THE ROLE OF pH AND SOIL BUFFER CAPACITY
IN
HEAVY METAL RETENTION IN CLAY SOILS

by

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March 1990

A thesis submitted to the Faculty of Graduate Studies
and Research in partial fulfillment of the requirements
for the degree of Doctor of Philosophy

ABSTRACT

The concept of soil buffer capacity was used in this study to investigate the capacity of soil to attenuate heavy metals when acid is involved in the soil system. Four soils were used in which three of them consisted mainly of clay minerals (kaolinite, illite, and montmorillonite) and one of them was a natural clay soil obtained from a landfill site in Quebec. Determination of soil buffer capacity was done by pH-acid titration. The buffer capacity of soil in this study was found to depend mainly on carbonate content and cation exchange capacity (C.E.C.) of soils. The magnitude of buffer capacity followed the order : illite>montmorillonite>natural clay soil>>kaolinite. Illite used in this study had higher carbonate content than the natural clay soil, and the montmorillonite and kaolinite had a very high and low C.E.C. respectively.

The study of heavy metal retention in soils was performed both by soil suspension test and soil column test. The results showed that as soils received increasing amounts of acid, high amounts of heavy metals (particularly Pb and Cu) could still be retained if the soils had a high enough buffer capacity to resist a change in pH such that it will not drop to < 5. In addition, an increasing acid input could lead to the exhaustion of soil buffer capacity which resulted in a rapid depletion of the amounts of heavy metals retained in soils. Illite had the capacity to retain high amounts of heavy metals for a larger range of acid input than the other soils. The amounts of heavy metals retained decreased as the application of heavy metals to soils changed from separately applied to compositely applied and to compositely applied with leachate collected from the landfill site.

Sequential extraction analyses performed in this study revealed that precipitation of heavy metals (both by hydroxide and carbonate phases) was the dominant mechanism when soil was at high soil solution pH whereas cation exchange mechanisms prevailed at low soil solution pH. Selectivity order of heavy metal retention in soils found by soil suspension tests followed the order $Pb > Cu > Zn > Cd$. The order changed to $Pb > Cd > Zn > Cu$ when soils were at low soil solution pH. Relative mobility of heavy metals found from the soil column test followed the order $Pb < Cu < Zn \leq Cd$. The heavy metals were very mobile in kaolinite whereas they were less mobile in illite and natural clay soil.

The relation of soil buffer capacity and heavy metal retention and movement in the clay soils found from this study revealed that the soil buffer capacity was a parameter that can be used in the prediction and prevention of heavy metal migration in soil. The soil buffer capacity is recommended, as a result of this study, as a parameter that should be included in the determination of soil properties particularly for the purpose of land application and disposal of wastes with leachates that could contain heavy metals.

RÉSUMÉ

Le concept " capacité tampon du sol " a été utilisé dans cette étude sur l' évaluation de la capacité du sol pour retenir les métaux lourds quand des acides sont appliqués sur le système du sol. Quatre sols ont été utilisés, trois d'entre eux étaient composés principalement de minéraux (kaolinite, illite, et montmorillonite) et un autre sol provenait d'un site d'enfouissement sanitaire au Québec. La détermination de la capacité tampon du sol a été obtenue par une titration acide du pH. Cette étude a démontré que la capacité tampon du sol dépend surtout de la teneure en carbonates et la capacité d'échange cationique (C.E.C) du sol. L'ampleur de la capacité tampon a suivi cet ordre: illite > montmorillonite > sol naturel >> kaolinite. Le sol illite utilisé dans cette étude a un contenu plus élevé de carbonates que le sol naturel. D'autre part, la montmorillonite et la kaolinite ont respectivement une très grande et une basse C.E.C..

L'étude de rétention de métaux lourds par des sols a été menée par des tests en suspension de sol et des tests en colonnes de sols. Les résultats montrent qu'au fur et à mesure que le sol reçoit des quantités plus grandes d'acide, des grandes quantités de métaux lourds (particulièrement Pb et Cu) peuvent être retenues si le sol a une grande capacité tampon de résister à un changement dans le pH sans devenir < 5. Pourtant, les résultats montrent qu' en augmentant la quantité d'acide une réduction de la capacité tampon du sol est provoquée, laquelle se traduit par une réduction de la quantité de métaux lourds retenus dans le sol. L'étude montre aussi que les quantités retenues de métaux lourds diminuent si l'application de métaux lourds sur le sol change d'une application individuelle à une application mixte ou mélangée avec des lixiviats cueillis sur le site d'enfouissement. Le sol de type illite a la capacité de retenir des quantités élevées de métaux lourds pour une charge acide de plus grande étendue que pour les autres sols.

Des analyses d'extraction séquentielle ont permis de révéler que le mécanisme de précipitation de métaux lourds (tant pour des phases carbonatées qu' hydratées) est le mécanisme dominant de rétention quand le pH du sol est haut. Pour le contraire, des mécanismes d'échange cationique sont dominants à bas pH. L'ordre de sélectivité pour la rétention des métaux lourds selon les tests en suspension est comme suit: $Pb > Cu > Zn > Cd$. L'odre change à $Pb > Cd > Zn > Cu$ quand les sols sont à bas pH. La mobilité relative de métaux lourds démontrée selon les tests en colonne est comme suit : $Pb < Cu < Zn < Cd$. Les métaux lourds furent très mobiles dans le cas de kaolinite et peu mobile dans le cas d'illite et du sol naturel.

La relation entre la capacité tampon et la rétention de métaux lourds et le mouvement dans le sol tel que découvertes dans cette étude montrent que la capacité tampon est un paramètre qui peut être utilisé pour la prédiction et la prévention de la migration des métaux lourds dans le sol. La capacité tampon du sol est recommandée dans cette étude comme étant un paramètre qui devrait être inclu dans la détermination des propriétés du sol, particulièrement dans l'utilisation de terrains pour l'élimination finale de déchets contenant des niveaux dangereux de métaux lourds.

ACKNOWLEDGEMENTS

The author wishes to thank Prof. R.N. Yong, William Scott Professor and Director of Geotechnical Research Center (GRC), Department of Civil Engineering and Applied Mechanics, for directing this research program and for his useful suggestions, constructive criticism and constant encouragement throughout the study. The author also wishes to avail herself of the opportunity to express her most sincere thanks and appreciation to him for providing the financial support covering the entire study program.

The author would like to thank Dr. Pakit Kiravanich, Deputy Permanent Secretary, Ministry of Science, Technology and Energy of Thailand who continuously encouraged the author during the entire Ph.D program.

Much appreciation is expressed for the support and assistance given by GRC staff members during the course of laboratory work and subsequent analysis of experimental data. Special thanks is given to Ms. Pat Lytle for her help in reading this manuscript.

Finally, a special debt is owed to her beloved parents, brothers, sister, and friends for their continuous inspiration, support, and encouragement and to Dr. Nophadol In-na for his understanding and invaluable help in many ways.

TABLE OF CONTENTS

TABLE OF CONTENTS *(Continued)*

LIST OF FIGURES

LIST OF FIGURES *(Continued)*

LIST OF FIGURES *(Continued)*

LIST OF FIGURES *(Continued)*

LIST OF FIGURES *(Continued)*

LIST OF TABLES

CHAPTER 1
INTRODUCTION

1.1 General

The accumulation of waste has greatly intensified in recent years due to an increase in world population and the rapid expansion of industrial and agricultural development. Consequently, land disposal of waste materials, landfilling, and waste containment ponds are increasing. Landfilling is at present considered as the most economical and practical means for disposal of municipal and industrial solid wastes, and as a means for containment of sludges and liquid concentrates of pollutants. However, societal concerns about the quality of soil and water have led to an increased interest in the safe containment and disposal of waste materials on land, i.e. land application. Researchers have devoted their time to study the potential problems associated with land application in order to help minimize the risk of soil and groundwater contamination.

In land disposal sites, infiltration of water from rainfall, snowmelt, and surface runoff into the area produces a leachate. These leachates contain several contaminants originating from the disposed wastes. The migration of the leachates through soil could lead to eventual groundwater contamination. As the leachates move downward, various contaminants interact with soil components resulting thereby in such processes as physisorption, chemisorption, precipitation or complexation. The result is the retention of contaminants by soil. However, soil has a limited capacity to retain contaminants. A continued load of contaminated leachates may diminish the capability of soil to act as a buffer against them.

The heavy metals form a group of contaminants commonly found in several kinds of wastes including sludges and landfill leachates (Stewart and Weber, 1976). Heavy metals are a group of contaminants that are highly toxic to human, animal, and aquatic life. Briceland (1976) referred to one incident concerning heavy metal contamination that took place in Illinois called "the Byron incident". The incident involved the dumping and burying of several barrels of cyanide plating waste, oil residues, solvents, and paint waste near the small town of Byron. This action resulted in the death of livestock that drank from a nearby stream. Monitoring of over 200 private drinking wells showed excessive levels of various heavy metals. This showed that heavy metals are contaminants that are hidden in several kinds of wastes. Insufficient knowledge and improper management of waste disposal could lead to eventual groundwater contamination of heavy metals.

Soil has been reported to have a capacity to retain heavy metals (Korte et al., 1976; Harter, 1979; Elliott et al., 1981; Yong et al., 1986). Studies have shown that the capacity of soil to retain heavy metals could be influenced by several factors depending on soil constituents, leachate and waste characteristics. The continued load of leachate may result in unfavorable conditions and the decrease in the capacity of soil to retain heavy metals. A major concern is that the capacity of soil to retain heavy metals may be exhausted resulting thereby in the rapid movement of heavy metals to groundwater and the increase in its concentration to potentially toxic levels.

Several studies have shown that soil pH is an important factor in the fate of heavy metal retention and movement in soils (Harter, 1983; Dowdy and Volk, 1983; Elliott et al., 1986). These studies have indicated that the direct correlation between soil pH and heavy metal retention and the change in soil pH could alter the retention or movement of heavy metals in soil. The ability of soil to retain heavy metals, therefore, depends on the resistance of soil to a change in pH or in other words the "soil buffer capacity". Although several studies have been done with regard to the effect of soil pH on heavy metal retention, very few have included the soil buffer capacity in the study. Recently, an increasing number of studies have focused on the effect of acid precipitation on soil productivity (Strayer and Alexander, 1981; Bitton and Boyland, 1985). In the field of land disposal, not only acid rain but also the presence of acids in solid or liquid wastes in landfill would effect the soil pH. Thus the ability of soil to retain heavy metals depends on the susceptibility of soil to change in pH. In this case, the soil buffer capacity would be a good parameter to help indicate the fate of heavy metals in soil

The present research was undertaken to investigate the role of soil buffer capacity in the retention of heavy metals in soil, with a view to developing a better understanding of heavy metal retention in soil and its role in the prevention of heavy metal contamination in soil and groundwater.

1.2 Statement of Problem

Several studies have been done in regard to the retention of heavy metals in soil (see e.g., Stewart and Weber, 1976; Frost and Griffin, 1977; Griffin and Shimp, 1978; Harter, 1983; Elliott et al., 1986). Stewart and Weber (1976) found that heavy metals tend to persist in surface soil, and that raising soil pH reduces the mobility of Cu, Zn, Ni, and Cd. Frost and Griffin (1977) found that the degree of removal of Cu, Zn, and Cd from a landfill leachate by kaolinite and montmorillonite clay suspensions increased with higher pH levels. Griffin and Shimp (1978) performed a column study on the attenuation of contaminants in municipal solid waste landfill leachate using mixtures of sand and clay. Their results showed that Pb, Cd, Hg, and Zn were strongly attenuated on the soil constituents. It is noted from the above studies that heavy metal retention in soil is influenced by pH.

Dowdy and Volk (1983) reviewed studies on movement of heavy metals in soil when sewage sludge was applied to soil. They concluded that heavy metal movement will most likely occur with large application of sewage sludge to a sandy, acidic, low organic matter soil which receives high rainfall or irrigation. In the study of leachate migration through a clay liner by Yong et al. (1986), it was shown that clay liners exhibit better attenuation of heavy metals than salts, provided that a high pH environment is maintained. However, they stated that the capability of soil to retain heavy metals continued to change with the continued passage of contaminants.

It can be seen from the above studies that the retention of heavy metals by soil is very much dependent on pH. High soil pH is preferable since the retention of heavy metals is enhanced. Considering landfill leachates, in the presence of certain acids in solid or liquid wastes in landfill or containment ponds, and also from the occurrence of *acid rain,* a leachate with low pH will sometimes result. The migration of the low pH leachate through soil would affect the soil pH and also the retention of heavy metals in soil. The effect might be small or large depending on the capacity of soil to resist a change in pH or so called ***soil buffer capacity*** which is dependent on the compositional characteristics of soil materials. Soils with high buffer capacity will have a high resistance to changes in their pH values, and conversely, soils with low buffer capacity are those which are easily susceptible to changes in pH (Yong and Warkentin, 1987). However, if an acidic leachate was to continually pass through soil, then the capacity of soil to act as a buffer would decrease. The resulting decrease in the buffer capacity would reduce the ability of the soil to retain heavy metals.

The concept of pH buffer capacity in solution chemistry has been well developed and has been used in the study of water and wastewater systems (Snoeyink and Jenkins, 1980). The term soil buffer capacity, based on the same concept of pH buffer capacity in solution chemistry, has been used for many years in agricultural practices (Buckman and Brady, 1969). These include the studies of soil acidity and soil alkalinity, the application of lime to soil to increase crop production and the effect of acid precipitation on forest and agricultural lands (Shoemaker et al.,1961; Keeney and Corey, 1963; McFee et al., 1977; Federer and Hornbeck, 1985; and Mowbray and Schlesinger, 1988).

However, in the field of land disposal of waste, little use has been made of the concept of soil buffer capacity in studying the differences among soils in the retention of contaminants. As mentioned above, for one group of contaminants such as heavy metals, the retention of heavy metals in soil is very much dependent on pH. Heavy metal retention can therefore be directly correlated with soil buffer capacity.

In view of the important role of the soil buffer capacity, the present thesis is thus directed towards research in the area of soil buffer capacity and determination of how it relates to heavy metal retention in soils. In Quebec, a natural clay soil barrier is considered to be a desirable feature in the siting of a land disposal site (Yong and Warkentin, 1987). The emphasis of the study is, therefore, on the relation of soil buffer capacity and heavy metal retention in *clay soils*. The study consists of three main parts. The first part is the determination of soil buffer capacity. The second part includes the soil suspension study on heavy metal retention and the third part includes the soil column study on heavy metal movement in clay soils.

1.3 Objectives and Tasks of the Study

The objectives of the research study were :

1) To determine the relationship between the pH, the buffer capacity of soil, and the retention of heavy metals in soil, and to study the retention mechanisms of heavy metals in soil with changes in the buffer capacity of the soils.
2) To recommend, through the use of the concept of soil buffer capacity, a rational approach to the selection and/or management of land disposal sites in order to minimize leaching of heavy metals to groundwater.

To implement the objectives, two distinct tasks were structured :

Task 1) To study the pH and buffer capacity of soil and the change in the soil buffer capacity as a function of acid input.

Task 2) To study the migration of heavy metals in soil column tests as the soil receives increasing amounts of acid input in relation to soil buffer capacity.

For Task 1, the experiments conducted utilised soil suspensions since these provided the kinds of information more amenable for interpretation in terms of relationships and mechanisms. Task 2 utilised soil columns for the experiments conducted.

1.4 Organisation of the Thesis

The thesis is arranged into five chapters and two appendices. The contents of the five chapters are as follows :

Chapter 1 : is an introductory chapter which presents the statement of the problem and the purpose of the study;

Chapter 2 : gives a review of the literature pertinent to the present study;

Chapter 3 : provides a description of the experimental methods, materials, and techniques employed in the study;

Chapter 4 : presents the results and discussion of the laboratory studies on

i) the soil pH and its buffer capacity,

ii) the relationship of the buffer capacity and the capacity of soil to retain heavy metals in soil suspension test,

iii) the retention mechanism of heavy metals in soil,

iv) the migration of heavy metals in soil column test;

Chapter 5 : contains the summary, concluding remarks and suggestions for further studies.

The content of the appendices are as follows :

Appendix A : presents the experimental results on soil suspension tests and soil column tests;

Appendix B : presents the input and output of the MINTEQ program used to calculate the probable equilibrium composition of heavy metals species present in the soil suspension system.

CHAPTER 2

LITERATURE REVIEW

In the following, a brief review of the previous studies concerning soil buffer capacity and the retention of heavy metals in soils are presented, together with some general remarks on the studies.

2.1 Soil Buffer Capacity

In solution chemistry, a buffer solution is a solution that in some way has the ability to maintain a stable composition when various components are added or removed. The pH buffers (solutions that resist a change in pH on the addition of a strong acid, H^+, or a strong base, OH^-) are the most commonly talked about buffers (Snoeyink and Jenkins, 1980). The capacity of a solution to resist a change in pH, or so–called "buffer capacity", was first introduced in solution chemistry in 1922 by Van Slyke. Since then this term has been used widely in the study of solution equilibria, aquatic chemistry, water and wastewater chemistry, etc. (Waser, 1967; Laitinen and Harris, 1975; Snoeyink and Jenkins, 1980; Stumn and Morgan, 1981). The aforementioned authors defined the term buffer capacity, β, or buffer intensity as it is sometimes called, as the moles/liter of strong base, C_B, (or OH^-) which when added to a solution causes a unit change in pH. Thus

$$\beta = \frac{dC_B}{dpH} = -\frac{dC_A}{dpH} \tag{2.1}$$

where C_A is the moles/liter of strong acid (or H^+) added. The buffer capacity can be determined experimentally and by computation at individual pH values. Experimental measurement involves determining a titration curve that shows the course of pH change with moles of strong acid or base added. The buffer capacity always has a positive value and is proportional to the reciprocal of the slope of the titration curve.

In the case of a soil, there is a distinct resistance to a change in the pH of a soil solution, as stated by Buckman and Brady (1969). They explained that the resistance to pH change depends on the equilibrium between the adsorbed H ions on the micelle of soil and the H ions in the soil solution.

$$\text{Adsorbed H ions in soil} \rightleftharpoons \text{H ions in soil solution}$$

In the case when H ions are added to a soil, this would give a temporary increase in the H ions in the soil solution. The equilibrium reaction above would immediately shift to the left and more H ions would become adsorbed on the micelle. They also explained that when liming materials are added to neutralize the H ions in the soil solution, the above reaction would be shifted to the right, resulting in more H ions moving out into the soil solution. As a consequence, the resulting pH rise would be negligibly small and would remain so until enough lime had been added to deplete the reserve H ions. The resultant pH change in the soil solution would be very small if the soil has a high buffer capacity. They stated that the higher the exchange capacity of soil, the greater will be its buffer capacity. They added that a high soil buffer capacity includes the presence of buffering compounds in soil such as organic matter, carbonates, and phosphates which would enable the soil to resist an appreciable change in pH.

Determination of soil buffer capacity can be done by computation and experimentation. For computational determination, Van Breeman and Wielemaker (1974a and 1974b) calculated buffer intensities of soil, based on the assumption that the soil is in an aqueous system. They calculated buffer intensities of a number of aqueous systems involving several soil and rock minerals using thermodynamic equilibrium, and expressed the unit of buffer intensity in terms of concentration of acid or base/pH ($equivalent\ liter^{-1} \cdot pH^{-1}$) as in solution chemistry. They found that silicate minerals, carbonates, and gibbsite provide strong buffering upon addition of strong acid under slightly alkaline to slightly acid conditions.

Since soil is a mixed system that consists of several constituents, most of the studies involving soil pH and buffer capacity used experimental means to determine the soil buffer capacity. The experiment is based on the same method as in solution chemistry, i.e., titration of soil with strong acid or base. The buffer capacity of soil is therefore the reciprocal of the slope of the titration curve. Soil titrations have been made for many years on agricultural soils as one way of measuring the amount of lime required to raise soil pH to neutral or some basic value, i.e., titration of soil in the base direction (Buckman and Brady, 1969). Recently, titration of soil in the acid direction has come into attention (Federer and Hornbeck, 1985; Magdoff and Barlett, 1985; Mowbray and Schlesinger, 1988), due to the increased interest in the effect of acid rain on soils and their productivity.

Federer and Hornbeck (1985) studied the buffer capacity of forest soils in New England and the effect of acid precipitation on the soils. They defined the buffer capacity of a soil as the number of mols of H^+ or OH^- that must be added to raise or lower the pH of 1 kg of soil by 1 pH unit. They expressed the unit of soil buffer capacity in $meq \quad H^+$ or $OH^- kg^{-1} \cdot pH^{-1}$. They found that the soils have buffer capacity to resist a change in pH due to acid rain for several years.

Magdoff and Barlett (1985), and Mowbray and Schlesinger (1988) used the same definition of soil buffer capacity as Federer and Hornbeck (1985) in the study of the buffer capacity of organic soils. Since the unit of "*cmol*" is often used in soil studies, they expressed the unit of acid in the titration curves in $cmol \quad H^+ \cdot kg^{-1} soil$ and buffer capacity in $cmol \quad H^+ \cdot kg^{-1} soil \cdot pH^{-1}$. These units are consistent with the SI unit. Therefore, in this research, the term $cmol \quad H^+ \cdot kg^{-1} soil$ and $cmol \quad H^+ \cdot kg^{-1} soil \cdot pH^{-1}$ are used as the units to express the concentration of acid applied to soil and the magnitude of soil buffer capacity.

2.2 Heavy Metal Retention in Soil

Heavy metals form a group of contaminants commonly found in several kinds of wastes including sludges and landfill leachates. Depending on the type and origin of wastes, the leachates generated may have undesirable levels of concentration of several heavy metals. Heavy metals that have received the most attention with regard to accumulation in soils, uptake by plants, and contamination of groundwater include lead(Pb), cadmium(Cd), copper(Cu), zinc(Zn), nickel(Ni), chromium(Cr), and mercury(Hg) (Martin et al., 1976; Dowdy and Volk, 1983). The concentration of these heavy metals may range from 0-100 ppm in municipal solid wastes to 100-10,000 ppm in sewage sludges, mining wastes, and various industrial wastes such as those originating from the electroplating, pulp and paper, and chemical industries (Walsh et al.,1976).

As mentioned in Chapter 1, many studies have been done regarding heavy metal retention and movement in soils. In the following, a summary and review of these studies are presented.

In a study involving kaolinite, illite, and montmorillonite clay suspensions, the uptake of heavy metal ions by the various clay suspensions was observed to increase with pH, with a marked jump in the amount of the metals retained occurring when the soil solution pH exceeded the value required for precipitation or formation of metal hydroxy species (Farrah and Pickering 1976a, 1976b, 1976c, 1977, 1979). Moreover, the following order of increasing attenuation capacity was observed for the clay minerals : kaolinite < illite < montmorillonite. The increase was found to correspond to the C.E.C. values of the clays.

Maguire et al. (1981) studied the influence of pH in heavy metal uptake by clay suspensions that were extracted from natural soils. They obtained the same results as Farrah and Pickering (1979) in that the amount of Cu, Zn, Pb, and Cd sorbed in clay soil increased with pH, and that when the pH of the soil solution was greater than 6, few metal ions were found in the soil solution. The authors concluded that the retention capacity at a fixed pH is less informative than pH dependence curves. They also stated from their study that it would be desirable if the leachates were present in an alkaline condition so as to enhance the precipitation of metal species.

Tyler and McBride (1982) studied the mobility of heavy metals (Cd, Cu, Ni, and Zn) in several soils by using soil columns. The results showed that the least mobility of metals was observed in a mineral soil with a relatively high pH, C.E.C., and exchangeable base content. Harter (1983) studied the adsorption and desorption of Pb, Cu, Ni, and Zn on pH-adjusted soil. He found that the amount of all metals retained was dependent upon pH of the soil sample, with retention dramatically increasing above pH 7.0 and 7.5. However, the sorbed metals were substantially extractable by 0.01 M HCl.

Yanful et al. (1988a) studied the heavy metal migration at a 15 year old landfill site in Ontario. They found that heavy metals such as Cu, Zn, and Pb had migrated through soil having pH close to 8 only up to 10 cm compared to 130 cm of Na^+ and Cl^- migration. The results obtained correspond to the study by Yong et al. (1986) on a landfill site in Quebec, which showed that natural clay liners exhibit better attenuation of heavy metals than cations (e.g. Na^+, K^+, and Ca^{2+}) provided that the high pH environment is maintained.

In terms of retention mechanisms of heavy metals in soils, Elliott et al. (1986) observed a common pH dependent trend of heavy metal sorption on their soils and explained that several mechanisms of metal retention are involved such as cation exchange, precipitation of solid phase (as oxides, hydroxides, carbonates, etc.), solubility and complexation reaction. They stated that the mechanisms are different at different soil pH conditions which make it difficult to predict the relative retention of heavy metals. Yanful et al.(1988b) used the selective dissolution or sequential extraction analysis method to find the phases of heavy metals that were retained in soils. The method is based on the fact that different forms of heavy metals that are retained in soil (e.g., as oxides, hydroxides, carbonates, bound with organic matter, and etc.) can be extracted selectively by using appropriate reagents (Tessier et al., 1979). The method can be used to investigate the retention mechanism of heavy metals in soil. From this method Yanful et al.(1988b) found that heavy metals were retained in their soil in the carbonate phase more than in the hydroxide phase and concluded that the presence of carbonates in their soil was the important factor which reduced the migration rate of the metals.

It can be seen from the review above that the experiments in the study of heavy metal retention in soils were performed either by soil suspension tests or soil column tests. The soil suspension test is less time consuming and can be used to determine the heavy metal retention capacity of soil and to investigate the heavy metal retention mechanism. The soil column test is considered as a useful method for predicting heavy metal movement in soils (Fuller, 1977). The results from both tests found from the above studies showed that heavy metal retention or movement in soils depend on pH and is highly affected by both soil pH and pH of leachates or solutions involved. However, most of the studies were performed on soil at its ambient pH or used pH adjusted soil in the experiments without paying any attention to the resistance in the change of pH or the buffer capacity of the soil. Moreover, those studies related the retention of heavy metal only with soil pH and did not consider the amounts of acid or base that were added to adjust the pH of the soil. In order to expand the knowledge in this field of study, this thesis uses the concept of soil buffer capacity in the study of heavy metal retention in soils.

2.3 General Remarks

From the review of the existing literature, it is clear that heavy metal retention in soil is very much dependent on pH whenever the soils used in the experiments are pure clay minerals or natural soils that have several constituents in them. The amount of heavy metals retained in soil depends on different heavy metals. However, the amount retained remains high at near neutral or alkaline pH. The mechanisms suggested from several studies for heavy metal retention include precipitation as solid phases (oxides, hydroxides, carbonates), ion exchange, and complexation reaction. At acidic pH values, heavy metals become mobile and adsorption on to clay soil particles becomes less effective due to competition at the exchange sites from the H^+ ions. The amount of heavy metals retained and selectivity of retention depend on soil and its composition.

Recently, an increasing number of studies have focused on the effect of acid precipitation on soil in order to determine the change in soil productivity after an acid input (Bitton and Boylan, 1985; De Vries and Breeuwsma, 1987; Lilieholm and Feagley, 1988). Regarding the pH value of acid rain, Likens and Bormann (1974) have noted that water in the atmosphere is generally in equilibrium with prevailing CO_2 pressure and will produce a pH of about 5.7. Fisher et al. (1968) report that weekly samples of precipitation collected over a 2 year period at the Hubbard Brook Experimental Forest were frequently less than 4.0. Mean annual values of 3.9, 3.9, and 4.0 have been reported for three locations in upper New York State (Likens and Bormann, 1974). Moreover, pH values as low as 2.1 have been observed in north central New Hampshire (Likens et al. , 1972). The increasing occurrence of acid rains could affect soil not only in terms of its productivity but also in terms of soil as a natural liner for waste disposal containment. In the vicinity of land disposal sites, infiltration of acid rain into the area could produce a low pH leachate. In addition, a low pH leachate could also be a result of the presence of acids in wastes. An increasing input of acid to soil from a continued load of low pH leachate would cause the change in the soil pH. As mentioned, heavy metal retention in soil is very much dependent on pH. Thus the ability of soil to retard the mobility of heavy metals depends on the susceptibility of the soil to change in pH. The soil buffer capacity would, therefore, be a reliable parameter to indirectly indicate the longevity of heavy metal retention in soil.

In the present study, the soil buffer capacity is determined by using the method of titration of a soil suspension system. Since the interest is on the capacity of soil to buffer against acid leachates, and since heavy metal retention in soils is more affected by acid than by base, only titration in the acid direction is considered. The pH-acid titration is used as a method to determine the soil buffer capacity. The study of heavy metal retention is performed using both soil suspension tests and soil column tests. Results from the study of both tests are then related to the soil buffer capacity.

In the soil suspension test, experiments are performed to assess the capacities of soils to retain heavy metals as they receive increasing known amounts of acid input. The pH of the soils are permitted to change according to its buffer capacity characteristics. In this way, the relation of heavy metal retention with soil pH and acid input can be compared and related with pH-acid titration curves in the determination of soil buffer capacity. The sequential extraction method (Tessier et al., 1979; Yanful et al., 1988b) is used to assist in the investigation of heavy metal retention mechanism at different soil buffering conditions.

For the case of soil column tests, the tests are performed in order to study the relation of soil buffer capacity on the movement of heavy metals along the soil column. The acidic leachates are continually applied to soil columns and the movements of heavy metals are determined. The results from the soil column test are then related with the soil buffer capacity and the results from the soil suspension test. Details of the materials and experimental methods used in the study are presented in the following chapter.

CHAPTER 3

MATERIALS AND METHODS

In order to achieve the objectives of the research work, the materials and methods used in this study are organized and divided into 5 different sections. These sections are i) soils used and determination of their properties, ii) determination of soil buffer capacity, iii) a study on heavy metal retention using soil suspensions, iv) an analysis of heavy metal retention mechanism by sequential extraction, and v) a study on heavy metal movement in soil columns. A summary of the experimental work is presented in the flow chart shown in Fig. 3.1. The results of all experiments performed in this chapter are presented in Chapter 4.

3.1 Soils and Determination of Soil Properties

In Quebec, a natural clay soil barrier is considered to be a desirable feature in the siting of land disposal sites (Yong and Warkentin, 1987). The value of clay soil as a physical and chemical barrier against the migration of leachates from disposal sites has been recognized due to its low hydraulic conductivity and its high adsorption capacity (Warith, 1987). In this experiment, the soils that were selected have clay as a major component. Different clay soils were used as well as a natural clay soil from Quebec.

Four clay soil types were used in this study. They were i) kaolinite identified as kaolinite hydrite PX obtained from Georgia Kaolin Company, ii) illite identified as seal-bond obtained from Canada Brick Company, iii) montmorillonite identified as southern bentonite (dixie bond) obtained from International Minerals & Chemical Corporation

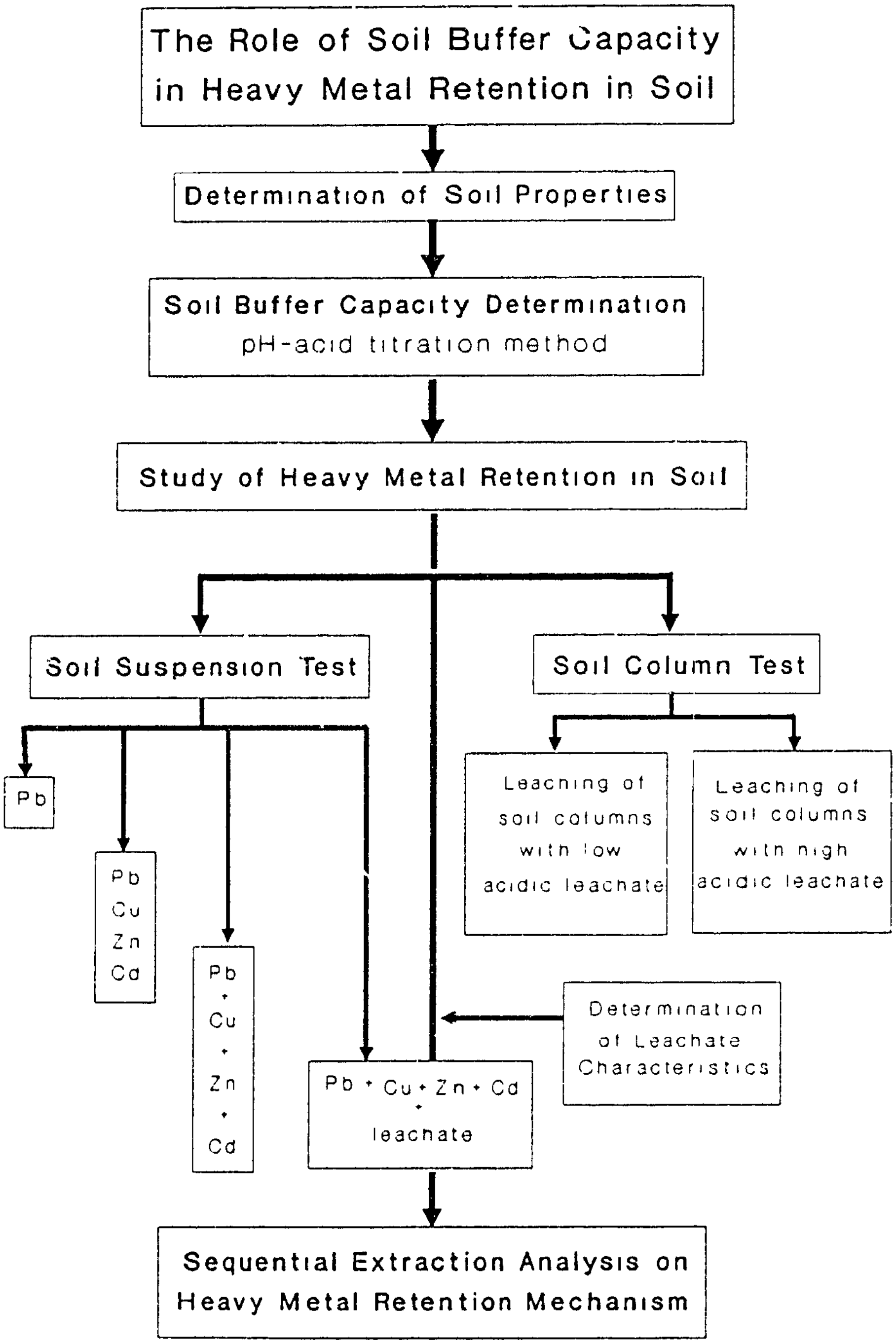


Figure 3.1 Flow chart of the experimental study.

(IMC) and iv) a natural clay soil obtained from an active landfill area (Lachenaie, 35 km east of Montreal, Quebec), at a depth of 2-3 m and at a point sufficiently remote from the actual disposal site to ensure that the clay soil sample was not contaminated by municipal solid waste landfilling.

The soils were air dried and ground to pass the 2 mm sieve. They were subjected to a variety of chemical and physical tests e.g., soil pH measurement, cation exchange capacity determination, surface area measurement, organic content determination, carbonate content determination, amorphous material determination, particle size analysis, and mineralogical analysis by X-ray diffraction.

Soil pH was measured in 1:10 soil:water solution ratio by a Beckman Φ^{TM} 12 pH/ISE meter. Cation exchange capacities were determined at pH 7 using the silver thiourea method (Chhabra et al., 1975). The surface areas were measured using ethylene glycol-monoethyl ether (EGME), according to the procedure described by Eltantaway and Arnold (1973). The organic contents were determined following the method described by Jackson (1956). The carbonate content determination was performed using the titration method (Hesse, 1971). Presence of amorphous materials was determined using the method of Segalen (1968). Percentages of clay were determined by the particle size analysis method which was performed according to ASTM Test No. D422-54 (1970). For determination of mineral composition, the soils were prepared and analyzed by X-ray diffraction using a Siemens D-500 X-ray diffractometer. The preparation and analysis were performed according to the method described by Starkey et al.(1984). Results of soil properties determination are given in section 4.1 of the following Chapter.

3.2 Determination of Soil Buffer Capacity

As mentioned in Chapter 2, the determination of soil buffer capacity was based on the titration method. Since the intent of this thesis is directed towards a study of the capacity of soil to buffer against acid, only titration in the acid direction was performed. In this experiment, the clay soil samples were titrated with increasing amounts of strong acid in soil suspension system. After the titration, data on the amounts of acid input and soil solution pH were plotted and the soil buffer capacity was calculated from the titration curve. In this experiment, nitric acid (HNO_3) was used as the titration acid. The ratio of soil:acid solution was 1:10. In the pH-acid titration of each clay soil, several 40 ml of acid solutions with concentrations of acid from 0, 0.01, 0.02 , 0.03 , ..., to 0.2 $mol \cdot L^{-1}$ were prepared and added to plastic tubes. Each tube contained 4 g of dry soil. The resultant soil suspensions obtained with acid input ranged from 0 to 200 $cmol \quad H^+ \cdot kg^{-1} soil$. After addition of the acid solutions, the resultant soil suspension samples obtained were equilibrated by shaking in an end-over-end shaker at 25^oC for 24 h (equal to the time used by Federer and Hornbeck,1985). The samples were then centrifuged at 5,000 rpm for 10 minutes. The pH of the soil solutions were measured using a Beckman Φ^{TM} 12 pH/ISE meter.

All four clay soils i.e., kaolinite, illite, montmorillonite, and natural clay soil were titrated. The titration curves which show the relationship between soil solution pH and amount of acid input (from 0-200 $cmol \quad H^+ \cdot kg^{-1} soil$) were plotted (e.g., Fig. 4.1). From the titration curves, the soil buffer capacity was determined from the negative of the inverse slope of the titration curve (as in the relation shown in eq.(2.1)). The buffer capacity, expressed as $cmol \quad H^+ \cdot kg^{-1} soil \cdot pH^{-1}$ was then plotted with increasing amounts of acid input, and soil solution pH. The results are presented in section 4.2 of Chapter 4.

3.3 Soil Suspension Study on Heavy Metal Retention

In the study of contaminant retention in soil, the soil suspension test was used because of its simplicity, rapidity, and reproducibility (Farrah and Pickering, 1977; Maguire et al.,1981; and Harter, 1983) . In this research work, the soil suspension test was conducted first in the study of the relationship of soil buffer capacity on heavy metal retention. The experimental procedure was planned based on the same principle as in pH-acid titration method for determination of soil buffer capacity. Heavy metal solutions were applied to the soils with increasing amounts of acid. The pH of soil solutions and amounts of heavy metals retained in soils with increasing amounts of acid were determined. Heavy metals that were used in this experiment are Pb, Cu, Zn, and Cd. Several soil suspension tests were performed from a simple soil-heavy metal solution system to more complex systems. They were i) soil-Pb solution (with different concentrations of Pb applied), ii) soil-Pb, Cu, Zn, and Cd solutions (applied separately), iii) soil-Pb+Cu+Zn+Cd solutions (applied compositely), and iv) soil-Pb+Cu+Zn+Cd-leachate solutions (applied compositely with leachate). The arrangement of these tests was made in order that the retention of heavy metals in soil could be easily studied from a simple system to a more complicated system. The details of each test are given in the following subsections.

3.3.1 Pb Retention in Soil-Pb Solution

Three different concentrations of Pb solutions were applied to each of the clay soil samples (kaolinite, illite, montmorillonite, and natural clay soil) with increasing amounts of acid input. The concentration of Pb solutions used are 5.0 x 10^{-5}, 5.0 x 10^{-4}, and 5.0 x 10^{-3} $mol \cdot L^{-1}$. These concentrations are equivalent to concentrations in ppm Pb of ≈ 10, 100, and 1000 ppm respectively. These concentrations were selected because they cover the range of Pb concentrations which are most commonly found in municipal solid wastes, some industrial wastes, and sewage sludges. For each concentration of Pb, a set of solutions with increasing concentrations of acid from 0, 0.01, 0.02, 0.03, ..., to 0.2 $mol \cdot L^{-1}$ was prepared. The Pb solutions were prepared by using Pb in the form of lead nitrate ($Pb(NO_3)_2$), and the acid used was nitric acid. The solutions of Pb with increasing amounts of acid were applied to each of the clay soil samples at 1:10 soil:solution ratio, using 4 g of dry soil and 40 ml of Pb solution.

The application of the three different concentrations of Pb as above was equivalent to Pb applied to soil of 0.05, 0.5, and 5 $cmol \cdot kg^{-1} soil$ in which each concentration of Pb applied had increasing amounts of acid input to soil ranging from 0 to 200 $cmol \quad H^{+} \cdot kg^{-1} soil$. After the solutions were applied to the clay soils, the soil suspension samples were equilibrated by shaking in an end-over-end shaker at 25^{o} C for 24 h, a time previously found to be sufficiently for equilibration (Elliott and Liberati, 1981). The samples were then centrifuged at 5,000 rpm for 10 minutes. The pH of the soil solutions were measured. The amounts of Pb remaining in the supernatant were analyzed by a GBC902 double beam atomic absorption spectrophotometer.

The amount of Pb retained in the soils was calculated as the difference in the Pb applied and Pb remaining in solution. The amount of Pb retained in each soil at different concentrations of Pb applied was then compared and related with the amounts of acid input and the soil solution pH values. The results and discussion of Pb retention in soil Pb-solution are given in section 4.3.1.

3.3.2 Heavy Metal Retention in Soil-Heavy Metal Solution

Four heavy metal solutions were separately applied to each clay soil at increasing amounts of acid. The solutions used were Pb, Cu, Zn, and Cd solutions. They were prepared at the concentration of 1.0 x 10^{-3} $mol \cdot L^{-1}$ from their nitrate salts ($Pb(NO_3)_2$, $Cu(NO_3)_2$, $Zn(NO_3)_2$, and $Cd(NO_3)_2$). The acid used was nitric acid. For each heavy metal solution, a set of solutions with increasing concentrations of acid from 0, 0.01, 0.02, 0.03, ..., to 0.2 $mol\ L^{-1}$ was prepared. The solutions were then applied to each of the clay soils at 1:10 soil:solution ratio, using 4 g of dry soil and 40 ml of the solution. This made the amount of each heavy metal applied to each soil equal to 1.0 $cmol \cdot kg^{-1} soil$ and amounts of acid input ranging from 0 to 200 $cmol\ H^{+} \cdot kg^{-1} soil$.

The soil suspension samples were equilibrated by shaking in an end-over-end shaker at 25° C for 24 h after the solutions were applied to soils. The samples were then centrifuged at 5,000 rpm for 10 minutes. The pH of the soil solutions were measured. The amount of heavy metal remaining in the supernatant was analysed by a GBC902 double beam atomic absorption spectrophotometer. The amount of heavy metal retained in the soils was calculated as the difference in the heavy metal applied and remained in solution. The amount of heavy metal retained in each soil was then compared and related with the amounts of acid input and the soil solution pH values. The results and discussion on this topic are shown in section 4.3.2.

3.3.3 Heavy Metal Retention in Soil-Composite Heavy Metal Solution

A composite solution of heavy metals having concentrations of Pb, Cu, Zn, and Cd in their nitrate forms of 1.0 x 10^{-3} $mol \cdot L^{-1}$ was applied to soils at increasing amounts of nitric acid. The solution was applied at 1:10 soil:solution ratio by using 4 g of dry soil and 40 ml of solution. The amount of heavy metal applied to soils was 1.0 $cmol \cdot kg^{-1} soil$ with increasing amounts of acid input of 0-200 $cmol \quad H^{+} \cdot kg^{-1} soil$.

The methods of pH and heavy retention measurements were the same as in 3.3.2. The amounts of heavy metals retained in each soil were then calculated and compared with the increasing amounts of acid input and soil solution pH values. Results and discussion on this subject are provided in section 4.3.3.

3.3.4 Heavy Metal Retention in Soil-Heavy Metal-Leachate Solution

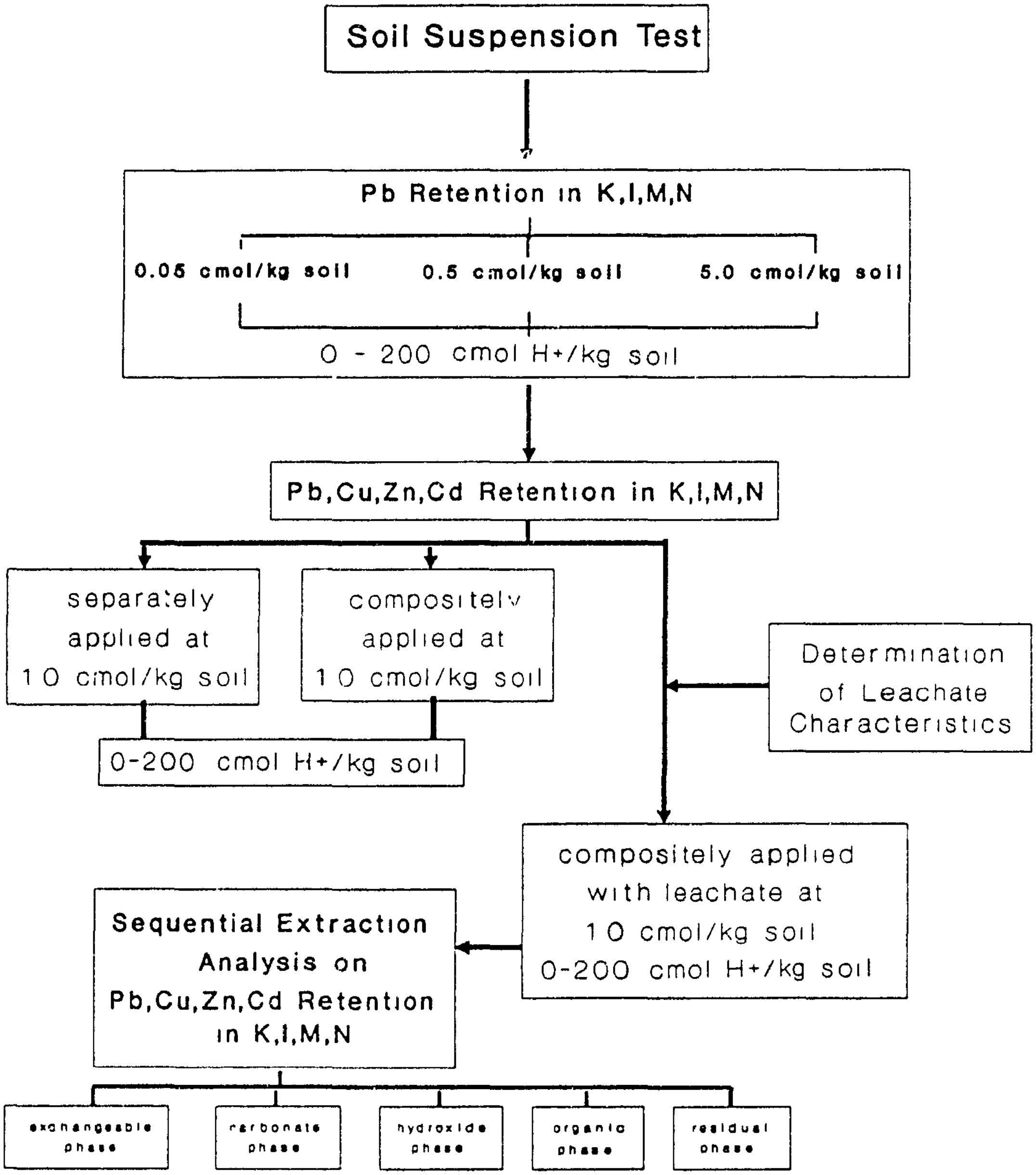
In the adsorption study of heavy metals on clay at various pH values, Frost and Griffin (1977) dissolved nitrate salts of Cd, Cu, and Zn into a leachate collected from the Dupage County, Illinois, sanitary landfill. They found differences in the adsorption of heavy metals in pure nitrate salt solution and in the leachate. Several constituents in the leachate interfered and/or competed with heavy metals for retention in the soil. In this experiment, a leachate collected from Lachenaie (an active landfill site, 35 km east of Montreal) was combined with heavy metals in order to prepare a heavy metal-leachate solution used in the tests. The purpose of this set of experiments is to work with a leachate that simulates a real field situation.

The leachate was collected directly from the basins designed to gather the leachate solution generated at the landfill site. Samples of the leachate solution were taken from a number of locations within the leachate basins, and were mixed together. To ensure that the composition of the leachate solution used in all laboratory tests remained constant, a large quantity of the solution was collected. Determination of leachate characteristics were conducted according to procedures described by the Environmental Protection Service (EPS, 1979), and ASTM Standards (1984).

Heavy metals in the form of Pb, Cu, Zn, and Cd nitrates and nitric acid were mixed into the leachate for the preparation of heavy metal-leachate solutions having increasing amounts of acid. A set of solutions, each solution having the same concentration of Pb, Cu, Zn, and Cd at 1.0 x 10^{-3} $mol \cdot L^{-1}$ but having increasing acid concentration from 0 to 2x10^{-3} $mol \cdot L^{-1}$, was applied to the soils at 1:10 soil:solution ratio (4 g of dry soil and 40 ml of solution). The amount of each heavy metal applied to soil as described is equivalent to 1.0 $cmol \cdot kg^{-1} soil$ with increasing acid input from 0 to 200 $cmol \quad H^{+} \cdot kg^{-1} soil$.

The methods of pH and heavy metal retention measurements were the same as in 3.3.2. The amounts of heavy metals retained in each soil were then calculated and compared with the increasing amounts of acid input and soil solution pH values. The results and discussion are given in section 4.3.4 of the following Chapter.

A summary of the soil suspension experiments are presented in a flow chart shown in Fig. 3.2.



Notes: K = kaolinite soil M = montmorillonite soil
I = illite soil N = natural soil

Figure 3.2 Experimental flow chart of the soil suspension study on heavy metal retention.

3.4 Sequential Extraction on Heavy Metal Retention

The forms of heavy metals retained in soils at different conditions are different (Yong et al., 1986). For example, heavy metals may be retained in soils in the form of oxides and hydroxides, carbonates, exchangeable cations, and/or bound to organic matter depending on the soil conditions and soil constituents (Yanful et al., 1988b). These forms of heavy metals can be extracted selectively by using appropriate reagents (Tessier et al., 1979). The procedure of selective dissolution or as it is often called, ***sequential extraction,*** for the study of heavy metal retention in soils and sediments has been developed by Chester and Hughes (1967), Gupta and Chen (1975), Tessier et al. (1979), and Yanful et al. (1988b). In this experiment, the sequential extraction method developed by the aforementioned was used in order to obtain information on the amounts and forms of heavy metals that were retained in the soil samples at different conditions of pH and acid input. The results from the experiment were used to help explain the retention mechanisms of heavy metals at different buffering conditions of the soils.

The experiment as in 3.3.4 was again performed but this time with only 1 g of dry soil and 10 ml of heavy metal-leachate solution having increasing amounts of acid were used. After the soil suspension sample was centrifuged, the supernatant was removed with a pipet and analyzed for heavy metals and pH. The residue was washed with 8 ml of distilled water. The sample was centrifuged again and the washed water was discarded. The soil residue was then used as a material for sequential extraction analyses – presented in Table 3.1. As can be seen from the Table, the extraction

Table 3.1 Sequential extraction procedure used in the fractionation of heavy metals retained in soils.

	Reagents and extraction method	Heavy metal phase released from soil
i)	Extraction of soil at room temperature with 8 ml of of potassium nitrate (KNO_3) for 1 h with continuous agitation	Exchangeable cations
ii)	Extraction of the residue from i) at room temperature with 8 ml of 1M sodium acetate (NaOAc) adjusted to pH 5.0 by acetic acid (HOAc) for 5 h with continuous agitation	Carbonates
iii)	Extraction of the residue from ii) with 20 ml of 0.04 M hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) in 25 % (v/v) HOAc at 96±3°C with occasional agitation for 6 h	Oxides and Hydroxides
iv)	Extraction of residue from iii) 1^{st} - with 3 ml of 0.02 M HNO_3 and 5 ml of 30 % H_2O_2 adjusted to pH 2 with HNO_3 at 85±2°C for 2 h with occasional agitation 2^{nd} - with 3 ml of 30 % H_2O_2 at pH 2 at 85±2°C for 3 h with intermittent agitation 3^{rd} - with 5 ml of 3.2 M ammonium acetate (NH_4OAc) in 20 % (v/v) HNO_3 diluted to 20 ml at room temperature with continuous agitation for 30 min	Bound to organic matter
v)	Digestion of the residue from (iv) with a 5:1 mixture of hydrofluoric acid (HF) and perchloric acid ($HClO_4$), dissolve the residue left from the digestion with 12 N hydrochloric acid (HCl) and dilute to 25 ml	Residual fraction

procedure involved treating a soil sample with the reagent under a certain condition and for a certain period of time.

In the first step of extraction, the KNO_3 solution was adjusted to the same pH value as in the original soil solution pH in order to sustain the same condition of pH for the extraction of exchangeable heavy metal cations. After the first treatment, the soil sample was centrifuged at 10,000 rpm for 10 min and the clear supernatant was analyzed for Pb, Cu, Zn, and Cd by atomic absorption spectroscopy (AAS). The residue was washed with distilled water, centrifuged and the supernatant was discarded. The residue was then passed on to the next stage of the extraction as outlined in Table 3.1. The amounts of heavy metals that were retained in each clay soil by different phases at increasing amounts of acid were calculated from the AAS data. The amounts of heavy metals retained in each clay soil by different phases were then plotted as a function of acid input and soil solution pH values.

In addition to this experiment, the computer program - MINTEQ (Metal Speciation Equilibrium Model for Surface and Groundwater), developed by U.S. Environmental Protection Agency (1988) was used to calculate the probable percentage distribution of different species of heavy metals present in the leachate solution at different solution pH conditions. This is to assist with the sequential extraction experiment in evaluation of the retention mechanism of heavy metals in the clay soils studied. The results and discussion on sequential extraction of heavy metal retention are provided in section 4.4 of Chapter 4.

3.5 Soil Column Study on Heavy Metal Movement

The soil column tests were conducted in order to study the relation of soil buffer capacity to the movement of heavy metals when a soil column receives a leachate having acid and heavy metals in it. Apart from results and information on heavy metal retention received from the soil suspension study, results from the soil column test added information on heavy metal migration or movement in soils when they receive increasing amounts of acid. The studies by O'Donnell et al.(1977), Fuller (1977), Fuller (1978), and Yong et al. (1986) indicated that the soil column technique is a useful method for predicting pollutant attenuation and pollutant movement in soils because of its capacity to be simple, rapid, reproducible, and reliable.

In this present study, soil column experiments were performed following the method of Fuller (1982) and Yong et al. (1986). A soil column, or as it is sometimes called leaching cell, was designed as shown in Fig. 3.3. The cell consists of a hollow Plexiglas cylinder with an inside diameter of 5 cm, and a length for soil packing of 10 cm.

A hollow Plexiglas cylinder having the same diameter and a length of 5 cm was used as a top cap and at the same time as a reservoir for a permeant solution. The Plexiglas top cap and a Plexiglas bottom plate were screwed to the top and bottom of a cylinder, and fitted with rubber O-rings to prevent leakage.

Three clay soil samples were used in this experiment : kaolinite, illite, and natural clay soil. Due to the possibility of swelling in a soil column, montmorillonite was not selected. Each clay soil was packed into two columns, one for receiving low acidic

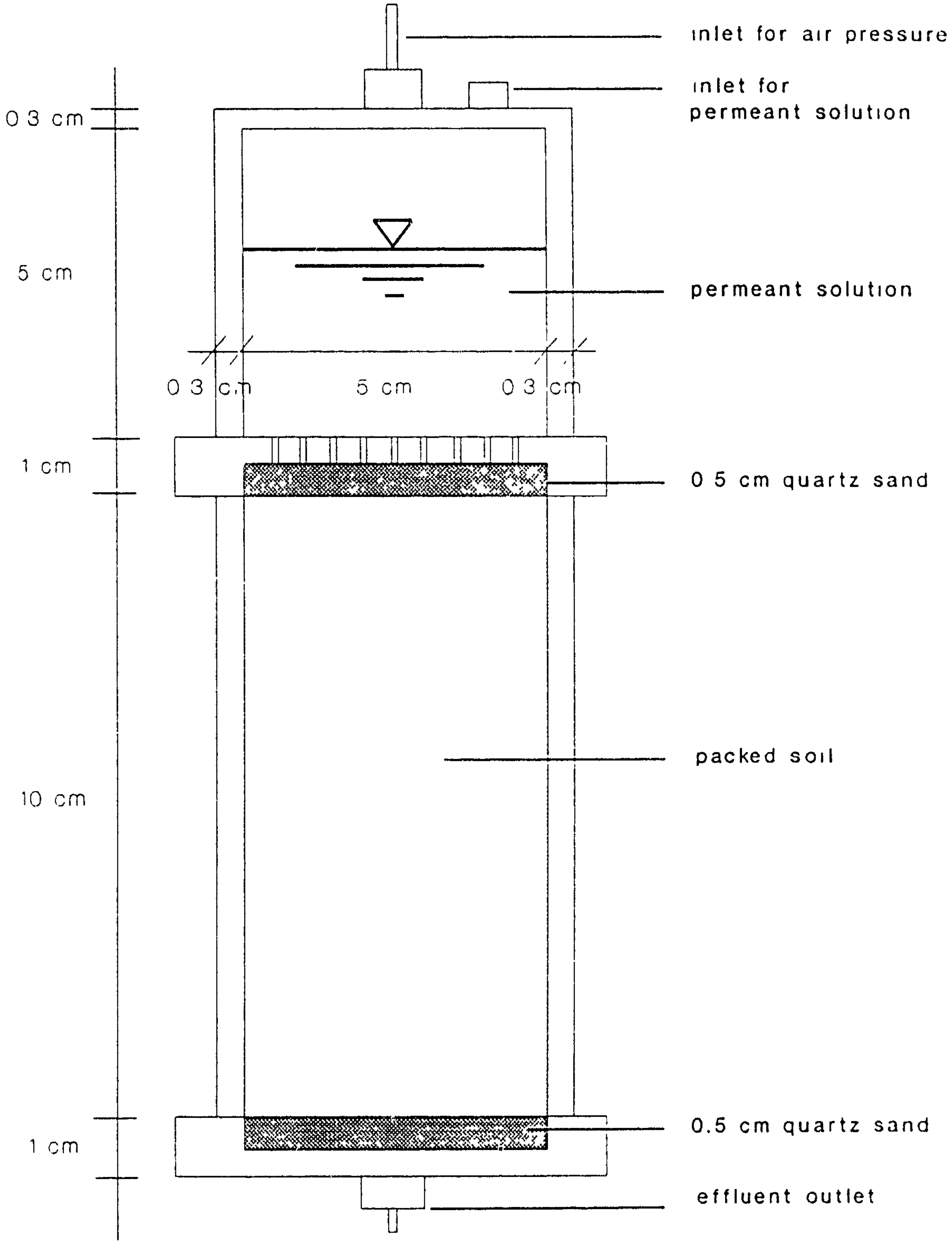


Figure 3.3 Schematic representation of a soil column used in this study

permeant solution and the other one for receiving high acidic permeant solution. The size of soil sample used for each column was approximately 250 g of dry soil. This amount of soil, when packed into a column, resulted in a pore volume of around 100 ml.

The calculation of a soil sample size used in order to obtain a pore volume of 100 ml is based on the relation of soil column porosity and column volume. If a specific gravity of the soil used and column volume are known, the amount of dry soil used at a fixed pore volume can be calculated. In this case, the specific gravity of kaolinite, illite, and natural clay soil used in this study were 2.58, 2.68, 2.67 g/cm^3 respectively. The column volume was known as calculated from its diameter and length of 5 and 10 cm. For a pore volume of 100 ml, the amounts of kaolinite, illite, and natural clay soil used were calculated to be 249, 258, and 257 g of dry soils respectively.

Packing of soil in a column was done according to Fuller (1982). A layer of air dried soil (1 2 cm thick) was spooned into a column, packed uniformly with a round ended durable glass rod and then repeated until the column was filled. In addition, pure quartz sand was used in the soil column as an inert - distribution layer at both ends of the soil column between the soil and the solution intake and outlet plates. The bulk density of the kaolinite soil column was 1.27 g/cm^3 whereas the bulk density of both the illite and natural clay soil columns were 1.31 g/cm^3. The porosity of all the three soil columns were about 0.51.

As mentioned earlier, two kinds of permeant solution were used : one with low acidic solution and the other one with high acidic solution. They were prepared from leachate collected from Lachenaie landfill as in section 3.3.4. Heavy metals Pb, Cu, Zn, and Cd, in the form of nitrate salts and nitric acid were added to the leachate. For the low acidic permeant solution, the solution was prepared such that the concentration of each heavy metal was equal to 1.0 x 10^{-3} $mol \cdot L^{-1}$ and the concentration of nitric acid was 0.025 $mol \cdot L^{-1}$. For the high acidic permeant solution, the solution had the same concentration of heavy metals but the concentration of nitric acid in the solution was 0.25 $mol \cdot L^{-1}$. The pH values were about 1.6 and 0.6 for low and high acidic permeant solutions respectively.

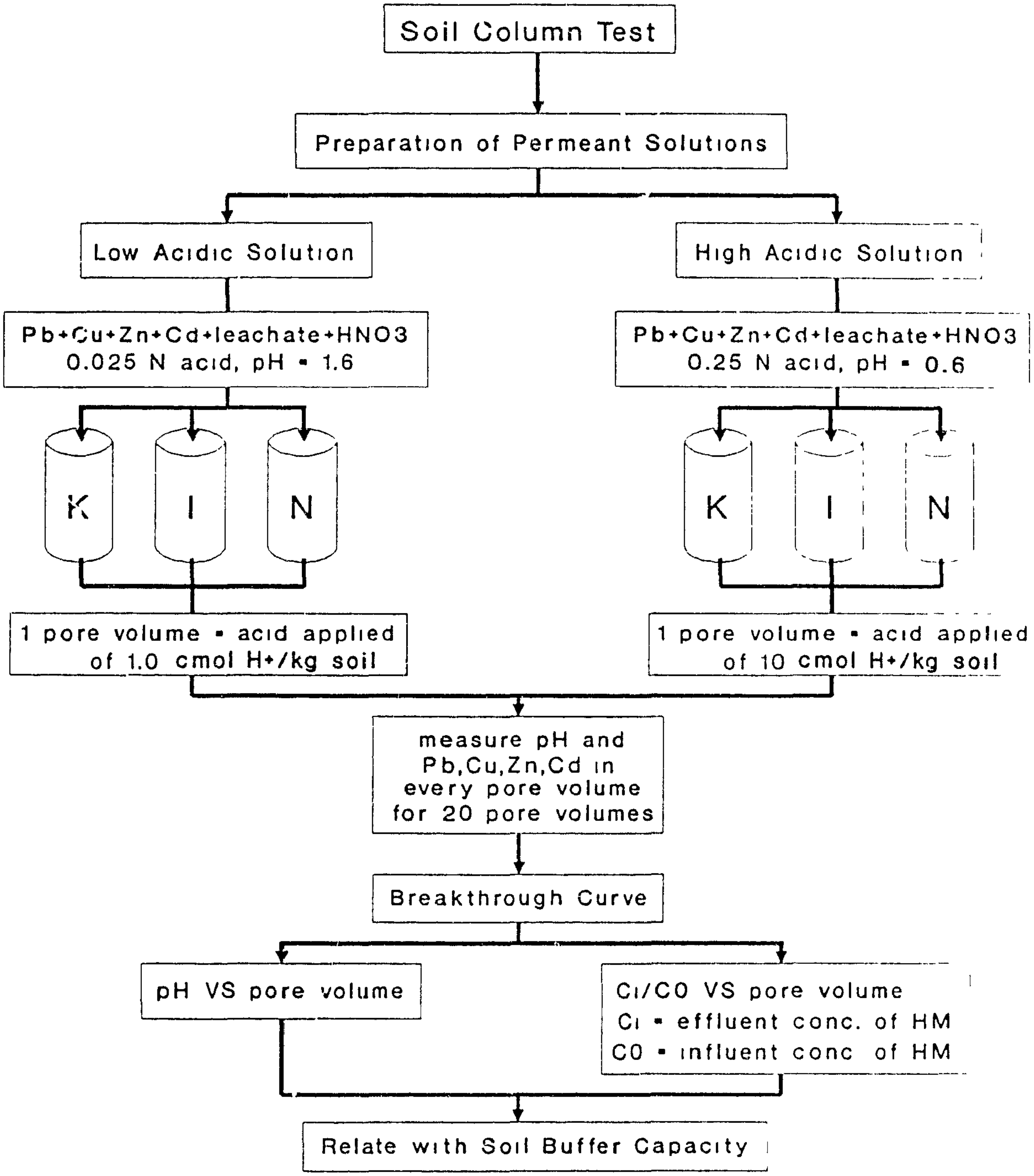
The concentrations of acid in the permeant solutions (0.025 and 0.25 $mol \cdot L^{-1}$) were prepared such that when one pore volume of leaching solutions was collected at 100 ml, the amounts of acid input to the soil column was equivalent to an increment of 1 $cmol \quad H^{+} \cdot kg^{-1} soil$ and 10 $cmol \quad H^{+} \cdot kg^{-1} soil$ for low and high acidic permeant solutions respectively. This was designed for ease of data comparison between the results of the soil column study and the soil suspension study–at the same increasing amount of acid input.

Each permeant solution was continuously leached through each of the soil columns that had been prepared. Three columns, each for kaolinite, illite, and natural clay soil were leached with low acidic leachate, and another three columns of the same soils were leached with high acidic leachate. Distilled water was first passed through the soil columns before leaching with permeant solutions. At least 1 pore volume of distilled water was used.

The permeant solutions were applied on top of the soil. An air pressure was applied to the permeant solution basin in order to regulate the flow rate of the solution through soil (see Fig.3.3). The pressure applied was equivalent to a hydraulic head of 6.25 m. This hydraulic head resulted in an effluent flow rate of around 0.5 pore volume displacement per 24 h which is the flow rate suggested by Fuller (1982) to be the most useful flow rate for gravity control in soil column test.

During the leaching period, effluent was collected in polyethylene bottles at every pore volume and analyzed for pH and concentration of the heavy metals by AAS. The total pore volume collected in each column was 20 pore volumes. The schematic diagram of the soil column study is presented in Fig. 3.4.

The results of pH and heavy metal concentrations in each soil column were then related with pore volumes and the amounts of acid applied by a breakthrough curve. The results and information received from this soil column test are presented in section 4.5. These results were also compared and related with the results from the soil suspension test and soil buffer capacity determination.



Note . HM = Heavy Metal

Figure 3.4 Schematic diagram of the experimental works used in the soil column study.

CHAPTER 4

RESULTS AND DISCUSSION

This chapter presents the results of all experiments described in the previous chapter. Discussion of the results is included in order to explain the relation of soil buffer capacity to heavy metal retention which is the main purpose of the study. The content of the chapter is divided into 5 sections corresponding to the experimental sections given in Chapter 3. The first section contains the results of the tests of the properties of the soils used whereas the second section gives the results and discussion on their buffer capacity. The experimental results with detailed discussion on soil suspension test, soil sequential extraction analysis, and soil column test are provided in sections 4.3, 4.4, and 4.5 respectively.

4.1 Soils and Soil Properties

Selected physical and chemical properties of kaolinite, illite, montmorillonite, and natural clay soil are presented in Table 4.1. The mineral composition of the clay soils are also included in the table.

The results from Table 4.1 reveal that illite, montmorillonite, and the natural clay soil have higher soil pH values than kaolinite. Among the four clay soils, montmorillonite has the highest C.E.C. value whereas kaolinite has the lowest C.E.C. value. The ranking of the values of surface area correspond to the ranking shown by the soil C.E.C. values, i.e., montmorillonite > illite > natural clay soil > kaolinite.

Table 4.1 : Selected properties and compositions of the four clay soils used in the study.

Parameters	kaolinite	illite	montmorillonite	natural clay soil
soil pH (1:10 soil:water)	4.5	8.2	7.7	7.8
C.E.C.				
$(\text{cmol}(+)\cdot\text{kg}^{-1})$	8	40	108	24
$(\text{cmol}(++)\cdot\text{kg}^{-1})$	4	20	54	12
surface area $(\text{m}^2\cdot\text{kg}^{-1} \text{ x } 10^{-3})$	12	92	843	80
organic content (% w/w)	0	0.9	0.3	1.9
carbonate content (% w/w)	0	14.7	0	9.7
amorphous content (% w/w)	1.2	6.1	0.2	11.0
clay (% < 2 micron)	86	40	42	56
mineral composition (given in decreasing abundance)	kaolinite	illite chlorite quartz feldspar calcite	montmorillonite quartz	quartz illite feldspar kaolinite chlorite dolomite

It is noted from the table that organic and carbonate contents were not detectable in the kaolinite. A higher amount of organic content was found in the natural clay soil than in illite and in montmorillonite. The carbonate contents in illite (14.7%) and the natural clay soil (9.7%) were considered to be significant. These high amounts of carbonate content may help to explain the high values of soil pH in the illite and natural clay soil. The amorphous contents in the natural clay soil and illite were larger than those in kaolinite and montmorillonite. The highest percentage of clay was found in kaolinite and the lowest was found in illite.

The illite clay soil used in this study not only has illite clay mineral as a main component but also has varying amounts of chlorite, quartz, feldspar, and calcite. The natural clay soil has several clay and non-clay minerals, some of which are also found in other clay soils. Kaolinite has only its clay mineral whereas montmorillonite has its clay mineral and quartz as a non-clay mineral.

The differences in the properties and compositions of these soils would cause them to have different buffer capacities. The results of their buffer capacity determination are provided in the following section.

4.2 Soil Buffer Capacity

As mentioned in the previous chapter, the soil buffer capacity was determined by the titration method. The titration curves of soil solution pH versus amounts of acid input in $cmol \quad H^{+} \cdot kg^{-1} soil$ for kaolinite, illite, montmorillonite, and natural clay soil suspensions are shown in Fig. 4.1. The titration curve of a blank (a solution in the absence of soil) is also plotted in Fig. 4.1 together with the titration curves of the four clay soils. As expected, the figure shows that the addition of acid reduced the pH of the soil solutions. However, the initial pH values and the reduction in the soil solution pH of different soils are different. The kaolinite suspension has a lower initial pH (pH 4.5 at 0 acid input) than the illite (pH 8.2 at 0 acid input), the montmorillonite (pH 7.7 at 0 acid input), and the natural clay soil suspensions (pH 7.8 at 0 acid input).

The titration curve of the illite in Fig. 4.1 shows that the illite suspension can resist addition of acid with small changes in pH by the slow drop of pH from 8 to 5. When the amount of acid input reaches 120 $cmol \quad H^+ \cdot kg^{-1} soil$ the soil solution pH drops sharply from 5 to 2. In the case of the titration curve of montmorillonite, the soil solution pH begins to drop sharply from about pH 5 to 2 when the amount of acid input exceeds 80 $cmol \quad H^+ \cdot kg^{-1} soil$. The natural soil shows its capacity to resist a change in pH until the amount of acid input reaches 60 $cmol \quad H^+ \cdot kg^{-1} soil$. Beyond that point the soil solution pH starts to drop gradually from 5 to 2.

In the case of kaolinite, there is an immediate drop in the soil solution pH upon addition of acid to an amount of about 25 $cmol \quad H^+ \cdot kg^{-1} soil$. Beyond this point, there is relatively little change in soil solution pH with further addition of acid. The curve shows almost the same pattern as the blank except that it is slightly displaced above the blank and that the pH at 0 acid input of kaolinite is lower (pH 4.5 at 0 acid input). These titration curves reveal that the illite has a higher resistance to pH changes than the montmorillonite and natural clay soils whereas the kaolinite does not seem to have any resistance to pH changes.

From the titration curves of Fig. 4.1, the buffer capacities of kaolinite, illite, montmorillonite, natural clay soil and the blank can be determined from the negative inverse slope of the curves, as shown plotted in relation to both acid input and pH in the two dimensional plots in Figs. 4.2 and 4.3 respectively. The buffer capacity of illite increases with increasing addition of acid and reaches the highest point at near 100

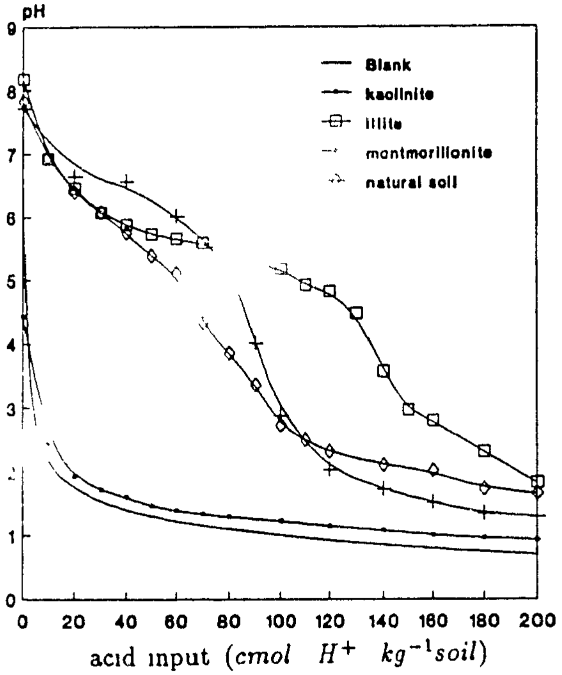
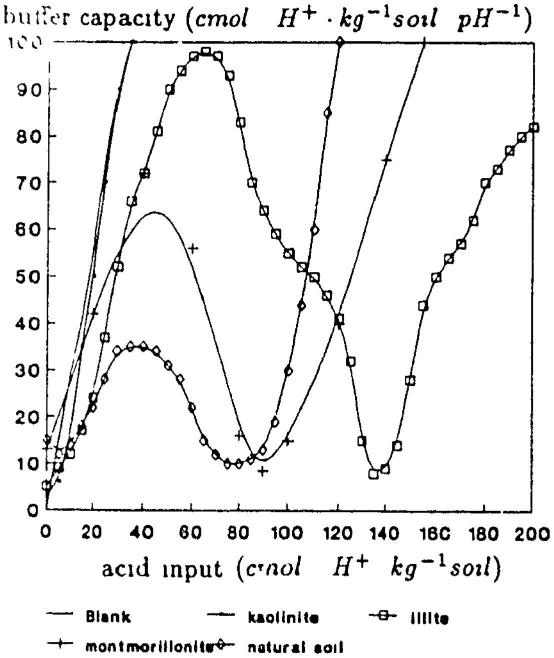


Figure 4.1 pH-acid titration curves of clay soils.



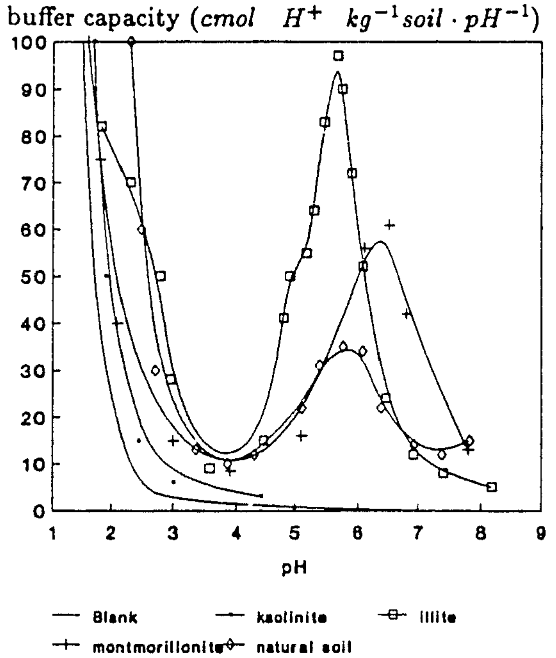


Figure 4.2 Buffer capacity curves of blank, kaolinite, illite, montmorillonite, and natural clay soil as a function of acid input.

Figure 4.3 Buffer capacity curves of blank, kaolinite, illite, montmorillonite, and natural clay soil as a function of soil suspension pH.

$cmol\quad H^{+} \cdot kg^{-1} soil \cdot pH^{-1}$ at an amount of acid input of 70 $cmol\quad H^{+} \cdot kg^{-1} soil$ (Fig. 4.2). The buffer capacity then begins to decrease and reaches its lowest point at the level of 10 $cmol\quad H^{+} \cdot kg^{-1} soil \cdot pH^{-1}$ when the acid input reaches 135 $cmol\quad H^{+} \cdot kg^{-1} soil$. These highest and lowest points correspond to the soil solution pH values of about 5.5 and 4 as seen in Fig. 4.3 when the buffer capacity is plotted as a function of soil solution pH.

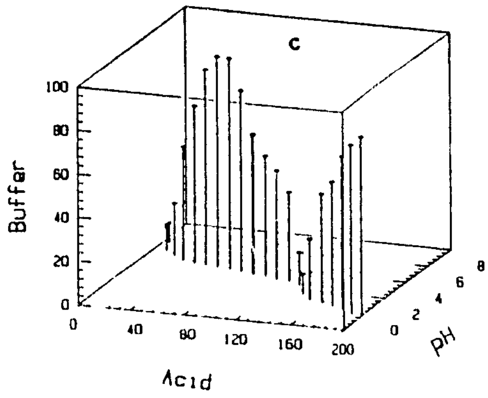
The buffer capacity curve of montmorillonite shows a trend similar to the buffer capacity curve of illite (Fig. 4.2). Its highest buffer capacity value is 60 $cmol\quad H^{+} \cdot kg^{-1} soil \cdot pH^{-1}$ at an acid input of 50 $cmol\quad H^{+} \cdot kg^{-1} soil$ which is lower than the highest buffer capacity value of illite. Its lowest point is about 10 $cmol\quad H^{+} \cdot kg^{-1} soil \cdot pH^{-1}$ which is at the same level of the lowest point of the buffer capacity value of illite, but at a smaller amount of acid input, i.e., at 90 $cmol\quad H^{+} \cdot kg^{-1} soil$. The highest buffer capacity is at a pH value around 6.5, whereas the lowest value is at a pH around 4, as shown in Fig. 4.3.

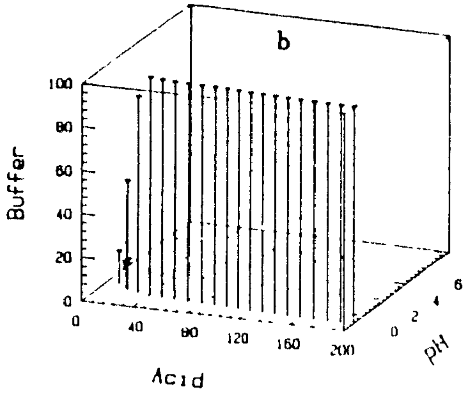
In the case of the natural clay soil, the buffer capacity curve exhibits a similar pattern to the montmorillonite. However, the highest buffer capacity value is lower (35 $cmol\quad H^{+} \cdot kg^{-1} soil \cdot pH^{-1}$ at an acid input of around 40 $cmol\quad H^{+} \cdot kg^{-1} soil$ in Fig. 4.2). The corresponding pH value for this highest point is around 6 (Fig. 4.3). The lowest point is at acid input of 80 $cmol\quad H^{+} \cdot kg^{-1} soil$, corresponding to a pH value of around 4 (Fig. 4.3). In contrast to the other three clay soils, the kaolinite buffer capacity curve is at its lowest point near the beginning of the curve, – similar to the case of the blank (Fig. 4.2). These lowest buffer capacity points correspond to a pH around 4 for kaolinite and 3 for the blank (Fig. 4.3).

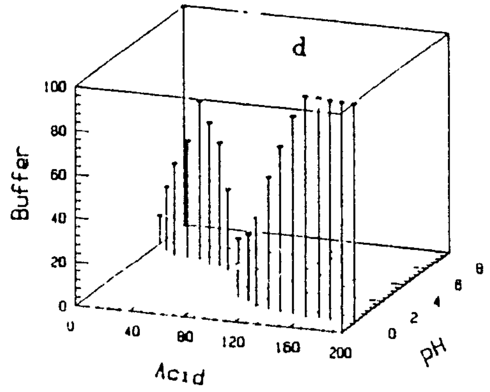
The relation of soil buffer capacity with amounts of acid input and soil solution pH can be clearly seen when the buffer capacity is plotted with acid and soil solution pH in the three dimensional plots shown in Figs. 4.4a–4.4e. It can be seen from these plots that when the soil solution pH is greater than 4, the buffer capacity of illite is higher than montmorillonite and natural clay soil and covers a larger range of acid input before the buffer capacity begins to decrease. In addition, it may seem to appear from the figures that when soil solution pH is lower than 4, the kaolinite has a much higher buffer capacity than that of the natural clay soil, montmorillnoite, and illite respectively. However, the slow change in soil solution pH at low pH does not reflect the high buffer capacity of the system, since the pH is a logarithmic scale and addition of acid in the blank provided the same pattern of buffer capacity at low pH, as can be seen from Fig. 4.4a.

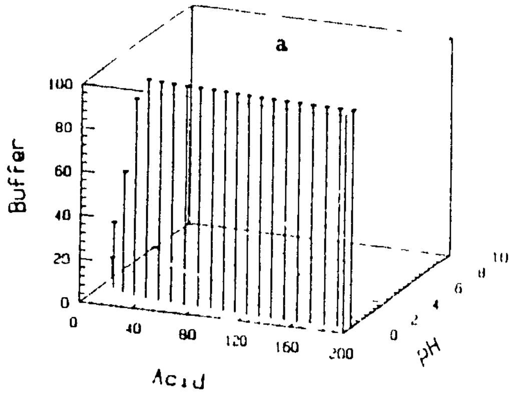
The experimental data for all the graphs that plotted in Figs. 4.1–4.4 are provided in Tables A-1, A-2, and A-3 in Appendix A.

The results shown in Figs. 4.1–4.4 indicate that the illite has a higher buffer capacity or higher resistance to pH changes than the montmorillonite and natural clay soil respectively. The kaolinite does not have any significant resistance to pH changes. One interprets from the results that the illite is able to adsorb more H^+ than the montmorillonite and natural clay soil before producing any significant changes in the pH. The adsorption of H^+ in the case of the illite, is not only due to adsorption onto the exchange sites but also due to the neutralization of H^+ by carbonates that are present in significant amounts in the illite. The mechanism resembles the neutralization of acid in soil by the addition of lime. Yanful et al. (1988b) also found from their experiment that their carbonate-rich soil (containing 37% carbonates) consistently gave equilibrium pH values around 8.2 during pH adjustment, and the amounts of acid input had to be









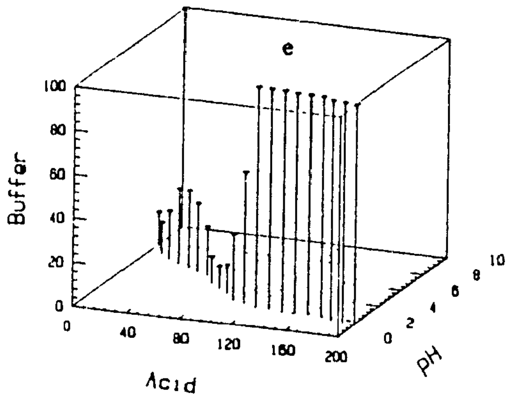


Figure 4.4 The relation of soil buffer capacity with acid input and soil suspension pH in . (4.4a) blank, (4.4b) kaolinite, (4.4c) illite, (4.4d) montmorillonite, and (4.4e) natural clay soil.

Notes ·
Buffer = Buffer capacity ($cmol\ \ H^{+}\ \ kg^{-1} soil\ \ pH^{-1}$)
Acid = Acid input ($cmol\ \ H^{+}\ \ kg^{-1} soil$)
pH = soil solution pH.

very high in order to exhaust the carbonates before producing any drop of the soil pH.

In the case of montmorillonite, the clay soil has a very high C.E.C. value but has little or no organic matter or carbonate content. Because of its high C.E.C., the resistance to pH changes in the montmorillonite can be explained by the adsorption of H^+ by cation exchange mechanisms. After the exchange sites are filled with H^+, the pH of soil suspension then begins to drop down. Farrah and Pickering (1979) found from experiments on H^+ uptake by pure clay suspensions that the amounts of H^+ uptake needed to lower the pH of clay suspensions down from 6.5 to 3 were greater for montmorillonite than for illite and kaolinite clays respectively. Their results showed that the montmorillonite clay suspension had higher resistance to pH changes than the illite clay suspension, i.e., 400 $mmolH^+ \cdot kg^{-1}$ were required to bring the pH of the montmorillonite clay suspension down from 6.5 to 3 whereas 150 $mmolH^+ \cdot kg^{-1}$ were required in the case of the illite clay suspension. However, it can be observed that although the illite used in this study has a lower C.E.C. value than the montmorillonite, it has a higher buffer capacity than montmorillonite. This means that carbonates present in the illite play an important role in buffering of the soil solution pH.

The natural clay soil, however, has much a lower C.E.C. than montmorillonite but does not show a much lower buffer capacity as might be expected from the C.E.C. alone. This is due to the presence of some amounts of soil constituents particularly carbonates. As mentioned above, carbonates play an important role in resisting a change of soil solution pH. Other soil constituents sush as organic matter and amorphous materials present in the natural soil have also been mentioned (e.g., Buckman and Brady, 1969) as being effective as buffering compounds in soil.

The kaolinite has a very low C.E.C. value, and does not have any significant amount of soil constituent in it, apart from its clay mineral. This results in its possessing the lowest buffer capacity among the four clay soils. In addition, it was found that at 0 acid input, the kaolinite suspension reduced the pH of the solution added from 7 to 4.5 (Fig. 4.1). Since kaolinite is a variable charge soil with a zero point of charge (ZPC) at pH of 4.2 (Yong and Ohtsubo, 1987), the addition of solutions with pH values above the ZPC could result in the situation where the soil tends to deprotonate or surrender H^+ from its edges, resulting thereby in a reduction of the soil solution pH.

The results of soil buffer capacity determination above show that the buffer capacity of the soils used in this study depends mainly on carbonate content and C.E.C. value. The illite has the highest buffer capacity due to its highest carbonate content. While montmorillonite does not have any significant amount of carbonates, it has the second highest buffer capacity because of its very high C.E.C. value. The natural clay soil has a lesser C.E.C. value and carbonate content than the illite, and thus shows a buffer capacity lower than that of the illite and montmorillonite – but still much higher than that of the kaolinite which has very low C.E.C. and no significant amount of any other soil constituent.

The differences in the buffer capacity of these clay soils would show interesting results in experiments on retention of heavy metals as they receive increasing amounts of acid. The following sections present the results and discussion of the experiments involved in the soil suspension study on heavy metal retention.

4.3 Soil Suspension Study on Heavy Metal Retention

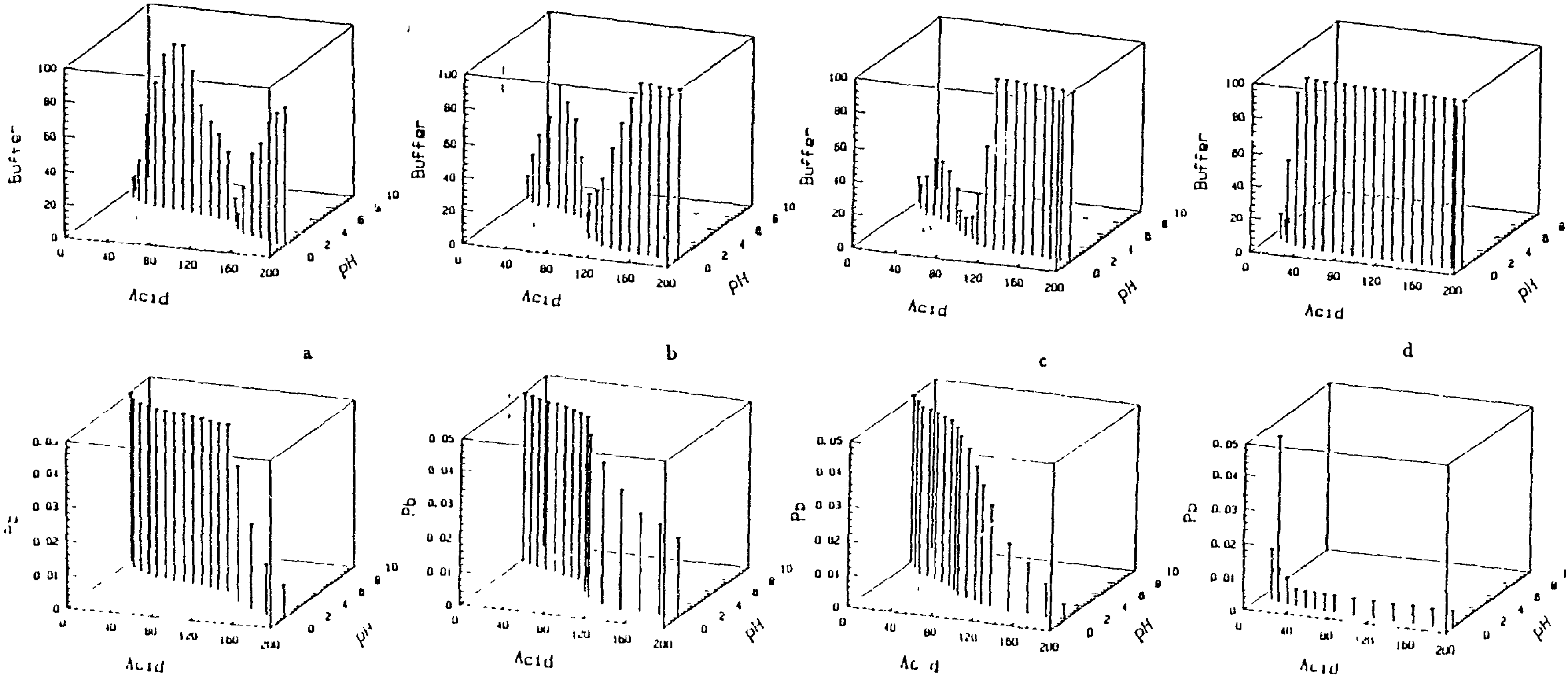
Several soil suspension tests were conducted to study heavy metal retention in the clay soils used as they received increasing amounts of acid. The first test used only Pb in the study (section 4.3.1). The other three tests used all four heavy metals, but were applied differently to the soils (sections 4.3.2, 4.3.3, and 4.3.4). The last test (section 4.3.4) includes the application of leachate to the soil suspension. Information is obtained not only on the relationship between the soil buffer capacity and the capacity of the clay soils to retain heavy metals, but also on the amounts and selectivity of the heavy metals retained as the soils receive increasing amounts of acid. The results and discussion on the four soil suspension tests are presented as follows :

4.3.1 Retention of Pb in Soil-Pb Solution

Three different concentrations of Pb, 5.0 x 10^{-5}, 5.0 x 10^{-4}, and 5.0 x 10^{-3} $mol \cdot L^{-1}$, equivalent to Pb applied to soil of 0.05, 0.5, and 5.0 $cmol \cdot kg^{-1} soil$, were applied to each of the four clay soils at increasing amounts of acid from 0-200 $cmol \quad H^{+} \cdot kg^{-1} soil$.

The relationship between the amounts of Pb retained in soil, the amounts of acid input, and the soil solution pH is illustrated in the three dimensional plots (Figs. 4.5a–4.5d), using the case of Pb applied to soil equal to 0.05 $cmol \cdot kg^{-1} soil$. In addition, the resulting plot of each clay soil is also compared with the three dimemsional plot of its buffer capacity in the same figures (Figs. 4.5a–4.5d).

It can be seen from Fig. 4.5a that high amounts of Pb (nearly 100% of Pb applied) were retained in illite as it received increasing amounts of acid until the amounts of acid input exceeded 120 $cmol \quad H^{+} \cdot kg^{-1} soil$, i.e., when the pH of the soil solution began to drop from 5. When the amounts of Pb retained are compared with the soil buffer capacity, it can be observed that the retention pattern of Pb in illite is closely related to



Notes :
Buffer = Buffer capacity ($cmol \quad H^{+} \quad kg^{-1} soil \cdot pH^{-1}$), Acid = Acid input ($cmol \quad H^{+} \quad kg^{-1} soil$),
pH = soil solution pH, and Pb = Amounts of Pb retained in soil ($cmol \cdot kg^{-1} soil$)

Figure 4.5 Comparison of soil buffer capacity and amounts of Pb retained as a function of acid input and soil solution pH at Pb applied of 0.05 $cmol \quad kg^{-1} soil$ in : (4.5a) illite, (4.5b) montmorillonite, (4.5c) natural clay soil, and (4.5d) kaolinite.

its buffer capacity pattern. It can be seen from the two graphs in Fig. 4.5a that when the buffer capacity begins to drop rapidly (at acid input of 120 $cmol \quad H^{+} \cdot kg^{-1} soil$), resulting in a drop of pH from 5 to 2, the amounts of Pb retained also decreases rapidly. The increase in buffer capacity of illite at low pH does not result in high amounts of Pb retained in the soil. This means that high amounts of Pb can be retained in illite, provided that the soil still has a high enough buffer capacity to resist changes in pH – so long as the pH remains above 5.

The same relationships were found for montmorillonite and natural clay soil as seen in Figs. 4.5b and 4.5c respectively. High amounts of Pb were retained until the buffer capacity of montmorillonite dropped when the acid input was 80 $cmol \quad H^{+} \cdot kg^{-1} soil$. In the natural clay soil, the amounts of Pb retained began to drop at 60 $cmol \quad H^{+} \cdot kg^{-1} soil$ when its buffer capacity was exhausted. It can also be noted here that the increase in the buffer capacity of the soils at low pH did not result in high amounts of Pb retained. In the case of kaolinite which has very low buffer capacity at high pH range ($pH > 4$), small amounts of Pb were retained (Fig. 4.5d). High buffer capacity of kaolinite at low pH ($pH < 4$) did not result in high amounts of Pb retained in the soil. It can be concluded here that high amounts of Pb can be retained in the clay soils used if the soil still has a high enough buffer capacity to resist a change in pH to not drop to < 5.

The differences in the retention of Pb in clay soils when higher concentrations of Pb were applied are investigated. The amounts of Pb retained in the clay soils at three different concentrations of Pb applied are plotted as a function of acid input as shown in Figs. 4.6a–4.6c. It can be seen from Figs. 4.6a–4.6c that the amounts of Pb retained in all the clay soils are higher with increasing concentrations of Pb applied. In addition, as the amounts of acid added increase, the amounts of Pb retained tend to decrease.

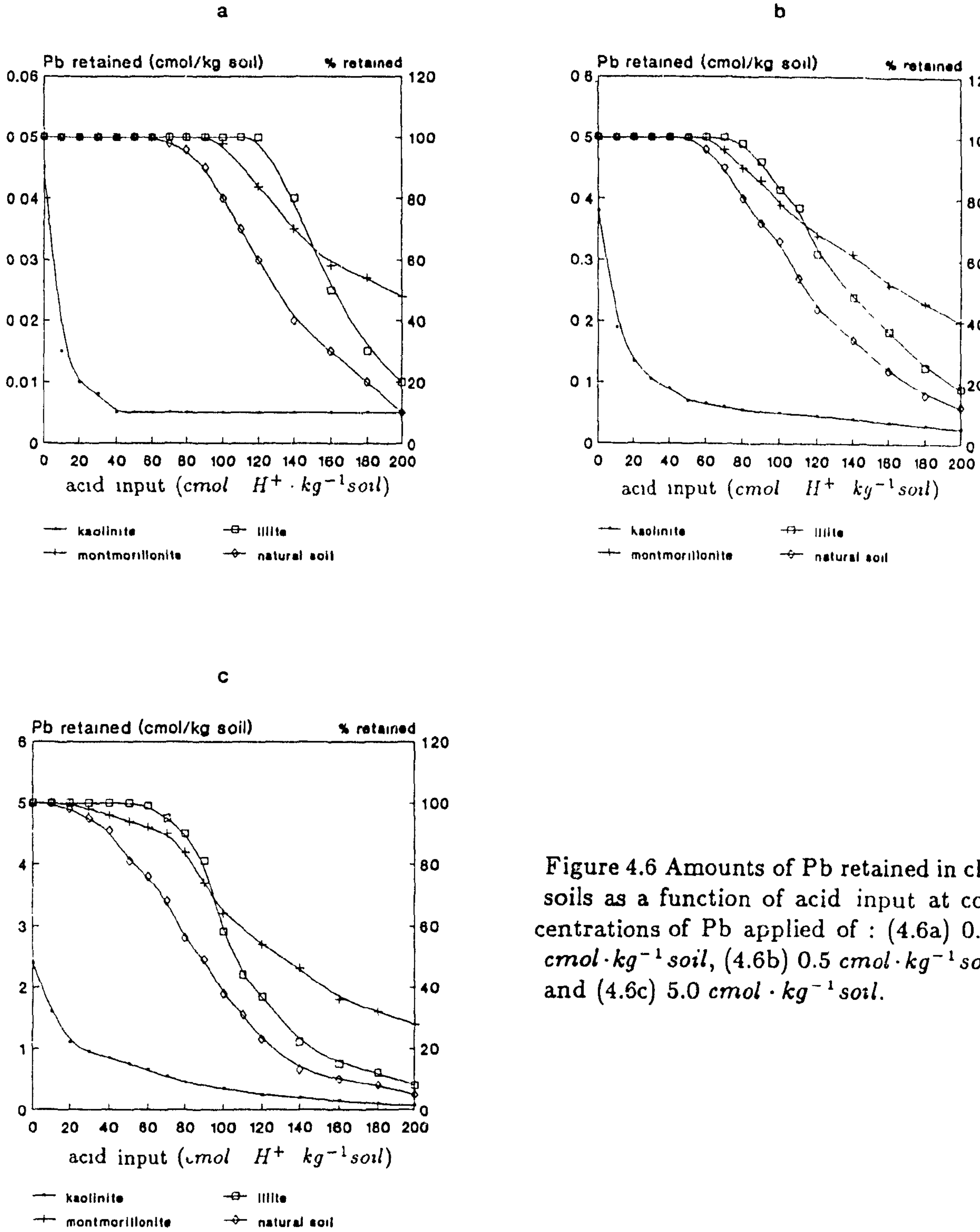
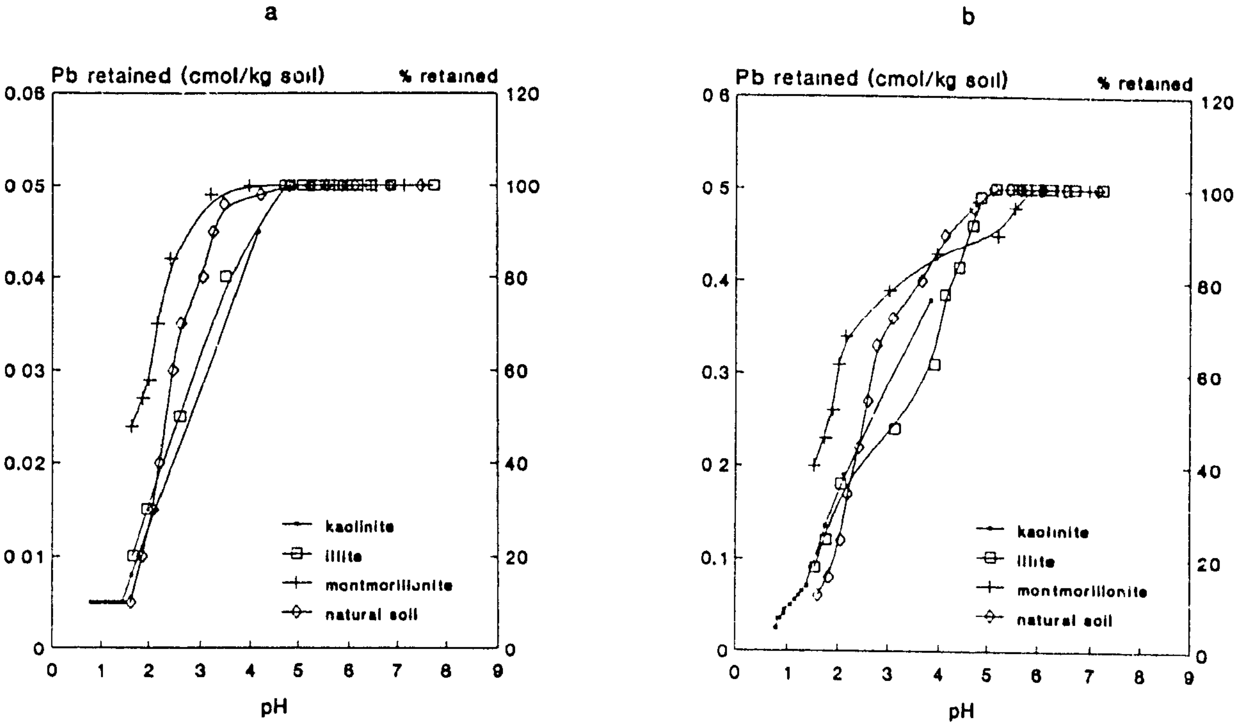


Figure 4.6 Amounts of Pb retained in clay soils as a function of acid input at concentrations of Pb applied of : (4.6a) 0.05 $cmol \cdot kg^{-1} soil$, (4.6b) 0.5 $cmol \cdot kg^{-1} soil$, and (4.6c) 5.0 $cmol \cdot kg^{-1} soil$.

The amounts of Pb retained in the four clay soils are different. In the case of kaolinite, the amounts of Pb retained is very much less than that of illite, montmorillonite, and natural clay soil. For illite, it is noted that illite retained higher amounts of Pb than natural clay soil throughout the range of acid input. On the other hand, illite retained higher amounts of Pb than montmorillonite for a certain range of acid input.

The amounts of Pb retained at different concentrations of Pb applied are also plotted with the equilibrium soil solution pH as shown in Figs. 4.7a–4.7c. The results show that the amounts of Pb retained increased with higher pH levels. When soil solution pH is > 5, 100% of Pb applied is retained in the soils whereas when soil solution pH is < 5 the amounts of Pb retained decrease rapidly. The amounts of Pb retained in montmorillonite when soil solution pH is < 5 are higher than in the other three soils.

The results correspond to the studies involving pure clays and natural soil clays by Farrah and Pickering (1977) and Maguire et al. (1981). Their results showed that at low pH (~ 2-4), Pb retention, as is true for most heavy metals, is by cation exchange with the difference being due to valence and ionic size. As the pH increases, soluble hydroxy species of Pb are formed and adsorbed onto the clay surface. When the pH exceeds the value required for formation of Pb hydroxides (> 5), retention is dominated by precipitation mechanisms which account for very high amounts of Pb being retained. In the partial precipitation region at intermediate pH (~ 4-6), various hydroxides species are formed, and retention of Pb by cation exchange and precipitation mechanisms is indistinguishable (Elliot et al., 1981). High amounts of Pb retained in soils at high pH could also be due to carbonates that are present in the soils. Yanful et al. (1988b) found in their experiments with carbonate-rich soil that when pH > 5.2, removal of heavy metals, and particularly Pb, increased significantly



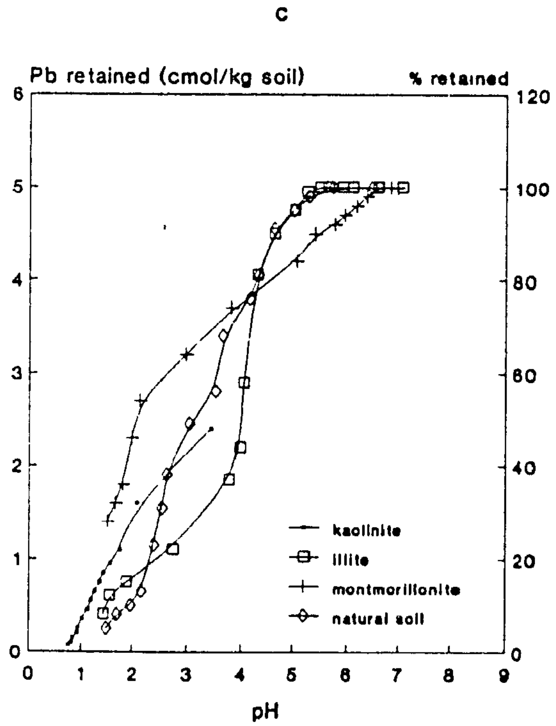


Figure 4.7 Amounts of Pb retained in clay soils as a function of soil solution pH at concentrations of Pb applied of : (4.7a) 0.05 $cmol \cdot kg^{-1} soil$, (4.7b) 0.5 $cmol \cdot kg^{-1} soil$, and (4.7c) 5.0 $cmol \cdot kg^{-1} soil$.

due to precipitation as carbonates.

It can be observed from Figs. 4.7a–4.7c that the retention curves of Pb in the clay soils as a function of varying concentrations of Pb applied and soil solution pH are similar. If the amounts of Pb retained in the soils are viewed in terms of pH dependency alone, the relation would not provide much information regarding the differences between Pb retention in each clay soil. The change in soil solution pH due to the amounts of acid input and the soil buffer capacity need to be considered in the investigation of the retention capacity of soils for Pb.

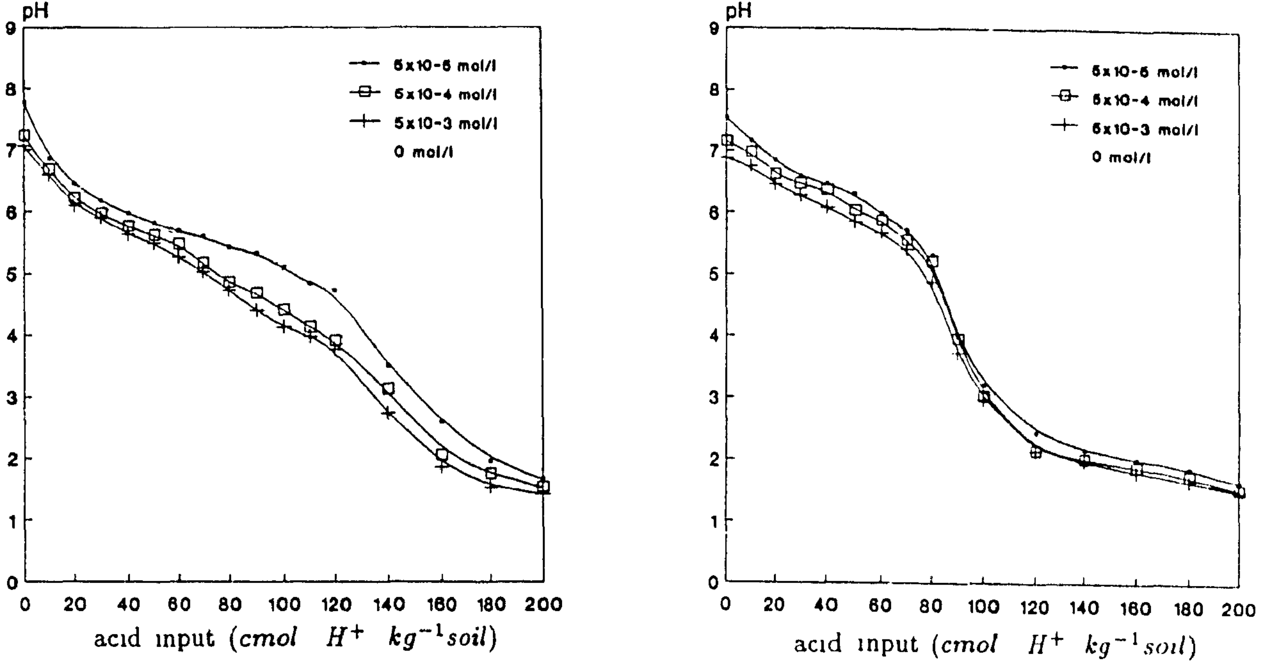
Figs. 4.8a, 4.8b, 4.8c, and 4.8d show the change in equilibrium pH of the soil solutions as a function of acid input after different concentrations of Pb were applied to illite, montmorillonite, natural clay soil, and kaolinite respectively. It can be seen from Fig. 4.8a that the higher the concentration of Pb applied in illite, the lower the resultant pH curves. All curves are obviously lower than the 0 $mol \cdot L^{-1}$ Pb added, i.e., the titration curve of the blank shown in Fig. 4.1. This observation can also be seen in Figs. 4.8b, 4.8c, and 4.8d in the case of montmorillonite, natural clay soil, and kaolinite. The reduction in pH of the soil solution with increasing additions of Pb could be due to the fact that the higher the concentration of Pb in the solution, the higher will be the concentration of H^+ obtained due to hydrolysis of Pb^{2+} in water, according to the following equation :

$$Pb^{2+}(aq) + nH_2O \rightleftharpoons Pb(OH)_n^{2-n} + nH^+. \tag{4.1}$$

This effect can be observed from the reduction in the pH of $Pb(NO_3)_2$ solution at higher concentrations of Pb prepared before adding to the soils. The pH reduced from 4.8 to 4.7 and to 4.6 for concentrations of Pb solutions of 5.0 x 10^{-5}, 5.0 x 10^{-4}, and 5.0 x 10^{-3} $mol \cdot L^{-1}$ respectively.

a
illite

b
montmorillonite



c
natural clay soil

d
kaolinite

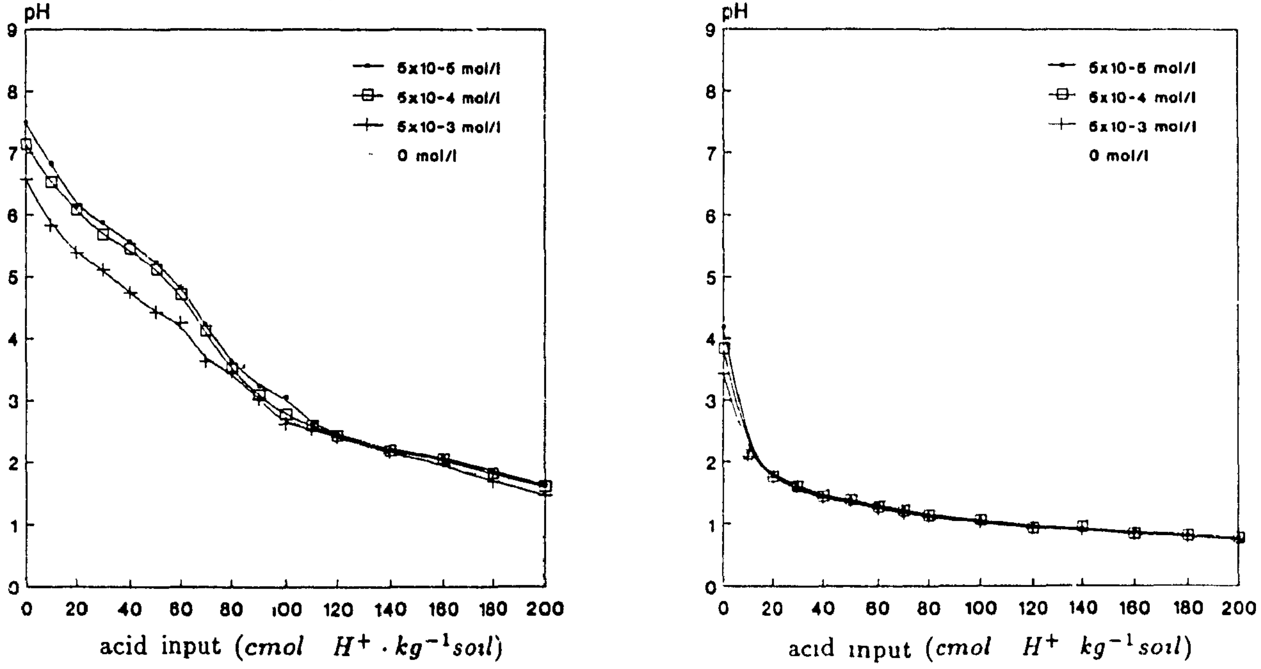


Figure 4.8 Equilibrium soil solution pH versus acid input at different concentrations of Pb applied in : (4.8a) illite, (4.8b) montmorillonite, (4.8c) natural clay soil, and (4.8d) kaolinite.

Another cause of the pH reduction of the soil solutions could be the competition of Pb ion species and H^+ for adsorption sites. Since Pb has a higher affinity than H^+ (Bohn, 1979), the higher the concentration of Pb applied, the higher will be the H^+ remaining in the solution. These effects indicate that the presence of Pb in the solution applied could affect the buffer capacity of the soils and also result in a reduction of the equilibrium soil solution pH.

From the results shown in Figs. 4.8a–4.8d and Figs. 4.6a–4.6c, it is noted that illite can retain higher amounts of Pb than the other clay soils. The amounts of Pb retained are as high as 100% of Pb applied when the amount of acid input does not exceed 120 $cmol \quad H^+ \cdot kg^{-1} soil$ for Pb applied at 5.0 x 10^{-5} $mol \cdot L^{-1}$. In comparison with the equilibrium pH of the illite suspension in Fig. 4.8a, when the value of acid added does not exceed 120 $cmol \quad H^+ \cdot kg^{-1} soil$, the pH values (at Pb applied of 5.0 x 10^{-5} $mol \cdot L^{-1}$) still remain high enough (> 5) for Pb to be retained in the soil by precipitation mechanisms. Beyond these values of acid input, the pH of the soil suspension decreases, resulting thereby in a change of the dominant retention mechanism, from precipitation to another mechanism such as cation exchange. This causes the rapid reduction in the amounts of Pb retained as the amounts of acid input exceed the value cited. The Pb retention curve of illite thus corresponds to its soil buffer capacity curve as previously shown by the three dimensional plots shown in Fig. 4.5a above.

However, when the concentrations of Pb applied to illite increased (0.5 and 5.0 $cmol \cdot kg^{-1} soil$), the soil retained Pb as high as 100% within the smaller range of acid input (0-80 and 0-60 $cmol \quad H^+ \cdot kg^{-1} soil$). After that range, the amounts of Pb retained decreased rapidly. This could be due to the decrease in the soil solution pH at higher concentration of Pb applied as described above.

For Pb retention in montmorillonite (Figs. 4.6a–4.6c), the amounts of Pb retained were as high as 100% until the amount of acid input exceed 100, 60, and 30 $cmol \quad H^+ \cdot kg^{-1} soil$ at Pb applied of 0.05, 0.5, and 5.0 $cmol \cdot kg^{-1} soil$ respectively. Beyond these points (i.e., amounts of acid input), the amounts of Pb retained decreased slowly but were higher than the amounts of Pb retained in illite at higher ranges of acid input. This is because montmorillonite has a higher C.E.C. value than illite. At the higher ranges of acid input, the decrease in pH of the soil suspension means that cation exchange is the more likely adsorption mechanism. The high C.E.C. value of montmorillonite helps it retain higher amounts of Pb than illite as the soil solution pH decreases.

In the case of the natural clay soil, characteristics similar to those of illite for the retention pattern of Pb are demonstrated. The principal difference is that the 100% of Pb retained occurred within a smaller range of acid input, i.e., when the amount of acid did not exceed 60, 50, and 30 $cmol \quad H^+ \quad kg^{-1} soil$ for Pb applied of 0.05, 0.5, and 5.0 $cmol \cdot kg^{-1} soil$ respectively. The amounts of Pb retained beyond these acid values are also lower, probably due to the fact that the natural clay soil has a lower C.E.C. value than illite, as shown in Table 4.1.

In the case of kaolinite, the amount of Pb retained is very much less than that in the other three soils, not only at the onset of acid input, but throughout the entire sequence of acid input. This is because the equilibrium pH of the soil suspension (Fig. 4.8d) is less than that required for precipitation of lead hydroxide (precipitation pH value of 5 as cited by Farrah and Pickering, 1977). Precipitation as a mechanism which can result in higher amounts of Pb retained in soil cannot be counted as a dominant mechanism for Pb retention in kaolinite. Instead, it would appear that the most likely retention mechanism is via cation exchange. The C.E.C. value of kaolinite is low compared to the others, as seen in Table 4.1. The amount of Pb retained, moreover, is far less than its C.E.C. and becomes gradually lower as the amount of acid increases. This is consistent with the situation where under low pH, Al is dissolved from the crystal structure and adsorbed on exchange sites (Bolland et al., 1980), thus blocking the adsorption of Pb on kaolinite as pH decreases.

The experimental data of all the graphs that are plotted in Figs. 4.5–4.8 are provided in Tables A-4 to A-7 in Appendix A.

The above results and discussion on Pb retention could be summarized here as follows :

(i) The soil buffer capacity is related directly with the capacity of the soil to retain Pb. As the clay soils receive increasing amounts of acid, high amounts of Pb can still be retained if the soil retains a sufficiently high buffer capacity to resist a change in pH – such that it will not drop to a low pH value where precipitation cannot occur.

(ii) Pb can be retained, as much as 100%, for a larger range of acid input in illite than in montmorillonite and natural clay soil due to its higher buffer capacity. Kaolinite has a very low capacity for retention of Pb.

(iii) It was also found that high concentrations of Pb applied to soils can affect the soil buffer capacity, resulting in a lower percentage of Pb retained in soils than when Pb is applied at low concentrations.

(iv) The results show that the relation of the amounts of Pb retained and pH alone cannot fully explain the differences in Pb retention in clay soils without consideration of the amounts of acid involved and the resistance of soil to pH change, i.e., without considering the concept of soil buffer capacity.

In addition to the relation of soil buffer capacity and Pb retention found above, the relation may also be applicable to other heavy metals such as Cu, Zn, and Cd since these heavy metals have similar pH-retention curves in soils (Maguire et al., 1981). In the next section, the results and discussion on Pb, Cu, Zn, and Cd retention in clay soils are presented.

4.3.2 Retention of Heavy Metals in Soil-Heavy Metal Solution

The solutions of Pb, Cu, Zn, and Cd at a concentration of 1.0 x 10^{-3} $mol \quad L^{-1}$ were separately applied to each of the four clay soils at increasing amounts of acid from 0 to 200 $cmol \quad H^{+} \quad kg^{-1} soil$. The amount of heavy metal applied to soil is equivalent to 1.0 $cmol \cdot kg^{-1} soil$ in every case.

In order to compare the amounts of heavy metals retained in all the clay soils, the amounts of Pb, Cu, Zn, and Cd retained in the soils are plotted with increasing amounts of acid input, as shown in Figs. 4.9a–4.9d, and with soil solution pH, as shown in Figs. 4.10a–4.10d. It can be seen from Figs. 4.9a–4.9d that as the amounts of acid increase, the amounts of heavy metals retained in soils tend to decrease. In the case of Pb retention in soils (Fig. 4.9a), the resultant curves are similar to those obtained in the previous section (see Figs. 4.6a–4.6c). Retention curves of Cu (Fig. 4.9b) are similar to the Pb retention curves, however, the amounts retained are a little less than in the case of Pb. The retention curves of Zn are similar to the retention curves of Cd (Figs. 4.9c–4.9d). It can be clearly seen from Figs. 4.9c–4.9d and Figs. 4.9a–4.9b that the amounts of Zn and Cd retained in the soils are less than the amounts of Pb and Cu retained particularly in illite and natural clay soil. The retention curves of the heavy metals in montmorillonite decrease slowly compared to the retention curves in the other clay soils which show that the amounts of heavy metals retained in montmorillonite are higher than in the other soils as the amounts of acid increase.

When the amounts of heavy metals retained are plotted with soil solution pH in Figs. 4.10a–4.10d, it is found that the amounts of all the heavy metals retained increases with increasing soil solution pH. Nearly 100% of heavy metals applied (1 $cmol \cdot kg^{-1} soil$) is retained when soil solution pH is $\geq$ 5 and 5.5 for Pb and Cu and

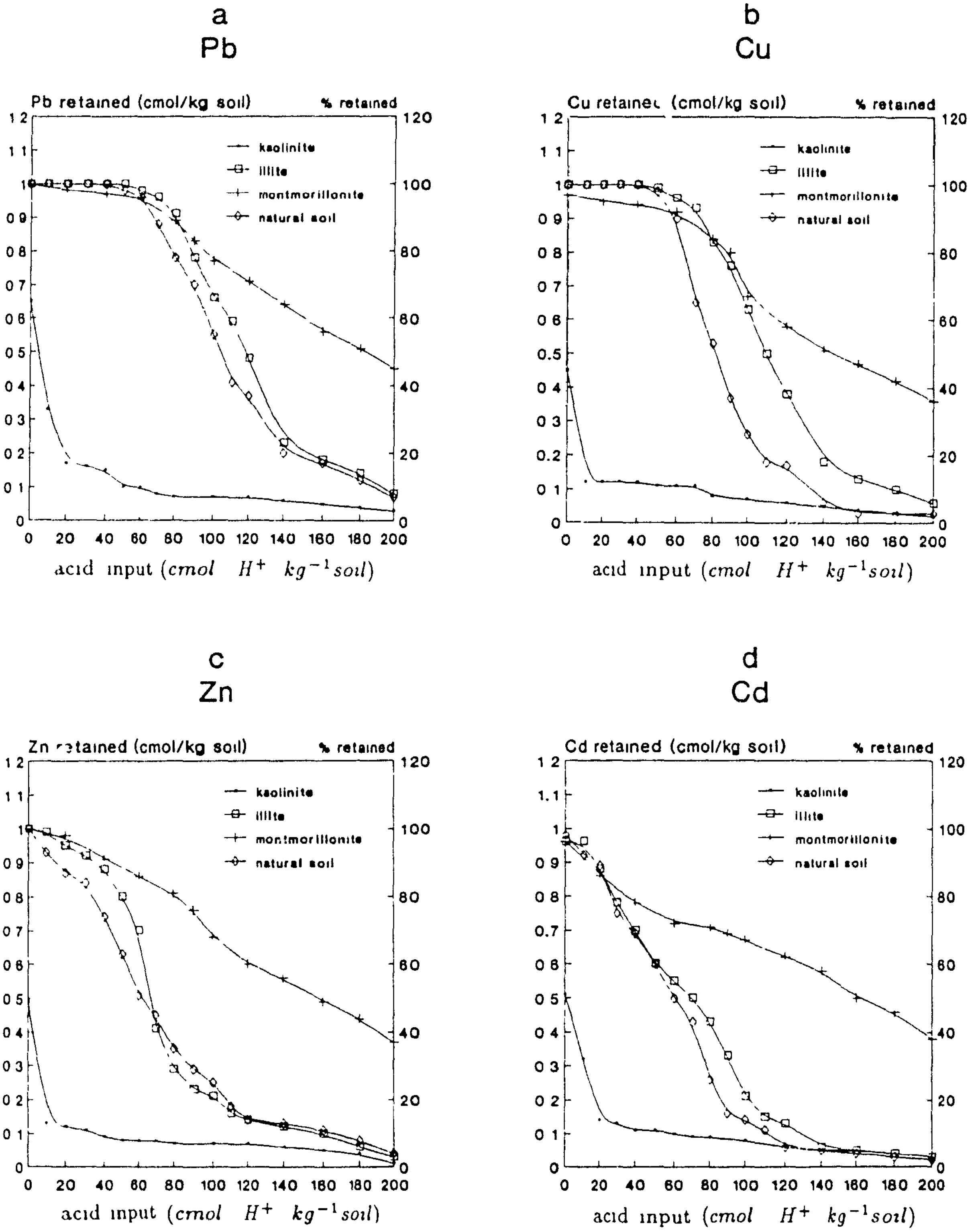


Figure 4.9 Amounts of heavy metals retained in kaolinite, illite, montmorillonite, and natural clay soil at increasing amounts of acid input for : (4.9a) Pb, (4 9b) Cu, (4.9c) Zn, and (4.9d) Cd when heavy metals were applied separately.

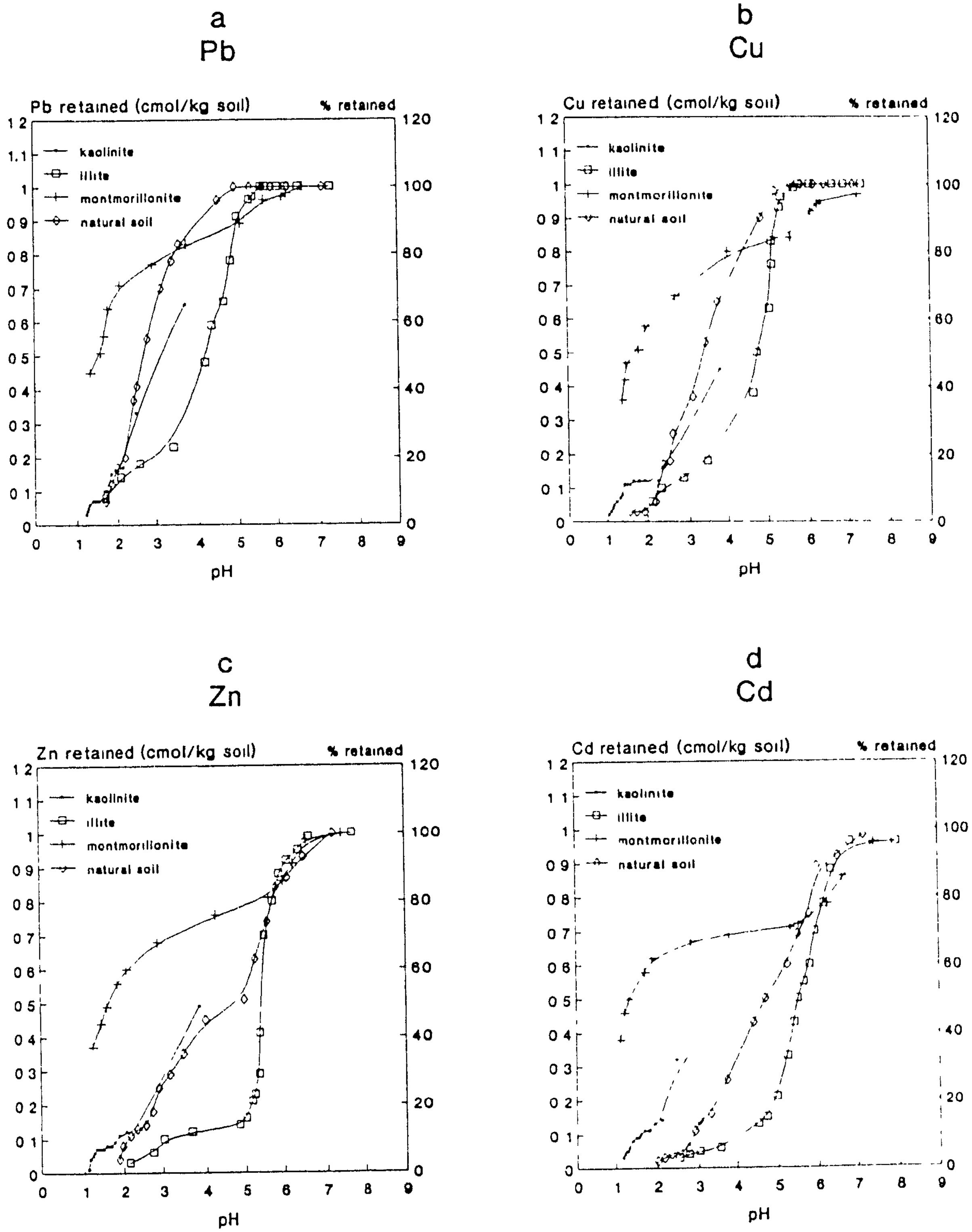


Figure 4.10 Amounts of heavy metals retained in the kaolinite, illite, montmorillonite, and natural clay soil as a function of soil solution pH for : (4.10a) Pb, (4.10b) Cu, (4.10c) Zn, and (4.10d) Cd when heavy metals were applied separately.

$\geq$ 7 and 7.5 in the case of Zn and Cd for the same results. The results correspond to the results from the study on influence of pH on heavy metal uptake in soil clays by Maguire et al. (1981).

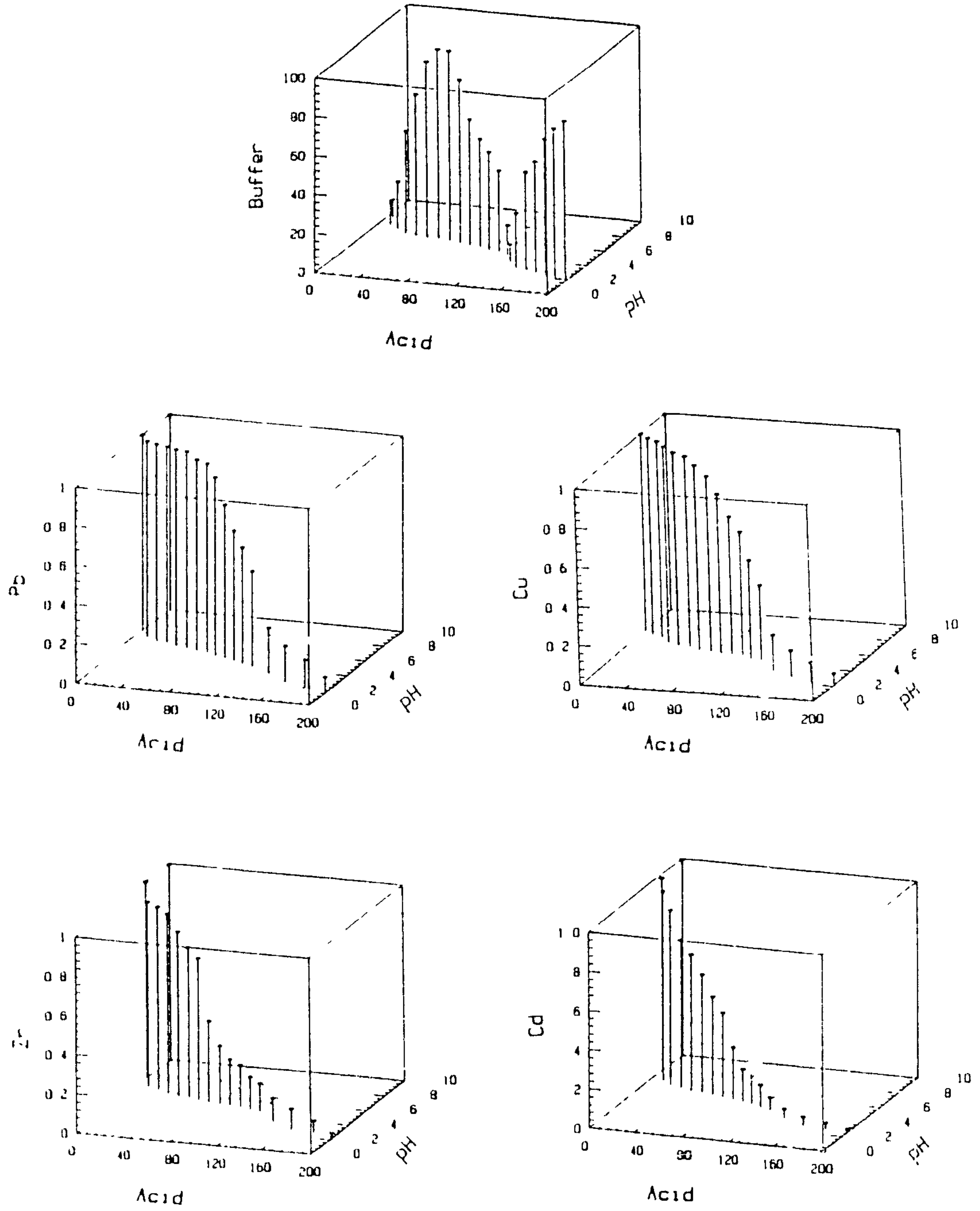
The amounts of heavy metals retained in illite and natural clay soil at high pH are about the same but a little less in the case of montmorillonite (Figs. 4.10a–4.10d). After those pH values (pH 5, 5.5, 7, and 7.5) the amounts of heavy metals retained dropped; the amounts of Pb and Cu retained are higher in montmorillonite than in natural clay soil, kaolinite, and illite respectively. On the other hand the amounts of Zn and Cd retained are higher in montmorillonite than in kaolinite, natural clay soil, and illite respectively.

In the case of kaolinite, it can be observed that the retention curves of kaolinite in Figs. 4.10a–4.10d are short, and end only at pH around 4. This is because when heavy metal-acid solutions were added into kaolinite which had initial pH around 4, the change in the soil solution pH only went downward in a lower pH direction. Therefore, the heavy metal retention curves in the case of kaolinite appeared only up to pH 4 when amounts of heavy metals retained are plotted with the soil solution pH. In order to extend the curves, a base has to be added instead of acid. This will make the kaolinite suspension system different from the others. This is beyond the scope of this study since this research is focused only on the titration of soils in the acid direction.

One can observe that the results of heavy metal retention in the clay soils are apparently different when they were plotted differently. For example, the amounts of heavy metals retained in illite when plotted with amounts of acid input (Fig. 4.9) are higher than those for kaolinite but become lower when plotted with soil solution pH (Fig. 4.10). If the results of heavy metal retention in the soils are shown by plotting with soil solution pH alone, it would appear as if illite has a lower capacity to retain heavy metals than kaolinite does. In fact, when kaolinite and illite received the same amounts of acid, illite retained higher amounts of heavy metal than kaolinite did (Fig. 4.9).

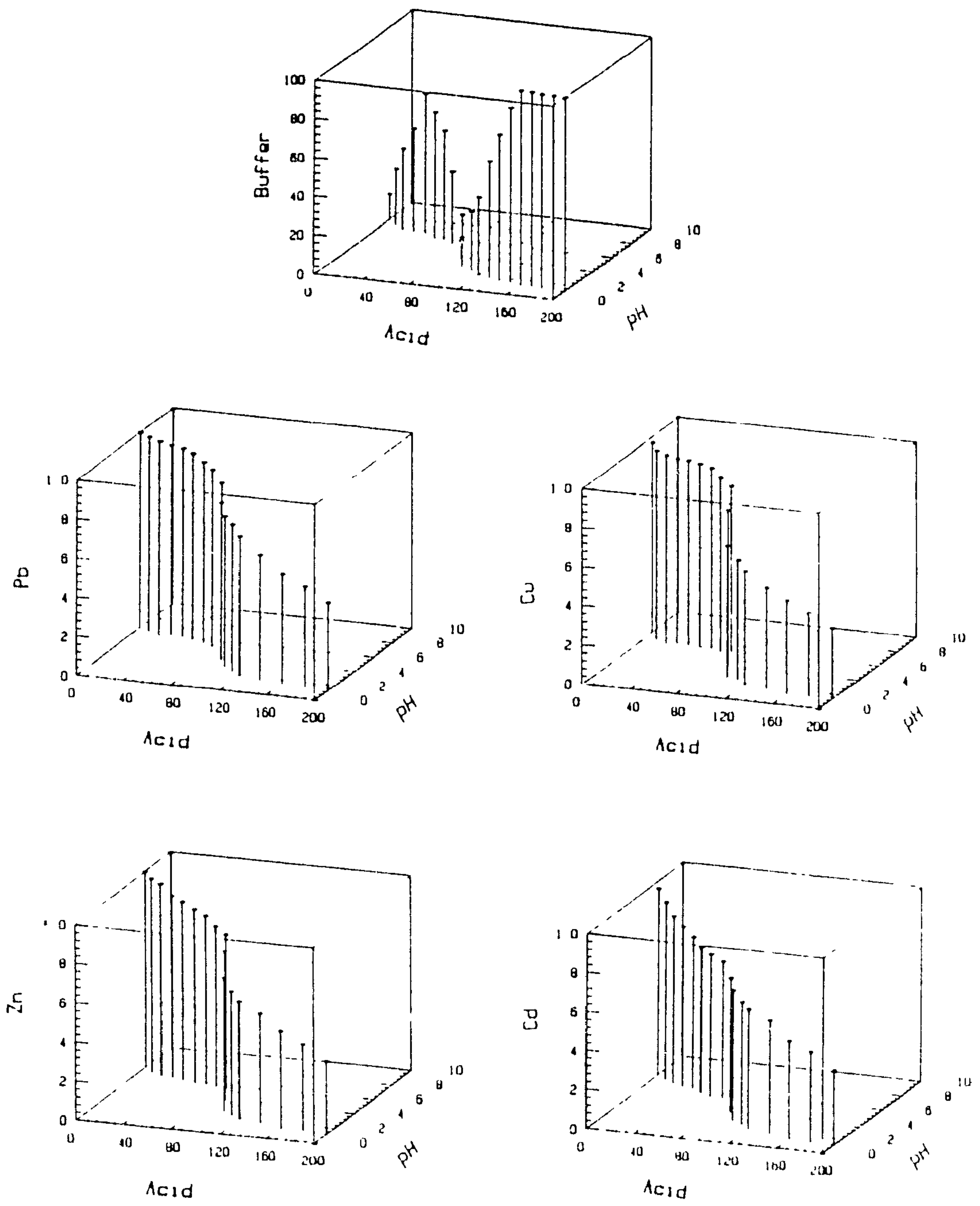
Since the method of data presentation should not change the physical property and response performance of the material, it is clear that if proper interpretations are to be made, the various parameters which participate in the relationship which describe the physical property need to be accounted for. Thus, it can be seen here that if pH control is only considered, the relation of the amounts of heavy metals retained cannot account for the differences observed in respect to heavy metal retention in the clay soils used. In this case the differences in the change of the soil solution pH due to the amounts of acid input (i.e., the soil buffer capacity) have also to be considered along with the retention of heavy metals in the soils.

The overall results of Pb, Cu, Zn, and Cd retention in illite, montmorillonite, natural clay soil, and kaolinite can be compared with the soils' buffer capacity in order to observe the relation of heavy metal retention in the soils and the soil buffer capacity. The buffer capacity and the heavy metal retention curves of each soil are presented as a function of both acid input and soil solution pH in the three dimensional plots for illite, montmorillonite, natural clay soil, and kaolinite respectively (Figs. 4.11a–4.11d). It can be generally seen from all four figures that the retention of heavy metals in the soils is closely related to the soil buffer capacity. High amounts of heavy metals are retained in the soils if the soil buffer capacity still remains high. As the soil buffer capacity decreases, the amounts of heavy metals retained also decrease. The relation is clearly seen in the case of Pb and Cu. In the case of Zn and Cd, the amounts retained drop more quickly than for Pb and Cu. It can be observed from Figs. 4.11a–4.11d that as the soils receive increasing amounts of acid, nearly 100% of heavy metals can



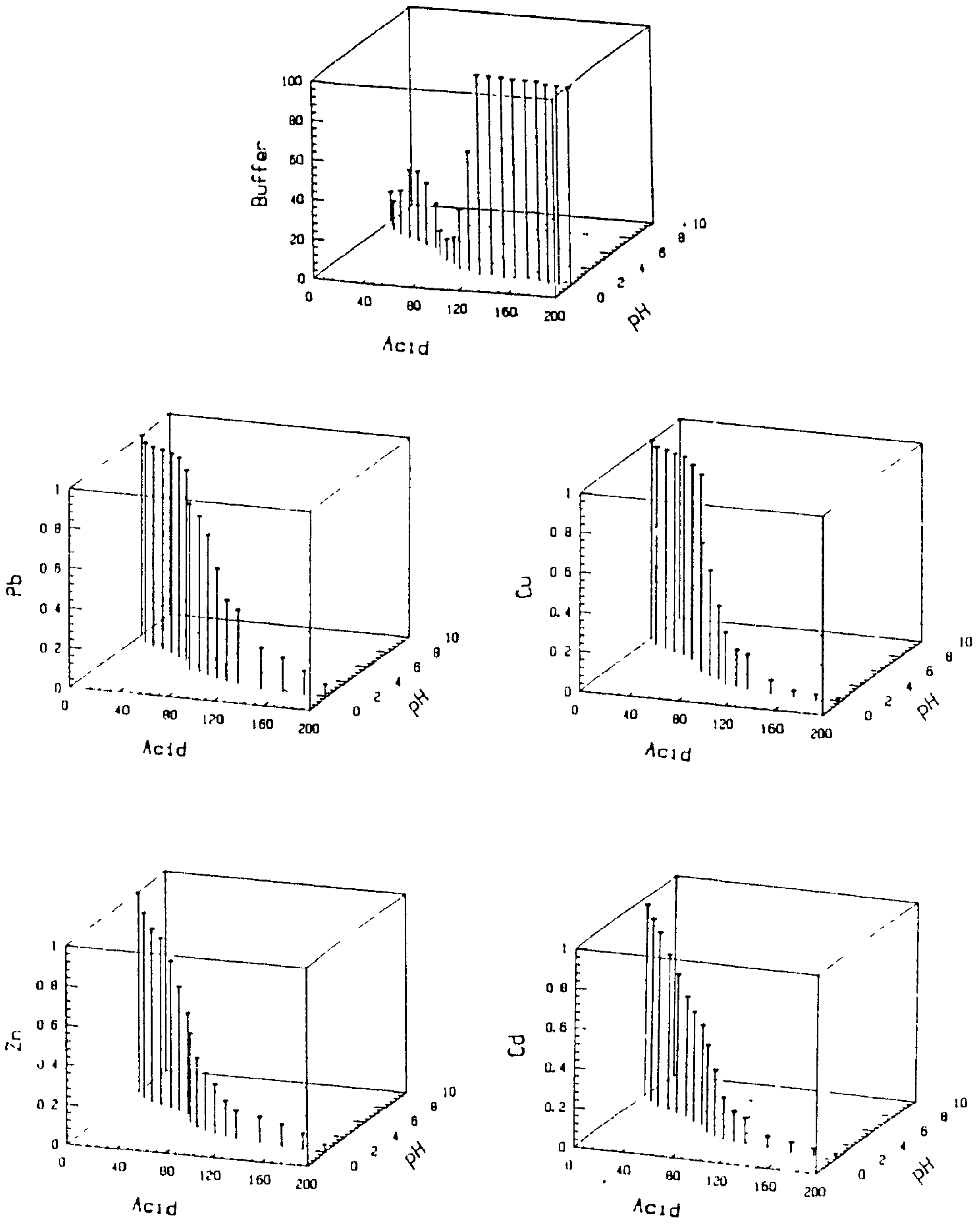
Notes :
Buffer = Buffer capacity ($cmol\ \ H^{+} \cdot kg^{-1} soil\ \ pH^{-1}$), Acid = Acid input ($cmol\ \ H^{+}$ $kg^{-1} soil$),
pH = soil solution pH, and Pb, Cu, Zn, and Cd = Amounts of Pb, Cu, Zn, and Cd retained in soil ($cmol\ \ kg^{-1} soil$).

Figure 4 11a Comparison of buffer capacity and amounts of heavy metals (Pb, Cu, Zn, and Cd) retained in illite as a function of acid input and soil solution pH in three dimensional plots.



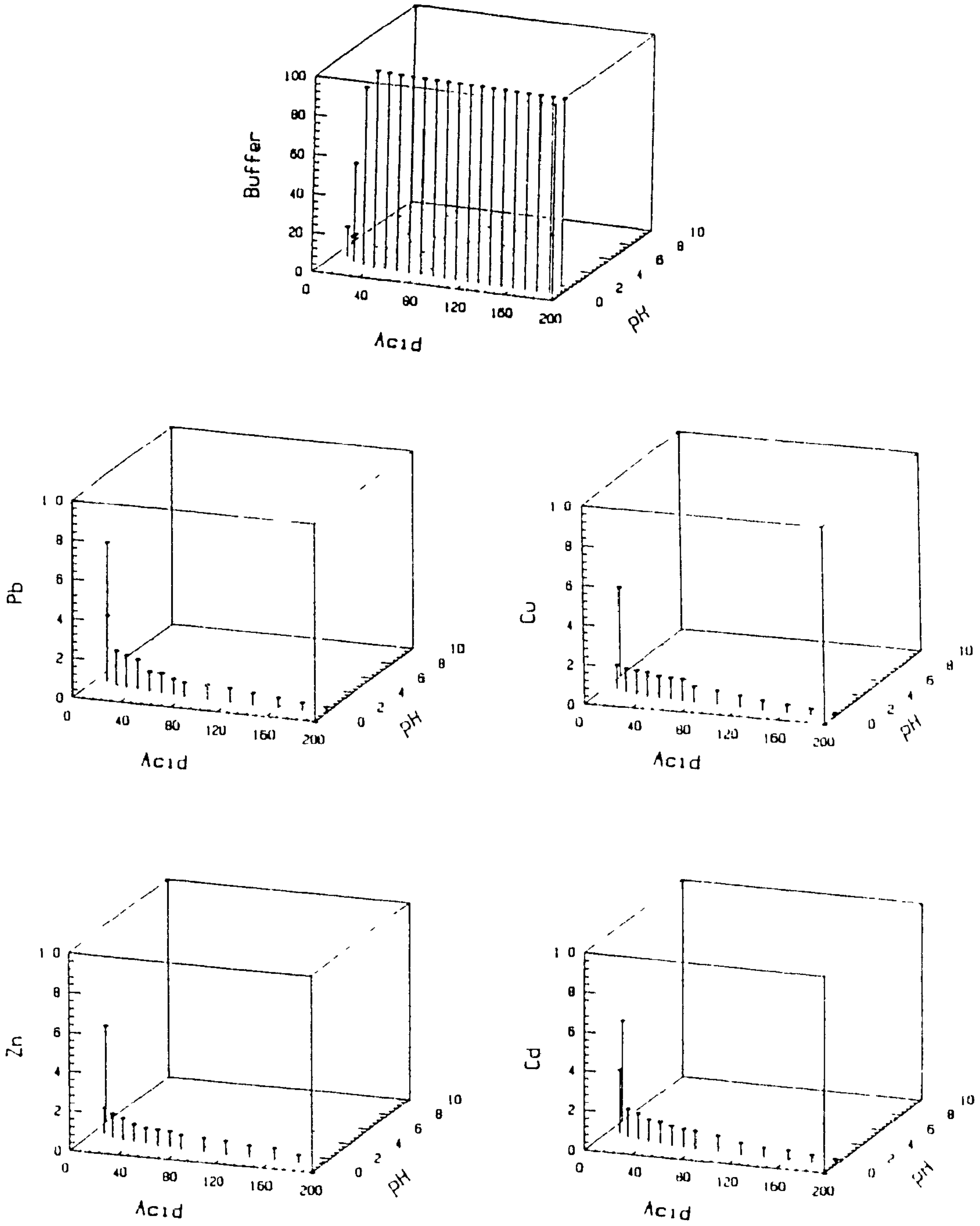
Notes :
Buffer = Buffer capacity ($cmol \quad H^+ \cdot kg^{-1} soil \quad pH^{-1}$), Acid = Acid input ($cmol \quad H^+ \; kg^{-1} soil$),
pH = soil solution pH, and Pb. Cu, Zn, and Cd = Amounts of Pb, Cu, Zn, and Cd retained in soil ($cmol \cdot kg^{-1} soil$).

Figure 4.11b Comparison of buffer capacity and amounts of heavy metals (Pb, Cu, Zn and Cd) retained in montmorillonite as a function of acid input and soil solution pH in three dimensional plots.



Notes .
Buffer = Buffer capacity ($cmol \quad H^{+} \cdot kg^{-1} soil \cdot pH^{-1}$), Acid = Acid input ($cmol \quad H^{+} \cdot kg^{-1} soil$),
pH = soil solution pH, and Pb, Cu, Zn, and Cd = Amounts of Pb, Cu, Zn, and Cd retained in soil ($cmol \cdot kg^{-1} soil$).

Figure 4.11c Comparison of buffer capacity and amounts of heavy metals (Pb, Cu, Zn, and Cd) retained in natural clay soil as a function of acid input and soil solution pH in three dimensional plots



Notes .
Buffer = Buffer capacity ($cmol\ \ H^{+} \cdot kg^{-1} soil \cdot pH^{-1}$), Acid = Acid input ($cmol\ \ H^{+}$ $kg^{-1} soil$),
pH = soil solution pH, and Pb, Cu, Zn, and Cd = Amounts of Pb, Cu, Zn, and Cd retained in soil ($cmol \cdot kg^{-1} soil$).

Figure 4 11d Comparison of buffer capacity and amounts of heavy metals (Pb, Cu, Zn, and Cd) retained in kaolinite as a function of acid input and soil solution pH in three dimensional plots.

be retained if the soil buffer capacity still remains high enough to resist a change in pH, so long as it does not drop to less than 5 in the case of Pb and Cu and less than 7 in the case of Zn and Cd. It can also be observed from the comparison that the high buffer capacity of soils when the soil solution pH is lower than 4, does not result in high amounts of heavy metals retained. This indicates that a high soil buffer capacity at low pH cannot contribute to high retention of heavy metals in the soil. As mentioned in section 4.2, a high buffer capacity of soil at low pH does not indicate a correspondingly high buffer capacity of the system. The results show that a high buffer capacity of soil is important for heavy metal retention when the pH of the soil is high. The comparison between the three dimensional plots of the buffer capacity and the retention of heavy metals in the clay soils used in this study (Figs. 4.11a–4.11d) show that a high soil buffer capacity can contribute to high retention of heavy metals when the soil solution is at pH 4-8.

It is noted here that heavy metal retention in the soils can be compared with soil buffer capacity because they have the same x-y plane of the pH-acid relations (Figs. 4.11a–4.11d). These pH-acid relations are the results of the resistance of the soils to pH change (the soil buffer capacity) as the soils receive increasing amounts of acid. In addition, the patterns of heavy metal retention in the soils are the results of these pH-acid relations. Therefore, it can be concluded here that the pH-acid titration of soil, which was obtained from the experiment, can be used as a representation of the soil buffer capacity for prediction of the retention of heavy metals in the soils tested.

Figs. 4.12a–4.12d show the relationship of the equilibrium soil solution pH (after the heavy metal solutions were applied to soils) versus the amounts of acid input, i.e., the pH-acid titration curves of the soils after heavy metals were applied. In the case of illite the pH-acid curves resemble the titration curve of illite (Fig. 4.12a). From

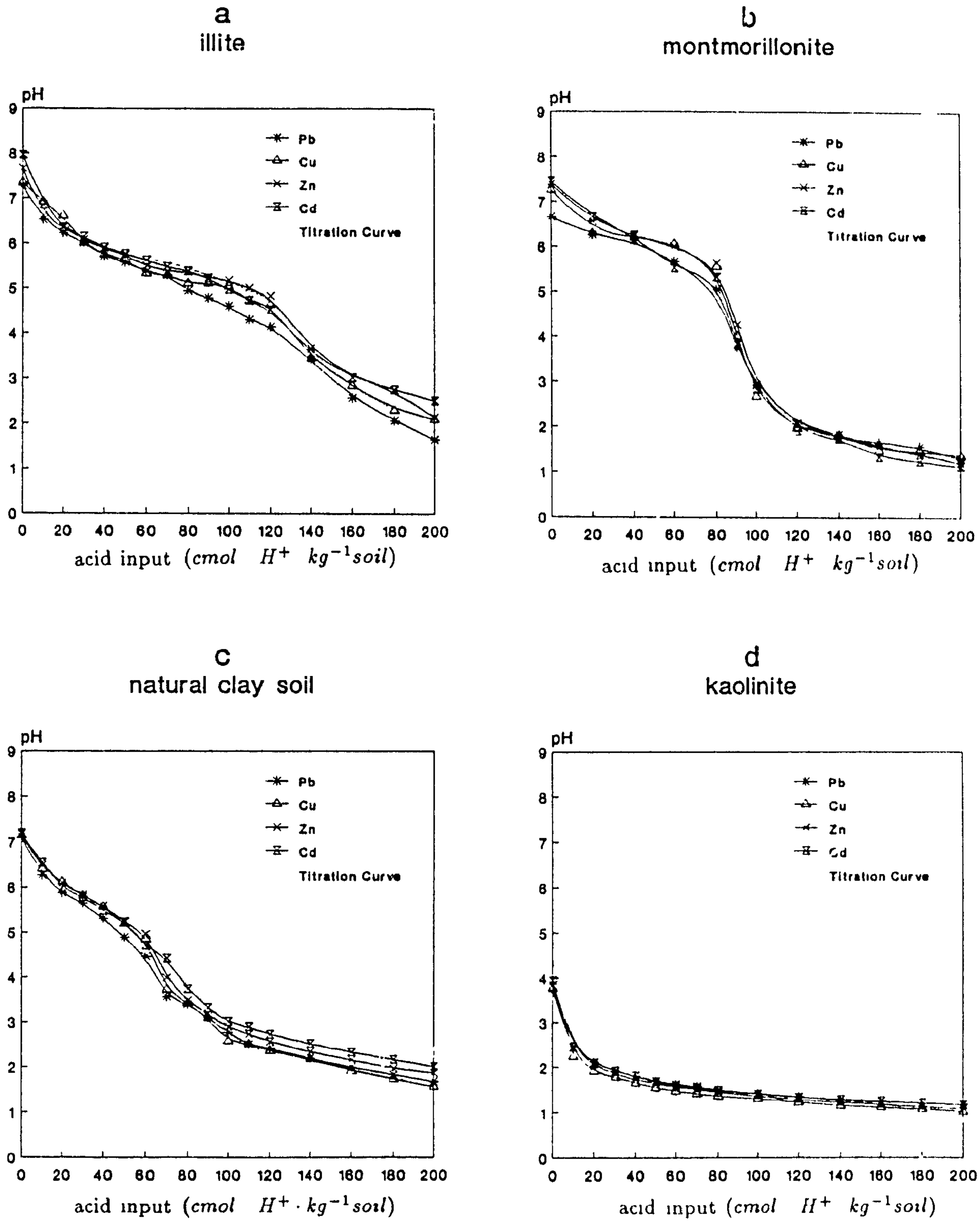


Figure 4.12 Equilibrium soil solution pH (after heavy metals were applied separately) as a function of acid input for : (4.12a) illite, (4.12b) montmorillonite, (4.12c) natural clay soil, and (4.12d) kaolinite.

the retention curves of heavy metals in illite as a function of pH (Figs. 4.10a–4.10d) it is expected, from the pH-acid titration curves of illite (Fig. 4.12a), that illite would retain high amounts of heavy metals for a large range of acid input before the amounts of heavy metals retained begins to decrease. Fig. 4.9a shows that illite can retain as high as 100% of Pb when the amounts of acid input does not exceed 80 $cmol \cdot kg^{-1} soil$. This is the amount of acid input where pH of the soil solution begins to drop to less than 5 (Fig. 4.12a). This pH value is the pH that the amounts of Pb retained begins to be as high as 100% of Pb applied (Fig. 4.10a). The same result is obtained for Cu retention in illite but 100% of Cu retained is at ≤ 70 $cmol \cdot kg^{-1} soil$ and at pH ≥ 5.5. In the case of Zn and Cd, it can be observed that solution pH of illite drops from 8 to less than 7 at the beginning of the curves (Fig. 4.12a). As mentioned earlier nearly 100% of Zn and Cd can be retained if soil solution pH is still ≥ 7 and 7.5 respectively (Figs. 4.10c and 4.10d). Therefore, the results show that nearly 100 % of Zn and Cd retention is only at the begining of acid input, and that the amounts retained decreases rapidly (Figs. 4.9c and 4.9d).

In the case of heavy metal retention in montmorillonite, it would be expected from the curves in Fig. 4.12b, that the soil would retain high amounts of heavy metals within the same range of acid input as in the natural clay soil. This is true for the retention of Pb and Cu as seen in Figs. 4.9a and 4.9b respectively. However, it is shown in Figs. 4.9c and 4.9d that the amounts of Zn and Cd retained in montmorillonite are higher than in the other soils. This could be due to the very high C.E.C. of montmorillonite which permits it to retain high amounts of Zn and Cd.

In the case of the natural clay soil, the titration curves (Fig. 4.12c) show a similar trend to the curves of illite (Fig. 4.12a) but the soil solution pH begins to drop at a smaller range of acid. This results in the drop of amounts of Pb, Cu, and Zn retained in the natural clay soil at smaller range of acid input than in illite as seen in Figs. 4.9a–4.9c. However, there are not many differences in the amounts of Cd retained in both soils as seen in Fig. 4.9d. This could be due to higher content of organic matter in the natural clay soil than in illite. The presence of organic matter in soils can help retain heavy metals, particularly Cd (Tyler and McBride, 1982).

As noted from the results, the solution pH of kaolinite was very low (Fig. 4.12d) compared to the soil solution pH of the other soils (Figs. 4.12a-4.12c). The curve resembles the pH-acid titration curve of kaolinite. This low pH resulted in low amounts of heavy metals retained in kaolinite (Figs. 4.9a–4.9d) and small retention curves of heavy metals when the amounts of heavy metals retained are plotted with the soil solution pH (Figs. 4.10a–4.10d).

When the amounts of heavy metals retained within the same soil are plotted with increasing amounts of acid input (Figs. 4.13a–4.13d) and with soil solution pH (Figs. 4.14a–4.14d), the affinity or selectivity orders of the heavy metals retention in the soils can be obtained.

In the case of illite, the selectivity order follows Pb>Cu>>Zn≈Cd (Figs. 4.13a and 4.14a). Two different orders were found in montmorillonite which are Pb>Cu>Zn>Cd for the first half of acid addition or when pH of the soil solution is $\geq$ 3 and Pb>Cd>Zn> Cu for the second half of acid input or when the pH is $\leq$ 3 (Figs. 4.13a and 4.14a). For the natural clay soil, the order was found to be Pb>Cu>Zn>Cd but changed to Pb>Zn>Cd>Cu at the very end of acid input or at the very low pH (Figs. 4.13c and 4.14c). Figs. 4.13d and 4.14d show that the amounts of Pb, Cu, Zn, and Cd retained in kaolinite are not much different but can be expressed in the order of Pb>Cd>Zn>Cu.

The dissimilarity of adsorption sequences is due to the differences in soil and heavy

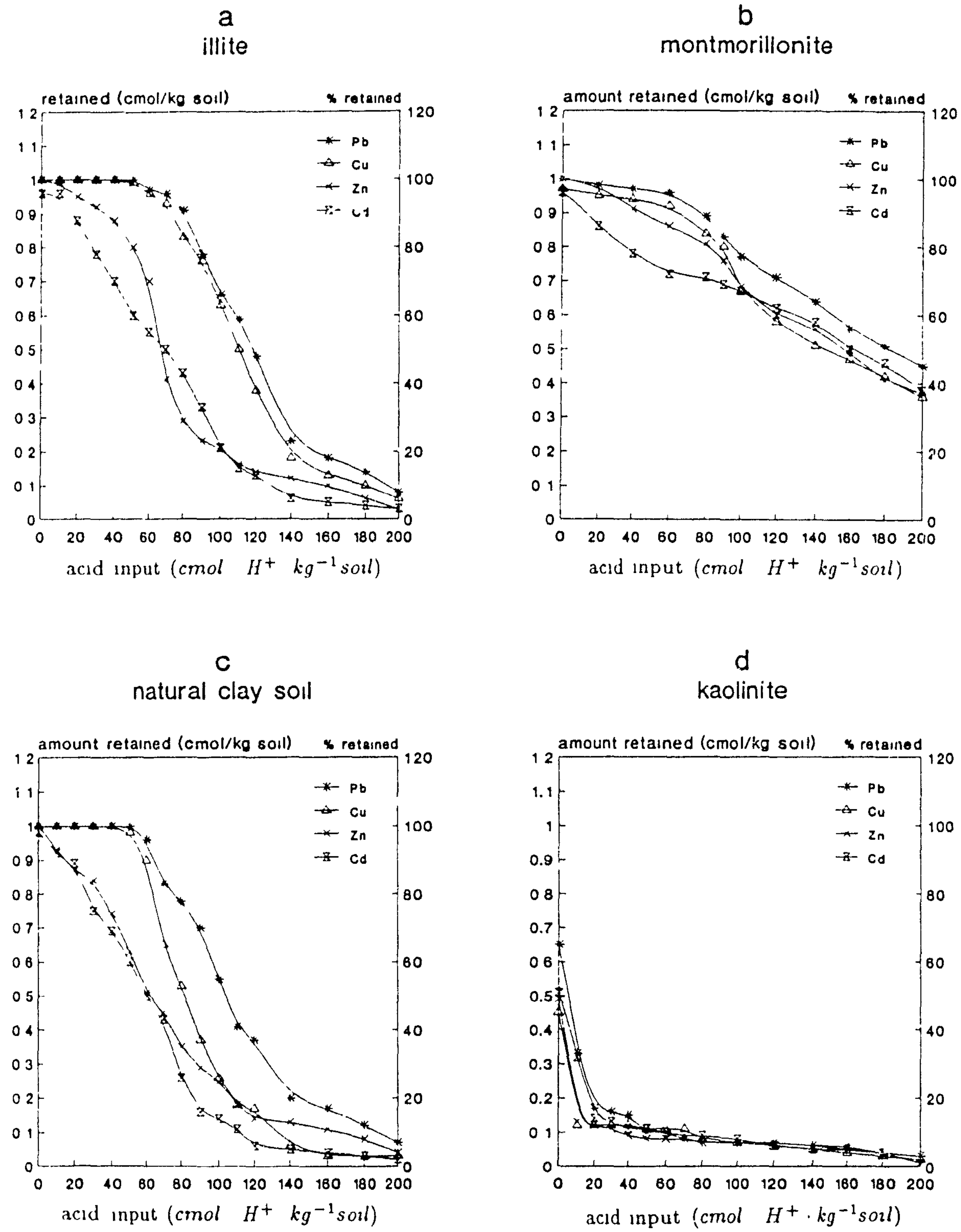


Figure 4.13 Amounts of Pb, Cu, Zn, and Cd retained as a function of acid input in : (4.13a) illite, (4.13b) montmorillonite, (4.13c) natural clay soil, and (4.13d) kaolinite when heavy metals were applied separately.

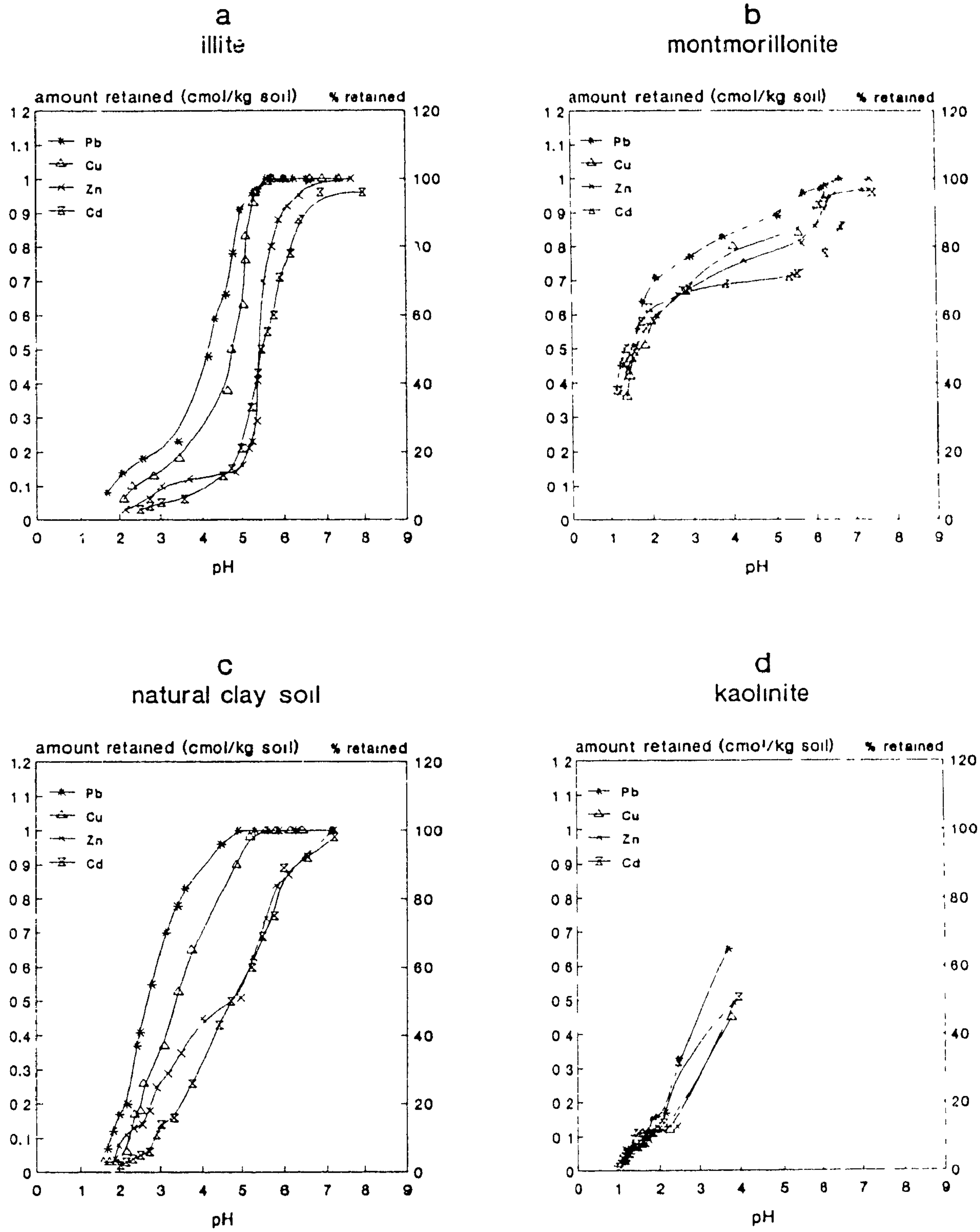


Figure 4.14 Amounts of Pb, Cu, Zn, and Cd retained as a function of soil solution pH in : (4.14a) illite, (4.14b) montmorillonite, (4.14c) natural clay soil, and (4.14d) kaolinite when heavy metals were applied separately

metal properties (Forbes et al., 1974). Table 4.2 shows selectivity orders of heavy metals found in different soils and soil constituents from several studies. It can be observed from the table that different selectivity orders were found depending on the soil and its conditions.

Table 4.2 Selectivity order of heavy metals in different soils and soil constituents

Material	selectivity order	Reference
kaolinite clay (pH 3.5-6)	Pb>Ca>Cu>Mg>Zn>Cd	Farrah and Pickering (1977)
kaolinite clay (pH 5.5-7.5)	Cd>Zn>Ni	Puls and Bohn (1988)
illite clay (pH 3.5-6)	Pb>Cu>Zn>Ca>Cd>Mg	Farrah and Pickering (1977)
montmorillonite clay (pH 3.5-6)	Ca>Pb>Cu>Mg>Cd>Zn	Farrah and Pickering (1977)
montmorillonite clay (pH 5.5-7.5)	Cd≈Zn>Ni	Puls and Bohn (1988)
Al oxides (amorphous)	Cu>Pu>Zn>Cd	Kinniburgh et al. (1976)
Mn oxides	Cu>Zn	Murray (1975)
Fe oxides (amorphous)	Pb>Cu>Zn>Cd	Benjamin and Leckie (1981)
Geothite	Cu>Pb>Zn>Cd	Forbes et al. (1974)
Fulvic acid (pH 5.0)	Cu>Pb>Zn	Schnitzer and Skinner (1967)
Humic acid (pH 4-6)	Cu>Pb>>Cd>Zn	Stevenson (1977)
Japanese soils dominated by volcanic parent material	Pb>Cu>Zn>Cd>Ni	Biddappa et al. (1981)
Mineral soils (pH 5.0) (with no organic)	Pb>Cu>Zn>Cd	Elliott et al. (1986)
Mineral soils (containing 20 to 40 $g \cdot kg^{-1}$ organic)	Pb>Cu>Cd>Zn	Elliott et al. (1986)

However, to begin an explanation on the arrangement of selectivity order, the ionic size of heavy metals need to be considered. For divalent heavy metals, when the concentrations applied to soil are the same, a correlation between ionic size and selectivity order may be expected (Elliott et al., 1986). The ease of exchange or the strength with which cations of equal charge are held is generally inversely proportional to the hydrated radii, or proportional to the unhydrated radii (Bohn, 1979). Therefore, the predicted order of selectivity based on unhydrated radii is Pb^{2+} (0.120 nm) > Cd^{2+} (0.097 nm) > Zn^{2+} (0.0.074m) > Cu^{2+} (0.072 nm) (Elliott et al., 1986). In this experiment, the sequence is true for the kaolinite soil for the whole range of acid input but for the latter half of acid input for the montmorillonite soil when the soil solution pH is ≤ 3, i.e., only when cation exchange mechanisms prevail.

At high pH levels, aqueous metal cations hydrolysed, resulting in a suite of soluble metal complexes according to the generalized expression for divalent metals as in the following equation (Elliot et al., 1986) :

$$M^{2+}(aq) + nH_2O \rightleftharpoons M(OH)_n^{2-n} + nH^+. \tag{4.2}$$

This hydrolysis, according to Elliott et al. (1986), results in precipitation of metal hydroxides onto soils, which is experimentally indistinquishable from removal of metals from solution by adsorption. The affinity of the heavy metals to be retained in soils could then be related to the pK of the first hydrolysis product of the metals (Forbes et al., 1974) where K is the equilibrium constant for the reaction in eq. 4.2 and when n=1. When the pK values of Pb, Cu, Zn, and Cd are ranked (Baes and Messmer, 1976; Elliott et al., 1986) the order follows Pb(6.2) > Cu(8.0)> Zn(9.0) > Cd(10.1). This order corresponds to the selectivity order of heavy metal retention found in illite, which is clearly seen when the soil solution pH remains high. This order was also found in montmorillonite for the first half of acid input, or when pH is > 3.

In addition to the precipitation of metal hydroxides onto soils, retention of heavy metals by precipitation with soil carbonates is also involved in the high retention capacity of heavy metals in soils at high pH. Yanful et al. (1988b) found from their results for soil with high carbonates, that at pH 5.5, Pb and Cu removal by carbonate-free soil was 72.5% and 22%, compared to 95% and 77% by carbonate-rich soil at a pH of 8.2. This means that Pb has a higher affinity to be retained in carbonate-rich soil than Cu does. Taking note that the illite and natural clay soil used in this study have some carbonates in them, the study by Yanful et al. (1988b) supports the results of the selectivity order of illite and natural clay soil, i.e., Pb has a higher affinity to be retained in the soils than Cu. The fact that the montmorillonite used in this study does not have any significant amount of carbonates could be the reason why the amounts of Pb and Cu retained in illite and natural clay soil at the beginning range of acid input (when the pH is still ≥ 5) is higher than that for montmorillonite (see Figs. 4.9a–4.9c and 4.10a–4.10d).

From the above results and discussion, some pertinent observations can be made as follows :

(i) As the clay soils receive increasing amounts of acid, the amounts of heavy metals retained in the soils depend on the soil solution pH, which is directly changed according to the soil buffer capacity. The change in the soil solution pH resulted in the change of the dominant retention mechanism of heavy metals in the soils. At high pH, precipitation mechanisms (by precipitating as hydroxides and/or as carbonates) prevail. As pH decreases, precipitation becomes less important, and cation exchange becomes dominant. High amounts of heavy metals are retained in the soils if the soil buffer capacity still remained high enough to resist a change in pH, such that it does not drop to low pH values where precipitation does not occur.

(ii) The pH-acid titration of the soils, which was obtained from the experiment, can be used as a representation of the soil buffer capacity for prediction of the retention of heavy metals in the soils.

(iii) The illite, montmorillonite, and natural clay soil have higher initial pH and buffer capacity than the kaolinite. This permitted them to retain high amounts of heavy metals, particulary Pb and Cu, for larger ranges of acid input before the amounts retained dropped.

(iv) The selectivity order of heavy metal retention in soils depends on the pH of soil solution. At high soil solution pH, when precipitation prevails, the order follows Pb>Cu>Zn>Cd which can be clearly seen in the case of illite, montmorillonite, and natural clay soil. At low soil solution pH, the order follows Pb>Cd>Zn>Cu, as can be seen in the case of kaolinite and montmorillonite.

(v) The presence of carbonates in the illite and natural clay soils not only enhanced the soil buffer capacity, but also helped retain heavy metals in soils at high pH. Due to the very high C.E.C. of montmorillonite, the drop in the amounts of heavy metals retained in the soil at increasing amounts of acid input is slow and becomes higher than the other soils at lower pH when cation exchange becomes more important.

All the experimental data used in Figs.4.9-4.14 are provided in Tables A-8 to A-11 in Appendix A.

In order to obtain a broader view of heavy metal retention in soil, an application of heavy metals to soils changed from separately applied to compositely (i.e., grouped together) applied. The results and discussion on this subject is presented in the following section.

4.3.3 Retention of Heavy Metals in Soil-Composite Heavy Metal Solution

The solutions of Pb, Cu, Zn, and Cd at a concentration of 1.0 x 10^{-3} $mol \cdot L^{-1}$ were compositely applied to each clay soil at increasing amounts of acid from 0 to 200 $cmol \quad H^{+} \cdot kg^{-1} soil$. The amount of each heavy metal applied is equivalent to 1.0 $cmol \quad kg^{-1} soil$. Competitive adsorption or retention among the heavy metals were involved in this case.

The amounts of Pb, Cu, Zn, and Cd retained in illite, montmorillonite, natural clay soil, and kaolinite are plotted with increasing amounts of acid as shown in Figs. 4.15a–4.15d and with pH as shown in Figs. 4.16a–4.16d respectively. It can be observed from these figures that the retention curves of heavy metals in each soil have similar patterns to the retention curves in Figs. 4.9a–4.9d and Figs. 4.10a–4.10d when the heavy metals were applied separately. The difference is that the retention curves in Figs. 4.15a–4.15d and Figs. 4.16a–4.16d are lower than the corresponding curves in Figs. 4.9a–4.9d and Figs. 4.10a–4.10d for every case.

Both sets of retention curves in Figs. 4.15–4.16 show similar trends of heavy metal retention in soils as in Figs. 4.9–4.10. In particular, the magnitude of retention varies directly with increasing amounts of acid input or decreasing pH. High amounts of heavy metals are retained at low acid input or when soil solution pH still remains high. But as the amounts of acid input increased, the pH of the soil solution begins to decrease (depending on the buffer capacity of soil) resulting in a drop in the amounts of heavy metals retained.

The lower curves of heavy metal retention indicate that the amounts of heavy metals retained are lower when the heavy metals are compositely applied to soil than

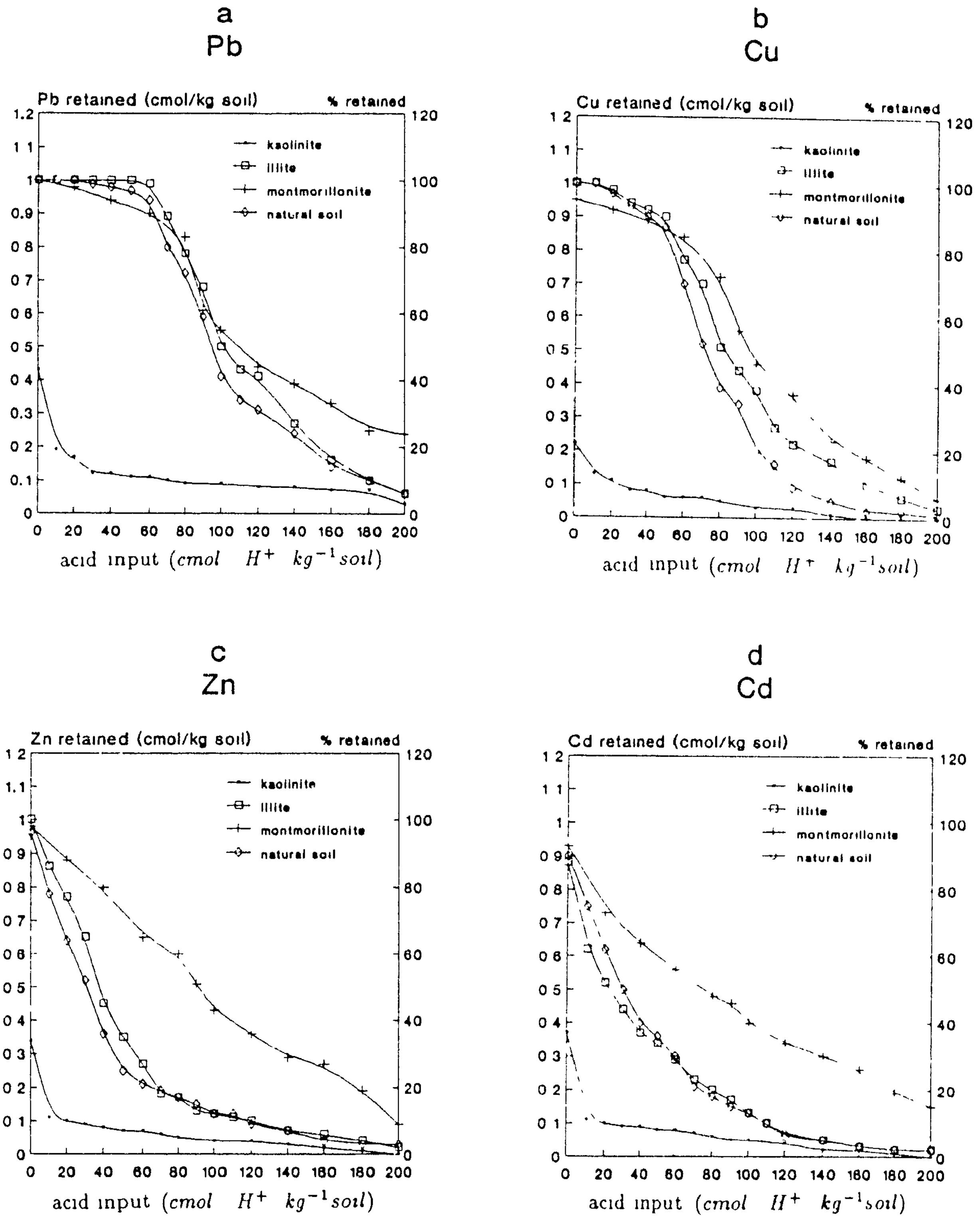


Figure 4.15 Amounts of heavy metals retained in kaolinite, illite, montmorillonite, and natural clay soil at increasing amounts of acid input, for : (4.15a) Pb, (4.15b) Cu, (4.15c) Zn, and (4.15d) Cd when heavy metals were applied compositely

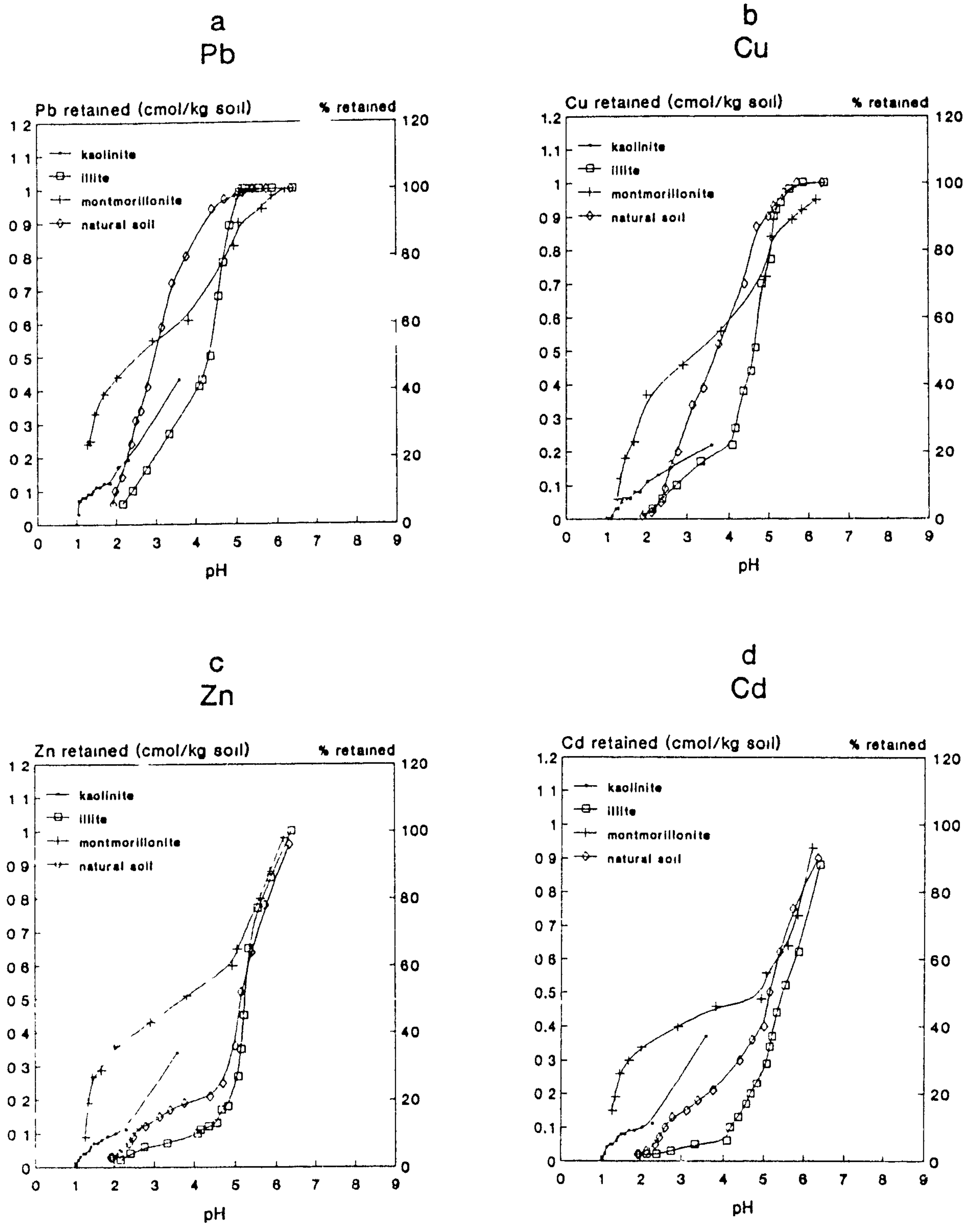


Figure 4.16 Amounts of heavy metals retained in kaolinite, illite, montmorillonite, and natural clay soil as a function of soil solution pH for : (4.16a) Pb, (4.16b) Cu, (4.16c) Zr, and (4.16d) Cd when heavy metals were applied compositely.

when they are separately applied. This could be due to the competitive effect among the heavy metals. In this case, not only competition for adsorption sites but also competition for precipitation on to soils need to be considered. When heavy metals were applied separately, a metal precipitated freely and competed only with H^+ for adsorption sites. But when they were applied compositely, different metals competed among themselves to precipitate onto soils at high pH. They also competed among each other and with H^+ for adsorption sites, resulting thereby in lower amounts of heavy metals retained in this case. The reduction in the amounts of heavy metals retained can also be further explained by the pH-acid titration curves of the soils.

The equilibrium pH of the soil solutions (after heavy metals were applied to the soils) are plotted with the amounts of acid input for illite, montmorillonite, natural clay soil, and kaolinite respectively (Figs. 4.17a–4.17d). It is observed from these figures that all curves are lower than the titration curves of the soils when there are no heavy metals. The reduction in the pH of the soil solution is due to the hydrolysis reaction of the metals in water according to the same equation shown in eq.4.2. When heavy metals were applied compositely, total concentration of the heavy metals was higher than when they were applied separately. The higher the concentration of heavy metal ions in the solution, the more the reaction will shift to the right in order to adjust itself to equilibrium (Laitinen and Harris, 1975). This resulted in higher concentration of H^+ which lowered the initial pH and the equilibrium pH of the soil solution for the whole range of acid input as seen in Figs. 4.17a–4.17d. It can also be observed from Figs. 4.17a–4.17d that the rapid reduction or the drop of the soil solution pH occurs at lower amounts of acid addition than in the titration curves. This means that the soils have lower resistances to pH changes or lower buffer capacities due to the faster drop

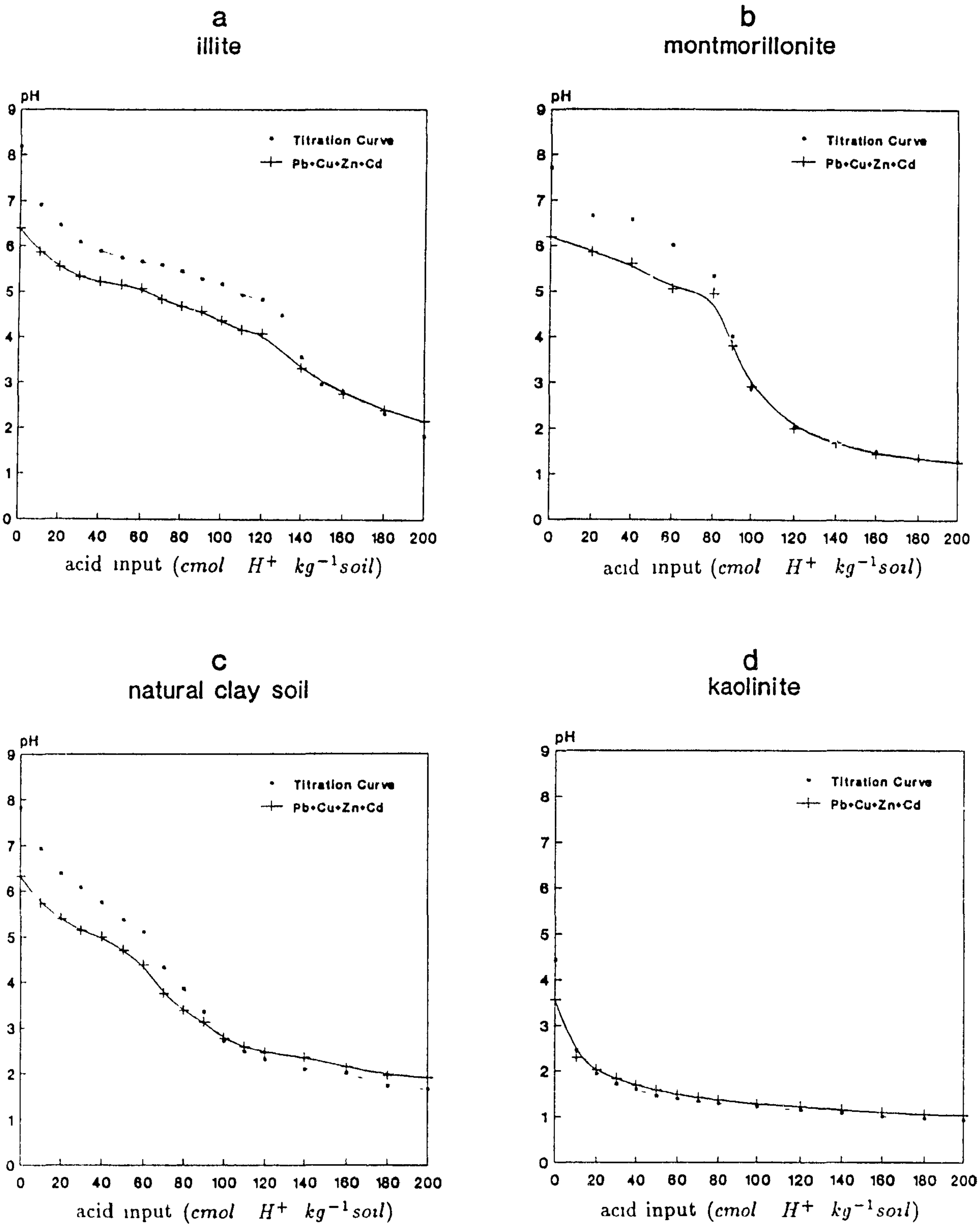


Figure 4.17 Equilibrium soil solution pH (after heavy metals were applied compositely) as a function of acid input for : (4.17a) illite, (4.17b) montmorillonite, (4.17c) natural clay soil, and (4.17d) kaolinite.

of the soil solution pH. This reduction of the pH-acid curves is similar to the reduction of the soil solution pH when the concentration of Pb applied increased as described in section 4.3.1.

As the soil solution pH decreases, the possibility of heavy metals retained in soil by precipitation also decreases, resulting in smaller amounts of heavy metals retained in soils. The reduction curves of the pH-acid relation as shown in Figs. 4.17a–4.17d can be used to explain why the amounts of heavy metal retained are lower when heavy metals are applied compositely than when they are applied separately. For example, it can be expected from the lower pH-acid curve of illite (Fig. 4.17a) that illite could retain nearly 100% of Pb and Cu when acid addition did not exceed 60 $cmol\quad H^+\quad kg^{-1}soil$ because this is the point where the soil solution pH starts to drop to < 5 (see Fig. 4.15a). As compared with the previous section, nearly 100% of Pb and Cu could be retained in illite when acid input did not exceed 80 $cmol\quad H^+ \cdot kg^{-1}soil$ (Fig. 4.9a). In addition, the reduction in pH-acid curves resulted in the smaller or shorter retention curves of heavy metals when plotted with pH (Figs. 4.16a–4.16d as compared with Figs. 4.10a–4.10d). This is due to the decrease in the initial pH of the soil solutions and also to the decrease in the overall soil solution pH throughout the entire range of acid addition.

When the amounts of heavy metals retained within the same soil for illite, montmorillonite, natural clay soil, and kaolinite are plotted with increasing amounts of acid input (Figs. 4.18a–4.18d) and with pH (Figs. 4.19a–4.19d), the selectivity orders of the competitive adsorption of the heavy metal retention in soils can be obtained. The resulting orders are the same as in section 4.3.2 when heavy metals were applied individually. For the illite soil the order was found to be Pb>Cu>>Zn≥Cd which is

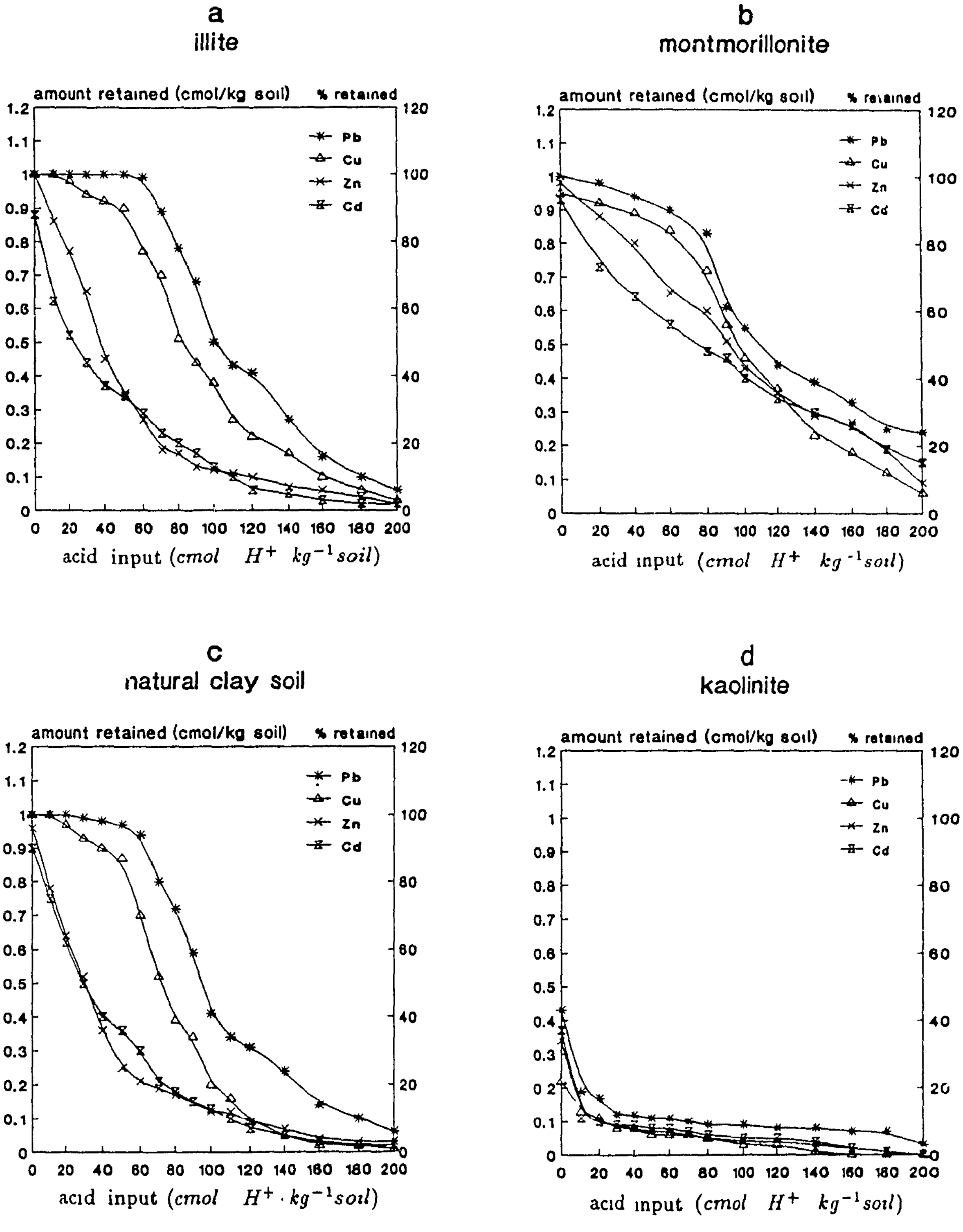


Figure 4.18 Amounts of Pb, Cu, Zn, and Cd retained as a function of acid input in : (4.18a) illite, (4.18b) montmorillonite, (4.18c) natural clay soil, and (4.18d) kaolinite when heavy metals were applied compositely.

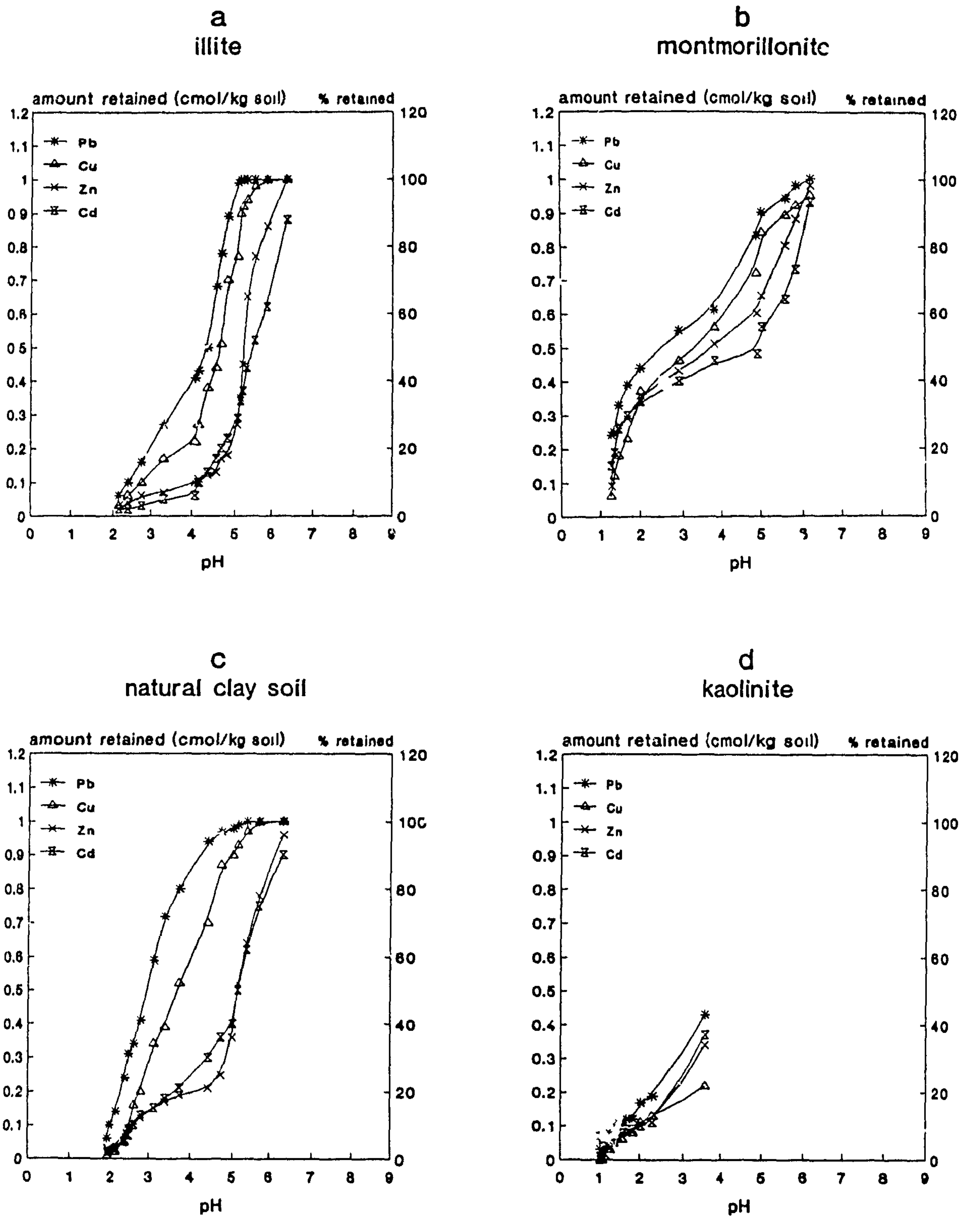


Figure 4.19 Amounts of Pb, Cu, Zn, and Cd retained as a function of soil solution pH in : (4.19a) illite, (4.19b) montmorillonite, (4.19c) natural clay soil, and (4.19d) kaolinite when heavy metals were applied compositely.

the same order found in the natural soil. In the case of the montmorillonite soil, the order of Pb>Cu>Zn>Cd was found in the first half of acid input whereas the order of Pb>Cd>Zn>Cu was found in the second half of acid input when pH is ≤ 3. For the kaolinite soil, though, the amounts of heavy metals retained were not much different, and the order was found to be Pb>Cd>Zn>Cu.

The results and discussion of this section as presented above can be summarized here as follows :

(i) When heavy metals were compositely applied to the soils, the soil buffer capacity was affected more than when the heavy metals were separately applied, as can be observed from the reduction of soil solution pH-acid curves. The effect is similar to the reduction of soil solution pH when the concentration of Pb applied increases.

(ii) The reduction in the soil solution pH resulted in lower amounts of heavy metals retained in the soils. However, the selectivity orders of the heavy metal retention in the soils still remained the same as in the previous section.

It can be seen from the above discussion that as the soil solution system has more solution components in it, the competitive effect could be higher. The soil buffer capacity could be affected more, resulting thereby in lower amounts of heavy metals retained in the soil.

In the next section, the heavy metals were compositely applied to soils together with leachate collected from the Lachenaie landfill site. These results and discussion are presented.

All the experimental data used in Figs. 4.15–4.19 are provided in Tables A-12 to A-15 in Appendix A.

4.3.4 Retention of Heavy Metals in Soil-Heavy Metal-Leachate Solution

As mentioned in section 3.3.4, a leachate collected from Lachenaie landfill site was combined with heavy metals in order to prepare a heavy metal-leachate solution. The purpose of the experiments performed is to form a system that more closely resembles the complex system of a real "field" situation, and to investigate how several constituents in a leachate will interfere with soil buffer capacity and the retention of heavy metals in the clay soils.

Heavy metals in the form of nitrates and nitric acid were added to the leachate to prepare the heavy metal-leachate solutions having increasing amounts of acid. A set of solutions, each solution having the same concentration of Pb, Cu, Zn, and Cd at 1.0 x 10^{-3} $mol \cdot L^{-1}$ but having increasing acid concentration from 0 to 2x10^{-3} $mol \cdot L^{-1}$, were applied to the clay soils. The amount of each heavy metal applied to the soils is equivalent to 1.0 $cmol \cdot kg^{-1} soil$ with increasing amounts of acid input from 0 to 200 $cmol \quad H^{+} \cdot kg^{-1} soil$. The soil suspensions in this case thus contained several compositions that came with the leachate.

The results of the analysis on leachate characteristics are shown in Table 4.3. It can be seen from the table that the leachate had high biochemical oxygen demand (BOD) and chemical oxygen demand (COD) values, indicating that the leachate contained organic materials. The leachate pH was near neutral whereas the specific electrical conductivity was high which indicated high amounts of ionic components.

The concentrations of cationic salts such as Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}, and anionic salts such as Cl^{-}, HCO_3^{-} were higher than the concentrations of heavy metals e.g., Pb, Cu, and Zn found in the leachate.

Table 4.3 Characteristics of leachate collected from Lachenaie landfill site

Parameter	ASTM Test No. (1984)	Concentration in ppm	Concentration in $mol \cdot L^{-1}$
BOD	D 888	440	-
COD	D1252	830	-
TOC	D2579	180	-
TC	D2579	270	-
pH	D1293	6.9 (pH unit)	-
Spec.Electrical Conductivity	D1125	1.8×10^3 (μmho/cm)	-
oil & grease	D4281	20	-
phenol	D1783	0.04	-
total iron (Fe)	D1068	5.0	9.0×10^{-5}
Na^+	D4191	140	6.1×10^{-3}
K^+	D4192	15	3.8×10^{-4}
Ca^{2+}	D 511	170	4.3×10^{-3}
Mg^{2+}	D 511	30	1.2×10^{-3}
NH_3	D1426	10	5.9×10^{-4}
Cl^-	D1253	200	5.6×10^{-3}
HCO_3^-	D 513	300	4.9×10^{-3}
Pb	D3551	1.0	4.8×10^{-6}
Cu	D1688	1.8	2.8×10^{-5}
Zn	D1691	2.4	3.7×10^{-5}

In this experiment, equal amounts of heavy metals as in the previous section were added to the leachate. The amounts of Pb, Cu, Zn, and Cd retained in soils were measured after the mixture (heavy metals and leachate) was applied to soils. The results of the amounts of Pb, Cu, Zn, and Cd retained in illite, montmorillonite, natural clay soil and kaolinite are plotted with increasing amounts of acid input (Figs. 4.20a–4.20d) and with soil solution pH (Figs. 4.21a–4.21d). The equilibrium soil solution pH of illite, montmorillonite, natural clay soil, and kaolinite are also plotted (Figs. 4.22a–4.22d). The retention curves in these figures reveal that the magnitude of retention varies with increasing amounts of acid input or decreasing soil solution pH. High amounts of heavy metals were retained at low acid input or when soil solution pH still remained high. As the amount of acid input increased, the pH of soil solution decreased, the amounts of heavy metals retained decreased rapidly particularly in the case of Zn and Cd.

The amounts of heavy metals retained within the same soil for illite, montmorillonite, natural clay soil, and kaolinite are plotted with increasing amounts of acid input and soil solution pH in Figs. 4.23a–4.23d and Figs. 4.24a–4.24d respectively. The selectivity order of heavy metals in each soil can be seen from these figures. The selectivity order of heavy metal retention in each soil was the same as in section 4.3.2 and 4.3.3 when heavy metals were applied separately and compositely. In addition, it can be observed that the retention curves of heavy metals in each soil presented in this section have similar patterns to the corresponding curves in sections 4.3.2 and 4.3.3. However, the differences in the retention curves are that the curves in this section are lower than in the previous two sections. This means that the soils retained smaller amounts of heavy metals when leachate was involved in the system.

The amounts of Pb, Cu, Zn, and Cd retained in each clay soil when heavy metals

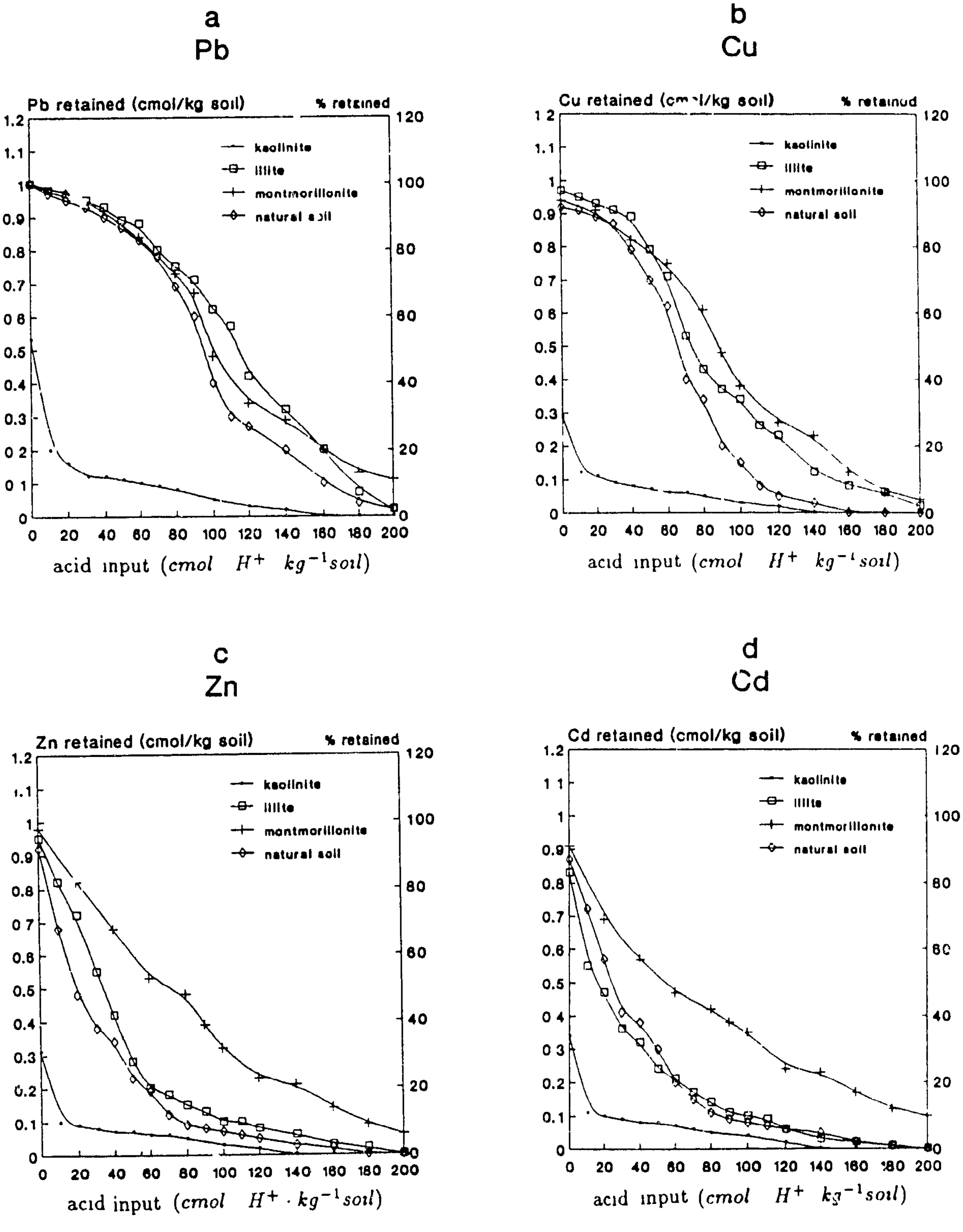


Figure 4.20 Amounts of heavy metals retained in kaolinite, illite, montmorillonite, and natural clay soil at increasing amounts of acid input for : (4.20a) Pb, (4.20b) Cu, (4.20c) Zn, and (4.20d) Cd when heavy metals were applied compositely with leachate.

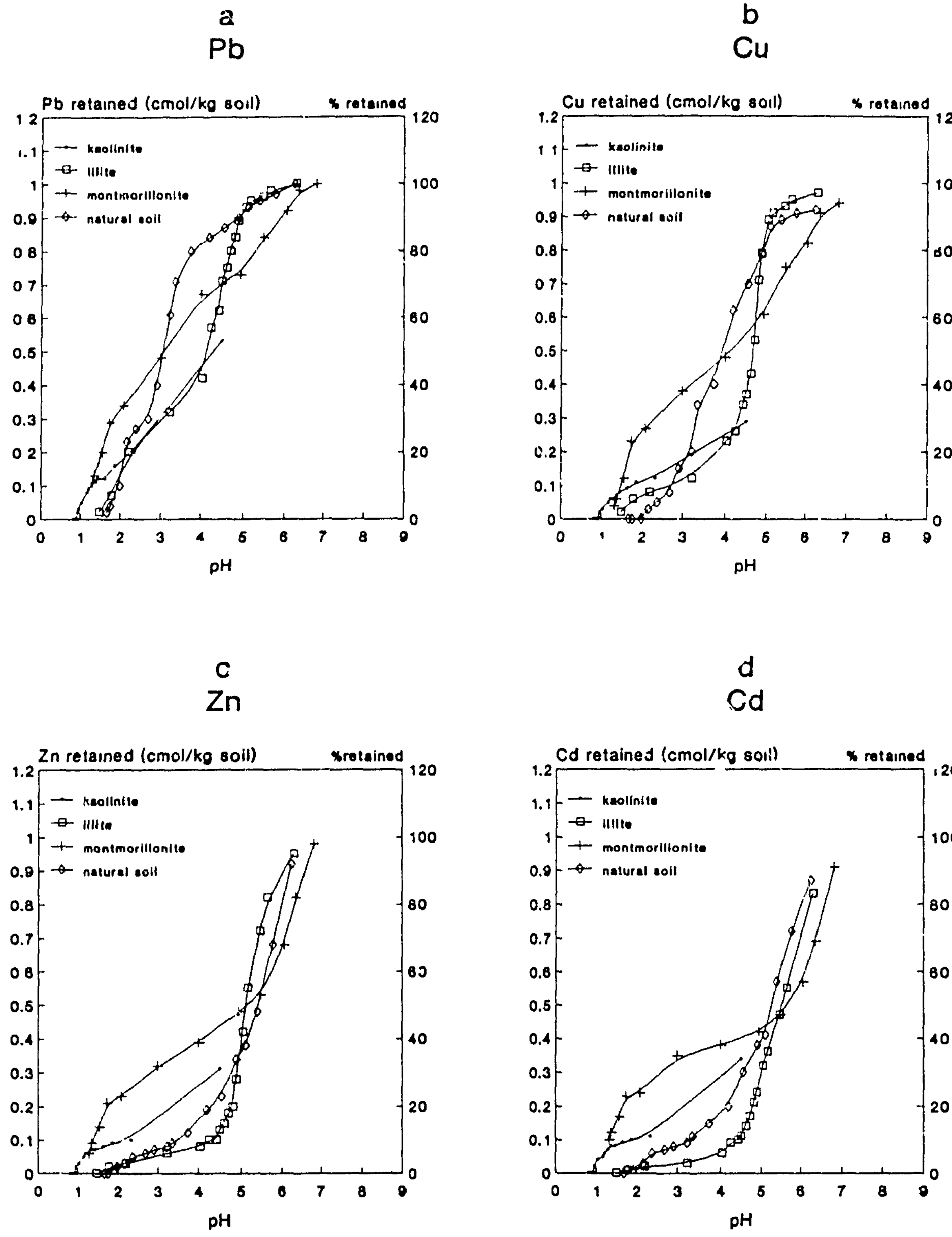


Figure 4.21 Amounts of heavy metals retained in kaolinite, illite, montmorillonite, and natural clay soil as a function of soil solution pH for : (4.21a) Pb, (4.21b) Cu, (4.21c) Zn, and (4.21d) Cd when heavy metals were applied compositely with leachate.

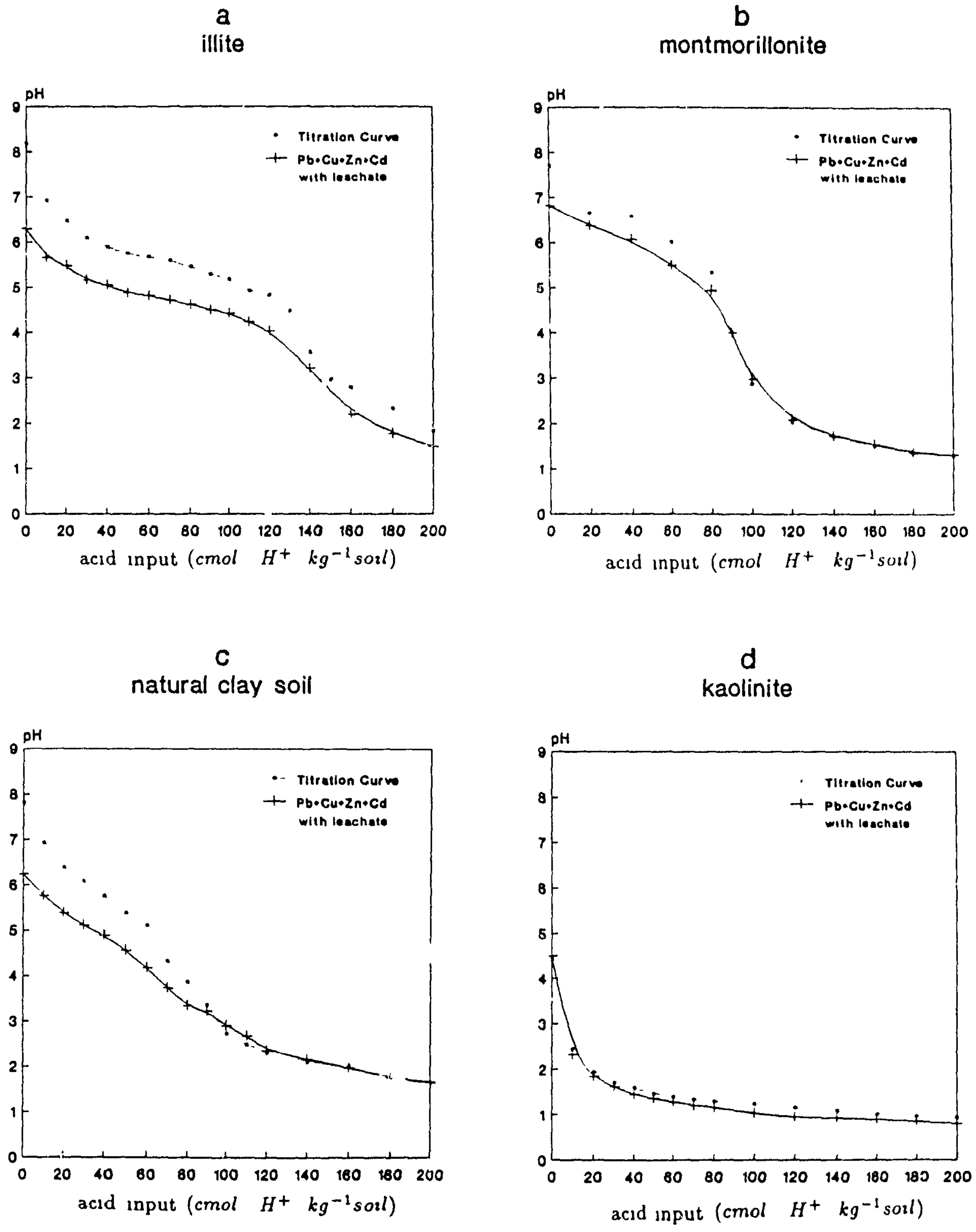


Figure 4.22 Equilibrium soil solution pH (after heavy metals were applied compositely with leachate) as a function of acid input for : (4.22a) illite, (4.22b) montmorillonite, (4.22c) natural clay soil, and (4.22d) kaolinite.

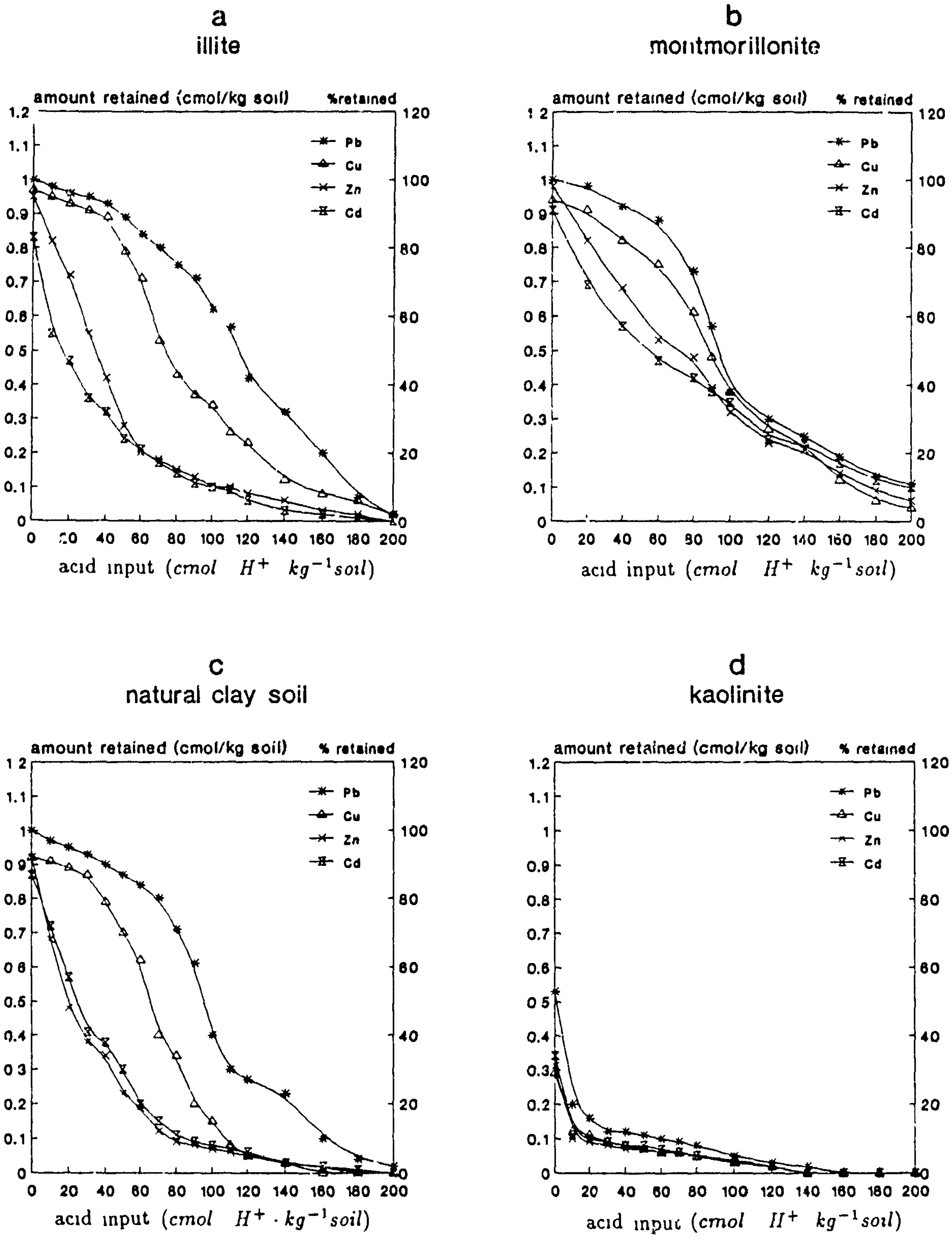
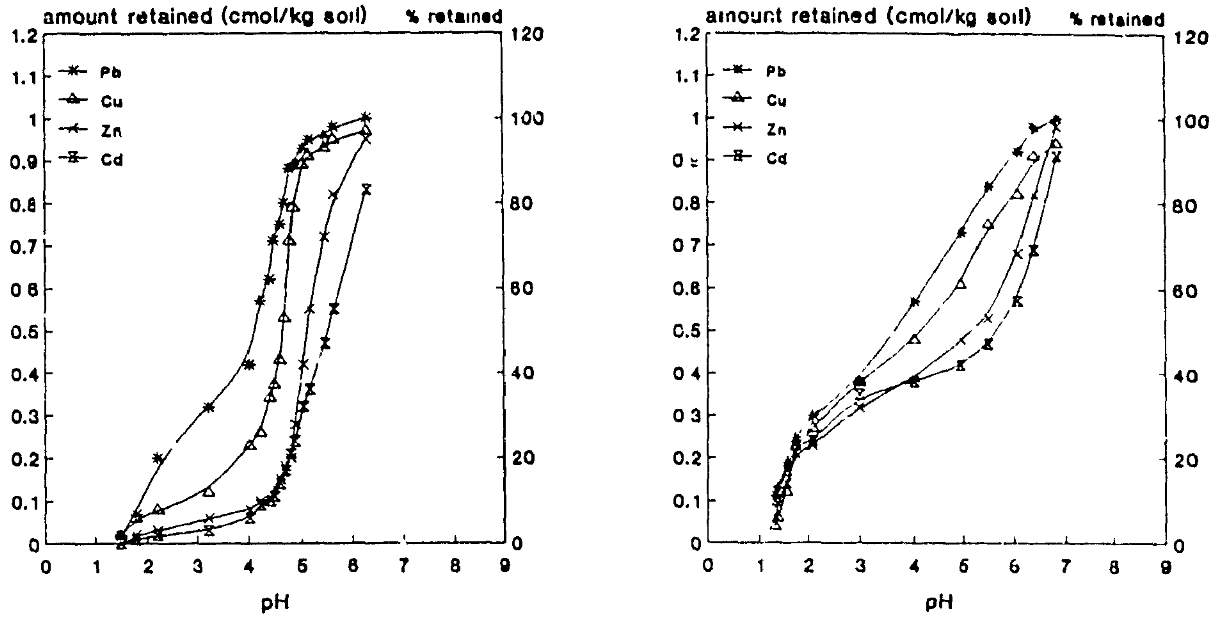
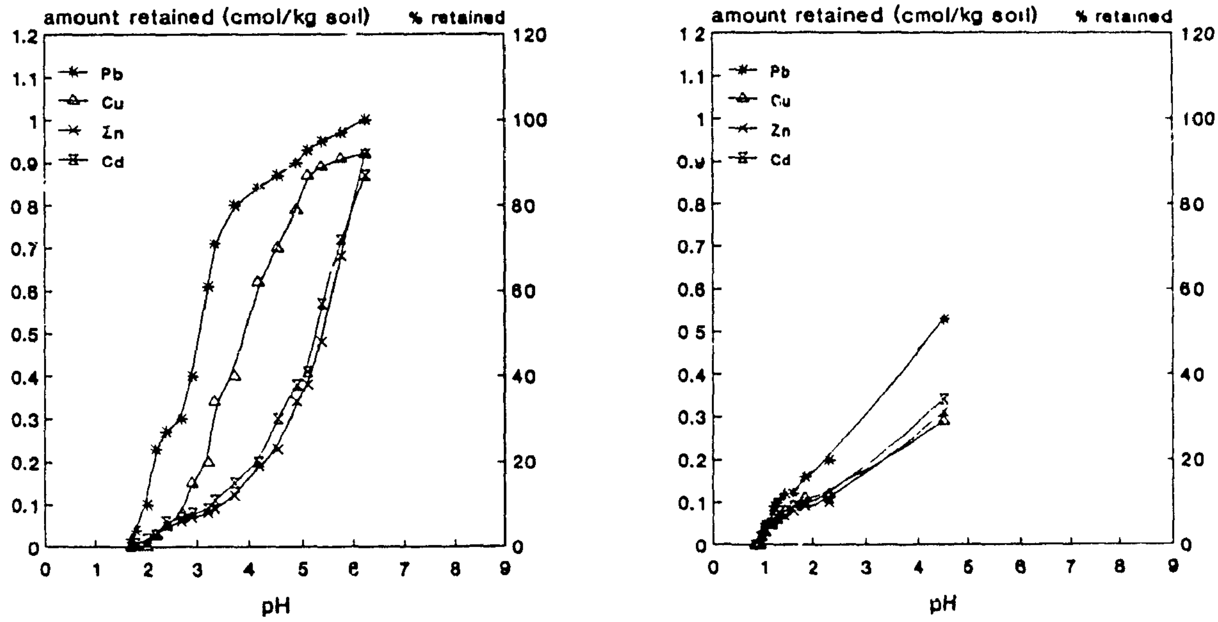


Figure 4.23 Amounts of Pb, Cu, Zn, and Cd retained as a function of acid input in : (4.23a) illite, (4.23b) montmorillonite, (4.23c) natural clay soil, and (4.23d) kaolinite when heavy metals were applied compositely with leachate.



a
illite

b
montmorillonite



c
natural clay soil

d
kaolinite

Figure 4.24 Amounts of Pb, Cu, Zn, and Cd retained as a function of soil solution pH in : (4.24a) illite, (4.24b) montmorillonite, (4.24c) natural clay soil, and (4.24d) kaolinite when heavy metals were applied compositely with leachate.

were separately applied, compositely applied, and compositely applied with leachate were compared by plotting with amounts of acid input (see Figs 4.25a–4.25d, 4.26a–4.26d, 4.27a–4.27d, and 4.28a–4.28d respectively). The decrease in the amounts of heavy metal retained in the soils by each application can be clearly seen from these figures. The reduction in the retention was low in kaolinite but high in montmorillonite.

The cause of reduction of heavy metal retention in soils could be due to several effects which may be described as follows :

Reduction of the soil solution pH

Figures 4.22a–4.22d show the relationship between the equilibrium soil solution pH values and the amounts of acid added for different soils. It can be seen from these figures that all curves are lower than the titration curves when heavy metals and leachates are not involved. This indicates that the application of heavy metal-leachate solution afftects the soil buffer capacity. As mentioned in the previous sections, when higher concentrations of heavy metals were applied to the soils, the buffer capacity of the soils was affected resulting in the lowering of the pH-acid curves. The reduction in the pH-acid curves resulted in lower amounts of heavy metals retained in the soils. It can be observed from Figs. 4.22a-4.22d that the magnitudes of the reduction in the soil solution pH seem to be more or less the same as in Figs. 4.17a–4.17d when heavy metals were compositely applied without leachate, however, the magnitudes of the reduction in heavy metal retention were greater as seen in Figs. 4.25-4.28 particularly in illite, montmorillonite, and natural clay soil. Therefore, there are some other effects apart from the reduction of the soil solution pH that are involved in the lower retention of heavy metals in the clay soils.

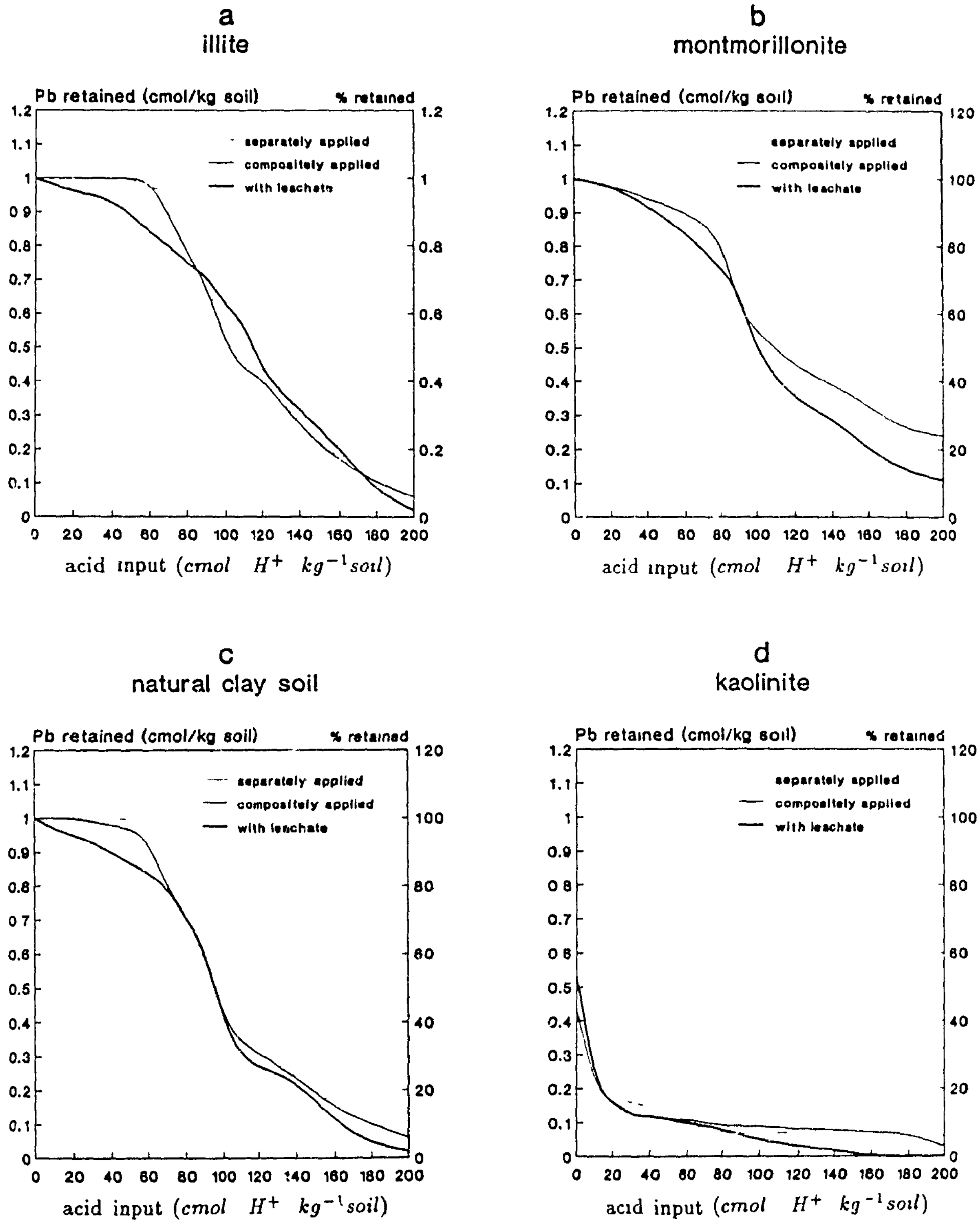
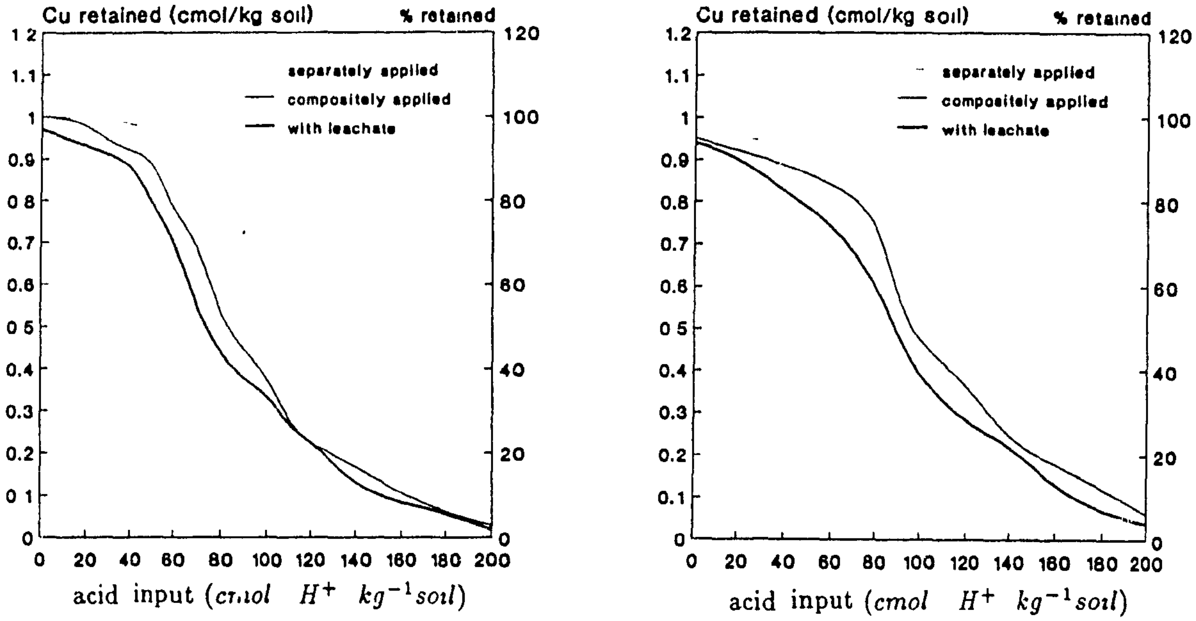


Figure 4.25 Amounts of Pb retained when heavy metals were applied separately, compositely, and compositely with leachate as a function of acid input in : (4.25a) illite, (4.25b) montmorillonite, (4.25c) natural clay soil, and (4.25d) kaolinite.

a
illite

b
montmorillonite



c
natural clay soil

d
kaolinite

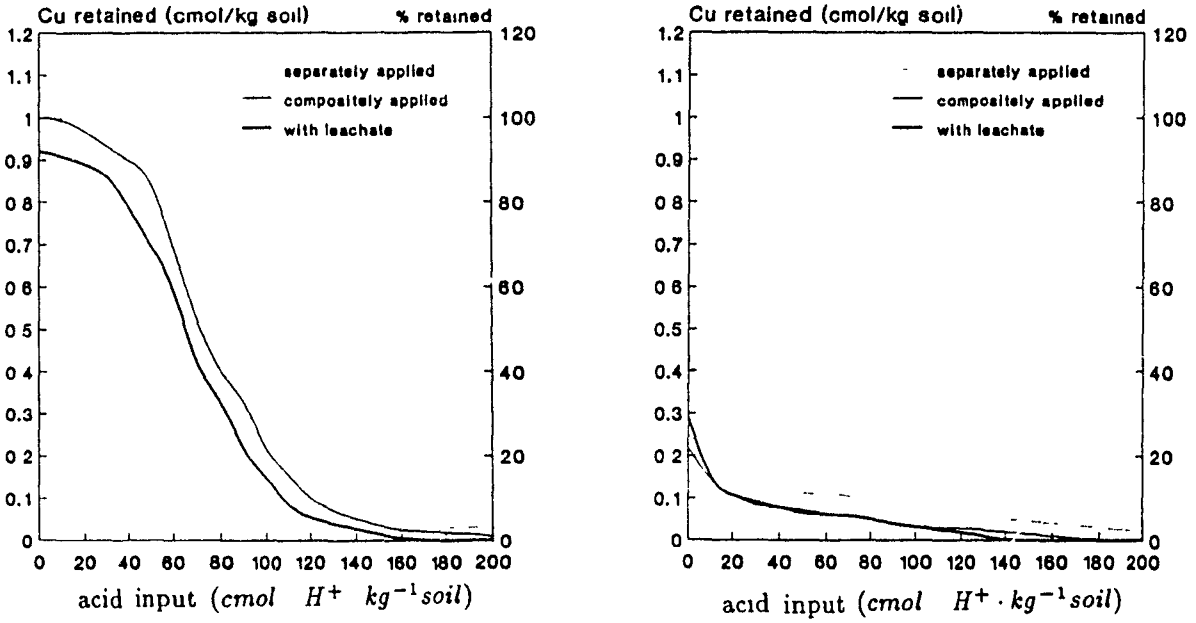


Figure 4.26 Amounts of Cu retained when heavy metals were applied separately, compositely, and compositely with leachate as a function of acid input in : (4.26a) illite, (4.26b) montmorillonite, (4.26c) natural clay soil, and (4.26d) kaolinite.

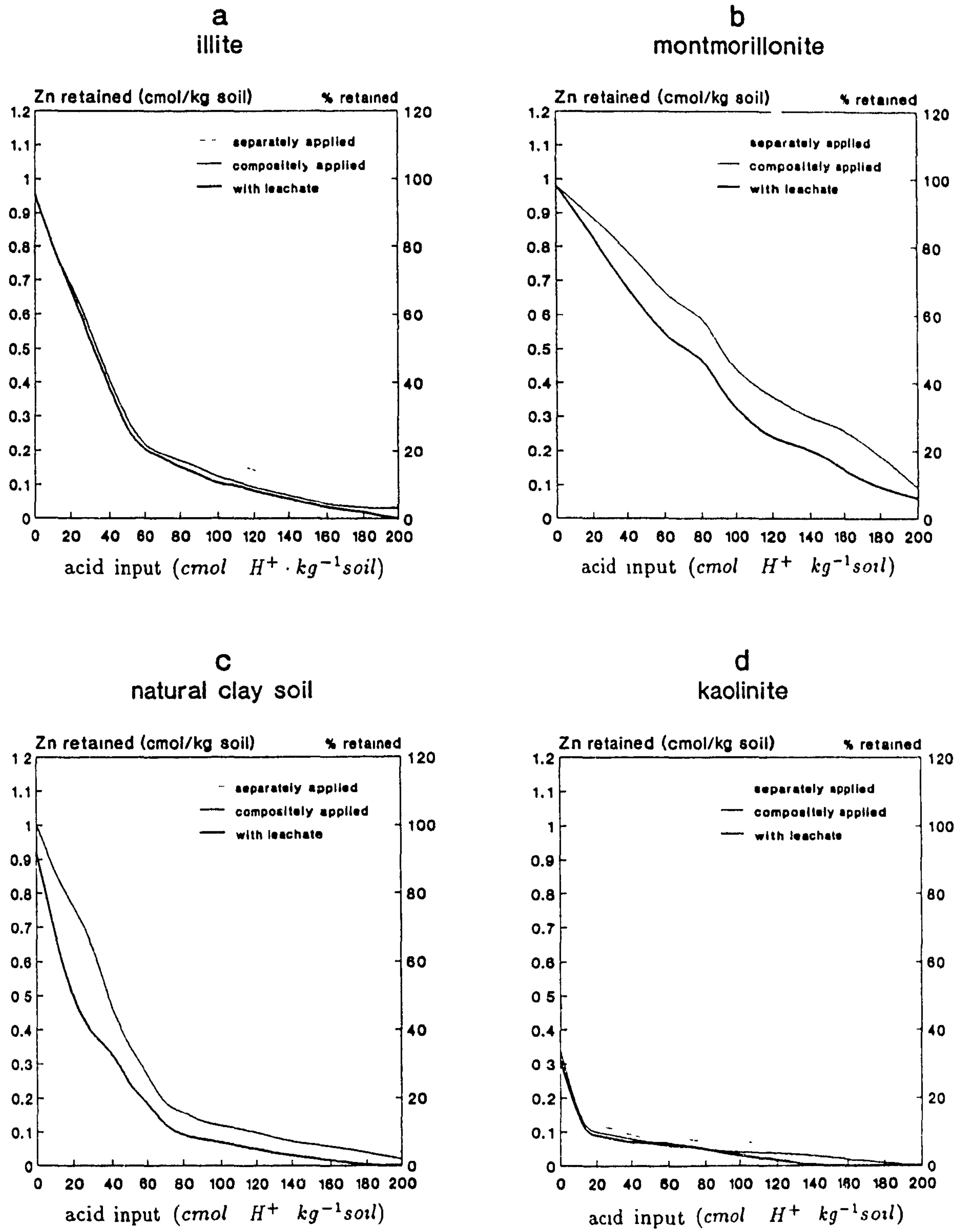
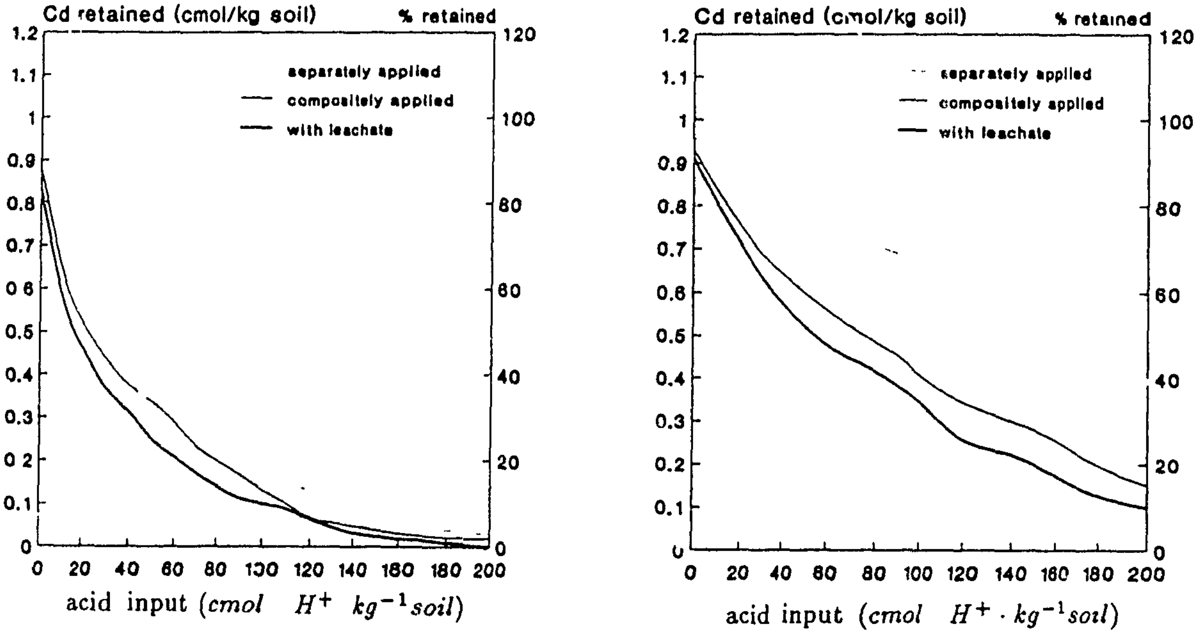


Figure 4.27 Amounts of Zn retained when heavy metals were applied separately, compositely, and compositely with leachate as a function of acid input in : (4.27a) illite, (4.27b) montmorillonite, (4.27c) natural clay soil, and (4.27d) kaolinite.

a
illite

b
montmorillonite



c
natural clay soil

d
kaolinite

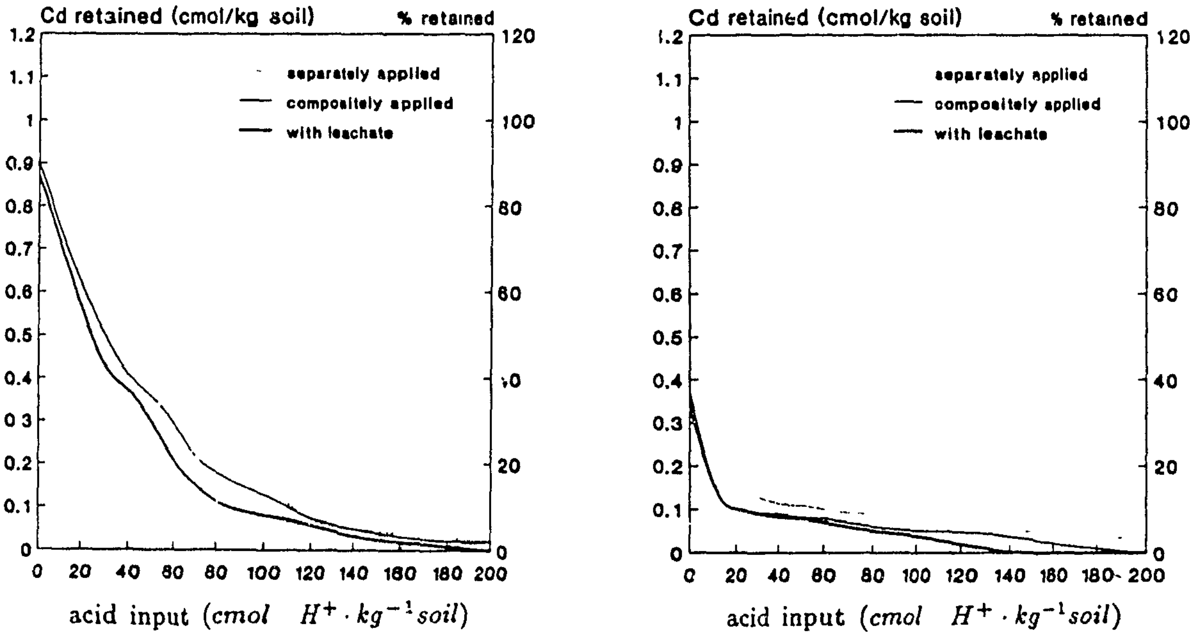


Figure 4.28 Amounts of Cd retained when heavy metals were applied separately, compositely, and compositely with leachate as a function of acid input in : (4.28a) illite, (4.28b) montmorillonite, (4.28c) natural clay soil, and (4.28d) kaolinite.

Effect of Competing Cations

As mentioned in section 4.3.3, when heavy metals were applied compositely, different heavy metals competed among themselves to adsorb onto soils. This made the amounts of heavy metals retained in soils, when heavy metals were applied compositely, less than when they were applied separately. When the leachate was included, the leachate had high concentrations of several cations such as Na^{+}, K^{+}, Ca^{2+}, and Mg^{2+} as seen in Table 4.3. These cations also competed with heavy metals for the cation exchange sites of the soils resulting in the decrease in the amounts of heavy metals retained in soils as seen Figs. 4.24–4.27. The effect can be seen clearly in montmorillonite (Figs. 4.25b, 4.26b, 4.27b, and 4.28b) where cation exchange dominates. A similar conclusion was reached by Griffin and Shimp (1976) and Frost and Griffin (1977) in their study on heavy metal adsorption using the mixture of leachate and heavy metals.

Precipitate Prevention by Organic Compounds

As seen in Table 4.3, the leachate has high BOD and COD indicating a high amount of organic materials. These organic materials could interfere with retention of heavy metals by preventing heavy metals from precipitating. Farrah and Pickering (1976, 1977) found that organic molecules such as oxalate, citrate, and tartrate could mask the formation of Pb, Zn, and Cd hydroxides, thus preventing retention of heavy metals in soil by precipitation. This effect can be seen, for example, in the results of Pb retention in illite at different applications of heavy metal applied in Fig. 4.25a. The results show that 100% of Pb can still be retained in the soil until acid input exceeded 80 and 60 $cmol \quad H^{+} \cdot kg^{-1} soil$ when heavy metals were applied separately and compositely. But when heavy metals were applied with leachate, 100% Pb retention is only at the beginning of the curves indicating that precipitation of Pb become less. The effect can be seen also in Pb and Cu retention in montmorillonite, natural clay soil, and including illite (Figs. 4.25-4.26).

Non Adsorption of Anionic and Uncharged Complex Species

Not only cations or organic compounds can prevent retention of heavy metals in soils, but anions such as chloride (Cl^-) can also reduce heavy metal retention. The presence of chloride in leachate can form uncharged and/or anionic complexes with heavy metals. These complexes cannot adsorb onto soils which have negative charge surfaces. Hahne and Kroontje (1973) found from their calculations that Cl^- can form complexes with heavy metals, particulary Cd, and become an uncharged form and anionic forms such as $CdCl_2$, $CdCl_3^-$, $CdCl_4^{2-}$. The complexation prevents heavy metals from forming hydroxides or from adsorbing onto soil exchange sites. Farrah and Pickering (1976) found from their experiments that organic acids such as tartaric acid and ethylenediamine tetra acetic acid (EDTA) could also form uncharged and anionic complexes with Cu. The formation of these complexes prevents Cu from adsorbing on soils by cation exchange. The leachate used in this study had Cl^- and may have had some organic acids that could form anionic and uncharged complexes with the heavy metals. The formation of these complexes when added to the other effects mentioned above resulted in lower amounts of heavy metals retained in the soils throughout the entire range of acid input when heavy metals were applied with leachate as seen in Figs. 4.25–4.28.

The above discussion in this section can be summarized here as follows :

(i) When heavy metals are compositely applied with leachate to the soils, the soil suspensions have several more solution compositions in the system than when leachate is not involved. These solution compositions such as cations, anions, organic molecules, etc. affect the soil buffer capacity and interfere with the retention of heavy metals on the clay soils resulting in lower amounts of heavy metals retained in the soils.

(ii) Several effects such as the reduction in soil solution pH, competition among cations, precipitation prevention, and formation of anionic or uncharged complex result in the reduction in amounts of heavy metals retained in soils. However, the selectivity orders of the heavy metal retention in the soils still remain the same as those in the sections 4.3.2 and 4.3.3.

It can be concluded in this section that the clay soils retain lower amounts of heavy metals when several solution compositions are involved in the suspensions system. However, the fact that soils can retain high amounts of heavy metals if they still have high buffer capacities to maintain their soil solution pH at a high level still remain the same.

From the results of sections 4.3.2, 4.3.3, and 4.3.4 when heavy metals are applied differently, it can be concluded that the capacity of the clay soils to retain heavy metals as they receive increasing amounts of acid depend on their buffer capacity. The degree or magnitude of heavy metal retention becomes less as the soil suspension system becomes more complex, particularly when the solution composition interferes with the retention process.

As concluded in the above sections, the retention mechanism changed in accord with the decrease in soil solution pH. The mechanisms such as precipitation (as hydroxides and carbonates), cation exchange, and complexation, have been mentioned as the mechanisms involved in the heavy metal retention in the clay soils used in the study. In order to qualify and quantify the retention of heavy metals in the soils by different mechanisms, the method of sequential extraction analysis was used. The analysis was performed in order to support, or used as a direct proof for the analysis made on heavy metal retention mechanisms in the soil suspension study in the previous sections.

In the following section, the results of the sequential extraction analysis are presented and discussed. The results could provide more information on how the heavy metals were retained and how the retention mechanisms were changed as the clay soils received increasing amounts of acid.

All the experimental data used in Figs.4.20-4.28 are provided in Tables A-9 to A-19 in Appendix A.

4.4 Sequential Extraction Analysis on Heavy Metal Retention

The method of sequential extraction, or selective dissolution, for the study of heavy metal retention in soils and sediments has been developed by Chester and Hughes (1967), Gupta and Chen (1975), and Tessier et al. (1979). Yanful et al. (1988b) used this method in studying the partitioning of heavy metals that were retained in the natural clay of a landfill site. In the experiments conducted in this part of the thesis study, the sequential extraction method was used in order to obtain information on the amounts and forms of heavy metals that are retained in the clay soils at different conditions of acid added and soil solution pH. The details of the method have been presented in section 3.4 of the previous chapter. The results from the experiments are used in the evaluation of the retention mechanism of heavy metals at different buffering conditions of soil.

The sequential extraction experiment was performed following heavy metal-leachate solution application to the soils. The pH and amounts of heavy metals retained in soils were measured and the soil samples were extracted sequentially by different reagents. Heavy metals that were first extracted by KNO_3 are referred to as exchangeable phase, i.e., they were retained in soil by cation exchange mechanism. The second extraction using NaOAc-HOAc reagent released heavy metals that were retained in the carbonate phase, i.e., precipitate with carbonates in soil. Hydroxylamine hydrochloride was the third reagent used to extract heavy metals that were retained by precipitating as hydroxides and/or absorbing on the oxides or amorphous hydroxides of the soil. The fourth reagent that was used to extract heavy metals which were retained by organic phase of soil was H_2O_2. The last extraction procedure included digestion of soil with strong acids. The heavy metals that were left in this step are referred to as the residual phase. This phase refers to heavy metals that are retained by other kind of mechanisms such as specific adsorption in the soil mineral lattice

The amounts of heavy metals retained in different phases in the clay soils are plotted as shown in Figs. 4.29–4.36. Figures 4.29a–4.29d show the amounts of Pb retained by different phases with increasing amounts of acid input for the illite, montmorillonite, natural clay soil, and kaolinite respectively. Figures 4.30a–4.30d show the amounts of Pb retained by different phases at various soil solution pH values. Figures 4.31–4.32, 4.33–4.34, and 4.35–4.36 present the plots of the same relations for retention of Cu, Zn, and Cd in the soils respectively. Details of the experimental data for Figs. 4.29–4.36 are provided in Table A-20 to Table A-35 in Appendix A.

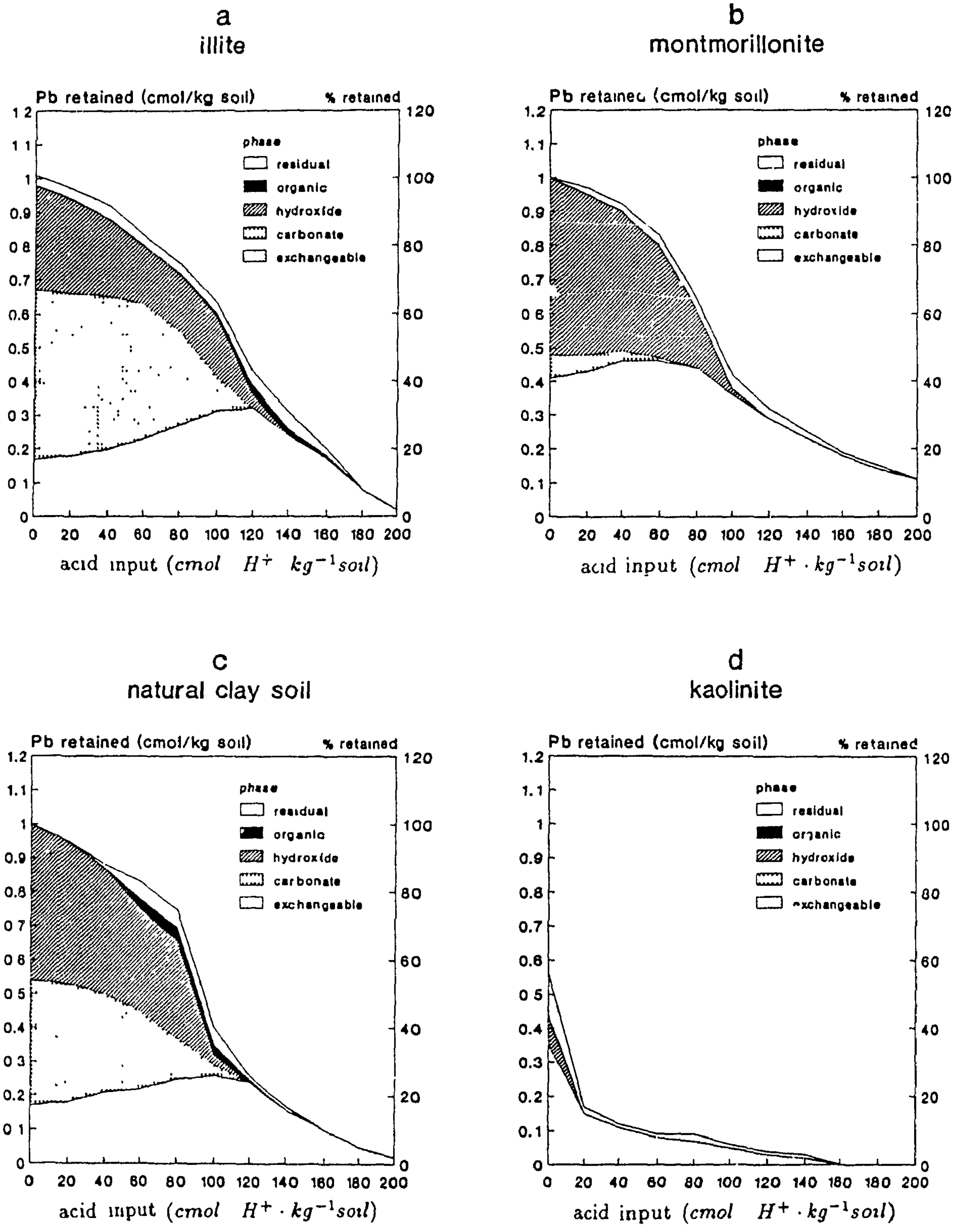


Figure 4.29 Amounts of Pb retained by different phases at increasing amounts of acid input using sequential extraction analysis in : (4.29a) illite, (4.29b) montmorillonite, (4.29c) natural clay soil, and (4.29d) kaolinite.

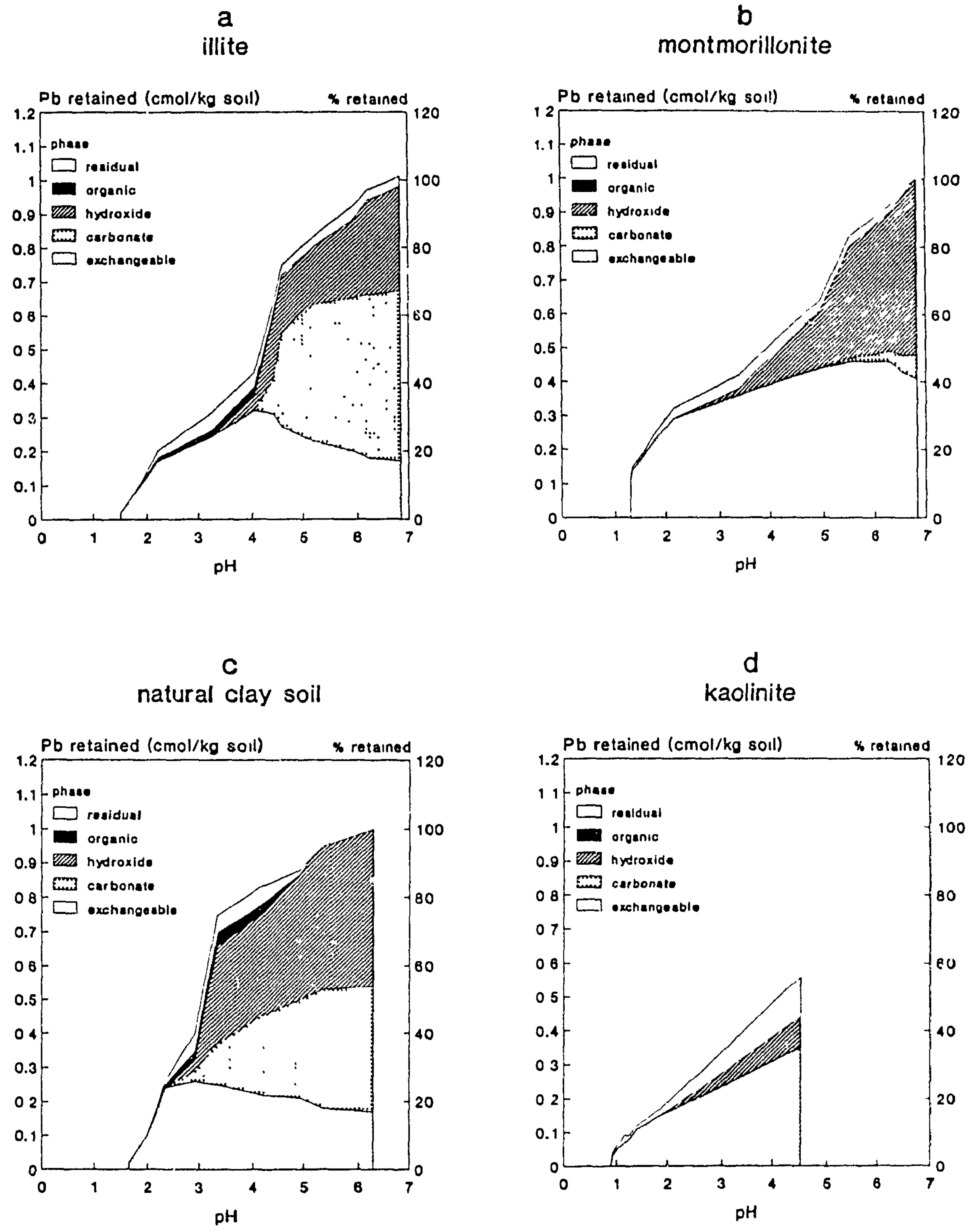


Figure 4.30 Amounts of Pb retained by different phases at various soil solution pH using sequential extraction analysis in : (4.30a) illite, (4.30b) montmorillonite, (4.30c) natural clay soil, and (4.30d) kaolinite.

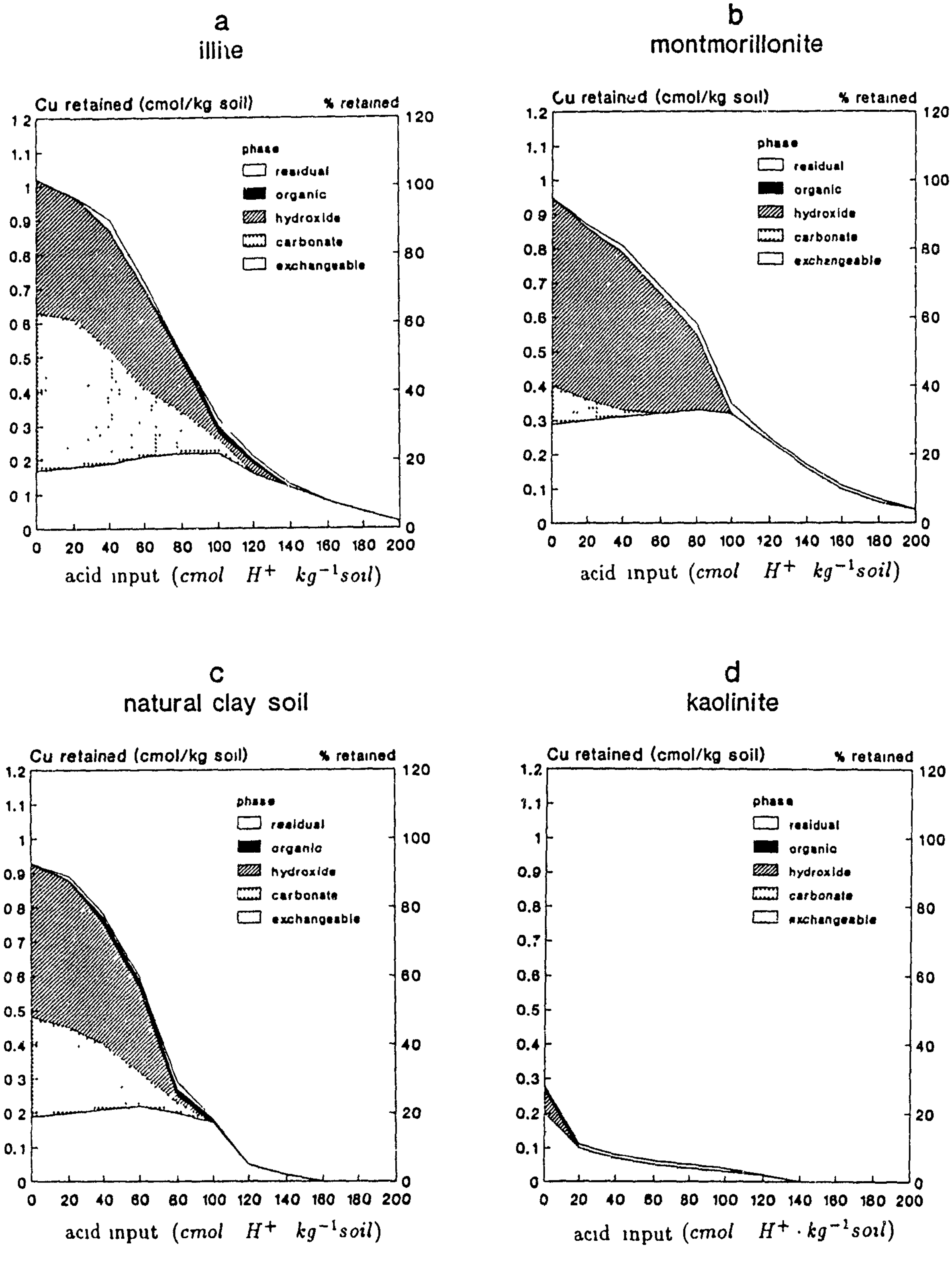


Figure 4.31 Amounts of Cu retained by different phases at increasing amounts of acid input using sequential extraction analysis in : (4.31a) illite, (4.31b) montmorillonite, (4.31c) natural clay soil, and (4.31d) kaolinite.

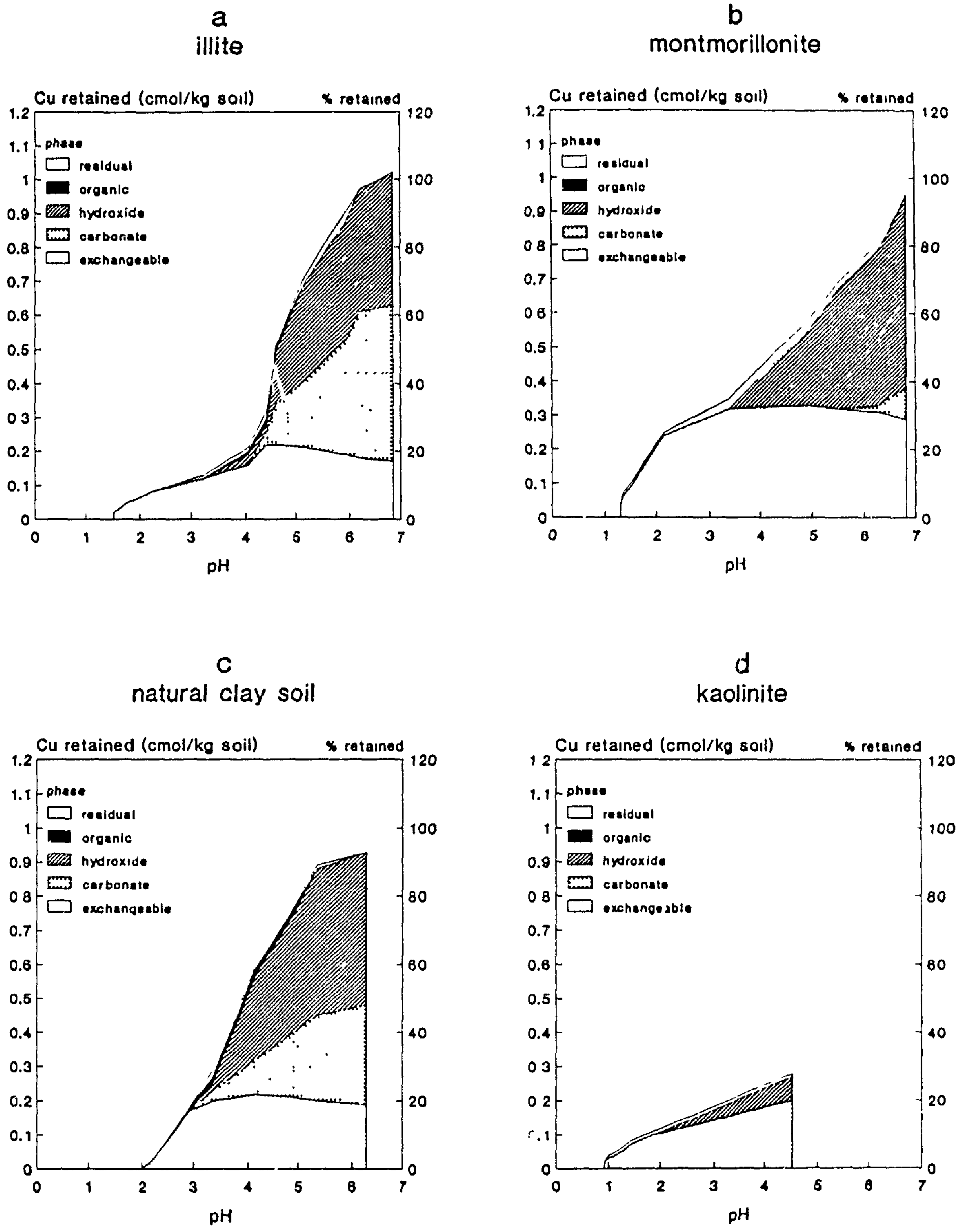


Figure 4.32 Amounts of Cu retained by different phases at various soil solution pH using sequential extraction analysis in : (4.32a) illite, (4.32b) montmorillonite, (4.32c) natural clay soil, and (4.32d) kaolinite.

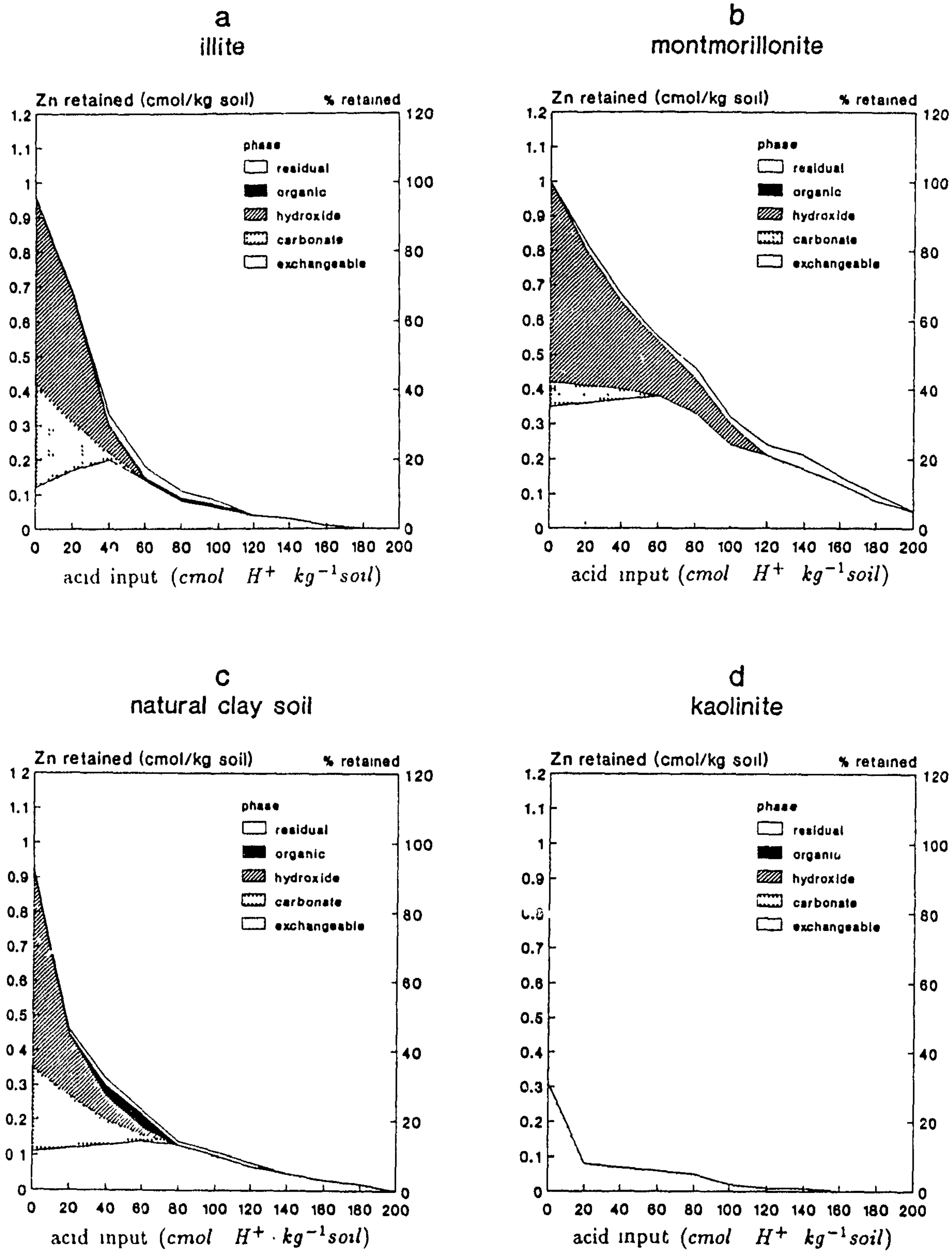


Figure 4.33 Amounts of Zn retained by different phases at increasing amounts of acid input using sequential extraction analysis in : (4.33a) illite, (4.33b) montmorillonite, (4.33c) natural clay soil, and (4.33d) kaolinite.

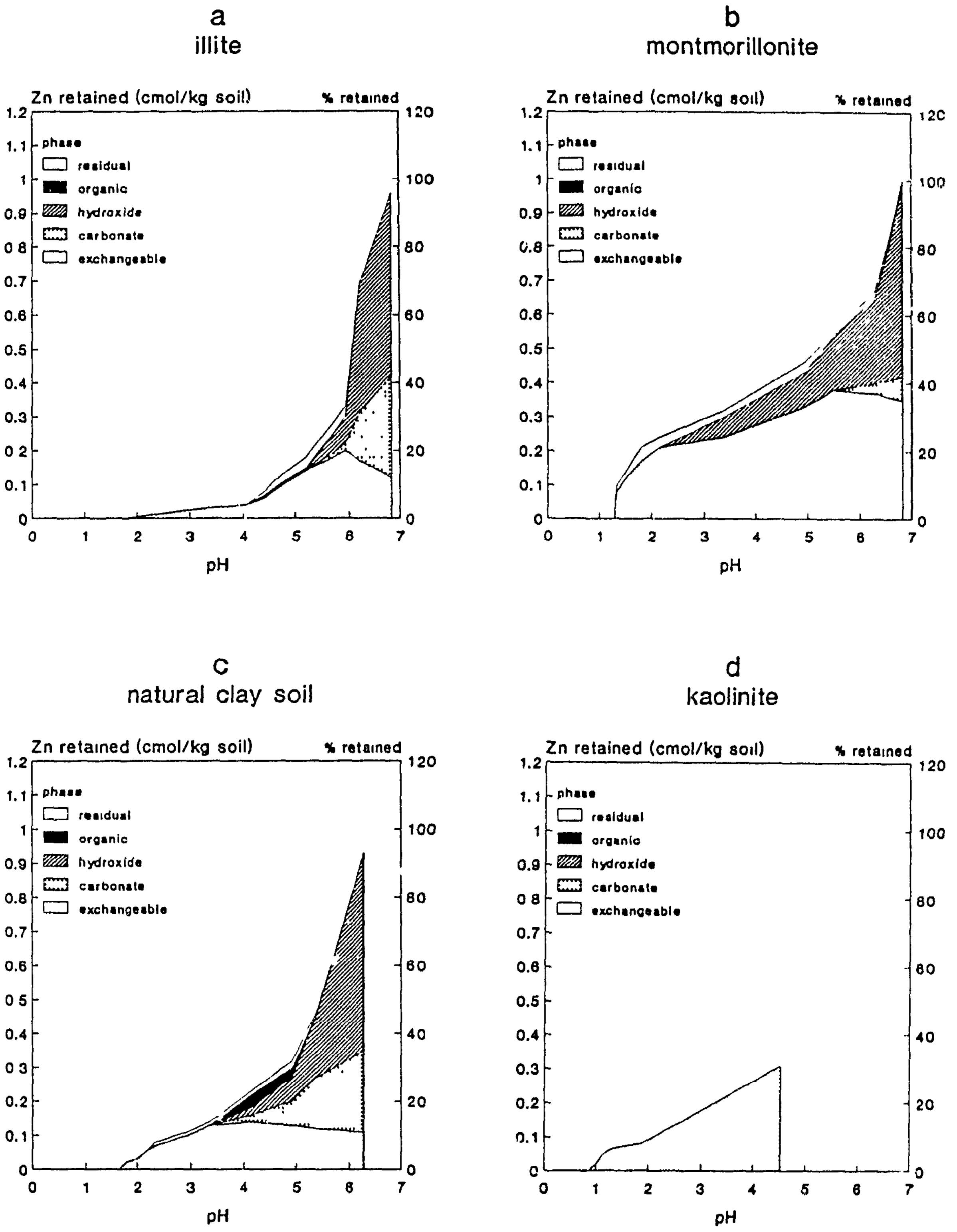


Figure 4.34 Amounts of Zn retained by different phases at various soil solution pH using sequential extraction analysis in : (4.34a) illite, (4.34b) montmorillonite, (4.34c) natural clay soil, and (4.34d) kaolinite.

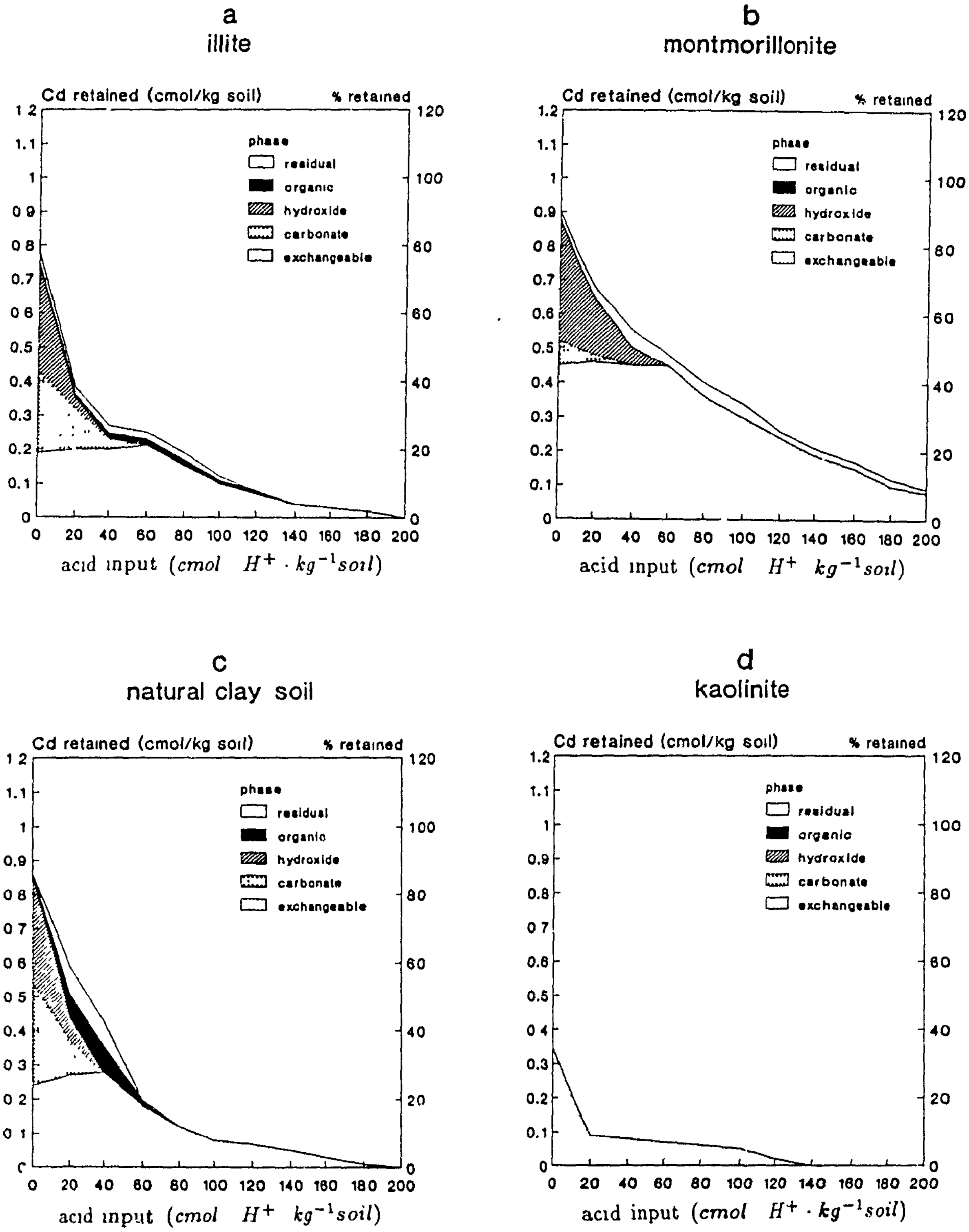


Figure 4.35 Amounts of Cd retained by different phases at increasing amounts of acid input using sequential extraction analysis in : (4.35a) illite, (4.35b) montmorillonite, (4.35c) natural clay soil, and (4.35d) kaolinite.

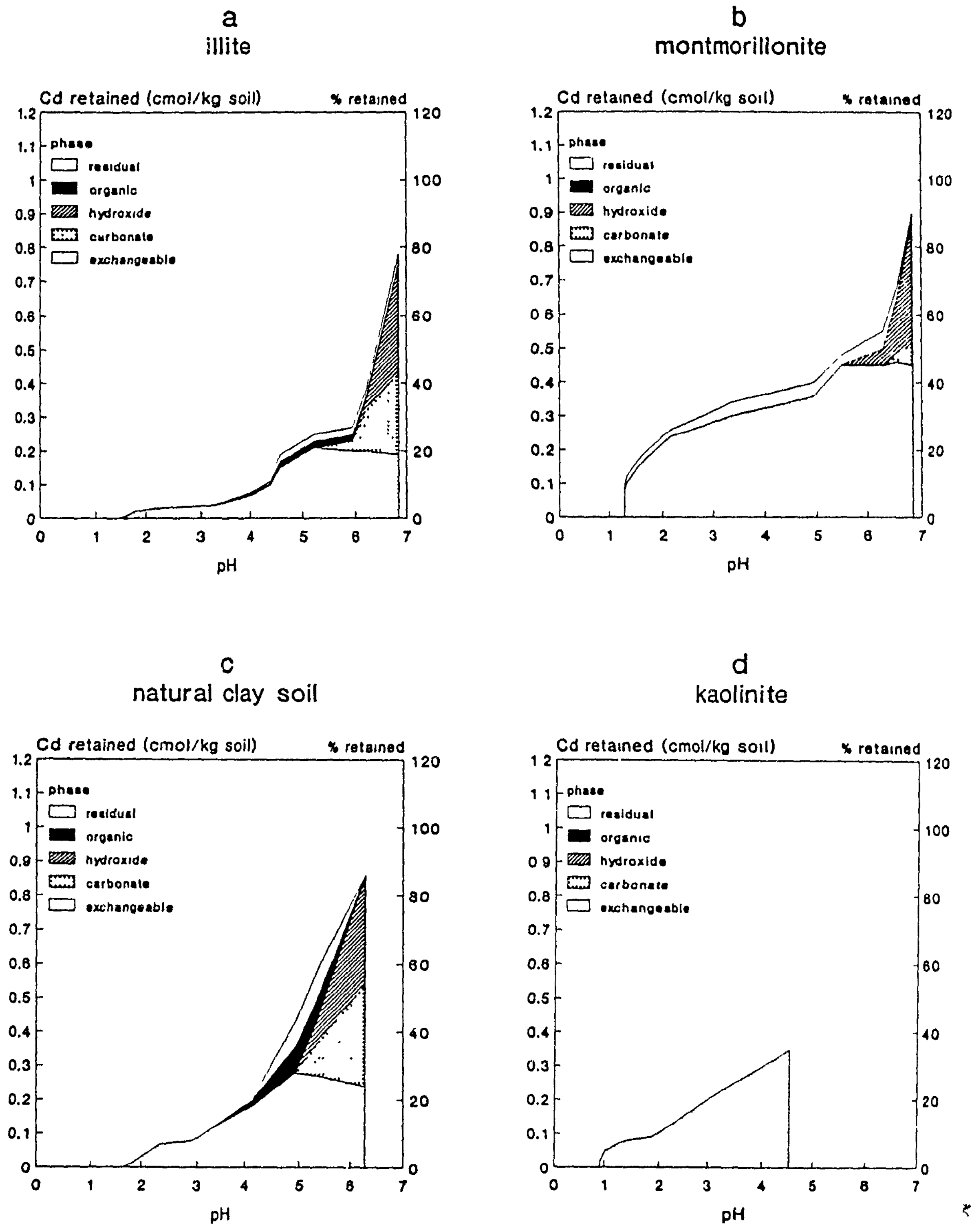


Figure 4.36 Amounts of Cd retained by different phases at various soil solution pH using sequential extraction analysis in : (4.36a) illite, (4.36b) montmorillonite, (4.36c) natural clay soil, and (4.36d) kaolinite.

In addition to the results in the above figures, the MINTEQ program was used to calculate the probable percent distribution of precipitated and dissolved species of heavy metals that could be present in the leachate solution at various solution pH values. Examples of the detailed program output are provided in Appendix B. The results are shown in Table 4.4. The information obtained from Table 4.4 is used to evaluate the retention of heavy metals in the soils.

It can be observed from Table 4.4 that as the pH increases, the form of heavy metal species in the solution changes from a simple form to a more complicated form. For example, about 88% of Pb remains as a free cation (Pb^{2+}) at pH 1–5. At pH 6, 70% of Pb precipitate whilst other species of Pb form in the solution. As the pH increases further, a higher percentage of Pb precipitates and the percentages of Pb hydroxide species increase. The same results are obtained for Cu, Zn, and Cd. However, Zn precipitates at a higher pH value than Pb and Cu, whereas Cd does not precipitate even at a pH value of 8. It can be expected from the distribution of the heavy metals that the retention mechanism of heavy metals in soils would change according to the difference in the speciation of heavy metals as the soil solution pH changes.

Figs. 4.29–4.36 reveal that in general, heavy metals were retained in soils by different phases. The amounts retained in each phase changed according to the change in soil solution pH as the soils received increasing amounts of acid.

The results in Figs. 4.29a–4.36a present the retention of Pb, Cu, Zn, and Cd in different phases in illite. The results show that in the first half of acid addition or when the pH of the soil solution $\geq$ 4, heavy metals were retained in soil by hydroxide, carbonate, and exchangeable phases resulting thereby in high amounts of total heavy metals retained. But as the amounts of acid increased or when pH becomes less ($\leq$ 4) only the exchangeable phase dominates, resulting in lower amounts of total heavy metals retained.

Table 4.4 Probable percent distribution of different heavy metal species present in heavy metal-leachate solution at various pH as calculated by MINTEQ.

Metal species	pH							
	1	2	3	4	5	6	7	8
Pb								
percent precipitated	0	0	0	0	0	70.4	99.7	100
percent dissolved	100	100	100	100	100	29.6	0.3	0
percent distribution of components among dissolved species								
Pb^{2+}	88.3	88.1	88.1	88.1	88.0	88.6	78.8	40.5
$PbCl^{+}$	9.6	9.8	9.8	9.8	9.8	10.1	9.3	4.9
$PbNO_3^{+}$	2.1	2.0	2.0	2.0	2.0	2.1	1.9	1.0
$PbOH^{+}$						1.1	9.9	51.8
$Pb(OH)_2^0$								1.7
Cu								
percent precipitated	0	0	0	0	0	92.5	99.8	100
percent dissolved	100	100	100	100	100	7.5	0.2	0
percent distribution of components among dissolved species								
Cu^{2+}	99.2	99.2	99.2	99.2	99.1	97.0	43.8	
$Cu(OH)_2^0$						1.2	52.7	98.6
$CuOH^{+}$							2.9	
Zn								
percent precipitated	0	0	0	0	0	0	0	97.3
percent dissolved	100	100	100	100	100	100	100	2.7
percent distribution of components among dissolved species								
Zn^{2+}	99.2	99.2	99.2	99.2	99.2	99.1	98.3	85.7
$ZnOH^{+}$								6.4
$Zn(OH)_2^0$								6.4
Cd								
percent precipitated	0	0	0	0	0	0	0	0
percent dissolved	100	100	100	100	100	100	100	100
percent distribution of components among dissolved species								
Cd^{2+}	78.9	78.5	78.5	78.5	78.5	77.6	77.3	76.0
$CdCl^{+}$	20.5	20.9	20.9	20.9	20.9	21.7	21.9	22.1
$CdOH^{+}$								1.0

It can be seen from Table 4.4 that when pH of the solution is high, a higher percentage of metals are precipitated and hydroxy species are formed, especially Pb and Cu. This enhances the retention of heavy metals in the soils as hydroxide phase. Moreover, it can be observed that the pH at which the heavy metals begin to be retained by hydroxide phase is lower than the pH at which the metals start to precipitate and form metal hydroxy species. For example, in Fig. 4.30a, Pb begins to be retained in the soil as hydroxide phase when pH $\geq$ 4 whereas in Table 4.4, the calculations show that Pb begins to precipitate and form hydroxy species when the pH is about 6. This means that heavy metals tend to easily form hydroxy species in the presence of soil. The results agree well with the studies by Farrah and Pickering (1979) and Maguire et al.(1981). In addition, it was suggested by James and Healy (1972) that the addition of an -OH group on the metal ion reduces the free energy required for adsorption. Adsorbed metal ions hydrolyze more readily with deprotonation of coordinated water molecules, followed thereafter by hydroxy bridging and polymer formation onto soil (Farrah and Pickering, 1979).

An interesting observation found in Fig. 4.30a is the decrease and increase in the amounts of Pb retained in different phases. The retention of the metal through cation exchange mechanism (as seen by exchangeable phase in the figure) increased as the pH increased, but decreased after the soil solution pH $>$ 4. As the soil solution pH exceeded 4 the amounts of Pb retained as hydroxides and carbonates increased. This is due to the change in heavy metal speciation as the soil solution pH changed as explained earlier from Table 4.4. In Fig. 4.30a, at pH 1-4, Pb was present in the solution as a free cation (Pb^{2+}). Therefore, the mechanism of Pb retained in the soil was by cation exchange and the amounts retained increased as pH increased. However, when the soil solution pH increased to a certain level, Pb began to form hydroxy species which resulted in the beginning of Pb retention on the soil as hydroxides. From this point, the amounts of Pb^{2+} decreased, thus, resulting in the drop of the curve of Pb retention by exchangeable phase. This phenomenon can also be seen in heavy metal retention in the montmorillonite, and natural clay soil (Figs. 4.30b–4.30c, 4.32b–4.32c, 4.34b–4.34c, and 4.36b–4.36c).

It can be observed from Figs. 4.35-4.36 that the amounts of Cd retained as hydroxide phase were small compared to the other heavy metals. This could be explained from the information in Table 4.4. Cd began to form hydroxy species at a very high pH and no precipitation occured even at pH 8. In addition, Cl^- which was present in considerable amounts in the leachate, affected the formation of Cd hydroxy species by forming Cd-Cl complexes. This led to less amounts of Cd retained in soils as hydroxides and also less total amounts retained in soils in comparison to the other metals.

In the case of the carbonate phase, when carbonates were present in the soil as in illite and the natural clay soil, heavy metals were also retained in the soils by precipitation as carbonates as seen in Figs. 4.29a–4.36a and 4.29c–4.36c. These results correspond to those obtained by Udo et al. (1970) and Yanful et al. (1988b). The amounts of heavy metals retained as carbonates in illite were higher than in the natural clay soil due to the higher amounts of carbonates in the illite (Table 4.1). The higher the carbonate content of the soil, the greater is the amount of heavy metals that can be retained by carbonate phase (Yanful et al., 1988b). It can also be observed that the amounts of heavy metal retained as carbonates in the illite and natural clay soil ceased when the pH decreased to < 4 (see, e.g., Fig. 4.30a). This is due to the fact that as pH decreases, carbonates tend to dissolve (Buckman and Brady, 1969) resulting in a drop in heavy metal retention as carbonates at low pH.

In the case of heavy metal retention in montmorillonite, the results shown in Figs. 4.29b–4.36b reveal that heavy metals were retained in hydroxide phase as much as they were as in exchangeable phase when the soil solution pH was ≥ 4, and no significant amounts of heavy metals were retained in carbonate phase. In the case of Cd retention, the area of exchangeable phase is higher than that of hydroxide phase (Fig. 4.36b). It is also observed that the amounts of heavy metals retained as exchangeable phase in the montmorillonite are higher than those in the other soils (Figs. 4.29b–4.36b). These results can be explained by the very high C.E.C. value of the montmorillonite soil (see Table 4.1). The high C.E.C. of montmorillonite provides a large number of exchangeable sites, thus increasing the possibility of heavy metal retention in the soil by exchangeable phase.

For heavy metal retention in the natural clay soil, it can be observed from the results shown in Figs. 4.29c-4.36c that the retention pattern of heavy metals in different phases is similar to that of illite. However, higher amounts of heavy metals were retained in organic phase in the natural clay soil than in illite (Figs. 4.29a-4.36a). On the other hand, less amounts of heavy metals were retained in carbonate phase in the natural clay soil than in illite. This could be due to the fact that the natural clay soil has higher amounts of organic content and has less amounts of carbonate content than illite (Table 4.1).

In the case of kaolinite, the results from Fig.4.29d-4.36d show that heavy metals were mainly retained in the soil by exchangeable phase. The calculations from MINTEQ (Table 4.4) show that at low pH (pH 1–5), most heavy metals remain in the leachate solution as free cations. This indicates that cation exchange mechanism predominates – due to the low pH of the kaolinite soil solution (≤ 4).

The results obtained from the sequential extraction analysis support the results of the soil suspension study in section 4.3. They may be summarized as follows :

(i) Heavy metals can be retained in the clay soils by several means, such as exchangeable, carbonate, hydroxide, and organic phases. However, the retention of heavy metals in any phase depends on soil solution pH, soil constituents, and heavy metals themselves. Illite, montmorillonite, and natural clay soil can retain heavy metals by hydroxide phase because they have high initial pH and can resist a change in pH for larger ranges of acid input. Kaolinite cannot retain the metals by hydroxide phase beacuse of its low initial pH. Retention of the metals as carbonates is possible in illite and natural clay soil because of the presence of carbonates in the soils. Montmorillonite retains larger amounts of the metals by exchangeable phase due to its high C.E.C. value. The amounts of Zn and Cd retained in the soils by precipitation phases are less than those of Pb and Cu because of their differences in speciation. The natural clay soil retains higher amounts of Cd than illite does because the natural soil has higher organic content than illite. In addition, at high soil solution pH, retention of heavy metal by precipitation mechanisms prevail whereas at low soil solution pH, cation exchange mechanism becomes dominant.

(ii) The results from the sequential extraction analysis support the conclusion regarding the significance of soil buffer capacity in relation to heavy metal retention. As soils receive increasing amounts of acid, high amounts of heavy metals can still be retained if the soils can resist a change in pH without allowing the pH to drop to the point where precipitation mechanisms do not prevail. The capacity of soils to retain high amounts of heavy metals as they receive increasing amounts of acid, therefore, depends directly on the soil initial pH and on their buffer capacity. Illite, montmorillonite, and natural clay soil retained high amounts of heavy metals when retention in precipitation phases were involved, whereas kaolinite could not retain high amounts because the soil could not support the retention by precipitation phases due to its low initial pH and low buffer capacity.

Thus, it can be seen that the results of the soil suspension study from sections 4.2, 4.3, and 4.4 provided several pieces of information about the soil buffer capacity and its relation to the capacity of soil to retain heavy metals. However, in order to relate these findings with heavy metal migration in land disposal sites, a soil column study was conducted. The study provided the results of heavy metal movement as soil columns received increasing amounts of acid. The results are presented in the next section and these results are related to the information obtained from the soil suspension study.

4.5 Soil Column Study on Heavy Metal Movement

The experiments were performed according to section 3.5 of the previous chapter. The results from the tests are then related with the results from the soil suspension test.

Illite, natural clay soil, and kaolinite soil columns were prepared. The soil columns were leached with acidic permeant solutions. The solutions were prepared by adding nitric acid and heavy metals (Pb, Cu, Zn, and Cd) in the form of nitrate salts to the leachate. The resulting concentration of each heavy metal in the solution was 1.0 x 10^{-3} $mol \cdot L^{-1}$ which is the same concentration used in section 4.3.4 in the soil suspension test.

The concentration of acid used in the permeant solution was carefully considered. It was desired that the acidic permeant solution, when leached through the soil column, should give a cumulative acid applied of 0–200 $cmol \quad H^{+} \ kg^{-1} soil$ as the pore volume increased. This range of cumulative acid applied was equivalent to the range of the amounts of acid added which were used in the soil suspension test. The results from the soil column test could, therefore, be readily related to the results from the soil suspension test.

If the concentration of acid in the permeant solution had been prepared at 2.5 x 10^{-4} $mol \cdot L^{-1}$, the pH of solution would have been around 3.6. This level of pH is close to the pH of acid rain (Lilieholm and Feagley, 1988). However, if this solution had been used in the test, the numbers of pore volume required to achieve a cumulative acid applied of 0–200 $cmol \quad H^{+} \quad kg^{-1} soil$ would have been considerably time consuming. Therefore, in order to accerelate the process, the permeant solution was prepared by having an acid concentration of 0.25 $mol \quad L^{-1}$ with a pH of 0.6. The solution, when leached through the soil column, resulted in a cumulative acid applied to soil of 0, 10, 20, ... ,200 $cmol \quad H^{+} \cdot kg^{-1} soil$ at increasing pore volumes of 0, 1, 2, ... ,20.

Likewise, another permeant solution was also prepared at a lower acid concentration of 0.025 $mol \cdot L^{-1}$ with a pH of 1.6. This solution, when leached through the soil column, resulted in a cumulative acid applied of 0, 1, 2, ... ,20 $cmol \quad H^{+} \cdot kg^{-1} soil$

as a pore volume increased from 0, 1, 2, ... ,20 respectively.

In summary, two sets of the three soil columns were prepared. One set was leached with permeant solution having an acid concentration of 0.025 $mol \ L^{-1}$ with a pH of 1.6 (referred to as a low acidic permeant solution). The other set was leached with a permeant solution having an acid concentration of 0.25 $mol \cdot L^{-1}$ with a pH of 0.6 (referred to as a high acidic permeant solution). Effluents from the soil columns were collected at every pore volume up to 20 pore volumes. The effluent pH and effluent concentration of heavy metals in every pore volume were measured. The results of the measurement are provided in Table A–36 to A–41 of Appendix A.

Figures 4.37a and 4.37b show the effluent pH as a function of pore volume in the illite soil column when the low and high acidic permeant solutions were applied respectively. The same relationship is also given for the natural clay soil and kaolinite soil columns as shown in Figs. 4.38a–4.38b and Figs 4.39a–4.39b respectively. Note that the corresponding values of a cumulative acid applied for each pore volume are provided at the bottom of the graphs. The results of heavy metal movement in the illite, natural clay soil, and kaolinite are also plotted in the graphs in terms of a relative concentration (C_t/C_0) versus pore volume. Note also that the relative concentration is the ratio of the column effluent concentration (C_t) and the column influent concentration (C_0). The resultant curve is generally called the "breakthrough curve" and the breakthrough point of the curve for a given element is obtained when the column effluent concentration equals the influent concentration and has a relative concentration value of one. The value of one indicates that a soil column could no longer retain the element.

The decrease in the effluent pH at increasing pore volume of the illite soil column as shown in Fig. 4.37a was small as compared to the decrease in the effluent pH shown in Fig. 4.37b. When the low acidic permeant solution was used, the effluent slowly

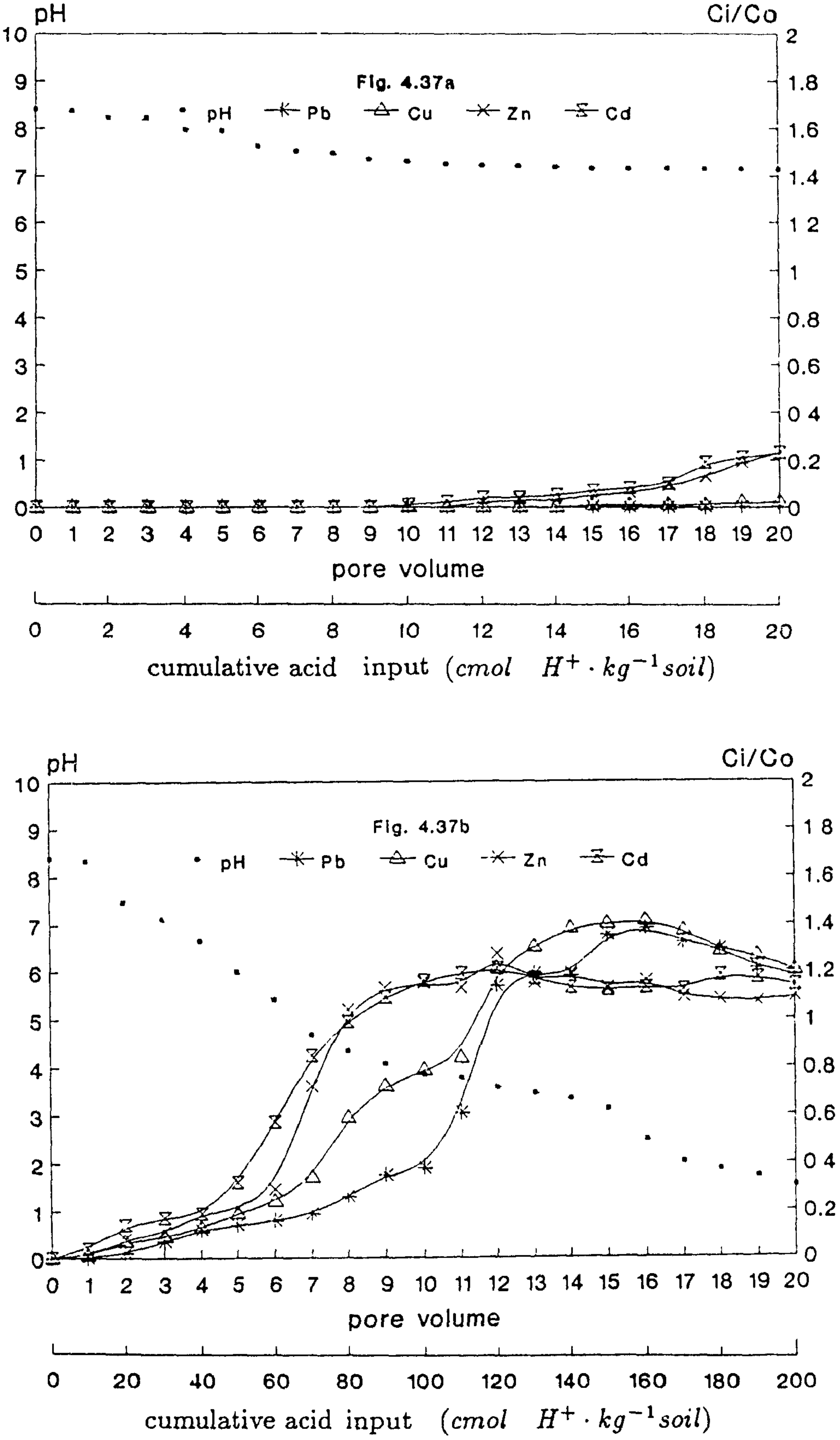


Figure 4.37 Breakthrough curves of pH and C_i/C_0 of Pb, Cu, Zn, and Cd versus pore volume of illite soil column when the columns were leached with (4.37a) low acidic permeant solution and (4.37b) high acidic permeant solution.

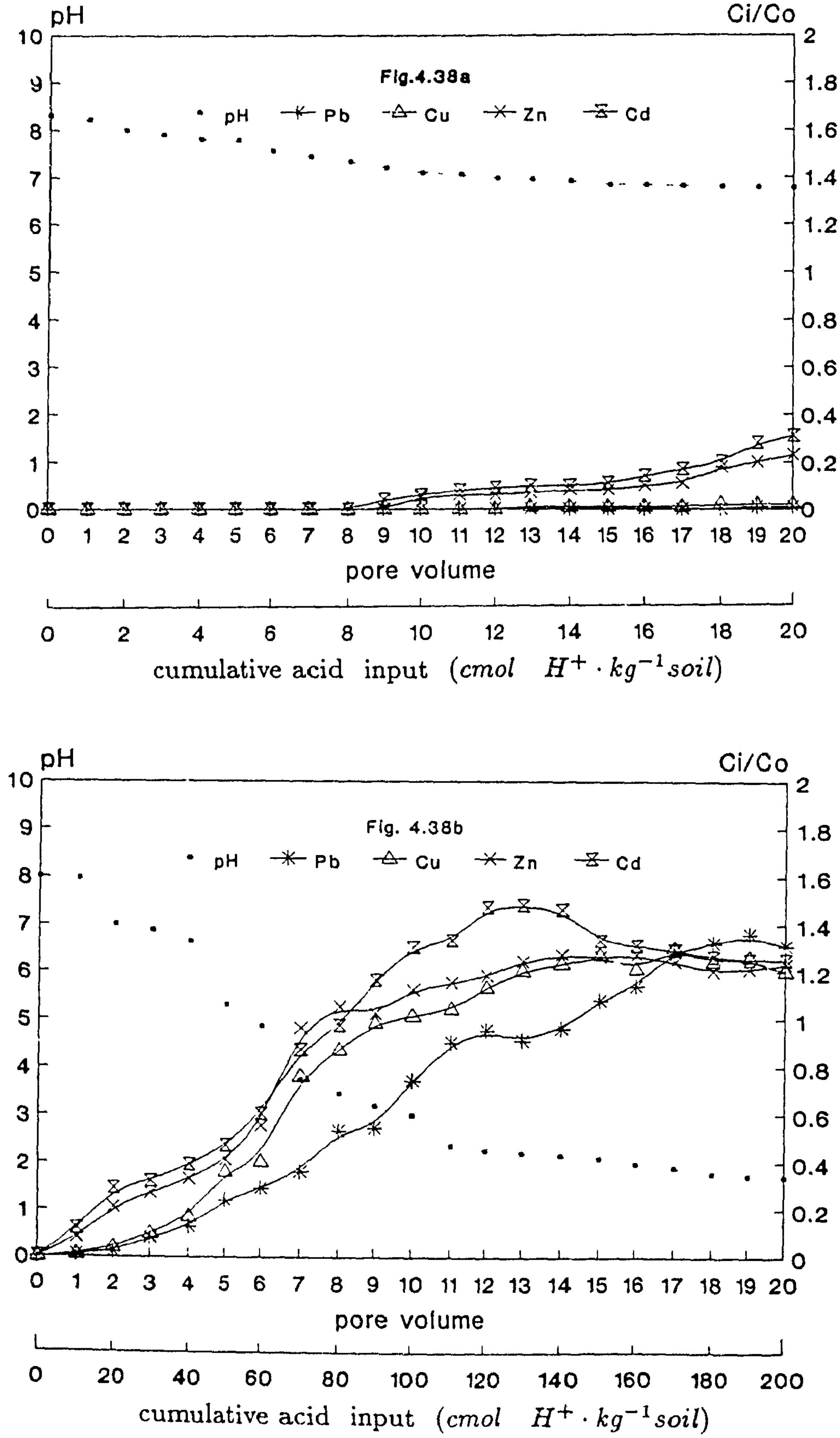


Figure 4.38 Breakthrough curves of pH and C_i/C_0 of Pb, Cu, Zn, and Cd versus pore volume of natural clay soil column when the columns were leached with (4.38a) low acidic permeant solution and (4.38b) high acidic permeant solution.

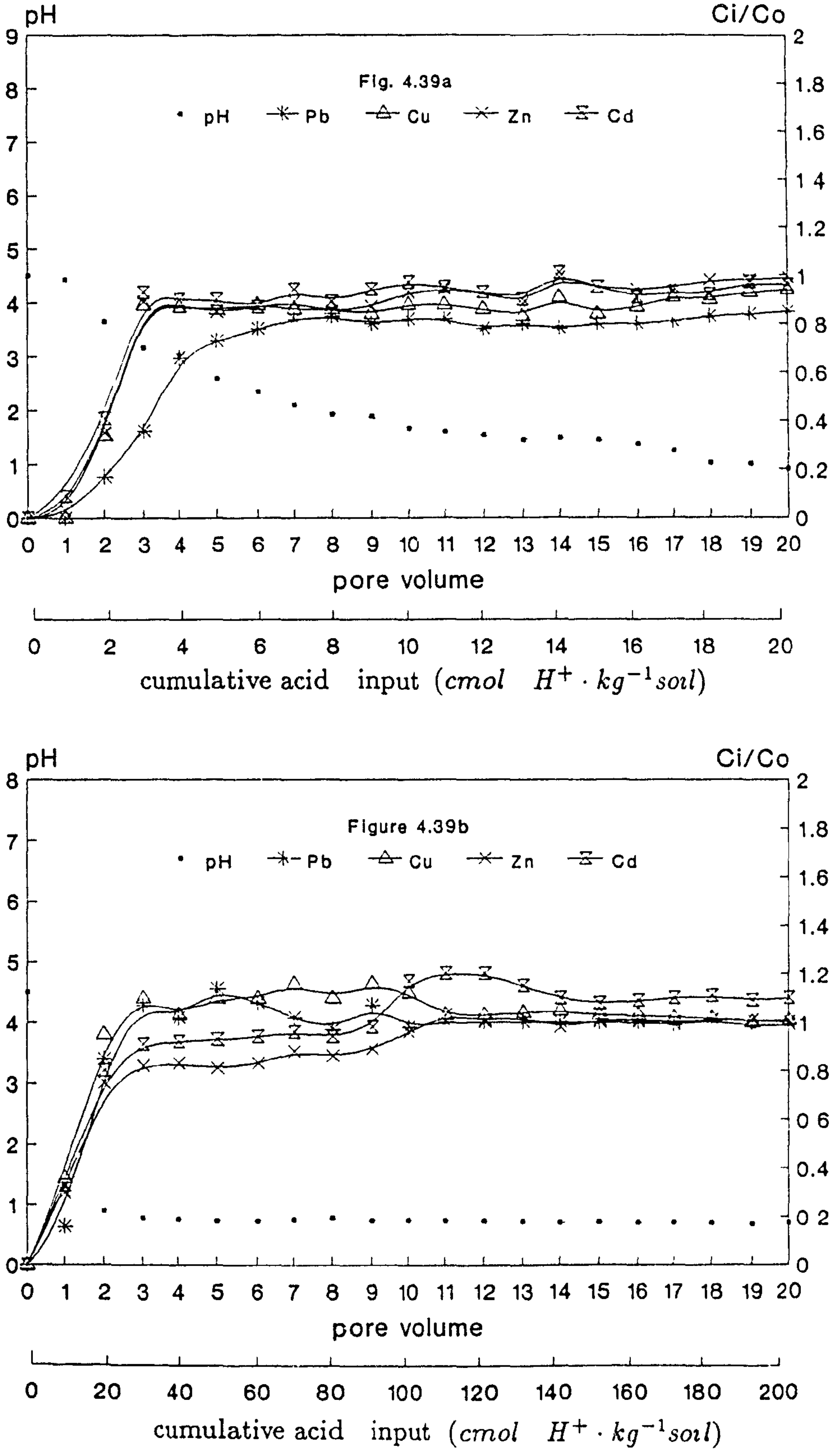


Figure 4.39 Breakthrough curves of pH and C_i/C_0 of Pb, Cu, Zn, and Cd versus pore volume of kaolinite soil column when the columns were leached with (4.39a) low acidic permeant solution and (4.39b) high acidic permeant solution.

dropped from 8 to 7 (from pore volume 1 to 20) whereas the effluent pH dropped from 8 to 3 at the same range of pore volume when the high acidic solution was used. The breakthrough curves of the metals in Fig. 4.37a are much lower than in Fig. 4.37b which mean that the metals were more mobile when the soil columns were leached with the high acidic permeant solution than with the low acidic permeant solution. The amount of acid input in the soil column when it was leached with the high acidic permeant solution is ten times greater than when it was leached with the low acidic one, thus resulted in a faster drop of the soil pH and a lower retention of heavy metals in the soil column.

In Fig. 4.37a, as the effluent pH slowly dropped from 8 to 7 (from pore volume 1 to 20), the relative concentration of Pb and Cu remained at zero, whereas the relative concentration of Zn and Cd began to rise at pore volume 10 (Fig. 4.37a). This indicates that Pb and Cu could still be retained in the soil column while Zn and Cd began to migrate from the column when the cumulative acid applied exceeded 10 $cmol \quad H^{+} \cdot kg^{-1} soil$. The results correspond to the results from the soil suspension test that the illite soil can retain less amount of Zn and Cd than Pb and Cu.

In the case when the high acidic permeant solution was used, the effluent pH decreased from 8 to 5 when the cumulative acid applied reached 60 $cmol \quad H^{+} \cdot kg^{-1} soil$ and from 5 to 3 when the cumulative acid applied exceeded 150 $cmol \quad H^{+} \cdot kg^{-1} soil$ (Fig. 4.37b). These changes of pH resulted in the changes of movement pattern of heavy metals. The relative concentrations of the metals, especially Pb and Cu, were still low at pore volume 1–6. After pore volume 6 (when the cumulative acid applied exceeded 60 $cmol \quad H^{+} \cdot kg^{-1} soil$), the effluent pH dropped to < 5 and the relative concentrations of the metals increased sharply, particularly Zn and Cd. The relative concentrations of Pb and Cu were lower than for Zn and Cd. These results indicate that the mobility order of the heavy metals in the illite soil column follows $Pb < Cu < Zn \leq Cd$. Tyler and McBride (1981) also found the same trend of heavy metal mobility order in their study. Also, the results correspond to the results from the soil suspension test that the selectivity order of the heavy metal retention in the soil are $Pb > Cu > Zn \geq Cd$.

It can be seen from Fig. 4.37b that the breakthrough points of Pb and Cu were around pore volume 12 and 11 when the cumulative acid applied reached 120 and 110 $cmol \quad H^+ \cdot kg^{-1} soil$ respectively, and the effluent pH became lower than 4. The breakthrough points of Zn and Cd were around the same pore volume of 8 (80 $cmol \quad H^+ \cdot kg^{-1} soil$) and the effluent pH became lower than 5. These breakthrough points reveal that the soil column could no longer retain the heavy metals. The relative concentration of the heavy metals increased beyond the breakthrough points (i.e., $C_i/C_0 > 1$), which indicates that the effluent concentrations of the heavy metals became higher than the influent concentrations. The plausible explanation of these results is that heavy metals which had already been retained in the soil became remobile. The remobilization of heavy metals could be due to the dissolution of heavy metals that are retained in soil by precipitation mechanisms. Another cause of remobilization includes the replacement of the heavy metals which are retained on exchangeable sites of the soil by H^+ as the cumulative acid applied increases. The phenomenon of $C_i/C_0 > 1$ was also observed by Warith (1987) but only in the case of cation such as Na^+, and K^+, – when the effluent pH of soil columns were around 7.

Figures 4.38a and 4.38b show the relationship of effluent pH and heavy metal relative concentrations as a function of pore volume in the natural clay soil columns. The reduction of effluent pH of the soil column when the low acidic permeant solution was used (Fig.4.38a) is similar to that of illite. This resulted in the similar curves of C_i/C_0 versus pore volume. All Pb and Cu were retained in the soil column but small amounts of Zn and Cd began to migrate from the soil column at pore volume 9 (1 pore volume less than illite). The reduction of effluent pH, when the high acidic leachate solution was leached, was higher in the natural clay soil than in illite (see Figs.4.37b and 4.38b). The relative concentrations of the heavy metals began to increase sharply after pore volume 5 or after the cumulative acid applied exceeded 50 $cmol \quad H^+ \quad kg^{-1} soil$ when the effluent pH dropped to ≤ 5. The relative mobility order of the metals in the natural clay soil column followed $Pb < Cu < Zn \leq Cd$ which is the same as for illite.

The breakthrough points of Pb and Cu were at pore volume 11 and 10 respectively whereas the breakthrough points Zn and Cd were at the same pore volume of 7.5. After the breakthrough points, the relative concentration values of the metals also increased as in illite. It can be seen from the above results that heavy metals were more mobile in the natural clay soil than in illite. Pb and to a lesser extent Cu were less mobile than Zn and Cd. No heavy metal migrated from the soil columns if the cumulative acid applied did not exceed 10 and 9 $cmol \quad H^+ \cdot kg^{-1} soil$ for the illite and natural clay soil respectively (for the low acidic permeant solution in Figs. 4.37a and 4.38a). A dramatic increase in the mobility of heavy metals (particularly Zn and Cd) occurred when the cumulative acid applied was ≥ 60 $cmol \quad H^+ \cdot kg^{-1} soil$ for the illite and ≥ 50 $cmol \quad H^+ \cdot kg^{-1} soil$ for the natural clay soil which are the points where the effluent pH dropped to ≤ 5.

For the kaolinite soil column, the changes in effluent pH as a function of pore volume and the breakthrough curves of heavy metals are shown in Figs. 4.39a and 4.39b. When the low acidic permeant solution was used, the effluent pH decreased from 4.5 to 1 as the pore volume increased from 1 to 20 (Fig. 4.39a). The effluent pH dropped sharply from 4.5 to 1 at the very beginning of the curve when the high acidic permeant solution was applied (Fig. 4.39b). The pH remained at the very low value of

≤ 1 throughout the whole range of pore volume. These drops of pH resulted in high values of relative concentration of the heavy metals which indicates the high mobility of heavy metals in the soil column as seen from the breakthrough curves in Fig. 4.39a and 4.39b. The mobility of the heavy metals in the soil column is not much different from each other.

It can be concluded from the above results that heavy metals are more mobile in the kaolinite than in the natural clay soil and illite respectively. The differences in the movement of heavy metals among the soil columns as the columns receive a continued load of acidic heavy metal-leachate solutions are due to the differences in the soil buffer capacity, i.e., the resistance of the soil to a change in pH which is caused by several soil constituents. The heavy metals are less mobile in the illite which has higher buffer capacity than the natural clay soil. High mobility of heavy metals occurs in the kaolinite because the soil has low initial pH and buffer capacity.

The relation between the soil buffer capacity and the heavy metals movement in soils can be clearly seen when the results from the soil suspension test are compared with the results from the soil column test. Fig. 4.40 compares the results of the pH-acid titration curves (Fig. 4.22a), the amounts of heavy metals retained as a function of acid addition (Fig. 4.23a), and the breakthrough curves (Figs. 4.37a–4.37b) of the illite.

It can be seen that the reduction of the soil solution pH when heavy metal and leachate is involved (Fig. 4.22a) is similar to the reduction of the effluent pH of the soil column (Fig. 4.37b). For example, the pH reduced to 5 when acid applied reached 60 $cmol\ \ H^{+} \cdot kg^{-1} soil$ and from 5 to 3 when acid applied exceeded 160 $cmol\ \ H^{+} \cdot kg^{-1} soil$. The retention curves of heavy metals (Fig. 4.23a) correspond to the breakthrough curves (Fig. 4.37b) in that heavy metals are less mobile when

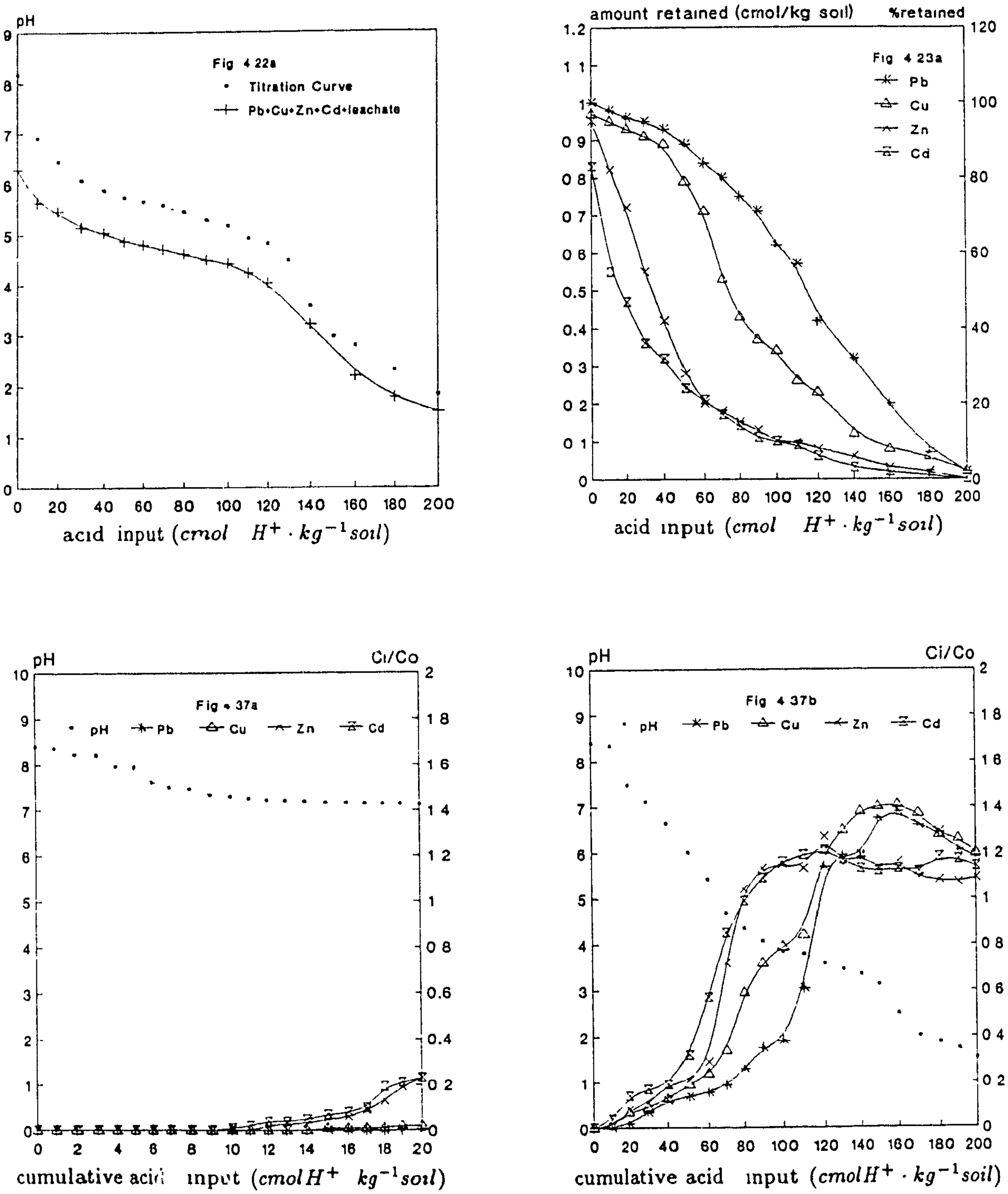


Figure 4.40 Comparison of the results from the soil suspension test and the soil column test of Illite.

high amounts of heavy metals are retained in the soil. Nearly 100% of Pb and Cu are retained when the amount of acid added does not exceed 60 $cmol\quad H^+ \cdot kg^{-1} soil$ (Fig. 4.23a) which is at the same point of cumulative acid applied when the mobility of Pb and Cu begin to increase sharply (Fig. 4.37b). This point is also the point that the soil solution pH and the effluent pH drop to < 5. In the case of Zn and Cd, nearly 100% of them retained only at the acid added of 1–10 $cmol\quad H^+ \cdot kg^{-1} soil$ (Fig. 4.23a) while Zn and Cd begin to migrate from the soil column as the cumulative acid applied exceeds 10 $cmol\quad H^+ \cdot kg^{-1} soil$ (Fig. 4.37a). This value of cumulative acid applied corresponds to the effluent pH of ≤ 7. In addition, the mobility order of the heavy metals in the soil column follows $Pb < Cu < Zn \leq Cd$ which corresponds to the selectivity order found in the illite in the soil suspension test (Fig. 4.23a).

Figure 4.41 compares the results of the pH-acid titration curves (Fig. 4.22c), the amounts of heavy metals retained as a function of acid addition (Fig. 4.23c), and the breakthrough curves (Figs. 4.38a–4.38b) of the natural clay soil. The same relationship between the results from the soil suspension test and the soil column test was found as in the case of illite. For example, the reduction soil solution pH (Fig. 4.22c) and effluent pH (Fig. 4.38b) are similar. The drop of Pb and Cu retention from 100% retained and a dramatic increase in the mobility of Pb and Cu occur at the same acid applied, i.e., 50 $cmol\quad H^+ \cdot kg^{-1} soil$ (Figs. 4.23c and 4.38b) where the soil solution pH and effluent pH decrease to < 5 (Fig. 4.22c). Zn and Cd begin to migrate from the soil column at the cumulative acid applied of 8 $cmol\quad H^+ \cdot kg^{-1} soil$ (Fig. 4.38a) where the amounts of Zn and Cd retained drop sharply (Fig. 4.23c). The mobility order of the heavy metals in the soil column follows $Pb < Cu < Zn \approx Cd$ which corresponds to the selectivity order found for the natural clay soil in the soil suspension test (Fig. 4.23c).

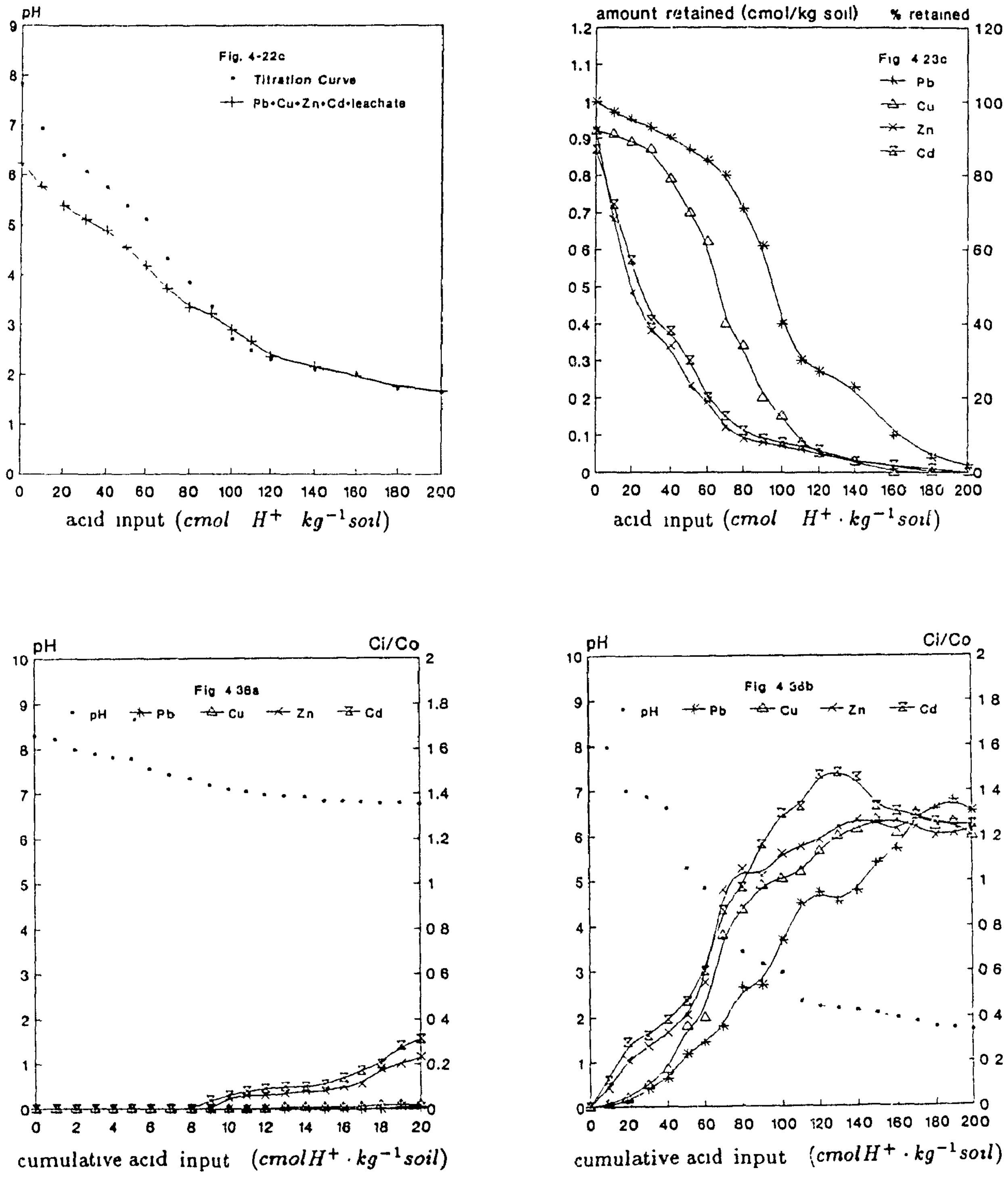


Figure 4.41 Comparison of the results from the soil suspension test and the soil column test of natural clay soil.

Figure 4.42 compares the results of the soil suspension test of kaolinite (Figs. 4.22d and 4.23d) with the results from the soil column test (Figs. 4.39a–4.39b). It can be seen from the above figures that the drop in effluent pH of the kaolinite soil column (Fig. 4.39b) corresponds to the drop in the kaolinite soil solution pH (Fig. 4.22d). As expected, the low initial pH of kaolinite and the dramatic decrease of the soil solution pH and the effluent pH result in the low retention and high mobility of heavy metals in kaolinite (see Figs. 4.23d, 4.39a, and 4.39d).

It can be clearly seen from the above comparison that the determination of the soil buffer capacity by pH-acid titration could give us some idea of how heavy metals might be retained or migrate in the soil. In addition, the study on heavy metal retention by soil suspension test could be used to predict the heavy metal movement in soil column.

The above results and discussion can be summarized as follows :

(i) The capacity of the soil column to retard or attenuate heavy metals as it receives a continual heavy metal-leachate solution depends on the concentration of acid in the solution and on the buffer capacity of the soil.

(ii) Movement of heavy metals in the clay soils follows the order illite < natural clay soil << kaolinite which corresponds to the results from the soil suspension test, i.e., the retention of heavy metals in the clay soils follows illite > natural clay soil >> kaolinite.

(iii) Mobility of heavy metals follows the order $Pb < Cu < Zn \leq Cd$ in the illite and $Pb < Cu < Zn \approx Cd$ in the natural clay soil whereas the mobility of heavy metals in the kaolinite does not show much difference for each heavy metals. The order corresponds to the selectivity order found in the soil suspension test.

(iv) The comparison of the results from the soil suspension test and the soil column test shows a very close relation of the results. This indicates that the soil suspension

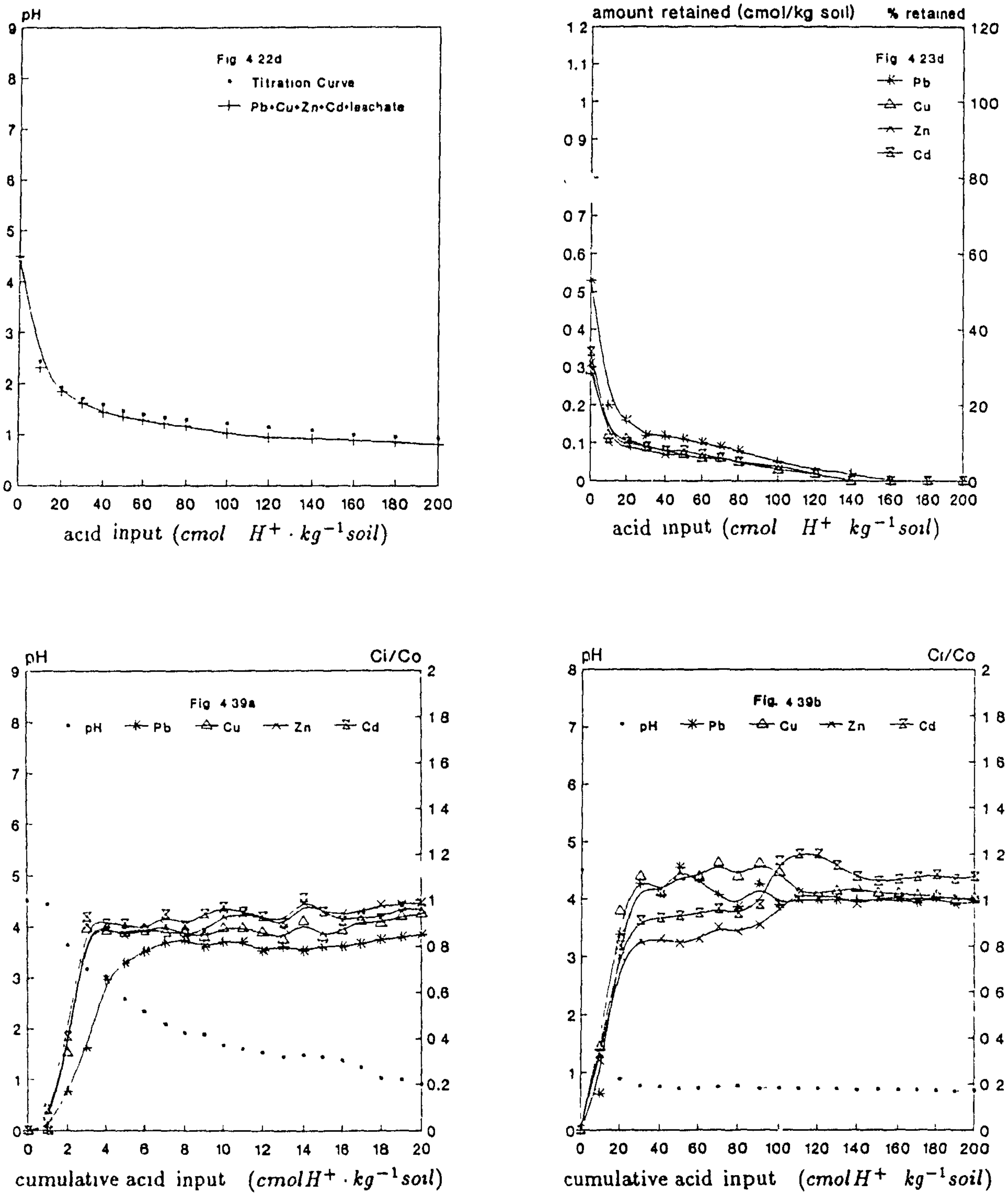


Figure 4.42 Comparison of the results from the soil suspension test and the soil column test of kaolinite.

test could be used to predict the heavy metal movement in soil. In addition, the determination of soil buffer capacity by pH-acid titration could give a general view of the change in the soil pH if the soil receives increasing amounts of acid.

(v) Without the experiment on heavy metal retention or heavy metal movement, the pH-acid curve could give us some idea of how heavy metals might be retained or migrate in the soil. Results of the experiment on heavy metal retention by soil suspension test or heavy metal movement by soil column test performed in this study confirm that the retention or movement of heavy metals in soil could be predicted by the pH-acid titration curve of the soil.

(vi) The results obtained from the determination of soil buffer capacity, the experiment on soil suspension test, the sequential extraction analysis, and the experiment from soil column study provide a good picture of the role of soil buffer capacity on the retention of heavy metals in soils.

(vii) An observation which could be drawn from these soil suspension and soil column tests is that if the pH of the leachate remains high (≥ 7), the heavy metal migration would not likely occur. This observation is also found in the study by Yong et al. (1986) and Yanful et al. (1988a and 1988b). However, if the pH of leachate is affected, for example by acid rain, the migration of heavy metals would possibly occur. The degree of migration depends on leachate pH, soil pH and its buffer capacity. The determination of soil buffer capacity would give information which could describe the susceptibility of the soil to retain heavy metals. Moreover, the determination of soil buffer capacity could help in the selection of a landfill site, along with other geolcgical and physical factors that have to be considered in the site selection.

CHAPTER 5

CONCLUSIONS

5.1 Concluding Remarks

This research work concentrated mainly on the study of the significance of pH and soil buffer capacity in the retention of heavy metals by clay soils. Due to an increased interest in the effect of acid rain and acid wastes on soils, the emphasis of the study was on the capacity of soil to retain heavy metals as soils received increasing amounts of acid. The investigation of the relation of soil buffer capacity and the capacity of soil to retain heavy metals was conducted both by soil suspension test and soil column test. The experiments for both kinds of tests gave several useful results which were discussed in the previous chapter. The interesting observations and conclusions of the study may be drawn here as follows :

(1) When soil receives increasing amounts of acid, changes in the soil pH could be small or large depending on the buffer capacity of the soil. Determination of soil buffer capacity by pH-acid titration gives useful information on the resistance pattern of the soil to pH changes. The buffer capacity of soil in this study depends mainly on soil carbonate content and soil C.E.C. value. The kaolinite used in this study has a low initial pH and very low buffer capacity due to its low C.E.C. value, and has no significant amount of any other soil constituent. The illite has a high initial pH and the highest buffer capacity because of its high carbonate content – in relation to the other clay soils used. The montmorillonite does not have any significant amount of carbonates; however, it has the second highest buffer capacity due to its very high

C.E.C. value. The natural clay soil has some significant amounts of amorphous and organic content but has less C.E.C. value and carbonate content than illite. The buffer capacity of the natural clay soil is lower than that of illite and montmorillonite but much higher than that of kaolinite.

(2) The capacity of soil to retain heavy metals as the soil receives acidic heavy metal solution depends directly on its buffer capacity. The soil with high buffer capacity has the capacity to retain high amounts of heavy metals for a larger range of acid input or for a longer period of time compared to soil with low buffer capacity. However, soil has a limited capacity to retain heavy metals if its buffer capacity diminishes. An increasing load of acid can lead to exhaustion of soil buffer capacity which results in rapid reduction of heavy metal retention in soil. It was found from this study that high amounts of heavy metals (particularly Pb and Cu) can still be retained in soils as long as the soils can resist a change in pH without allowing the pH to drop to less than 5. In addition, the retention curves of heavy metals presented as a function of soil solution pH alone cannot fully explain the differences in heavy metal retention among soils without considering the concept of soil buffer capacity.

(3) The buffer capacity of soil and the capacity of soil to retain heavy metals are affected when the solution of heavy metals applied has several solution compositions within. The amounts of heavy metals retained in soils decrease as the application of heavy metal solution to soils changes from separately applied to compositely applied and compositely applied with leachate. Competitive effects among heavy metals and interference of several components from the leachate are involved. However, the selectivity order of heavy metal retention remains the same. The order follows $Pb > Cu > Zn > Cd$ in illite, montmorillonite, and natural clay soil particularly when the soils are at high pH. The order follows to $Pb > Cd > Zn > Cu$ in kaolinite and

when montmorillonite soil is at low pH.

(4) Sequential extraction analysis performed in this study reveals that the dominant retention mechanisms of heavy metals are precipitation mechanisms when soil is at high pH. It was found that as soil pH decreases, precipitation mechanisms become less important; cation exchange mechanism becomes more dominant resulting in the reduction of amounts of heavy metals retained in soil. Heavy metals can precipitate as hydroxides and/or carbonates depending on soil components. Precipitation of heavy metals by both phases are responsible for high amounts of heavy metals retained in the illite and natural clay soil whereas precipitation by hydroxide and cation exchange phases are responsible for high amounts of heavy metals retained in the montmorillonite soil.

(5) It was found from the soil column study that the capacity of soil to retard or attenuate heavy metals as it receives continual heavy metal-leachate solution depends on the concentration of acid in the solution and the buffer capacity of soil. Migration of heavy metals is very high in the kaolinite soil compared to the other soils. Heavy metals are less mobile in the illite soil than in the natural soil. No movement of heavy metals out of the soil column occurs while the effluent pH of the soil column is still high. Relative mobility of the metals in soil columns follows the order $Pb < Cu < Zn \leq Cd$. The results correspond to the results of heavy metal retention in the soil suspension test.

(6) The experiments on soil buffer capacity determination, heavy metal retention by soil suspension test, and heavy metal movement in soil column test provided the relation of soil buffer capacity with the capacity of soil to attenuate heavy metals when acid is involved. The results obtained reveal that determination of soil buffer capacity by pH-acid titration can be used as an indirect tool to predict heavy metal migration

in soil.

From the above conclusions, it is recommended from this study that the soil buffer capacity is a parameter that should be included in the determination of soil properties along with other parameters such as C.E.C., pH, surface area, mineral composition, etc. The determination of soil buffer capacity by pH-acid titration is basically simple, less time consuming, and reliable. This recommendation is directed primarily toward the determination of soil properties for the purpose of la[illegible]sposal site selection where the effect of acid rain or acid wastes could be involve[illegible]he recommendation is also toward land application of sludge, waste streams or leachate, where changes in pH and accumulations of heavy metals in topsoils are likely to occur.

In addition, the experimental method for heavy metal retention by soil suspension test performed in this study could be applicable in the prediction and prevention of groundwater contamination. This is a contamination that could be caused by disposal of industrial and municipal wastes to landfills, where the wastes may drastically alter the pH and composition of leachate.

5.2 Suggestions for Further Studies

(1) The concept of soil buffer capacity should also be applied to other groups of contaminants in which their retention in soil could be affected by pH such as organic acids.

(2) There could be an extension of the present work on the buffer capacity of the other groups of soils such as organic soils.

(3) As well as physical and chemical parameters that are used in the development of a mathematical model for predictive purposes of heavy metal migration in soil, the

addition of the soil buffer capacity in the model should be exercised. The model would provide better results of heavy metal movement in soil.

(4) The concept of soil buffer capacity could be used in the study of the effect of simulated acid rain on soils and its capacity to attenuate contaminants.

(5) Further study should be performed on the use of soil with high buffer capacity in the treatment of acid wastes such as mining wastes or some industrial wastes with considerable concentration of heavy metals.

(6) A study on the application of materials such as lime to increase the buffer capacity of soil which act as a barrier in a landfill site could be further conducted.

STATEMENT OF ORIGINALITY

To the best of the author's knowledge, this study represents the following contribution toward the practical approach in the area of heavy metal contamination problem in land application and disposal of wastes :

(1) The concept of soil buffer capacity was first applied in the field of land disposal to investigate the capacity of soils to attenuate heavy metals.

(2) The soil buffer capacity was found to be directly related with the retention of heavy metals in soils when acid is involved in the system.

(3) The use of sequential extraction analysis provided a clear picture of how heavy metals were retained in soil at different soil bufferring conditions.

(4) The soil buffer capacity was recommended as a parameter that should be included in the determination of soil properties for the purpose of land application and disposal of wastes.

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APPENDIX A

Experimental Data

Table A-1 : pH-acid titration data of the four clay soils

acid input $(cmolH^+/kgsoil)$	pH of soil solution				
	blank	kaolinite	illite	montmorillonite	natural soil
0	7.00	4.43	8.17	7.71	7.82
1	3.00	4.00	7.82		7.44
10	2.06	2.44	6.91		6.93
20	1.75	1.93	6.45	6.64	6.39
30	1.52	1.71	6.07		6.07
40	1.40	1.60	5.88	6.56	5.75
50	1.30	1.46	5.73		5.38
60	1.22	1.39	5.65	6.01	5.11
70	1.15	1.33	5.58		4.32
80	1.10	1.29	5.44	5.33	3.85
90	1.05		5.28	4.01	3.36
100	1.00	1.22	5.17	2.87	2.72
110	0.96		4.92		2.49
120	0.92	1.14	4.82	2.03	2.31
130			4.48		
140	0.85	1.08	3.57	1.72	2.10
150			2.96		
160	0.80	1.00	2.79	1.51	2.01
180	0.74	0.96	2.31	1.34	1.72
200	0.70	0.93	1.82	1.29	1.65

Table A-2 : Acid input and buffer capacity data of the four clay soils.

acid input(1)[1] and buffer capacity(2)[2] of soils									
blank		kaolinite		illite		montmorillonite		natural soil	
(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
0	0.1	0	3	0	5	0	13	0	15
5	15	5	6	5	9	20	42	5	12
10	30	10	15	10	12	40	72	10	14
15	40	15	35	15	17	60	56	15	18
20	55	20	50	20	24	80	16	20	22
25	75	25	70	25	37	90	8.5	25	28
30	90	30	90	30	52	100	15	30	34
35	100	35	100	35	66	120	40	35	35
				40	72	140	75	40	35
				50	90	170	120	45	34
				60	97	200	200	50	31
				70	97			55	28
				80	83			60	22
				90	64			65	15
				100	55			70	12
				110	50			75	10
				120	41			80	10
				130	15			85	11
				140	9			90	13
				150	28			95	19
				160	50			100	30
				170	57			105	44
				180	70			110	60
				190	77			115	85
				200	82			120	100

[1] unit = $cmol\ \ H^{+} \cdot kg^{-1} soil$

[2] unit = (cmol/kg soil)/pH

Table A-3 : pH and buffer capacity data of the four clay soils.

pH(1) and buffer capacity(2)* of soils									
blank		kaolinite		illite		montmorillonite		natural soil	
(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
1 51	100	1.70	100	1.82	82	1.40	100	2.31	100
1.52	90	1.71	90	2.31	70	1.80	75	2.49	60
1.68	50	1.90	50	2.79	50	2 10	40	2.72	30
1.90	30	2.44	15	2.96	28	3.00	15	3.36	13
2.10	20	3.00	6	3.57	9	3.90	8.5	3.85	10
2.25	12	4.43	3	4.48	15	5.10	16	4.32	12
2.50	5			4.82	41	6.10	56	5.11	22
3.00	1			4.92	50	6.50	72	5.38	31
7.00	0.1			5.17	55	6.80	42	5.75	35
				5.28	64	7.80	13	6 07	34
				5.44	83			6.38	22
				5.58	97			6.93	14
				5.65	97			7.39	12
				5.73	90			7.82	15
				5.88	72				
				6.07	52				
				6.45	24				
				6.91	12				
				7.41	9				
				8.17	5				

* unit = (cmol/kg soil)/pH

Table A-4 : pH and Pb retention in illite at different concentrations of Pb applied to the soil and at increasing amounts of acid input.

acid input	5.0 x 10^{-5} (0.05 cmol·kg^{-1} soil)		5.0 x 10^{-4} (0.5 cmol kg^{-1} soil)		5.0 x 10^{-3} (5.0 cmol·kg^{-1} soil)	
(cmol/kg soil)	pH[1]	retained[2]	pH[1]	retained[2]	pH[1]	retained[2]
0	7.76	0.05	7.23	0.5	7.06	5.0
10	6.86	0.05	6.67	0.5	6.59	5.0
20	6.45	0.05	6.21	0.5	6.10	5.0
30	6.18	0.05	5.96	0.5	5.90	5.0
40	5.97	0.05	5.76	0.5	5.63	5.0
50	5.82	0.05	5.61	0.5	5.49	5.0
60	5.68	0.05	5.47	0.5	5.26	4.95
70	5.59	0.05	5.16	0.5	5.03	4.75
80	5.42	0.05	4.85	0.49	4.63	4.5
90	5.33	0.05	4.68	0.46	4.30	4.05
100	5.09	0.05	4.40	0.415	4.03	2.9
110	4.83	0.05	4.12	0.385	3.98	2.2
120	4.72	0.05	3.90	0.31	3.77	1.85
140	3.50	0.04	3.12	0.24	2.74	1.1
160	2.60	0.025	2.05	0.18	1.87	0.75
180	1.96	0.015	1.75	0.12	1.54	0.6
200	1.67	0.01	1.54	0.09	1.42	0.4

[1] of soil solution

[2] amount of Pb retained in cmol·kg^{-1} soil

Table A-5 : pH and Pb retention in montmorillonite at different concentrations of Pb applied to the soil and at increasing amounts of acid input.

acid input	5.0×10^{-5} (0.05 cmol·kg^{-1} soil)		5.0×10^{-4} (0.5 cmol·kg^{-1} soil)		5.0×10^{-3} (5.0 cmol·kg^{-1} soil)	
(cmol/kg soil)	pH[1]	retained[2]	pH[1]	retained[2]	pH[1]	retained[2]
0	7.53	0.05	7.15	0.5	6.98	5.0
10	7.16	0.05	6.97	0.5	6.84	5.0
20	6.84	0.05	6.61	0.5	6.56	5.0
30	6.59	0.05	6.47	0.5	6.38	4.9
40	6.47	0.05	6.36	0.5	6.19	4.8
50	6.30	0.05	6.04	0.5	5.95	4.7
60	5.98	0.05	5.87	0.5	5.77	4.6
70	5.72	0.05	5.55	0.48	5.41	4.5
80	5.31	0.05	5.21	0.45	5.08	4.2
90	3.99	0.05	3.95	0.43	3.82	3.7
100	3.21	0.049	3.02	0.39	2.97	3.2
120	2.43	0.042	2.15	0.34	2.14	2.7
140	2.17	0.035	2.01	0.31	1.98	2.3
160	2.01	0.029	1.69	0.26	1.81	1.8
180	1.88	0.027	1.74	0.23	1.66	1.6
200	1.65	0.024	1.53	0.20	1.50	1.4

[1] of soil solution

[2] amount of Pb retained in cmol·kg^{-1} soil

Table A-6 : pH and Pb retention in natural clay soil at different concentrations of Pb applied to the soil and at increasing amounts of acid input.

acid input	5.0×10^{-5} (0.05 cmol·kg^{-1} soil)		5.0×10^{-4} (0.5 cmol·kg^{-1} soil)		5.0×10^{-3} (5.0 cmol·kg^{-1} soil)	
(cmol/kg soil)	pH^1	retained^2	pH^1	retained^2	pH^1	retained^2
0	7.50	0.05	7.14	0.5	6.48	5.0
10	6.84	0.05	6.53	0.5	5.73	5.0
20	6.13	0.05	6.08	0.5	5.29	4.9
30	5.87	0.05	5.67	0.5	5.01	4.75
40	5.57	0.05	5.45	0.5	4.64	4.55
50	5.23	0.05	5.11	0.5	4.33	4.05
60	4.83	0.05	4.71	0.48	4.16	3.8
70	4.23	0.049	4.12	0.45	3.64	3.4
80	3.47	0.048	3.64	0.40	3.51	2.8
90	3.25	0.045	3.09	0.36	3.03	2.45
100	3.05	0.04	2.77	0.33	2.63	1.9
110	2.62	0.035	2.59	0.27	2.54	1.55
120	2.46	0.03	2.42	0.22	2.40	1.15
140	2.21	0.02	2.19	0.17	2.17	0.65
160	2.09	0.015	2.05	0.12	1.96	0.5
180	1.87	0.01	1.82	0.08	1.69	0.4
200	1.63	0.005	1.61	0.06	1.48	0.25

[1] of soil solution

[2] amount of Pb retained in cmol·kg^{-1} soil

Table A-7: pH and Pb retention in kaolinite at different concentrations of Pb applied to the soil and at increasing amounts of acid input.

acid input	5.0×10^{-5} (0.05 $\text{cmol}\cdot\text{kg}^{-1}$ soil)		5.0×10^{-4} (0.5 $\text{cmol}\cdot\text{kg}^{-1}$ soil)		5.0×10^{-3} (5.0 $\text{cmol}\cdot\text{kg}^{-1}$ soil)	
(cmol/kg soil)	pH[1]	retained[2]	pH[1]	retained[2]	pH[1]	retained[2]
0	4.17	0.045	3.82	0.38	3.43	2.40
10	2.14	0.015	2.11	0.19	2.08	1.60
20	1.79	0.01	1.75	0.135	1.75	1.10
30	1.64	0.008	1.60	0.105	1.56	0.95
40	1.47	0.005	1.45	0.09	1.42	0.85
50	1.40	0.005	1.38	0.07	1.35	0.75
60	1.30	0.005	1.27	0.065	1.25	0.65
70	1.24	0.005	1.21	0.06	1.18	0.55
80	1.15	0.005	1.14	0.055	1.12	0.45
100	1.07	0.005	1.05	0.05	1.02	0.35
120	0.96	0.005	0.93	0.045	0.93	0.25
140	0.92	0.005	0.9	0.04	0.9	0.2
160	0.87	0.005	0.84	0.035	0.84	0.15
180	0.82	0.005	0.81	0.03	0.8	0.1
200	0.78	0.005	0.77	0.025	0.75	0.075

[1] of soil solution

[2] amount of Pb retained in $\text{cmol}\cdot\text{kg}^{-1}$ soil

Table A-8 : pH and heavy metal retention in illite at increasing amounts of acid input when heavy metals were applied separately.

acid input (cmol/kg soil)	Pb		Cu		Zn		Cd	
	pH[1]	retained[2]	pH[1]	retained[2]	pH[1]	retained[2]	pH[1]	retained[2]
0	7.27	1.00	7.35	1.00	7.65	1.00	7.96	0.96
10	6.52	1.00	6.91	1.00	6.60	0.99	6.85	0.96
20	6.23	1.00	6.61	1.00	6.36	0.95	6.35	0.88
30	6.02	1.00	6.01	1.00	6.08	0.92	6.15	0.78
40	5.71	1.00	5.75	1.00	5.89	0.88	5.91	0.70
50	5.58	1.00	5.64	0.99	5.73	0.80	5.77	0.60
60	5.38	0.97	5.33	0.96	5.50	0.70	5.62	0.55
70	5.28	0.96	5.29	0.93	5.37	0.41	5.47	0.50
80	4.94	0.91	5.11	0.83	5.36	0.29	5.38	0.43
90	4.78	0.78	5.10	0.76	5.24	0.23	5.22	0.33
100	4.60	0.66	5.04	0.63	5.17	0.21	4.97	0.21
110	4.30	0.59	4.72	0.50	5.00	0.16	4.72	0.15
120	4.14	0.48	4.63	0.38	4.82	0.14	4.52	0.13
140	3.41	0.23	3.44	0.18	3.66	0.12	3.56	0.06
160	2.57	0.18	2.84	0.13	3.01	0.10	3.01	0.05
180	2.06	0.14	2.30	0.10	2.74	0.06	2.75	0.04
200	1.65	0.08	2.10	0.06	2.14	0.03	2.51	0.03

[1] of soil solution

[2] amount retained in cmol·kg^{-1} soil

Table A-9 : pH and heavy metal retention in montmorillonite at increasing amounts of acid input when heavy metals were applied separately.

acid input (cmol/kg soil)	Pb		Cu		Zn		Cd	
	pH[1]	retained[2]	pH[1]	retained[2]	pH[1]	retained[2]	pH[1]	retained[2]
0	6.65	1.00	7 26	0.97	7 39	1.00	7.45	0.96
20	6.26	0.98	6.31	0.95	6.56	0.98	6.65	0.86
40	6.1[illegible]	0.97	6 23	0 94	6.24	0.91	6.26	0.78
60	5.67	0.96	6.06	0.92	6.00	0.86	5.52	0.72
80	5.05	0 89	5.56	0.89	5.63	0.81	5.32	0.71
90	3.75	0.83	4.01	0.80	4.26	0 76	3 82	0.69
100	2.94	0.77	2.68	0.67	2.90	0.68	2.84	0.67
120	2.07	0.71	1.97	0.58	2.08	0.60	1.92	0.62
140	1.76	0.64	1.82	0.51	1.84	0.56	1.74	0.58
160	1 66	0.56	1.49	0.47	1.56	0.49	1.34	0 50
180	1 57	0 51	1.46	0 42	1.41	0.44	1.24	0.46
200	1.31	0.45	1.39	0.36	1.21	0.37	1.13	0.38

[1] of soil solution

[2] amount retained in cmol·kg^{-1} soil

Table A-10. pH and heavy metal retention in natural clay soil at increasing amounts of acid input when heavy metals were applied separately.

acid input (cmol/kg soil)	Pb		Cu		Zn		Cd	
	pH[1]	retained[2]	pH[1]	retained[2]	pH[1]	retained[2]	pH[1]	retained[2]
0	7 10	1.00	7.15	1.00	7.17	1.00	7.19	0.98
10	6 27	1 00	6.41	1.00	6.49	0.93	6 54	0.92
20	5 88	1.00	6.13	1.00	6 09	0.87	5.99	0.89
30	5.64	1.00	5.82	1.00	5.82	0.84	5.78	0.75
40	5.31	1.00	5.57	1.00	5.58	0.74	5.49	0 69
50	4.89	1.00	5 19	0.98	5.25	0.63	5.23	0.60
60	4.47	0.96	4.85	0.90	4.97	0.51	4.71	0.50
70	3 57	0.83	3.73	0 65	3.99	0.45	4.42	0.43
80	3.40	0 78	3.42	0 53	3.48	0.35	3.75	0.26
90	3.12	0.70	3.09	0.37	3.18	0.29	3.32	0.16
100	2.78	0.55	2.59	0.26	2.90	0.25	3.01	0.14
110	2.51	0.41	2.52	0.18	2.74	0.18	2.90	0.11
120	2.42	0.37	2.36	0.17	2.57	0.14	2.73	0.06
140	2.19	0 20	2.18	0.06	2.34	0.13	2.52	0.05
160	1.99	0.17	1.92	0.03	2.16	0.11	2.33	0.04
180	1.83	0.12	1.73	0.03	1.96	0.08	2.16	0.03
200	1.68	0.07	1.57	0 03	1.87	0.04	2.01	0.02

[1] of soil solution

[2] amount retained in cmol·kg^{-1} soil

Table A-11 : pH and heavy metal retention in kaolinite at increasing amounts of acid input when heavy metals were applied separately.

acid input (cmol/kg soil)	Pb		Cu		Zn		Cd	
	pH[1]	retained[2]	pH[1]	retained[2]	pH[1]	retained[2]	pH[1]	retained[2]
0	3.70	0.65	3 78	0 45	3 85	0.49	3 95	0 51
10	2.46	0.33	2.24	0.12	2.43	0 13	2.45	0 32
20	2.12	0.17	1.92	0.12	2.05	0 12	2 10	0.14
30	1.92	0.16	1 78	0.12	1.86	0.11	1.93	0 13
40	1.81	0.15	1.66	0 12	1.73	0 09	1 81	0 11
50	1.70	0.10	1.56	0.11	1.65	0 08	1.69	0 11
60	1.63	0.10	1 48	0.11	1.57	0 08	1 60	0 10
70	1.59	0.08	1.42	0.11	1.53	0.08	1.56	0 09
80	1.49	0.07	1 36	0.08	1.45	0.07	1 50	0 09
100	1.42	0.07	1.31	0.07	1.36	0 07	1.41	0 08
120	1 35	0.07	1.23	0 06	1.28	0.07	1.33	0 06
140	1.26	0.06	1.15	0.05	1 22	0.06	1.29	0.05
160	1.24	0.05	1.12	0.04	1.19	0.06	1 25	0 05
180	1.21	0.04	1.07	0.03	1.12	0 04	1 21	0 04
200	1.18	0 03	1.02	0 02	1.09	0 01	1 17	0 03

[1] of soil solution

[2] amount retained in cmol·kg^{-1} soil

Table A-12 : pH and heavy metal retention in illite at increasing amounts of acid input when heavy metals were applied compositely.

acid input (cmol/kg soil)	pH	amount retained in cmol/kg soil			
		Pb	Cu	Zn	Cd
0	6.39	1.00	1.00	1.00	0.88
10	5 87	1 00	1.00	0.86	0.62
20	5 54	1.00	0.98	0.77	0.52
30	5.32	1.00	0.94	0 65	0.44
40	5.21	1 00	0.92	0.45	0.37
50	5.14	1.00	0.90	0.35	0 34
60	5.07	0.99	0.77	0.27	0.29
70	4.82	0.89	0.70	0.18	0 23
80	4.67	0.78	0.51	0 17	0.20
90	4 56	0.68	0.44	0.13	0.17
100	4.35	0.50	0.38	0.12	0.13
110	4.15	0 43	0.27	0.11	0.10
120	4.08	0.41	0.22	0.10	0.06
140	3.32	0.27	0.17	0 07	0.05
160	2.74	0.16	0.10	0.06	0.03
180	2.39	0.10	0.06	0.04	0.02
200	2.15	0 06	0.03	0.02	0.02

Table A-13 : pH and heavy metal retention in montmorillonite at increasing amounts of acid input when heavy metals were applied compositely.

acid input (cmol/kg soil)	pH	amount retained in cmol/kg soil			
		Pb	Cu	Zn	Cd
0	6.19	1.00	0.95	0.98	0.93
20	5.85	0.98	0.92	0.88	0.73
40	5.61	0.94	0.89	0.80	0.64
60	5.05	0.90	0.84	0.65	0.56
80	4.94	0.83	0.72	0.60	0.48
90	3.81	0.61	0.56	0.51	0.46
100	2.91	0.55	0.46	0.43	0.40
120	2.01	0.44	0.37	0.36	0.34
140	1.69	0.39	0.23	0.29	0.30
160	1.46	0.33	0.18	0.27	0.26
180	1.35	0.25	0.12	0.19	0.19
200	1.27	0.24	0.06	0.09	0.15

Table A-14 : pH and heavy metal retention in natural clay soil at increasing amounts of acid input when heavy metals were applied compositely.

acid input (cmol/kg soil)	pH	amount retained in cmol/kg soil			
		Pb	Cu	Zn	Cd
0	6.33	1.00	1.00	0.96	0.90
10	5.73	1.00	1.00	0.78	0.75
20	5.40	1.00	0.97	0.64	0.62
30	5.14	0.99	0.93	0.52	0.50
40	5.00	0.98	0.90	0.36	0.40
50	4.71	0.97	0.87	0.25	0.36
60	4.39	0.94	0.70	0.21	0.30
70	3.75	0.80	0.52	0.19	0.21
80	3.39	0.72	0.39	0.17	0.18
90	3.33	0.59	0.34	0.15	0.15
100	2.78	0.41	0.20	0.12	0.13
110	2.60	0.34	0.16	0.11	0.10
120	2.47	0.31	0.09	0.09	0.07
140	2.36	0.24	0.05	0.07	0.05
160	2.14	0.14	0.02	0.04	0.03
180	1.96	0.10	0.02	0.03	0.02
200	1.91	0.06	0.01	0.03	0.02

Table A-15 : pH and heavy metal retention in kaolinite at increasing amounts of acid input when heavy metals were applied compositely.

acid input (cmol/kg soil)	pH	amount retained in cmol/kg soil			
		Pb	Cu	Zn	Cd
0	3.57	0.43	0.22	0 34	0 37
10	2.29	0.19	0.13	0 11	0.11
20	2.02	0.17	0.11	0.10	0.10
30	1.83	0.12	0.08	0.09	0.09
40	1.69	0.12	0 08	0.08	0.09
50	1.59	0.11	0.06	0.07	0.08
60	1.49	0.11	0.06	0.07	0.08
70	1.42	0.10	0.06	0.06	0 07
80	1.37	0.09	0.05	0.05	0.06
100	1.27	0.09	0.03	0 04	0.05
120	1.22	0.08	0.03	0.04	0.05
140	1.14	0.08	0.02	0.03	0.04
160	1.09	0.07	0.01	0.02	0.02
180	1.04	0.07	0	0.01	0.01
200	1.03	0.03	0	0	0

Table A-16 : pH and heavy metal retention in illite at increasing amounts of acid input when heavy metals were applied compositely with leachate.

acid input (cmol/kg soil)	pH	amount retained in cmol/kg soil			
		Pb	Cu	Zn	Cd
0	6.29	1.00	0.97	0.95	0.83
10	5.64	0.98	0.95	0.82	0.55
20	5.46	0.96	0.93	0.72	0.47
30	5.15	0.95	0.91	0.55	0.36
40	5.04	0.93	0.89	0.42	0.32
50	4.87	0.89	0.79	0.28	0.24
60	4.80	0.88	0.71	0.20	0.21
70	4.70	0.80	0.53	0.18	0.17
80	4.61	0.75	0.43	0.15	0.14
90	4.49	0.71	0.37	0.13	0.11
100	4.42	0.62	0.34	0.10	0.10
110	4.23	0.57	0.26	0.10	0.09
120	4.03	0.42	0.23	0.08	0.06
140	3.21	0.32	0.12	0.06	0.03
160	2.19	0.20	0.08	0.03	0.02
180	1.77	0.07	0.06	0.02	0.01
200	1.48	0.02	0.02	0	0

Table A-17 : pH and heavy metal retention in montmorillonite at increasing amounts of acid input when heavy metals were applied compositely with leachate.

acid input (cmol/kg soil)	pH	amount retained in cmol/kg soil			
		Pb	Cu	Zn	Cd
0	6.81	1.00	0.94	0.98	0.91
20	6.36	0.98	0.91	0.82	0.69
40	6.06	0.92	0.82	0.68	0.57
60	5.49	0.84	0.75	0.53	0.47
80	4.94	0.73	0.61	0.48	0.42
90	4.00	0.57	0.48	0.39	0.38
100	2.98	0.38	0.38	0.32	0.35
120	2.09	0.30	0.27	0.23	0.24
140	1.73	0.25	0.23	0.21	0.23
160	1.55	0.19	0.12	0.14	0.17
180	1.36	0.13	0.06	0.09	0.12
200	1.31	0.11	0.04	0.06	0.10

Table A-18 : pH and heavy metal retention in natural clay soil at increasing amounts of acid input when heavy metals were applied compositely with leachate.

acid input (cmol/kg soil)	pH	amount retained in cmol/kg soil			
		Pb	Cu	Zn	Cd
0	6.24	1.00	0.92	0.92	0.87
10	5.76	0.97	0.91	0.68	0.72
20	5.38	0.95	0.89	0.48	0.57
30	5.11	0.93	0.87	0.38	0.41
40	4.89	0.90	0.79	0.34	0.38
50	4.55	0.87	0.70	0.23	0.30
60	4.18	0.84	0.62	0.19	0.20
70	3.73	0.80	0.40	0.12	0.15
80	3.34	0.71	0.34	0.09	0.11
90	3.22	0.61	0.20	0.08	0.09
100	2.90	0.40	0.15	0.07	0.08
110	2.68	0.30	0.08	0.06	0.07
120	2.36	0.27	0.05	0.05	0.06
140	2.16	0.23	0.03	0.03	0.03
160	1.98	0.10	0	0.02	0.02
180	1.76	0.04	0	0	0.01
200	1.67	0.02	0	0	0

Table A-19 : pH and heavy metal retention in kaolinite at increasing amounts of acid input when heavy metals were applied compositely with leachate.

acid input (cmol/kg soil)	pH	amount retained in cmol/kg soil			
		Pb	Cu	Zn	Cd
0	4.50	0.53	0.29	0.31	0.34
10	2.32	0.20	0.12	0.10	0.11
20	1.84	0.16	0.11	0.09	0.10
30	1.62	0.12	0.09	0.08	0.09
40	1.44	0.12	0.08	0.07	0.08
50	1.35	0.11	0.07	0.07	0.08
60	1.28	0.10	0.06	0.06	0.07
70	1.20	0.09	0.06	0.06	0.06
80	1.16	0.08	0.05	0.05	0.05
100	1.02	0.05	0.03	0.03	0.04
120	0.94	0.03	0.02	0.02	0.02
140	0.92	0.02	0	0	0
160	0.89	0.0	0	0	0
180	0.85	0.0	0	0	0
200	0.80	0.0	0	0	0

Table A-20 : Pb retention in illite in different phases by sequential extraction analysis when heavy metals were applied compositely with leachate.

acid input (cmol/kg soil)	pH	amount retained in different phases in cmol/kg soil				
		exchangeable	carbonate	hydroxide	organic	residual
0	6 85	0.17	0.50	0.31	0	0.03
20	6.21	0.18	0.48	0.28	0	0.03
40	5.93	0.20	0.45	0.23	0	0.04
60	5.19	0.23	0.41	0.17	0	0.03
80	4.59	0.27	0.28	0.17	0	0.03
100	4.41	0.31	0.10	0.18	0.01	0.03
120	4.05	0.32	0	0.04	0.03	0.04
140	3.24	0.24	0	0	0.02	0.05
160	2.21	0.17	0	0	0.01	0.02
180	1.78	0.08	0	0	0	0
200	1.50	0.02	0	0	0	0

Table A-21 : Pb retention in montmorillonite in different phases by sequential extraction analysis when heavy metals were applied compositely with leachate.

acid input (cmol/kg soil)	pH	amount retained in different phases in cmol/kg soil				
		exchangeable	carbonate	hydroxide	organic	residual
0	6.83	0.41	0.07	0.52	0	0
20	6.55	0.43	0.05	0.47	0	0.02
40	6.29	0.46	0.03	0.41	0	0.02
60	5.48	0.46	0.01	0.33	0	0 03
80	4.93	0.44	0	0.17	0	0.03
100	3.37	0.36	0	0.02	0	0.04
120	2.15	0.29	0	0	0	0.03
140	1.80	0.23	0	0	0	0.02
160	1.55	0.18	0	0	0	0.01
180	1.34	0.14	0	0	0	0.01
200	1.30	0.11	0	0	0	0

Table A-22 : Pb retention in natural clay soil in different phases by sequential extraction analysis when heavy metals were applied compositely with leachate.

acid input (cmol/kg soil)	pH	amount retained in different phases in cmol/kg soil				
		exchangeable	carbonate	hydroxide	organic	residual
0	6.29	0.17	0.37	0.46	0	0
20	5.36	0.18	0.35	0.42	0	0
40	4.93	0.21	0.29	0.37	0	0.01
60	4.15	0.22	0.23	0.30	0.03	0.05
80	3.35	0.25	0.12	0.29	0.04	0.05
100	2.92	0.26	0.03	0.03	0.03	0.05
120	2.34	0.24	0	0	0.01	0.01
140	2.17	0.16	0	0	0	0.01
160	1.99	0.10	0	0	0	0
180	1.77	0.05	0	0	0	0
200	1.64	0.02	0	0	0	0

Table A-23 : Pb retention in kaolinite in different phases by sequential extraction analysis when heavy metals were applied compositely with leachate.

acid input (cmol/kg soil)	pH	amount retained in different phases in cmol/kg soil				
		exchangeable	carbonate	hydroxide	organic	residual
0	4.52	0.35	0	0.09	0	0.12
20	1.86	0.15	0	0	0	0.02
40	1.42	0.11	0	0	0	0.01
60	1.25	0.08	0	0	0	0.01
80	1.15	0.07	0	0	0	0.02
100	1.01	0.05	0	0	0	0.01
120	0.92	0.03	0	0	0	0.01
140	0.91	0.02	0	0	0	0.01
160	0.88	0	0	0	0	0
180	0.86	0	0	0	0	0
200	0.81	0	0	0	0	0

Table A-24 : Cu retention in illite in different phases by sequential extraction analysis when heavy metals were applied compositely with leachate.

acid input (cmol/kg soil)	pH	amount retained in different phases in cmol/kg soil				
		exchangeable	carbonate	hydroxide	organic	residual
0	6.85	0.17	0.46	0.39	0	0
20	6.21	0.18	0.43	0.36	0	0
40	5.93	0.19	0.33	0.35	0	0.03
60	5.19	0.21	0.20	0.29	0	0.02
80	4.59	0.22	0.12	0.15	0.02	0
100	4.41	0.22	0.04	0.02	0.02	0.02
120	4.05	0.16	0	0.03	0.01	0.01
140	3.24	0.12	0	0	0	0.01
160	2.21	0.08	0	0	0	0
180	1.78	0.05	0	0	0	0
200	1.50	0.02	0	0	0	0

Table A-25 : Cu retention in montmorillonite in different phases by sequential extraction analysis when heavy metals were applied compositely with leachate.

acid input (cmol/kg soil)	pH	amount retained in different phases in cmol/kg soil				
		exchangeable	carbonate	hydroxide	organic	residual
0	6.83	0.29	0.09	0.57	0	0
20	6.55	0.30	0.06	0.50	0	0.01
40	6.29	0.31	0.02	0.46	0	0.02
60	5.48	0.32	0	0.35	0	0.02
80	4.93	0.33	0	0.22	0	0.03
100	3.37	0.32	0	0	0	0.01
120	2.15	0.24	0	0	0	0.01
140	1.80	0.16	0	0	0	0.01
160	1.55	0.10	0	0	0	0.01
180	1.34	0.06	0	0	0	0.01
200	1.30	0.04	0	0	0	0

Table A-26 : Cu retention in natural clay soil in different phases by sequential extraction analysis when heavy metals were applied compositely with leachate.

acid input (cmol/kg soil)	pH	amount retained in different phases in cmol/kg soil				
		exchangeable	carbonate	hydroxide	organic	residual
0	6.29	0.19	0.29	0.45	0	0
20	5.36	0.20	0.25	0.43	0	0.01
40	4.93	0.21	0.19	0.35	0.02	0.01
60	4.15	0.22	0.10	0.30	0.02	0.01
80	3.35	0.20	0.03	0.02	0.02	0.02
100	2.92	0.17	0	0	0.01	0
120	2.34	0.05	0	0	0	0
140	2.17	0.02	0	0	0	0
160	1.99	0	0	0	0	0
180	1.77	0	0	0	0	0
200	1.64	0	0	0	0	0

Table A-27 : Cu retention in kaolinite in different phases by sequential extraction analysis when heavy metals were applied compositely with leachate.

acid input (cmol/kg soil)	pH	amount retained in different phases in cmol/kg soil				
		exchangeable	carbonate	hydroxide	organic	residual
0	4.52	0.20	0	0.07	0	0.01
20	1.86	0.10	0	0	0	0.01
40	1.42	0.07	0	0	0	0.01
60	1.25	0.05	0	0	0	0.01
80	1.15	0.04	0	0	0	0.01
100	1.01	0.03	0	0	0	0.01
120	0.92	0.02	0	0	0	0
140	0.91	0	0	0	0	0
160	0.88	0	0	0	0	0
180	0.86	0	0	0	0	0
200	0.81	0	0	0	0	0

Table A-28 : Zn retention in illite in different phases by sequential extraction analysis when heavy metals were applied compositely with leachate.

acid input (cmol/kg soil)	pH	amount retained in different phases in cmol/kg soil				
		exchangeable	carbonate	hydroxide	organic	residual
0	6.85	0.12	0.30	0.54	0	0
20	6.21	0.17	0.14	0.38	0	0
40	5.93	0.20	0.02	0.08	0.01	0.03
60	5.19	0.14	0	0	0.01	0.03
80	4.59	0.08	0	0	0.01	0.02
100	4.41	0.06	0	0	0	0.01
120	4.05	0.04	0	0	0	0
140	3.24	0.03	0	0	0	0
160	2.21	0.01	0	0	0	0
180	1.78	0	0	0	0	0
200	1.50	0	0	0	0	0

Table A-29 : Zn retention in montmorillonite in different phases by sequential extraction analysis when heavy metals were applied compositely with leachate.

acid input (cmol/kg soil)	pH	amount retained in different phases in cmol/kg soil				
		exchangeable	carbonate	hydroxide	organic	residual
0	6.83	0.35	0.07	0.58	0	0
20	6.55	0.36	0.05	0.39	0	0.02
40	6.29	0.37	0.03	0.25	0	0.02
60	5.48	0.38	0	0.16	0	0.01
80	4.93	0.33	0	0.10	0	0.03
100	3.37	0.24	0	0.06	0	0.02
120	2.15	0.21	0	0	0	0.03
140	1.80	0.17	0	0	0	0.04
160	1.55	0.13	0	0	0	0.02
180	1.34	0.08	0	0	0	0.02
200	1.30	0.05	0	0	0	0

Table A-30 : Zn retention in natural clay soil in different phases by sequential extraction analysis when heavy metals were applied compositely with leachate.

acid input (cmol/kg soil)	pH	amount retained in different phases in cmol/kg soil				
		exchangeable	carbonate	hydroxide	organic	residual
0	6.29	0.11	0.24	0.58	0	0
20	5.36	0.12	0.15	0.18	0	0
40	4.93	0.13	0.07	0.07	0.03	0.01
60	4.15	0.14	0.02	0.02	0.04	0.02
80	3.35	0.13	0	0	0	0.01
100	2.92	0.10	0	0	0	0.01
120	2.34	0.07	0	0	0	0.01
140	2.17	0.05	0	0	0	0
160	1.99	0.03	0	0	0	0
180	1.77	0.02	0	0	0	0
200	1.64	0	0	0	0	0

Table A-31 : Zn retention in kaolinite in different phases by sequential extraction analysis when heavy metals were applied compositely with leachate.

acid input (cmol/kg soil)	pH	amount retained in different phases in cmol/kg soil				
		exchangeable	carbonate	hydroxide	organic	residual
0	4.52	0.31	0	0	0	0
20	1.86	0.08	0	0	0	0
40	1.42	0.07	0	0	0	0
60	1.25	0.06	0	0	0	0
80	1.15	0.05	0	0	0	0
100	1.01	0.02	0	0	0	0
120	0.92	0.01	0	0	0	0
140	0.91	0.01	0	0	0	0
160	0.88	0	0	0	0	0
180	0.86	0	0	0	0	0
200	0.81	0	0	0	0	0

Table A-32 : Cd retention in illite in different phases by sequential extraction analysis when heavy metals were applied compositely with leachate.

acid input (cmol/kg soil)	pH	amount retained in different phases in cmol/kg soil				
		exchangeable	carbonate	hydroxide	organic	residual
0	6.85	0 19	0.24	0.32	0	0.03
20	6.21	0.20	0.12	0.03	0.01	0.02
40	5.93	0.20	0.03	0	0.02	0.02
60	5.19	0.21	0	0	0.02	0.02
80	4.59	0.15	0	0	0.02	0.02
100	4.41	0.10	0	0	0.01	0.01
120	4.05	0.07	0	0	0.01	0
140	3.24	0 04	0	0	0	0
160	2.21	0.03	0	0	0	0
180	1.78	0.02	0	0	0	0
200	1.50	0	0	0	0	0

Table A-33 : Cd retention in montmorillonite in different phases by sequential extraction analysis when heavy metals were applied compositely with leachate.

acid input (cmol/kg soil)	pH	amount retained in different phases in cmol/kg soil				
		exchangeable	carbonate	hydroxide	organic	residual
0	6.83	0.45	0.07	0.36	0	0 02
20	6.55	0.46	0.02	0.17	0	0.03
40	6.29	0.45	0	0.05	0	0.05
60	5.48	0.45	0	0	0	0.03
80	4.93	0.36	0	0	0	0.04
100	3.37	0.30	0	0	0	0.04
120	2.15	0.24	0	0	0	0.02
140	1.80	0.19	0	0	0	0.02
160	1.55	0.15	0	0	0	0.02
180	1.34	0.10	0	0	0	0.02
200	1.30	0.08	0	0	0	0.01

Table A-34 : Cd retention in natural clay soil in different phases by sequential extraction analysis when heavy metals were applied compositely with leachate.

acid input (cmol/kg soil)	pH	amount retained in different phases in cmol/kg soil				
		exchangeable	carbonate	hydroxide	organic	residual
0	6.29	0.24	0.30	0.32	0	0
20	5.36	0.27	0.10	0.07	0.07	0.08
40	4.93	0.28	0	0	0.08	0.07
60	4.15	0.18	0	0	0.02	0
80	3.35	0.12	0	0	0	
100	2.92	0.08	0	0	0	
120	2.34	0.07	0	0	0	0
140	2.17	0.05	0	0	0	0
160	1.99	0.03	0	0	0	0
180	1.77	0.01	0	0	0	0
200	1.64	0	0	0	0	0

Table A-35 : Cd retention in kaolinite in different phases by sequential extraction analysis when heavy metals were applied compositely with leachate.

acid input (cmol/kg soil)	pH	amount retained in different phases in cmol/kg soil				
		exchangeable	carbonate	hydroxide	organic	residual
0	4.52	0.35	0	0	0	0
20	1.86	0.09	0	0	0	0
40	1.42	0.08	0	0	0	0
60	1.25	0.07	0	0	0	0
80	1.15	0.06	0	0	0	0
100	1.01	0.05	0	0	0	0
120	0.92	0.02	0	0	0	0
140	0.91	0	0	0	0	0
160	0.88	0	0	0	0	0
180	0.86	0	0	0	0	0
200	0.81	0	0	0	0	0

Table A-36 : Results of soil column study on illite when illite soil column was leached with low acidic permeant solution.

pore volume	cumulative acid input (cmol/kg soil)	pH	C_t/C_0^* Pb	Cu	Zn	Cd
1	1	8.36	0	0	0	0
2	2	8.23	0	0	0	0
3	3	8.21	0	0	0	0
4	4	7.96	0	0	0	0
5	5	7.95	0	0	0	0
6	6	7.62	0	0	0	0
7	7	7.51	0	0	0	0
8	8	7.47	0	0	0	0
9	9	7.34	0	0	0	0
10	10	7.30	0	0	0	0.01
11	11	7.25	0	0	0	0.02
12	12	7.22	0	0	0.02	0.04
13	13	7.21	0	0	0.03	0.04
14	14	7.19	0	0	0.03	0.05
15	15	7.16	0	0.01	0.05	0.07
16	16	7.16	0	0.01	0.06	0.08
17	17	7.15	0	0.01	0.09	0.10
18	18	7.14	0	0.01	0.13	0.19
19	19	7.14	0	0.02	0.19	0.21
20	20	7.13	0	0.02	0.23	0.23

* C_t = effluent concentration
C_0 = influent concentration

Table A-37 : Results of soil column study on illite when illite soil column was leached with high acidic permeant solution.

pore volume	cumulative acid input (cmol/kg soil)	pH	C_t/C_0^*			
			Pb	Cu	Zn	Cd
1	10	8.34	0	0.01	0.01	0.04
2	20	7.48	0.02	0.07	0.08	0.14
3	30	7.12	0.07	0.09	0.11	0.17
4	40	6.65	0.12	0.13	0.19	0.19
5	50	6.01	0.14	0.19	0.21	0.32
6	60	5.42	0.16	0.24	0.29	0.57
7	70	4.68	0.19	0.34	0.72	0.85
8	80	4.35	0.26	0.59	1.04	0.99
9	90	4.07	0.35	0.72	1.13	1.09
10	100	3.85	0.38	0.79	1.15	1.16
11	110	3.79	0.61	0.84	1.13	1.19
12	120	3.58	1.14	1.21	1.27	1.21
13	130	3.46	1.19	1.30	1.15	1.17
14	140	3.35	1.18	1.38	1.19	1.13
15	150	3.13	1.35	1.40	1.13	1.12
16	160	2.49	1.38	1.41	1.16	1.13
17	170	2.01	1.32	1.37	1.09	1.12
18	180	1.87	1.29	1.28	1.08	1.18
19	190	1.72	1.21	1.26	1.07	1.17
20	200	1.52	1.18	1.20	1.09	1.14

* C_t = effluent concentration
C_0 = influent concentration

Table A-38 : Results of soil column study on kaolinite when kaolinite soil column was leached with low acidic permeant solution.

pore volume	cumulative acid input (cmol/kg soil)	pH	C_t/C_0^*			
			Pb	Cu	Zn	Cd
1	1	4.43	0	0	0.03	0.09
2	2	3.64	0.17	0.34	0.35	0.41
3	3	3.16	0.36	0.88	0.89	0.93
4	4	3.02	0.66	0.87	0.88	0.90
5	5	2.59	0.73	0.86	0.85	0.90
6	6	2.34	0.78	0.88	0.87	0.87
7	7	2.09	0.82	0.86	0.89	0.94
8	8	1.92	0.83	0.86	0.85	0.89
9	9	1.89	0.80	0.84	0.87	0.94
10	10	1.66	0.82	0.88	0.93	0.97
11	11	1.60	0.82	0.88	0.94	0.95
12	12	1.53	0.78	0.86	0.93	0.93
13	13	1.44	0.80	0.83	0.88	0.90
14	14	1.48	0.78	0.91	0.99	1.01
15	15	1.44	0.80	0.84	0.95	0.95
16	16	1.37	0.80	0.87	0.94	0.91
17	17	1.23	0.81	0.91	0.95	0.93
18	18	1.01	0.83	0.90	0.98	0.92
19	19	0.99	0.84	0.93	0.98	0.97
20	20	0.90	0.85	0.94	0.99	0.96

* C_t = effluent concentration
C_0 = influent concentration

Table A-39 : Results of soil column study on kaolinite when kaolinite soil column was leached with high acidic permeant solution.

pore volume	cumulative acid input (cmol/kg soil)	pH	C_t/C_0^*			
			Pb	Cu	Zn	Cd
1	10	1.30	0.16	0.36	0.30	0.33
2	20	0.89	0.85	0.95	0.75	0.80
3	30	0.77	1.07	1.10	0.82	0.91
4	40	0.76	1.02	1.03	0.83	0.92
5	50	0.73	1.14	1.10	0.81	0.93
6	60	0.73	1.08	1.10	0.83	0.94
7	70	0.75	1.02	1.16	0.88	0.96
8	80	0.77	0.97	1.10	0.86	0.94
9	90	0.73	1.07	1.16	0.89	0.98
10	100	0.74	0.98	1.12	0.96	1.17
11	110	0.73	1.00	1.03	1.03	1.20
12	120	0.73	1.00	1.03	1.01	1.20
13	130	0.72	1.00	1.04	1.02	1.15
14	140	0.70	1.00	1.05	0.98	1.10
15	150	0.71	1.00	1.03	1.01	1.08
16	160	0.70	1.00	1.03	1.01	1.09
17	170	0.70	0.99	1.02	1.00	1.10
18	180	0.69	1.01	1.02	1.01	1.11
19	190	0.67	0.98	1.00	1.01	1.09
20	200	0.69	0.99	1.01	1.00	1.10

* C_t = effluent concentration
C_0 = influent concentration

Table A-40 : Results of soil column study on the natural clay soil when the natural clay soil column was leached with low acidic permeant solution.

pore volume	cumulative acid input (cmol/kg soil)	pH	C_t/C_0^*			
			Pb	Cu	Zn	Cd
1	1	8.23	0	0	0	0
2	2	7.99	0	0	0	0
3	3	7.90	0	0	0	0
4	4	7.81	0	0	0	0
5	5	7.79	0	0	0	0
6	6	7.56	0	0	0	0
7	7	7.43	0	0	0	0
8	8	7.33	0	0	0	0
9	9	7.19	0	0	0	0.04
10	10	7.09	0	0	0.05	0.06
11	11	7.05	0	0	0.06	0.08
12	12	6.97	0	0	0.06	0.09
13	13	6.95	0	0.01	0.07	0.10
14	14	6.92	0	0.01	0.08	0.10
15	15	6.83	0	0.01	0.08	0.11
16	16	6.82	0	0.01	0.10	0.14
12	12	6.97	0	0.01	0.11	0.17
13	13	6.95	0	0.02	0.18	0.20
14	14	6.92	0.01	0.02	0.20	0.28
15	15	6.83	0.01	0.02	0.23	0.31

* C_t = effluent concentration
C_0 = influent concentration

Table A-41 : Results of soil column study on the natural clay soil when the natural clay soil column was leached with high acidic permeant solution.

pore volume	cumulative acid input (cmol/kg soil)	pH	C_t/C_0^*			
			Pb	Cu	Zn	Cd
1	10	7.96	0.01	0.01	0.08	0.12
2	20	7.01	0.02	0.04	0.21	0.29
3	30	6.87	0.08	0.10	0.27	0.32
4	40	6.63	0.13	0.17	0.33	0.39
5	50	5.29	0.24	0.36	0.41	0.47
6	60	4.84	0.29	0.40	0.55	0.60
7	70	3.73	0.36	0.76	0.96	0.87
8	80	3.43	0.53	0.97	1.05	0.97
9	90	3.16	0.54	0.98	1.02	1.16
10	100	2.98	0.74	1.01	1.12	1.30
11	110	2.34	0.90	1.04	1.15	1.33
12	120	2.24	0.95	1.13	1.18	1.47
13	130	2.19	0.91	1.20	1.24	1.48
14	140	2.15	0.96	1.23	1.27	1.46
15	150	2.09	1.08	1.27	1.26	1.33
16	160	1.98	1.14	1.21	1.27	1.31
17	170	1.90	1.29	1.30	1.24	1.29
18	180	1.77	1.32	1.24	1.20	1.26
19	190	1.73	1.36	1.26	1.21	1.25
20	200	1.69	1.31	1.20	1.23	1.25

* C_t = effluent concentration
C_0 = influent concentration

APPENDIX B

Example of MINTEQ Program Output

```
EXAMPLE
EX1

----------------------------------------------------------------------------- -
-
 Temperature (Celsius):  25.00
 Units of concentration: MOLAL
 Ionic strength to be computed.
 If specified, total carbonate concentration represents total inorganic carbo
 Do not automatically terminate if charge imbalance exceeds 30%
 Precipitation is allowed for all solids in the thermodynamic database and
   the print option for solids is set to: 3
 The maximum number of iterations is: 200
 The method used to compute activity coefficients is: Debye-Huckel equation
 Print the full species database including gram-formula weights and Debye-Huck
   parameters.

-----------------------------------------------------------------------------

    500  0.610E-02    -2.21
    410  0.380E-03    -3.42
    150  0.430E-02    -2.37
    460  0.120E-02    -2.92
    180  0.560E-02    -2.25
    600  0.100E-02    -3.00
    231  0.100E-02    -3.00
    950  0.100E-02    -3.00
    160  0.100E-02    -3.00
    330  0.100E-06    -7.00
    492  0.300E-02    -2.52
    280  0.900E-04    -6.00
    490  0.590E-03    -5.00

 H2O HAS BEEN INSERTED AS A COMPONENT
  3    1
    330       7.0000       0.0200
INPUT DATA BEFORE TYPE MODIFICATIONS

   ID          NAME          ACTIVITY GUESS     LOG GUESS    ANAL TOTAL
   500   Na+1                     6.156E-03        -2.210     6.100E-03
   410   K+1                      3.802E-04        -3.420     3.800E-04
   150   Ca+2                     4.266E-03        -2.370     4.300E-03
   460   Mg+2                     1.202E-03        -2.920     1.200E-03
   180   Cl-1                     5.623E-03        -2.250     5.600E-03
   600   Pb+2                     1.000E-03        -3.000     1.000E-03
   231   Cu+2                     1.000E-03        -3.000     1.000E-03
   950   Zn+2                     1.000E-03        -3.000     1.000E-03
   160   Cd+2                     1.000E-03        -3.000     1.000E-03
   330   H+1                      1.000E-07        -7.000     1.000E-07
   492   NO3-1                    3.020E-03        -2.520     3.000E-03
   280   Fe+2                     1.000E-06        -6.000     9.000E-05
   490   NH4+1                    1.000E-05        -5.000     5.900E-04
     2   H2O                      1.000E+00         0.000     0.000E-01
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 PERCENTAGE DISTRIBUTION OF COMPONENTS AMONG          dissolved and adsorbed s
cies

Na+1
               100.0     PERCENT BOUND IN SPECIES #    500   Na+1

K+1
               100.0     PERCENT BOUND IN SPECIES #    410   K+1

Ca+2
               100.0     PERCENT BOUND IN SPECIES #    150   Ca+2

Mg+2
               100.0     PERCENT BOUND IN SPECIES #    460   Mg+2

Cl-1
                95.8     PERCENT BOUND IN SPECIES #    180   Cl-1
                 3.9     PERCENT BOUND IN SPECIES #1601800   CdCl +

NO3-1
                99.9     PERCENT BOUND IN SPECIES #    492   NO3-1

Fe+2
                99.8     PERCENT BOUND IN SPECIES #    280   Fe+2

Zn+2
                98.3     PERCENT BOUND IN SPECIES #    950   Zn+2

Cd+2
                77.3     PERCENT BOUND IN SPECIES #    160   Cd+2
                21.9     PERCENT BOUND IN SPECIES #1601800   CdCl +
NH4+1
                99.5     PERCENT BOUND IN SPECIES #    490   NH4+1

Pb+2
                78.8     PERCENT BOUND IN SPECIES #    600   Pb+2
                 9.3     PERCENT BOUND IN SPECIES #6001800   PbCl +
                 9.9     PERCENT BOUND IN SPECIES #6003300   PbOH +
                 1.9     PERCENT BOUND IN SPECIES #6004920   PbNO3 +

Cu+2
                43.8     PERCENT BOUND IN SPECIES #    231   Cu+2
                 3.9     PERCENT BOUND IN SPECIES #2313300   CuOH +
                52.7     PERCENT BOUND IN SPECIES #2313301   Cu(OH 2 AQ
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H2O
              1.4       PERCENT BOUND IN SPECIES #2803300   FeOH +

             13.2       PERCENT BOUND IN SPECIES #2313301   Cu(OH)2 AQ

             55.0       PERCENT BOUND IN SPECIES #9503300   ZnOH +

             10.9       PERCENT BOUND IN SPECIES #9503301   Zn(OH)2 AQ

              6.6       PERCENT BOUND IN SPECIES #9501804   ZnOHCl AQ

              3.1       PERCENT BOUND IN SPECIES #1603300   CdOH +

              5.9       PERCENT BOUND IN SPECIES #1601803   CdOHCl AQ

              2.4       PERCENT BOUND IN SPECIES #6003300   PbOH +


H+1
             17.8       PERCENT BOUND IN SPECIES #3304900   NH3 AQ

              1.2       PERCENT BOUND IN SPECIES #2803300   FeOH +

             10.8       PERCENT BOUND IN SPECIES #2313301   Cu(OH)2 AQ

             45.2       PERCENT BOUND IN SPECIES #9503300   ZnOH +

              8.9       PERCENT BOUND IN SPECIES #9503301   Zn(OH)2 AQ

              5.4       PERCENT BOUND IN SPECIES #9501804   ZnOHCl AQ

              2.6       PERCENT BOUND IN SPECIES #1603300   CdOH +

              4.8       PERCENT BOUND IN SPECIES #1601803   CdOHCl AQ

              2.0       PERCENT BOUND IN SPECIES #6003300   PbOH +


                   ------------------------------------------------------
                   ----------- EQUILIBRATED MASS DISTRIBUTION -----------

IDX      NAME              DISSOLVED              SORBED             PRECIPITATED
                      MOL/KG    PERCENT     MOL/KG   PERCENT      MOL/KG    PERCENT

500   Na+1          6.100E-03   100.0    0.000E-01     0.0    0.000E-01     0.0
410   K+1           3.800E-04   100.0    0.000E-01     0.0    0.000E-01     0.0
150   Ca+2          4.300E-03   100.0    0.000E-01     0.0    0.000E-01     0.0
460   Mg+2          1.200E-03   100.0    0.000E-01     0.0    0.000E-01     0.0
180   Cl-1          5.600E-03   100.0    0.000E-01     0.0    0.000E-01     0.0
492   NO3-1         3.000E-03   100.0    0.000E-01     0.0    0.000E-01     0.0
280   Fe+2          9.000E-05   100.0    0.000E-01     0.0    0.000E-01     0.0
950   Zn+2          1.000E-03   100.0    0.000E-01     0.0    0.000E-01     0.0
160   Cd+2          1.000E-03   100.0    0.000E-01     0.0    0.000E-01     0.0
490   NH4+1         5.900E-04   100.0    0.000E-01     0.0    0.000E-01     0.0
600   Pb+2          3.232E-06     0.3    0.000E-01     0.0    9.958E-04    99.7
231   Cu+2          1.642E-06     0.2    0.000E-01     0.0    9.984E-04    99.8
  2   H2O           1.315E-05   100.0    0.000E-01     0.0    0.000E-01     0.0
330   H+1          -1.600E-05   100.0    0.000E-01     0.0    0.000E-01     0.0
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