vermiculite, illite and kaolinite. The original concentration levels of the four elements: 100 ppm, 250 ppm, 500 ppm, 1000 ppm, 1500 ppm, 2000 ppm and 3000 ppm. The experiments were conducted at working pH of 4, 5, 6 and 7.

Competition Study: This experiment was conducted at the single pH 5.0. Quintaplate samples of 0.2 g adsorbent were shaken with 25 ml equivalent mixture of cadmium, lead, copper and zinc and the pH adjusted to 5.0 with NaOH or HNO<sub>3</sub>. The adsorbents used were Na-montmorillonite and Na-kaolinite. The original levels of adsorbate chosen were 0.025, 0.05, 0.1, 0.5, 1.0, 5.0, 10.0, 20.0 and 50 me/litre. The equilibration time was set for 18 hours; the samples were then centrifuged and the supernatant solution analyzed for cadmium, lead, copper and zinc by atomic absorption spectrophotometry.

#### Cation Exchange Capacity

Duplicate samples (0.2 g) of the minerals were saturated with 25 ml of 1.0 N NaNO<sub>3</sub>, shaken for 5 minutes, allowed to stand overnight and shaken for 30 minutes prior to centrifuging.

The samples were equilibrated with two additional 25 ml portions of 1.0 N  $\text{NaNO}_3$  followed by two washings with 25 ml aliquots of isopropanol-water (1:1) mixture. The sodium was displaced by washing with 3 successive 25 ml portions of 1.0 N  $\text{KNO}_3$  and the supernatant liquid brought to volume in a 100 ml volumetric flask, before analysis for Na by atomic absorption spectrophotometry.

### Data Treatment

The original readings were computed on an arithmetic mean basis and relevant data have been presented in Appendices (XI-XV). Because adsorption isotherms indicate primarily adsorption patterns, all the average values were incorporated into the Langmuir and Freundlich equations by the least square technique, which was run on the IBM 360 computer using the UBC Trip program.

## RESULTS AND DISCUSSION

### Individual Study

The results obtained from these sets of experiments are presented in the form of graphs, with amount adsorbed ( $x/m$ ) on the y-axis and equilibrium concentration ( $C$ ) on the x-axis. Averages from triplicate readings are reported in the corresponding Appendices (XI to XIV). The results have been summarized and presented in Tables VII to XI. Standard error of 'a'

values, from the Freundlich equations, are reported in linear units and not in logarithmic units. Large standard error values obtained for some regression equations are probably because the triplicate observations were averaged and, so far as the computer program was concerned, the number of replications was only one.

Cation exchange capacities of the clay minerals as determined by the sodium nitrate method, did not change significantly with increasing pH. On the average, the values obtained were 77.6 me/100 g for montmorillonite, 109.1 me/100 g for vermiculites, 17.5 me/100 g for illite and 7.5 me/100 g for kaolinite.

Adsorption maxima/cation exchange capacity ratios for each metal with montmorillonite and vermiculite were calculated and are reported in Tables IX and XII; it is envisaged that these ratios would allow certain generalizations to be made regarding heavy metal adsorption in a nitrate system.

When adsorption patterns were considered (Fig. 2-5), it was observed that in all cases, there was an increase in sorption with increasing pH.

Montmorillonite: Figure 2 illustrates the adsorption patterns for cadmium, lead and zinc at pH 4, 5, 6 and 7 respectively; and for copper at pH 4, 5 and 6. Irrespective of heavy metal, the sorption characteristics of montmorillonite

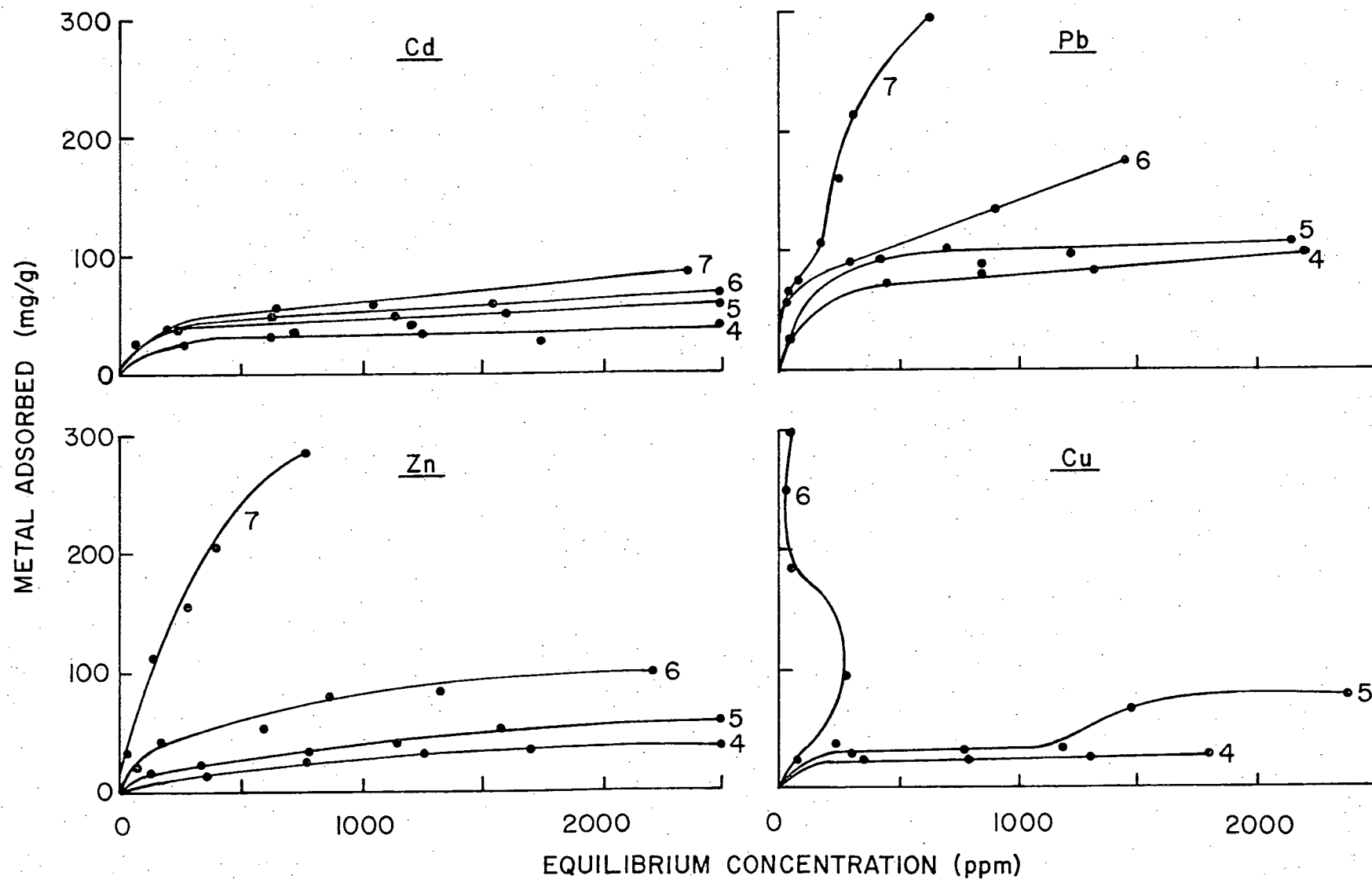


FIG. 2. HEAVY METAL ADSORPTION BY MONTMORILLONITE AT FOUR pH-VALUES

Table VII    Langmuir constants and statistical analysis of heavy metal adsorption  
on montmorillonite with four heavy metals at four pH values\*.

Montmorillonite	Constant a	Regression Coefficient b	F(ratio) b	Standard Error a	Standard Error b	Standard Error y	Coefficient of determination $r^2$
pH 4							
Cadmium	3.85	0.025	77.5	3.80	0.003	6.92	0.939
Lead	0.88	0.010	352.7	0.56	0.001	1.11	0.986
Copper	1.14	0.039	118.7	3.53	0.004	5.84	0.967
Zinc	9.17	0.020	45.2	4.04	0.003	7.14	0.900
pH 5							
Cadmium	3.99	0.018	76.9	2.54	0.002	4.64	0.939
Lead	1.11	0.009	369.1	0.48	0.001	0.94	0.989
Copper	7.89	0.012	9.2	4.84	0.004	8.54	0.649
Zinc	8.66	0.015	28.5	3.58	0.003	6.32	0.851
pH 6							
Cadmium	2.59	0.015	188.3	1.35	0.001	2.52	0.974
Lead	1.27	0.006	47.6	0.58	0.001	1.10	0.905
Copper	0.23	0.019	8.8	0.92	0.006	1.80	0.638
Zinc	3.44	0.009	60.9	1.26	0.001	2.33	0.924
pH 7							
Cadmium	2.75	0.012	56.9	1.72	0.002	3.19	0.934
Lead	1.12	0.002	15.6	0.12	0.001	0.20	0.796
Copper	0.06	-0.001	0.1	0.03	0.004	0.03	0.024
Zinc	0.86	0.003	86.7	0.10	0.001	0.17	0.956

\* Model  $y = a + bx$

Table VIII Freundlich constants and statistical analysis of heavy metal adsorption  
on montmorillonite with four heavy metals at four pH values\*.

Montmorillonite	Constant a	Regression Coefficient b	F(ratio) b	Standard Error a	Standard Error b	Standard Error y	Coefficient of determination $r^2$
pH 4							
Cadmium	2.76	0.164	35.0	1.07	0.028	0.06	0.875
Lead	3.12	0.265	14.6	1.18	0.069	0.18	0.745
Copper	2.75	0.127	17.1	1.08	0.031	0.64	0.810
Zinc	2.46	0.186	15.6	1.14	0.047	0.11	0.757
pH 5							
Cadmium	2.69	0.209	52.0	1.08	0.029	0.07	0.912
Lead	2.67	0.325	15.9	1.21	0.082	0.18	0.761
Copper	1.96	0.322	25.6	1.18	0.063	0.12	0.837
Zinc	2.59	0.197	11.3	1.17	0.058	0.16	0.693
pH 6							
Cadmium	2.68	0.240	48.4	1.09	0.034	0.08	0.906
Lead	2.11	0.473	41.1	1.18	0.073	0.15	0.892
Copper	8.54	-0.164	0.1	2.12	0.432	0.62	0.027
Zinc	2.68	0.275	19.6	1.17	0.062	0.17	0.797
pH 7							
Cadmium	2.74	0.252	29.6	1.12	0.046	0.11	0.881
Lead	1.15	0.857	199.8	1.13	0.061	0.08	0.981
Copper	3.43	1.079	5.6	4.68	0.454	0.28	0.585
Zinc	1.88	0.640	293.9	1.08	0.037	0.47	0.986

\* Model  $y = ax^b$

Table IX

Bonding energy constants ( $K_1$ ) and adsorption maxima ( $K_2$ ) for cadmium, lead, copper and zinc by montmorillonite at indicated pH values for original concentration of 0-3000 ppm.

pH	$K_1$	$K_2$ mg/g	$K_2$ me/100 g	$K_2$ /C.E.C.
<u>Cadmium</u>				
4	0.0066	39.6	70.46	0.91
5	0.0044	56.4	100.36	1.29
6	0.0060	64.9	115.46	1.49
7	0.0044	83.3	148.16	1.91
<u>Lead</u>				
4	0.0139	81.3	78.47	1.01
5	0.0081	108.4	104.59	1.35
6	0.0044	178.6	172.40	2.22
7	0.0014	641.0	618.75	7.97
<u>Copper</u>				
4	0.0348	25.3	79.55	1.02
5	0.0016	81.2	255.62	3.29
6	0.0910	51.2	161.37	2.07
<u>Zinc</u>				
4	0.0022	48.76	149.15	1.92
5	0.0018	65.90	201.65	2.60
6	0.0027	108.24	331.10	4.27
7	0.0030	382.84	1171.15	15.09



appeared to be similar up to pH 5.0. In the case of cadmium the upward trend with increasing pH was similar up to pH 7; for zinc similarity was only up to pH 6.0; there was a sharp increase in sorption for lead beyond an equilibrium concentration of approximately 1000 ppm at pH 6.0 and above; and for copper, the sharp increase in sorption started to appear at pH 5.0 beyond an equilibrium concentration of approximately 1500 ppm. Sharp increase in sorption with increasing pH has been reported (Reddy and Perkins, 1973; Anon, 1974); these would seem to suggest that more than one mechanism takes place during adsorption.

Statistical analysis of the montmorillonite data illustrated that not all data fitted the Langmuir and Freundlich equations (Tables VII and VIII). Experimental data for cadmium were in accord with both equations at all pH's, with the regression equations being significant at the 5% level. Coefficients of determination ( $r^2$ ) for the Langmuir equation ranged from 0.94 at pH 4.0 to 0.93 at pH 7.0; and for the Freundlich equation the  $r^2$  values varied from 0.87 at pH 4.0 to 0.88 at pH 7.0. Though lead adsorption patterns at pH 6 and 7 were different than that of cadmium, still good conformity with Langmuir and Freundlich were obtained, since the  $r^2$  values for Langmuir were (0.98-0.80) and for Freundlich (0.74-0.98). Copper adsorption showed marked differences in conforming with Langmuir; values

of  $r^2$  at pH 4.0 and 5.0 were 0.81-0.84 and values at pH 6.0 and 7.0 were 0.64 and 0.02 respectively. Similar trends were observed for the Freundlich model. Coefficient of determination for zinc showed similarity with that of cadmium for both Langmuir and Freundlich models (Tables VII and VIII); suggesting some similarity in sorption characteristics such as binding energies.

The Freundlich constant  $K$  for cadmium varied between 2.6 and 2.7 irrespective of pH change; for lead it decreased from 3.1 at pH 4.0 to 1.1 at pH 7.0. Copper showed no trend with a value of 2.7 at pH 4.0, and the constant for zinc was observed to be 2.5 at pH 4.0 falling to 1.9 at pH 7.0. With such inconsistencies in the Freundlich values, it is difficult to comment on the intensity of adsorption.

The slope and intercept values from Table VII were used to calculate the binding energy constants and maximum sorption capacities, (Table IX). Bonding energy constants ( $K_1$ ) for zinc were twice as large for vermiculite than montmorillonite; for copper, the intensity of adsorption was greater on montmorillonite than vermiculite. Lead was found to be more strongly sorbed on vermiculite than montmorillonite; and cadmium was adsorbed with almost similar binding strength on both montmorillonite and vermiculite.

Variation in bonding energy with surface coverage was also observed by Tiller and Hodgson (1962), and, inferred that as bonding energy decreases, it becomes increasingly difficult to distinguish from non-specific electrostatic bonding. They also suggested that silicate clays adsorb zinc reversibly by cation exchange and irreversibly by lattice penetration. McBride and Mortland (1974) quoted from recent studies by infra-red and electron spin resonance spectroscopy that exchangeable copper on montmorillonite is strongly hydrated as the  $\text{Cu}(\text{H}_2\text{O})_6^{2+}$  suspension, but upon air-drying, loses bound-water to form the interlamellar  $\text{Cu}(\text{H}_2\text{O})_4^{2+}$  species. Since the hydrated nature is important in considering the possibility of proposed specific adsorption mechanisms exhibited by heavy metals, McBride and Mortland (1974), investigate the nature of copper, cadmium and zinc bonding through physical methods such as infra-red and electron spin resonance spectroscopy; they found no evidence for specific adsorption; instead copper adsorption on montmorillonite interlamellar surfaces occurred through its strongly held ligand water by co-valent bonding. Several heat treatments showed no lattice penetration of either copper, cadmium or zinc to occur at ambient temperatures; the ionic radii of Cu, Zn and Cd are respectively, 0.72°A, 0.74°A and 0.97°A.

Based upon the above evidence, it would therefore appear reasonable to exclude the possibility of lattice penetration under the experimental conditions of this study. From the binding energy constant values obtained, it would seem that zinc and cadmium exhibit close similarity in binding to 2:1 expanded layer silicates such as montmorillonite and vermiculite; and that, lead and copper get bound with different energies. Weakness in the ability to evaluate the binding energy constants arises from the fact that ionic species in kind and amount vary with pH conditions, solubility product, intrinsic solubility and ionic medium; and, that it would be difficult to isolate the species. Variation in binding energies would seem to indicate that the energy of interaction between montmorillonite and the metals vary from metal to metal, with pH conditions and ionic strength.

Adsorption is a result of unbalanced forces at an interface. With clay minerals, unbalanced forces at the surface are satisfied by adsorbing ions; they can be sorbed by weak physical ( $<10$  K cal/mole) and strong chemical attractive forces ( $>10$  K cal/mole). The mechanisms responsible for charge on clay surfaces are

1. Isomorphous substitution
2. Broken bonds in tetra or octahedral layer  
along edges, and
3. Lattice defects.

The amount of heavy metal adsorbed per gram of clay mineral depends on

1. its specific surface area,

2. its surface charge density,
3. the interlamellar spacing in the case of 2:1 expanded type,
4. the temperature and pressure,
5. the equilibrium solute concentration in the solution, and
6. the nature of the ionic medium.

It may be noted that ancient environmental conditions conducive for clay formation, have resulted in clays of different shape; clays are found to exist in the form of clay platelets, clay crystals, clay aggregates, clay conglomerates or a combination of them depending upon the environmental conditions and the purity and type of clay mineral (Sankaran and Rao, 1974). These foregoing considerations would partly explain variations not only in their cation exchange capacities, but also in their ability to bind metals.

Under the conditions of this study (varying pH conditions and the nitrate system), the probable existence of different ionic species have significantly affected the sorption characteristics of the clay minerals.

In the case of cadmium-montmorillonite interaction, it is seen that cadmium had an adsorption maxima ( $K_2$ ) of 70.46 me/100 g at pH 4.0, and at pH 7.0, it was 148.2 me/100 g

(Table IX). The sorption capacity for lead varied from 78.5 me/100 g at pH 4.0 to 618.7 me/100 g at pH 7.0. Though for copper a  $K_2$  value was calculated at pH 6.0, it would not be worthy of interpretation since the regression equation was not significant at the 5% level; the data for pH 4.0 and 5.0 were observed to be 79.5 and 255.6 me/100 g, respectively. In the case of Zinc, at pH 4.0, the adsorption maximum ranged from 149.1 to 331.1 me/100 g at pH 6.0, followed by a sudden increase to 117.1 me/100 g at pH 7.0. Since it is customary and practical to quantify exchange reactions, through either the mass-balance or statistical thermodynamic approaches, it was felt appropriate in this investigation, to establish  $K_2$ /CEC ratios. For montmorillonite, the ratios are reported in Table VIII.

From these ratios, it became evident that at pH 4.0 and 5.0, the sorption capacity of montmorillonite for cadmium was equivalent to its cation exchange capacity; at pH 6.0, the ratio was 1:5 and approximately twice at pH 7.0. It has been reported (Hahne, 1974) that at pH 7.0, the predominant ion is still  $\text{Cd}^{2+}$ ;  $\text{Cd}(\text{OH})^+$  starts forming at pH 7.0-7.5 and peaks at pH 8.2-9.0. Cadmium hydroxide begins at pH 9.0 and peaks at 11.0;  $\text{Cd}(\text{OH})_3^-$ ,  $\text{Cd}(\text{OH})_4^{2-}$  complexes at pH >11.0. In the case of lead, the adsorption maximum was observed to be twice the CEC at pH 6.0, but at pH 7.0, the ratio was observed to be 8.0.

A rapid increase in sorption is believed to be associated with precipitation. Precipitation should not be regarded as unimportant, because of the intrinsic solubility of the precipitate, and secondly as quoted from studies by Hahne (1974), hydroxyl groups of neutral molecular species may display adsorption affinities through hydrogen bonding. As is evident from the figures and from studies quoted by Ellis and Knezek (1972), precipitation is indicated by a rapid increase in adsorption with a small change in equilibrium concentration solution. DeMumbrum and Jackson (1956a) found sorption of zinc on montmorillonite from  $\text{Zn}(\text{OH})_2$  to be faster than from  $\text{Zn}_3(\text{PO}_4)_2$ . DeMumbrum and Jackson (1956a) concluded that above pH 6.2, precipitation of the metal oxide (copper) was a major factor in the non-stoichiometry of the exchange mechanism.

Though it is believed that the form of lead precipitated is lead hydroxide, Abel (1973) suggested that in a nitrate system, addition of NaOH would precipitate the basic forms of lead  $\text{Pb}(\text{NO}_3)_2 \cdot \text{Pb}(\text{OH})_2 \cdot 5\text{Pb}(\text{OH})_2$ ; even at pH 12.0, there is no precipitation of  $\text{Pb}(\text{OH})_2$  as such.

Copper adsorption to montmorillonite at pH 5.0 was three times its CEC compared to an equivalent amount at pH 4.0; the ratio reported at pH 6.0 is not considered to be meaningful, since the regression equation was not significant at the 5%

level. Bingham, Page and Sims (1964) reported similar findings; they found that at pH <5.5 (too acid for the formation of  $\text{Cu}(\text{OH})_2$ ), the amounts of Cu and Zn retained by montmorillonite were equal to the CEC. Because of close similarity in certain chemical properties of zinc and cadmium, one would have expected similar sorption capacities; instead at pH 6.0, the ratio for zinc was twice that noted at pH 4.0 and 15 times at pH 7.0.

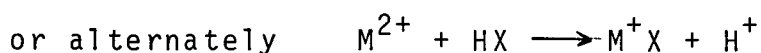
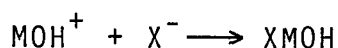
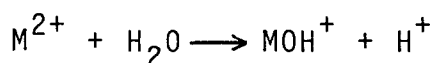
It is clearly seen from the above that irrespective of heavy metal, there was an increase in sorption with increasing pH; secondly up to pH 5.0, twice the amount of heavy metal as the CEC was adsorbed by montmorillonite; but beyond pH 6.0, a sharp increase in sorption occurred.

Sorption in excess of cation exchange capacity has been reported by several workers (Bingham, Page and Sims, 1964; Menzel and Jackson, 1950; DeMumbrum and Jackson, 1956b; Anon, 1974). Proposed mechanisms were postulated to be the result of adsorption of the hydrolyzed form or in the case of Zn and Cu as the hydroxides. Results obtained from this study support that in a nitrate system, similar inferences can be made.

Since adsorption was measured in the presence of a large excess of sodium, a constant ionic environment was maintained; hence ionic strength and all activity coefficients are assumed to remain constant. Several phenomena can cause such patterns



of adsorption; generally they can arise from unbalanced forces due to variations in the structural arrangement of the minerals, and the differing chemical properties of the metals. The nature of ions present would vary primarily with the pH of the medium. Polyvalent metals such as copper, lead, zinc and cadmium hydrolyze easily; Hodgson (1964) postulated the following to occur:



and that both mechanisms occur with certain surface reactions controlled by hydrolysis (bonding of metal ions to clays) and others by surface exchange.

Heavy metal hydrolysis in the region of pH 6.0 as  $MOH^+$  has been reported for several heavy metals. The ratio of  $Cu^{2+}/CuOH^+$  and  $Zn^{2+}/ZnOH^+$  decreases 1000 fold from pH 4.0 to pH 6.0 (DeMumbrum and Jackson, 1957). Menzel and Jackson (1950) reported that at least 5% of the copper was adsorbed in the hydrolyzed form by montmorillonite and kaolinite.

The sorption capacity to CEC ratio is based on the assumption that ion-exchange on a stoichiometric basis is taking place. Hahne (1974) stated rightly: "Determinations of ionic adsorption phenomena on colloidal surfaces are often

based on the valency of ions which may lead to erroneous interpretations if formation of inorganic complexes is omitted." Santillan-Medrano (1974) arrived at a value of twice the CEC while applying correction solely for the ion-pair effect.

Varying effects of different anions have also been reported to affect heavy metal solubility. Hahne (1974) quoted studies on mercury adsorption; at pH 4.6-4.9, bentonite adsorbed 50% of added Hg in 0.01 M  $\text{Ca}(\text{NO}_3)_2$  whereas in 0.01 M  $\text{CaCl}_2$ , only 8.4% was adsorbed. Zinc solubility at higher pH levels has been observed and is considered to be due to the precipitate changing from a granular to gelatinous form, making the analysis of the supernatant liquid uncertain, especially above pH 8.5 (Jurinak and Inouye, 1962). From oxysalts of nitrates, zinc oxide precipitates at lower pH than the more stable ones such as osysulphate or oxycarbonate which require higher pH. This may explain in part, the high sorption ratio obtained for zinc in this study.

The solubility products of Cd, Pb, Zn and copper hydroxide are  $2.0 \times 10^{-14}$ ,  $4.0 \times 10^{-15}$ ,  $5.0 \times 10^{-17}$  and  $1.69 \times 10^{-19}$  (Sopper and Kardos, 1973); these values partly explain the higher ratios obtained for zinc and lead between pH 6.0 and 7.0; and that no reliable fit of experimental data into the

Langmuir equation at pH 6.0 and above occurred. Hahne (1974) stated that precipitation of  $\text{Zn}(\text{OH})_2$  occurs if the concentration of Zn as  $\text{Zn}(\text{OH})_2$  exceeds 160 ppm (in other words 160 ppm Zn can exist as soluble  $\text{Zn}(\text{OH})_2$  in a pure system). The intrinsic solubilities of  $\text{Zn}(\text{OH})_2$ ,  $\text{Cd}(\text{OH})_2$  and  $\text{Pb}(\text{OH})_2$  are respectively  $2.45 \times 10^{-3}$  moles/litre,  $158 \times 10^{-3}$  ppm and  $474 \times 10^{-6}$  ppm. At pH 7.0, 50% of the zinc occurs as  $\text{Zn}(\text{OH})_2$  and only 5% as  $\text{Zn}^{2+}$  (Hahne, 1974); the zincate ion exists above pH 9.0 (Lindsay, 1972).

Vermiculite: Heavy metal sorption with changes in pH followed similar trends (Fig. 3) as those obtained for montmorillonite. This is as expected since both vermiculite and montmorillonite belong to the smectite group of layer silicates. When regression equations were computed (Table X), it was observed that with the exception of lead and copper adsorption at pH 7.0, in all cases the coefficient of determinations ranged from 0.97 at pH 4.0 to 0.91 at pH 7.0 indicating conformity with the Langmuir model. An  $r^2$  of 0.89 observed for copper at pH 6.0 was not expected, since at the same pH, an  $r^2$  of only 0.63 was obtained for montmorillonite; this would seem to suggest that copper adsorption at this pH to 2:1 expanded type clay minerals is affected by the nature of the clay surface; it could be that specific sorption of

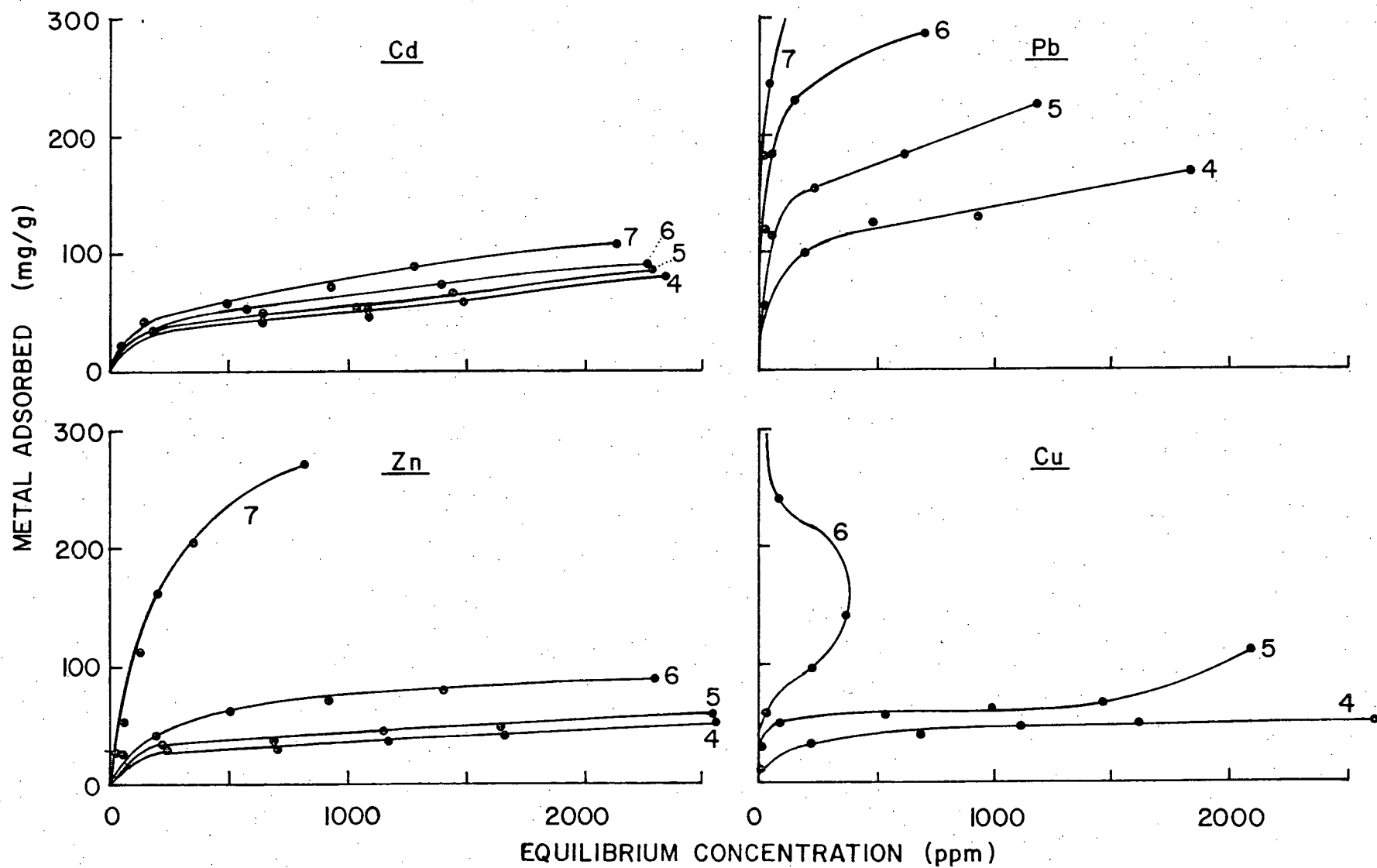


FIG.3. HEAVY METAL ADSORPTION BY VERMICULITE AT FOUR pH-VALUES

Table X Langmuir constants and statistical analysis of heavy metal adsorption  
on vermiculite with four heavy metals at four pH values\*.

Vermiculite	Constant a	Regression Coefficient b	F(ratio) b	Standard Error a	Standard Error b	Standard Error y	Coefficient of determination $r^2$
pH 4							
Cadmium	3.46	0.013	50.2	2.06	0.002	3.79	0.909
Lead	0.36	0.007	245.3	0.11	0.001	0.23	0.998
Copper	1.34	0.020	775.1	0.94	0.001	1.74	0.994
Zinc	2.92	0.020	175.1	1.92	0.001	3.52	0.972
pH 5							
Cadmium	2.58	0.012	44.3	2.09	0.002	3.90	0.899
Lead	0.35	0.004	209.4	0.16	0.001	0.33	0.977
Copper	1.91	0.010	29.3	2.06	0.002	3.88	0.854
Zinc	2.66	0.018	173.6	1.75	0.001	3.23	0.972
pH 6							
Cadmium	1.98	0.012	73.4	1.51	0.001	2.84	0.936
Lead	0.17	0.003	348.6	0.05	0.001	0.11	0.986
Copper	0.05	0.007	41.0	0.20	0.001	0.39	0.891
Zinc	1.57	0.011	321.2	0.68	0.001	1.30	0.985
pH 7							
Cadmium	1.57	0.009	92.1	1.01	0.001	1.94	0.949
Lead	0.21	0.001	0.5	0.09	0.002	0.18	0.089
Copper	0.16	0.009	0.6	0.09	0.013	0.11	0.104
Zinc	0.51	0.003	49.6	0.16	0.001	0.32	0.908

\* Model  $y = a+bx$

Table XI Freundlich constants and statistical analysis of heavy metal adsorption  
on vermiculite with four heavy metals at four pH values\*.

Vermiculite	Constant a	Regression Coefficient b	F(ratio) b	Standard Error a	Standard Error b	Standard Error y	Coefficient of determination $r^2$
pH 4							
Cadmium	2.38	0.292	204.5	1.05	0.020	0.04	0.976
Lead	3.15	0.340	58.7	1.10	0.044	0.12	0.921
Copper	3.07	0.172	59.4	1.06	0.022	0.06	0.922
Zinc	2.99	0.169	398.2	1.02	0.008	0.02	0.988
pH 5							
Cadmium	3.18	0.209	57.6	1.07	0.028	0.08	0.920
Lead	3.05	0.427	20.6	1.21	0.094	0.22	0.805
Copper	3.38	0.214	19.6	1.12	0.048	0.15	0.797
Zinc	3.06	0.174	190.0	1.03	0.013	0.03	0.974
pH 6							
Cadmium	3.25	0.215	50.2	1.08	0.030	0.09	0.909
Lead	3.46	0.482	7.6	1.33	0.175	0.35	0.602
Copper	3.31	0.457	8.0	1.33	0.162	0.34	0.615
Zinc	3.04	0.246	186.7	1.05	0.018	0.05	0.974
pH 7							
Cadmium	3.42	0.225	47.6	1.08	0.033	0.10	0.905
Lead	3.68	0.554	2.5	1.56	0.347	0.47	0.337
Copper	2.47	1.391	6.0	1.57	0.567	0.39	0.546
Zinc	2.87	0.472	191.1	1.07	0.004	0.85	0.974

\* Model  $y = ax^b$

Table XII

Bonding energy constants ( $K_1$ ) and adsorption maxima ( $K_2$ ) for cadmium, lead, copper and zinc by vermiculite at indicated pH values for original concentration range of 0-3000 ppm.

pH	$K_1$	$K_2$ mg/g	$K_2$ me/100 g	$K_2$ /C.E.C.
<u>Cadmium</u>				
4	0.0036	79.36	141.21	1.29
5	0.0047	81.70	145.37	1.33
6	0.0059	86.13	153.26	1.40
7	0.0060	106.10	188.79	1.73
<u>Lead</u>				
4	0.0195	144.6	139.63	1.28
5	0.0128	227.5	219.57	2.01
6	0.0186	306.6	296.00	2.71
7	0.0052	909.0	877.41	N.A.
<u>Copper</u>				
4	0.0153	48.7	153.49	1.41
5	0.0055	95.1	299.39	2.74
6	0.1333	133.9	421.24	3.86
<u>Zinc</u>				
4	0.0068	50.3	153.95	1.41
5	0.0069	54.5	166.89	1.53
6	0.0071	89.28	273.13	2.50
7	0.0063	311.10	951.79	8.72

cupric hydroxide may have taken place, through its ligand water. At pH 7.0, the copper data did not fit the Langmuir equation ( $r^2 = 0.10$ ).

When the experimental data were incorporated into the Freundlich equation, similar trends of  $r^2$  values as found for Langmuir were obtained.

Bonding energy constants computed from the slope and intercept data in Table X are presented in Table XII. Values for cadmium varied from 0.004 to 0.006; for lead, a constant value of 0.019 was observed up to pH 6.0, which is different than that observed for montmorillonite where a decrease in  $K_1$  with increasing pH was observed. In the case of copper, there was a decrease in the  $K_1$  value from 0.015 to 0.005; a similar decrease was also noted in the case of montmorillonite. With zinc adsorption, the binding energies stayed almost constant irrespective of pH changes from 0.007 at pH 4.0 to 0.006 at pH 7.0; such constancy was not found in the case of montmorillonite.

Vermiculite adsorbed 141.2 me of Cd/100 g of clay mineral at pH 4.0 and 188.8 me/100 g at pH 7.0, thus producing  $K_2/CEC$  ratios varying from 1.29 at pH 4.0 to 1.73 at pH 7.0 (Table XI). These data support the findings that 2:1 expanded type clay minerals approximately adsorb an amount of cadmium equivalent to its CEC at pH 4.0 and twice the amount at pH 7.0.



In the case of lead, sorption capacities ranged from 139.6 me/100 g at pH 4.0 to 296.0 at pH 6.0, followed by a sharp increase at pH 7.0 to 877.4 me/100 g. The ratio for lead at pH 7.0 was not computed since the data did not fit the Langmuir equation. Similar adsorption ratios were obtained as for montmorillonite, with an amount equivalent to the CEC at pH 4.0, twice the amount at pH 5.0 and almost three times the amount at pH 6.0.

The sorption capacity of copper was 1.4 times the cation exchange capacity at pH 4.0 and approximately 3 times at pH 5.0; a finding which appears analogous to that observed for copper adsorption by montmorillonite.

Zinc adsorption maxima (Table XII) were not similar to that obtained for montmorillonite (Table IX); 1.5 times the CEC was adsorbed at pH 5.0, 2.5 times at pH 6.0 and 8.7 times at pH 7.0. There appear to be two possible explanations for this phenomenon; one possibility is that adsorption increased due to uncertainty in the analysis of the supernatant liquid, which may be caused by the gelatinous nature of the precipitated forms; secondly, reaction with surface charges on the clay minerals may have behaved differently, thus allowing excessive precipitation of zinc compounds in the case of the montmorillonite system.

From Fig. 2, it is evident that at pH 4.0, montmorillonite sorbed Cd, Pb and Cu in amounts equivalent to its CEC but Zn in excess of its CEC (Cd: 70.5 me/100 g, Pb: 78.5 me/100 g, Cu: 79.5 me/100 g and Zn: 149.1 me/100 g). When values obtained for vermiculite are compared (Fig. 2), no significant differences in sorption existed between the metals at pH 4.0 indicating that vermiculite adsorbed them in amounts exceeding its cation exchange capacity (Cd: 141.2 me/100 g, Pb: 139.6 me/100 g, Cu: 153.5 me/100 g, Zn: 153.9 me/100 g). These findings can be summarized as follows:

Adsorption maxima (pH 4.0)

Montmorillonite      Cd:Pb:Cu:Zn = 1:1:1:2

Vermiculite              Cd:Pb:Cu:Zn = 1:1:1:1

Comparisons in terms of me/100 g adsorbent are considered to be more meaningful than expressed in mg/g adsorbent, since at pH 4.0, at least 95% of the ionic species would be in the form of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ ; and consequently complete stoichiometric exchange reactions could occur. Another significant observation made when comparing adsorption between minerals is that at this pH, vermiculite adsorbed twice the amount of Cd, Pb and Cu than montmorillonite, but zinc was adsorbed to the same extent by both minerals.

At pH 5.0, the sorption capacities can be summarized as follows:-

Adsorption maxima ratio

Montmorillonite	Cd:Pb:Cu:Zn = 1:1:2.5:2
Vermiculite	Cd:Pb:Cu:Zn = 1:1.5:2:1.1

It was also noted that under this pH condition, compared to pH 4, the margin of difference in adsorption between montmorillonite and vermiculite was reduced by 50% (Tables IX and XII); still approximately twice the amount of lead was adsorbed by vermiculite than by montmorillonite. The margin of difference for copper adsorption was not as wide as that observed at pH 4.0. The pattern of zinc adsorption was reversed; in fact, more zinc was adsorbed by montmorillonite than by vermiculite at pH 5.0 than at pH 4.0.

When the sorption reactions at pH 6.0 from the 'me' column were computed, the ratios for montmorillonite were Cd:Pb:Zn = 1:1.5:2.9; and in the case of vermiculite Cd:Pb:Zn = 1:1.9:1.8. Under this pH condition, stoichiometric exchange may hold true in the case of cadmium but not with lead, copper, and zinc since possibility of metal hydrolysis, polyhydroxy complexes and precipitation have been reported to start beyond pH 6.0.

When the  $K_2$  values at pH 7.0, were compared, the ratios of Cd to Pb to Zn with montmorillonite were 1:4.2:7.9, and Cd:Zn with vermiculite were 1:5.

The significant findings from these studies have indicated that up to pH 5.0, and, irrespective of heavy metal, montmorillonite or vermiculite can adsorb approximately twice their cation exchange capacities; at pH 6.0, the sorption capacities varied between two and three times their CEC. Finally, since stoichiometric exchange reactions become less meaningful at pH 7.0 and above, it was observed that, with the exception of cadmium, high ratios were obtained, thus supporting the postulate that metal hydrolysis, polyhydroxy complexes and precipitation to be the main phenomena contributing to the sorption capacity.

Illite: Fig. 4 describes the adsorption patterns for cadmium, lead, copper and zinc. Experimental data for Pb at pH 6.0 and 7.0, Zn at pH 6.0 and copper at pH 7.0 have not been reported since wide variations in the original readings were recorded. From Fig. 4, it was observed that for cadmium there was a consistent trend in increment of adsorption with increasing pH, but no similar trends were obtained for lead, copper and zinc. The adsorption patterns would seem to show that adsorption is partly influenced by

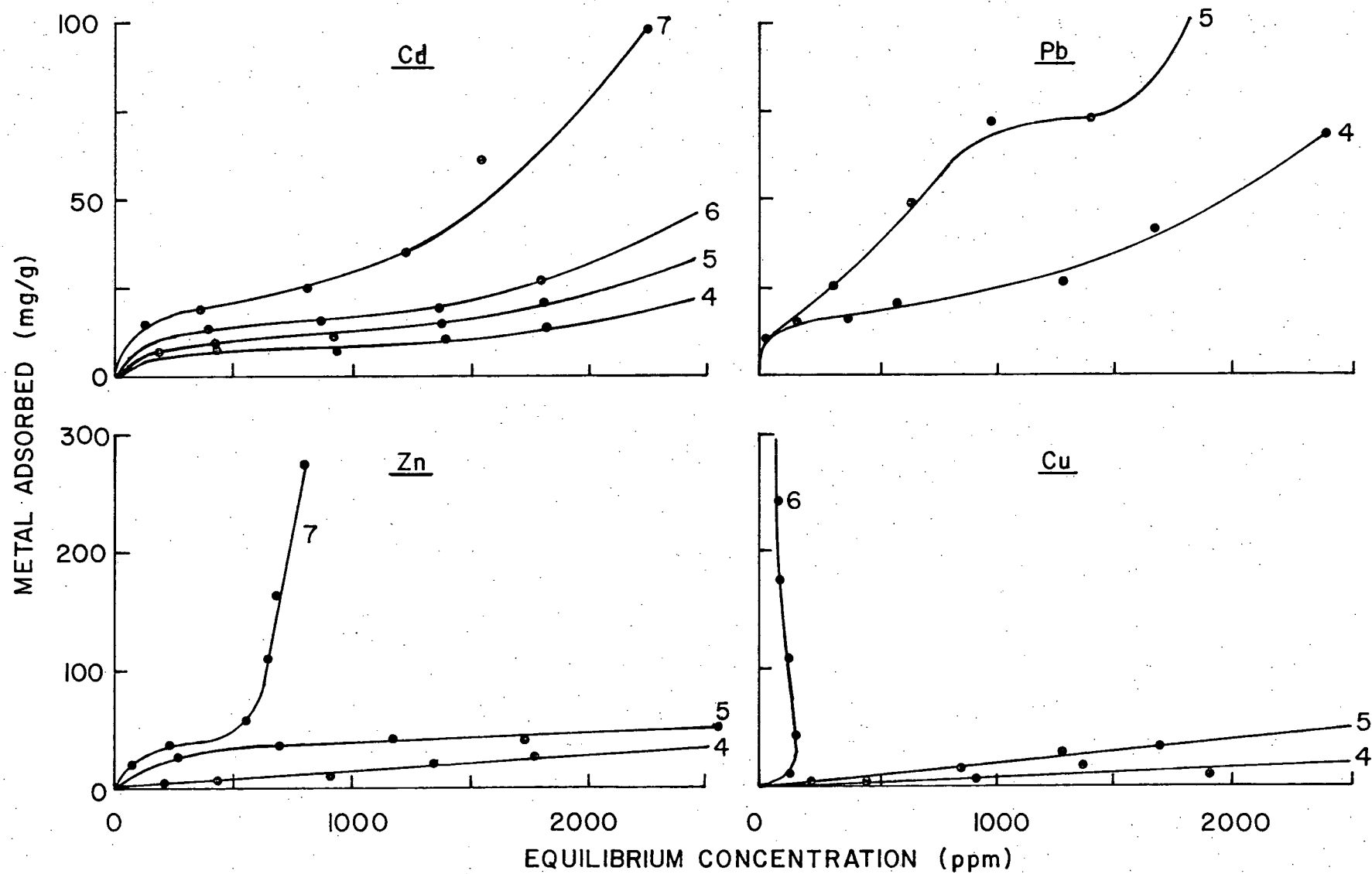


FIG. 4. HEAVY METAL ADSORPTION BY ILLITE AT FOUR pH-VALUES

Table XIII Freundlich constants and statistical analysis of heavy metal adsorption on illite with four heavy metals at four pH values\*.

Illite	Constant a	Regression Coefficient b	F(ratio) b	Standard Error a	Standard Error b	Standard Error y	Coerricient of determination r <sup>2</sup>		
pH 4									
Cadmium	0.77	0.647	41.4	1.35	0.100	0.09	0.912		
Lead	2.83	0.094	6.2	1.09	0.038	0.09	0.676		
Copper	2.12	0.549	13.9	1.59	0.147	0.10	0.874		
Zinc	2.07	0.969	212.3	1.22	0.066	0.06	0.981		
pH 5									
Cadmium	0.44	0.645	24.5	1.47	0.130	0.12	0.859		
Lead	0.47	0.483	125.3	1.09	0.043	0.08	0.984		
Copper	0.21	0.953	122.0	1.29	0.086	0.07	0.968		
Zinc	2.73	0.192	15.9	1.47	0.048	0.06	0.799		
pH 6									
Cadmium	0.74	0.536	23.8	N.A.	1.38	0.109	0.10	0.856	
Lead									
Copper	4.28	0.230	0.1			3.27	0.651	0.65	0.024
Zinc									
pH 7									
Cadmium	0.77	0.632	19.0	N.A.	1.52	0.145	0.15	0.826	
Lead									
Copper	2.91	1.029	4.5			1.56	0.485	0.42	0.474
Zinc	1.98	0.458	12.4			1.41	0.438	0.27	0.756

\* Freundlich model  $Y = ax^b$

the nature of ions or compounds present and that, beyond a certain pH, precipitation overrides other phenomena.

A plot of  $\frac{C}{x/m}$  vs C did not produce linearity with the Langmuir model regardless of pH condition and metal type. Since the regression equations were not significant at the 5% level, the computer analysis data have not been reported. Such a significant finding would seem to indicate that with illite (a non-expanded 2:1 layer silicate) no monolayer adsorption takes place.

Because no adsorption maxima can be derived, saturation peaks from Fig. 4 were estimated. In all cases, adsorption increased with increasing pH; Reddy and Perkins (1974) made similar observations while working with zinc and illite. In this study, the amount of zinc adsorbed at pH 5.0 was approximately 50 mg/g illite, with the curve rising sharply at an equilibrium concentration of 500 ppm at pH 7.0. Copper adsorption at pH 5.0 reached the plateau at approximately 40 mg/g illite, but at pH 6.0, practically all of the copper adsorbed appeared to be in the precipitated form since a very rapid increment in adsorption was observed for a very small change in equilibrium concentration.

Experimental data for lead adsorption by illite at high pH, lacked precision; consequently, data for pH 4.0 and pH 5.0

only have been illustrated (Fig. 4). In the case of cadmium adsorption, it would seem that irrespective of pH, and, beyond an equilibrium concentration of 1250 ppm, there was a steady upward trend of the sorption curve.

Table XIII illustrates the results obtained when the experimental data were fitted into the Freundlich equation. The coefficients of determination ( $r^2$ ) ranged from 0.67 for Pb to 0.98 for Zn at pH 4.0; at pH 5.0 from 0.79 for zinc to 0.98 for Pb. At pH 6.0 and 7.0, only cadmium conformed to the Freundlich relationship. No consistent trends were observed with the Freundlich's constants, indicating that the latter can hardly be used to properly predict heavy metal adsorption.

Kaolinite: The results of this part of the study are illustrated in Fig. 5. Experimental data under all pH conditions did not conform to the Langmuir relationship as found by regression analysis of variance test of significance. Departure from Langmuir curve has also been reported in other studies (Pleiss and Burger, 1971) quoted by McLaren and Crawford (1973) while examining specific sorption by clays and clay fractions.

The statistical results obtained from this study and from that of adsorption by illite, permits inference that adsorption by 1:1 layer and 2:1 non-expanded layer silicates may be governed by mechanisms which are different than that for the 2:1 expanded types.



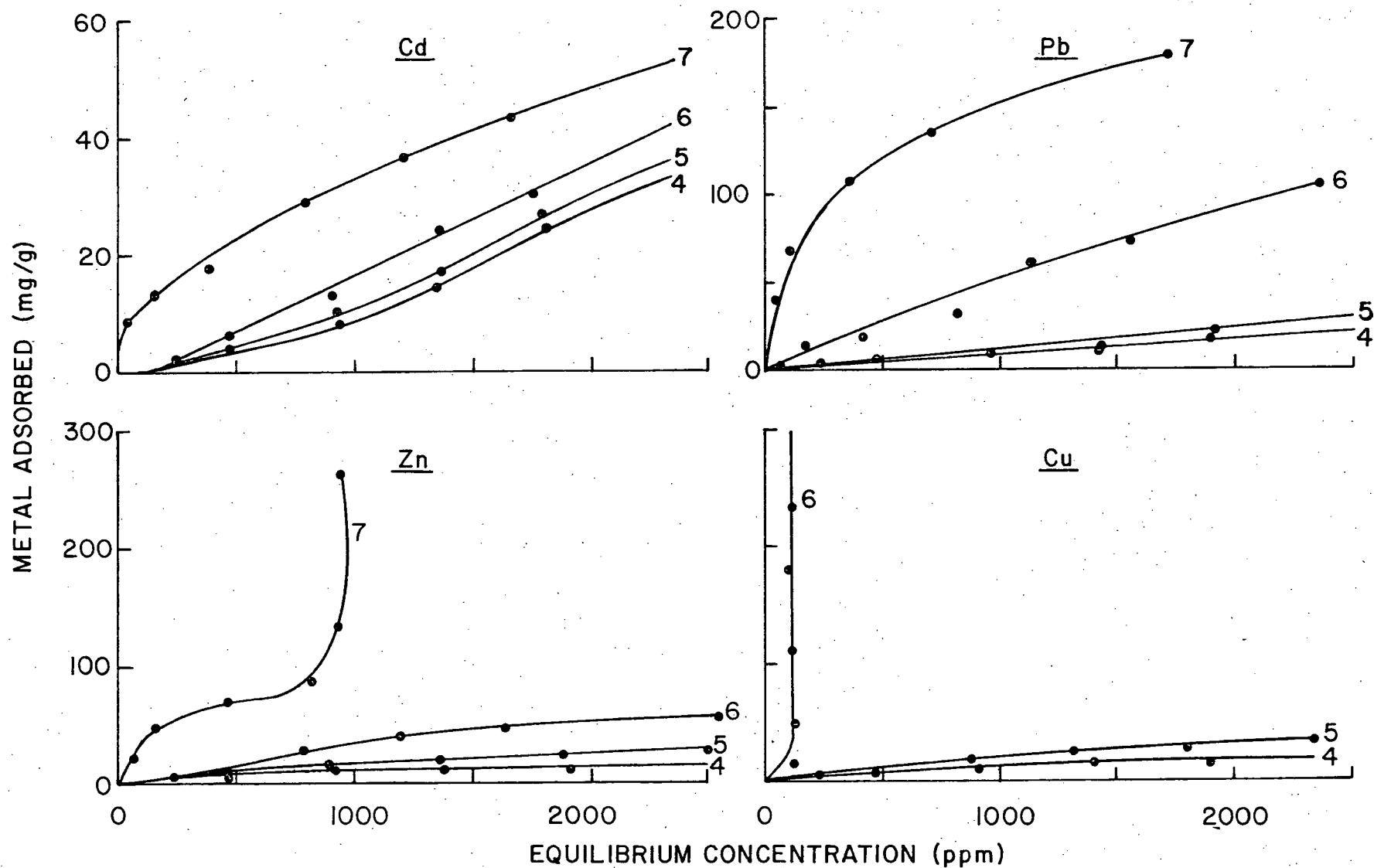


FIG. 5. HEAVY METAL ADSORPTION BY KAOLINITE AT FOUR pH-VALUES

Table XIV Freundlich constants and statistical analysis of heavy metal adsorption on kaolinite with four heavy metals at four pH values\*.

Kaolinite	Constant a	Regression Coefficient b	F(ratio) b	Standard Error a	Standard Error b	Standard Error y	Multiple Coefficient of determination $r^2$
pH 4							
Cadmium	0.06	1.287	242.5	1.28	0.083	0.07	0.984
Lead	0.19	0.854	213.6	1.18	0.058	0.07	0.097
Copper	0.31	0.728	125.6	1.19	0.065	0.07	0.969
Zinc	0.88	1.319	65.8	0.48	0.163	0.14	0.943
pH 5							
Cadmium	0.04	1.449	71.3	1.67	0.172	0.15	0.947
Lead	0.25	0.792	81.4	1.29	0.088	0.11	0.942
Copper	0.34	0.815	45.2	1.41	0.121	0.16	0.900
Zinc	0.17	0.957	399.0	1.15	0.048	0.04	0.992
pH 6							
Cadmium	0.08	1.237	1322.0	1.11	0.034	0.03	0.997
Lead	0.42	0.827	215.7	1.17	0.056	0.07	0.986
Copper	0.06	-0.494	0.7	2.88	0.576	0.69	0.285
Zinc	0.16	1.084	53.6	1.55	0.148	0.13	0.931
pH 7							
Cadmium	1.26	0.433	133.6	1.11	0.037	0.06	0.964
Lead	1.89	0.493	36.6	1.21	0.081	0.15	0.901
Copper	3.52	1.200	9.1	1.30	0.397	0.34	0.646
Zinc	1.06	0.706	20.2	1.51	0.157	0.17	0.855

\* Freundlich model  $Y = ax^b$

Below pH 5.0, (Fig. 5) kaolinite seemed to adsorb approximately the same amounts of lead, zinc and copper, but more cadmium. It would be difficult to estimate saturation peaks from the graphs, since the plateaux are not clearly defined. Generally speaking, heavy metal adsorption increased with increasing pH; a fact which has been noted above and also reported in the literature (Heydeman, 1959; Anon, 1974; Reddy and Perkins, 1973). Kishk and Hassan (1973) found kaolinite to retain more copper than its CEC at pH 5.0; similar results (Fig. 5) have been obtained in this study for all metals.

The experimental data did conform to the Freundlich relationship (Table XIII) thus indicating that this process of adsorption with increasing equilibrium concentration can go on indefinitely. Heydeman (1959) also observed this Freundlich relationship. The coefficients of determination at pH 4.0 varied from 0.94 (Zn) to 0.98 (Cd); at pH 5.0, the  $r^2$  values ranged from 0.90 (Cu) to 0.99 (Zn); at pH 6.0, from 0.12 (Cu) to 0.99 (Cd); and at pH 7.0 an  $r^2$  of 0.64 for Cu to 0.96 for Cd. Again, as in the case of adsorption by illite, no consistent trends in Freundlich constants were obtained thus limiting further inference about the adsorption mechanisms.

It is known that unbalanced forces in clay minerals are regulated by the pH of the medium. Clay minerals such as illite and kaolinite carry a greater fraction of the CEC from pH dependent charges than do the 2:1 expanded types. McClean and Bittnecourt (1973) observed illite to carry 30% and bentonite approximately 10% of the CEC from pH dependent-charges; Baweja and McClean (1975) reported 6.9% for vermiculite and 18% for kaolinite. In this study, as determined by the sodium nitrate method, cation-exchange capacity values from pH 4 to pH 7.0, did not vary more than 10% for montmorillonite and vermiculite; and did more than 15% for kaolinite and illite. Consequently, increase in sorption with increasing pH cannot be satisfactorily explained to arise from an increase in the pH dependent cation-exchange capacity of the minerals.

Several workers (Fordham, 1969; Menzel and Jackson, 1950; Kishk and Hassan, 1973) have reported on divalent-metal sorption on kaolinite. Fordham (1969) using Fe, suggested polymerization as the initial stage in the formation of a precipitate on kaolinite. Menzel and Jackson (1950) suggested that the simplest type of exchange to occur at low pH was in the form of  $\text{Cu}^{2+}$ , but as copper concentration increases, and, in the absence of cupric hydroxide precipitate, hydroxy cupric ions are sorbed; adsorption of the latter was more pronounced with kaolinite than montmorillonite (Menzel and Jackson, 1950).

From the sets of experiments, it became evident that use of the Langmuir equation over a wide concentration range has allowed slight understanding of heavy metal adsorption on 2:1 expanded type layer silicates; and, secondly, both expanded and non-expanded layer silicates conformed to the Freundlich relationship. However, conformity with Langmuir on one hand, by vermiculite and montmorillonite, and not by illite and kaolinite may partly explain that at low pH, two different adsorption mechanisms take place. It is accepted that at pH below 5.0, divalent exchange would be the main form of exchange reaction; consequently, effects such as ion-pairing, hydrolyzed metal ion species, polyhydroxy polynuclear species and other solid phases of the metals would be absent.

Several ion-exchange theories have been used to explain the behaviour of ion-exchange processes using adsorption as the basic principle. Babcock (1963) stated that in the statistical thermodynamics model, the mutual interaction energy of the adsorbed ions is the same for the ions of the same valence, and that, when a polyvalent ion of valency  $Z_i$  replaces  $Z_i$  monovalent ions (in this study,  $\text{Na}^+$ ), the mutual interaction energy is decreased by the interaction energy of the monovalent ions. This postulate would become questionable when the adsorbate is subject to hydrolysis, since theories of ion-exchange are based on the premise that the exchanging ions

retain their identity (Marinsky, 1966). The constant ( $K_1$ ) of the Langmuir equation is assumed to describe bonding energies. Under low pH condition, one would have expected (in the case of vermiculite and montmorillonite) to obtain uniform values regardless of metal type; since no consistent trend in  $K_1$  values was observed, it can be inferred that the bonding energy constant from the Langmuir equation cannot be used to support the statistical thermodynamics model. Probably they should not correlate, since the principle behind the Langmuir theory is based on uniform monolayer adsorption, whereas the statistical thermodynamics model (discrete phases of solid and solution) describes the adsorbing surface to be composed of identical discrete sites with unit electric charge, and, the adsorbed ions are localized. The distribution of mobile positive ions near the solid surface follows the Poisson-Boltzmanns distribution (Eriksson, 1952).

In the diffuse double layer theory (no distinct boundary between solid and solution), at equilibrium, the same number of ions enter the double layer (sorbed) as compared to the same amount leaving it (desorbed). Increasing the concentration of the electrolyte compacts the double layer and reduces the energy barrier between the solution and the solid phase. The double layer concept fails to consider the effect of ionic size, because it considers ions as point charges and the charge density on the surface of the particles to be uniform; it also fails to consider specific reactions between the adsorbent and adsorbate as well as between adsorbate molecules or ions.

From the  $K_2$ /CEC ratios obtained, it would appear that below pH 5.0, the divalent species retain their identity and that the heavy metals are concentrated in the double layer of both vermiculite and montmorillonite with different energies of interaction. In the case of kaolinite and illite, the adsorbed metal ions are probably localized at low pH and consequently do not conform to the Langmuir relationship. At high pH, the behaviour of the exchange processes is masked by the loss of identity of the exchanging ions that it becomes difficult to properly understand the mechanism.

Using the diffuse double layer concept, increasing the concentration of the solution phase no doubt reduces the energy barrier between surface and electrolyte thus partly explaining adsorption in excess of cation-exchange capacity. Santillan-Medrano (1974) considering ion-pair associations and heavy metal adsorption applied a correction due to ion-pairs only, to be equivalent to the CEC of the soil.

### Competition Study

In this phase of the study, the approach taken was more empirical than in the individual study. This approach was taken to amass data for comparing the affinities of heavy metals when in competition for adsorption on montmorillonite and kaolinite. The results of this study are illustrated in

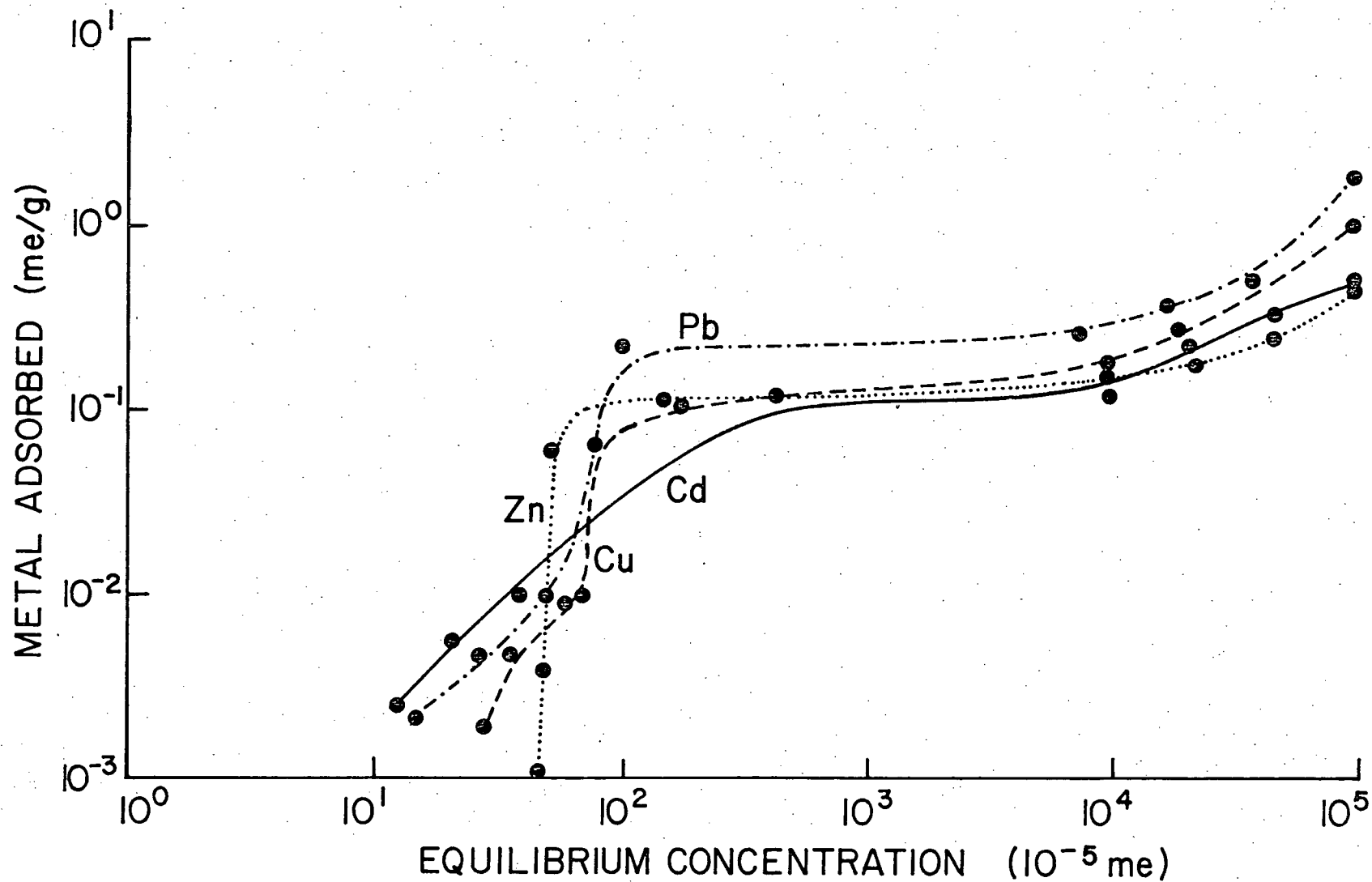


FIG. 6. HEAVY METAL ADSORPTION BY MONTMORILLONITE AT pH 5.0 FROM AN EQUIVALENT MIXTURE (1:1:1:1) OF Cd, Pb, Cu, Zn



Table XV    Langmuir constants and statistical analysis of heavy metal adsorption on montmorillonite with an equivalent mixture (1:1:1:1) of Cd, Pb, Cu and Zn at pH 5.0\*.

Montmorillonite	Constant a	Regression Coefficient b	F(ratio) b	Standard Error a	Standard Error b	Standard Error y	Coefficient of Determination $r^2$
cadmium	0.19	$0.168 \times 10^{-4}$	34.7	0.12	$0.28 \times 10^{-5}$	0.30	0.853
Lead	0.12	$0.761 \times 10^{-5}$	14.5	0.07	$0.20 \times 10^{-5}$	0.18	0.675
Copper	0.23	$0.121 \times 10^{-4}$	11.9	0.14	$0.35 \times 10^{-5}$	0.36	0.628
Zinc	0.31	$0.189 \times 10^{-4}$	41.1	0.13	$0.29 \times 10^{-5}$	0.31	0.872

\* Langmuir model  $Y = a + bx$

Fig. 6 and Fig. 7 and the data in Appendix XV.

Montmorillonite: Sharp upward trends were observed (Fig. 5) for all metals at dilute concentration ranges with the curves flattening at an equilibrium concentration of  $10^{-1}$  me; beyond this point, irrespective of metal a sharp upward trend was again observed. When the data were incorporated into the Langmuir equation, coefficients of determination ( $r^2$ ) obtained for cadmium and Zinc were (0.85 and 0.87, respectively); but, for lead and copper, they were respectively 0.67 and 0.63. The linear regression analysis data (Table XV and Table VII) clearly indicate that in both competition and individual studies, heavy metal adsorption by montmorillonite conforms to the Langmuir equation at pH 5.0. Sharp upward trends at the higher concentration ranges can be interpreted to represent the precipitated forms of the heavy metals following neutralization of the unbalanced forces on the minerals.

When the adsorption maxima ( $K_2$ ) were computed (Table XVI) lead was found to be sorbed to a much greater extent (131.4 me/100 g) followed by copper (82.3 me/100 g), cadmium (59.5 me/100 g) and zinc (52.7 me/100 g). The interesting findings from these data are that, despite low pH condition of 5.0 and competition effects, lead is adsorbed in excess of the cation

Table XVI

Bonding energy constants ( $K_1$ ) and adsorption maxima ( $K_2$ ) for cadmium, lead, copper and zinc in competition by montmorillonite at pH 5.0, for original concentration of 0-50.0 me/l.

	$K_1$	$K_2$ (me/100 g)
Cadmium	0.09	59.5
Lead	0.06	131.4
Copper	0.05	82.3
Zinc	0.05	52.7

exchange capacity of montmorillonite, copper to the same extent; and, cadmium and zinc less than its CEC. If it is assumed that at this pH, almost 95% of the metal ions are in the divalent form, and, that, ion-exchange processes are the only processes occurring between the solution and the mineral surface, then the sorption capacity of montmorillonite from one equivalent mixture of copper, lead, zinc and cadmium would be the sum of their adsorption maxima (Table XVI), which in this case would be 325.8 me/100 g. This value is approximately 4-5 times the CEC of montmorillonite.

Excluding the possibility of inorganic complexes at this pH such as ion-pairs or polyhydroxy complexes, it would appear that two kinds of reactions could happen; either the working concentration was so high (50 me/litre), that the energy barrier between the solid phase and solution was drastically reduced thus allowing increased adsorption through an extension of the diffuse layer; or due to ionic interactions between the metal ions and the solvent molecules, the conditional solubilities were exceeded thus causing the metals to be physically adsorbed in their precipitated forms.

Absorption maxima values for cadmium, copper and zinc, individually at pH 5.0 were 2, 3 and 4 times greater respectively than the values found in this experiment.

In the case of lead, more was absorbed in the competition study, which could be probably caused by precipitation.

Since an equivalent mixture of  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  was used, and having made the assumption that the same divalent species existed following equilibration, one can talk of relative affinities while considering the absorption maxima. From the foregoing considerations and Table XVI, it could be interpreted that montmorillonite had the following affinities while  $\text{Na}^+$  was being displaced:  $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+}$ ; in the case of individual studies, the sorption capacities at the same pH were as follows:  $\text{Cu} > \text{Zn} > \text{Pb} > \text{Cd}$ . Bittell and Miller (1974) derived selectivity coefficients for Pb and Cd and found  $\text{Pb}^{2+}$  adsorption to be favoured over  $\text{Ca}^{2+}$  on montmorillonite, illite and kaolinite, but little difference was observed between  $\text{Cd}^{2+}$  and  $\text{Ca}^{2+}$  exchange.

Sorption capacities or affinities for a metal would be closely related to interaction energy; in this part of the study, the binding energy constants for Cu and Zn were similar (0.05), for Pb (0.06) and for Cd (0.09) (Table XVI). These binding energy values were higher than the ones obtained for the individual studies. It would be difficult to delineate the exact causes since many factors are involved; cation exchange equilibria are primarily dominated by coulombic interactions between the

Table XVII Freundlich constants and statistical analysis of heavy metal adsorption  
(a) montmorillonite and (b) kaolinite with an equivalent mixture (1:1:1:1)  
of Cd, Pb, Cu and Zn at pH 5.0\*.

	Constant a	Regression Coefficient b	F(ratio) b	Standard Error a	Standard Error b	Standard Error y	Coefficient of Determination $r^2$
(a) <u>Montmorillonite</u>							
Cadmium	9.82	0.499	26.8	1.34	0.096	0.39	0.817
Lead	8.71	0.593	37.4	1.36	0.097	0.41	0.842
Copper	8.21	0.552	25.9	1.43	0.108	0.45	0.787
Zinc	8.71	0.505	10.1	1.73	0.159	0.63	0.626
(b) <u>Kaolinite</u>							
Cadmium	2.40	0.736	129.2	1.26	0.065	0.23	0.949
Lead	7.83	0.535	60.0	1.27	0.691	0.31	0.909
Copper	5.48	0.576	63.8	1.28	0.072	0.29	0.901
Zinc	2.16	0.735	158.0	1.23	0.058	0.21	0.958

\* Freundlich model  $Y = ax$

counter ions (in various hydrated forms) and the fixed groups of the exchanger; and also by ion-dipole or induced dipole interactions between the counter-ions and the water molecules (ionic hydration).

The data also conformed to the Freundlich equation (Table XVII), with  $r^2$  values for Cd, Pb, Cu and Zn being, respectively 0.82, 0.84, 0.79 and 0.63. The Freundlich's constants for the metals did not differ significantly (8.2 to 9.8) indicating that at this pH when in competition, the energy of interaction did not vary widely.

Kaolinite: The adsorption data when plotted (Fig. 7) did not give consistent patterns as obtained for montmorillonite (Fig. 6); it would therefore be difficult to derive any interpretation from their description. When data for the kaolinite study were incorporated into the Langmuir equation lack of conformity was obtained (very low  $r^2$  values); consequently F-tests showed the regression equations to be insignificant; the results have not been reported. Lack of the Langmuir relationship in both individual and competition studies indicated that the monolayer theory of adsorption cannot be applied to heavy metal adsorption by kaolinite and probably by the kaolin group of minerals. It would also seem that the concept of uniform distribution of charge-density cannot therefore be applied to

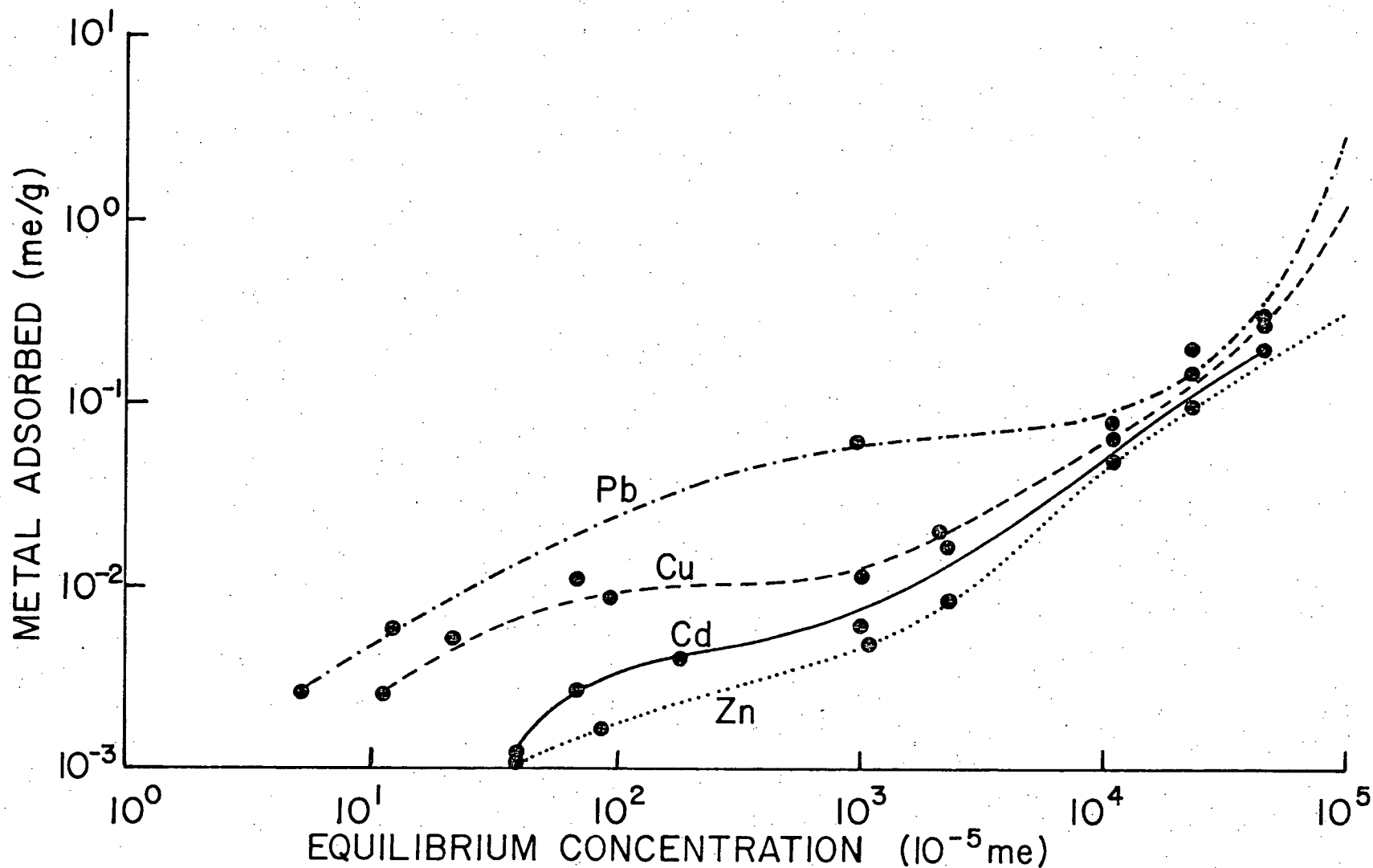


FIG. 7. HEAVY METAL ADSORPTION BY KAOLINITE AT pH 5.0 FROM AN EQUIVALENT MIXTURE (1:1:1:1) OF Cd,Pb,Cu,Zn



minerals such as kaolinite; instead charges can be considered to be localized, and, consequently, the adsorbed ions are localized which would therefore partly explain failure of the monolayer adsorption.

The experimental data did conform to the Freundlich relationship (coefficients of determination  $>0.90$  for all metals). The Freundlich's constants were not spread narrowly as they were for adsorption on montmorillonite; in this case, zinc and cadmium had almost the same values (2.1-2.4), (Table XVII); lead, 7.8 and copper 5.4. These values would seem to suggest that when the metals compete for localized sites, their energies of interaction are different; whereas when they compete for charge density sites (probably uniform) on montmorillonite, their energies of interaction are almost similar (it should be noted that at pH 5.0, they all behave primarily as divalent species).

Deductions from the use of Freundlich and Langmuir equations are not sufficient for interpreting the mechanisms, since identification of fundamental entities (atoms, ions, charge density, etc.) in the solid-solution system were not possible. The generalizations derived from this phase of the study are of predictive value, though they do not provide an understanding as such of the phenomena.

An extension of the physico-chemical approach used in these clay mineral studies, to soil systems, would be also useful for predicting availability of heavy metals in soil solution under different conditions of pH and concentration ranges. Such an attempt will be made in the next section to investigate the retention mechanisms of some agricultural soils and surrounding sediment of the Salmon River Watershed.

### CONCLUSIONS

Adsorption isotherms were obtained for the heavy metals cadmium, lead, copper and zinc on montmorillonite, vermiculite, illite and kaolinite. Heavy metal adsorption in all cases was found to increase with increasing pH.

When the data for montmorillonite and vermiculite were incorporated into the Langmuir equations, cadmium, lead and zinc adsorption conformed to the Langmuir relationship; in the case of copper, experimental data beyond pH 5.0 did not obey the relationship.

Conformity with Langmuir, allowed the computation of adsorption maxima on montmorillonite and vermiculite. These ratios have served as sorption indices for both individual and competition studies. At pH 4.0, montmorillonite adsorbed Cd, Pb, Cu and Zn in the ratios of 1:1:1:2, respectively, but vermiculite was found to adsorb them in the ratio of 1:1:1:1.

At pH 5.0, the ratios for montmorillonite were 1:1:2.5:2, whereas for vermiculite, they were 1:1.5:2:1.1.

Irrespective of heavy metal, montmorillonite could adsorb approximately twice its CEC at pH 5.0; at pH 6.0, the sorption capacities varied between two to three times the CEC. Beyond pH 6.0, with the exception of cadmium, high ratios were obtained; it was difficult to identify the processes, since the extent of chemical to physical sorption, formation of inorganic complexes or precipitation could not be delineated.

Results of the studies with illite and kaolinite showed non-conformity with Langmuir, thus failing to show monolayer adsorption of the heavy metals; instead adsorption at localized sites is being suggested.

Heavy metal adsorption on the 2:1 expanded, 2:1 non-expanded and 1:1 clay minerals also followed the Freundlich relationship under all working pH conditions and concentration range of 0 to 3000 ppm.

Competition studies showed conformity with Langmuir for montmorillonite at pH 5.0 for all metals; no relationship was observed with kaolinite. Computation of adsorption maxima for montmorillonite showed the latter to have affinities in the order  $Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+}$ . The sorption maximum of montmorillonite at pH 5.0, was at least four times its CEC in the competition study. Experimental data for both kaolinite and montmorillonite were significant at the 5% level when incorporated into the Freundlich equation.

## PART III

Heavy Metal and Sorption Isotherms for some  
Soils and Sediment of the Salmon River Area  
(British Columbia)

## INTRODUCTION

The amounts of some of the heavy metals responsible for acute intoxication are fairly well established and have been recently reviewed (National Research Council 1973; Friberg, 1973; National Academy of Sciences, 1974). For example, poisoning caused by cadmium has been well exemplified in the Jintsu River Valley of Japan (Kobayashi, 1971). The biological effects of continuous exposure to the lesser amounts present in the modern environments are largely unknown.

Numerous surveys have been carried out to identify the nature and extent of heavy metal pollution of the physical environment: (a) soils and plants (Lagerweff, 1967, 1971; Chow, 1970; John, 1971, 1972b, 1973; Takijima and Katsumi, 1973; Warren et al, 1971); (b) sea-water (Preston et al., 1972); (c) rainfall (Hallsworth and Adams, 1973), estuaries and rivers

(Carmody, 1973) and glacier contamination (Weiss and Koide, 1971). Knowledge pertaining to uptake by life-forms is slowly accumulating. It appears that levels of heavy metal pollution vary with man's activity within a geographic region and the sources may be from any or a combination of the following: mining and smelting operations, gasoline and fossil fuel combustion (Lagerweff, 1967), biocides (Lisk, 1972), limestone and phosphate fertilizers (Williams and David, 1973; Schroeder, 1963) and, sewage and industrial sludge applications to agricultural (Webber, 1975; Purves and MacKenzie, 1973) and forested lands (Sopper and Kardos, 1973). Since the hydrological cycle interacts with the cycle of rocks, heavy metal transport from soils is related to their presence in the sediments of rivers, lakes and estuaries. Winds, sewer outfalls, storm and river runoff have been identified as transporting agents for heavy metal addition to sediments (Bruland, et al., 1974). Contamination of Cu, Pb, Ni, Zn in surface sediments near waste disposal areas were found to be ten to hundred times greater than in uncontaminated sediments (Carmody, 1973); the wastes consisted of dredge spoils from inner harbour, sewage sludge from treatment plants and chemical discharges from industry. Slow enrichment of heavy metals in sediments would reduce biological activity in urban aquatic environments.

Ion exchange equilibria in the soil system would be a function of: unbalanced forces arising from the net charge on the clay minerals, secondly, from the ionic and non-ionic groups exhibited by the organic fraction and thirdly by amorphous oxides. Stevenson and Ardakani (1972) described two groups of soil organic compounds to react with metals; the first group of naturally occurring compounds such as polyphenols, organic acids, amino-acids, proteins, polysaccharides and, the second group to be of secondary origin, namely humic and fulvic acids.

The solubility and mobility of heavy metal compounds in soils are becoming increasingly important. Since mobility affects levels in waters and availability to life-forms, it is imperative to understand the mechanisms controlling availability in soil solution. Availability in soil solution is controlled by:

1. adsorption on clay colloids,
2. complexing with organic matter (organo-metallic and organo-metallic clay complexes), and
3. solubility of the ionic species and nature of the solid phase of the metal.

Heavy metal sorption studies on a wide range of soils are needed before generalizations can be made regarding heavy metal

transport in natural systems. Considerations have been given by Tiller et al. (1969) to specific and non-specific sorption of isotopically labelled cobalt; and by McLaren and Crawford (1973) on the specific sorption of copper at very low concentration in a chloride system. The sorptive capacities for zinc by soils rich in calcium (Udo et al., 1970) and soils of varying organic matter and clay content (Shuman, 1975), for lead sorption on soils of differing texture (Anon, 1974), and for cadmium sorption in a chloride system (John, 1972b) with pH unadjusted have been reported. Other observed phenomena studied have dealt with the adsorption of Pb and Cd on hydrous oxides of Mn (Anon, 1974) and heavy metal complexing with iron oxide (Leeper, 1972). Santillan-Medrano (1974) emphasized the importance of ion-pair formation in adsorption of Pb and Cd to soils. Lagerweff and Brower (1973) found lead adsorption to be greater in Ca-treated soils than Al-treated soils. In leaching studies (Anon, 1974) it was found that only 1/3 of the Pb retained in the soil can be removed by  $\text{CaCl}_2$ , but most of it by leaching with EDTA. A survey of the literature revealed that in Western Canada and in particular British Columbia, very few heavy metal studies have been undertaken to identify the intensity of soil contamination (Warren, Delavault and Fletcher, 1971, John, 1971, 1972c). Potential sources of pollution in the province would be

primarily from the forestry and mining industries and municipal wastes. The agricultural industry commonly regarded as a non-point source of pollution has been assessed but the sorptive capacities of agricultural soils have not been determined. The Salmon River Watershed is an important agricultural area in the Lower Mainland of British Columbia and the Salmon River is a tributary of the Fraser River.

Some of the inorganic constituents (clay minerals) commonly found in the soils were the subject of investigation in Part II. Since clay minerals in soils do not react singly, but intermingle in various proportions with the other soil constituents, adsorption results obtained, could be quite different than that exhibited by soils.

It is the purpose in this part of the study to investigate further the adsorptive behaviour of cadmium, lead, copper and zinc when sorbed individually as well as when in competition on some selected soils and sediment of the watershed. Causal relationships between sorption capacities and soil properties are also examined. A wide concentration range of the nitrate ion was chosen to simulate conditions of nitrate pollution.



## MATERIALS AND METHODS

### Description and Preparation of Samples

Three surface horizons (Ap) representative of the soils found in the watershed and a surface sediment were chosen for this part of the study. They have been referred to in Part I as Site I, Site III and Site IV and Sediment sample  $S_2$ .

Selected physical and chemical properties of these samples have been reported in Appendices.

Na saturation: Samples were air-dried and ground to pass 100 mesh stainless steel sieve before sodium-saturation.

The procedure used was similar to that for the clay minerals and has been described in Part II page 56.

Stock solutions: The preparation of stock solutions of Cd, Pb, Cu and Zn have been described in Part II page 57.

### Analytical Method

#### a. Individual study

In the individual studies, i.e. between adsorbent and single absorbate, the procedure described in Part II page 58 was used.

Experiments were conducted between the heavy metals (Cd, Pb, Cu and Zn) with soil samples from Sites I, III and V and sediment sample  $S_2$ . These studies were conducted at pH 5.

In addition experiments with lead and soil samples from Sites I and III at pH values of 4, 6 and 7 were conducted as lead was found to be more pH dependant than the other elements.

b. Competition Study

This study was conducted at single pH 5.0 using equivalent mixture of cadmium, lead, copper and zinc and the procedure described in Part II (Page 59) was used.

Cation Exchange Capacity

Procedure was similar to that described in Part II (Page 59) with the exception that 2.5 g of (<100 mesh) soil and sediment samples were taken.

Treatment of data: The data were treated in a similar manner to the clay mineral studies and are described in Part II page 60.

## RESULTS AND DISCUSSION

### Individual Studies

Lead sorption: All experimental data were incorporated into both the Langmuir and Freundlich equations using the least square technique. The results have been summarized and presented in Tables XVIII-XIX and Appendix XVI. Selected chemical and physical properties of the samples are reported in Appendices IV,VI. Mineralogical properties are reported in Appendix VIII.

Cation exchange capacities of the samples as determined by  $\text{NaNO}_3$  for alluvium, outwash, marine loam and sediment were found to be 42 me/100 g, 15.1 me/100 g, 19.5 me/100 g and 18.7 me/100 g respectively.

Fig. 8 (a) and Fig. 8 (b) illustrate the adsorption patterns for lead at pH 4, 5, 6 and 7 on the surface horizons of marine loam and glacial outwash. The sorption characteristics at pH 4.0 and 5.0 were almost similar for both soils. At pH 6.0 and beyond an equilibrium concentration of about 1200 ppm, the adsorption isotherms for both soils rose steeply. At pH 7.0, and low equilibrium concentrations, the curves rose steeply and remained close to the Y-axis. From these adsorption isotherms, it became clearly evident that at pH 6.0 and 7.0, phenomena other than ion-exchange seemed to occur.

It has been suggested (Anon, 1974) that very little hydrolysis of  $\text{Pb}^{2+}$  occurs at pH 6.0 and that adsorption involves  $\text{Pb}^{2+}$  only. The sharp upward trends in sorption observed beyond pH 6.0 (Fig. 8) were also observed in the clay mineral studies. These would seem to support the suggestion that whenever a rise in the isotherm accompanied by a small change in equilibrium concentration takes place, precipitation of the heavy metal is the most likely phenomenon. Specific sorption of lead through metal hydrolysis would probably not be able to account for such sharp upward trends in the case of both soils and clay minerals.

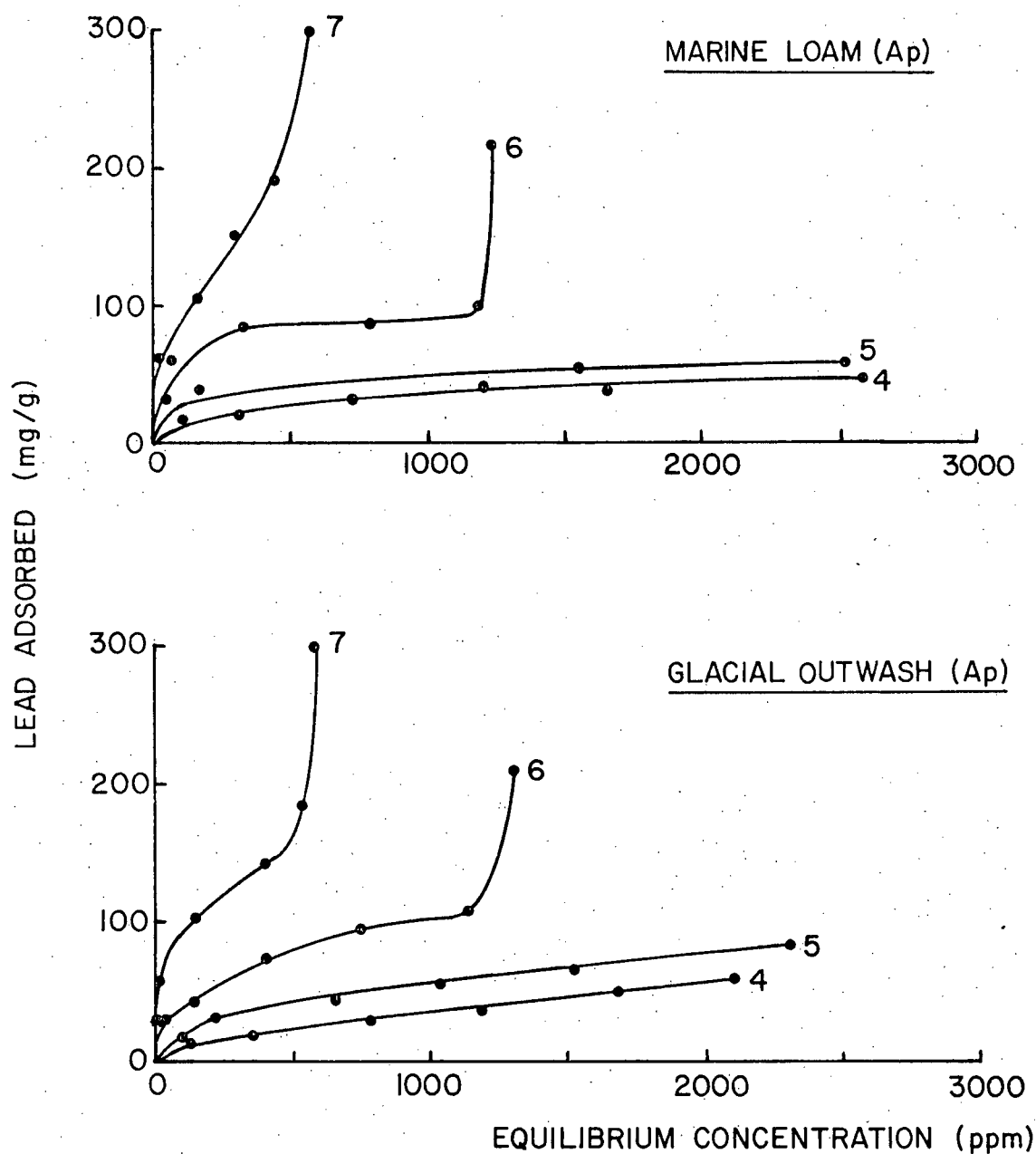


FIG. 8. LEAD ADSORPTION BY MARINE LOAM (Ap) AND GLACIAL OUTWASH (Ap) AT FOUR pH-VALUES.

Regression analysis of the data (Table XVIII) showed conformity with the Langmuir equation over all working pH conditions; with coefficient of determination ( $r^2$ ) varying from 0.90-0.96 up to pH 5.0 for both marine loam and out-wash surface horizons and 0.70 to 0.78 beyond pH 6.0.

Analogous results were obtained for the smectite group of clay minerals; these would indicate that adsorption phenomena of heavy metals on soils of differing texture are similar to that occurring with the smectite group.

Variation in the nature of the solid phase (soil) arises from the nature of the clay minerals, amorphous oxides and organic constituents. Adsorption of heavy metals on amorphous oxides of Fe, Al and Mn is well known; adsorption of Pb, Cd, and Zn on hydrous manganese oxide were favoured with increases in pH; and the sorptive capacity was found to follow the order:  $Pb > Zn > Cd$  (Anon, 1974). It has been suggested that adsorption on hydrous oxides can be treated as surface complex formation or as an ion exchange process. Reactions of heavy metals with organic soil colloids have been extensively reported. Functional groups such as hydroxyls, carboxyl, phenolic, imino groups, etc. are responsible for holding metal ions in pentagonal or hexagonal chelate structure (Leeper, 1972). Nature of complexing in the

Table XVIII    Langmuir constants and statistical analysis of lead adsorption  
on marine loam and glacial outwash at four pH values\*.

	Constant a	Regression Coefficient b	F(ratio) b	Standard Error a	Standard Error b	Standard Error y	Coefficient of Determination $r^2$
pH	Marine Loam						
4	5.99	0.019	120.8	2.23	0.002	3.90	0.970
5	3.96	0.017	40.8	3.43	0.003	5.91	0.911
6	0.81	0.007	15.4	1.38	0.002	2.58	0.755
7	0.30	0.004	18.6	0.28	0.001	0.52	0.788
	Glacial Outwash						
4	8.45	0.020	61.2	2.97	0.002	5.00	0.924
5	4.47	0.012	49.9	1.91	0.002	3.46	0.909
6	1.68	0.006	12.2	1.26	0.002	2.26	0.709
7	0.38	0.004	16.5	0.35	0.001	0.64	0.767

\* Langmuir model  $Y = a + bx$

Table XIX Freundlich constants and statistical analysis of lead adsorption on marine loam and glacial outwash at four pH values\*.

	Constant	Regression Coefficient b	F(ratio) b	Standard Error a	Standard Error b	Standard Error y	Coefficient of Determination $r^2$
pH	Marine Loam						
4	2.14	0.262	49.9	1.10	0.037	0.07	0.926
5	2.93	0.186	11.1	1.16	0.055	0.16	0.735
6	3.10	0.320	38.1	1.12	0.121	0.15	0.884
7	3.51	0.400	76.4	1.09	0.046	0.13	0.939
	Glacial Outwash						
4	1.83	0.302	47.0	1.13	0.044	0.08	0.904
5	2.81	0.227	27.1	1.12	0.044	0.12	0.844
6	2.89	0.332	51.7	1.12	0.046	0.13	0.912
7	3.21	0.416	65.4	1.11	0.051	0.14	0.929

\* Freundlich model  $Y = ax^b$

case of copper-humic acid was found to occur with the nitrogen of porphyrin groups (Goodman and Chesire, 1973); whereas laboratory made complexes with humic acid have been linked to carboxyl and phenolic groups. Chelated metals remain in solution at much higher pH values than do the inorganic forms since the protected cations are not subject to precipitation as insoluble hydroxides. Stability complexes with humic acid (Anon, 1974), followed the order  $\text{Cu} > \text{Pb} > \text{Cd} > \text{Zn}$ ; and similarly in the case of fulvic acid complexes,  $\text{Cu} > \text{Pb} > \text{Zn}$  (Stevenson and Ardakani, 1972).

In the present study, the soil matrix is considered to be a mixture of different kinds of adsorbents acting singly and also interacting with each other. It would therefore be difficult to differentiate the distribution of the charge density; despite this fact, adsorption similar to the monolayer type is exhibited. It would appear that under high pH, pH effects such as precipitation overrides chemical and mineralogical properties since both soils produced almost similar sorption capacities (Table XX). The adsorption maxima at pH 4.0 for both soils were analogous; but at pH 5.0, more lead was sorbed on glacial outwash than on marine loam.



Table XX

Bonding energy constants ( $K_1$ ) and adsorption maxima ( $K_2$ ) for lead on two soils at four pH values for original concentration of 0-3000 ppm.

pH	$K_1$	$K_2$ me/100 g	$K_2/C.E.C.$
Marine Loam (Ap)			
4	0.0031	51.44	2.63
5	0.0042	57.79	2.96
6	0.0092	130.78	6.71
7	0.0128	247.73	12.70
Glacial Outwash (Ap)			
4	0.0023	48.67	3.22
5	0.0026	82.42	5.45
6	0.0036	166.67	11.03
7	0.0111	228.87	15.15

The bonding energy constants ( $K_1$ ) (Table XX) increased with a rise in pH for both soils; values ranged from 0.003 to 0.013 for lead adsorption on marine loam and 0.002 to 0.011 on glacial outwash. These would seem to suggest that irrespective of the nature of the parent material and texture, the average bonding energy for lead is the same for both soils.

Data incorporated into the Freundlich equation also showed conformity (Table XIX). The constants are reported in actual units and were observed to increase with increasing pH; values ranged from 2.14 at pH 4.0 to 3.5 at pH 7.0 for marine loam, and, 1.83 to 3.21 at pH 7.0 for outwash.

#### Heavy metal sorption at pH 5.0

To evaluate the sorptive capacities of the soils and the sediment for various metals, adsorption at a single pH was determined. The pH of 5.0 was chosen because it was close to that exhibited by the samples under natural conditions (Appendix IV).

Fig. 9 illustrates the adsorption patterns of Cd, Pb, Cu, and Zn on the surface horizons of glacial outwash, alluvium and marine loam soils, as well as on the surface sediment ( $S_2$ ). The original readings are reported in Appendices XVII and XVIII.

Adsorption of copper on the outwash followed a different pattern than that observed on alluvium, marine loam and sediment.

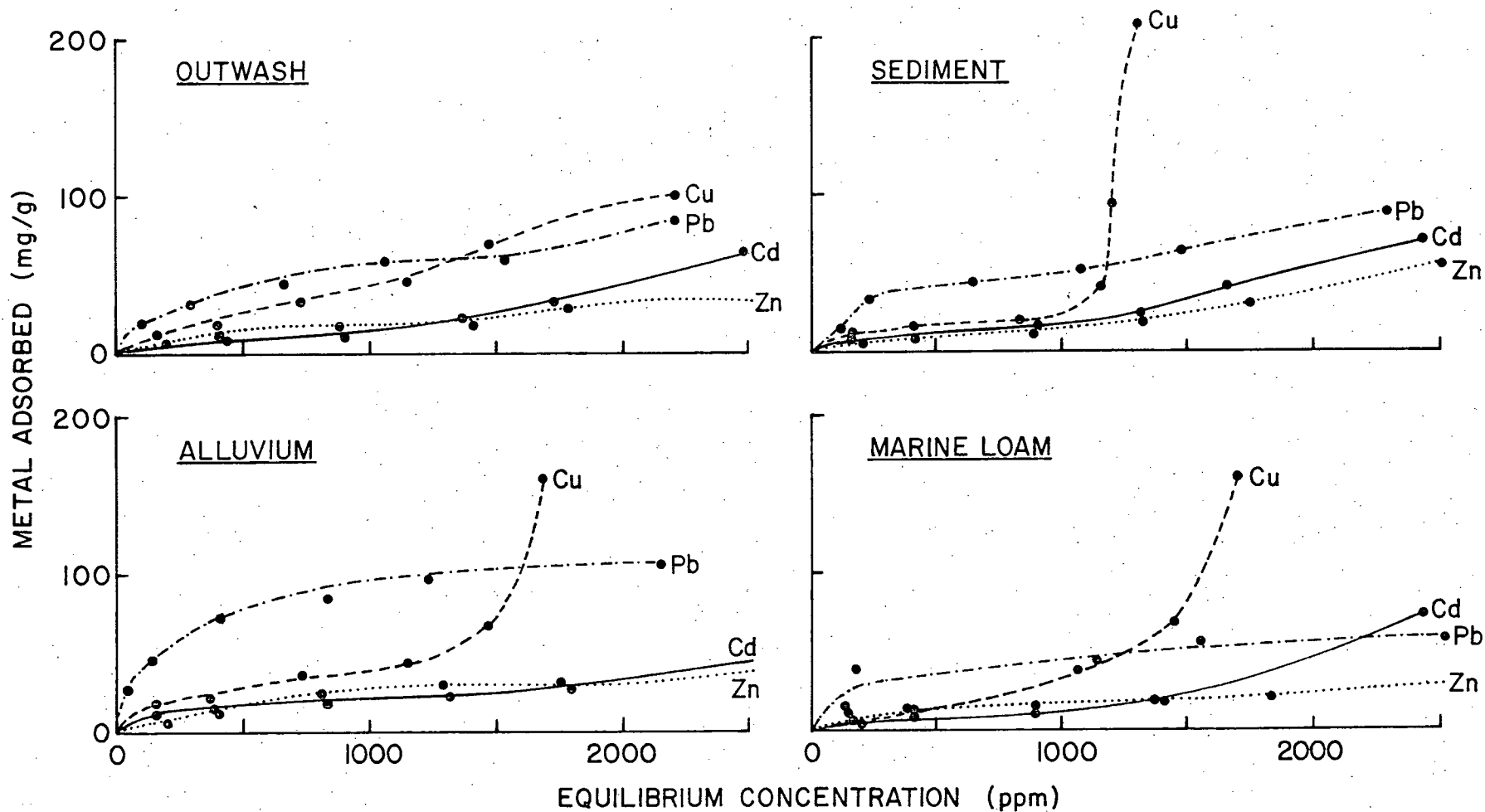


FIG.9. HEAVY METAL ADSORPTION BY SOILS AND SEDIMENT AT pH 5.0

In the case of the outwash, at an equilibrium concentration of approximately 1250 ppm, no sharp increase in adsorption was observed, whereas for the other samples and at the same equilibrium concentration, steep rises in the copper curves were noted (Fig. 9). Since differences in clay and organic matter contents and CEC could not explain this phenomenon, it might be inferred that adsorption on outwash was primarily due to  $\text{Cu}^{2+}$  and practically no precipitation as  $\text{Cu}(\text{OH})_2$  occurred. In the case of the heavy metals Pb, Cd and Zn, the adsorption patterns were similar for all samples. Curves for zinc and cadmium gave plateaux up to an equilibrium concentration of 1300 ppm on outwash, marine loam and sediment; beyond the 1300 ppm equilibrium concentration, steep rise in the curves could be the result of precipitated forms. Adsorption isotherms of Zn and Cd on the alluvial horizon were smooth (Fig. 9), indicating that total adsorption occurs as  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$ . At pH 5.0, it is regarded that the most prevalent ionic species would be divalent species. Since the alluvial horizon contained the highest amount of clay (33.3%), CEC (52.4 me/100 g) and OM (21.3%), it could be inferred that more surface area is available and therefore more uniform adsorption is possible. Consequently, it would seem that the solubility products of zinc hydroxide and cadmium hydroxide were not exceeded, whereas they did in the other cases.

When the four samples were compared (Fig. 9), it became evident that irrespective of soil or sediment, sorptive capacities were almost similar up to an equilibrium concentration of 1250 ppm with adsorption following the order  $Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+}$ . When the experimental data for the working range of 0-3000 ppm were incorporated into the Langmuir equation, it was observed to lack conformity in some cases Table XXI. For instance, adsorption of Cd, Pb and Zn on alluvium followed Langmuir ( $r^2 = 0.72$  to  $0.98$ ); in the case of copper adsorption, the  $r^2$  value was only  $0.20$ , but when data for a working range of 0 to 1500 ppm were incorporated, an  $r^2$  of  $0.75$  was achieved. Conformity for Cu adsorption was poor even at the 0 to 1500 ppm concentration range for all other samples. The same remarks can be made for cadmium adsorption since  $r^2$  values at 1500 ppm concentration range varied from  $0.97$  (alluvium) to  $0.90$  (sediment); whereas they ranged from  $0.72$  to  $0.09$  in the working range (0-3000 ppm) (Table XXI). These data would seem to suggest that before generalizations can be made regarding heavy metal adsorption, the concentration range as well must be taken into account, since it seems to influence adsorption phenomena. The Langmuir relationship was obeyed for the adsorption of Zn and Pb in the working range of 0 to 3000 ppm since the regression equations were significant at the 5% level (Table XXI). Data obtained

Table XXI    Langmuir constants and statistical analysis of heavy metal  
adsorption on some soils and sediment at pH 5.0\*.

	Constant a	Regression Coefficient a	F(ratio) b	Standard Error a	Standard Error b	Standard Error y	Coefficient of Determination $r^2$
<u>Alluvium</u>							
Cadmium	5.09 14.32	0.040 0.020	109.7 13.2	2.78 7.36	0.004 0.005	4.13 12.76	0.973 0.725
Lead	1.17	0.009	364.1	0.48	0.001	0.93	0.986
Copper	6.16 10.59	0.019 0.006	8.8 1.3	4.05 5.37	0.006 0.005	5.98 8.73	0.745 0.202
Zinc	15.59	0.202	23.7	5.57	0.004	9.66	0.826
<u>Glacial Outwash</u>							
Cadmium	19.06 35.73	0.046 0.009	14.7 0.4	8.99 13.59	0.012 0.010	12.76 22.58	0.830 0.138
Lead	4.47	0.012	49.9	1.91	0.002	3.46	0.909
Copper	10.64 14.66	0.016 0.005	2.6 1.5	6.22 4.95	0.009 0.004	8.85 8.37	0.465 0.232
Zinc	25.81	0.023	14.5	8.35	0.006	14.29	0.743
<u>Marine Loam</u>							
Cadmium	13.05 34.47	0.059 0.009	49.9 0.5	6.41 17.62	0.008 0.012	9.18 29.15	0.943 0.093
Lead	3.96	0.017	40.8	3.43	0.003	5.91	0.912
Copper	10.52 15.14	0.016 0.003	2.4 0.2	6.54 6.30	0.010 0.006	9.33 10.05	0.439 0.045
Zinc	18.51	0.029	30.1	7.34	0.005	12.65	0.857

\* Model  $Y = a + bx$

Table XXI (continued) Langmuir constants and statistical analysis of heavy metal adsorption on some soils and sediment at pH 5.0\*.

	Constant a	Regression Coefficient b	F(ratio) b	Standard Error a	Standard Error b	Standard Error y	Coefficient of Determination $r^2$
<u>Sediment</u>							
Cadmium	10.86	0.043	26.5	6.24	0.008	9.06	0.898**
	24.73	0.011	1.4	11.61	0.009	19.51	0.214
Lead	4.37	0.011	43.3	1.94	0.002	3.50	0.896
Copper	13.58	0.020	2.9	8.00	0.011	11.20	0.496**
	19.02	0.001	0.0	10.07	0.011	14.75	0.002**
Zinc	12.33	0.041	24.9	6.08	0.008	8.76	0.892
	24.26	0.015	4.5	9.53	0.007	16.18	0.473

\* Model  $y = a + bx$

\*\* Data for original concentration of 0-1500 ppm.

Table XXII

Bonding energy constants ( $K_1$ ) and adsorption maxima ( $K_2$ ) for some soils and sediment at pH 5.0 for original concentrations of 0-3000 ppm and 0-1500 ppm.

	$K_1$	$K_2$ me/100 g	$K_2$ /C.E.C.
Alluvium (Ap)			
Cadmium	0.0079	43.9	1.0*
	0.0014	88.5	2.1
Lead	0.0078	105.4	2.5
Copper	0.0031	163.9	3.9*
Zinc	0.0013	151.4	3.6
Outwash (Ap)			
Cadmium	0.0024	38.9	2.6*
Lead	0.0026	82.4	5.5
Copper	0.0015	199.2	13.2*
Zinc	0.0009	133.0	8.8
Marine loam (Ap)			
Cadmium	0.0045	30.1	1.5*
Lead	0.0042	57.8	3.0
Copper	0.0015	197.9	10.1*
Zinc	0.0016	105.6	5.4
Sediment			
Cadmium	0.0023	40.9	2.2*
Lead	0.0026	86.2	4.6
Copper	0.0015	153.2	8.2*
Zinc	0.0033	74.4	4.0*

\* 0-1500 ppm.



from the present study would seem to indicate that although adsorption patterns are analogous (Fig. 9), they do not explain the nature of adsorption. Application of the Langmuir relationship indicates that heavy metal adsorption on soils varies partly with the nature of the metal, the working concentration range and pH condition.

The bonding energy constants ( $K_1$ ) are reported in Table XXII; values ranged from 0.001 for cadmium and zinc to 0.007 for lead;  $K_1$  values determined from both working concentration range of 0 to 3000 ppm and 0 to 1500 ppm, stayed within the mentioned values, thus indicating that little difference in energies of interaction existed between the metals and Ap horizons derived from different parent materials. McLaren and Crawford (1973II) reported bonding energy constants at pH 5.5 to range from 0.30 to 1.93 for copper sorption on soils. John (1972) also found the bonding energy of Cd on soils to vary considerably.

Adsorption maxima ( $K_2$ ) are presented in Table XXII. It was assumed that all ions were divalent and their activities unity. In all cases, at pH 5.0, the amount of heavy metal sorbed exceeded the cation exchange capacity. Similar findings have been reported for the adsorption of heavy metals on clay minerals (See Part II) and soils (Santillan-Medrano, 1974; Anon, 1974). Santillan-Medrano (1974) stressed the presence of ion-

pairs; he derived an exchange function for the determination of sorption capacity from experimental isotherm data of Cd and Pb; the maximum correction applied while determining the sorptive capacity was twice the CEC of the soil. The CEC of the soil does not change, but the divalent ions after forming ion-pairs with non-valent ligands require only one equivalent exchange site to be adsorbed rather than two. He did not differentiate whether the heavy metal was adsorbed or precipitated; but rather regarded both phenomena to be responsible as a general sink for a given heavy metal; he also suggested that the main mechanism for lead fixation in soil to be precipitation, and exchange to be the more important mechanism for Cd fixation. In this study, the adsorption maxima (Table XXII) showed greater equivalent amounts of zinc and copper sorbed than lead, with cadmium the least; however, when the isotherms (Fig. 9) were compared, beyond an equilibrium concentration of 1250 ppm, the sorption peaks followed the order  $Cu > Pb > Cd > Zn$ . Udo et al. (1970) suggested while studying adsorption of zinc on soils with carbonate that at moderately high levels of Zn, zinc precipitated as  $Zn(OH)_2$ . It has been stated (Ellis, 1973; Lindsay, 1972) that inorganic solid phases (precipitates) participate in the dynamic equilibria involving soil solution, soil exchange complex, adsorption surfaces, uptake and release of nutrients by micro-organisms and removal of nutrients by plants.

Adsorption maxima for lead on alluvium, outwash and sediment were almost similar (82.6 - 88.5 me/100 g), but only 57.8 me/100 g was adsorbed on marine loam. Ratios for zinc adsorption on sediment were not calculated for the 0-3000 ppm range; but rather for the 0-1500 ppm range. The  $K_2$  values showed more zinc to be adsorbed than lead and cadmium by all samples. Values reported for copper were not regarded as meaningful since the regression equations were not significant at the 5% level. McLaren and Crawford (1973II) found  $K_2$  values for Cu at pH 5.5 in a chloride system to vary between 340-5,780  $\mu\text{g/g}$  soil. The  $K_2/\text{CEC}$  ratios presented in Table XXII are useful for comparing the sorptive capacities of heavy metals within the same soil sample, but not quite practical to compare between soils. It would seem that comparing adsorption maxima ( $K_2$ ) would be more meaningful. The higher ratios obtained at pH 5.0 on soils compared to those for the 2:1 or 1:1 type clay minerals, indicated that, use of a soil property such as cation exchange capacity alone would not explain the observed differences.

It would appear that surface areas contribution by the presence of amorphous oxides of Fe, Al, Mn, Si as well as the various organic components are important parameters that

must be taken into account. McLaren and Crawford (1973I) fractionated soil copper into five fractions: (1) soil solution and exchangeable copper (2) copper weakly bound to specific sites (3) organically bound copper (4) copper occluded by oxide material and (5) residual copper mainly in clay lattice structures. Organic matter extracts such as humic and fulvic acids have also been found to be effective in complexing heavy metals in soils and sediments. The equilibria of such metal complexes or chelates have been reviewed (Schnitzer and Khan, 1972; Norvell, 1972; Geering and Hodgson, 1969; Santillan-Medrano, 1974). It is considered that organo-metallic complexes are ubiquitous in nature. Humic and fulvic acids from both soluble and insoluble stable complexes with polyvalent cations (Stevenson and Aldakani, 1972; Tan et al., 1971), and that, fulvic acids because of relatively low molecular weights and high acidities form mobile metal complexes. Rashid and Leonard (1973) emphasized the important role of humic acids in accumulating metals in sedimentary deposits; they found sedimentary humic matter or its acid-hydrolyzate to adsorb metals up to 628 mg/g of organic matter from their insoluble salts. The scavenging nature of hydrous oxides towards heavy metals has been well exemplified; for example enrichment of Co and Ni in manganese nodules in ocean bottoms

(Anon, 1974). The change in the surface charge of hydrous oxides with pH as well as the mechanism responsible for heavy metal sorption are not well understood. Recent studies (Anon, 1974) found lead was adsorbed much more strongly than Cd, Zn, K, Mg, Ca on the same hydrous manganese oxide sample. McLaren and Crawford (1973II) showed adsorption maxima for copper to follow the order  $\text{MnO}_2 > \text{organic matter} > \text{iron oxides} > \text{clay minerals}$ .

Table XXIII reports the regression equations obtained when the experimental data at pH 5.0 were incorporated into the Freundlich's equation. All the regression equations were significant at the 5% level for the working concentration range (0-3000 ppm). The Freundlich's constant (a) Table XXIII for, lead varied between 2.8-3.0, cadmium 0.9-2.1; copper 0.6-1.8 and zinc 1.2-1.6. These values would indicate that for the concentration range studied, this parameter varies within narrow limits for all samples; the same applies for zinc but not to the same extent for cadmium. It would appear that in the case of copper, probably, forms of Cu other than  $\text{Cu}^{2+}$  were adsorbed in a different manner.

Table XXIII Freundlich constants and statistical analysis of heavy metal adsorption on some soils and sediment at pH 5.0\*.

	Constant a	Regression Coefficient b	F(ratio) b	Standard Error a	Standard Error b	Standard Error y	Coefficient of Determination $r^2$
<u>Alluvium</u>							
Cadmium	2.09	0.228	12.3	1.19	0.06	0.13	0.711
Lead	3.05	0.278	1505.0	1.08	0.07	0.21	0.997
Copper	1.82	0.374	8.6	1.40	0.13	0.27	0.632
Zinc	1.56	0.310	16.4	1.24	0.08	0.14	0.766
<u>Glacial Outwash</u>							
Cadmium	0.90	0.482	10.8	1.51	0.15	0.23	0.683
Lead	2.81	0.227	27.1	1.12	0.05	0.13	0.844
Copper	1.07	0.529	22.1	1.36	0.11	0.18	0.815
Zinc	1.21	0.364	16.0	1.29	0.09	0.15	0.762
<u>Marine Loam</u>							
Cadmium	0.97	0.467	7.9	1.59	0.16	0.25	0.614
Lead	2.92	0.186	11.1	1.16	0.06	0.16	0.735
Copper	N.A.						
Zinc	1.35	0.333	72.0	0.10	1.12	0.04	0.935
<u>Sediment</u>							
Cadmium	1.62	0.313	5.4	1.45	0.13	0.25	0.521
Lead	2.81	0.232	28.7	1.12	0.04	0.12	0.852
Copper	0.61	0.745	8.8	1.97	0.25	0.34	0.639
Zinc	1.32	0.365	11.4	1.35	0.11	0.18	0.695

\* Freundlich model  $Y = ab^x$

### Correlation Studies:

When correlation studies were performed between the Langmuir adsorption maxima of Pb, Cd and Zn at pH 5.0 and selected soil properties (Table XXIV), they were all positively correlated with % clay, % carbon and CEC. With clay, highest correlation was obtained for lead ( $r = 0.94$ ) followed by Cd (0.84) and Zn (0.63). In the case of zinc, a high correlation with Pb or Cd was obtained with carbon content and CEC. Udo *et al.*, (1970) found the  $K_2$  values for zinc to be also related to clay content, OM and CEC with  $r$  values 0.75, 0.67 and 0.75, respectively. Negative correlations were obtained for both Pb and Cd with oxalate-Fe and oxalate-Al; but zinc was positively correlated.

Table XXIV. Correlation between Langmuir adsorption maxima and some soil properties

	clay	carbon	oxalate-Fe %	oxalate-Al	CEC
Pb	0.94	0.68	-0.20	-0.56	0.67
Cd	0.84	0.50	-0.39	-0.59	0.51
Zn	0.63	0.74	0.71	0.37	0.70

Positive correlations of Cd and Pb were also observed with increasing CEC (Santillan-Medrano, 1974). However Tiller *et al.*; (1969) working with very low concentrations of cobalt

found positive correlations between Langmuir sorption capacity, clay content and pH but not with organic matter.

An examination of the dominant soil properties affecting the sorption capacity of lead was undertaken. Adsorption maxima data for marine loam, outwash, alluvium and sediment samples under all working pH conditions were used for multiple regression analysis by the elimination technique. The dependent variables chosen were pH, % clay, % carbon, % oxalate-Fe, % oxalate-Al and CEC. The multiple regression obtained was as follows:

$$\begin{aligned} \text{Adsorption maxima (mg Pb/g soil)} = & -249.3 + 64.33 \text{ pH} + 0.49 \text{ clay} - 25.8 \text{ oxalate-Fe} \\ & + 14.88 \text{ oxalate-Al} + 0.67 \text{ CEC.} \end{aligned}$$

The statistical results showed pH the only independent variable to be significant at the 5% level. The pH effect was as expected; probably due to lack of sufficient observations and variability in the soil properties, the independent variables other than pH were not significant at the 5% level. Multiple regression analysis (Hassett, 1974) revealed on the other hand that soil properties such as CEC, OM, high surface area and high clay content showed a greater effect on lead sorption than pH did; but McLaren and Crawford (1973I) also by multiple regression analysis found OM and free  $\text{MnO}_2$  to be the dominant constituents contributing towards specific sorption of soil copper.



### Competition Studies:

Surface horizons from the outwash and marine loam parent materials were used in this part of the study. The experimental data are reported in Appendices (XIX). When they were incorporated into the rearranged form of the Langmuir equation ( $C$  as the independent variable and  $C/x/m$  as the dependent variable) on the computer program, poor correlations were obtained in all cases. In the case of the outwash sample,  $r$  values between  $C$  and  $C/x/m$  were as follows: Cd (-0.37), Pb (0.54), Cu (0.29) and Zn (-0.17); the correlation coefficient values for competitive adsorption on the marine loam were found to be: Cd (0.46, Pb (0.29, Cu (0.35) and Zn (-0.02). Consequently, the independent variable  $C/x/m$  was found to be non-significant at the 5% level and no meaningful adsorption maxima could be calculated.

Fig. (10) illustrates the shape of the isotherms obtained for competitive adsorption of the metals on glacial outwash surface soil. Adsorption patterns showed adsorption to increase with increasing concentration. All the curves rose sharply beyond an equilibrium concentration of 0.01 me mixture of the heavy metals. The adsorption isotherms obtained for the glacial marine surface soil were almost identical (Fig. 11). This was as expected since both soils did not differ significantly in physical, chemical and mineralogical properties (Appendices

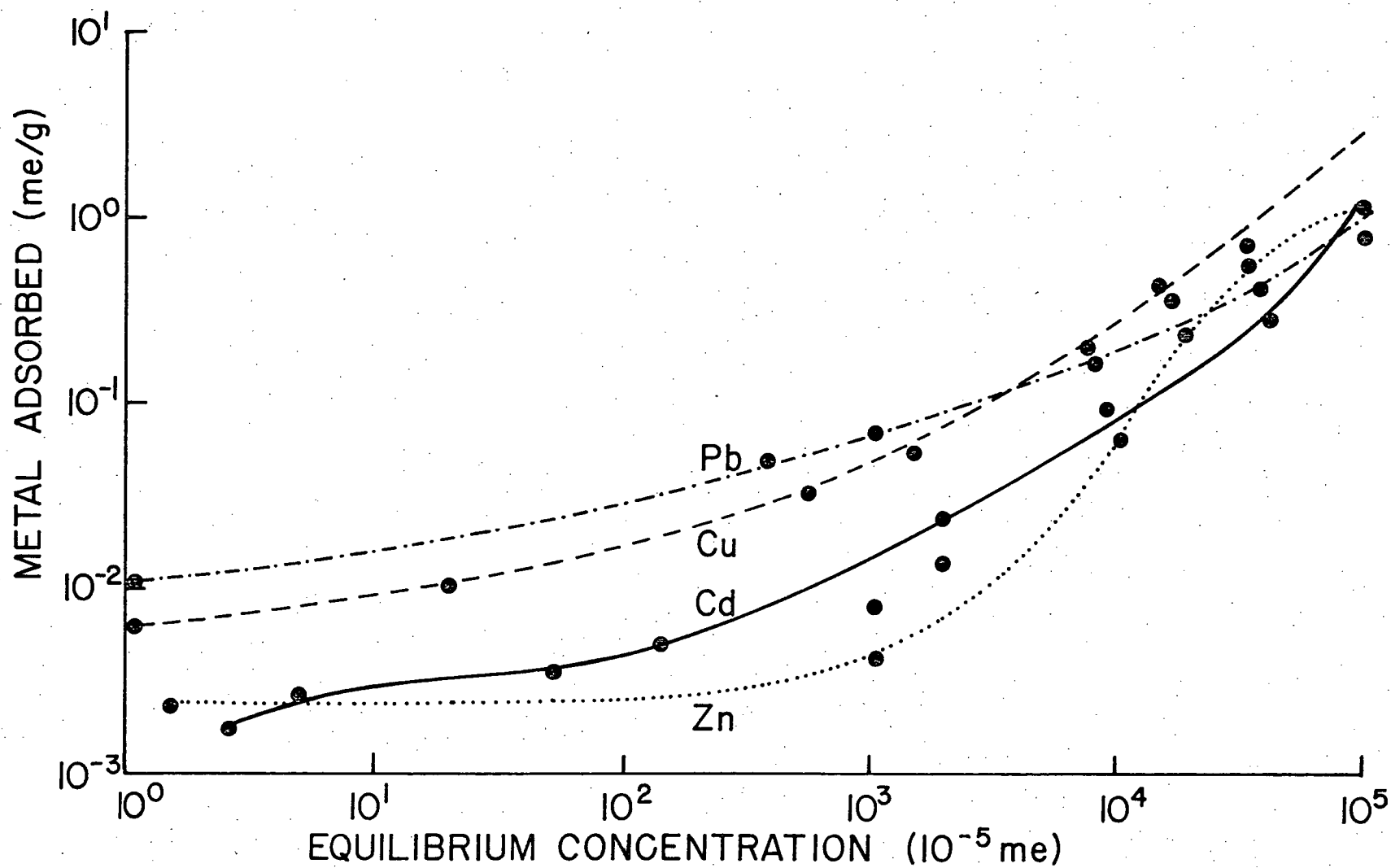


FIG.10. HEAVY METAL ADSORPTION BY GLACIAL OUTWASH SOIL FROM AN EQUIVALENT MIXTURE (1:1:1:1) OF Cd, Pb, Cu, Zn

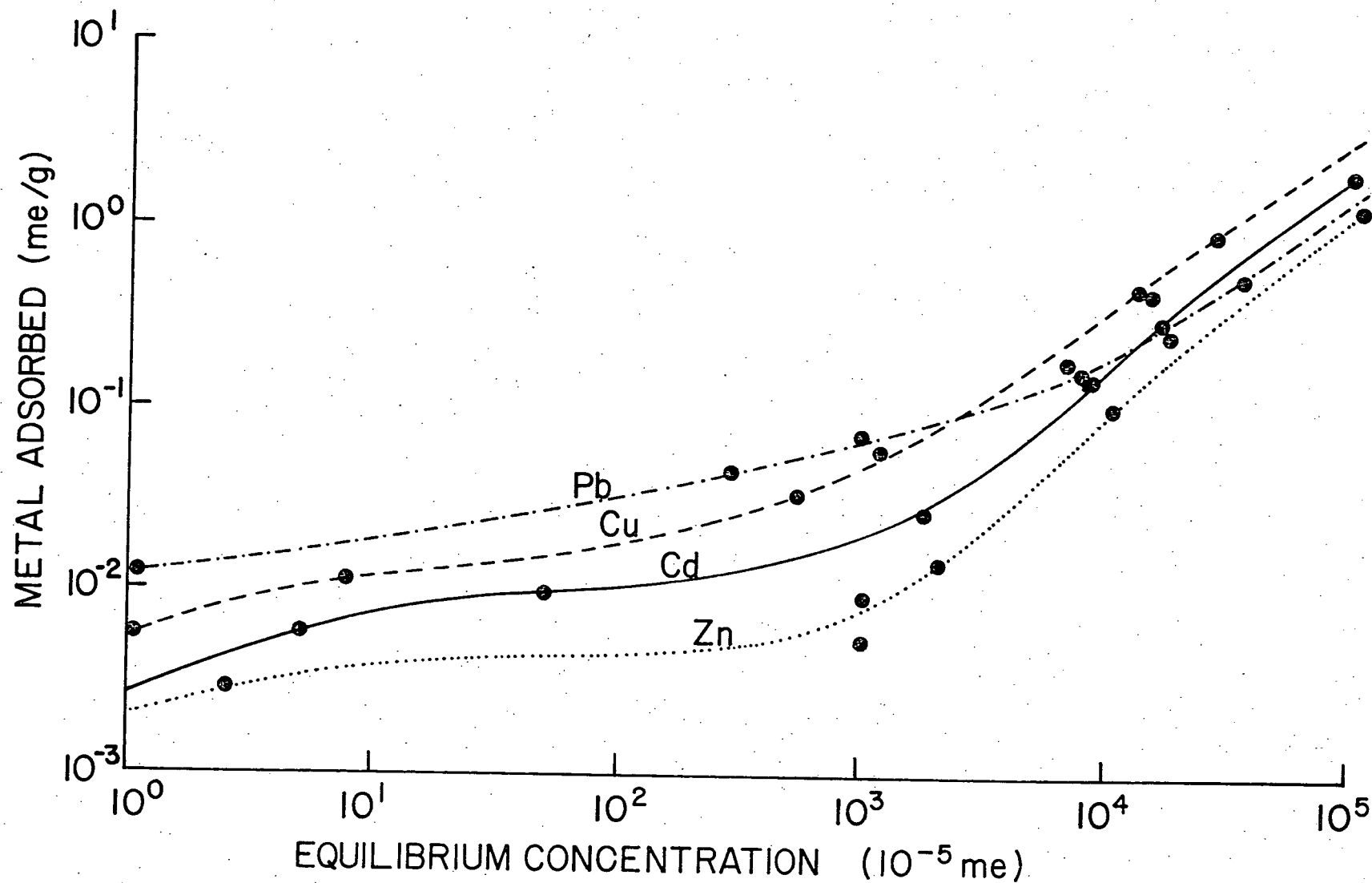


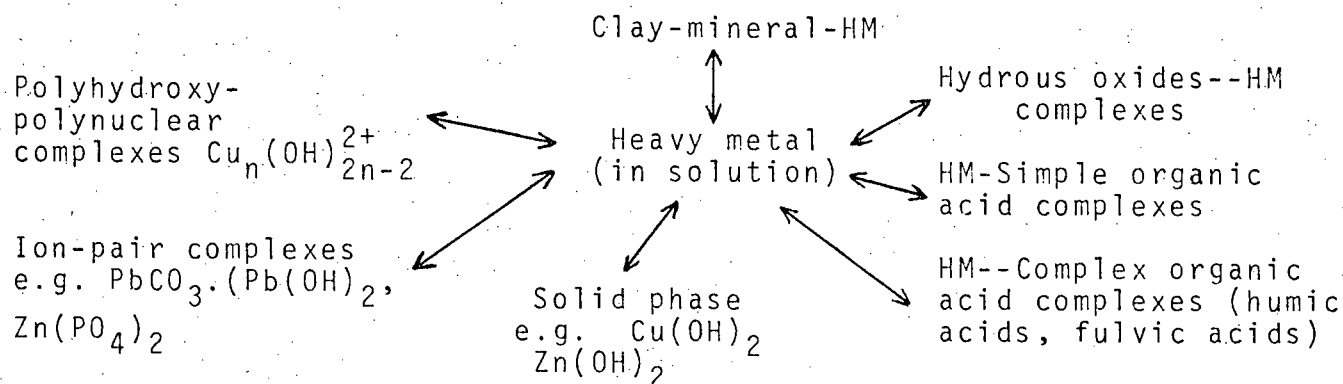
FIG. II. HEAVY METAL ADSORPTION BY GLACIAL MARINE SOIL FROM AN EQUIVALENT MIXTURE (1:1:1:1) OF Cd, Pb, Cu, Zn

IV, VI and VIII). Competitive adsorption below an equilibrium concentration of 0.01 me followed the order  $Pb > Cu > Cd > Zn$ . At higher concentrations, more copper than lead was sorbed on both soils, caused probably by greater precipitation of  $Cu(OH)_2$ .

Comparing the results obtained in this competition study with those for competitive adsorption on montmorillonite and kaolinite (see Part II), it could be suggested that the adsorption phenomena on soils was different than that on montmorillonite. Lack of conformity with the rearranged Langmuir plot for both, soils and kaolinite does not necessarily mean that similar adsorption phenomena occurred for adsorbing equivalent mixtures of heavy metals. In the case of competition of heavy metals on soils, several interacting factors could affect the adsorptive behaviour; some of these factors would no doubt arise from the nature and composition of the inorganic and organic constituents as well as interactions between these two groups from variations in charge-densities in these different fractions; and from the ionic strength of the medium.

Though the competition studies on soils have not been able to predict sorptive capacities, the adsorption isotherms have provided evidence that heavy metal adsorption when in competition does not behave in a similar fashion as the adsorption of individual metals.

From the foregoing studies and literature surveyed, it would appear that heavy metal deposition in natural environments such as soils, sediments and waters is regulated by many factors. A hypothetical soil-heavy metal model that may regulate mobility is presented below:



### CONCLUSIONS

The ability of agricultural soils and surface sediments to sorb lead was found to increase with increasing pH. Regression analysis of the lead data showed conformity with both Langmuir and Freundlich equations over the 0 to 3000 ppm range at all pH values studied; thus indicating similarity in adsorption phenomena with the smectite group of clay minerals. No differences in bonding energy of lead were observed between the soils at the same pH.

Heavy metal sorption in excess of cation exchange capacity was observed by both soils and sediment at low pH values.

Irrespective of soil or sediment, sorptive capacities were similar up to an equilibrium concentration of 1250 ppm, with adsorption following the order  $Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+}$ . There was conformity with Langmuir in the concentration range of 0-3000 ppm at pH 5.0 for Pb and Zn but not for Cu and Cd; conformity with Freundlich was obtained for all metals in the 0-3000 ppm range.

In all cases at pH 5.0, the amount of heavy metal sorbed exceeded the respective cation-exchange capacity; similar findings were observed with the clay minerals.

Application of the Langmuir relationship has permitted the inference that heavy metal adsorption phenomena on soils vary with metal type, concentration range and pH.

Langmuir adsorption maxima at pH 5.0 of Pb, Cd and Zn on the samples were positively correlated with clay content, organic carbon and cation-exchange capacity. Negative correlations were obtained for both Pb and Cd with oxalate-Fe and oxalate-Al, but zinc was positively correlated.

Adsorption isotherms for Cd, Pb, Cu and Zn when in competition showed sorption on soils to increase with increasing original concentration; however, data incorporated into the Langmuir equation lacked conformity, thus indicating different adsorption phenomena than individual metal adsorption.

## SUMMARY

The effects of short term and long term exposure to heavy metals by life forms are not clearly understood. Both urban and rural areas of British Columbia often receive substantial amounts of heavy metals through industry, that, it has become a matter of concern for the Province.

Empirical and mechanistic approaches were used to study the fate and behaviour of heavy metals in soils. Recovery of added elements Cd, Pb, Cu and Zn to soils of British Columbia showed that 0.1 N HCl and 0.05 M E.D.T.A. were better extractants than nitric and acetic acid. Irrespective of heavy metal, differences in organic matter and cation exchange capacity between surface and sub-surface samples showed significant differences in per cent recovery. No significant differences at the 5% level existed between per cent recovery of added heavy metals and extraction shaking periods of two and six hours.

Lead, cadmium and zinc levels decreased with depth in the different soils of the Salmon River Watershed; however, copper distribution in the profiles stayed constant. Lead was retained to a greater extent than the other metals and correlated strongly with organic matter and to a lesser extent with cation exchange capacity.

Comparative data from soils under different land use practices showed Pb and possibly Cd to be associated with traffic proximity.

Analysis of sediments from the Salmon River indicated higher metal values in industrial, intensive agricultural and near estuary sites than from upstream rural sites. Mineralogical composition of the less than two micron fraction of sediments showed only very small differences between composition of soil clay and sediment clay within the watershed.

In studying the retention mechanisms by the predominant clay minerals present in the soils studied, it was observed that clay minerals such as montmorillonite, vermiculite, illite and kaolinite adsorbed Cd, Pb, Cu and Zn beyond their cation exchange capacity; and that, adsorption increased with increasing pH. However, only the 2:1 expanded type of clay minerals conformed to the Langmuir relationship, whereas the 2:1 non expanded illite and 1:1 kaolinite did not. Data for all minerals conformed with the Freundlich equation under all working pH conditions and the concentration range of 0-3000 ppm.

Competition studies with an equivalent mixture (1:1:1:1) of Cd, Pb, Cu and Zn on montmorillonite at pH 5.0, showed conformity with Langmuir but Kaolinite failed to obey the relationship. The Langmuir fit allowed computation of adsorption



maxima for montmorillonite and vermiculite.

An extension of this physico-chemical approach to soils and sediments, provided adsorption maxima that are of predictive value for the metals Cd, Pb, Cu and Zn. Similar sorptive behaviour by the soils, as for the smectite group of minerals, were observed with increasing pH, for lead, over the 0-3000 ppm range. The ability of agricultural soils to sorb lead was found to increase with increasing pH. No differences in bonding energy of lead were observed between the soils at the same pH. Heavy metal sorption in excess of the cation exchange capacity was also observed by both soils and sediment at low pH values.

Conformity with Langmuir in the concentration range of 0-3000 ppm at pH 5.0 was obtained for lead and zinc, but not for copper and cadmium; data for all metals fitted the Freundlich equation in the 0-3000 ppm range. Adsorption of Pb, Cd and Zn on soils and sediment at pH 5.0, were positively correlated with clay content, organic matter and cation exchange capacity; negative correlations by Pb and Cd were observed with oxalate-Fe and oxalate-AL, but zinc was positively correlated.

Adsorption from the mixture (1:1:1:1) in equivalent of Cd, Pb, Cu and Zn on two soils of differing texture and organic matter content did not fit the Langmuir equation over the 0-50 me/l range, thus indicating adsorption to be other than the monolayer type.

## REFERENCES

- ABEL, E.W. (1973). Lead. In Bailar, C.J. (ed). Comprehensive Inorganic Chemistry. Volume 2, 105-146. Pergamon Press.
- ADAMSON, A.W. (1967). Physical Chemistry of surfaces. Interscience Publishers Incorporation, New York.
- AIR POLLUTION CONTROL DIRECTORATE. (1973). Exploratory lead studies in high traffic density areas in Vancouver, Toronto and Montreal. Report E.P.S.5-AP-73-2. Environment Canada.
- ALLAWAY, W.H. (1968). Agronomic controls over the environmental cycling of trace elements. Advances in Agronomy 20, 235-274.
- ANON, (1974). Institute for environmental studies. An interdisciplinary study of environmental pollution by lead and other metals. Progress report (PR4). University of Illinois N8F. Rann Grant. G1 31605.
- AYLETT, J.B. (1973). Zn and Cd. In Bailar, C.J. (ed). Comprehensive Inorganic Chemistry. Volume 3, 187-328. Pergamon Press.
- BABCOCK, L.K. (1963). Theory of the chemical properties of soil colloidal systems at equilibrium. Hilgardia 34.
- BAILAR, C.J., EMELENS, J.H., NYHOLM, R., AND TROTMAN-DICKENSON. 1973. Comprehensive Inorganic Chemistry. Pergamon Press.
- BAWEJA, S.A., and MCLEAN, E.O. (1975). Bonding of calcium and kaolinite clays as affected by H-clay addition. Soil Science Society America Proceedings. Vol. 39, 48-50.
- BHUIYA, H.R.M. and CORNFIELD, H.A. (1972). Effects of addition of 1000 ppm Cu, Ni, Pb and Zn on carbon dioxide release during incubation of soil alone and after treatment with straw. Environmental Pollution 3, 173-177.
- BINGHAM, T.F., PAGE, L.A. and SIMS, R.J. (1964). Retention of Cu and Zn by H-montmorillonite. Soil Science Society of America Proceedings, Volume 28, 351-355.

- BITELL, E.J. and MILLER, J.R. (1974). Lead, cadmium and calcium selectivity coefficients on a montmorillonite, illite and kaolinite. *Journal of Environmental Quality* 3, 250-253.
- BLACK, C.A. (1965). Methods of soil analysis. Part 2. Agronomy Number 9. American Society of Agronomy. Madison, Wisconsin, U.S.A.
- BOGDEN, J.D., SINGH, P.N. and JOSELOW, M.M. (1974). Cadmium, lead and zinc concentrations in whole blood samples of children. *Environmental Science and Technology* 8, 740-742.
- BOWER, C.A. and TRUOG, E. (1941). Base exchange capacity determination as influenced by nature of cation employed and formation of basic exchange salts. *Soil Science Society of American Proceedings* 5, 86-89.
- BROWN, A.L., QUICK, J. and EDDINGS, L.J. (1971). A comparison of analytical methods for soil zinc. *Soil Science Society of American Proceedings* 35, 105-107.
- BRULAND, K.W., BERTINE, K., KOIDE, M. and GOLDBERG, E. (1974). History of metal pollution in Southern California coastal zone. *Current Research* 8, 425-432.
- CARMODY, J.D. (1973). Trace metals in sediments of New York Bight. *Marine Pollution Bulletin* 4, 132-135.
- CHOW, T.J. (1970). Lead accumulation in roadside soil and grasses. *Nature (London)*. 225 (5229): 295-296.
- DANILOV, V.V. (1971). Ammonia complexes of cadmium. *Zhurnal Prikladnoi Khimi* 44, 3-6.
- DAVIES, C.W. (1962). Ion Association Washington, D.C. Butterworth.
- DEMUMBRUM, L.E. and JACKSON, (1956a). Copper and zinc exchange from dilute neutral solutions by soil colloidal electrolytes. *Soil Science* 81, 353-357.
- DEMUMBRUM, L.E. and JACKSON, M.L. (1956b). Infra-red absorption evidence on exchange reaction mechanism of copper and zinc with layer silicate clays and peat. *Soil Science Society of American Proceedings* 20, 334-337.

- DEMUMBRUM, E.L. and JACKSON, L.M. (1957). Formation of basic cations of copper, zinc, iron and aluminium. Soil Science Society of America Proceedings 21, 662.
- DOLLAR, S.G. and KEENEY, D.R. (1971). Availability of Cu, Zn and Mn in Wisconsin soils. Journal of Agriculture and Food Science 22, 273-278.
- ELGABALY, M.M. and JENNY, H. (1943). Cation and anion interchange with zinc montmorillonite clays. Journal of Physical Chemistry 47, 399-408.
- ELLIS, G.B. and KNEZEK, D.B. (1972). Adsorption reactions of micronutrients in soils. In. J. J. Mortvedt. (ed). Micronutrients in Agriculture. Soil Science Society of America Incorporation. Madison. Wiscon. U.S.A.
- ENNIS, M.T. and BROGAN, J.C. (1961). The availability of copper from copper-humic complexes. Irish Journal of Agricultural Research 1, 35-42.
- ERIKSSON, E. (1952). Cation exchange equilibria on clay minerals. Soil Science 74, 106-113.
- FEDEROV, V.M.A. (1971). Mixed chloride sulphate complexes of Zn and Cd. Zhurnal Neorganicheskoi. Khimii 16, 325-329.
- FORDHAM, W.A. (1969). Sorption and precipitation of iron on kaolinite. 11 Sorption isotherms and their interpretation in terms of iron (III) ionic equilibrium. Australian Journal of Soil Research 7, 199-212.
- FORDHAM, A.W. (1969a). Sorption and precipitation of iron on kaolinite I. Factors involved in sorption equilibria Australian Journal of Soil Research 7, 185-197.
- FRIBERG, L. (1973). Cadmium in the environment. Chemical Rubber Press. Cleveland. Ohio.
- GAYNOR, D.J. (1973). Lettuce growth on sewage sludge amended soils. Soil horizons 14 (2).
- GEERING, H.R. and HODGSON, F.J. (1969). Micro-nutrient cation complexes in soil solution : III, Characterization of soil solution ligands and their complexes with  $Zn^{2+}$  and  $Cu^{2+}$ . Soil Science Society America. Proceedings 33, 54-59.

- GOODMAN, A.B. and CHESIRE, M.V. (1973). Electron paramagnetic resonance evidence that copper is complexed in humic acid by the nitrogen of porphyrin groups. *Nature New Biology* 244, 158-159.
- HAGHIRI, F. (1973). Cadmium uptake by plants. *Journal of Environmental Quality* 2, 93-96.
- HAHNE, H. (1974). Significance of pH and pCl in heavy metal ion reactions and mercury (II) adsorption by soil materials. Ph.D Thesis. Virginia Polytechnic Institute and State University.
- HALL, J.K., KOCH, A.F. and YESAKI, I. (1975). Further investigations into water quality conditions in the Lower Fraser River System. Technical Report Number 4, August 1974. Westwater Research Centre. University of British Columbia. Vancouver.
- HALLSWORTH, E.G. and ADAMS, A.W. (1973). The heavy metal content of rainfall in the East Midlands. *Environmental Pollution* 4, 231-235.
- HASSETT, J.J. (1974). Capacity of selected Illinois soils to remove lead from aqueous solution. *Communications in Soil Science and Plant Analysis* 5, 499-506.
- HEYDEMAN, A. (1959). Adsorption of copper on clay minerals and quartz. *Geochim-Cosmochim Acta* 15, 305-329.
- HODGSON, J.F., TILLER, G.K. and FELLOWS, M. (1964). The role of hydrolysis in the reaction of heavy metals with soil forming materials. *Soil Science Society of America Proceedings* 28, 42-46.
- HOPPS, C.H. (1974). Overview.- In *Geochemistry and the Environment*. Volume (I). National Academy of Sciences.
- JOHN, M.K. (1971). Lead contamination of some agricultural soils in Western Canada. *Environmental Science and Technology* 5, 1199-1203.
- JOHN, M.K., VAN LEARHOVEN, C.J. and CHUAH, H.H. (1972). Factors affecting plant uptake and phytotoxicity of cadmium added to soils; *Environmental science Technology* 6, 1005-1009.
- JOHN, M.K. (1972a). Influence of soil properties and extractable zinc on zinc availability. *Soil Science* 113, 222-227.

- JOHN, M.K. (1972b). Cadmium adsorption maxima of soils as measured by the Langmuir isotherm. *Canadian Journal of Soil Science* 52, 343-350.
- JOHN, M.K. (1972c). Lead availability related to soil properties and extractable lead. *Journal of Environmental Quality* 1, 295-298.
- JOHN, M.K. (1973). Cadmium uptake by eight food crops as influenced by various soil levels of cadmium. *Environmental Pollution* 4, 7-15.
- JOHN, M.K. (1974). Extractable and plant available zinc in horizons of several Fraser River alluvial soils. *Canadian Journal of Soil Science* 54, 125-132.
- JONES, J.S. and HATCH, M.B. (1937). The significance of inorganic spray residue accumulations in orchard soils. *Soil Science* 44, 37-64.
- JONES, L.R., HINESLY and ZIEGLER, L.E. (1973). Cadmium content of soybean grown in sewage sludge amended soil. *Journal of Environmental Quality* 2, 351-353.
- JURINAK, J.J. and INOUE, T.S. (1962). Some aspects of zinc and copper phosphate formation in aqueous systems. *Soil Science Society of America Proceedings* 26, 144-147.
- KING, D.L. and MORRIS, H. (1972). Land disposal of liquid sewage sludge: II. The effect on soil pH, Mn, Zn and growth, and chemical composition of rye. *Journal of Environmental Quality* 1, 425-429.
- KISK, M.F. and HASSAN, N.M. (1974). Sorption and desorption of copper by and from clay minerals. *Plant and Soil* 39, 497-505.
- KLINE, J.R. and RUSE, R.H. (1966). Fractionation of Cu in neutron activated soil. *Soil Science Society America Proceedings* 30, 188-192.
- KOBAYASHI, J. (1971). Relation between the itai-itai disease and the pollution of river water by cadmium from a mine. In, *Proceedings of the Fifth International Water Pollution Research Conference, San Francisco* p 1-7.

- KRAUSKOPF, B.K. (1972). Geochemistry of Micronutrients. In J.J. MORTVEDT (ed). Micronutrients in agriculture. Soil Science Society of America Incorporation. Madison. U.S.A.
- LAGERWEFF, J.V. (1967). Heavy metal contamination of soils. p 343-364. In N.C. BRADY (ed). Agriculture and the quality of our environment. American Association for the Advancement of Science. Washington, D.C.
- LAGERWEFF, J.V., and SPECHT, W.A. (1970). Contamination of roadside soil and vegetation with Cd, Ni, Pb and zinc. Environmental Science and Technology 4, 583-585.
- LAGERWEFF, V.J. (1971). Uptake of cadmium, lead and zinc by radish from soil and air. Soil Science 111, 129-133.
- LAGERWEFF, V.J. (1972). Lead, mercury and cadmium as environmental contaminants. In J.J. Mortvedt (ed). Micronutrients in Agriculture. Soil Science Society of America. Madison, Wisconsin, U.S.A.
- LAGERWEFF, J.V. and BROWER, L.D. (1973). Exchange adsorption or precipitation of lead in soils treated with chlorides of aluminium, calcium and sodium. Soil Science Society America Proceedings 37, 11-13.
- LEEPER, W.G. (1972). Reactions of heavy metals with soils with special regard to their application in sewage wastes. Prepared for Department of the Army Corps of Engineers, Directorate of Civil Works. Washington. D.C. Contract Number DACW-73-73-C-0026.
- LEWIS, T. (1974). The soils of the West Coast Trail, Vancouver Island, B.C. DINA, Parks Branch, Ottawa.
- LINDSAY, L.W. (1972). Inorganic phase equilibria of micronutrients in soils. In J.J. Mortvedt (ed). Micronutrients in agriculture. Soil Science Society of America Incorporation. Madison, Wisconsin, U.S.A.
- LISK, J.D. (1972). Trace metals in soils, plants and animals. In N.C. Brady (ed). Advances in Agronomy 24, 267-311.
- LUND, J.L., KOHNKE, H. and PAULET, M. An interpretation of reservoir sedimentation II. Clay Mineralogy. Journal of Environmental Quality; 1, 303-307.

- MARINSKY, A.J. (1966). Ion-exchange - A series of advances. Marcel Dekker. Incorporation. New York.
- MARTENS, D.C. (1968). Plant availability of extractable boron, copper and zinc as related to selected soil properties. Soil Science 106, 23-28.
- MARTENS, D.C., CHESTERS, G. and PETERSON, L.A. (1966). Factors controlling extractability of soil zinc. Soil Science Society America Proceedings 30, 67-69.
- MASSEY, G.A. (1973). Copper. In Bailar C.J. (ed). Comprehensive Inorganic Chemistry, Volume 3, 1-78.
- MCBRIDE, B.M. and MORTLAND, M.M. (1974). Copper (II) Interactions with montmorillonite: Evidence from physical methods. Soil Science Society America 38, 408-415.
- MCLAREN, G.R. and CRAWFORD, V.D. (1973). Studies on soil copper. I. The fractionation of copper in soils. Journal of Soil Science 24, 173-181.
- MCLAREN, G.R. and CRAWFORD, V.D. (1973). The specific adsorption of copper by soils. Journal of Soil Sciences 24, 444-451.
- MCLEAN, O.E. and BITTENCOURT, C.V. (1973). Complementary ion effects on potassium, sodium and calcium displacement from bi-ionic bentonite and illite systems as affected by pH-dependent charges. Soil Science Society America Proceedings 37, 375-379.
- MACLEAN, K.S., HALSTEAD, C.R. and FIN, J.B. (1969). Extractability of added lead in soils and its concentration in plants. Canadian Journal of Soil Science 49, 327-334.
- MACLEAN, K.S. and LONGVILLE, W.M. (1973). Heavy metal studies of crops and soils in Nova Scotia. Communications in Soil Science and Plant Analysis 4, 495-505.
- MENZEL, R. and JACKSON, M.L. (1950). Sorption of copper from acid systems by kaolinite and montmorillonite. Transactions International Soils Conference, 125-128.
- MENZEL, R. and JACKSON, L.M. (1951). Mechanism of sorption of hydroxy cupric ion by clays. Soil Science Society America Proceedings 15, 122-124.



- NATIONAL ACADEMY OF SCIENCES. (1974). Geochemistry and the Environment. Volume I. The relation of selected trace elements to health and disease.
- NATIONAL RESEARCH COUNCIL. (1973). Lead in the Canadian environment. Associate Committee on scientific criteria for environmental quality.
- NORTHCOTE, G.T., JOHNSTON, T.N. and TSUMURA, K. (1975). Trace metal concentrations in Lower Fraser River fishes. Technical Report Number 7, June 1975. Westwater Research Centre. University of British Columbia. Canada
- NORVELL, W.A. and LINDSAY, L.W. (1969). Reactions of E.D.T.A. complexes of Fe, Zn, Mn and Cu with soils. Soil Science Society America Proceedings 33, 86-91.
- NORVELL, A.W. (1972). Equilibria of metal chelates in soil solution. In J.J. Mortvedt (ed). Micronutrients in agriculture, p 131. Soil Science Society of America Incorporation Madison, Wisconsin, U.S.A.
- OLIVER, J. and KINRADE, D. (1972). Heavy metal concentrations in Ottawa River and Rideau River sediments. Scientific Series, Number 14. Inland Waters Branch. Environment Canada.
- PAGE, L.A. and BINGHAM, T.F. (1973). Cadmium residues in the environment. In Gunther.F.(ed). Residue Reviews. Volume 48, 1-44 Springer-Verlag. New York.
- PAGE, L.A., BINGHAM, F.T. and NELSON, C. (1972). Cadmium absorption and growth of various plant species as influenced by solution cadmium concentration. Journal of Environmental Quality 1, 288-291.
- PIETZ, R.I., ADAMS, R.S. and MACGREGOR, M.J. (1970). Effects of different aqueous buffers on the zinc extractability of dithizone. Soil Science Society America Proceedings 34, 698-699.
- PLEISS, S.F. DU and BURGER, R. DU.T. (1971). Die spesifiekte adsorpie van koperdeur kleiminerales en grandfraksies. Agrochemophysica 3, 1-10.

- PRESANT, E.W. and TUPPER, W.M. (1965). Trace elements in some New Brunswick soils. *Canadian Journal of Soil Science* 45, 305-310.
- PRESTON, A., JEFFERIES, D., DUTTON, R.W., HARVEY, R.B. and STEELE, A.K. (1972). British Isles coastal waters: The concentrations of selected heavy metals in sea-water, suspended matter and biological indicators-a pilot survey. *Environmental Pollution* 3, 69-82.
- PURVES, D. (1972). Consequences of trace element contamination of soils. *Environmental Pollution* 3, 17-24.
- PURVES, D. and MACKENZIE, E.J. (1973). Effects of applications of municipal compost on uptake of copper, zinc and boron by garden vegetables. *Plant and soil* 39, 361-371.
- QURAIISHI, I.S.M. and CORNFIELD, H.A. (1973). Incubation study of nitrogen mineralization and nitrification in relation to soil pH and level of Copper (II) addition. *Environmental Pollution* 4, 159-163.
- RASHID, M.A. (1973). Role of humic acids of marine origin and their different molecular weight fractions in complexing di and tri-valent metals. *Soil Science* 111, 298-306.
- RASHID, M.A. and LEONARD, D.J. (1973). Modifications in the solubility and precipitation behaviour of various metals as a result of their interaction with sedimentary humic acid. *Chemical Geology* 11, 89-97.
- REDDY, R.M. and PERKINS, F.H. (1974). Fixation of zinc by clay minerals. *Soil Science Society of America Proceedings* 38, 229-231.
- REUTHER, W. and SMITH, P.F. (1953). Effects of high copper content of sandy soil on growth of citrus seedlings. *Soil Science* 75, 219-224.
- ROSE, W.A. (1974). The mode of occurrence of trace elements in soils and stream sediments applied to geochemical exploration. *International Geochemical Congress*.
- SANKARAN, S.K. and RAO, V.D. (1974). Mechanistic response of clays. *Soil Science* 118, 289-297.
- SANTILLAN-MEDRANO, M.J. (1974). Behaviour and translocation of Cd and Pb in soils. Ph.D. Thesis. Utah State University.

- SCHNITZER, M. (1969). Reactions between fulvic acid, a soil humic compound and inorganic soil constituents, Soil Science Society America Proceedings 33, 75-81.
- SCHNITZER, M. and SKINNER, S.M. (1970). Organo-metallic interactions in soils. 8: An evaluation of methods for the determination of stability constants of metal-fulvic acid complexes. Soil Science 109, 333-340.
- SCHNITZER, M. (1971). Metal organic matter interactions in soils and waters. (In. S.J. FAUST and J.V. HUNTER (ed). Organic compounds in aquatic environments. Marcel Dekker, New York.
- SCHNITZER, M. and KHAN, S.U. (1972). Humic substances in the environment. Marcel Dekker. New York.
- SCHROEDER, H.A. (1963). Cadmium: Uptake by vegetables from super-phosphate in soil. Science 140(36568) :819.
- SHARPLESS, G.R., WALLIHAN, F.E. and PETERSON, F.F. (1969). Retention of zinc by some arid zone soil materials treated with zinc sulphate. Soil Science Society America Proceedings 33, 901-904.
- SHUMAN, M.L. (1975). The effect of soil properties on zinc adsorption by soils. Soil Science Society America Proceedings 39, 454-458.
- SNEED, C.M. and BRASTED, C.R. (1955). Comprehensive Inorganic Chemistry, Volume IV. Zn, Cd. Hg. D. Van Nostrand.
- SOPPER, W.E. and KARDOS, T.L. (1973). Recycling treated municipal wastewater and sludge through forest and cropland. Pennsylvania State University Press.
- STEVENSON, J.F. and ARDAKANI, S.M. (1972). Organic matter reactions involving micronutrients in soils. In J.J. MORTVEDT (ed). Micronutrients in agriculture p 79-110. Soil Science Society America Incorporation Madison, Wisconsin. U.S.A.
- TAKIJIMA, Y. and KATSUMI, F. (1973). Cadmium contamination of soils and rice plants caused by zinc mining. Use of soil amendment for the control of cadmium uptake by plants. Soil Science and Plant Nutrition 19, 235-244.

- TAN, H.K., KING, D. and MORRIS, D.H. (1971). Complex reactions of zinc with organic matter extracted from sewage, sludge. Soil Science Society America Proceedings 35, 748-751.
- TILLER and HODGSON (1962). Sorption of zinc by layer silicates. Clays and Minerals 9, 393-402.
- TILLER, K.G., HONEYSETT, J.L. and HALLSWORTH, G.E. (1969). The isotopically exchangeable form of native and applied cobalt in soils. Australian Journal of Soil Research 7, 43-56.
- TUCKER, G.T. and KURTZ, T. (1955). A comparison of several chemical methods with the bio-assay procedure for extracting zinc from soils. Soil Science Society America Proceedings 19, 477-481.
- UDO, E.J., BOHN, H. and TUCKER, C.T. (1970). Zinc adsorption by calcareous soils. Soil Science Society America Proceedings 34, 405-407.
- VIETS, G.F. and LINDSAY, L.W. (1973). Testing soils for Zn, Cu, Mn and Fe. In L.M. WALSH and J.D. BEATON (ed). Soil testing and plant analysis. Soil Science Society Incorporation 73-75560.
- WALSH, L.M. (1972). Effect of high rates of Zn on several crops grown in irrigated plain field sand., Communication in Soil Science and Plant Analysis 3, 187-195.
- WARREN, H.V., DELAVAUULT, R.E. and FLETCHER (1971). Metal pollution - A growing problem in industrial and urban areas - Canadian Mining and Metallurgical Bulletin p 1-12.
- WEBBER, D.M. (1975). Metal availability in soils. Paper presented at the Ontario Soil Management Research Committee Workshop on Metals in Agriculture. Guelph, Canada.
- WEISS, H.V. and KOIDE, M. (1971). Hg in a Greenland ice-sheet. Science 174-692-694.
- WILLIAMS, C.H. and DAVID, J.D. (1973). The effect of superphosphate on the cadmium content of soils and plants. Australian Journal of Soil Research 11, 43-56.

# APPENDIX I

Heavy metal distribution following sample fortification and six hours shaking  
(without pH adjustment)

<u>Supernatant Solution</u> ppm (Average)					<u>Extract</u> ppm (Average)				
	Cd	Pb	Cu	Zn		Cd	Pb	Cu	Zn
Ah	8.3	0.2	2.3	8.7	5.0 % CH <sub>3</sub> COOH	4.1	0.0	8.0	5.7
Bgf	9.3	2.6	7.3	-		2.0	11.7	7.3	2.3
Ah	8.3	0.4	2.4	8.5	10.0 % CH <sub>3</sub> COOH	4.3	3.1	9.6	5.4
Bgf	9.1	2.3	7.4	-		2.0	14.7	7.7	6.0
Ah	8.3	0.4	2.2	8.5	0.1N HCl	6.0	14.3	18.1	6.0
Bgf	9.5	2.7	7.4	-		2.1	28.8	9.2	3.8
Ah	8.2	0.4	2.2	8.9	1.0N HCl	4.8	27.0	23.7	8.0
Bgf	9.2	2.7	7.4	-		2.1	31.6	10.2	5.8
Ah	8.1	0.4	2.2	8.3	0.05M EDTA	5.7	22.0	26.1	6.3
Bgf	9.3	2.8	7.4	-		2.0	31.1	9.4	3.4
Ah	8.1	0.4	2.1	8.4	1.0 NHNO <sub>3</sub>	6.1	12.3	20.1	7.4
Bgf	9.2	2.2	7.3	-		2.0	26.5	9.2	2.5

# APPENDIX II (a)

Heavy metal distribution following sample fortification  
and two hours shaking

		<u>Supernatant Solution</u> ppm (Average)				<u>Extract</u> ppm (Average)			
		Cd	Pb	Cu	Zn	Cd	Pb	Cu	Zn
0.1N HCl	Ah	5.4	N.D	1.1	7.0	10.1	19.3	21.7	10.6
	Bgf	8.1	2.1	4.8	9.3	5.9	26.6	15.5	5.5
1.0N HCl	Ah	5.9	N.D	1.3	7.3	12.1	34.9	30.6	14.6
	Bgf	7.9	2.4	4.5	9.1	4.6	23.9	14.0	5.2
0.05M EDTA	Ah	6.2	N.D	1.4	7.4	11.3	31.3	30.1	11.2
	Bgf	8.4	3.1	5.5	9.5	5.4	29.2	15.2	5.0

# APPENDIX II (b)

Heavy metal distribution following sample fortification and  
pH adjustment with six hours shaking

		<u>Supernatant Solution</u> ppm (Average)				<u>Extract</u> ppm (Average)			
		Cd	Pb	Cu	Zn	Cd	Pb	Cu	Zn
0.1N HCl	Ah	5.0	N.D	1.0	6.1	15.6	16.8	23.7	15.4
	Bgf	8.2	1.9	5.1	9.0	4.7	23.8	14.1	5.1
1.0N HCl	Ah	6.5	N.D	1.5	7.7	12.1	33.2	31.5	12.6
	Bgf	8.1	2.2	4.9	9.0	6.4	30.7	12.9	6.9
0.05M EDTA	Ah	6.4	N.D	1.6	7.7	14.1	31.7	31.2	13.3
	Bgf	7.0	2.8	6.2	9.6	7.7	37.6	18.9	7.7

### APPENDIX III

Heavy metal distribution following sample fortification and  
pH adjustment with two hours shaking

		<u>Supernatant Solution</u> ppm (Average)				<u>Extract</u> ppm (Average)			
		Cd	Pb	Cu	Zn	Cd	Pb	Cu	Zn
0.1N HCl	Ap (Site I)	1.4	N.D	0.21	2.0	29.1	21.6	28.0	9.2
	Ap (Site III)	6.0	N.D	1.30	2.0	11.1	24.4	27.1	23.0
1.0N HCl	Ap (Site I)	1.4	N.D	0.19	7.1	28.2	29.4	36.3	21.8
	Ap (Site III)	6.0	N.D	1.30	7.1	10.9	32.4	32.0	10.5
0.05M EDTA	Ap (Site I)	1.3	N.D	N.D	2.1	39.0	46.2	46.1	36.2
	Ap (Site III)	6.3	N.D	1.30	6.6	13.3	41.5	31.9	14.2



# APPENDIX IV

## Selected chemical properties of some soils of the Salmon River watershed

Parent Material	Horizon	Depth (cm)	pH (1:1) H <sub>2</sub> O	pH (1:1) H <sub>2</sub> O	O.M %	Total N %	P ppm	C/N	Exchangeable cations				C.E.C.
									Ca	Mg	K	Na	
									m.e/100 g				
Alluvium (Site I)	Ap	0-25	5.1	4.3	21.3	2.15	13.9	5.7	2.85	0.47	0.02	N.D	52.42
	Bg	25-40	5.6	4.6	2.1	0.11	9.6	11.0	1.42	0.54	0.01	-	16.70
	C	40+	5.6	4.7	2.9	0.12	9.6	13.9	1.30	0.52	N.D	-	15.83
Alluvium (Site II)	Ap	0-20	5.5	4.5	12.8	1.44	35.6	5.1	12.25	2.17	0.79	-	42.75
	Bg	20-40	5.5	4.4	4.2	0.22	33.8	11.0	6.52	1.68	0.86	0.07	39.28
	C	40+	5.4	4.5	2.1	0.10	14.0	12.4	10.06	3.42	0.18	0.21	32.42
Glacial Outwash (Site III)	Ap	0-12	5.4	4.6	7.1	0.44	23.9	9.4	3.00	0.46	0.31	N.D	25.27
	B	12-90	5.6	4.6	2.0	0.08	30.2	14.2	0.44	0.11	0.25	-	21.20
	C	90+	5.8	4.6	0.8	0.03	39.8	14.7	0.27	0.07	0.20	-	11.65
Glacial Outwash (Site IV)	A	0-10	5.1	4.3	11.2	0.92	47.5	7.1	2.22	0.32	0.10	-	30.35
	B	10-40	5.2	4.1	3.1	0.10	20.0	18.3	0.75	0.08	0.05	0.02	17.94
	C	40+	5.5	4.1	0.9	0.03	13.0	17.0	0.59	0.20	0.04	0.01	12.25
Marine Loam (Site V)	Ap	0-10	5.1	4.0	8.4	0.84	12.9	5.8	3.59	0.36	0.06	0.03	28.60
	B	10-70	5.6	4.5	5.4	0.21	9.7	15.0	2.49	0.62	0.03	0.08	27.03
	C	70+	5.9	4.5	0.6	0.04	25.5	8.5	2.36	1.79	0.02	0.24	10.73
Marine Loam (Site IV)	H	0-4	3.6	3.1	24.1	0.49	19.6	28.5	5.48	1.10	0.31	0.03	59.80
	Bf	4-75	4.4	3.9	7.1	0.24	14.9	17.3	0.03	0.08	0.08	0.02	30.55
	C	75+	4.9	4.3	1.7	0.06	13.0	16.8	0.15	0.07	0.02	0.03	15.96

## APPENDIX V

Selected chemical properties of some surface sediments of Salmon River

Surface Sediment	pH (H <sub>2</sub> O) 1:1	pH (H <sub>2</sub> O) 1:1	Org.C	0.M	Total	P	c/n	Ca	Exchangeable cations			
			—————	%	—————	ppm			Mg	K	Na	C.E.C.
									me/100 g —————			
Site 1	5.5	4.7	0.90	1.5	0.060	37.5	15.0	5.00	1.02	0.19	0.16	10.59
Site 2	5.3	4.2	3.48	6.0	0.234	42.0	15.1	7.12	1.34	0.29	0.27	24.90
Site 3	5.6	4.7	0.99	1.7	0.040	17.3	24.7	5.25	1.44	0.33	0.73	5.06
Site 6	5.6	4.7	0.19	0.3	0.003	17.2	63.3	1.62	0.29	0.10	0.06	3.70
Site 7	5.6	4.9	0.34	0.6	0.004	34.7	85.0	1.62	0.24	0.11	0.05	4.11

# APPENDIX VI

Particle-size distribution of the < 2mm fraction of surface horizons and surface sediment of watershed

Parent Material	Sand	Silt %	Clay	Texture Class
Alluvium (Site I - Ap)	21.0	45.7	33.3	Clay loam
Outwash (Site III - Ap)	30.4	51.6	18.0	Silt loam
Marine (Site V - Ap)	40.9	47.6	11.5	Loam
<u>Sediment</u>				
S1	24.4	63.0	12.6	Silt loam
S2	44.5	37.1	13.4	Silt loam
S3	83.9	7.9	3.2	Sand
S6	93.0	5.6	1.4	Sand
S7	91.8	6.5	1.7	Sand

## APPENDIX VII

Extractable iron and aluminum from the soils and sediments studied

<u>Parent Material</u>		<u>Sodium pyrophosphate</u>		<u>Ammonium oxalate</u>	
		Fe	Al	Fe	Al
		— % —	— % —	— % —	— % —
Alluvium (Site I)	Ap	15.4	14.5	1.07	0.60
	Bg	2.3	2.1	0.49	0.12
	C	3.2	2.5	0.47	0.12
Alluvium (Site II)	Ap	13.6	14.9	1.38	0.80
	Bg	11.6	17.8	1.62	0.98
	C	5.4	9.2	0.79	0.40
Outwash (Site III)	Ap	6.6	16.3	0.93	1.70
	Bg	1.2	8.6	0.97	2.00
	C	0.8	4.9	0.33	0.98
Outwash (Site IV)	Ap	8.5	17.3	0.95	1.43
	Bg	3.6	12.6	0.81	1.88
	C	0.9	6.7	0.26	0.94
Glacial Marine (Site V)	Ap	13.2	16.9	1.20	1.37
	Bg	16.3	19.7	1.20	1.58
	C	2.6	4.0	0.14	0.13
Glacial Marine (Site VI)	H	9.8	10.5	0.59	0.48
	Bg	9.5	20.3	1.04	1.84
	C	1.9	9.4	0.20	1.01
<u>Surface Sediment</u>					
	S1	2.9	1.4	0.50	0.14
	S2	5.5	5.3	0.51	0.31
	S3	5.0	3.5	0.06	0.25
	S6	0.2	0.4	0.11	0.08
	S7	1.3	2.1	0.16	0.17

## APPENDIX VIII

X-ray mineralogy of  $<2\mu$  fraction of some  
soils of the Salmon River watershed

Parent Material	Horizon	Dominant	Mineral	
			Moderate	Minor
Alluvium (Site I)	Ah	Vt	Kt	Ct, It, Mt.
	B	Vt	It, Kt, Ct	Mt, Mt-Lt-Vt, Q, F.
	C	Vt	Kt, Ct.	Mt, Mt-It-Vt, Q, F.
Alluvium (Site II)	Ap	Vt	It, Kt, Ct	It-Vt, Q, F.
	B	Vt	Kt, Ct, Kt	It-Vt, Q, F.
	C	Vt	Kt, Ct	Mt, It, It-Vt, Q, F.
Glacial Outwash (Site III)	Ap	Kt	Ct	Vt, Q.
	B	Ct	Kt	Vt, Q.
	C	Ct	Mt or It, Kt.	Vt, Q.
Glacial Outwash (Site IV)	A	Vt	Kt	Mt or It, Q.
	B	Vt	Kt	Mt or It, Q.
	C	Vt	Kt, Ct	It, Qt.
Marine Loam (Site V)	Ap	Vt	Kt	Q
	B	Vt	Kt	Q
	C	Ct	Kt	It, Vt.
Marine Loam (Site VI)	H	Vt	Kt	Q, F.
	Bf	Vt	Kt	Q, F.
	C	Vt	Kt, Ct	Q, F.

Vt : Vermiculite  
 Mt : Montmorillonite  
 Kt : Kaolinite  
 It : Illite  
 Ct : Chlorite  
 F : Feldspars  
 Q : Quartz  
 A : Amphibole  
 M : Mica

## APPENDIX IX

X-ray mineralogy of  $<2\mu$  fraction of the surface  
sediment of the Salmon River

Sediment Sample	Dominant	Mineral Moderate	Minor
S <sub>1</sub>	Vt	Kt, Mor It	Mt, Q, F
S <sub>2</sub>	Vt	Mt, Kt	Ct, Mt, It
S <sub>3</sub>	Vt	Mt, Kt	Mt, It, Q, F
S <sub>6</sub>	Vt	Ct, Kt	Mt, It, Q, F
S <sub>7</sub>	Vt	Kt	Ct, It, A, Q, F

# APPENDIX X

Single correlation coefficients (v) between % recovery of heavy metals and some soil properties for three extractants: (a) 0.1N HCl (b) 0.0N HCl and (c) 0.05M EDTA

	Lead			Copper			Cadmium			Zinc		
	0.1N HCl	1.0N HCl	0.05M EDTA	0.1N HCl	1.0N HCl	0.05M EDTA	0.1N HCl	1.0N HCl	0.05M EDTA	0.1N HCl	1.0N HCl	0.05M EDTA
Pyr-Al	+0.99	+0.91	-0.07	+0.96	-0.19	-0.99	-0.99	-0.90	-0.99	+0.89	+0.99	-0.93
Pyr-Fe	-0.99	-0.91	+0.97	-0.96	+0.19	+0.99	+0.99	+0.90	+0.99	-0.89	-0.99	+0.93
Ox-Al	+0.99	+0.91	-0.97	+0.96	-0.19	-0.99	-0.99	-0.90	-0.99	+0.89	+0.99	-0.93
Ox-Fe	-0.99	-0.91	+0.97	-0.96	+0.19	+0.99	+0.99	+0.90	+0.99	-0.89	-0.99	+0.93
0.M	-0.99	-0.91	-0.97	-0.96	+0.18	+0.99	+0.99	+0.90	+0.99	-0.89	-0.99	+0.93
Clay	-0.99	-0.91	+0.97	-0.96	+0.18	+0.99	+0.99	+0.90	+0.99	-0.89	-0.99	+0.93

Pyr = Na-pyrophosphate extractable

Ox = Acid ammonium oxalate extractable

# APPENDIX XI

Experimental values for cadmium adsorption under four pH conditions on  
montmorillonite, vermiculite, illite and kaolinite

	Original concentration ppm	pH							
		4		5		6		7	
		C ppm	x/m mg/g	C ppm	x/m mg/g	C ppm	x/m mg/g	C ppm	x/m mg/g
Montmorillonite	100	5.0	11.88	4.3	11.96	5.7	11.79	5.0	11.87
	250	51.0	24.87	36.0	26.75	22.0	28.50	14.0	29.50
	500	282.5	27.19	268.3	28.96	245.8	31.78	215.0	35.64
	1000	755.0	30.62	721.7	34.79	624.0	46.88	622.3	47.19
	1500	1243.0	31.35	1201.7	37.29	1115.7	48.01	1057.5	55.30
	2000	1760.0	30.00	1602.5	49.50	1547.5	56.60	N.A.	N.A.
	3000	2655.0	43.13	2545.0	56.90	2481.7	64.80	2340.0	82.50
Vermiculite	100	5.3	11.90	1.0	12.40	1.3	12.40	1.0	12.40
	250	56.5	24.20	11.0	29.90	5.7	30.60	2.3	31.00
	500	199.0	37.60	147.0	44.00	132.5	45.90	125.0	46.90
	1000	641.5	44.80	632.5	46.00	580.8	52.40	505.0	61.90
	1500	1109.0	48.80	1095.0	50.30	1045.0	56.90	923.0	72.30
	2000	1505.0	61.90	1455.0	68.40	1408.0	73.90	1285.0	89.40
	3000	2345.0	81.90	2308.0	86.50	2285.0	89.40	2135.0	108.00
Illite	100	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
	250	217.3	4.10	200.0	6.18	176.3	9.20	135.0	14.40
	500	455.6	5.50	445.8	6.80	397.5	12.80	359.1	17.60
	1000	947.5	6.57	928.3	9.00	877.0	15.30	812.3	23.50
	1500	1408.0	11.45	1385.0	14.40	1342.7	19.60	1225.7	34.30
	2000	1828.0	13.45	1830.0	21.30	1797.5	25.30	1526.0	59.40
	3000	2816.7	22.93	2730.0	33.75	2608.0	48.90	2250.0	93.70



# APPENDIX XI (Cont'd)

		pH							
	Original concentration ppm	4		5		6		7	
		C ppm	x/m mg/g	C ppm	x/m mg/g	C ppm	x/m mg/g	C ppm	x/m mg/g
Kaolinite	100	N.A	N.A	N.A	N.A	N.A	N.A.	31.0	8.60
	250	237.0	1.62	242.0	0.94	229.7	2.54	139.5	13.81
	500	465.0	4.37	452.0	5.90	456.7	5.41	359.2	17.60
	1000	926.2	9.22	921.9	9.75	895.0	13.10	776.7	27.90
	1500	1335.8	20.52	1366.0	16.70	1310.0	23.75	1211.7	36.04
	2000	1797.0	25.30	1785.0	26.80	1758.0	30.20	1655.0	43.10
	3000	2730.0	33.75	2690.0	38.80	2613.3	48.30	2520.0	60.00

# APPENDIX XII

Experimental values for lead adsorption on kaolinite, montmorillonite and vermiculite under four pH conditions

	Original concentration ppm	pH							
		4		5		6		7	
		C ppm	x/m mg/g	C ppm	x/m mg/g	C ppm	x/m mg/g	C ppm	x/m mg/g
Kaolinite	100	91.0	1.13	89.7	1.29	59.3	3.83	16.6	10.42
	250	231.7	2.29	223.7	3.29	159.0	11.41	20.5	28.69
	500	465.8	4.27	448.3	6.56	391.0	13.50	93.5	50.80
	1000	951.7	6.04	940.0	7.50	812.5	23.40	353.7	80.70
	1500	1422.0	9.79	1432.5	8.44	1122.0	47.00	692.5	100.94
	2000	1895.0	13.13	1855.0	18.12	1556.0	55.40	N.A	N.A
	3000	2800.0	25.42	2791.7	26.04	2340.0	82.50	1710.0	161.25
Montmoril- lonite	100	7.0	11.63	9.7	11.28	12.5	11.33	14.3	10.71
	250	8.3	30.25	30.3	27.46	25.0	28.12	25.3	28.08
	500	25.8	59.25	25.0	59.40	42.5	57.19	N.A	N.A
	1000	440.0	69.98	433.0	70.83	303.0	87.08	163.7	104.50
	1500	845.8	81.77	841.0	82.20	705.8	99.26	227.3	159.06
	2000	1330.0	83.80	1218.0	97.71	915.0	137.50	309.0	211.39
	3000	2203.3	99.58	2150.0	106.25	1463.3	175.80	633.0	295.83
Vermiculite	100	2.3	12.20	5.3	11.84	3.7	12.04	6.0	11.71
	250	5.3	30.60	7.7	30.29	9.3	30.09	9.7	30.04
	500	30.0	58.70	8.3	61.46	15.8	60.52	15.8	60.52
	1000	196.7	100.42	60.8	117.39	7.5	124.06	3.3	124.59
	1500	488.3	126.46	248.3	156.46	20.0	185.00	7.5	186.00
	2000	945.0	131.88	633.3	170.80	173.3	228.33	47.5	244.07
	3000	1856.7	142.92	1185.0	226.88	716.7	285.42	135.0	358.13

# APPENDIX XIII

Experimental values for copper adsorption on montmorillonite, vermiculite  
illite, and kaolinite under four pH conditions

		pH							
	Original concentration ppm	4		5		6		7	
		C ppm	x/m mg/g	C ppm	x/m mg/g	C ppm	x/m mg/g	C ppm	x/m mg/g
Montmorillonite	100	6.0	11.70	12.0	11.10	10.0	11.20	N.A	31.00
	250	80.3	21.00	75.3	21.80	62.3	23.40	2.0	61.70
	500	312.5	23.40	303.7	24.50	244.2	31.90	6.7	123.90
	1000	793.3	25.80	785.0	26.90	268.7	91.40	9.2	186.50
	1500	1332.0	21.00	1203.3	37.00	337.5	182.80	8.3	249.40
	2000	1781.7	27.30	1482.0	64.60	27.0	246.70	5.0	249.40
	3000	N.A	N.A	2375.2	78.10	10.0	373.70	13.3	373.30
Vermiculite	100	1.6	12.30	2.3	12.2	3.0	12.10	4.0	12.00
	250	20.7	28.70	2.3	31.0	2.0	31.00	2.0	31.00
	500	226.2	34.20	87.5	51.6	31.2	59.90	3.3	62.10
	1000	705.0	36.90	550.8	56.1	225.5	97.20	10.8	123.60
	1500	1115.0	48.00	990.0	53.7	370.0	141.30	9.2	186.40
	2000	1630.0	47.50	1472.3	66.3	88.0	238.70	10.0	248.80
	3000	2619.0	47.80	2095.0	113.1	78.3	365.20	7.5	374.10
Illite	100	225.0	3.10	N.A	N.A	9.3	11.40	1.7	12.30
	250	457.5	5.30	226.6	4.00	143.0	13.40	3.7	30.80
	500	922.5	9.70	425.5	9.30	150.0	43.70	14.2	60.70
	1000	1325.0	21.9	861.2	17.30	95.8	113.00	13.3	123.30
	1500	1920.0	9.40	1285.0	26.90	60.8	176.20	15.8	185.50
	2000	1925.0	9.38	1705.0	36.90	50.2	243.60	8.3	248.40
	3000	N.A	N.A	2691.7	38.50	50.2	368.60	6.7	374.00

# APPENDIX XIII (Cont'd)

	Original concentration ppm	pH							
		4		5		6		7	
		C ppm	x/m mg/g	C ppm	x/m mg/g	C ppm	x/m mg/g	C ppm	x/m mg/g
Kaolinite	100	84.5	1.90	76.0	3.00	60.5	4.90	0.7	12.40
	250	226.0	3.0	191.0	7.40	102.0	18.50	3.1	30.90
	500	456.7	5.40	431.0	8.70	100.8	49.90	4.7	61.90
	1000	906.0	11.70	876.5	15.50	98.7	112.60	5.3	124.30
	1500	1380.0	14.90	1291.7	26.00	85.0	176.90	9.4	186.30
	2000	1886.6	14.20	1785.5	26.50	115.0	235.60	5.3	249.30
	3000	N.A	N.A	2330.0	83.70	5.0	374.30	4.4	374.40

# APPENDIX XIV

Experimental values for zinc adsorption on montmorillonite, vermiculite,  
illite and kaolinite under four pH conditions

	Original concentration ppm	pH							
		4		5		6		7	
		C ppm	x/m mg/g	C ppm	x/m mg/g	C ppm	x/m mg/g	C ppm	x/m mg/g
Montmorillonite	100	3.0	12.12	1.3	12.30	1.0	12.50	N.A	N.A
	250	128.3	15.21	125.0	15.63	117.7	16.50	23.7	28.30
	500	368.3	16.43	356.7	17.91	163.7	42.03	47.5	56.60
	1000	779.2	27.60	783.2	27.10	590.0	51.23	132.5	108.40
	1500	1261.3	29.90	1168.7	41.40	871.5	78.53	282.5	152.20
	2000	1715.0	35.60	1585.0	51.90	1340.0	82.50	397.5	200.30
	3000	2644.0	47.25	2542.5	57.20	2230.0	96.20	757.0	280.0
Vermiculite	100	1.0	12.38	1.0	12.50	1.0	12.50	1.0	12.50
	250	47.6	25.29	32.7	27.20	15.7	29.30	8.0	30.20
	500	246.6	31.67	221.7	34.80	196.7	37.90	62.5	54.70
	1000	708.7	36.40	703.3	37.10	510.0	61.00	126.2	109.20
	1500	1180.0	40.00	1152.5	43.40	930.0	71.50	202.5	162.20
	2000	1665.0	41.90	1630.0	46.30	1350.3	81.30	356.7	205.40
	3000	2585.0	51.90	2552.5	55.96	2310.0	86.30	825.0	271.00
Illite	100	N.A	N.A	N.A	N.A	--	--	4.3	12.00
	250	219.3	3.83	63.7	23.29	--	--	N.A	N.A
	500	456.7	5.42	277.5	27.80	--	--	220.0	35.01
	1000	902.5	12.18	705.0	36.90	--	--	548.0	56.40
	1500	1346.7	19.17	1170.0	41.20	--	--	638.7	107.60
	2000	1786.0	76.67	1730.0	33.75	--	--	685.0	164.40
	3000	2693.0	38.30	2571.0	53.54	--	--	807.0	274.00

# APPENDIX XIV (Cont'd)

	Original concentration ppm	pH							
		4		5		6		7	
		C ppm	x/m mg/g	C ppm	x/m mg/g	C ppm	x/m mg/g	C ppm	x/m mg/g
Kaolinite	100	N.A	N.A	N.A.	N.A	N.A	N.A	N.A	N.A
	250	242.3	0.96	227.0	2.90	212.0	4.80	69.0	22.60
	500	477.5	2.80	452.5	5.90	435.0	8.13	145.8	44.30
	1000	913.0	10.80	905.0	11.90	771.7	28.56	458.7	67.60
	1500	1373.0	12.80	1350.0	18.70	1170.0	41.00	808.3	86.40
	2000	1905.0	11.90	1875.0	21.40	1620.0	47.50	928.3	134.00
	3000	2773.0	28.36	2760.0	30.10	2555.0	55.00	931.7	258.00

# APPENDIX XV

Experimental values for heavy metal adsorption from an equivalent mixture (1:1:1:1)  
of Cd, Pb, Cu and Zn on montmorillonite and kaolinite at pH 5.0.

Original concentration  m.e/l	<u>Cadmium</u>		<u>Lead</u>		<u>Copper</u>		<u>Zinc</u>	
	C	x/m	C	x/m	C	x/m	C	x/m
	m.e	m.e/g	m.e	m.e/g	m.e	m.e/g	m.e	m.e/g
	-5	-5	-5	-5	-5	-5	-5	-5
	x10	x10	x10	x10	x10	x10	x10	x10
<u>Montmorillonite</u>								
0.025	12.0	250.0	15.0	237.5	25.0	187.5	42.0	102.5
0.050	21.0	518.7	27.5	487.5	37.5	437.5	46.7	391.2
0.100	40.0	1050.0	50.0	1000.0	60.0	950.0	N.A	N.A
0.500	150.0	5500.0	75.0	5900.0	75.0	5900.0	50.0	6000.0
1.000	157.0	11725.0	100.0	12250.0	175.0	11000.0	150.0	12020.0
5.000	10000.0	12500.0	7100.0	27000.0	9250.0	15700.0	9750.0	13750.0
10.000	20750.0	21250.0	17080.0	39580.0	19800.0	26000.0	21062.0	18080.0
20.000	N.A	N.A	39750.0	51250.0	44000.0	30000.0	43750.0	31250.0
50.000	113500.0	57500.0	96500.0	142500.0	108500.0	90600.0	115000.0	50000.0
<u>Kaolinite</u>								
0.025	38.5	120.0	5.0	287.5	11.2	256.2	37.5	125.0
0.050	65.5	297.5	12.5	562.5	22.5	512.5	87.5	187.5
0.100	171.0	395.0	68.5	907.5	92.5	787.5	180.0	350.0
0.500	1130.0	600.0	900.0	5800.0	1000.0	1250.0	1150.0	500.0
1.000	2230.0	1350.0	N.A	N.A	2080.0	2100.0	2300.0	850.0
5.000	11500.0	5000.0	11000.0	7500.0	11300.0	6000.0	11500.0	5000.0
10.000	22250.0	13750.0	22250.0	13750.0	22250.0	13750.0	23000.0	10000.0
20.000	46250.0	18750.0	45000.0	25000.0	45000.0	25000.0	46000.0	18750.0
50.000	108700.0	81250.0	87500.0	187500.0	99060.0	129600.0	115000.0	50000.0

# APPENDIX XVI

Experimental values for lead adsorption under four pH conditions on two  
soils: Ap (marine loam) and Ap (glacial outwash)

Soil	Original concentration ppm	pH							
		4		5		6		7	
		C ppm	x/m mg/g	C ppm	x/m mg/g	C ppm	x/m mg/g	C ppm	x/m mg/g
Ap (Marine Loam)	100	9.0	11.4	0.0	12.5	0.0	12.5	0.0	12.5
	250	125.0	15.6	124.0	15.5	22.0	28.5	2.0	31.0
	500	327.5	21.5	175.0	40.6	37.7	59.6	7.5	61.5
	1000	740.0	32.5			327.5	84.1	167.0	104.0
	1500			1215.0	35.6	805.0	86.9	290.0	151.2
	2000	1665.0	41.9	1558.0	55.0	1215.0	98.1	455.0	193.1
	3000	2600.0	50.0	2525.0	59.4	1245.0	219.6	576.7	302.9
Ap (Outwash)	100	16.0	10.5	0.0	12.5	0.0	12.5	0.0	12.5
	250	141.0	13.6	106.0	18.0	20.0	28.7	9.0	30.1
	500	357.5	17.8	230.0	33.7	150.0	43.7	10.0	61.2
	1000	783.3	27.0	657.5	42.8	413.2	73.3	192.5	100.0
	1500	1217.5	35.4	1057.5	55.4	745.0	94.4	367.5	141.5
	2000	1687.5	39.0	1520.0	60.0	1140.0	107.5	535.0	183.1
	3000	2130.0	46.2	2330.0	83.7	1308.3	211.4	585.0	301.9



# APPENDIX XVII

Experimental values for the adsorption of Cd, Pb, Cu and Zn on alluvial soil (Ap) and glacial outwash soil (Ap) at pH 5.0.

Original Concentration ppm	<u>Cadmium</u>		<u>Lead</u>		<u>Copper</u>		<u>Zinc</u>	
	C	x/m	C	x/m	C	x/m	C	x/m
	ppm	mg/g	ppm	mg/g	ppm	mg/g	ppm	mg/g
<u>Alluvium (Ap)</u>								
100	10.0	11.2	0.0	12.5	6.0	11.7	22.0	9.7
250	150.0	12.5	22.5	28.5	130.0	15.0	183.0	8.4
500	380.0	15.0	127.5	46.6	362.0	17.1	395.0	13.1
1000	832.5	20.9	417.5	72.8	720.0	35.0	800.0	25.1
1500	1312.5	23.4	825.0	84.4	1137.5	45.4	1277.5	27.8
2000	1750.0	31.2	1235.0	95.6	1450.0	68.7	1770.0	28.7
3000	2595.0	50.6	2143.0	107.6	1696.7	162.7	2641.6	44.8
<u>Glacial outwash (Ap)</u>								
100	42.0	7.2	0.0	12.5	26.0	9.2	38.0	7.7
250	204.0	5.7	106.0	18.0	156.0	11.7	204.0	5.7
500	427.0	9.1	230.0	33.7	392.0	13.4	412.5	10.9
1000	894.0	13.2	657.5	42.8	727.5	34.0	877.5	15.3
1500	1350.0	18.7	1057.0	55.4	1137.5	45.4	1352.0	18.4
2000	1725.0	34.4	1520.0	60.0	1455.0	68.1	1770.0	28.7
3000	2475.0	65.6	2330.0	83.7	2205.0	99.4	2725.0	34.4

# APPENDIX XVIII

Experimental values for the adsorption of Cd, Pb, Cu and Zn on marine  
loam soil (Ap) and surface sediment at pH 5.0.

Original concentration ppm	<u>Cadmium</u>		<u>Lead</u>		<u>Copper</u>		<u>Zinc</u>	
	C ppm	x/m mg/g	C ppm	x/m mg/g	C ppm	x/m mg/g	C ppm	x/m mg/g
<u>Marine Loam Soil (Ap)</u>								
100	40.0	7.5	0.0	12.5	25.0	9.4	44.0	7.0
250	192.0	7.2	124.5	15.5	154.0	12.0	178.0	9.0
500	427.5	9.1	175.0	40.6	395.0	13.1	392.0	13.4
1000	900.0	12.5	N.A	N.A	720.0	35.0	877.5	15.3
1500	1375.0	15.6	1215.0	35.6	1137.5	45.4	1340.7	19.9
2000	1645.0	44.0	1558.0	55.0	1450.0	68.7	1820.0	22.5
3000	2425.0	71.9	2525.0	59.4	1710.0	161.2	2730.0	33.1
<u>Surface Sediment</u>								
100	14.0	10.7	0.0	12.5	41.0	7.4	28.0	9.0
250	182.0	8.5	102.0	18.5	164.0	10.7	194.0	7.0
500	412.5	10.9	222.5	34.7	402.5	12.1	398.0	12.7
1000	868.3	16.4	642.5	44.7	830.0	21.2	870.0	16.0
1500	1330.0	21.2	1070.0	53.7	1165.0	41.7	1327.5	21.6
2000	1638.3	45.2	1490.0	63.7	1210.0	98.7	1740.0	32.0
3000	2430.0	71.8	2290.0	88.0	1292.5	213.4	2560.0	55.0

# APPENDIX XIX

Experimental values for heavy metal adsorption from an equivalent mixture (1:1:1:1)  
of Cd, Pb, Cu and Zn on outwash soil (Ap) and marine soil (Ap) at pH 5.0.

Original Concentration  m.e/l	<u>Cadmium</u>		<u>Lead</u>		<u>Copper</u>		<u>Zinc</u>	
	C	x/m	C	x/m	C	x/m	C	x/m
	m.e	m.e/g	m.e	m.e/g	m.e	m.e/g	m.e	m.e/g
	-5 x10	-5 x10	-5 x10	-5 x10	-5 x10	-5 x10	-5 x10	-5 x10
<u>Glacial outwash soil (Ap)</u>								
0.025	5.0	287.5	N.A	N.A	0.0	625.0	1.5	250.0
0.050	76.7	350.0	N.A	N.A	20.0	1150.0	N.A	N.A
0.100	145.0	525.0	0.0	1250.0	590.0	3300.0	N.A	N.A
0.500	1090.0	800.0	370.0	4400.0	1550.0	4750.0	1167.0	415.0
1.000	2020.0	2400.0	1110.0	6950.0	8775.0	18625.0	2205.0	1475.0
5.000	10620.0	9400.0	8900.0	18000.0	16720.0	41400.0	11150.0	6750.0
10.000	18350.0	33250.0	17500.0	37500.0	35250.0	73750.0	20370.0	23150.0
20.000	44370.0	28150.0	41350.0	43250.0	64120.0	304400.0	38370.0	58150.0
50.000	105587.0	96650.0	88000.0	185000.0	N.A	N.A	106000.0	95000.0
<u>Glacial marine soil (Ap)</u>								
0.025	2.5	300.0	N.A	N.A	N.A	N.A	2.5	300.0
0.050	5.0	600.0	N.A	N.A	0.0	625.0	N.A	N.A
0.100	52.0	990.0	0.0	1250.0	7.5	1212.0	N.A	N.A
0.500	1040.0	1050.0	297.0	4765.0	562.0	3440.0	1135.0	575.0
1.000	1940.0	2800.0	1010.0	7450.0	1207.0	6465.0	2172.0	1640.0
5.000	9175.0	16625.0	8000.0	22500.0	7625.0	24375.0	10150.0	11750.0
10.000	18725.0	31250.0	15700.0	46500.0	15250.0	48750.0	19100.0	29500.0
20.000	N.A	N.A	38500.0	57500.0	30750.0	96250.0	N.A	N.A
50.000	101870.0	115650.0	82550.0	212250.0	58870.0	330650.0	104120.0	104400.0