SORPTION OF CADMIUM, COPPER, LEAD, AND ZINC AS INFLUENCED BY IONIC STRENGTH, pH, AND SELECTED SOIL COMPONENTS

by
Wonae Bong Fike

Dissertation submitted to the Faculty of the
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of
Doctor of Philosophy
in
Crop and Soil Environmental Sciences

APPROVED:

R. B. Reneau, Jr., Co-chairperson

D. C. Martens, Co-chairperson

L. W. Zelazny

D. F. Berry

J. S. Radcliffe

August 24, 2001
Blacksburg, Virginia

Sorption of Cadmium, Copper, Lead, and Zinc as influenced by pH, ionic strength and selected soil components

by

Wonae Bong Fike

Dr. Raymond B. Reneau, Jr., Co-chairperson

Dr. David C. Martens, Co-chairperson

Crop and Soil Environmental Sciences

(ABSTRACT)

Metals sorption in soils is influenced by several factors, including pH, ionic strength, the presence of ionic composition or organic ligands, total amount of metals, and adsorbent loading. These conditions should be considered when evaluating metal sorption capacity of soil material or when applying laboratory results to field conditions. Metal sorption experiments were conducted on Bertie sandy and Starr-Dyke clay loam soils from long-term field studies in which soils received annual applications of copper-rich pig manure for 16 years.

Adsorption of Cd, Cu, Pb, and Zn as affected by different background electrolytes at various concentrations was investigated. Electrolytes were Na^+, Ca^{2+}, or Al^{3+} in perchlorate solution, and their concentrations ranged from 0.001 to 0.5 $mol_c\ L^{-1}$. Increasing ionic strength decreased metal adsorption capacity. Electrolyte cation composition had a greater effect on adsorption than did electrolyte concentration. The order of sensitivity to cation composition of the electrolyte was Zn > Cd > Cu > Pb, and this effect was greater in Bertie sandy loam than Starr-Dyke clay loam soils. Little difference in Cu and Pb adsorption was observed between Na^+ and Ca^{2+} in background solution.

Most added Cu was adsorbed at low concentrations regardless of pH, but at high concentrations Cu sorption was strongly related to solution pH. Increases in pH resulted in greater Cu sorption due to pH-dependent negative charges and precipitation. The USEPA recommends that soil systems receiving high metal loading rates be maintained

at pH 6.5 or above because of the increased metal adsorption. However, pig manure applications to the Bertie soil resulted in greater Cu in soil solution than in control (no manure) soil at $pH > 6.5$ due to soluble organic matter.

Using the Langmuir equation to determine adsorption maxima for soil systems does not always give adequate estimates of adsorption and values from the equations are highly dependent upon soil environmental parameters. Given the limitations in prediction of adsorption maxima, and given that the amount of nonsorbed metal is as important as the adsorbed amount, the isolines of metal remaining in soil solution were provided with a given set of soil environmental factors.

IN MEMORY OF
JONGHA BONG

This dissertation is dedicated to the memory of my father, Jongha Bong. It was his encouragement that led me to pursue the Ph. D. degree, and this support never flagged. Even during a losing battle with cancer he continued to push me to stay in school and stay on track rather than returning home. During times of struggle, it has been his memory that has sustained me and filled me with persistence.

My father lived in a world torn by conflicts not of his making. He lived through the turmoil of two wars, losing much of his family. This thought often steeled my resolve in the face of the various obstacles I have faced. Without him it has taken much more time to get back on track, but without his memory I could not have finished this work.

Now, a namesake for Jongha Bong, Jonah Paul Bong Fike, fills me with enthusiasm and the desire to push on.

ACKNOWLEDGEMENTS

This length of time involved in this dissertation has reduced my memory of the many people that have helped me along the way.

The author would like to thank the members of her committee for their input on this work. Thanks particularly to advisors Dr. Ray B. Reneau and Dr. David C. Martens for their guidance and patience. Without their support, encouragement, and friendship I would not have finished. Thanks to Dr. Lucian Zelazny and Dr. Duane Berry for their insightful comments and efforts to make me a better scientist. Thanks to Dr. J. Scott Radcliffe for accepting a role on my committee after the tragic death of Dr. E. T. Kornegay.

Special thanks to Mr. Hubert Walker and Mr. Mike Saluta for their assistance in the laboratory and to Mr. Wes Atkinson for help gathering the samples used in these studies.

Thanks to my friends and colleagues in the department, listed alphabetically: Martha Anderson, Alec Hayes, Liming He, Jie Huang, Mike Jones, Alfredo Lopez, Regine Mankolo, Stewart Reed, Barry Stewart, Sunetra Wijisundara, and An and Hans Willems.

Thanks to the Korean Agricultural Science Institute for its assistance in directing me to seek a Ph.D. in the USA and for their financial support. The American Association of University Women (AAUW) Educational Foundation played a large role in my education by providing a scholarship at a time when other financial resources were no longer available.

To my family, who has continued to love, support, and be patient with me during this long process. To my mother, Sung-Soon Jung, who has prayed for me without ceasing, thank you for the prayers – which have often been answered beyond your wildest expectations! The Lord does move in mysterious ways. To my brother, Wonil Bong, who supported my family rather than pursuing his own advanced degree – you have given much financial and emotional support to this dissertation and I thank you with

great gratitude. To Wonja Bong, you have listened to me more than any other when I have faced times of struggle. Thank you for your willingness to share your time with me and for all your good advice.

Thanks to Herschel and Shirley Fike. Mom and Dad, you have given much encouragement, shared your wisdom and happiness, and perhaps most importantly, provided “Jonah-care” during the final stage of writing.

Special thanks to my husband, John Herschel Fike. A list of your doings is not necessary because you have given me everything and you have kept me going. To our son, Jonah, I give thanks to you and thank God for you. You fill our lives with joy, and your energy and enthusiasm for life (“Let’s Do It!”) have been great motivators and distracters during times of difficulty.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

Heavy metals exist in a wide variety of natural systems including waters, soils, rocks and sediments. Many industrial products and processes require heavy metals, and some heavy metals are used as feed ingredients for livestock. Waste products such as biosolids and animal manures often are landfilled or recycled via agricultural utilization or composting. Though application to agricultural land is a favored outlet for biosolids and animal manures, their application may cause environmental problems. The wastes usually contain large concentrations of heavy metals such as cadmium (Cd), copper (Cu), lead (Pb) and zinc (Zn) but chemical composition of the waste products is highly dependent on their origin. High levels of copper sulfate ($CuSO_4$) are added to swine diets because of the desirable effect of increasing weight gains and feed efficiency (Thomas and Kornegay, 1973; Stahly et al. 1980). Supplemental $CuSO_4$ in swine diets causes increased Cu concentrations in manure and consequent Cu application to soils. Thus, interest in heavy metals has grown with the recognition that increased metal concentrations in crops, soils, and waters could be both an environmental and human health hazard.

Application rates of waste products to agricultural land have been determined entirely or in part on the ability of the waste product to supply a crop's requirement for nutrients such as nitrogen (N) and phosphorus (P). In addition to valuable plant nutrients, biosolids and manures contain a variety of organic and inorganic trace constituents that potentially are harmful to plants and their consumers. Many heavy metals, including Cu and Cd, have shown appreciable mobility within the food chain, posing a substantial threat to human health (Peterson and Alloy, 1979; Wittmann, 1981). In addition, groundwater contamination by metals is possible under certain conditions such as a high water table with concomitant formation of mobile, neutral or anionic metal complexes and with high infiltration rates over a long period of time. Because of these potential environmental hazards, disposal or recycling of biosolids and animal manures via application to agricultural lands must be carried out in a way that provides benefit to the crop without causing pollution problems associated with accumulation of the trace metals.

The solid-aqueous solution interface has been studied because of its importance relative to the behavior and fate of trace metals in all natural water systems (Sposito, 1984). Because the characteristics of complexed heavy metals differ significantly from those of non-complexed metal ions, a better understanding of the chemical processes by which metal ions interact with other soil components is needed to understand potential metal behaviors in various environments. Metals are associated with soil components in several ways, including: i) adsorption onto soil particle surfaces, ii) co-precipitation with major hydroxide or carbonate phases, iii) occlusion in iron or manganese (oxy)hydroxides as coatings on soil particles, iv) binding with organic matter, or v) binding in lattice positions in aluminosilicates (Patterson and Passino, 1987). As the behavior of heavy metals is controlled to some extent by surface reactions (Sposito and Page, 1984), clay and organic colloids can be the primary soil components affecting metal retention. The reactive surfaces of solids are excellent scavengers for trace metals. Organic compounds such as humic and fulvic acids form stable complexes with metal ions because of their high content of oxygen-containing functional groups, and factors influencing the quantity of metal ions bound by humic substances include pH, ionic strength, molecular weight, and functional group content (Rashid, 1971; Guy et al., 1975). Research regarding metal retention by organic matter should not ignore inorganic constituents in soil systems however, because the metal ion-organic matter-mineral interactions are significant chemical processes in maintaining low metal availability. Inorganic materials such as phosphates, silicates, and Fe-, Al-, and Mn oxides, which commonly exist in soils, can provide long-term retentive capacity for some heavy metals (McLaren and Crawford, 1973; Mandal and Mandal, 1986; Mench et al., 1994). McBride and Bouldin (1984), using electron spin resonance, reported that the form of Cu^{2+} adsorbed in long-term contaminated soil was probably largely inorganic.

An understanding of metal complexation with soil components is important for determining which substrates act as a sink for metal ions. Thus, the chemical properties of soil and characteristics of inorganic and organic matter need to be better described before predictions about the long-term fate of heavy metals can be made. Individual soil component interactions with metals are difficult to quantify and vary from soil to soil, depending on pH, composition of soil solution, type and amount of clay minerals, organic matter concentration and characteristics, and management practices. However, because the partitioning of metals into soils and groundwaters is related to various chemical processes involving complexation, adsorption, coagulation, etc., the chemical form of metals probably will be the most important characteristic for determining metal reactions. To understand the long-term fate of heavy metals in soil systems, it will be very important to elucidate the factors controlling their solubility.

Adsorption data may aid in the determination of maximum metal loading levels on soils used for application of waste that contain more than one metal. The purpose of this research is to evaluate the influence of soil environmental conditions on sorption of Cd, Cu, Pb, and Zn with a sandy loam and a clay loam soil.

REFERENCES

Guy, R.D., C.L. Chakrabarti, and L.L. Schramn. 1975. The application of a simple chemical model of natural waters to metal fixation in particulate matter. Canadian J. Chem. 53:661-669.

Mandal, L.N., and B. Mandal. 1986. Zinc fractions in soil in relation to zinc nutrition of lowland rice. Soil Sci. 132:141-148.

McBride, M. B., and D.R. Bouldin. 1984. Long-term reactions of copper (II) in a contaminated calcareous soil. Soil Sci. Soc. Am. J. 48:56-59.

McLaren, R. G., and D. V. Crawford. 1973. Studies on soil copper. I. The fractionation of copper in soils. J. Soil Sci. 24:172-181.

Mench, M.J., V.L. Didier, M. Löffler, A. Gomez, and P. Masson. 1994. A mimicked insitu remediation study of metal-contaminated soils with emphasis on cadmium and lead. J. Environ. Qual. 23:58-63.

Patterson, J.W., and R. Passino. 1987. Metals speciation, separation, and recovery. Lewis Publishers, Inc. p. 201-224.

Peterson, P.J., and B.J. Alloway. 1979. Cadmium in soils and vegetation. *In* M. Webb (ed.) The chemistry, biochemistry and biology of cadmium. Elsevier/North Holland Biomedical Press. New York.

Rashid, M.A. 1971. Role of humic acids of marine origin and their different molecular weights in complexing di- and tri- valent metals. Soil Sci. 111:298-306.

Sposito, G. 1984. The surface chemistry of soils. Clarendon Press. Oxford.

Sposito, G., and A.L. Page. 1984. Cycling of metals in the soil environment. *In* Sigel, H. (ed.) Metal ions in biological systems. vol.18. Circulation of metals in the environment. Marcel dekker,Inc. New York.

Stahly, T. S., G. L. Cromwell, and H. J. Monegue. 1980. Effects of the dietary inclusion of copper and(or) antibiotics on the performance of weanling pigs. J. Anim. Sci. 51:1347-1351.

Thomas, H. R., and E. T. Kornegay. 1973. Feed additives for swine. 3. Comparison of copper and antibiotics for grower rations. Research Division, Virginia Polytechnic Institute and State University. Report 150.

Wittmann, G.T.W. 1981. Toxic metals. *In* U.Förstner, and G.T.W. Witmann (ed.) Metal pollution in the aquatic environments. Springer-Verlag. New York.

CHAPTER II

METALS ADSORPTION AS INFLUENCED BY ELECTROLYTE CATIONS AND IONIC STRENGTH

ABSTRACT

Most adsorption studies have been conducted with background solutions that are expected to have limited effect on the adsorption of the ion under consideration. However, ions that are normally present in soil solutions impact ion adsorption reactions. This research was conducted to estimate the effects of Na^+, Ca^{2+}, and Al^{3+} cations in perchlorate solution and their variable concentrations (0.001 to 0.5 mol_c L^{-1}) on the adsorption of Cd, Cu, Pb, and Zn for Bertie sandy loam and Starr-Dyke clay loam soils.

Increased ionic strength decreased metal adsorption capacity, and the effect of electrolyte cation composition on adsorption was greater than that of electrolyte concentration. The order of sensitivity to electrolyte cation composition was Zn > Cd > Cu > Pb, and this effect was greater in Bertie sandy loam than in Starr-Dyke clay loam soils. Little difference in Cu and Pb adsorption was observed between Na^+ and Ca^{2+} in background solution.

The character of the adsorption isotherms tended to change from L-curve to C-curve type when adsorbed amounts decreased due to high ionic strength of background electrolytes or low initial concentrations. Using the Langmuir equation to determine adsorption maxima for soil systems does not always give adequate estimates of adsorption maximums and values from the equations are highly dependent upon soil environmental parameters. Given the limitations in prediction of adsorption maxima, and given that the amount of nonsorbed metal is as important as the adsorbed amount, the isolines of metal concentration remaining in soil solution were provided for a given set of soil environmental factors.

INTRODUCTION

Heavy metals naturally exist in soil systems, and their concentrations are variable, depending upon parent materials. Most occur at low concentrations and are incorporated into soil minerals by isomorphous substitution in the crystal lattice (Alloway, 1990). Increased soil concentrations of heavy metals may result from anthropogenic activities such as biosolid and manure application, landfilling, and mining. These activities are usually accompanied by addition of salts into the soil systems that may impact metal reactions.

Metal retention in soils can be greatly influenced by other ion species and concentrations in the environments. Thus, these conditions should be considered when evaluating metal sorption capacity of soil material or when applying laboratory results to field conditions. Many researchers have focused on selecting background solutions in an attempt to minimize the impact of changes in ionic strength for adsorption isotherms (Cline and O'Connor, 1984; Harsh and Doner, 1984; Turner et al., 1984; Ritchie and Jarvis, 1986). Addition of background electrolytes can result in competitive interactions between ions from the background electrolyte and adsorbed solute. Ionic strength effects on metal adsorption have been studied by changing either solute activity or diffuse electrical double layer thickness. These effects depend on the concentration, composition, and charge of the ionic species in solution. Garcia-Miragaya and Page (1976) showed the anion effects on Cd sorption by montmorillonite. They indicated that Cl^- and SO_4^{2-} had a greater effect than other anions in altering the distribution of Cd. Cadmium behaves mainly as a neutral species ($CdCl_2^0$) and an anion ($CdCl_3^-$ and $CdCl_4^{2-}$), rather than a cation (Cd^{2+}) in soil with high Cl^- concentrations. Also, the SO_4^{-2} system showed that $CdSO_4^0$ exists in solution as a fraction of the Cd present. In dilute solution, Cd sorption was greatest in the presence of $CaSO_4$, followed in decreasing order by $Ca(ClO_4)_2$, and $CaCl_2$. However, there were significant differences between the dilute $CaSO_4$ and $CaCl_2$ systems and the $Ca(ClO_4)_2$ and $CaCl_2$ systems (O'Connor et al., 1984).

In Ni adsorption studies, Mattigod et al. (1979) found that more Ni was adsorbed on Na-kaolinite than on Ca-kaolinite. Cavallaro and McBride (1978) studied Cd and Cu adsorption in the presence of 0.01 M $CaCl_2$. They observed that both adsorption maxima were reduced by Ca^{2+} competition. Zhu and Alva (1993) studied the relative effect of Ca, Mg, and K on the adsorption of Zn and Cu. Adsorption of both Cu and Zn decreased with an increase in concentrations of either Ca or Mg. This reduction in adsorption was attributed to increased competition for exchange sites with increased ionic strength and was greatest on soils with low pH levels. The inhibitory effect of added cations on metal adsorption was greater for Zn than Cu. These kinds of cation inhibition on metal adsorption have been reported (Lagerweff and Brower, 1972; Garcia-Miragaya and Page, 1977), however, Na^{+} and Ca^{2+} effects on Cu sorption was negligible at pH 7.4 (Misra and Tiwari, 1962; 1966). The amount of Cd adsorbed on the montmorillonite surface depended on the cation species present, decreasing in the order Na < K < Ca < Al. However, as ionic strength of the electrolyte increases, the activity of solute changes less because of the shielding effect of neighboring ions (Roy et al., 1992). Thus, ionic strength can affect both ion exchange and adsorption reactions.

Background electrolytes can be used to establish a specific conceptual model of the adsorbent-solute system. Many adsorption isotherm equations have been useful for characterizing solid-liquid phase systems since the early stages of adsorption research. Application of the adsorption isotherm equations to the analysis of metal adsorption data in soils has been a common practice, although it is questionable whether the adsorption mechanism is actually fulfilling the theoretical assumption of the adsorption models. When a model accurately describes or predicts a given set of data, it is sometimes assumed correct. However, different models frequently predict a given data set equally well, but are accurate only under a given set of conditions. Empirical models may be developed using mathematical parameters but they may lack physical or chemical meaning. Some parameters have been developed to represent physicochemical characteristics, but their correlation with these characteristics may be based on unproven assumptions. Thus, specific parameter values may not be applicable with generalized adsorption models. The two most common equations in metal adsorption studies on soils, soil minerals, and sediments are the Langmuir equation and the van Bemmelen-

Freundlich equation. The expressions have utility in that derived parameters can be used for comparison of relative affinities of surfaces under identical experimental conditions.

Recently, surface complexation models have been utilized to obtain information about the nature of metal complexes adsorbed at solid surfaces. Adsorption of metals by the soil solid phase involves formation of either an inner-sphere or an outer-sphere surface complex depending on the properties of metals and the charge density of the solid phase. Changes in metal adsorption as a function of ionic strength could serve as a method to distinguish between inner- and outer-sphere complexes. Using the Triple-Layer Model (TLM), Pb^{2+} and Cd^{2+} ion adsorption were tested against ionic strength-pH data at the goethite/water interface (Hayes and Leckie, 1987). Their research indicated that Pb^{2+} and Cd^{2+} adsorption were relatively unaffected by changing ionic strength. These observations indicated that Pb^{2+} and Cd^{2+} adsorptions as a function of ionic strengths were best modeled as inner-sphere surface reactions. In applying surface complexation models for natural soil systems a significant difficulty is that K_a (Intrinsic equilibrium constant) and C_{site} (concentration of adsorption sites) are rarely reported.

Both types of surface analysis require help to interpret and predict solid/liquid systems in heterogeneous geomedia, but neither model provides definitive proof as to the physical characteristics of the adsorbed species nor information on adsorption rates (Schulthess and Sparks, 1991).

This research was conducted to evaluate the effect of background electrolytes on the relative bond strength of adsorbed metal ions. The effect of differing ionic strength and cation composition of background electrolytes on sorption of Cd, Cu, Pb, and Zn were investigated in both Bertie sandy loam and Starr-Dyke clayey loam soils, either with or without applied pig manure. The effect of changes in background electrolyte concentration (in this case $NaClO_4$) on the adsorption of Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} in sandy and clayey soils is presented in this chapter.

MATERIALS AND METHODS

Soils

Soils used in this research were Bertie fine sandy loam (fine-loamy, mixed, thermic Aquic Hapludults) from the Virginia Coastal Plain, and Starr-Dyke clay loam (fine-loamy, mixed, thermic Fluventic Dystochrept and clayey, mixed, mesic Typic Rhodudults) from the Virginia Piedmont. Soil samples were collected from control plots and plots that received applications of Cu-rich pig manure from existing studies at both sites. The Cu-rich pig manure was applied annually and resulted in a cumulative application rate of 1299 mt ha^{-1} over 16 years. These manure treatments supplied 384 and 379 kg Cu ha^{-1} to the Bertie and Starr-Dyke soils, respectively. Soil pH levels in the Ap horizon in each of the soils were maintained above pH 6.5 with dolomitic limestone. Soils were sampled from the upper 15 cm of the Ap horizon, air-dried, and passed through a 1 mm stainless steel sieve. Soil properties were determined by standard methods (Page et al., 1982) and are listed in Tables 2.1 and 2.2. Qualitative and quantitative mineral analyses of clay-sized fraction were determined by x-ray diffraction analysis (Rich and Barnhisel, 1977; Whittig and Allardice, 1986). Specific surface area was measured by desorption of ethylene glycol monoethyl ether (EGME) on the soil sample (Cater et al., 1965).

Sorption experiments

In these adsorption studies, Na-, Ca-, and Al-perchlorate were used as background solutions. Perchlorate was chosen as the anionic background solution because it does not form ion pairs with metal ions (Sposito et al., 1983). LeClaire (1985) indicated that $NaClO_4$ reagent may be contaminated with Pb, thus $NaClO_4$ stock solutions were passed through a column containing Sephadex 100, a 1% cross-linked polystyrene matrix with methyl iminodiacetic acid residues on aromatic rings. Sephadex 100 preferentially binds divalent metal ions over monovalent ions at an approximate ratio of 5000 to 1. All laboratory wares were soaked with acid solution and rinsed with distilled deionized water. The metal adsorption studies were performed with a 10:1 solution to soil ratio.

Table 2.1. Soil chemical properties.

Soil	Treatment	Exchangeable			------------ DTPA ------------				Free	Free	Organic	pH	CEC†
Series		K	Ca	Mg	Cu	Zn	Fe	Mn	Fe_2O_3	MnO_2	C	(1:1)	
		--------------------			$\mu g\ g^{-1}$		--------------------		$mg\ g^{-1}$	$\mu g\ g^{-1}$	$mg\ g^{-1}$		$cmol_c\ kg^{-1}$
Bertie	control	117	419	80	1.9	5.4	32.3	9.5	2.7	46	12.1	5.65	8.0
	pig manure	164	698	93	18.3	11.7	27.2	17.0	2.6	56	12.1	6.13	9.5
Starr-Dyke	control	403	946	368	14.2	17.3	16.6	160.3	63.7	3900	14.6	5.57	16.3
	pig manure	591	1516	421	51.9	29.3	21.4	183.7	68.0	3602	18.8	6.02	22.1

† Ca/Mg exchange, at soil pH (Zhu et al., 1991).

Table 2.2. Soil physical and mineralogical properties.

Soil Series	Particle size fraction			Minerals of < 0.002 mm clay fraction	Surface Area‡
	Sand	Silt	Clay		
	----------------	%	----------------		--- m^2 g^{-1} ---
Bertie	67.8	29.0	3.2	HIV (58), Kaolinite (22), Vermiculite (8), Quarz (5), Mica (4), Gibbsite (3)†	-
Starr-Dyke	16.9	45.6	37.5	Kaolinte (55), HIV (28),Quartz (12), Gibbsite, Vermiculite, Mica (Trace)	229.57

† Numbers in ( ) represent percentage of minerals.

‡ Specific surface area by EGME method (Cater et al., 1965).

Three gram samples of air-dried soils were weighed into polycarbonate bottles and 30 ml of each background solution was added. Soil suspensions were shaken for 24 h in an oscillating chamber at 120 rpm and 25°C. The kinetics of Cu adsorption were determined for Bertie and Starr-Dyke soils at a concentration of 1 mmol $Cu(ClO_4)_2$ (Appendix, Fig. A.1). Copper adsorption was rapid, occurring in less than 0.5 h, and was followed by a gradual continuous adsorption. After equilibration, pH and electrical conductivity of the supernatants were measured, and the supernatants were analyzed for each metal by flame absorption spectrophotometry on a Perkin-Elmer model 3300 Atomic Absorption Spectrophotometer. Soil suspension pH was not adjusted in this experiment because the presence of cations in soil solution also can cause pH changes.

To evaluate the effects of cation species in background electrolyte, soils were suspended with 1 mM of either Cd, Cu, Pb, or Zn in the presence of a 0.02 $mol_c\ L^{-1}$ background solution of either $NaClO_4$, $Ca(ClO_4)_2$, or $Al(ClO_4)_3$. A background solution of 0.02 $mol_c\ L^{-1}$ was chosen because the electrical conductivity of the saturated soil solutions was similar to that of the 0.02 $mol_c\ L^{-1}$ of $NaClO_4$ solution (Appendix, Table A.1). Also, soils were suspended with 1 mM of Cu using either $NaClO_4$, $Ca(ClO_4)_2$, or $Al(ClO_4)_3$ as background electrolytes at concentrations of 0.001, 0.005, 0.01, 0.02, 0.03, 0.05, 0.1, 0.2, and 0.5 $mol_c\ L^{-1}$ to determine the influence of solution ionic strength on Cu sorption. Cadmium, Pb, and Zn at 1 mM concentrations were also studied in a series of $NaClO_4$ background solutions. Ionic strength (I in the molar unit) of the solution was calculated based on the relationship: $I = 0.013 \times EC$, where EC is in mS cm^{-1} (Griffin and Jurinak, 1973; Alva et al., 1991).

Batch type adsorption experiments were conducted to determine the effect of background electrolytes on Cd, Cu, Pb, and Zn sorption. For Cu, soil samples were treated with $Cu(ClO_4)_2$ ranging in concentration from 0.1 to 4.0 mM. Background electrolyte solutions were 0.02 mol_c $NaClO_4$ L^{-1}; 0.01, 0.02, and 0.05 mol_c $Ca(ClO_4)_2$ L^{-1}; and 0.02 mol_c $Al(ClO_4)_3$ L^{-1}. Calcium is most capable of competing with metal in sorption equilibrium, and $CaCO_3$ often is added to soils to increase pH when metal-laden materials are applied. This research employed different concentrations of Ca in order to mimic real situations in which an elevated Ca concentration in the soil results from the application of phosphorus fertilizer, lime, and gypsum. For Cd, Pb, and Zn, soil samples were treated with $Cd(ClO_4)_2$, $Pb(ClO_4)_2$, and $Zn(ClO_4)_2$ from 0.1 to 1.0 mM using the same background electrolytes as for Cu adsorption isotherms. Soils used in Cu adsorption studies were the Bertie and Starr-Dyke soils, with or without addition of Cu-rich pig manure. Unlike Cu adsorption, only the control treatments on the Bertie and Starr-Dyke soils were used for Cd, Pb, and Zn adsorption isotherms.

Adsorption isotherms

Originally, adsorption model equations were developed to describe gaseous or extremely diluted sorbent adsorption by solids (Langmuir, 1918). Thus, adsorption model assumptions might not be applicable to soil systems. The Langmuir and Freundlich equations have been the most popular equations for describing metal sorption by soils. The mathematical description of the L-curve isotherm almost invariably involves either the Langmuir or the van Bemmelen-Freundlich equation. In this research, four adsorption models including Langmuir, extended Langmuir (Sibbesen, 1981), two-site Langmuir (Syers et al., 1973), and Freundlich were used for comparing the adsorption capacities of each soil under different environmental conditions. From the adsorption data pairs (Γ, and C_{eq}), the Langmuir equation is written as

$$\Gamma = \frac{\Gamma_m b C_{eq}}{1 + b C_{eq}}$$

where Γ is the quantity of the adsorbed phase, and Γ_m and b are adjustable parameters. The parameter Γ_m is considered as the maximum adsorption at equilibrium concentration (C_{eq}) under the assumption of a complete monomolecular layer. Parameter b determines the magnitude of the initial slope of the isotherm. The Γ_m and b values can be obtained by using linear or nonlinear least square regression analyses. The linearized Langmuir equation may introduce some bias toward fitting low adsorption data better than high adsorption data because of the inverse of the adsorption values in the linearization. Also, plotting of the concentration against itself may reduce data variability and provide a statistically significant correlation coefficient (Schulthess and Dey, 1996; Harter,1984). The Langmuir equation assumes the adsorption energy term (b) is constant and no lateral interactions occur between adsorbate particles. However, since b tends to decrease with increasing surface coverage in heterogeneous surfaces, Sibbesen (1981) proposed an extended Langmuir equation. In the extended Langmuir equation, b is combined with C_{eq}^{-d}, so the adsorption energy term decreases with increasing ion concentration. The equation is written as

$$\Gamma = \frac{\Gamma_m b C_{eq}^{-d} C_{eq}}{1 + b C_{eq}^{-d} C_{eq}}$$

where d is a constant. The two-site Langmuir equation was proposed so that the nonuniformity of sites on the surfaces could be characterized by different adsorption energy and adsorption maxima (Syers et al., 1973). The equation is expressed as

$$\Gamma = \frac{\Gamma_{m1} b_1 C_{eq}}{1 + b_1 C_{eq}} + \frac{\Gamma_{m2} b_2 C_{eq}}{1 + b_2 C_{eq}}$$

where subscripts 1 and 2 represent two different sorption sites. The Freundlich equation is a well-known empirical equation that describes ion adsorption in soils. The equation is written as

$$\Gamma = k C_{eq}^{1/n}$$

where k and n are positive, adjustable parameters, with n constrained to be greater than 1. White and Zelazny (1986) reported that the Freundlich parameter k is highly correlated with Langmuir Γ_m. However, this equation has been criticized by several researchers because it is an empirical equation with the constants having no physico-chemical meaning (Olsen and Watanabe, 1957; Holford et al., 1974).

Effect of ionic strength on metal sorption at various pH levels

Bertie sandy and Starr-Dyke clayey soils were used for Cd, Cu, Pb, and Zn sorption at various pH levels. Equilibrations were performed in 0.01, 0.02, and 0.05 mol_c L^{-1} of $NaClO_4$ solutions at a 1:10 soil-to-solution ratio. The suspension pH was incrementally adjusted by either addition of $HClO_4$ or NaOH solution, and pH ranged from 3.0 to 7.5. The total volume of suspension was limited to less than 1% change due to addition of acid or base. The effect of ionic strength and pH on metals sorption was evaluated at constant metals concentration. One mM of each metal-perchlorate was added to the soil suspension. Soil suspensions were shaken for 24 h in an oscillating chamber at 120 rpm and 25°C. After equilibration, pH of each solution was measured, and the supernatants were analyzed for each metal by flame absorption spectrophotometry on a Perkin-Elmer model 3300 Atomic Absorption Spectrophotometer.

RESUTS AND DISCUSSION

The degree of metal adsorption depends upon soil type, cations in background solution, and metal species (Petruzzelli et al., 1985; Zhu and Alva, 1993). In this study, the trend in adsorption capacity for Cd, Cu, Pb, and Zn was similar among soils and background electrolytes (Fig. 2.1). Cation species in background solution had the greatest effect on metals adsorption, followed by metal species, and soil properties, respectively. The observed cation species effect was primarily attributable to valence. At constant ionic strength, the greater the valence of the background electrolyte the larger the reduction in adsorption for all four metals. However, little difference in Cu or Pb adsorption was observed between Na^+ and Ca^{2+} in the background electrolyte because both Cu and Pb can be tightly bound by soil materials. Copper and Pb competed strongly with Ca^{2+} for exchange sites in Starr-Dyke soils, even though Ca^{2+} concentration was 10 times greater than the concentration of either metal. Cadmium and Zn in Bertie soils exhibited little ability to compete for adsorption sites when Ca^{2+} was present in the background solution. Zinc adsorption was less than 10% in the Bertie fine sandy loam

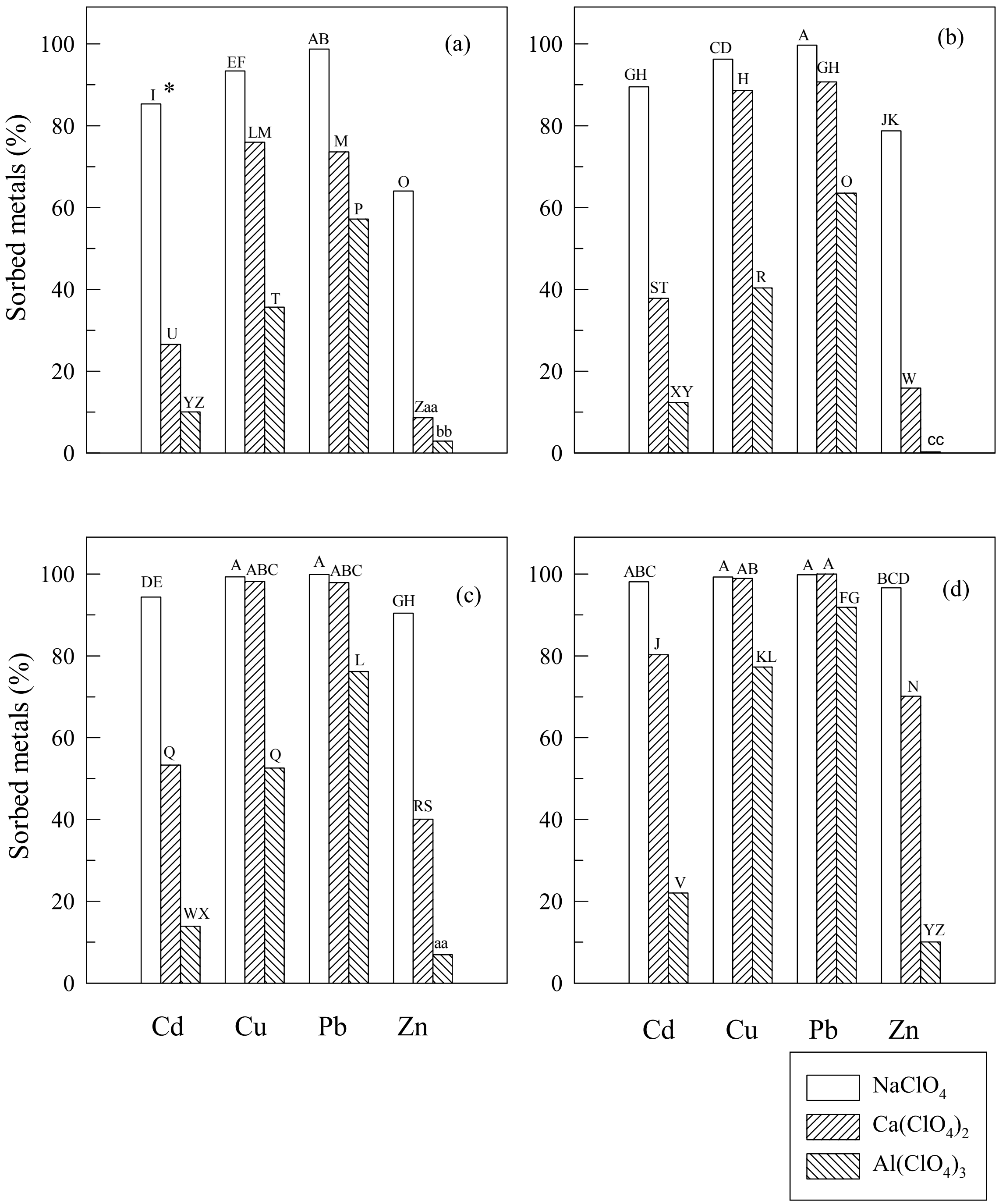

Fig. 2.1. Effect of different cations in background solution (concentration = 0.02 mol_c L^{-1}) on metals adsorption for Bertie soil (a), Bertie soil + applied pig manure (b), Starr-Dyke soil (c), and Starr-Dyke soil + applied pig manure (d).

* Means among treatments followed by the same letters are not different by LSD test at 0.05 level.

soil in the presence of 0.02 mol_c Ca L^{-1}. Zhu and Alva (1993) reported that Zn adsorption was completely inhibited at 0.015 mol_c Ca L^{-1} in a sandy Florida soil. Bittel and Miller (1974) found that Ca^{2+} competes effectively with Cd^{2+} but not with Pb^{2+} for adsorption sites on various clay minerals. In the presence of Al^{3+}, Cd and Zn adsorption decreased by more than 90% when compared to Na^+ in the background solution. The order of sensitivity to cation composition of the electrolyte was Zn >Cd > Cu > Pb, and this effect was greater in Bertie sandy than in Starr-Dyke clay loam soils. Cations in background solution change the soil suspension pH with the degree of change largely dependent upon the valence of the cation species. In these experiments, pH was not controlled at a constant value, so pH also may have affected metal adsorption (Appendix, Table A.3).

Adsorption of all metals was increased by amendment with pig manure, but the amount of adsorption varied depending upon the characteristics of soils or metals. Starr-Dyke soils were shown to have a large capacity for heavy metals retention. This may be due to their large portion of free Fe_2O_3 and/or MnO_2 (Table 2.1). The Starr-Dyke soil that received pig manure adsorbed 92% of the Pb in the presence of $Al(ClO_4)_3$, even though Al^{3+} is the predominant species at $pH < 4.7$ (Lindsay, 1979). Pig manure application reduced the sensitivity of the cation effect on metals adsorption. The order of adsorption capacity for heavy metals was Starr-Dyke + pig manure > Starr-Dyke control > Bertie + pig manure > Bertie control ($p > 0.05$). Long-term application of Cu-rich manure to soils increased their adsorption capacity (Zhu et al., 1991). An increase in the ability of manure-amended soils to adsorb metals was related to an increase in organic matter content of these soils. John (1972) also reported that the coefficient of binding energy for Cd decreased as follows: organic > heavy clay > sandy and silt loam > sandy soils.

Copper adsorption changed little with increasing ionic strength of background solution in the presence of Na^+ for all four soils (Fig. 2.2). Starr-Dyke soils had greater affinity for Cu than Bertie soils, thus increasing ionic strength of Ca^{2+} in background solutions had minimal effect on Cu adsorption. Soils that received Cu-rich pig manure

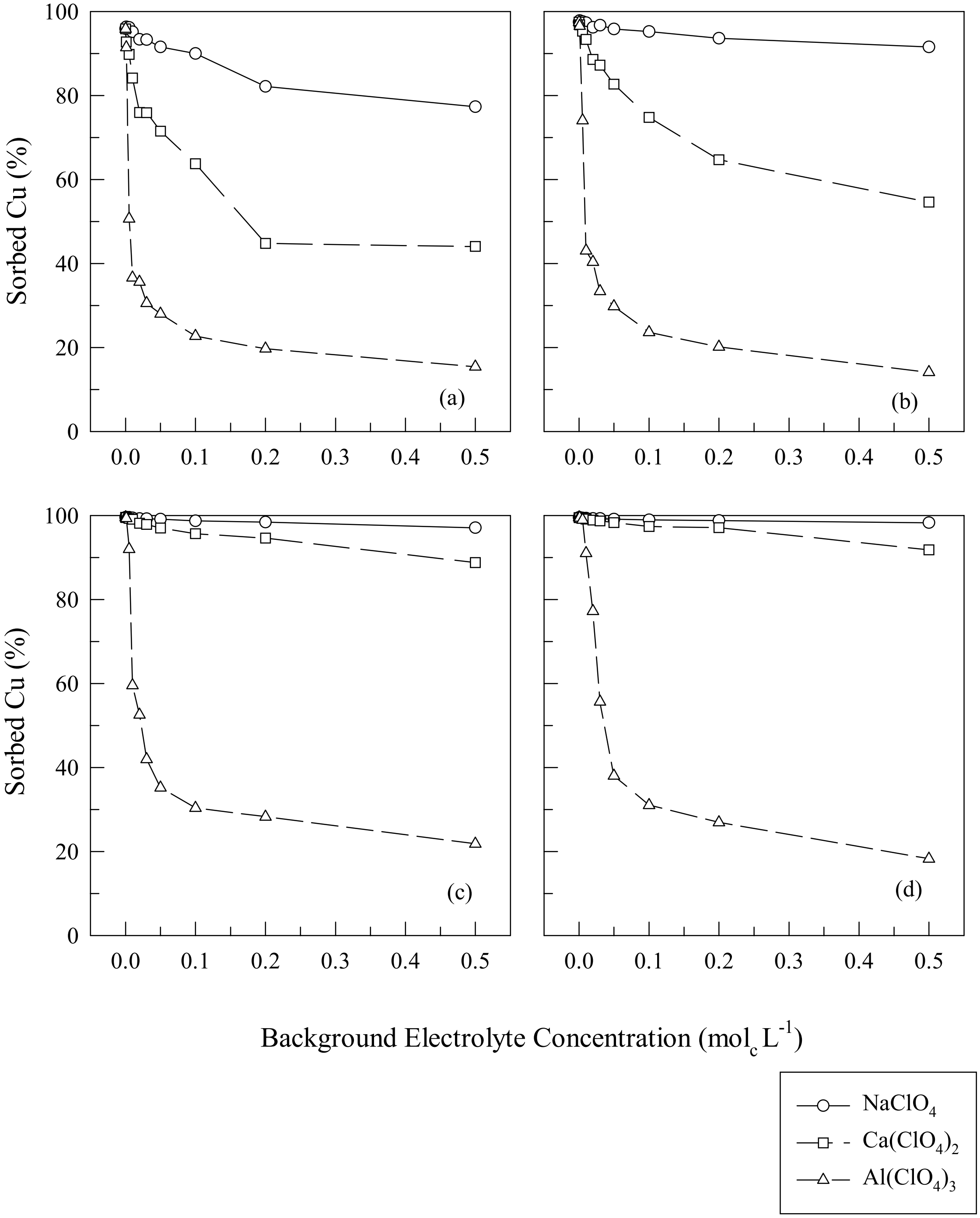

Fig. 2.2. Effect of different ionic strengths on Cu adsorption for Bertie soil (a), Bertie soil + pig manure (b), Starr-Dyke soil (c), and Starr-Dyke soil + pig manure (d).

had greater Cu adsorption capacity than control soils even though the pig manure amended soils had received, on average, an additional 258 mg Cu kg^{-1} over the past 16 y. In the Bertie sandy loam soil, Cu did not compete with Al^{3+} for adsorption sites at concentrations greater than 0.0003 mole of $Al(ClO_4)_3$ in background electrolyte and sorption capacity rapidly decreased above that concentration. At the greatest ionic strengths of $NaClO_4$, $Ca(ClO_4)_2$, and $Al(ClO_4)_3$, pH of the soil suspension decreased 0.3, 0.4, and 1.7 units, respectively (Table 2.3). The decrease in Cu adsorption with increasing concentration of exchange cations could be due to both a decrease in the activity of Cu^{2+} as a result of an increase in ionic strength and the ionic competition for the exchange sites (Garcia-Miragaya and Page, 1976; Zhu and Alva, 1993). More than half of the total decrease in Cu adsorption occurred at high levels of ionic strength (0.0075~0.015) in the presence of $NaClO_4$ or $Ca(ClO_4)_2$ background solutions (Fig. 2.3). In the presence of $Al(ClO_4)_3$, however, Cu adsorption decreased rapidly below ionic strengths of 0.003 (60%, 57%, and 47% for Bertie, Bertie + pig manure, and Starr-Dyke soil, respectively). Cadmium, Cu, Pb, and Zn adsorption are presented with increasing concentrations of $NaClO_4$ background electrolytes (Fig. 2.4). Cadmium adsorption decreased with increasing ionic strength of Na^+ in background solution. Lead adsorption was unaffected by ionic strength in any of the soils, because Pb was strongly bound by all soils. Copper reacted similarly to Cd in Bertie soil and to Pb in Starr-Dyke soil. Fewer differences in metals adsorption existed at different ionic strengths in Starr-Dyke soils than in Bertie soils. Soils that received pig manure had less sensitivity to ionic strength for all four metals. Unlike other metals, Zn adsorption in both control soils first decreased and then increased with increasing ionic strength. The specific minerals controlling the solubility of Zn^{2+} in soils are not known (Linsay, 1979). Krauskopf (1972) also reported that sorption of Zn by soil constituents seems a much more likely control mechanism. One of the major problems in studying sorption of Zn in soils has been the failure to consider which of the various species of Zn in solution are sorbed. Also, the mechanisms and constituents involved in Zn sorptions are not fully understood. Metal chelation is another important factor, which influences the solubility and

Table 2.3. Solution pH after Cu adsorption with increasing concentration of three different background electrolytes.

Concentration	Bertie soil			Bertie + pig manure		
(mol_c L^{-1})	$NaClO_4$	$Ca(ClO_4)_2$	$Al(ClO_4)_3$	$NaClO_4$	$Ca(ClO_4)_2$	$Al(ClO_4)_3$
0.001	5.20	4.25	4.25	5.32	4.60	4.47
0.005	5.12	4.30	3.79	5.33	4.34	3.99
0.01	5.12	4.22	3.61	5.22	4.37	3.65
0.02	5.06	4.18	3.58	5.33	4.20	3.62
0.03	5.04	4.14	3.52	5.30	4.22	3.49
0.05	5.04	4.12	3.44	5.31	4.21	3.47
0.1	5.09	4.21	3.33	5.24	4.26	3.34
0.2	5.13	4.15	3.20	5.19	4.21	3.19
0.5	4.90	4.13	2.89	5.20	4.06	2.90

Concentration	Starr-Dyke soil			Starr-Dyke + pig manure		
(mol_c L^{-1})	$NaClO_4$	$Ca(ClO_4)_2$	$Al(ClO_4)_3$	$NaClO_4$	$Ca(ClO_4)_2$	$Al(ClO_4)_3$
0.001	5.52	5.07	4.57	6.22	5.78	5.87
0.005	5.45	4.67	4.23	6.28	5.60	4.51
0.01	5.50	4.78	3.82	6.03	5.31	4.16
0.02	5.38	4.72	3.76	6.09	5.25	3.94
0.03	5.58	4.51	3.63	6.04	4.81	3.69
0.05	5.44	4.55	3.47	5.91	4.65	3.46
0.1	5.53	4.94	3.43	5.98	5.34	3.34
0.2	5.52	4.76	3.31	5.90	4.98	3.26
0.5	5.45	4.89	2.97	5.88	4.72	2.98

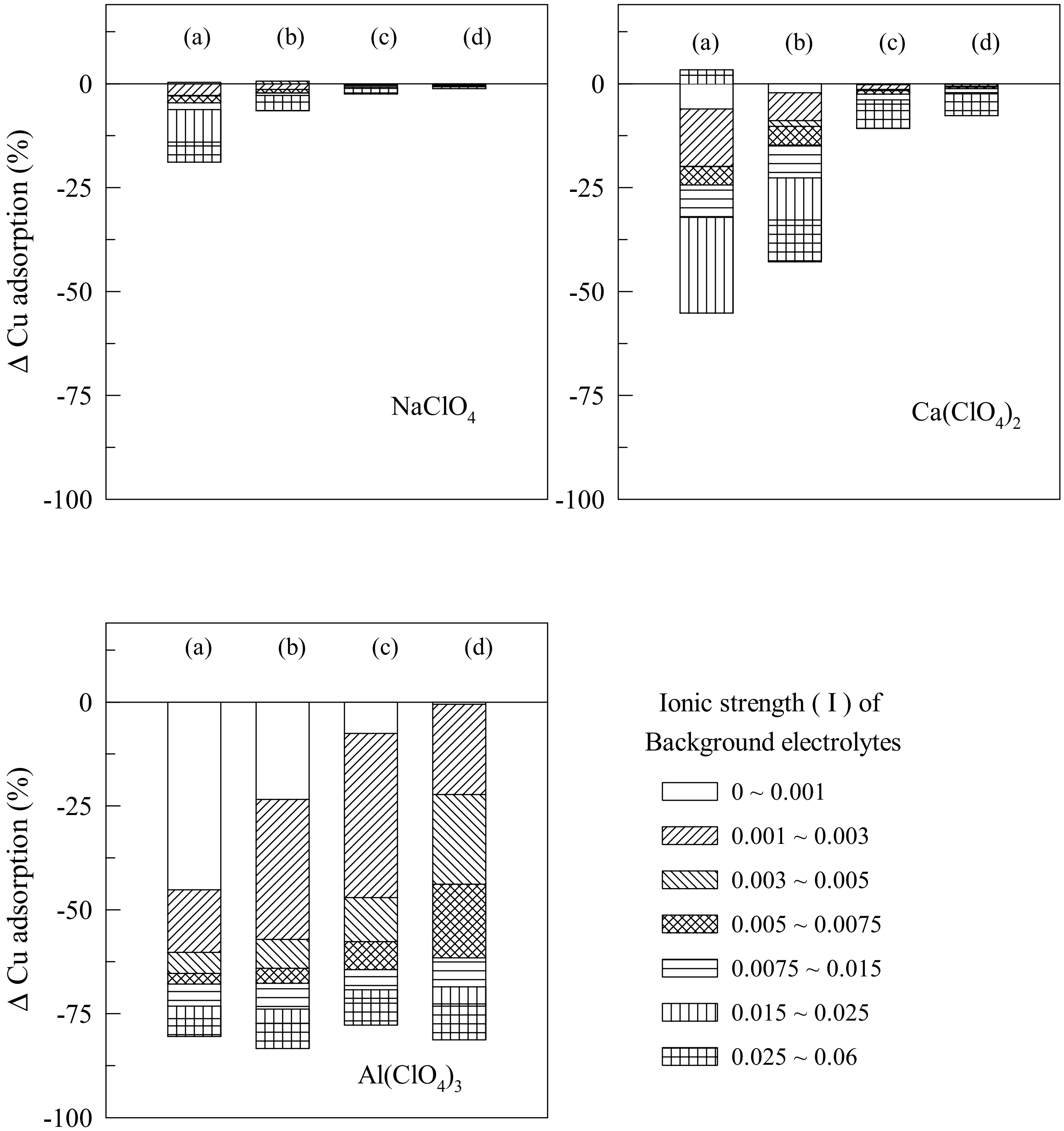

Fig. 2.3. Change in adsorption of Cu with changing ionic strength for Bertie soil (a), Bertie soil + applied pig manure (b), Starr-Dyke soil (c), and Starr-Dyke soil + applied pig manure (d).

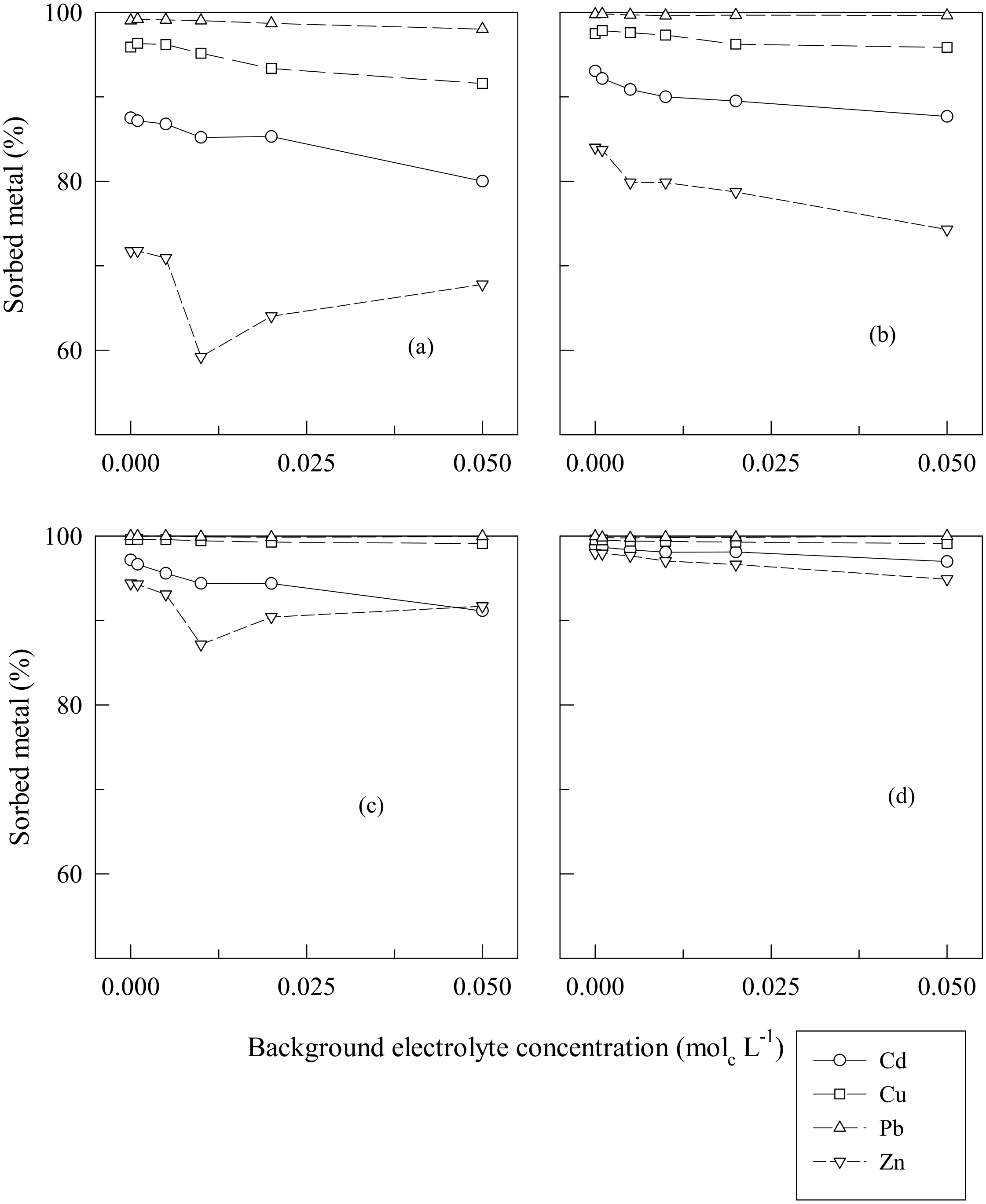

Fig. 2.4. Effect of different ionic strengths on metal adsorption in presence of $NaClO_4$ for Bertie soil (a), Bertie soil + applied pig manure (b), Starr-Dyke soil (c), and Starr-Dyke soil + applied pig manure (d).

movement of metals in soils. Zinc adsorption was most sensitive to ionic strengths between 0.002 and 0.003 in control soils where $NaClO_4$ was used as the background solution, but Cd adsorption was most sensitive at the highest range (0.003~0.007) of ionic strength (Fig. 2.5).

In most studies, several methods have been used to determine the ionic strength of background electrolytes. Normality ($mol_c\ L^{-1}$), molality (moles kg^{-1}), molarity (moles L^{-1}), ionic strength (μ; unitless), and electrical conductivity (mS cm^{-1}) have been used in differing ionic strength. To obtain the ionic strength (μ), all ion species in solution should be identified and their concentrations determined. Thus, many researchers have often used either the initial concentration of background electrolytes or electrical conductivity to determine μ. There are difficulties associated with both of these procedures for determining μ. Adding background solution to soils causes exchange reactions on the surface of soil particles, so ions with weak binding strength release from the surface. Another problem is that changes in concentration affect the activities of ion species. Also, different ionic species in solutions showed varying relationships between either concentration or ionic strength and electrical conductivity (Appendix; Figs. A.2 and A.3).

Typically, the number of protons released by the soil surface is related to the quantity of cations adsorbed. Proton-release values (χ; $\Delta[H^+]$/adsorbed [metal]) for all metals were less than 0.04 for the Bertie and 0.1 for the Starr-Dyke soils, respectively (Fig. 2.6). Perona and Leckie (1985) reported that χ values for Cd, Cu, Pb, and Zn were 1.80, 1.88, 1.65, and 3.20, respectively. Their values were obtained at relatively low adsorbate concentrations (10^{-5} M or less) and with amorphous hydrous ferric oxide. The number of protons released due to metal adsorption depends upon soil suspension pH, adsorption density, and source of adsorbents (Harvey et al., 1983; Kinniburgh, 1983). However, the apparent nonstoichiometric exchange may result from (1) failure to measure displaced cations other than H^+, (2) varying ratio of monodentate to bidentate mineral surface sites becoming occupied by the adsorbate as loading increases, (3) changes in both surface and aqueous speciation as a result of ligand and cation

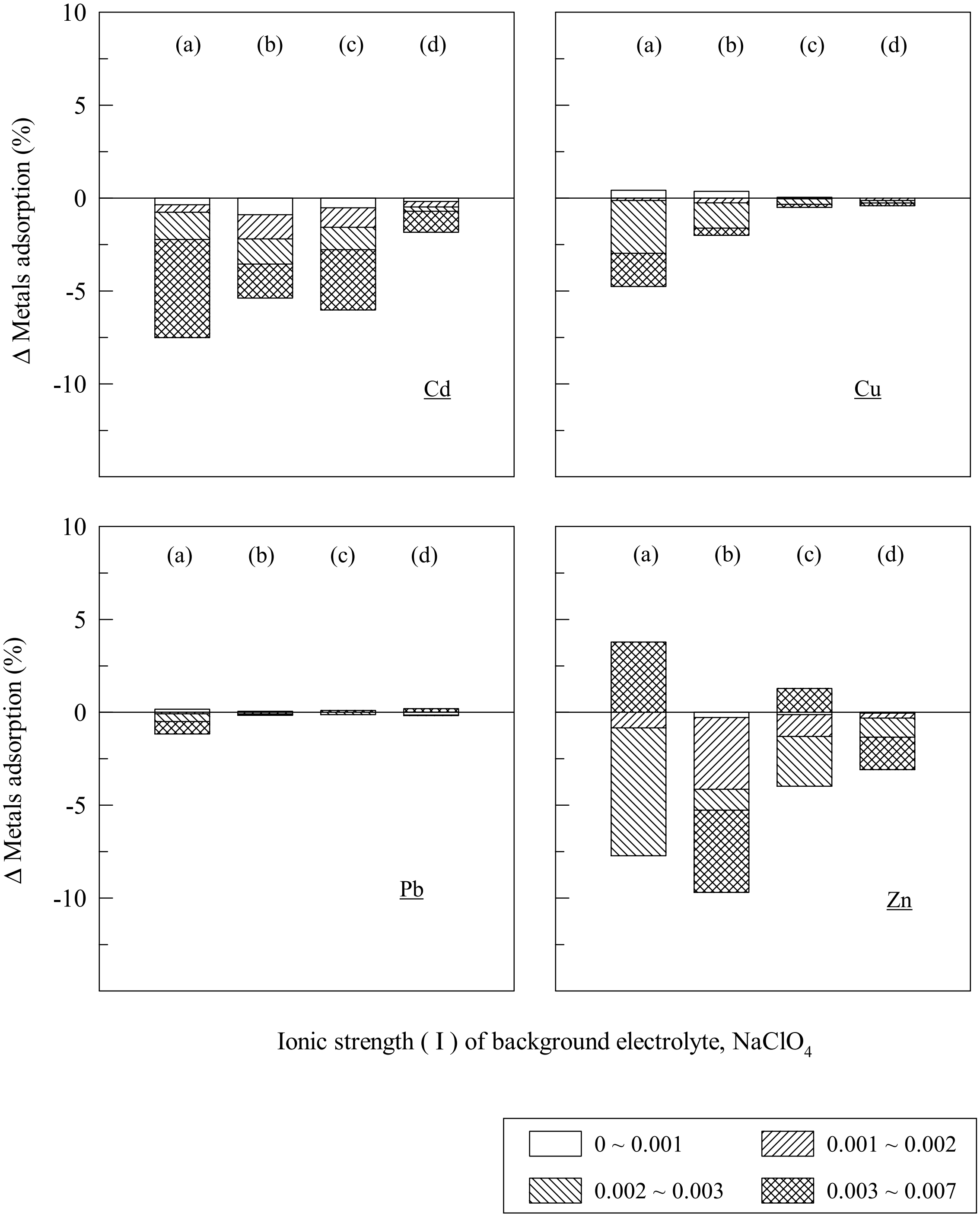

Fig. 2.5. Change in metal adsorption with different ionic strengths of $NaClO_4$ background electrolyte for Bertie soil (a), Bertie soil + applied pig manure (b), Starr-Dyke soil (c), and Starr-Dyke soil + applied pig manure (d).

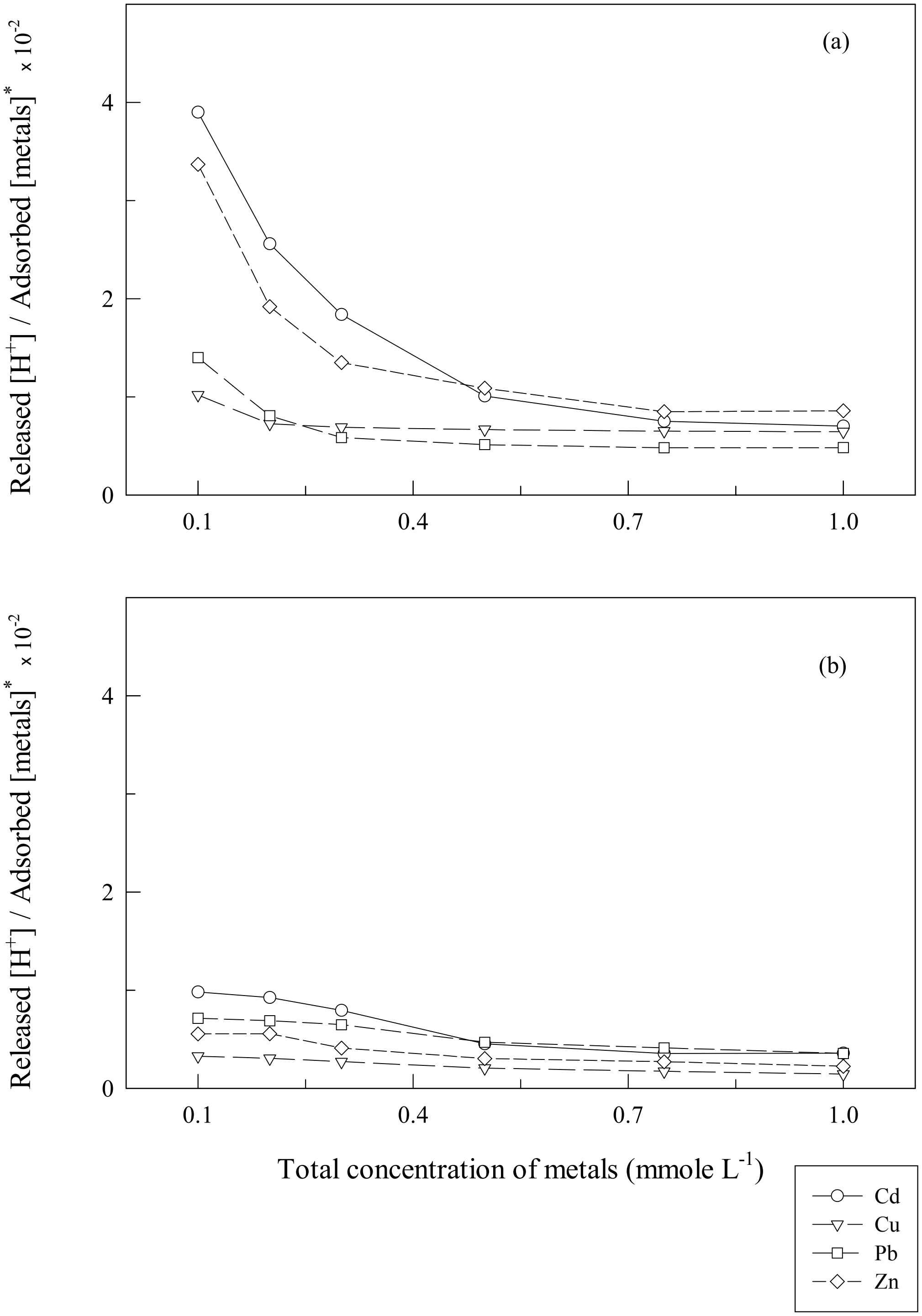

Fig. 2.6. Ratio of $\Delta[H^+]$ to adsorbed metal with increasing metal concentration in 0.02 mol_c $Ca(ClO_4)_2$ L^{-1} solution for Bertie soil (a) and Starr-Dyke soil (b).

* Released $[H^+]$ was calculated by changing $[H^+]$ in solution.

(particularly of H^+) adsorption or desorption, and (4) changes in the net surface charge (Benjamin, 1979). The $[H^+]/[M^{2+}]$ exchange stoichiometry may depend upon the extent of protonation of the mineral surface $–OH_2$ ligands and functional groups of organic matter following metal adsorption (Fig. 2.7). The χ values obtained with Bertie and Starr-Dyke soils were considerably smaller than those reported by Perona and Leckie (1985). This is attributed to the predominately negative soil surface charge at pH 5 (Fig. D.1). Metal adsorption could be attributed to a combination of the formation of positive charge through the specific adsorption, and to ionic strength induced surface charge on variable charge surfaces. As shown in Figure 2.7, a negative surface charge did not result in the release of H^+. Also, the new surface created by M^{2+} adsorption may itself be capable of adsorbing additional M^{2+} without releasing H^+, thus χ value would decrease with increasing adsorption density. However, the χ values calculated by changing $[H^+]$ in soil suspension might not be accurate because released H^+ can come from soil surfaces as a result of metal adsorption or from H_2O resulting from the consumption of OH^- in solution that forms MOH^+ or $M(OH)_2$.

To obtain adsorption isotherms, adsorption data pairs were plotted against equilibrium concentration (C_{eq}) with amount of metal adsorbed (Γ) as a dependant variable. Adsorption isotherms were illustrated by shapes of slope (Giles et al., 1960) or by the Langmuir, extended Langmuir, two-site Langmuir, and Freundlich equations (White and Zelazny, 1986). Giles et al. (1974) classified four different adsorption isotherms (C-, L-, H-, and S-type) based on initial slopes. They concluded that initial slope depends on the rate of change of site availability with increase in adsorption, and the magnitude of the slope is probably related to the heat of solution. The initial curvature of L-curve shows that as more substrate sites are filled, it becomes more difficult for the adsorbing molecule to find available sites. With increasing concentration, the adsorbate on the soil particle increases and the amount of adsorbing surface decreases.

The C-curve isotherm is characterized by an initial slope that remains independent of the concentration of a substance in the soil solution. The H-curve

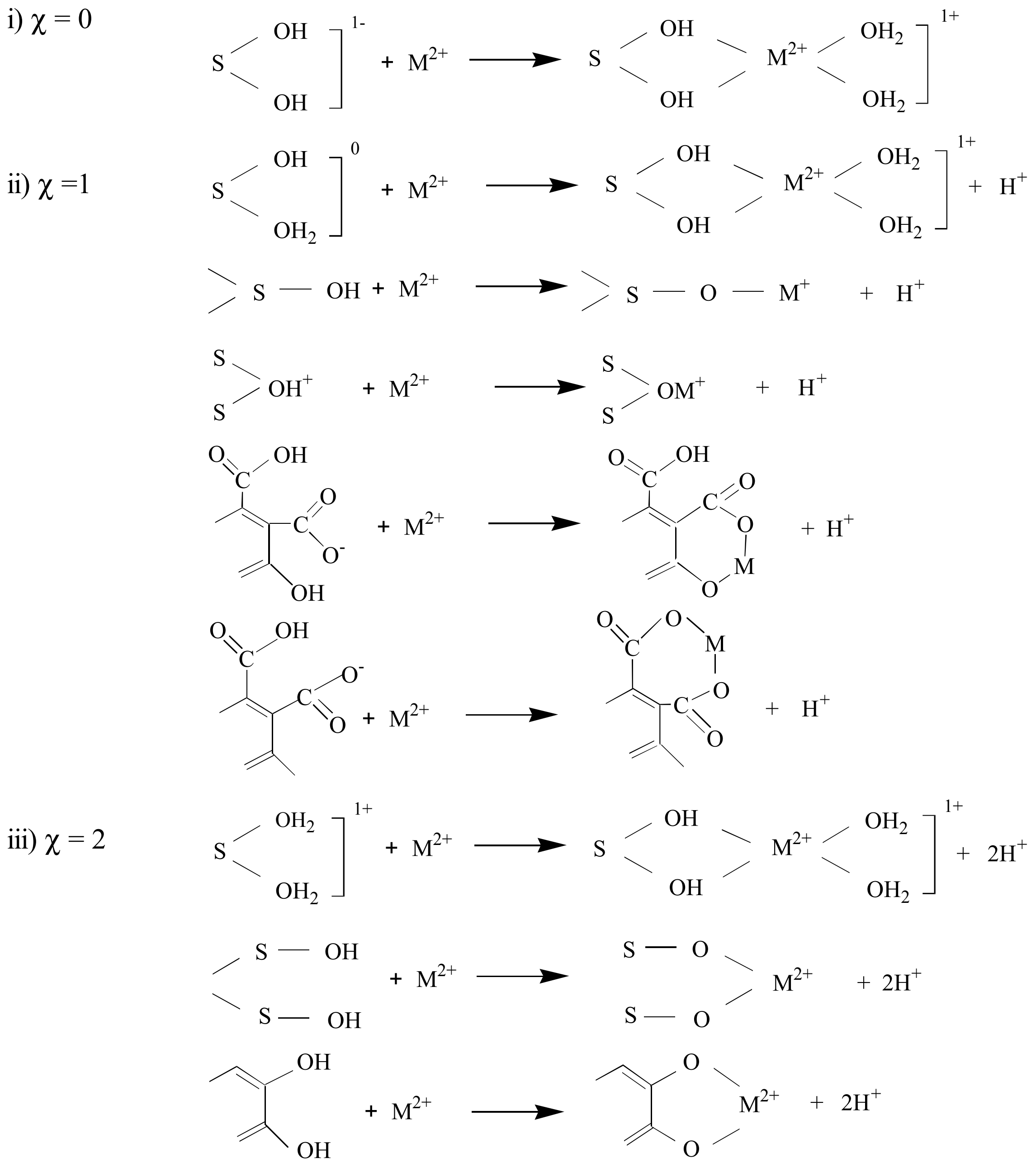

Fig. 2.7. Diagram of hypothetical metal adsorption based on different χ, where χ = (released [H^+])/(adsorbed [metal]) and S represents a surface. (Kinniburgh, 1983; Stevenson, 1982; McBride,1994)

isotherm is an extreme version of the L-curve isotherm. Its characteristic large initial slope suggested a very high relative affinity of the soil solid phase for an adsorbing substance. However, the S-curve shows that the relative affinity of soil solid phase at low concentration is less than the affinity of the soil solution. This mechanism is due to effective competition with surface functional groups for the metal cation when the complexation capacity of the compound is exceeded at which point the slope of the isotherm increases (Sposito, 1984).

The Cd adsorption isotherms are presented by soil type under different ionic strengths and electrolyte cations (Fig. 2.8). The concentration and composition of support electrolyte had a marked effect on the amount of Cd adsorbed by both soils, but the effect was greater for the Bertie soil than the Starr-Dyke soil. Increasing background electrolyte concentration and increasing valence of electrolyte cations significantly reduced Cd adsorption in both soils. However, the cations in background solution had a greater effect on Cd adsorption isotherms than did ionic strength. With increasing background electrolytes in Bertie soil Cd adsorption decreased, and the character of the adsorption isotherms tended to change from that of L-curve to C-curve (Appendix, Figs. B.1 and B.3). Adsorption of Cd in Starr-Dyke soil exhibited L-curve character in the presence of all background electrolytes except Al^{3+} (Appendix, Figs. B.2 and B.4). The Cd adsorption data fit all adsorption isotherm models (adjusted $R^2 > 0.99$) except when Al^{3+} ions were present in the background solution (Appendix, Figs. B.3 and B.4). Aluminum ions easily displace cations, even H^+ on soil surfaces and the surfaces of soil minerals. These reactions are probably similar to those associated with weathering processes. Five Israeli soils had L-curve shapes (Navrot et al., 1978) at initial concentrations up to 900 μg Cd ml^{-1}, while adsorption isotherms for Cd in Indian soils were linear at initial concentrations as high as 100 μg ml^{-1} of Cd Cadmium adsorption isotherms measured on alkaline soils from India have been shown to follow L-shape curves at initial concentration of 100 μg Cd ml^{-1} (Ramachandran and D’Souza, 1999) and have higher adsorption maxima values than acidic soils.

Copper adsorption isotherms were very similar when $NaClO_4$ and $Ca(ClO_4)_2$ were

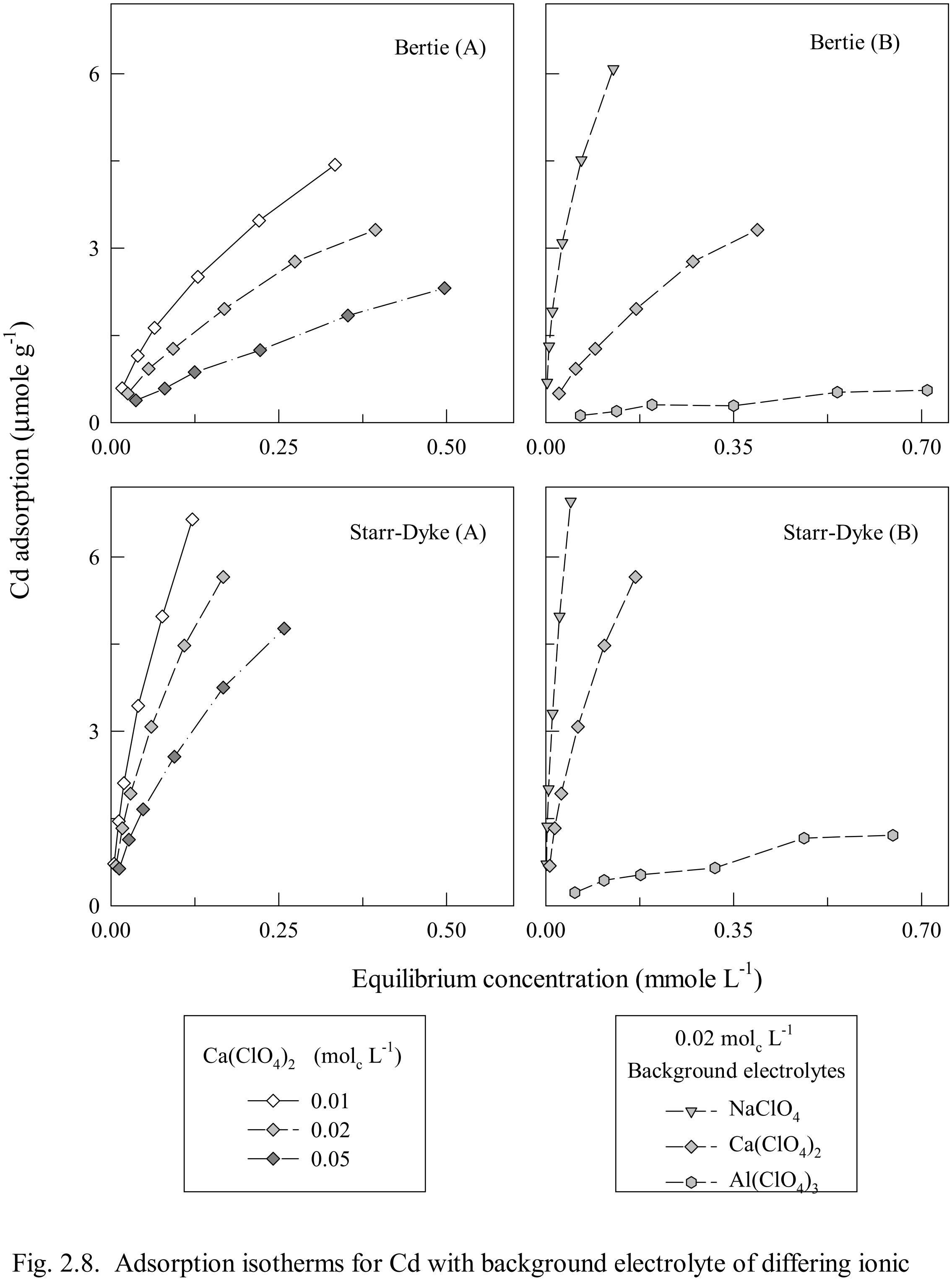

Fig. 2.8. Adsorption isotherms for Cd with background electrolyte of differing ionic strengths (A) and with background electrolyte of differing cations (B) for Bertie soil and Starr-Dyke soils.

used as background solutions (Fig. 2.9). This similarity implies that the Cu binding strength with soil particles was much greater than that of Ca and Na. Adsorption was greater in Starr-Dyke soil than in Bertie soil when Na^+ and Ca^{2+} ions were used in the background solution. However, Cu adsorption was much lower in both soils when Al^{3+} ions were present in the background solution instead of Na^+ and Ca^{2+}. The application of pig manure to the Bertie and Starr-Dyke soils had a greater effect on adsorption isotherms than the use of differing ionic strengths in background electrolytes (Fig. 2.10). The soils that received pig manure had greater amounts of Cu adsorbed than soils where pig manure was not applied. The Starr-Dyke soil again exhibited more available adsorption sites than Bertie soil at the same level of Cu treatment. This result possibly comes from the high organic matter content of Starr-Dyke soil that received pig manure (Table 2.1). Copper adsorption isotherms showed a typical L-type curve in Bertie and Starr-Dyke soils with initial concentrations from 0.1 mM to 1.0mM (Appendix, Figs. B.5 and B.6), while those with the high initial concentration (0.1 mM to 4.0 mM) had H-curve types, which are extreme case of L-curves (Appendix, Figs. B.7, and B.8). The slope decreased with increasing solution concentration of the metal. However, McLaren et al. (1981) reported that the sorption isotherms for Cu on soil materials at low solution concentrations (0.1~10 μg Cu ml^{-1}) were essentially linear. An adsorption isotherm with L-curve characteristics was observed for Cu sorption by the soil separate, after removal of soluble organic matter from the whole soil (LeClair, 1985). Addition of soluble organic matter to the soil separate produced an S-curve for Cu sorption. This mechanism is due to effective competition with surface functional groups for the metal cation, and when the complexation capacity of the compound is exceeded the slope of the isotherm increases (Sposito, 1984). Copper adsorption increases as the sorption sites of organic matter are shifted toward the surface coating (Davis, 1984). All Cu adsorption data fit well with adsorption isotherm model equations even when Al^{3+} was used as the cation in background electrolyte.

In the Bertie soil, Pb adsorption increased with decreasing concentration of $Ca(ClO_4)_2$ as the background solution (Fig. 2.11). In contrast Pb adsorption in Starr-

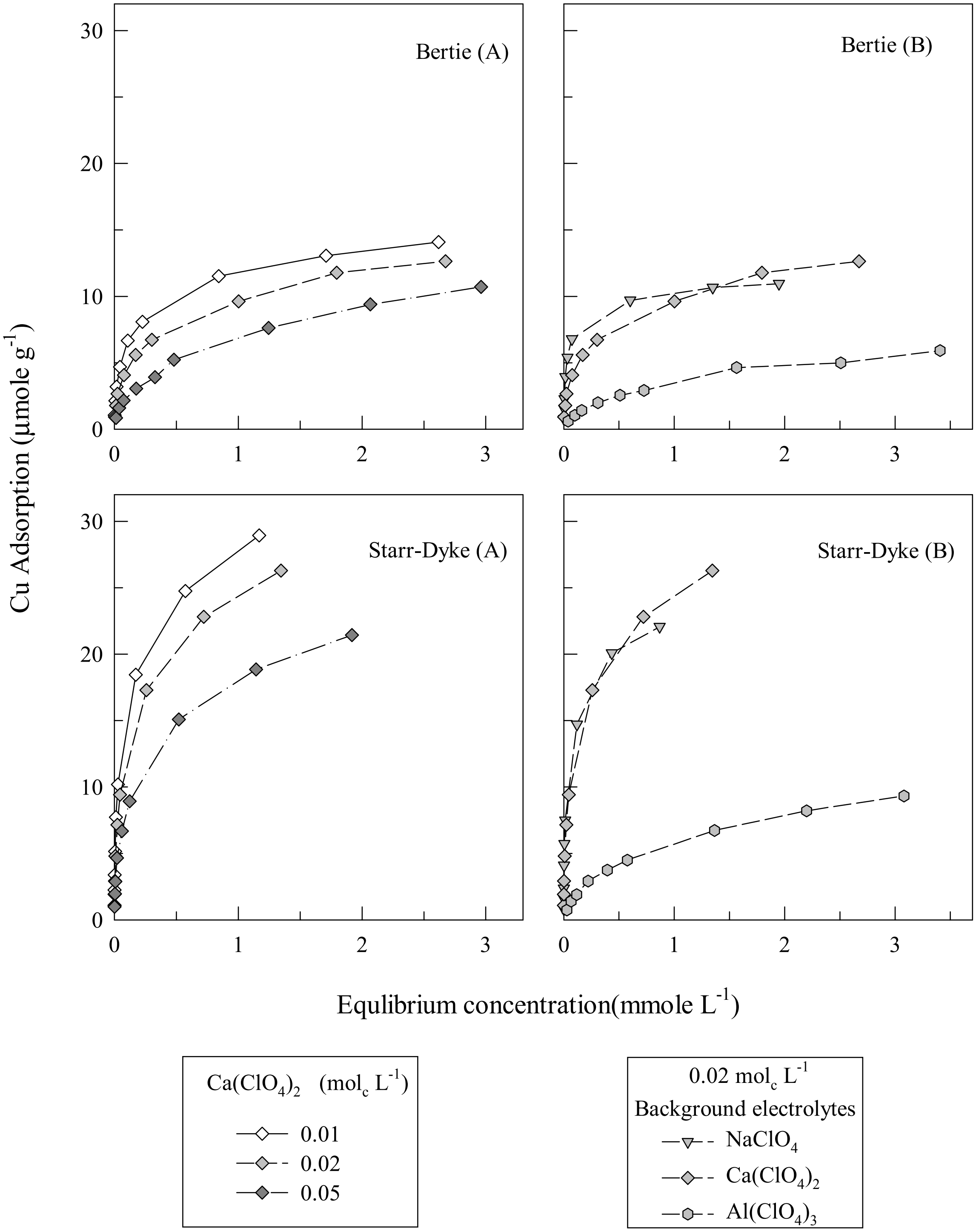

Fig. 2.9. Adsorption isotherms for Cu with background electrolyte of differing ionic strengths (A) and with background electrolyte of differing cations (B) for Bertie soil and Starr-Dyke soils.

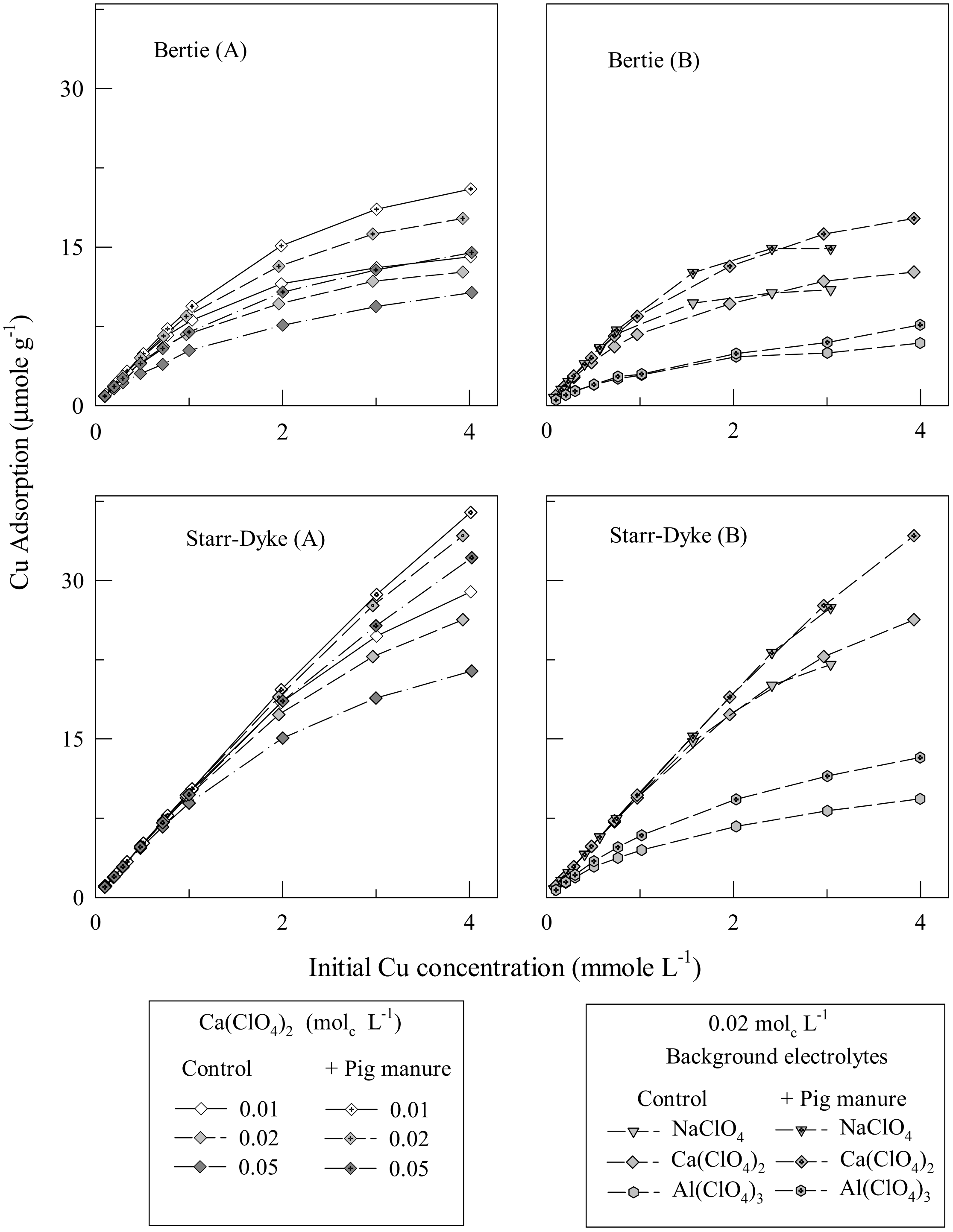

Fig. 2.10. Adsorption isotherms for Cu with background electrolyte of differing ionic strengths (A) and with background electrolyte of differing cations (B) for Bertie and Starr-Dyke soils with or without applied pig manure.

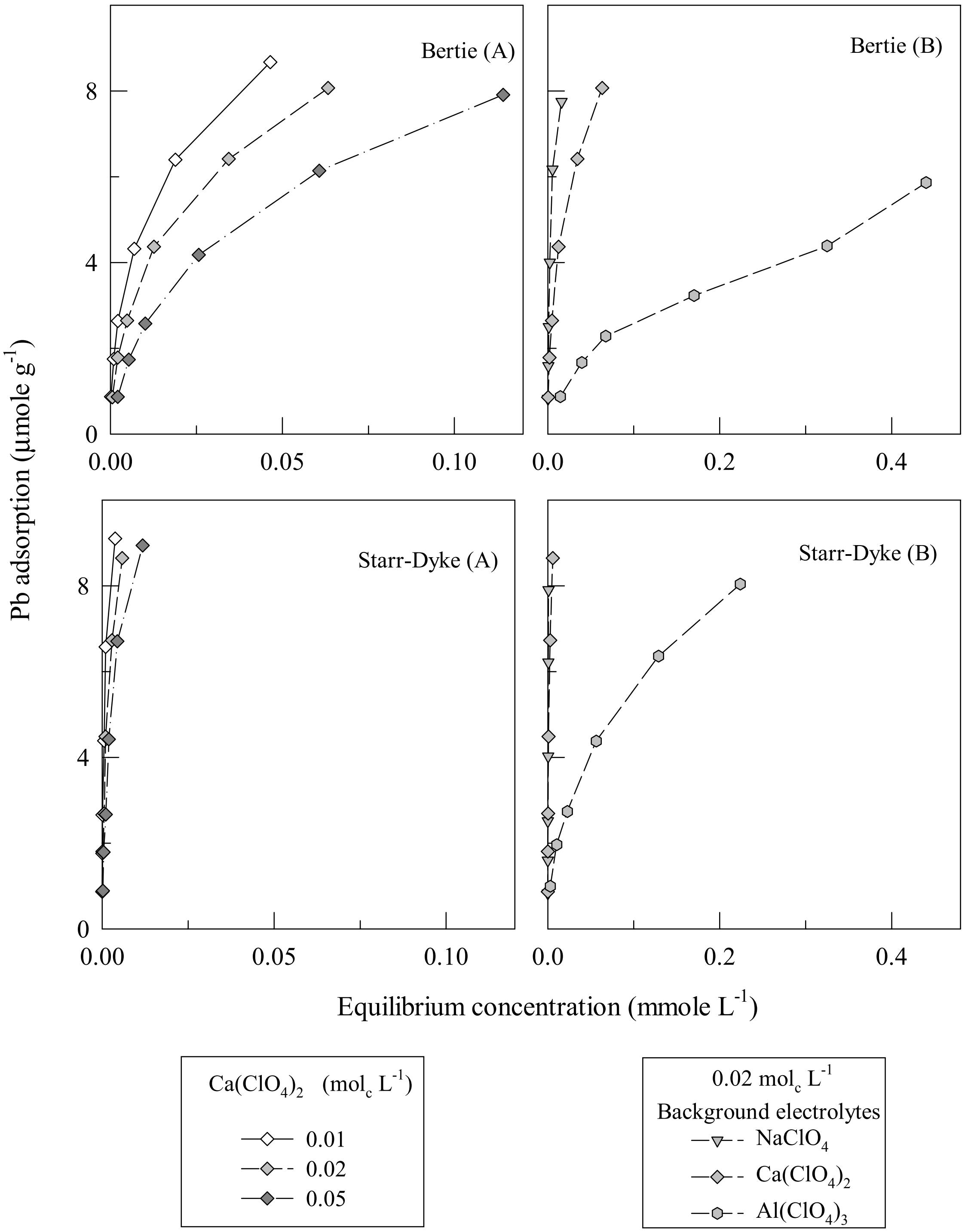

Fig. 2.11. Adsorption isotherms for Pb with background electrolyte of differing ionic strengths (A) and with background electrolyte of differing cations (B) for Bertie soil and Starr-Dyke soils.

Dyke soil showed very little difference between background solutions of 0.01 and 0.05 mol_c $Ca(ClO_4)_2$ L^{-1}. While there was some difference between Na^+ and Ca^{2+} in the background solutions for the Bertie soil, no difference was observed with the Starr-Dyke soil. Conversely, when Al^{3+} was present in the background solution, greater amounts of Pb^{2+} remained in the solution than when Na^+ and Ca^{2+} were the background electrolytes. However, Griffin and Au (1977) observed that Pb adsorption was markedly reduced in 0.1 mol_c $Ca(ClO_4)_2$ L^{-1} solution due to competition between Pb and Ca for cation exchange sites on montmorillonite. Azizian and Nelson (1998) report that Ca and Na compete with Pb, but only below pH 5 on $Fe(OH)_3$ coated sand. In many surface waters the activity of Pb^{2+} is regulated by $PbCO_3$ or $Pb_3(OH)_2(CO_3)_2$ (Hem, 1976). Dolomite ($CaMg(CO_3)_2$) was applied to soils to maintain the pH at 6.5 for 16 y in this research. Most of the adsorption isotherm equations fit the Pb adsorption data, though a little difference in correlation coefficients displayed within various background electrolytes (Appendix, Figs. B.9 and B.10). Some authors reported that the sorption of Pb by soil could be described by the Langmuir equation (Hassett, 1974 ; Zimdahl and Skogerboe, 1977). With increasing adsorption capacity, Pb adsorption changed from L-curve type to L-subgroup 4 curve type. This subsequent rise represented the development of a second layer.

Zinc adsorption was similar to Cd adsorption for these soils (Fig. 2.12). As Zn adsorption decreased, the character of the adsorption isotherms tended to change from L-curve to C-curve type in Bertie soil (Appendix, Figs. B.11 and B.12). However, Zn adsorption showed L-curve in Starr-Dyke soil because Starr-Dyke soil had greater adsorption capacity than Bertie-soil. In the Al^{3+} background solution, more Zn^{2+} was released from soils than adsorbed. Therefore, Zn adsorption data in presence of Al^{3+} did not fit any adsorption isotherm equations. There was a good fit for Zn adsorption to adsorption isotherm equation with the other background electrolytes.

When comparing metals adsorption, Pb adsorption was higher than any other metals in this research (Figs. 2.13). In Bertie soil metal adsorption was decreased with the order of Pb > Cu > Cd > Zn, while Starr-Dyke soil showed adsorption was reduced

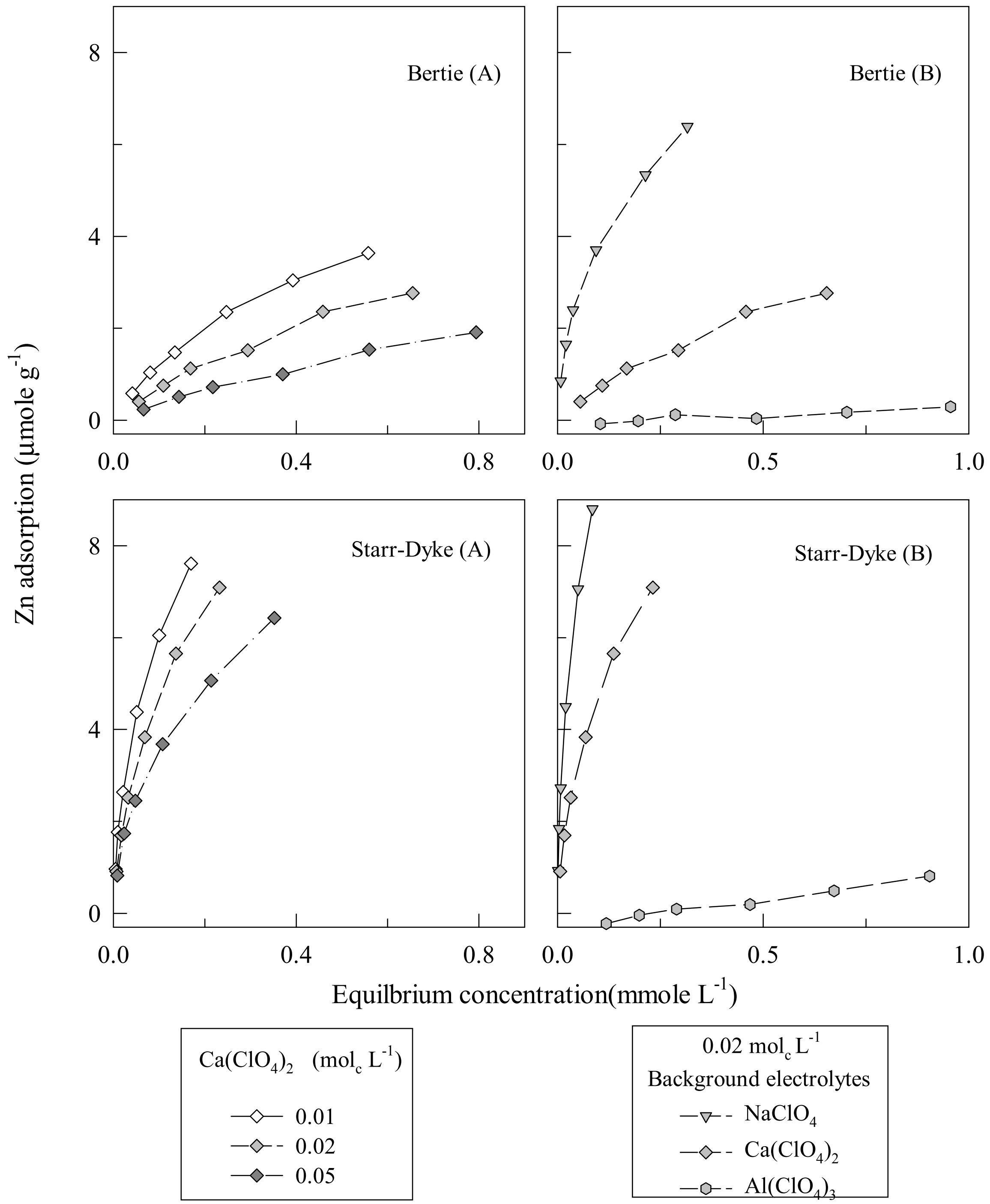

Fig. 2.12. Adsorption isotherms for Zn with background electrolyte of differing ionic strengths (A) and with background electrolyte of differing cations (B) for Bertie soil and Starr-Dyke soils.

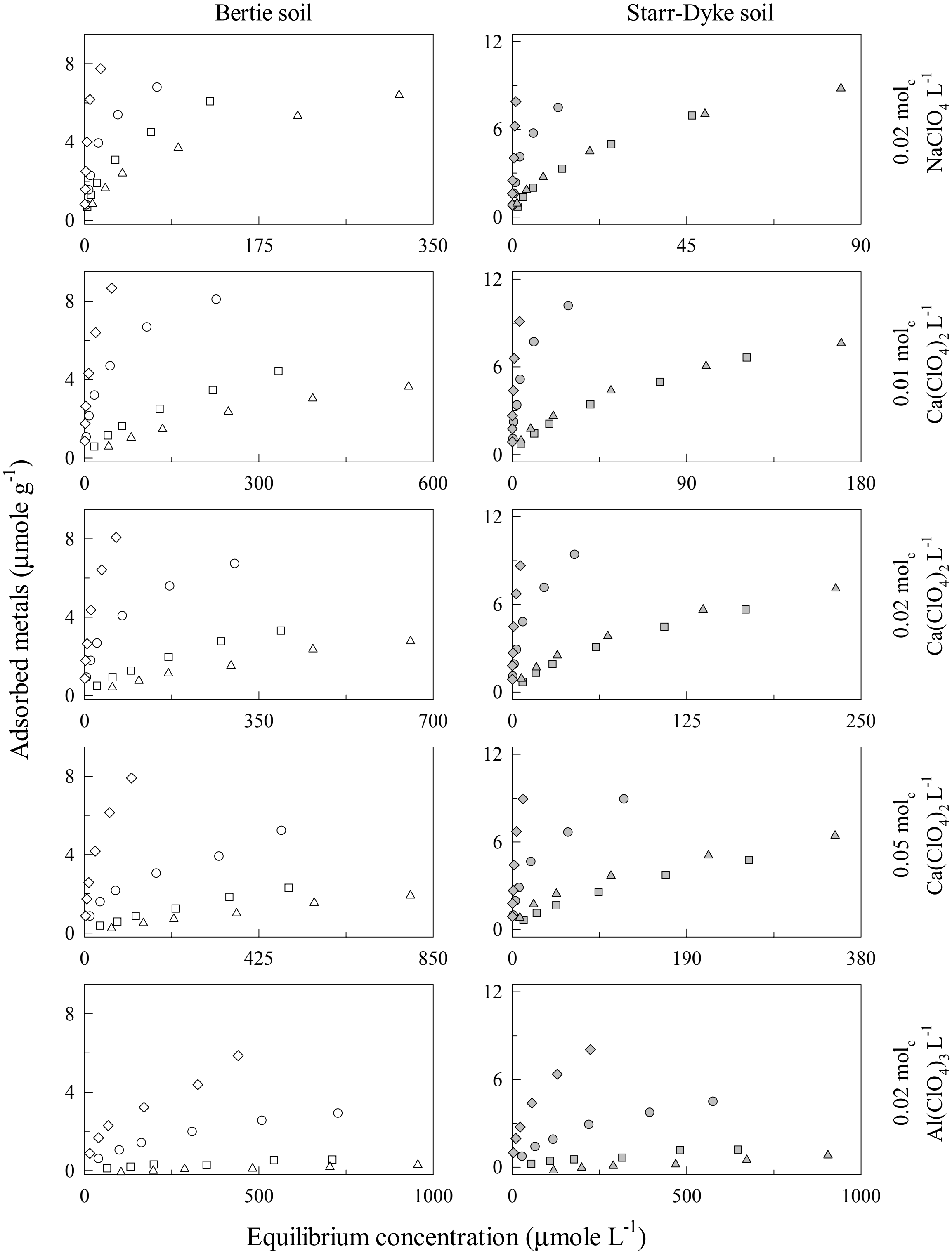

Fig. 2.13. Comparison of Cd (□ , ■), Cu (○ , ●), Pb (◇ , ◆), and Zn (△ , ▲) adsorption isotherms with various background electrolytes for Bertie and Starr-Dyke soils. Open and filled symbols represent Bertie soil and Starr-Dyke soils

with the order of Pb > Cu > Cd ≈ Zn. Other experimental studies of the adsorption of Cd, Cu, Pb, and Zn by soils indicated that bonding energy coefficients for these heavy metals decreased in the order Cu > Pb > Cd > Zn (Kiekens, 1983). However, between pH 3 and 7, the following order for decreasing solubility has been observed Cd > Zn > Cu > Pb. Kuo and Baker (1980) also found that Cu was preferentially sorbed over Zn and Cd. Exchange was the dominant force for Ca, Cd, and Zn retention (Garcia-Miragaya et al., 1977) while Cu and Pb were tightly bound by specific adsorption (Reed, 1993).

Though the experimental adsorption data to a particular adsorption equation provides no evidence of the actual mechanism of an adsorption process (Sposito, 1984), the models are used to compare and generalize experimental adsorption data. Four adsorption isotherm models are compared with Cd, Cu, Pb, and Zn adsorption data in Bertie and Starr-Dyke soils (Tables 2.4, 2.5, 2.8, and 2.9). The parameters of adsorption isotherms are presented according to the concentration of competing cations and loading metal concentration. In most cases, the adsorption of metals with various background electrolytes can successfully be explained by Langmuir and Freundlich equations. Despite the good fits obtained between the experimental data and the adsorption isotherm plots, some parameters in the model equations may not be reliable because of their dependency on other parameters. However, the parameters of adsorption equations varied with ionic strength and composition of the background solution. For all metals, the "b" term in Langmuir differed markedly due to cation species of the background electrolytes, and in the same background solution the "b" terms were decreased with increasing concentration. The pattern for the b values of the Langmuir equation appeared similar to the pattern of the k values of the Freundlich equation. Values varied from metal to metal, from soil to soil, and from background solution to background solution (Figs. 2.14 and 2.15). However, the n values showed distinctive ranges among metals. For Pb, the parameters ("b" in the Langmuir, and k, n in the Freundlich equation) displayed broad ranges of values except the parameter "Γ_m", and showed the highest among metals. The parameters of Zn adsorption isotherms followed a similar tendency as Cd adsorption i.e. very close values in the parameters "b" and "k". Navrot et al.

Table 2.4. Cadmium adsorption isotherms with different ionic strengths and cations in background electrolytes for Bertie and Starr-Dyke soils.†

Adsorption Isotherm Models

A. Bertie soil

Background		--- Langmuir ---		--- Extended Langmuir ---			------- Two-site Langmuir -------				--- Freundlich ---	
Electrolytes§		b	Γ_m	b	Γ_m	d	b_1	Γ_{m1}	b_2	Γ_{m2}	k	n ‡
$NaClO_4$	0.02	0.210^{***}	881^{***}	0.088^{**}	2175^{**}	0.38^{***}	1.30^{***}	228^{***}	0.043^{**}	1231^{***}	179.7^{***}	1.97^{***}
$Ca(ClO_4)_2$	0.01	0.037^{***}	841^{***}	0.023^{***}	1973^{***}	0.26^{***}	0.18^{**}	180^{**}	0.007^{*}	1611^{**}	51.6^{***}	1.59^{***}
	0.02	0.026^{***}	701^{***}	0.021^{**}	1170^{*}	0.18^{*}	21.04^{NS}	19^{NS}	0.018^{*}	803^{**}	31.2^{***}	1.52^{***}
	0.05	0.013^{***}	607^{***}	0.004^{NS}	3375^{NS}	0.24^{*}	27.73^{NS}	20^{NS}	0.006^{NS}	1003^{NS}	14.0^{***}	1.38^{***}
$Al(ClO_4)_3$	0.02	0.017^{*}	108^{***}	0.006^{NS}	671^{NS}	0.36^{NS}	0.09^{NS}	28^{NS}	0.001^{NS}	778^{NS}	4.3^{**}	1.63^{*}

B. Starr-Dyke soil

Background		--- Langmuir ---		--- Extended Langmuir ---			------- Two-site Langmuir -------				--- Freundlich ---	
Electrolytes§		b	Γ_m	b	Γ_m	d	b_1	Γ_{m1}	b_2	Γ_{m2}	k	n
$NaClO_4$	0.02	0.345^{***}	1184^{***}	0.069^{NS}	4632^{NS}	0.35^{***}	2.68^{NS}	223^{*}	0.071^{NS}	2126^{*}	297.9^{***}	1.70^{***}
$Ca(ClO_4)_2$	0.01	0.103^{***}	1249^{***}	0.038^{*}	3772^{*}	0.29^{***}	0.48^{*}	306^{*}	0.009^{NS}	4321^{NS}	144.8^{***}	1.59^{***}
	0.02	0.077^{***}	1057^{***}	0.048^{***}	2026^{***}	0.23^{***}	0.53^{*}	150^{*}	0.029^{*}	1431^{***}	103.0^{***}	1.60^{***}
	0.05	0.047^{***}	918^{***}	0.025^{**}	2396^{**}	0.27^{***}	0.73^{NS}	79^{*}	0.021^{*}	1228^{***}	64.6^{***}	1.58^{***}
$Al(ClO_4)_3$	0.02	0.014^{*}	276^{**}	0.005^{NS}	1443^{NS}	0.29^{NS}	0.30^{NS}	25^{NS}	0.003^{NS}	622^{NS}	8.1^{**}	1.50^{***}

† The concentration of adsorption isotherms ranged from 0.1 mM to 1.0 mM of $Cd(ClO_4)_2$.

‡ Units of parameters are as follows: b, ml μg^{-1}; Γ_m, $\mu g\ g^{-1}$; k, ml g^{-1}; and d, n are dimensionless.

§ Units of background electrolytes are $mol_c\ L^{-1}$.

*** Significant at < 0.01, ** significant at < 0.05, * significant at < 0.1, and NS significant at > 0.1 of P value.

Table 2.5. Copper adsorption isotherms with different ionic strengths and cations in background electrolytes for Bertie and Starr- Dyke soils.†

Adsorption Isotherm Models

A. Bertie soil

Background		--- Langmuir ---		--- Extended Langmuir ---			------- Two-site Langmuir -------				--- Freundlich ---	
Electrolytes§		b	Γ_m	b	Γ_m	d	b_1	Γ_{m1}	b_2	Γ_{m2}	k	n ‡
$NaClO_4$	0.02	0.993***	521***	0.977***	525***	-0.01^{NS}	1.13^{NS}	472^{NS}	0.002^{NS}	3173^{NS}	227.3***	2.21***
$Ca(ClO_4)_2$	0.01	0.506***	563***	0.311***	815***	-0.36***	3.16*	167**	0.154**	512***	192.6***	2.61***
	0.02	0.332***	469***	0.171***	893***	-0.43***	1.72*	170**	0.057*	503***	133.6***	2.49***
	0.05	0.109**	395***	0.018^{NS}	3400^{NS}	-0.50*	0.79^{NS}	130*	0.001^{NS}	9094^{NS}	62.7***	2.10***
$Al(ClO_4)_3$	0.02	0.054***	256***	0.052***	410***	-0.28***	1.15^{NS}	26*	0.031**	275***	27.0***	1.96***

B. Starr-Dyke soil

Background		--- Langmuir ---		--- Extended Langmuir ---			------- Two-site Langmuir -------				--- Freundlich ---	
Electrolytes§		b	Γ_m	b	Γ_m	d	b_1	Γ_{m1}	b_2	Γ_{m2}	k	n
$NaClO_4$	0.02	7.626***	538***	2.722*	685***	-0.25**	13.60*	366*	0.066^{NS}	3007^{NS}	554.8***	2.35***
$Ca(ClO_4)_2$	0.01	3.055***	746***	1.242*	989***	-0.29**	42.96^{NS}	108^{NS}	1.654^{NS}	719***	522.5***	2.41***
	0.02	1.968**	667***	0.217^{NS}	2240^{NS}	-0.51***	47.83^{NS}	126*	0.634*	727***	390.3***	2.40***
	0.05	0.831**	613***	0.215*	1444*	-0.47***	2.91*	300**	0.023^{NS}	1879^{NS}	247.1***	2.44***
$Al(ClO_4)_3$	0.02	0.062***	403***	0.058***	588*	-0.22**	0.37^{NS}	68^{NS}	0.029^{NS}	432*	41.9***	1.86***

† The concentration of adsorption isotherms ranged from 0.1 mM to 1.0 mM of $Cu(ClO_4)_2$.

‡ Units of parameters are as follows: b, ml μg^{-1}; Γ_m, μg g^{-1}; k, ml g^{-1}; and d, n are dimensionless.

§ Units of background electrolytes are mol$_c$ L^{-1}.

*** Significant at < 0.01, ** significant at < 0.05, * significant at < 0.1, and NS significant at > 0.1 of P value.

Table 2.6. Copper adsorption isotherms with different ionic strengths and cations in background electrolytes for Bertie and Starr-Dyke soils treated with high concentration of copper.†

Adsorption Isotherm Models

A. Bertie soil

Background Electrolytes§		--- Langmuir ---		--- Extended Langmuir ---			------- Two-site Langmuir -------				--- Freundlich ---	
		b	Γ_m	b	Γ_m	d	b_1	Γ_{m1}	b_2	Γ_{m2}	k	n ‡
$NaClO_4$	0.02	0.538^{***}	675^{***}	0.504^{***}	726^{***}	0.27^{***}	1.13^{***}	469^{***}	0.031^{**}	292^{***}	239.4^{***}	4.22^{***}
$Ca(ClO_4)_2$	0.01	0.156^{***}	864^{***}	0.190^{***}	1205^{***}	0.47^{***}	1.14^{***}	347^{***}	0.028^{***}	661^{***}	223.3^{***}	3.56^{***}
	0.02	0.077^{***}	810^{***}	0.094^{***}	1545^{***}	0.52^{***}	0.80^{***}	280^{***}	0.014^{***}	280^{***}	153.0^{***}	3.03^{***}
	0.05	0.026^{***}	779^{***}	0.024^{**}	2601^{*}	0.49^{***}	0.67^{*}	134^{***}	0.009^{***}	866^{***}	70.1^{***}	2.29^{***}
$Al(ClO_4)_3$	0.02	0.019^{***}	444^{***}	0.028^{***}	792^{**}	0.36^{***}	0.30^{NS}	68^{NS}	0.008^{*}	467^{***}	32.1^{***}	2.17^{***}

B. Starr-Dyke soil

Background Electrolytes§		--- Langmuir ---		--- Extended Langmuir ---			------- Two-site Langmuir -------				--- Freundlich ---	
		b	Γ_m	b	Γ_m	d	b_1	Γ_{m1}	b_2	Γ_{m2}	k	n
$NaClO_4$	0.02	0.880^{**}	1300^{***}	0.348^{***}	2024^{***}	0.53^{***}	10.74^{***}	426^{***}	0.110^{***}	1136^{***}	479.9^{***}	3.55^{***}
$Ca(ClO_4)_2$	0.01	0.383^{**}	1717^{***}	0.214^{***}	2973^{*}	0.53^{***}	4.65^{***}	560^{***}	0.058^{***}	1554^{***}	515.4^{***}	3.29^{***}
	0.02	0.223^{***}	1616^{***}	0.153^{***}	2988^{***}	0.53^{***}	3.95^{**}	436^{***}	0.047^{***}	1528^{***}	409.2^{***}	3.08^{***}
	0.05	0.108^{***}	1364^{***}	0.100^{***}	2750^{***}	0.52^{***}	2.21^{***}	347^{***}	0.026^{***}	1320^{***}	271.0^{***}	2.91^{***}
$Al(ClO_4)_3$	0.02	0.022^{***}	699^{***}	0.028^{***}	1396^{***}	0.38^{***}	0.15^{***}	181^{***}	0.005^{***}	817^{***}	52.0^{***}	2.15^{***}

† The concentration of adsorption isotherms ranged from 0.1 mM to 4.0 mM of $Cu(ClO_4)_2$.

‡ Units of parameters are as follows: b, ml μg^{-1}; Γ_m, $\mu g\ g^{-1}$; k, ml g^{-1}; and d, n are dimensionless.

§ Units of background electrolytes are $mol_c\ L^{-1}$.

*** Significant at < 0.01, ** significant at < 0.05, * significant at < 0.1, and NS significant at > 0.1 of P value.

Table 2.7. Copper adsorption isotherms with different ionic strengths and cations in background electrolytes for Bertie and Starr-Dyke soils received Cu-enriched pig manure treated with two different initial Cu concentrations. †

Adsorption Isotherm Models

A. Bertie soil received pig manure

Cu Treatment		Low initial concentration				High initial concentration			
Background Electrolytes §		Langmuir		Freundlich		Langmuir		Freundlich	
		b	Γ_m	k	n	b	Γ_m	k	n
$NaClO_4$	0.02	0.530***	826***	266.6***	1.50***	0.408***	954***	282.3***	3.49***
$Ca(ClO_4)_2$	0.01	0.613***	738***	260.1***	2.10***	0.181***	1263***	301.0***	3.18***
	0.02	0.464***	652***	200.9***	2.11***	0.136***	1105***	239.3***	3.09***
	0.05	0.191***	534***	109.8***	2.12***	0.050***	975***	133.0***	2.59***
$Al(ClO_4)_3$	0.02	0.042***	295***	23.3***	1.77***	0.010***	668***	22.6***	1.75***

B. Starr-Dyke soil received Cu-riched pig manure

Cu Treatment		Low initial concentration				High initial concentration			
Background Electrolytes		Langmuir		Freundlich		Langmuir		Freundlich	
		b	Γ_m	k	n	b	Γ_m	k	n
$NaClO_4$	0.02	0.470^{NS}	1828^{NS}	614.1***	1.18***	0.345***	1932***	504.4***	2.34***
$Ca(ClO_4)_2$	0.01	1.738***	978***	607.9***	1.87***	0.334***	2441***	644.0***	2.50***
	0.02	1.642***	911***	565.4***	1.74***	0.266***	2261***	558.3***	2.55***
	0.05	1.146***	805***	387.5***	2.02***	0.147***	2134***	413.6***	2.47***
$Al(ClO_4)_3$	0.02	0.042***	691***	44.7***	1.55***	0.022***	1032***	68.6***	2.03***

† The low concentration of adsorption isotherms ranged from 0.1 mM to 1.0 mM of $Cu(ClO_4)_2$; the high concentration ranged from 0.1 mM to 4 mM.

‡ Units of parameters are as follows: b, ml μg^{-1}; Γ_m $\mu g\ g^{-1}$; k is ml g^{-1}; and n is dimensionless.

§ Units of background electrolytes are $mol_c\ L^{-1}$.

*** Significant at the 0.01 level, and NS represents P > 0.1 level.

Table 2.8. Lead adsorption isotherms with different ionic strengths and cations in background electrolytes for Bertie and Starr-Dyke soils.†

Adsorption Isotherm Models

A. Bertie soil

Background		--- Langmuir ---		--- Extended Langmuir ---			------- Two-site Langmuir -------				--- Freundlich ---	
Electrolytes§		b	Γ_m	b	Γ_m	d	b_1	Γ_{m1}	b_2	Γ_{m2}	k	n ‡
$NaClO_4$	0.02	1.612^{***}	1926^{***}	1.797^{***}	1869^{***}	-0.06^{NS}	1.6^{NS}	1586^{NS}	1.580^{NS}	340^{NS}	1024.8^{***}	2.36^{***}
$Ca(ClO_4)_2$	0.01	0.704^{**}	1954^{***}	0.144^{*}	6152^{*}	0.53^{***}	38.9^{NS}	339^{**}	0.253^{**}	2046^{***}	762.2^{***}	2.60^{***}
	0.02	0.386^{***}	1914^{***}	0.170^{***}	3882^{***}	0.42^{***}	4.9^{NS}	398^{*}	0.129^{*}	2025^{***}	562.1^{***}	2.32^{***}
	0.05	0.159^{***}	2004^{***}	0.114^{***}	3278^{***}	0.32^{***}	0.7^{***}	669^{***}	0.034^{***}	2284^{***}	369.1^{***}	2.09^{***}
$Al(ClO_4)_3$	0.02	0.028^{*}	1540^{***}	0.007^{NS}	16219^{NS}	0.45^{NS}	0.3^{NS}	353^{NS}	0.003^{NS}	4092^{NS}	107.9^{***}	1.91^{***}

B. Starr-Dyke soil

Background		--- Langmuir ---		--- Extended Langmuir ---			------- Two-site Langmuir -------				--- Freundlich ---	
Electrolytes§		b	Γ_m	b	Γ_m	d	b_1	Γ_{m1}	b_2	Γ_{m2}	k	n
$NaClO_4$	0.02	6.104^{NS}	2910^{*}	0.043^{NS}	91418^{NS}	0.45^{NS}	755.2^{NS}	325^{NS}	0.117^{NS}	60357^{NS}	3844.4^{***}	1.83^{***}
$Ca(ClO_4)_2$	0.01	10.780^{NS}	2025^{***}	0.026^{NS}	83283^{NS}	0.63^{NS}	442.9^{NS}	338^{NS}	4.372^{NS}	2026^{NS}	2137.4^{***}	2.76^{***}
	0.02	3.609^{*}	2152^{***}	0.044^{NS}	39671^{NS}	0.60^{NS}	1402.6^{NS}	310^{NS}	1.614^{NS}	2250^{NS}	1675.0^{***}	2.54^{***}
	0.05	1.733^{***}	2279^{***}	1.010^{NS}	2784^{NS}	0.21^{NS}	2.4^{NS}	1759^{NS}	0.070^{NS}	2433^{NS}	1293.2^{***}	2.22^{***}
$Al(ClO_4)_3$	0.02	0.081^{***}	2023^{***}	0.035^{**}	7832^{**}	0.47^{***}	1.4^{*}	371^{**}	0.025^{**}	2423^{***}	283.9^{***}	2.16^{***}

† The concentration of adsorption isotherms ranged from 0.1 mM to 1.0 mM of $Pb(ClO_4)_2$.

‡ Units of parameters are as follows: b, ml μg^{-1}; Γ_m, $\mu g\ g^{-1}$; k, ml g^{-1}; and d, n are dimensionless.

§ Units of background electrolytes are $mol_c\ L^{-1}$.

*** Significant at < 0.01, ** significant at < 0.05, * significant at < 0.1, and NS significant at > 0.1 of P value.

Table 2.9. Zinc adsorption isotherms with different ionic strengths and cations in background electrolytes for Bertie and Starr-Dyke soils.†

Adsorption Isotherm Models

A. Bertie soil

Background	Electrolytes§	--- Langmuir ---		--- Extended Langmuir ---			------- Two-site Langmuir -------				--- Freundlich ---	
		b	Γ_m	b	Γ_m	d	b_1	Γ_{m1}	b_2	Γ_{m2}	k	n ‡
$NaClO_4$	0.02	0.164***	519***	0.094**	1051**	0.36***	0.55**	215***	0.012^{NS}	1137^{NS}	96.2***	2.05***
$Ca(ClO_4)_2$	0.01	0.035***	421***	0.035***	462***	0.05^{NS}	0.04^{NS}	329^{NS}	0.003^{NS}	364^{NS}	24.2***	1.56***
	0.02	0.019***	413***	0.018*	472^{NS}	0.05^{NS}	0.02^{NS}	355^{NS}	0.003^{NS}	146^{NS}	12.2***	1.38***
	0.05	0.010**	377***	0.006^{NS}	739^{NS}	0.12^{NS}	0.03^{NS}	94^{NS}	0.001^{NS}	1391^{NS}	5.5***	1.26***
$Al(ClO_4)_3$	0.02	0.001^{NS}	1418^{NS}	0.001^{NS}	154^{NS}	-1.02^{NS}	0.03^{NS}	2^{NS}	0.001^{NS}	108^{NS}	0.1^{NS}	0.52*

B. Starr-Dyke soil

Background	Electrolytes§	--- Langmuir ---		--- Extended Langmuir ---			------- Two-site Langmuir -------				--- Freundlich ---	
		b	Γ_m	b	Γ_m	d	b_1	Γ_{m1}	b_2	Γ_{m2}	k	n
$NaClO_4$	0.02	0.582***	730***	0.183***	1661***	0.38***	8.64***	113***	0.221***	843***	250.5***	2.02***
$Ca(ClO_4)_2$	0.01	0.261***	650***	0.134**	1230***	0.33***	1.93^{NS}	131^{NS}	0.087	757***	148.3***	1.96***
	0.02	0.157***	646***	0.095***	1187***	0.30***	2.46^{NS}	72**	0.077**	734***	109.7***	1.86***
	0.05	0.135***	532***	0.056^{NS}	1630^{NS}	0.42***	0.76**	162**	0.019^{NS}	896*	90.0***	2.03***
$Al(ClO_4)_3$	0.02	0.001^{NS}	4404^{NS}	0.001^{NS}	84^{NS}	-2.38^{NS}	0.01^{NS}	269^{NS}	0.001^{NS}	269^{NS}	0.1^{NS}	0.46**

† The concentration of adsorption isotherms ranged from 0.1 mM to 1.0 mM of $Zn(ClO_4)_2$.

‡ Units of parameters are as follows: b, ml μg^{-1}; Γ_m, $\mu g\ g^{-1}$; k, ml g^{-1}; and d, n are dimensionless.

§ Units of background electrolytes are $mol_c\ L^{-1}$.

*** Significant at < 0.01, ** significant at < 0.05, * significant at < 0.1, and NS significant at > 0.1 of P value.

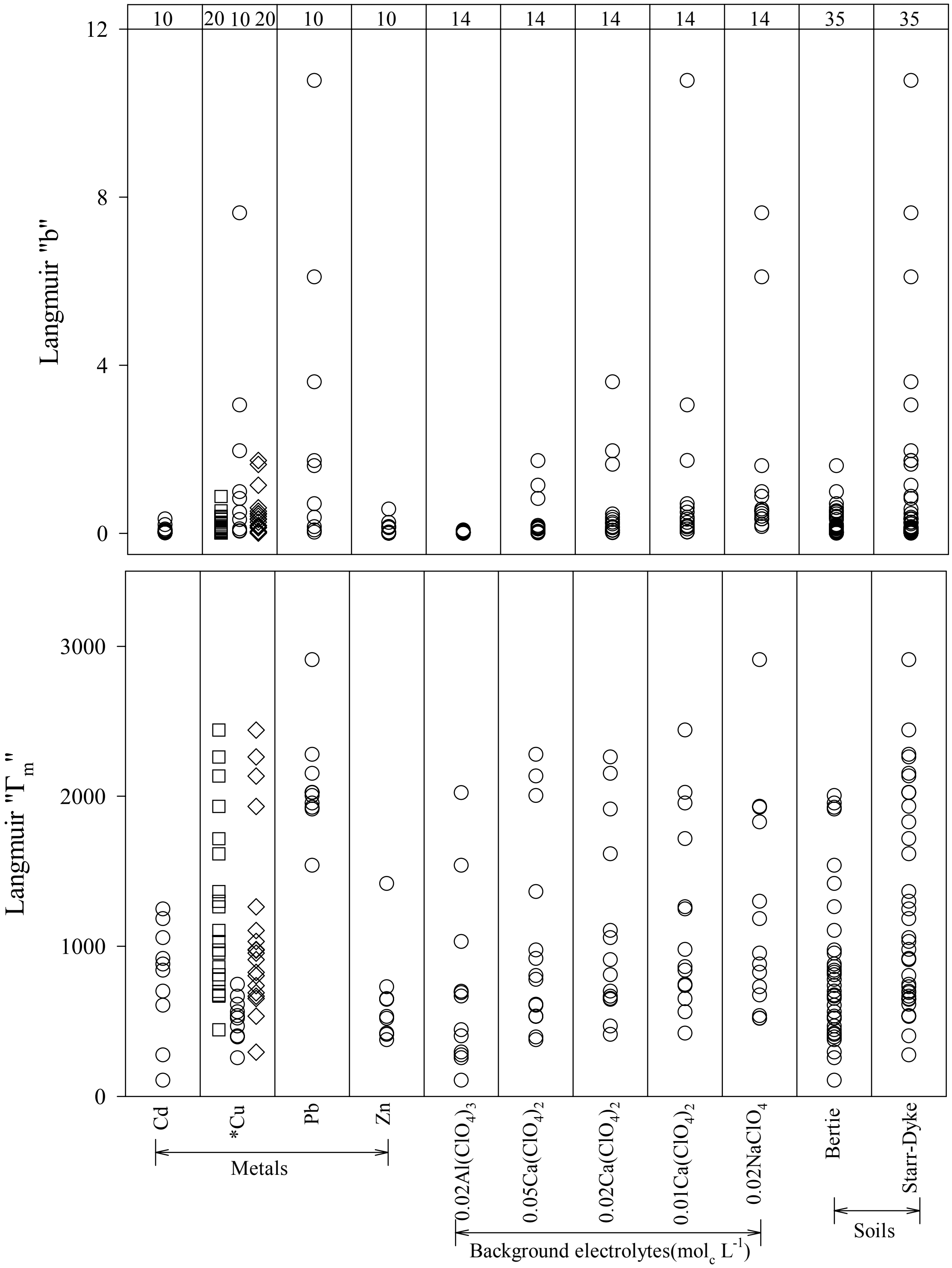

Fig. 2.14. Distribution of the parameters of the Langmuir equation with different metals, background electrolytes, and soils.

Number of the parameters within each column.

* □ represents high initial concentration (~ 4 mM) of Cu; ◇ represents soils treated with Cu-enriched pig manure.

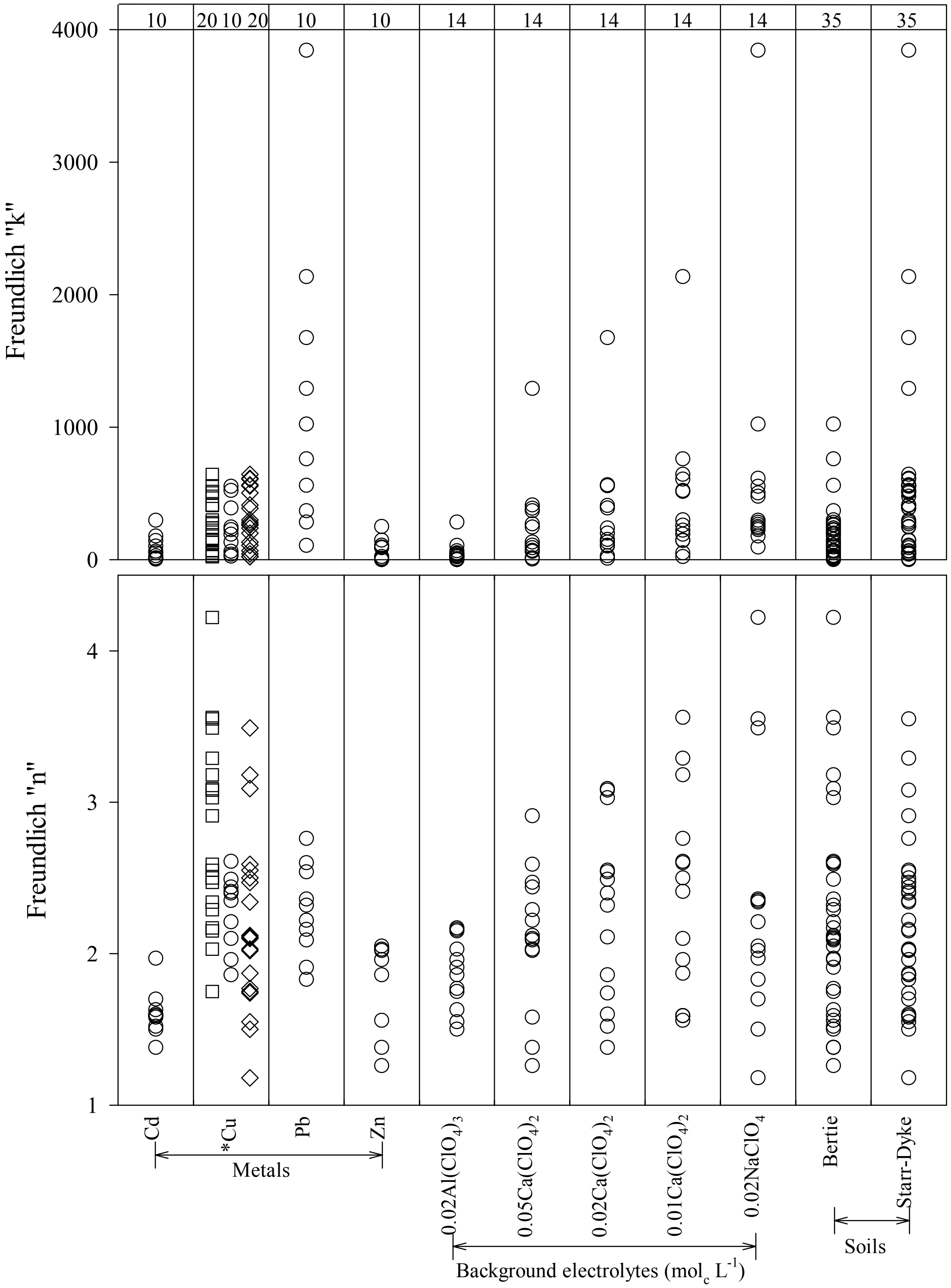

Fig. 2.15. Distribution of the parameters of the Freundlich equation with different metals, background electrolytes, and soils.

Number of the paramerters within each column.

* □ represents high initial concentration (~ 4 mM) of Cu; ◇ represents soils treated with Cu-enriched pig manure.

(1978) presented the Langmuir parameters for Cd retention. The ranges were from 4,730 μg g^{-1} to 10,040 μg g^{-1} for Γ_m, and from 0.034 to 0.225 for bonding energy constant, b. Their adsorption maxima values were much greater and values for parameter b were much less than those of this research. Although the differences may be due to several factors, effect of initial concentration likely had the greatest influence on the difference in values observed. Garcia-Miragaya et al. (1985) found that Cd sorption data at relatively low solution concentrations conformed to the van Bemmelen-Freundlich equation, but not to the Langmuir equation.

The parameters of Cu adsorption isotherms were calculated over two different concentration ranges (Tables 2.5, 2.6 and 2.7). Adsorption intensity ("b" in Langmuir equation) values were greater at the low rather than high range of initial Cu concentration. However, adsorption maxima (Γ_m) were greater when initial Cu concentration was in the high range (0.1 ~ 4.0 mM) rather than the low range (0.1 ~ 1.0 mM). These results were marked in Starr-Dyke soils. The different values resulted from the method of fitting the regression model equation (Figs. C.1 and C.2). Each nonlinear regression analysis creates different isotherms, and each seems equally reasonable but yields dramatically different conclusions. Klotz (1982) also pointed out dangers in estimating sorption maxima from sorption data, which do not approach maximum. The Langmuir equation has been classified as a mechanistic model; however, it may be considered empirical when used with soil systems because the equation contains parameters whose magnitude cannot be definitely determined or whose physicochemical correlation is based on unproven assumptions. McLaren and Crawford (1973) found that Cu conforms to the Langmuir equation in sorption isotherms. Sorption maxima followed the order organic matter > oxides > clay minerals. The results from this research followed the same pattern. Organic matter had greater influence on "Γ_m" values than soil minerals, and the order of sorption maxima was Starr-Dyke + pig manure > Bertie + pig manure > Starr-Dyke soil > Bertie soil. The extended and two-site Langmuir equations fit only adsorption isotherms with treatments of high initial concentration.

When using the Langmuir equation, numerous researchers have used linear regression analysis to determine the values of "b" and "Γ_m". A plot c/Γ vs. c will yield an intercept = $1/(\Gamma_m b)$ and a slope = $1/\Gamma_m$. This linearization was originally suggested by Langmuir (1918). However, such a regression can yield different Langmuir constants when compared with the nonlinear least squared regression method (Schulthess and Dey, 1996). The "b" values using linear regression analysis were greater than those using nonlinear regression, while "Γ_m" values were slightly less than the values using nonlinear regression (Fig. 2.16). It has also been noted that the adsorption maximum calculated by reciprocal of the slope underestimates the amount of adsorbate that can actually be retained (Harter, 1984). Also, the curvilinear forms are commonly observed in the linear transformation of the Langmuir equation (Figs. C.3, C.4, C.5, and C.6). This phenomenon is due to the fact that one of the Langmuir's assumptions (uniform adsorption energy in solid system) does not apply to soil systems. Harter and Baker (1977) suggested that the curvilinear nature comes from not considering the effect of desorbed ions in the equilibrium solution. In addition, the constant "b" of the Langmuir equation is not simply related to the bonding energy of the adsorbed ion, but to the ratio of adsorbed and desorbed ion bonding energies. However, in response, Holford (1978) insisted that the curvilinear relationship of c/Γ vs. c plot more likely comes from multiple energy bonding sites (Holford and Mattingly, 1975) based on two fundamental assumptions: uniformity of adsorption energy over the entire surface, and absence of interactions between the adsorbate molecules. A number of researchers have also shown that sorption data applied to the Langmuir equation can be described by multiple, linear portions, and two-linear portions frequently have been adapted to obtain the adsorption maxima. However, the degree of accuracy depends on visually noting the number of data points that lie on one or the other line. In contrast, the curvilinear relationship is very accurately described with an exponential equation of the form $y = ax^b$, where the slope is expressed as $1/\Gamma_m$. The slope is expressed as the derivative of the equation ($y' = abx^{b-1}$) and indicates that the calculated Γ_m in this method is highly dependent upon the value of x (the equilibrium concentration).

Researchers have continued to use the Langmuir equation in order to determine

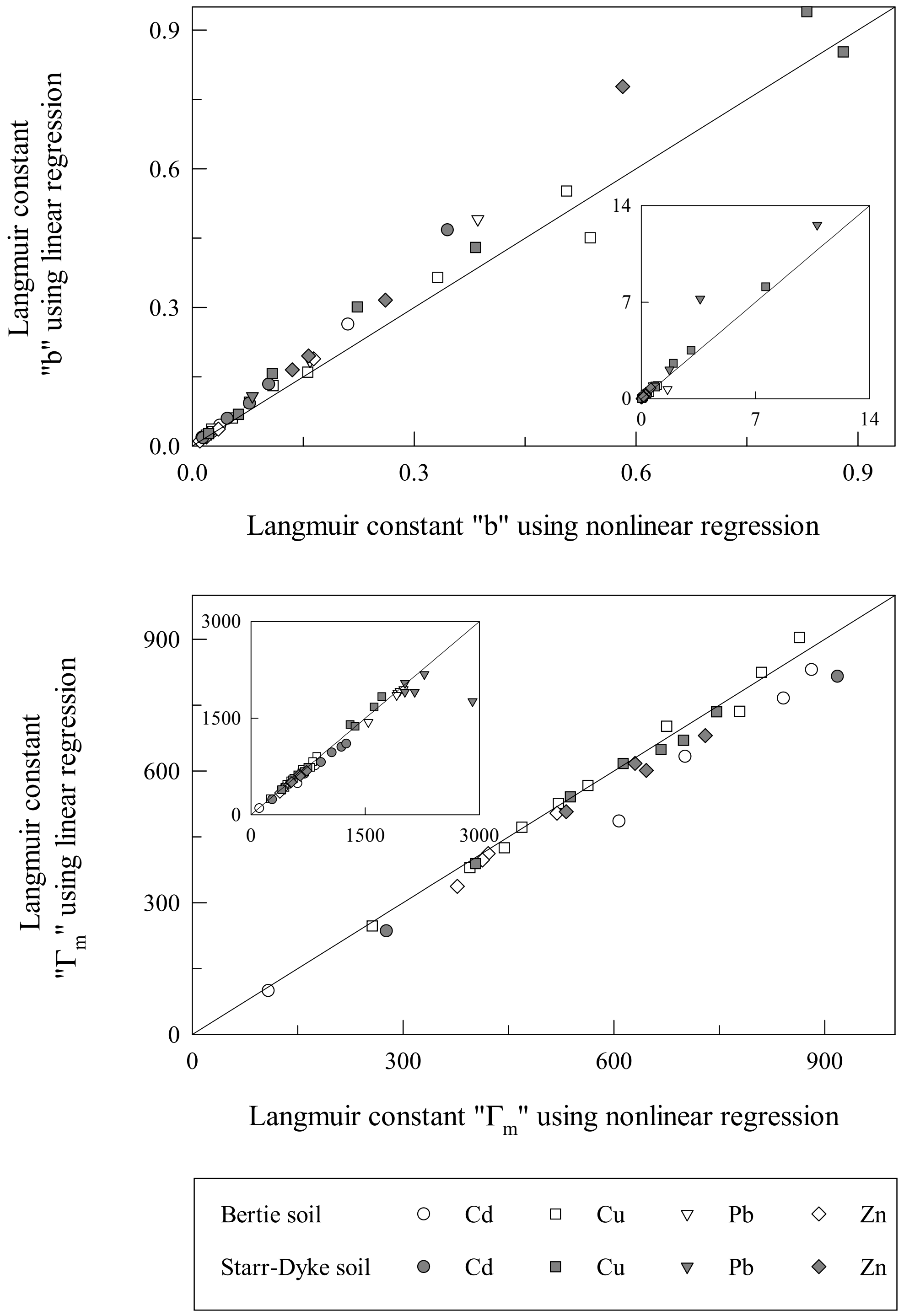

Fig. 2.16. Comparison of Langmuir constants "b" and "Γ_m" using both nonlinear regression least squares analyses and linear regression analyses.

adsorption maxima for soil systems but the equation does not always adequately estimate maximum adsorption. This problem has been resolved by assuming that the theory is obeyed only at low equilibrium concentration levels. Harter (1984) reported that estimates of the adsorption maximum using Langmuir could have error rates greater than 50% when the adsorption isotherms do not have the “correct” shape and only low concentration data are used. When the equation is used with data from low equilibrium concentrations to calculate adsorption maxima, errors may arise due to the imprecision in measuring small concentrations of ions in solution. Also, it should be noted that if concentration is low enough that $bC<<1$, the equation becomes $\Gamma = b\Gamma_m C$.

For comparison, adsorption maxima, Γ_m, were calculated using four different methods all based on the Langmuir equation (Tables 2.10 and 2.11). Values of Γ_m depended upon the method used and were or were not similar depending on soil, adsorbate, and background electrolyte concentration. Several authors have pointed out that using the Langmuir equation to describe soil systems is not appropriate given the equation cannot account for exchange reactions at solid interfaces and desorbed species from surfaces (Harter and Smith, 1981; Harter and Baker, 1977), differentiation between adsorption and secondary precipitation (Veith and Sposito, 1977), and impact of the concentration of competing ions on binding strengths of surfaces (Hendrickson and Cory, 1981). Regardless of these limitations, if use of the equation is to continue, a simple and accurate method of assessing whether data fits the equation model is necessary (Harter, 1984).

The primary reason for trying to determine adsorption maxima is to know maximum levels of metal(s) that soil systems can retain with no harmful effects on the environment. Given the limitations in prediction of adsorption maxima, and given that the amount of nonsorbed metal is as important as the adsorbed amount, a better approach to understanding potential for environmental contamination is to describe the concentration of metals in soil solution provided a given set of environmental factors. Metal concentrations in soil solution are dependent upon initial concentration, background electrolytes, and soil type (Figs. 2.17, 2.18, 2.19, 2.20, and 2.21). The

Table 2.10. Comparison of Cd, Cu, Pb, and Zn adsorption maxima with various background electrolytes for Bertie and Starr-Dyke soils calculated by different methods. Initial concentration ranged from 0.1 mM to 1.0 mM of $Me(ClO_4)_2$.

		"Γ_m" [†]calculated by different approaches								
		Bertie soil					Starr-Dyke soil			
Background electrolytes		linear	two-line linear		interpolation theorem ‡	nonlinear	linear	two-line linear		interpolation theorem	nonlinear
Cd											
$Ca(ClO_4)_2$,	0.01	766	453	972	961	841	1106	544	1409	1214	1249
mol_c L^{-1}	0.02	633	324	775	754	701	968	557	1197	1190	1057
	0.05	486	207	830	612	607	816	409	1063	1060	918
Cu											
$Ca(ClO_4)_2$,	0.01	567	319	624	618	563	735	325	778	776	746
mol_c L^{-1}	0.02	472	261	550	541	469	649	230	749	665	667
	0.05	380	205	563	424	395	617	281	704	669	613
Pb											
$Ca(ClO_4)_2$,	0.01	1920	631	2211	2131	1954	2048	1129	2259	2354	2025
mol_c L^{-1}	0.02	1858	758	2133	2064	1914	1907	571	2213	2273	2152
	0.05	1949	1090	2227	2172	2004	2184	829	2316	2421	2279
Zn											
$Ca(ClO_4)_2$,	0.01	412	293	420	418	421	617	316	733	660	650
mol_c L^{-1}	0.02	397	553	529	303	413	601	298	722	719	646
	0.05	337	436	598	304	377	507	269	631	617	532

† Γ_m is the proposed adsorption maximum of thr Langmuir equation, expressed in $\mu g\ g^{-1}$.

‡ An extrapolation of a graph of K_d vs. Γ to cut Γ-axis leads directly to an estimate of β_0, which equal to the Γ_m (Sposito, 1982).

Table 2.11. Comparison of Cu adsorption maxima for Bertie and Starr-Dyke soils with or without applied pig manure using various background electrolyte concentrations.

Cu		“Γ_m”† calculated by different approaches				
Background electrolytes	Soil	linear	two-line linear		interpolation theorem ‡	nonlinear
$Ca(ClO_4)_2$, 0.01 mol_c L^{-1}	Bertie	904	386	944	932	864
	Bertie + pig manure	1320	524	1371	1319	1263
	Starr-Dyke	1836	622	1955	1990	1717
	Starr-Dyke + pig manure	2462	551	2623	2527	2442
$Ca(ClO_4)_2$, 0.02 mol_c L^{-1}	Bertie	825	326	891	883	810
	Bertie + pig manure	1144	435	1199	1156	1105
	Starr-Dyke	1675	520	1806	1872	1616
	Starr-Dyke + pig manure	2262	778	2446	2565	2260
$Ca(ClO_4)_2$, 0.05 mol_c L^{-1}	Bertie	736	297	862	824	779
	Bertie + pig manure	963	282	1053	1040	975
	Starr-Dyke	1377	490	1521	1431	1364
	Starr-Dyke + pig manure	2099	811	2526	2155	2130

† Γ_m is the proposed adsorption maximum of thr Langmuir equation, expressed in μg g^{-1}.

‡ An extrapolation of a graph of K_d vs. Γ to cut Γ-axis leads directly to an estimate of β_0, which equal to the Γ_m (Sposito, 1982).

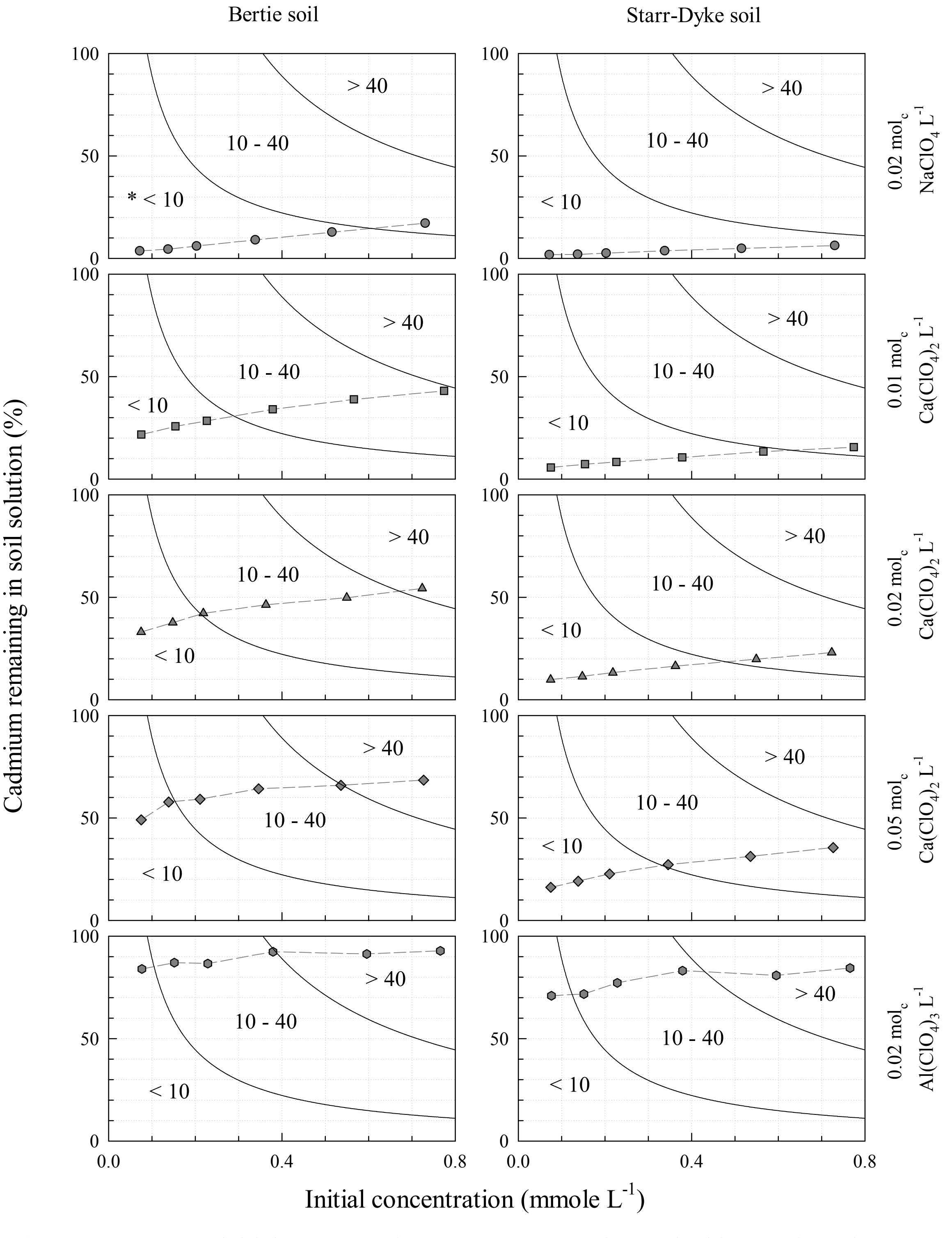

Fig. 2.17. Effect of initial concentration on percent of Cd unsorbed by Bertie and Starr-Dyke soils in the presence of different background electrolytes.

* Numbers within each zone represent the estimated concentration (mg L^{-1}) of Cd in soil solution.

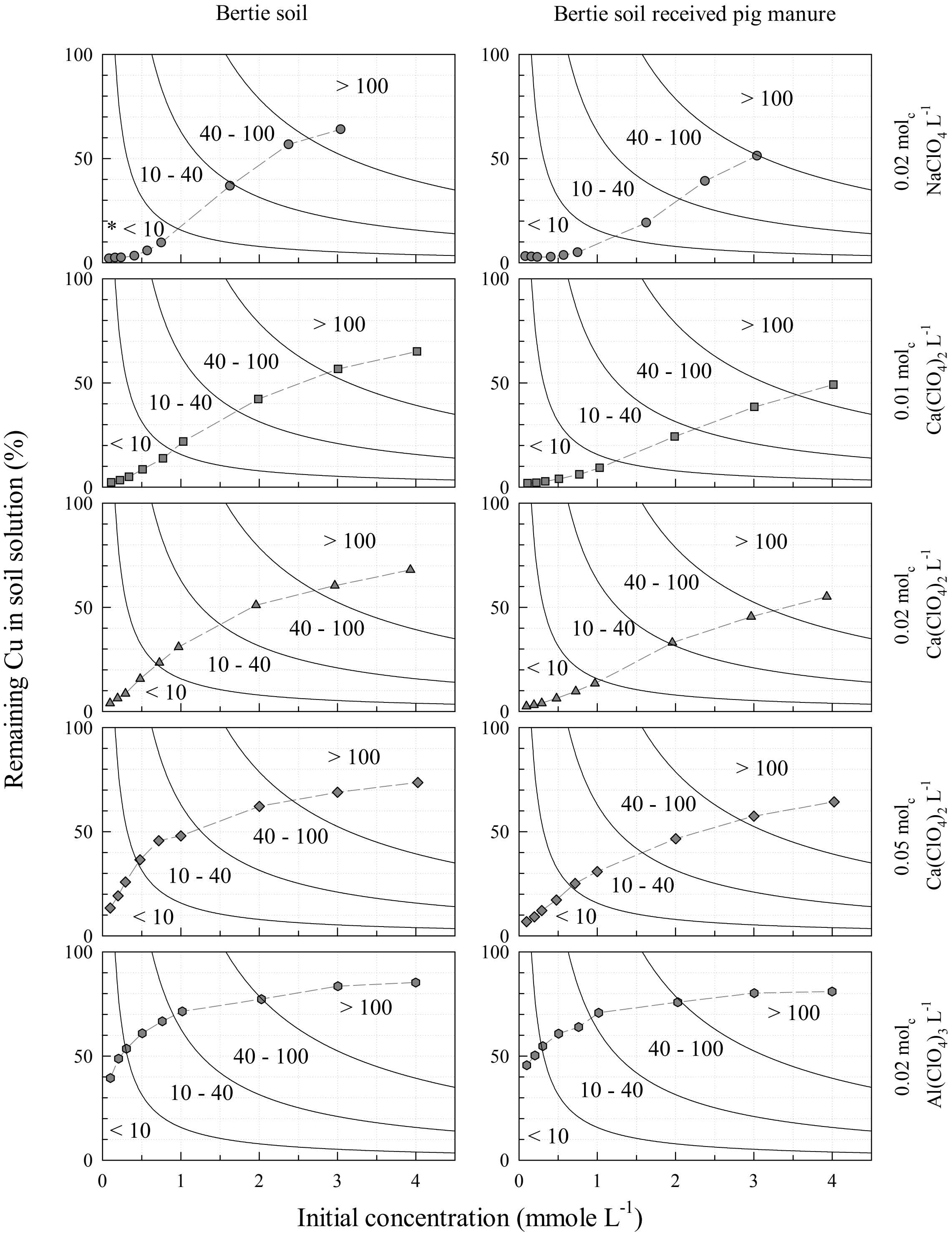

Fig. 2.18. Effect of initial concentration on percent of Cu unsorbed by Bertie soil with or without applied pig manure in the presence of different background electrolytes.

* Numbers within each zone represent the estimated concentration (mg L^{-1}) of Cu in soil solution.

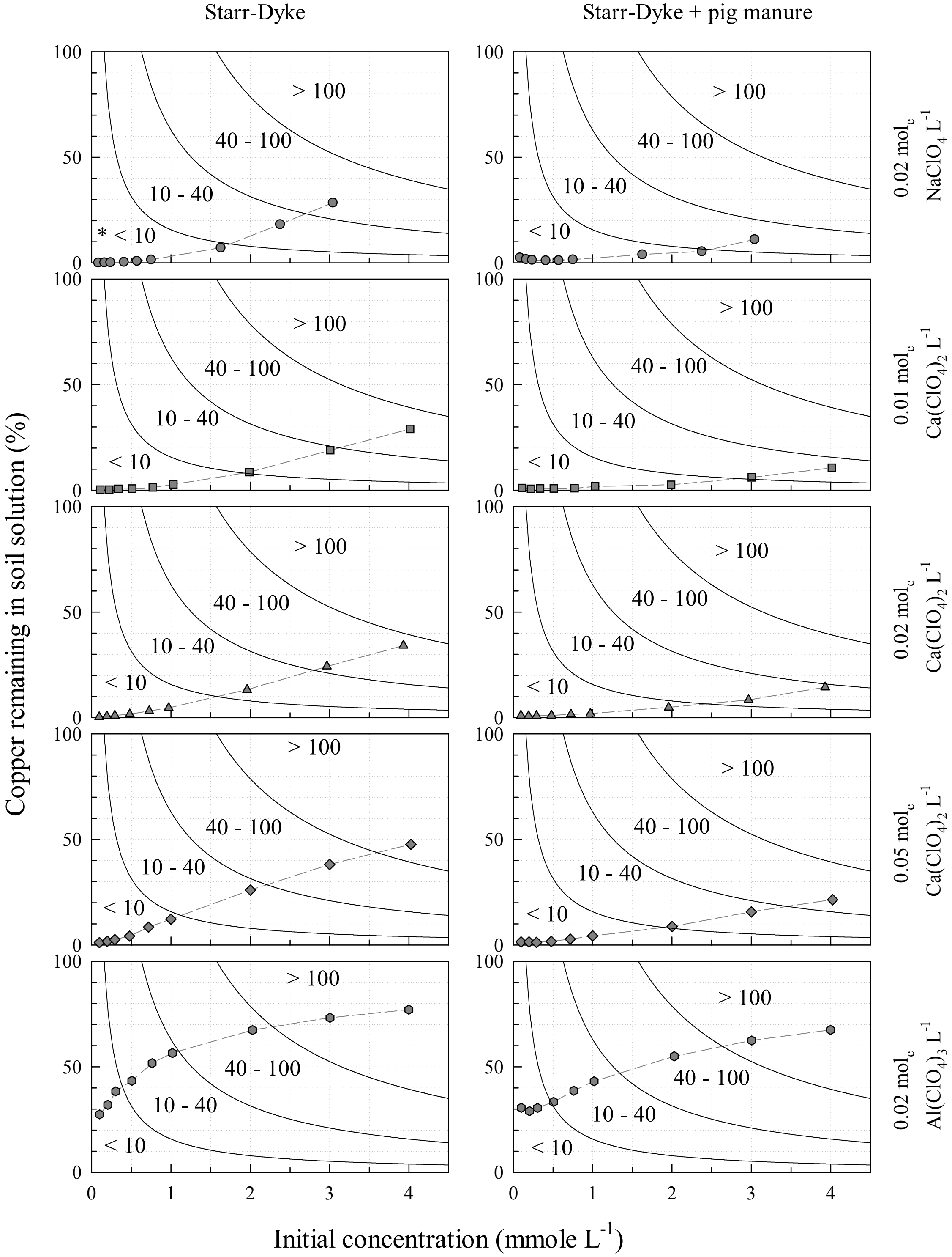

Fig. 2.19. Effect of initial concentration on percent of Cu unsorbed by Starr-Dyke soil with or without applied pig manure in the presence of different background electrolytes.

* Numbers within each zone represent the estimated concentration (mg L^{-1}) of Cu in soil solution.

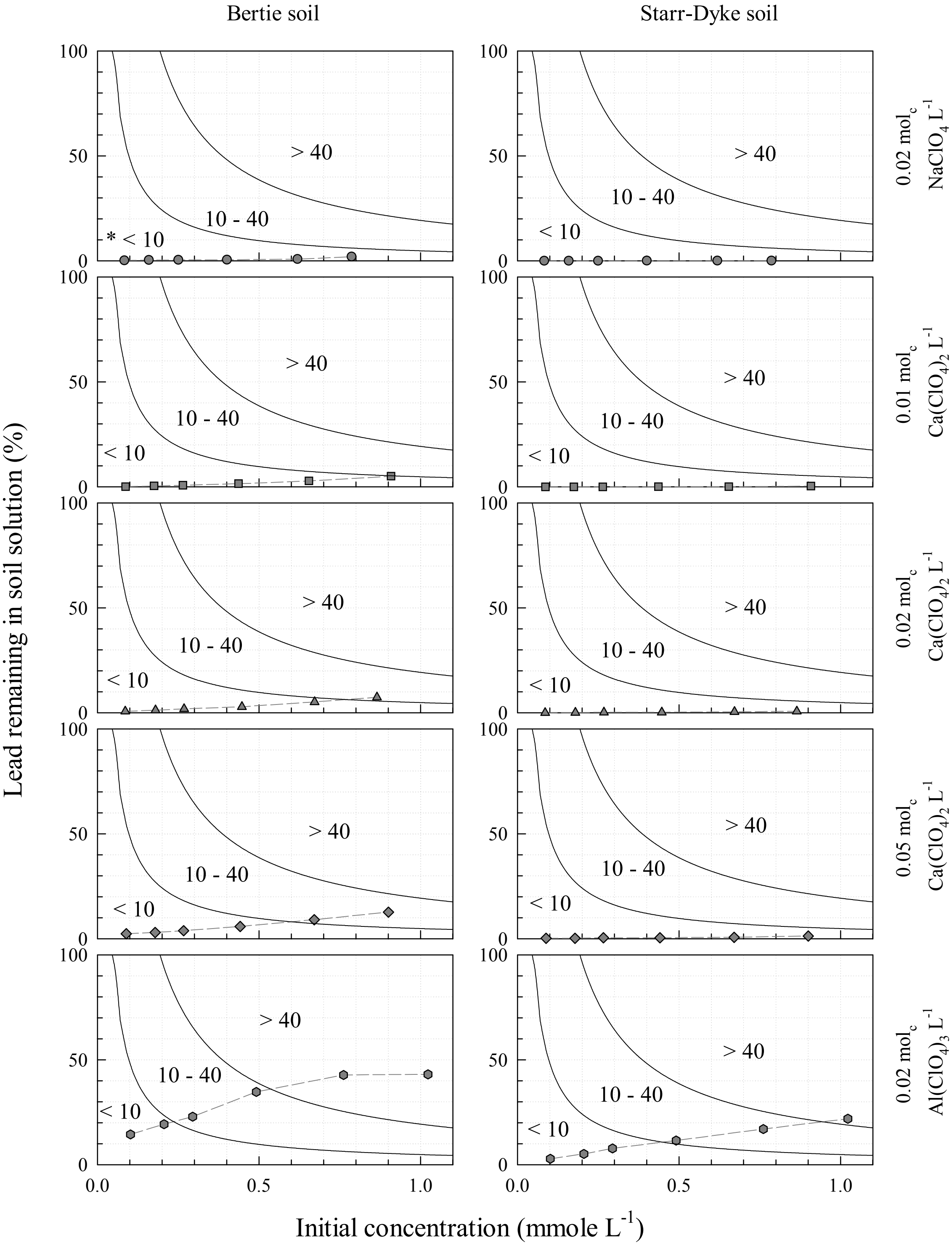

Fig. 2.20. Effect of initial concentration on percent of Pb unsorbed by Bertie and Starr-Dyke soils in the presence of different background electrolytes.

* Numbers within each zone represent the estimated concentration (mg L^{-1}) of Pb in soil solution.

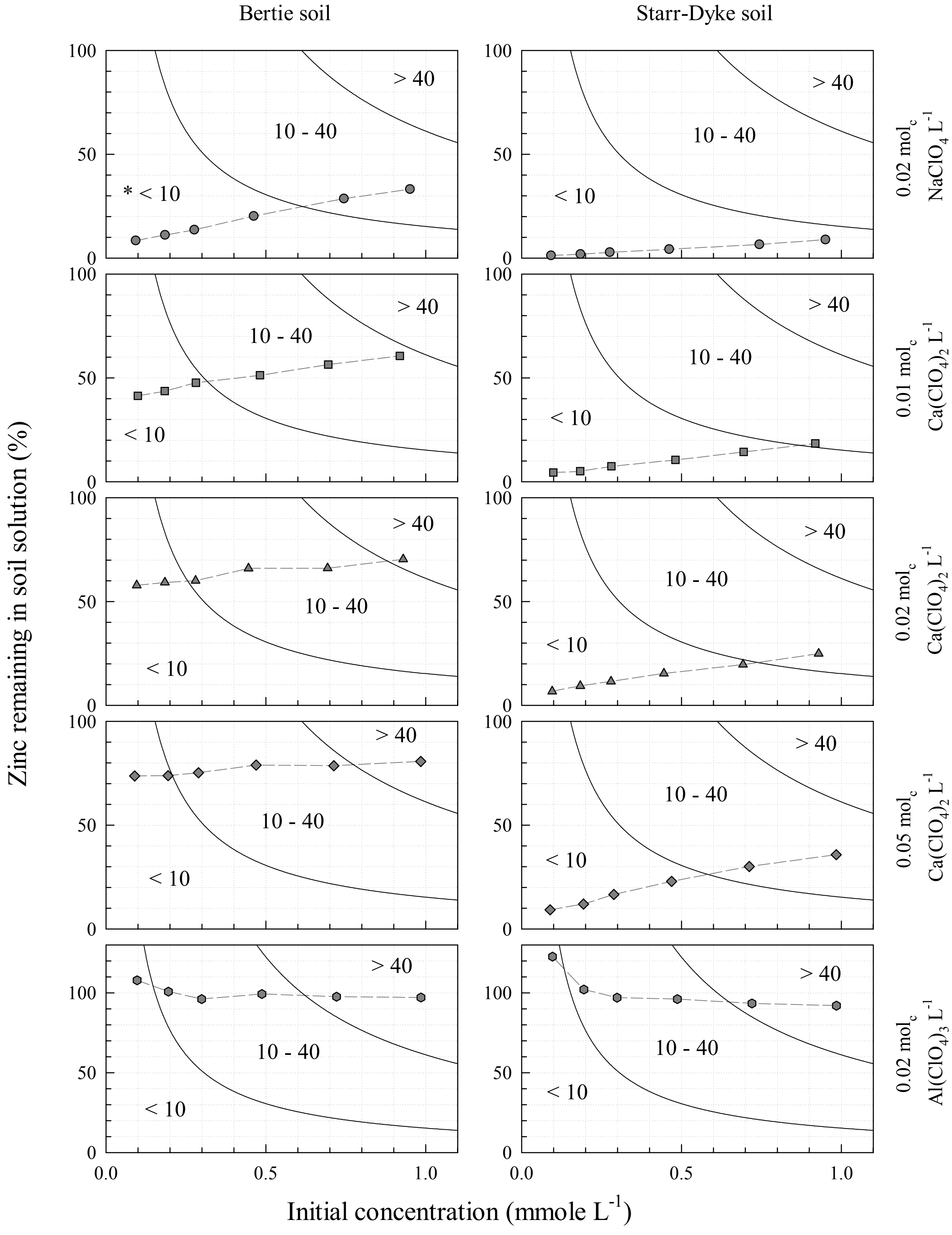

Fig. 2.21. Effect of initial concentration on percent of Zn unsorbed by Bertie and Starr-Dyke soils in the presence of different background electrolytes.

* Numbers within each zone represent the estimated concentration (mg L^{-1}) of Zn in soil solution.

isolines indicate levels of metal concentration remaining in soil solutions. For example, to attain Cd concentrations in soil solution of less than 10 mg L^{-1}, initial treatments should be approximately 0.6, 0.3, 0.21, 0.15, and 0.1 mmolar of Cd for 0.02 mol_c $NaClO_4$ L^{-1}, 0.01, 0.02, 0.05 mol_c $Ca(ClO_4)_2$ L^{-1}, respectively, and 0.02 mol_c $Al(ClO_4)_3$ background solution with Bertie soil. For Starr-Dyke soil, desirable solution concentrations are achievable at greater initial Cd concentration than with Bertie soil. Initial treatment of 0.8, 0.6, 0.5, 0.35, and 0.12 mmolar of Cd resulted in soil solution concentrations less than 10 mg L^{-1} for each of the respective background electrolytes (Fig. 2.17). For all metals in Starr-Dyke soils, soil solution concentrations were less than 10 mg L^{-1} in the presence of 0.02 mol_c $NaClO_4$ L^{-1} when initial concentration was 1 mmolar or less. In addition, pig manure application decreased Cu concentrations in soil solution for both soils except in the presence of Al^{3+}, and the effect was greater with Starr-Dyke than with Bertie soil. Only low Pb concentrations were measured in soil solution in both soil types and under most background conditions. Even in the presence of Al^{3+} in background electrolyte, Pb concentrations in soil solution were less than 40 mg L^{-1} when initial Pb concentrations were approximately 0.5 and 0.9 mmole L^{-1} with Bertie and Starr-Dyke soil, respectively. Starr-Dyke soils had much greater effect on Zn remaining in soil solution than Bertie soil, especially in the presence of $Ca(ClO_4)_2$.

The pH at which significant metal adsorption begins depends upon the strength of interaction of the metal and surface adsorption sites, and the concentration of $S{:}OH^0$ sites (Schindler, 1981). The increase in adsorption capacity with increasing pH presumably is due to the conversion of positively charged $S{:}OH_2^+$ sites to $S{:}OH^0$ sites and these in turn are converted to negatively charged $S{:}O^-$ sites. Metals adsorption by the Bertie and Starr-Dyke soils was not influenced by ionic strengths of $NaClO_4$ background solutions from pH 3 to pH 7 (Figs. 2.22 and 2.23). Jenne (1998) also reported that metals compete more effectively for pH-dependent sites than for pH-independent, fixed charge adsorption sites, as indicated by the minimal effect of electrolytes on adsorption. When pH is raised from an initially low value, the aqueous concentration of $Al(OH)_x^{3-x}$ becomes significant relative to Al^{3+} in clay systems. With 1 mM treatment of Cd, Cu, Pb, and Zn, the

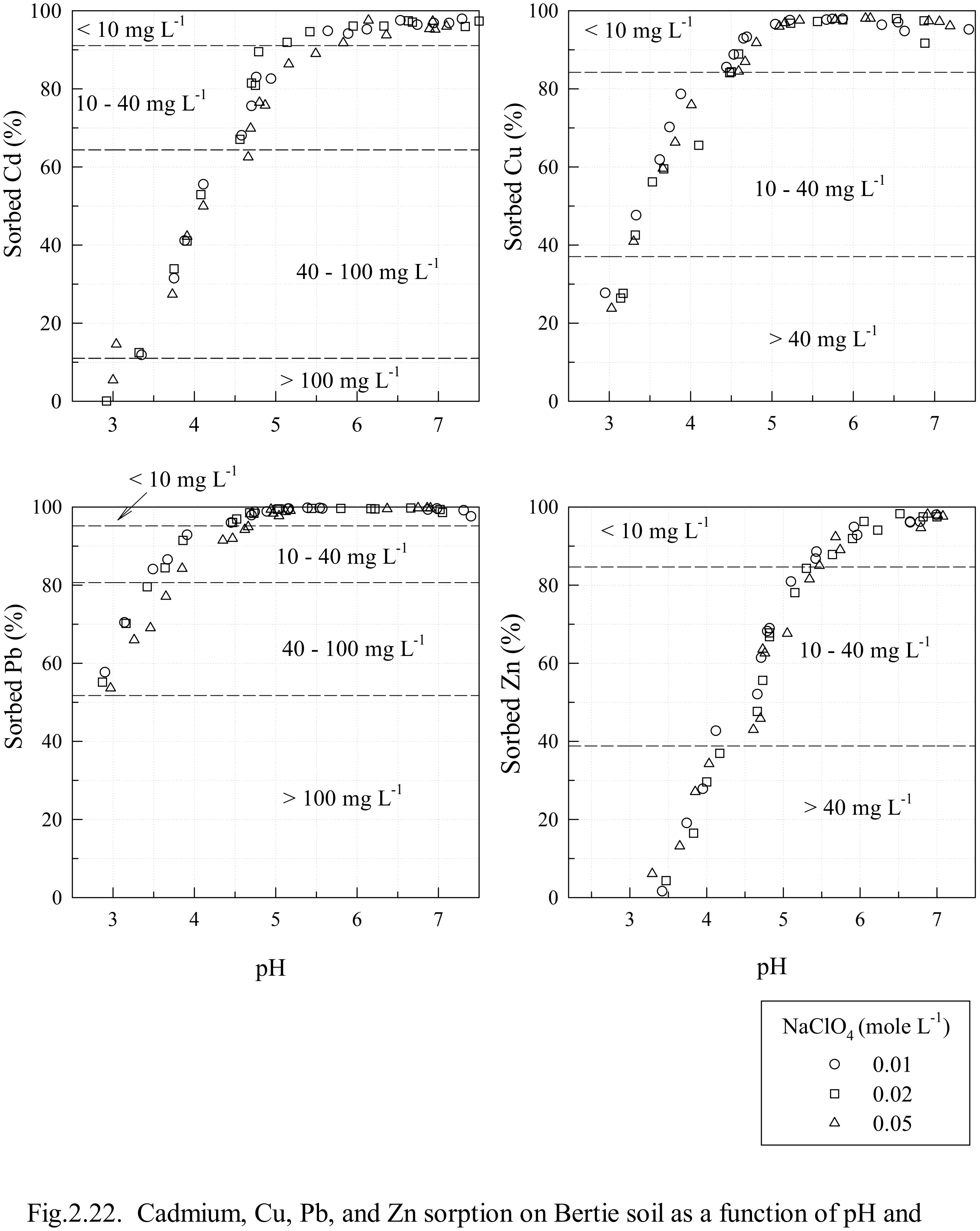

Fig.2.22. Cadmium, Cu, Pb, and Zn sorption on Bertie soil as a function of pH and ionic strengths of NaClO$_4$ background electrolytes.

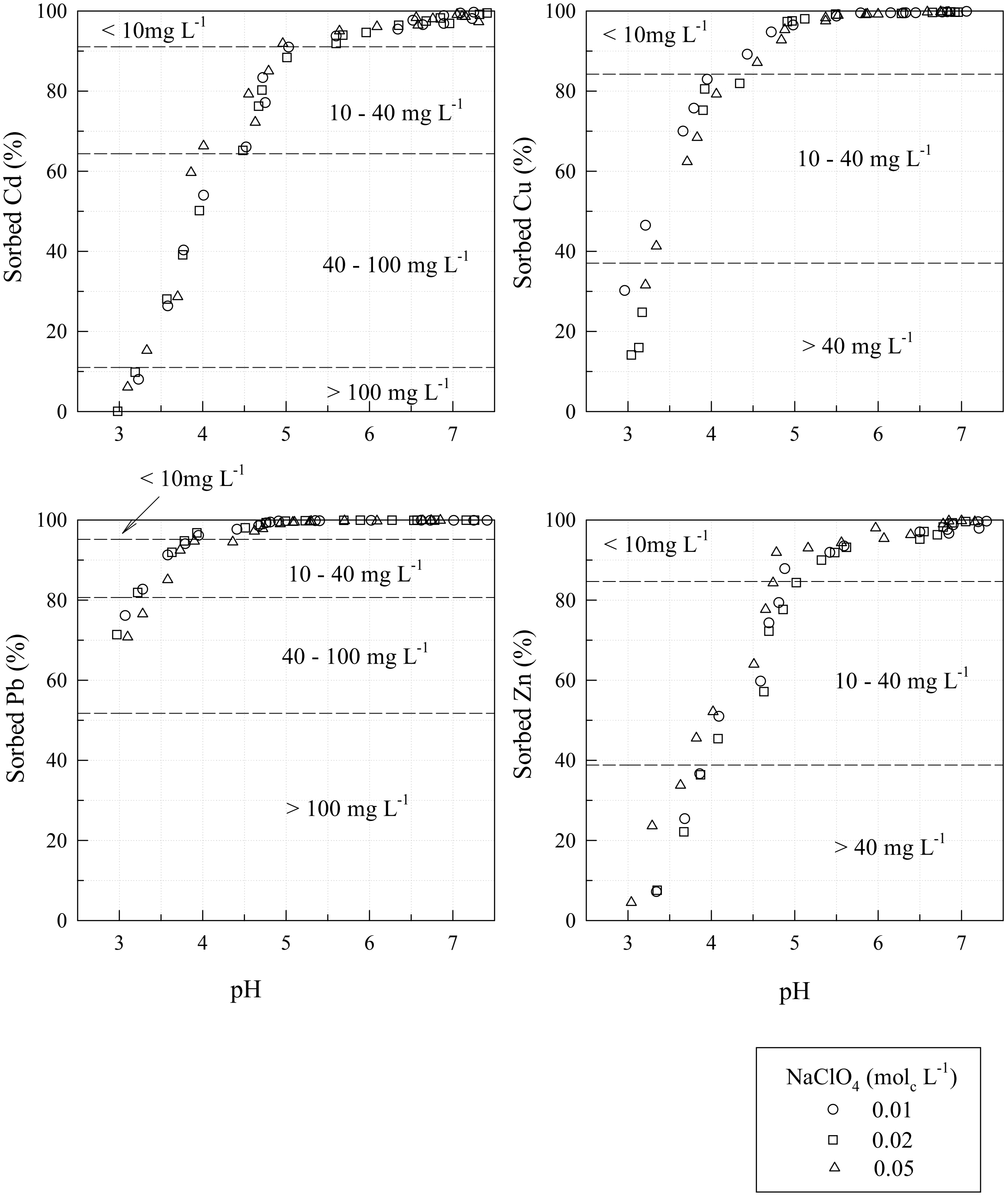

Fig.2.23. Cadmium, Cu Pb, and Zn sorption on Starr-Dyke soil as a fuction of pH and ionic strengths of NaClO$_4$ background electrolytes.

solution concentration of these metals was <10 mg L^{-1} in soil solution at pH values above 5.25, 4.5, 4.25, and 5.3, respectively, for Bertie soil, and 5, 4.5, 4, and 5, respectively, for Starr-Dyke soil. The replacement of a surface proton by metal or ligand exchange for a hydroxyl is considered to be equivalent to the formation of an inner-sphere complex (Schindler et al., 1976). An inner-sphere surface complex being one, which contains no water molecule between the surface site and adsorbed cation (Sposito, 1984). Davis (1977) also found that background electrolyte ions are involved in the development of surface charge. He interpreted the indifference in calculated acidity constants with varying ionic strength as inner-sphere formation between a surface site and background electrolyte cation. However, decreased adsorbate adsorption due to increases in the concentration of a background electrolyte are typically attributed to ionic strength effects and interpreted as evidence of nonspecific adsorption, i.e., formation of outer-sphere complexes as occurs on pH-independent charge sites (Hayes and Leckie, 1987; Zachara and McKinley, 1993). One difficulty in applying surface complexation models to a whole soil system is that soil parameters (e.g., surface acidity constants (K_a), adsorbent site concentration, etc.) are rarely reported. The K_a and pK_a are normally measured for individual minerals or amorphic solids rather than mixtures such as soils. Indeed, a given surface complex may change from predominantly an inner-sphere to predominantly an outer-sphere surface complex with pH or concentration of background electrolytes, because the data fitting includes identifying the number of the adsorption reactions (aqueous adsorbate and competing cation species) needed to adequately quantify the adsorption reaction (Ong and Leckie, 1998).

CONCLUSIONS

Cadmium, Cu, Pb and Zn adsorptions were affected by concentration of background electrolytes [$NaClO_4$, $Ca(ClO_4)_2$, and $Al(ClO_4)_3$] with the degree of adsorption dependent upon metal species and soil type. Also, the parameters of adsorption isotherms varied with ionic strength and composition of the background solution. Therefore, background electrolytes used in laboratory analysis should be considered when attempting to simulate real situations. Copper adsorption changed little with increasing ionic strength of Na^+ for Bertie sandy or Starr-Dyke clayey soils. Starr-Dyke soil, which contains a large amount of Fe_2O_3 and MnO_2, had minimal effect on Cu adsorption even with increasing ionic strength of Ca^{2+} in background solutions. In the presence of Na^+, Cd and Zn adsorption decreased with increasing ionic strength, while Pb adsorption was unaffected by ionic strength in any of the soils. Fewer differences in metals adsorption at different ionic strengths existed in Starr-Dyke soil than in Bertie soil. Soils with Cu-rich pig manure treatments had less difference in metals adsorption than control soils at different background ionic strengths. Enhanced adsorption of metals in those soils was attributed to preferential bonding of these metals by organic material.

Adsorption isotherms often were dependent upon the concentration range over which the experiments were conducted and a sufficiently large concentration range was not likely to have a C-curve characteristic (linear form). Jenne (1998) also concluded that the apparent success of Freundlich or Langmuir equations might depend on the concentration range of adsorbent, the adsorption capacity of the adsorbent, and the $C_{geomedia}$ (solid concentration). However, in most cases, Langmuir and Freundlich equations can successfully explain the adsorption of metals with various background electrolytes. Despite the good fits obtained between the experimental data and adsorption plots, some parameters in the model equations may not be reliable because of their dependency on other parameters. Numerous researchers have used the Langmuir equation to determine adsorption maxima for soil systems. Even though using the same set of experimental data, the equation values are often variable and dependent upon the methods of fitting the regression model equation. Klotz (1982) also pointed out dangers in estimating sorption maxima that do not approach maximum. Regardless of these limitations, the prime reason for trying to determine adsorption maxima is to estimate maximum levels of metals that soil systems can retain with no harmful effects on the environment. One approach to understanding the potential for environmental contamination is to determine the metal concentration in soil solution provided a given set of environmental factors. Initial treatments of Cd, Cu, Pb, and Zn should be 0.21, 0.7, 0.78, and 0.27 mM, respectively for Bertie soil in the presence of 0.02 mol_c Ca L^{-1} if metal concentrations remaining in soil solution are to be less than 10 mg L^{-1} based on concentration isolines. With 1 mM treatment of each metal, Cd, Cu, Pb, and Zn remained within 10 mg L^{-1} in soil solution at pH of approximately 5.25, 4.5, 4.25, and 5.3 respectively for Bertie soil, and 5.0, 4.5, 4.0, and 5.0 respectively for Starr-Dyke soil. Using isolines, metal-loading rates could be estimated with desirable metal concentration in soil solution dependent upon background electrolytes, soil type, pH, and possibly other factors.

REFERENCES

Alloway, B.J. 1990. The origin of heavy metals in soil. p. 29-39 . *In* B.J. Alloway (ed.) Heavy metals in soils. John Wiley & Sons, New York.

Alva, A.K., M.E. Summer, and W.P. Miller. 1991. Relationship between ionic strength and electrical conductivity for soil solutions. Soil Sci. 152: 239-242.

Azizian, M.F., and P.O. Nelson. 1998. Lead sorption, chemically enhanced desorption, and equilibrium modeling in an iron-oxide-coated sand and synthetic groundwater system. p. 165-180. *In* E.A. Jenne (ed.) Adsorption of metals by geomedia. Academic Press.

Benjamin, M.M. 1979. Effects of competing metals and complexing ligands on trace metal adsorption at the oxide/solution interface. Ph.D. Dissertation. Standford Univ., Standford, CA.

Bittel, J.E., and R.J. Miller. 1974. Lead, cadmium, and calcium selectivity coefficients on a montmorillonite, illite, and kaolinite. J. Environ. Qual. 3: 250-253.

Carter, D.L., M.D. Heilman, and C.L. Gonzales. 1965. Ethylene glycol monoethyl ether for determining surface area of silicate minerals. Soil Sci. 100: 356-360.

Cavallaro, N., and M.B. McBride. 1978. Copper and cadmium adsorption characteristics of selected acid and calcareous soils. Soil Sci. Soc. Am. J. 41: 550-556.

Cline, G.R., and G.A. O'Connor. 1984. Cadmium sorption and mobility in sludge-amended soil. Soil Sci. 138: 248-254.

Davis, J.A. 1977. Adsorption of trace metals and complexing ligands at oxide/water interface. Ph.D. Dissertation. Standford Univ., Standford, CA.

Davis, J.A. 1984. Complexation of trace metals by adsorbed natural organic matter. Geochim. et Cosmochim. Acta. 48: 679-691.

Garcia-Miragaya, J., and A.L. Page. 1976. Influence of ionic strength and inorganic complex formation on the sorption of trace amounts of Cd by montmorillonite. Soil Sci. Soc. Am. J. 48: 749-752.

Garcia-Miragaya, J., and A.L. Page. 1977. Influence of exchangeable cation on the sorption of trace amounts of cadmium by montmorillonite. Soil Sci. Soc. Am. J. 41: 718-721.

Garcia-Miragaya, J., J.R. Cardenas, and A.L. Page. 1985. Surface loading effect on Cd and Zn sorption by kaolinite and montmorillonite from low concentrations. Water, Air, Soil Pollut. 27:181-190.

Giles, C.H., T.H. MacEwan, S.N. Nakhwa, and D. Smith. 1960. Studies in adsorption. Part XI. A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids. J. Chem. Soc. 1960: 3973-3993.

Giles, C.H., D. Smith, and A. Huitson. 1974. A general treatment and classification of the solute adsorption isotherm. I. Theoretical. J. Colloid Interface Sci. 47: 755-765.

Griffin, R.A., and A.K. Au. 1977. Lead adsorption by montmorillonite using a competitive Langmuir equation. Soil Sci. Soc. Am. J. 41: 880-882.

Griffin, G.P., and J.J. Jurinak. 1973. Estimation of activity coefficients from the electrical conductivity and other natural aquatic systems and soil extracts. Soil Sci. 116: 26-30.

Harsh, J.B., and H.E. Doner. 1984. Specific adsorption of copper on a hydroxy-aluminum-montmorillonite complex. Soil Sci. Soc. Am. J. 48: 1034-1039.

Harter, R.D. 1984. Curve-fit errors in Langmuir adsorption maxima. Soil Sci. Soc. Am. J. 40: 658-663.

Harter, R.D., and D.E. Baker. 1977. Applications and misapplications of the Langmuir equation to soil adsorption phenomena. Soil Sci. Soc. Am. J. 41: 1077-1080.

Harter, R.D., and G. Smith. 1981. Langmuir equation and alternate methods of studying "adsorption" reactions in soils. p. 167-182. *In* R.H. Dowdy, et al. (ed.) Chemistry in the soil environment. Spec. publ. No. 40. American Society of Agronomy, Inc. Madison, WI.

Harvey, D.T., Fulghum, J.E., and Linton, R.W. 1983. Determination of adsorption stoichiometry for zinc adsorption on amorphous hydrous ferric oxide. J. Colloid Interface Sci. 94: 276-278.

Hassett, J.J. 1974. Capacity of selected Illinois soils to remove lead from aqueous solution. Comm. Soil Sci. Plant Anal. 5: 499-505.

Hayes, K.F., and J.O. Leckie. 1987. Modeling ionic strength effects on cation adsorption at hydrous oxide/solution interfaces. J. Colloid Interface Sci. 115: 564-572.

Hem, J.D. 1976. Geochemical control on lead concentrations in stream water and sediments. Geochim. Cosmochim. Acta. 40: 599-609.

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

Holford , I.C.R. 1978. Soil adsorption phenomena and the Langmuir equation. Soil Sci. Soc. Am. J. 42: 986-987.

Holford, I.C.R., and G.E.G. Mattingly. 1975. The high and low energy phosphate adsorbing surfaces in calcareous soils. J. Soil Sci. 26: 407-417.

Holford , I.C.R., R.W.M. Wedderburn, and G.E.G. Mattingly. 1974. A Langmuir two-surface equation as a model for phosphate adsorption by soil. J. Soil Sci. 25: 242-255.

Jenne, E.A. 1998. Adsorption of metals by geomedia: Data analysis, modeling, controlling factors, and related issues. p. 1-73. *In* E.A. Jenne (ed.) Adsorption of metals by geomedia. Academic Press.

John, M.K. 1972. Cadmium adsorption maxima of soils as measured by the Langmuir isotherm. Can. J. Soil Sci. 52: 343-350.

Kiekens, L. 1983. Behavior of heavy metals in soils. p. 126-134. *In* S. Berglund, R.D. Davis, and P.L'Hermite. (ed.) Utilization of sewage sludge on land: Rates of application and long-term effects of metals. D. Reidel Publishing Company.

Kinniburgh, D.G. 1983. The H^+/M^{2+} exchange stoichiometry of calcium and zinc adsorption by ferrihydrite. J. Soil Sci. 34: 759-768.

Klotz, I.M. 1982. Number of receptor sites from Scatchard graphs: facts and fantasies. Science 217: 1247-1249.

Krauskopf, K.B. 1972. Geochemistry of micronutrients. p. 7-40. *In* J.J. Morvedt et al. (ed.) Micronutrients in agriculture. Soil Science Society of America, Inc. Madison, WI.

Lagerwerff, J.V., and D.L. Brower. 1972. Exchange adsorption of trace quantities of cadmium in soils treated with chlorides of aluminum, calcium, and sodium. Soil Sc. Soc. Am. Proc. 36: 734-737.

Langmuir, I. 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. J. Amer. Chem. Soc. 40: 1361-1403.

LeClaire, J.P. 1985. Adsorption of copper and cadmium onto soils: Influence of organic matter. Ph. D. Dissertation, University of California, Riverside.

Lindsay, W.L. 1979. Chemical equilibria in soils. John Wiley & Sons, New York

Mattigod, S.V., A.S. Gibali, and A.L. Page. 1979. Effect of ionic strength and ion pair formation on the adsorption of nickel by kaolinite. Clays and Clay Miner. 27: 411-416.

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

McLaren, R.G., R.S. Swift, and J.G. Williams. 1981. The adsorption of copper by soil materials at low equilibrium solution concentrations. J. Soil Sci. 32: 247-256.

Misra, S.G., and R.C. Tiwari. 1962. Studies on the adsorption and release of copper by soils. Effects of cations. Soil Sci. Plant Nutr. 8: 93-96.

Misra, S.G., and R.C. Tiwari. 1966. Retention and release of copper and zinc by Indian soils. Soil Sci. 101: 465-471.

Navrot, J., A. Singer, A. Banin. 1978. Adsorption of cadmium and its exchange characteristic in some Israeli soils. J. Soil Sci. 29: 505-511.

O'Connor, G.A., C. O'Connor, and G.R. Cline. 1984. Sorption of cadmium by calcareous soils: Influence of solution composition. Soil Sci. Soc. Am. J. 48: 1244-1247.

Olsen, S.R., and F.S. Watanabe. 1957. A method to determine a phosphorus adsorption maximum of soils as measured by the Langmuir isotherm. Soil Sci. Soc. Am. Pro. 21: 144-149.

Ong, C.G., and J.O. Leckie. 1998. Surface and solution speciation of Ag^I in a heterogeneous ferrihydrite-solution system with thiosulfate. p. 317-331. *In* E.A. Jenne (ed.) Adsorption of metals by geomedia. Academic Press.

Page, A.L., R.H. Miller, and D.R. Keeney. 1982. Methods of soil analyses. Part 2. Chemical and microbiological properties. 2nd ed. American Society of Agronomy. Madison, Wis., USA.

Perona, M.J., and J.O. Leckie. 1985. Proton stoichiometry for the adsorption of cations on oxide surfaces. J. Colloid Interface Sci. 106: 64-69.

Petruzzelli, G., G. Guidi, and L. Lubrano. 1985. Ionic strength effect on heavy metal adsorption by soil. Commun. Soil Sci. Plant Anal. 16: 971-986.

Ramachandran, V., and T.J. D'Souza. 1999. Adsorption of cadmium by Indian soils. Water, Air, and Soil Pollut. 111: 225-234.

Reed, S.T. 1993. Copper adsorption/desorption characteristics on copper amended soils. Ph. D. Dissertation, Virginia Polytechnic Institute and State University. Blacksburg, VA.

Rich, C.I., and R.I. Barnhisel. 1977. Preparation of clay samples for x-ray diffraction analysis. p. 797-808. *In* J.B. Dixon and S.B. Weed (eds.). Minerals in soil environments. Soil Science Society of America, Inc. Madison, Wis.

Ritchie, G.S.P., and S.C. Jarvis. 1986. Effects of inorganic speciation on the interpretation of copper adsorption by soils. J. Soil Sci. 37: 205-210.

Roy, W.R., I.G. Krapac, S.F.C. Chou, and R.A. Griffin. 1992. Batch-type procedures for estimating soil adsorption of chemicals. U.S.E.P.A. EPA/530/SW-87/006-F.

Schindler, P.W. 1981. Surface complexes at oxide-water interfaces. p. 1-49. *In* M.A. Andrson and A.J. Rubin (eds.). Adsorption of inorganics. Ann Arbor Science, Ann Arbor, MI.

Schindler, P.W., B. Fürst, R. Dick, and P.U. Wolf. 1976. Ligand properties of surface silanol groups. I. Surface complex formation with Fe^{3+}, Cu^{2+}, Cd^{2+}, and Pb^{2+}. J. Colloid Interface Sci. 55: 469-475.

Schulthess, C.P., and D.K. Dey. 1996. Estimation of Langmuir constants using linear and nonlinear least squares regression analyses. Soil Sci. Soc. Am. J. 60: 433-442.

Schulthess, C.P., and D.L. Sparks. 1991. Equilibrium-based modeling of chemical sorption on soils and soil constituents. Adv. Soil Sci. 16: 121-163.

Sibbesen, E. 1981. Some new equations to describe phosphate sorption by soils. J. Soil Sci. 32: 67-74.

Sposito, G. 1984. The surface chemistry of soils. Clarendon Press. Oxford.

Sposito, G., K.M. Holtzclaw, L. Charlet, C. Jouany, and A.L. Page. 1983. Sodium-calcium and sodium-magnesium exchange on Wyoming bentonite in perchlorate and chloride background ionic media. Soil Sci. Soc. Am. J. 47: 51-56.

Syers, J.K., M.G. Browman, G.W. Smillie, and R.B. Corey. 1973. Phosphate sorption by soils evaluated by the Langmuir adsorption equation. Soil Sci. Soc. Am. Proc. 37: 358-363.

Turner, M.A., L.L. Hendrickson, and R.B. Corey. 1984. Use of chelating resins in metal adsorption studies. Soil Sci. Soc. Am. J. 48: 763-769.

U.S. Environmental Protection Agency. 1993. Clean water act. Section 503. Vol. 58. No. 32. USEPA, Washington, DC.

Veith, J.A., and G. Sposito. 1977. On the use of the Langmuir equation in the interpretation of "Adsorption" phenomena. Soil Sci. Soc. Am. J. 41: 697-702.

White, G.N., and L.W. Zelazny. 1986. Charge properties of soil colloids. p.39-81. *In* Sparks, D.L. (ed.) Soil physical chemistry. CRC Press, Inc., Boca Raton, FL.

Whittig, L.D., and W.R. Allardice. 1986. X-ray diffraction techniques. p. 331-362. *In* Klute, A. (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. American Society of Agronomy. Madison, Wis.

Zachara, J.M., and J.P. McKinley. 1993. Influence of hydrolysis on the sorption of metal cations by smectites: Importance of edge coordination reactions. Aquatic Sci. 55: 250-261.

Zhu, B and A.K. Alva. 1993. Differential adsorption of trace metals by soils as influenced by exchangeable cations and ionic strength. Soil Sci. 155: 61-66.

Zhu, Y., D.F. Berry, and D.C. Martens. 1991. Copper availability in two soils amended with eleven annual applications of copper-enriched hog manure. Commun. Soil Sci. Plant Anal. 22: 769-783.

Zimdahl, R.L., and R.K. Skogerboe. 1977. Behavior of lead in soil. Environ. Sci.

Technol. 11: 1202-1207.

CHAPTER III

COPPER SORPTION AS INFLUENCED BY pH AND SELECTED SOIL COMPONENTS

ABSTRACT

The effect of pH on Cu sorption by Bertie sandy and Starr-Dyke clay loam soils was investigated. Copper-rich pig manure was applied to each soil for 16 years. Most added Cu was adsorbed at low concentrations regardless of pH, but at high concentrations Cu sorption was strongly related to solution pH. Increases in pH resulted in greater Cu sorption due to pH-dependent negative charges and precipitation. The USEPA suggested that soil pH be maintained above 6.5 where high concentrations of metals are land applied because of the impact of soil pH on metal sorption. However, pig manure applications to Bertie soil resulted in greater Cu in soil solution than in control (no manure) soil at pH > 6.5 due to soluble organic matter. Adsorption isotherms indicated that in Bertie soil sorption of Cu changed from L-curve type to L-subgroup 4 curve type at pH > 5.5 while most of the Cu adsorption isotherms from Starr-Dyke soil were L-type curve except at pH 7.0. The subsequent rise in Cu sorption in Bertie soil likely represented the development of a second layer. These curves could be due to soluble organic matter, precipitation with inorganic ions or both. Therefore, determination of adsorption maxima for Bertie soil at pH > 5.5 was not possible because the adsorption curves did not follow the L-type. In both soils, the best fit across all models (Langmuir, extended Langmuir, two-site Langmuir, and Freundlich) was observed at pH 5.0. With increasing concentration, Cu sorption was more linear when pH was maintained at 5.5 than when pH was not controlled. When pH was not controlled, increased Cu concentration reduced solution pH, resulting in decreased Cu sorption. Organic matter, manganese oxide, and free iron oxide were removed with H_2O_2, $NH_2OH{\cdot}HCl$, and DCB (Dithionite-Citrate-Bicarbonate) respectively. In contrast with reports of other researchers, negligible effect on Cu sorption was observed after

removal of free Mn oxides with $NH_2OH \cdot HCl$ treatment. This conflicting result comes from differences between sequential extraction procedures and soil separates after removal of free Mn oxides with $NH_2OH \cdot HCl$ treatment. Further research needs to be conducted to elucidate the effects of chemical reagents on soil components.

INTRODUCTION

Copper is widely distributed in nature, interacting with soil minerals and organic components. The distribution of Cu among various soil phases determines its mobility, availability and toxicity to organisms. Secondary mineral forms of Cu^{2+} include oxides, carbonates, silicates, sulfates, and chlorides. However, these minerals do not persist at low pH and under strong leaching conditions (McBride, 1981). At low pH, adsorbed Cu^{2+} on layer silicates may tumble freely as hexaquo $Cu(H_2O)_6{}^{2+}$ species in interlayers or external surface positions and the ions are readily exchanged from surfaces by other ions (McBride, 1976). Cupric carbonate ($CuCO_3{}^0$) has been suggested as the major inorganic form of complexed Cu in neutral and alkaline soil solution (Mattigod and Sposito, 1977; Sanders and Bloomfield, 1980), but a number of studies have shown that at high pH, natural Cu^{2+} in soil solutions is largely complexed with soluble organic compounds (Hodgson et al., 1965; 1966).

Control of Cu solubility in soil-water systems is characterized by precipitation/dissolution reactions, or by surface chemical control. With precipitation and dissolution of the discrete solid phase, metal ions dominate the variation of metal concentration as a function of solution parameters and time, while with surface chemical control, insoluble phases provide sites for adsorption or interfacial reactions (James and MaNaughton, 1977). The reactions between metals and soil constituents are influenced by several factors. Numerous studies have shown the importance of pH as a factor controlling the extent of cation adsorption by soils. Anderson and Christensen (1988) reported that pH was more influential than any other soil property in determining distribution coefficients of Cd, Co, Ni, and Zn in 38 Danish soils. As pH increases, adsorbed Cu becomes much less exchangeable. An increase in pH makes the surface electrostatically more suitable for adsorption (Mckenzie, 1980). Parfitt (1980) reported that divalent metal ions can also be adsorbed as MOH^+ or $M(OH)_2{}^0$, depending on the pH of the equilibrium solution. Less adsorption of Cu by clay minerals and gibbsite was observed at lower pH due to competition of protons, $Mg^{2+}(aq)$, $Fe^{3+}(aq)$, and $Al^{3+}(aq)$ (Kishk and Hassan, 1973). The increase of Cu sorption may be explained by the precipitation of

$Cu(OH)_2$ at high pH. The precipitation of $Cu(OH)_2$ and $Zn(OH)_2$ can result in excess retention of Cu and Zn by bentonite (Bingham et al., 1964). Since co-precipitation of Cu^{2+} in Al- and Fe hydroxides occurs readily, non-diffusible Cu in soils may reside within oxide structures (McBride, 1978). This non-diffusible form exists largely in the residual Cu form. A portion of the residual Cu released by HF treatment may originate from crystalline silicate clays, because Cu^{2+} undergoes isomorphous substitution in octahedral positions of layer silicate clays.

As the behavior of heavy metals is controlled to some extent by surface reactions (Sposito and Page, 1984), clay and organic colloids can be major soil factors in metal retention. McLaren and Crawford (1973) reported a fractionation scheme that revealed an association between Cu and MnO_2. This possibly represents occlusion of the ion, but much of the labile Cu was associated with organic matter. Organic matter can have important effects on the behavior of heavy metal release or retention in soils due to its decomposition rate. In addition, organic matter has quite different effects on heavy metal uptake by plants, depending upon whether it is soluble (fulvic acid) or insoluble (humic acid). Research to date has resulted in the development of two contradictory theories about application of metal-enriched organic wastes to soil systems (McBride, 1995). The biosolid protection theory has been supported by evidence that metal adsorption capacity due to added biosolid persists as long as the heavy metals of concern persist in the soil (Chaney and Ryan, 1993). Short-term field experiments have shown that the adsorptive properties of biosolids often prevent excessive crop uptake of many of the constituent heavy metals, a protection attributable largely to the added organic matter except in the first year. Availability of metals to plants generally is the highest immediately following application of biosolid to soil and then diminished (Bidwell and Dowdy, 1987; Chang et al., 1987). Mullins et al. (1982) also reported that a portion of Cu in soil amended either with $CuSO_4$ or Cu-rich pig manure reverted to unavailable forms with time. Others found that extractable Cu decreased with time in Cu-amended histosols (Levesque and Mather, 1986).

A contrasting theory is made based on the fact that added organic matter eventually decomposes (Kononova, 1966). According to the theory, following cessation of waste product application, soil organic matter concentrations over the very long-term should return to a value not greater than that in the original soil (Bell et al., 1991; Terry et al., 1979). The theory is often termed the biosolid time bomb hypothesis because the slow mineralization of organic matter in biosolids could release metals in soluble forms. Long-term field observations often show that biosolid-applied metals can remain sufficiently available even in nonacid soils (Campbell and Beckett, 1988; Alloway, 1990). Reports of a high degree of EDTA-extractable Cd, Cu, Pb, and Zn in old biosolid application sites suggest that a large proportion of these metals are probably associated with organic matter in the biosolid (McGrath and Cegarra, 1992; Baldwin et al., 1983). The results also imply that many heavy metals added to soils through biosolid application have limited ability to diffuse or coprecipitate into soil minerals over time. Thus, a large fraction of certain heavy metals from biosolids remain in potentially plant-accessible forms.

Application of Cu-rich manure significantly increased Cu content of the upper 10 cm of soil each year, and plowing after the first year increased Cu levels in the 10-20 cm depth with a small increase in the 20-30 cm depth (Kornegay et al., 1974). Cabrera et al. (1989) reported that adding 14 tons of urban compost ha^{-1} yr^{-1} to a soil caused a noticeable increase in total and available soil Cu and Zn. Organic matter supplied to soil by biosolid application over a number of years probably enters into the humification-mineralization processes that tend to mitigate, with time, the direct effect of immediate partial incorporation into native soil humic acid. Organic matter binds Cu^{2+}, forming an inner sphere complex that is pH dependent (McBride, 1978). Effects of pH on Cu sorption by soil organic substances are due to both metal hydrolysis and the weak acid nature of exchange sites (Cavallaro and McBride, 1984). With any concentration of soluble metal in the system, the pH value had a more significant effect on systems containing soluble organic ligands (Sposito and Page, 1984).

This research was designed to evaluate Cu sorption in soil systems. Soils with or without applied pig manure were used to determine Cu sorption across a range of pH levels. Specific soil constituents were removed by chemical treatment to assess their impact on Cu sorption.

MATERIALS AND METHODS

Soils

In 1978, field plots were established to determine the long-term effect of Cu-rich pig manure application to agricultural soils. The soils used for this study were Bertie fine sandy loam (fine-loamy, mixed, thermic Aquic Hapludults) from the Virginia Coastal Plain, and Starr-Dyke clay loam (fine-loamy, mixed, thermic Fluventic Dystochrept and clayey, mixed, mesic Typic Rhodudults) from the Virginia Piedmont. The Cu concentration of the pig manure collected for field experiments averaged 1320 mg kg^{-1} (dry weight basis). At both sites, soil samples were obtained from control plots and plots receiving applications of Cu-rich pig manure. The Cu-rich pig manure was applied annually to the plots for 16 years at the cumulative rate of 1300 mt ha^{-1}, and treatments supplied 384 and 379 kg Cu ha^{-1} to the Bertie and Starr-Dyke soils, respectively. Soil pH levels in the Ap horizon of each soil were maintained above pH 6.5 with dolomitic limestone. Soils were sampled from the upper 15 cm of the exposed surface, air-dried, and passed through a 1-mm sieve. Soil properties, determined by standard methods (Page et al., 1982), are listed in Table 2.1 and Table 2.2.

Sorption Experiments

For each soil series, three grams of air-dried soil were sieved and placed in Teflon Erlenmeyer flasks with 30 ml of 0.02 mol$_c$ $NaClO_4$ L^{-1} solution. Sodium perchlorate was used as the background solution because perchlorate is a weak ligand that does not form complexes with metal ions (Sposito and Holtzclaw, 1979; Sposito et al., 1983). The $NaClO_4$ stock solutions were passed through a column containing Sephadex 100, a 1% cross-linked polystyrene matrix with methyl iminodiacetic acid residues on aromatic rings. Sephadex 100 preferentially binds divalent metal ions over monovalent ions at an approximate ratio of 5000 to 1. All laboratory wares were soaked with acid solution and rinsed with distilled deionized water. The background concentration of 0.02 mol$_c$ L^{-1} was chosen because the electrical conductivity of the saturated soil solutions was similar to that of the 0.02 mol_c L^{-1} of $NaClO_4$ solution (Appendix, Table A.1).

In each series of experiments, $Cu(ClO_4)_2$ was added to the $NaClO_4$ solution and concentrations ranged from 0.1 mM to 6 mM. Five replicates of soil suspensions were adjusted using either $HClO_4$ or NaOH to achieve desired pH levels from 3 to 7. Suspensions were allowed to equilibrate for 24 hrs in an oscillating chamber at 120 rpm and 25°C and pH was readjusted as needed and the procedure was repeated until solution pH was stable. The total volume of suspension was limited to less than 1% change due to addition of acid or base. After equilibration, the supernatants were analyzed for each metal by flame absorption spectrophotometry on a Perkin-Elmer model 3300 Atomic Absorption Spectrophotometer.

Soil Separates

Bertie and Starr-Dyke soils were treated to remove organic matter, and Fe and Mn oxides. The organic matter was removed by repeated treatment with H_2O_2 at 70 °C (Douglas and Fiessinger, 1971; Kunze and Dixon, 1982). The Mn oxides were removed by $NH_2OH{\cdot}HCl$ (Chao, 1972). Free iron oxides were separated from soil with dithionite-citrate-bicarbonate (DCB), which removes free Fe_2O_3 with minimum destructive action to the clay minerals (Mehra and Jackson, 1960). After chemical treatments, all soil separate samples were washed with 0.01 mol_c $NaClO_4$ L^{-1} solution before use for sorption studies. The chemical properties of soil separates are listed in Table 3.1.

Kaolinite (Kga-2) also was used as adsorbent for the adsorption studies. The poorly crystallized kaolinite was purchased from the Source Clay Minerals Repository, Clay Minerals Society, Department of Geology, University of Missouri. The kaolinite sample, from Warren County, Georgia, has a N_2 gas surface area of 23.6 m^2 g^{-1} and a CEC of 3.3 $cmol_c$ kg^{-1} (van Olphen and Fripiat, 1979).

Table 3.1. The chemical properties of Bertie and Starr-Dyke soils and their separates with H_2O_2, $NH_2OH·HCl$, and DCB for removing organic matter, free MnO_2, and free Fe_2O_3.

Soil fraction	pH	EC	Organic C	Exchangeable K	Exchangeable Ca	Exchangeable Mg	Free MnO_2	Mn in solution	Free Fe_2O_3	Fe in solution	Moisture
	(1:5)	(mS cm^{-1})	μg g^{-1}	------	mg L^{-1}	------	mg L^{-1}	mg L^{-1}	μg g^{-1}	mg L^{-1}	μg g^{-1}
Whole Bertie Soil	5.84	0.044	12.1	117	419	80	46.23	-	2.68	-	4.9
Whole Bertie Soil + pig manure	5.97	0.076	14.6	164	698	93	56.29	-	2.63	-	5.1
Bertie Separates*											
H_2O_2	7.12	1.152	2.1	34	233	9	9.05	0.553	5.02	19.31	4.9
$NH_2OH·HCl$	4.74	0.174	10.8	17	30	9	1.39	0.101	2.46	3.04	1.3
DCB	6.58	4.770	16.0	86	0.3	24	1.02	0.712	0.05	25.06	15.2
Whole Starr-Dyke Soil	6.58	0.081	12.1	403	946	368	3900.36	-	6.369	-	20.1
Whole Starr-Dyke Soil + pig manure	6.51	0.167	18.8	591	1516	421	3601.77	-	6.803	-	20.5
Starr-Dyke Separates*											
H_2O_2	7.98	1.420	4.0	182	238	28	1311.97	1.692	6.845	1.22	635.4
$NH_2OH·HCl$	4.75	0.638	11.4	90	202	82	337.70	50.721	6.729	0.49	549.5
DCB	9.72	4.765	12.0	384	18	8	47.39	0.618	0.248	28.32	420.1

* The chemical reagents, H_2O, H_2O_2, $NH_2OH·HCl$, and DCB, are used for removal of soluble organic matter, organic matter, free MnO_2, and free Fe_2O_3.

RESULTS AND DISCUSSION

Copper in soil solution decreased with increasing pH for both soils (Fig. 3.1). The effect of pH on Cu sorption by soils is likely due to edge charges or precipitation with hydroxyl groups. Adsorbed Cu has been observed as $CuOH^+$ rather than the aquo species $Cu(H_2O)_6{}^{2+}$ at pH 5 (Koppleman and Dillard, 1977). The addition of OH^- to the copper aquo ion $(Cu(H_2O)_6)^{2+}$ (aq) to increase pH causes successive displacement of water molecules from the hydration sheath and stepwise formation of Cu complexes. Harter (1983) reported that the amount of Cu, Pb, Ni, and Zn retained was dependent upon pH of the soil sample, with retention dramatically increasing at pH > 7.0 to 7.5. However, Kuo and Baker (1980) reported that in an acidic sandy soil Cu adsorption increased as suspension pH increased up to pH 6. In this study, most Cu was sorbed at pH 6.5, even when 6 mM of Cu was added to the soils.

At pH values above 6.5, Cu in soil solution increased with increasing pH in the Bertie sandy soil with applied pig manure (Fig. 3.2). Solution pH had less effect on the Starr-Dyke clay soil, however, and remaining Cu in soil solution was decreased with increasing pH from 6.5 to 7.5. This may be due to the association of Cu ions with organic matter-clay mineral interactions, so fewer soluble organics are available to complex Cu^{2+}. It is possible that the formation of soluble organic complexes increased the equilibrium concentration in Bertie sandy soil, especially at high pH. With increasing pH, the stability constant of metal-fulvic complexes increases due to the dissociation of functional –COOH and –OH groups in the fulvic acid molecules (Stevenson and Ardakani, 1972). Both soils treated with pig manure had more Cu in equilibrium solution than soils without applied pig manure at pH > 6.5 (Fig. 3.3). The Bertie soil solution was yellowish brown at high pH, and Stevenson (1991) reported that a large part of heavy metals present in soil solution and in surface waters appears to be linked in a yellowish compound with fulvic acid. In a soil leachate, Kiekens (1983) observed that 93% of soluble Cu was bound with fulvic acid. Stevenson and Fitch (1985) reported that the metal-organic ligand complex might remain soluble at pH values at which the uncomplexed metals would normally precipitate. LeClair (1984) reported that the Cu-

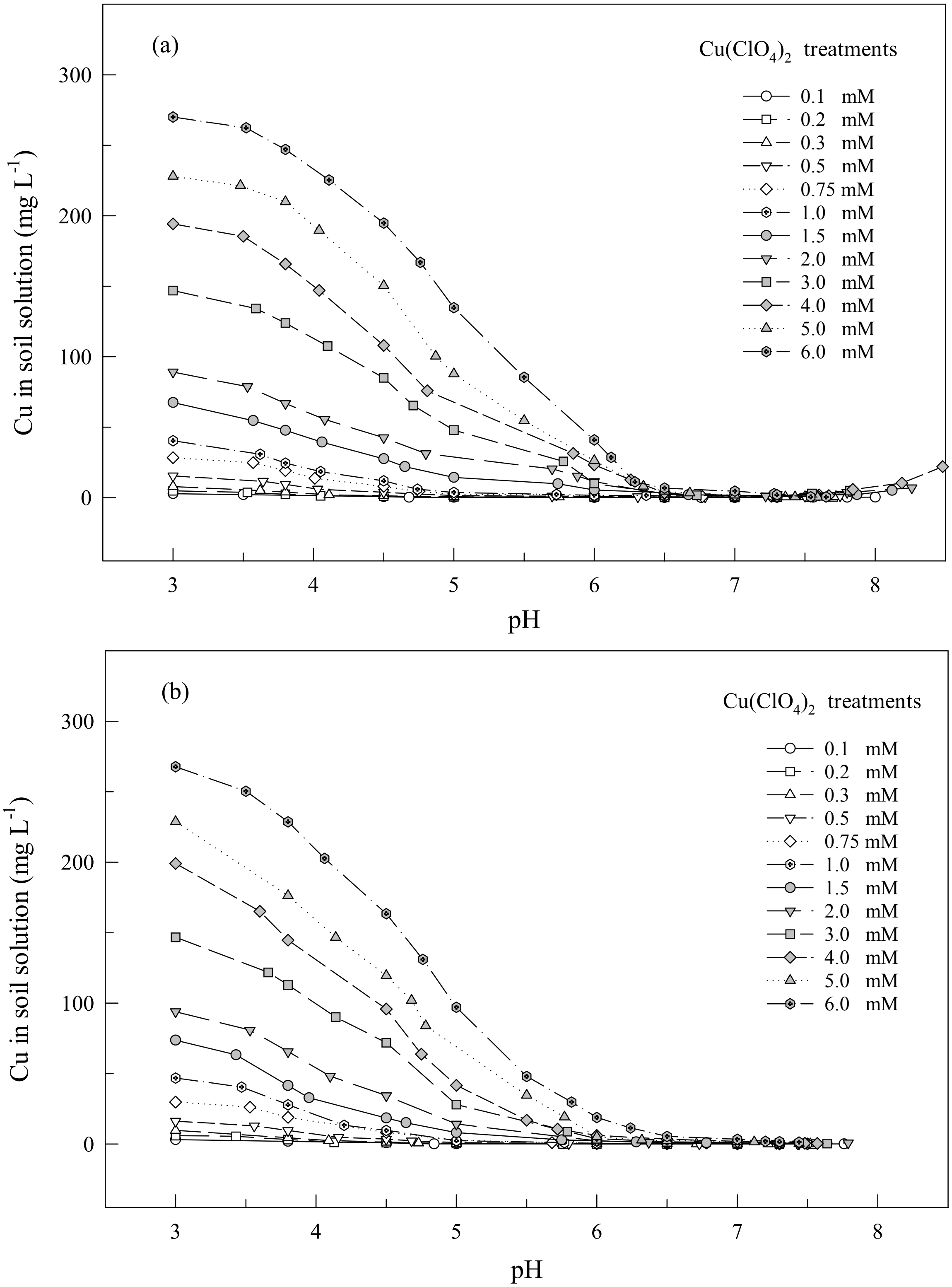

Fig. 3.1. Effect of pH on Cu sorption for Bertie sandy (a) and Starr-Dyke clay (b) soils.

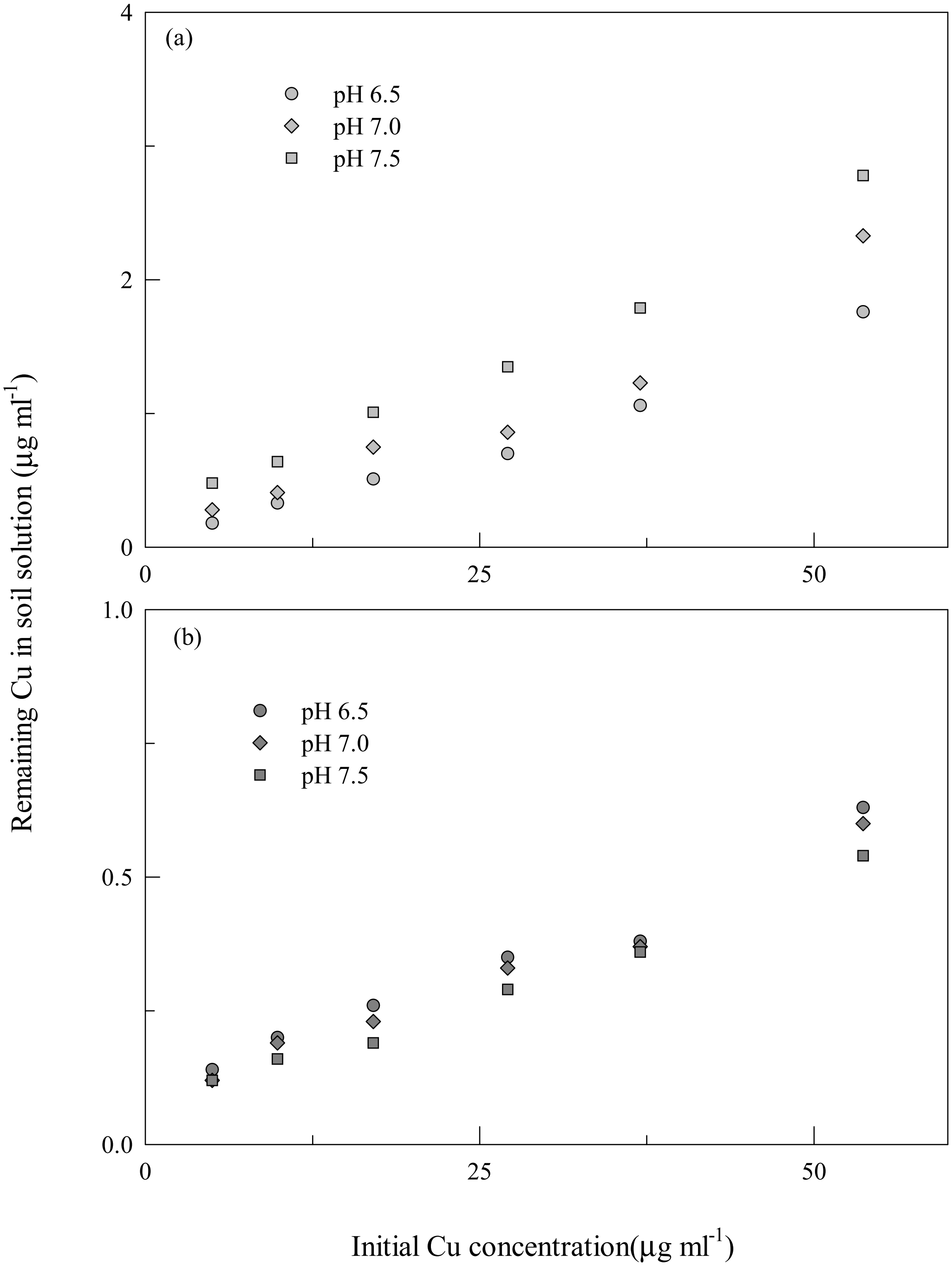

Fig. 3.2. Remaining Cu in soil solution at three different pH levels in Bertie sandy soil (a) and Starr-Dyke clay soil (b). Both soils had received pig manure annually for 16 years.

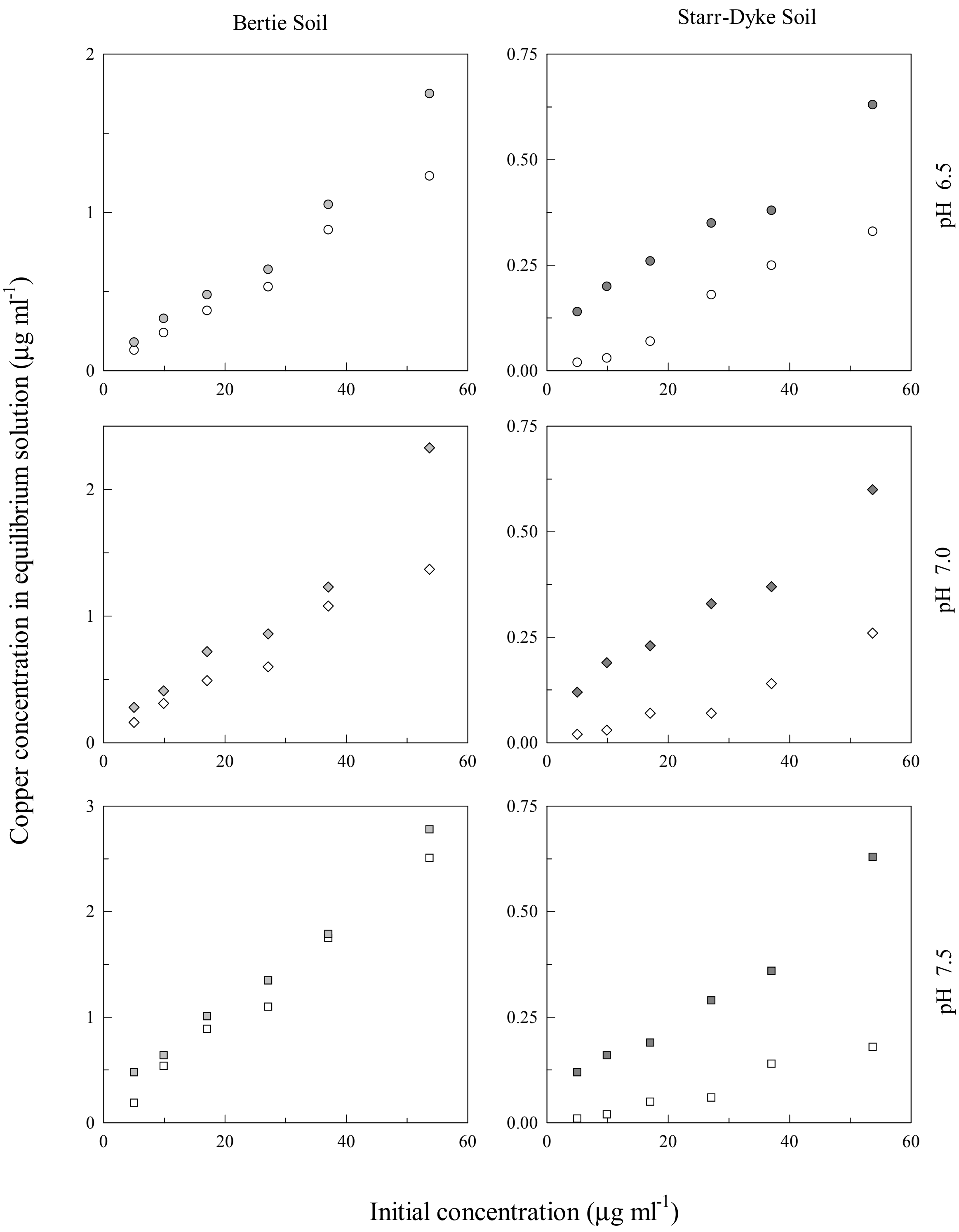

Fig. 3.3. Copper concentration in equlibrium solution of Bertie sandy, and Starr-Dyke clay soil at pH 6.5, 7.0, and 7.5. Soils were from long term field sites treated without (open symbols) or with (filled symbols; grey & dark grey) Cu-enriched pig manure.

fulvate complex was not sorbed by the soil surface, and much of the "labile" Cu was associated with organic matter. USEPA Regulations (1993) suggested that soil pH be maintained at pH 6.5 or higher when applying biosolids or animal manures to soil systems, but no guidelines were given regarding other soil characteristics. In light of these data the USEPA Regulations should be reconsidered. The chemical properties of soil and characteristics of the inorganic and organic fractions need to be better described before predictions about the long-term fate of heavy metals can be made.

Copper equilibrium concentration in soil at various pH levels is presented in Fig. 3.4. At pH 6.5, most Cu added was sorbed in both Bertie and Starr-Dyke soils. Although not measured, it is likely that Cu precipitated primarily with hydroxyl groups from NaOH that was added to the solution to adjust pH. Without soils, precipitates were not observed at pH below 5.5, while Cu started to precipitate at pH 6.5. When 5.0 mM of Cu was added to the solution, final Cu concentration after precipitation was 1 mM. LeClair (1985) reported that hydrolysis reactions occur which change the equilibrium speciation of Cu, such that $Cu(H_2O)_n^{2+}(aq)$ is no longer the dominant species in aqueous solution above pH 5.5. However, adsorption by soil surface and precipitation cannot be distinguished due to the mixed and heterogeneous nature of these kinetic processes.

Copper sorption was very dependent on pH (Figs. 3.5 and 3.6), but the increase in sorption occurred over a wider range of pH than often reported. For example, Davis (1977) reported that in the critical range, a change of about 1 pH unit resulted in abrupt increases in the percentage of metal sorbed, with increases from near 0 to nearly 100 % in hydrous metal oxide-aqueous systems. However, more complex systems such as soil-solution would be expected to have a wider pH range in which the percentage sorbed shows dramatic pH-dependence (Elliott, 1983). To obtain less than 1 mg Cu L^{-1} in soil solution when 0.1, 0.2, 0.3, and 0.5 mM of Cu were added to Bertie soil, pH values should be raised above 4.24, 4.64, 4.71, and 5.77, respectively. When 0.75 mM of Cu was added to Bertie soil, concentrations of soil solution were less than 1 mg Cu L^{-1} in the pH range between 6.60 and 7.19. Kuo and Baker (1980) also found that Cu sorption by some acid soils reached a maximum near pH 6. However, regardless of pH, no Bertie soil

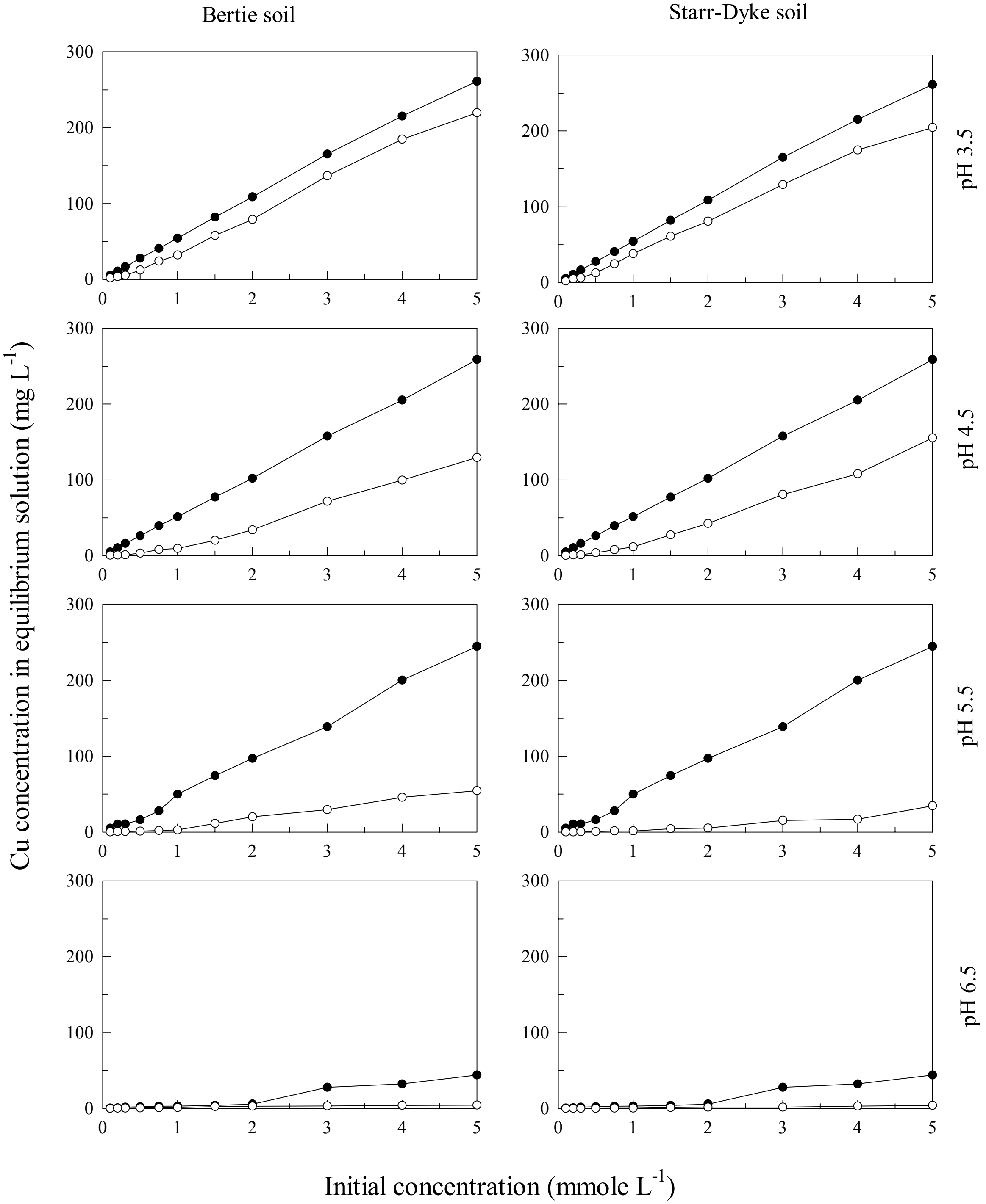

Fig. 3.4. Difference between equilibrium soil Cu concentration (○) and initial concentration (•) at varying pH values. Initial concentration was measured after pH was adjusted.

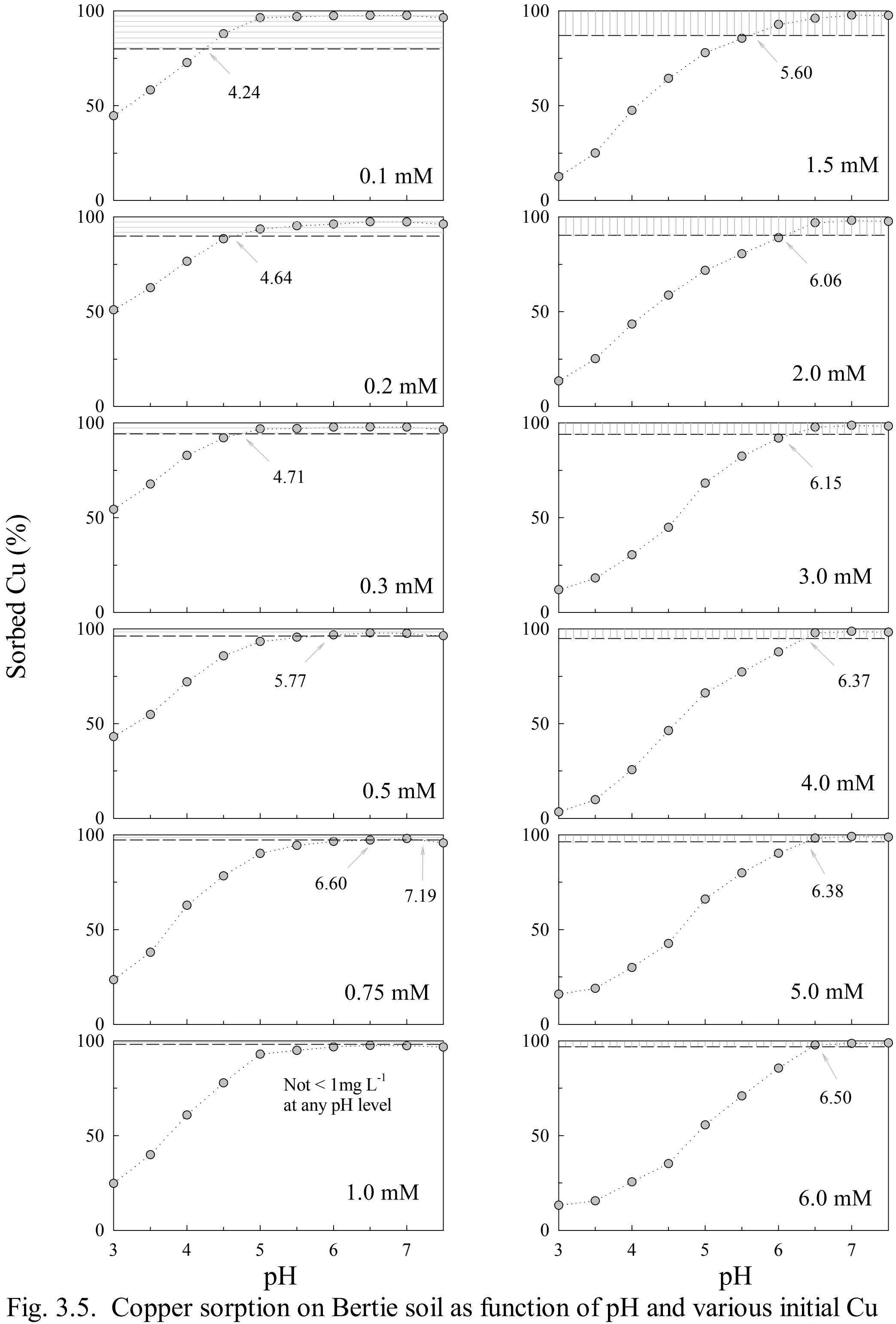

Fig. 3.5. Copper sorption on Bertie soil as function of pH and various initial Cu treatments. Area of horizontal lines represents concentration < 1 mg L^{-1} in solution, and area of vertical lines represents concentration < 10 mg L^{-1}.

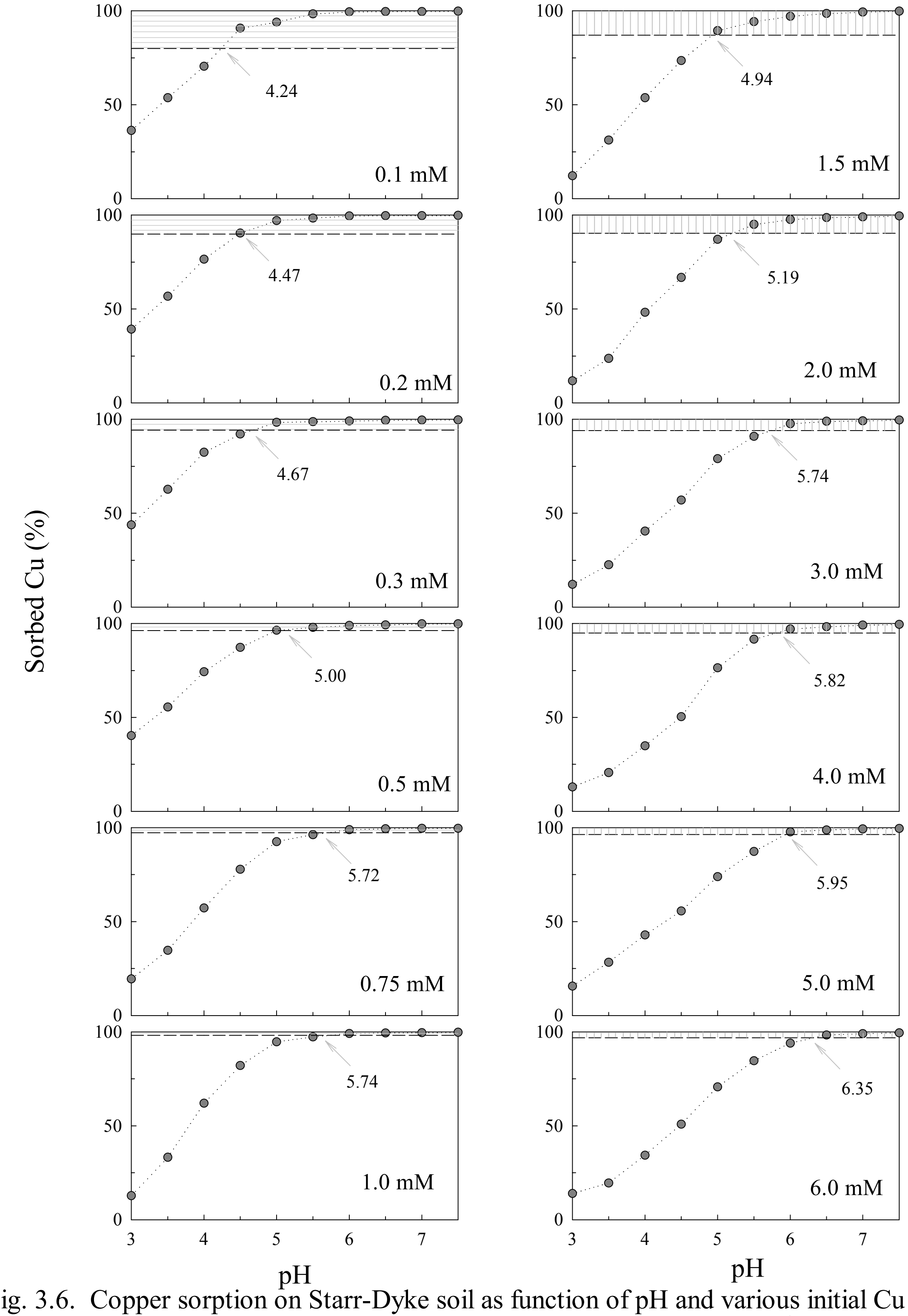

Fig. 3.6. Copper sorption on Starr-Dyke soil as function of pH and various initial Cu treatments. Area of horizontal lines represents concentration < 1 mg L^{-1} in solution, and area of vertical lines represents concentration < 10 mg L^{-1}.

solution had Cu concentration < 1 mg Cu L^{-1} when 1.0 mM of Cu was added. Similar responses were observed with Starr-Dyke clay soil though at slightly lower pH values than for the Bertie sandy soil. This same interpretation applies when greater concentrations of Cu were added to the soil systems.

Adjusting the pH of Bertie and Starr-Dyke soils had a major impact on their ability to retain Cu (Fig. 3.7). At the higher pHs, Cu sorption was similar between the two soils, but as pH decreased Cu sorption by Bertie soil was less than that of Starr-Dyke soil. Kishk and Hassan (1973) concluded that reduced sorption at lower pH values is due to the competition from H^+ and other cations for adsorption sites. As pH increases, the hydrogen ion activity decreases and pH-dependent negative charge on mineral surfaces increases, thus increasing sorption. However, Farrah et al. (1976, 1980) proposed that the pH dependence of Cu resulted from a surface-induced precipitation of a polynuclear complex, $(CuOH^+)_n$. Both mechanisms certainly cannot be determined by macroscopic experiments of this nature (Sposito, 1981; 1984). In these studies Cu sorption exhibited adsorbate characteristics at lower pH levels, while precipitation effects were observed at higher pH levels and at higher pH levels differences of Cu sorption between Bertie sandy soil and Starr-Dyke clay soil were less pronounced.

In most cases, simple L-type curves were observed in Bertie and Starr-Dyke soils (Figs. 3.8 and 3.9; Appendix, Figs. E.1. and E.2.). More complex isotherms were observed above pH 5.5 in Bertie soil. With increases of solution concentration greater than 0.026 μmole Cu ml^{-1} at pH 6.5, and 0.018 μmole Cu ml^{-1} at pH 7.0, additional Cu was sorbed by Bertie soil as a second layer. It is likely that soluble organic matter is the primary factor for explaining differences in sorption curves between pH levels above and below 5.5. LeClair (1985) reported the same features of Cu sorption in clay, silt, and sandy loam soils at pH 5.5. He described the isotherms as sigmoid shaped curves. When soluble organic matter was removed from the soils, L-curve isotherms were observed for Cu. His interpretation of this phenomenon was that soluble ligands in aqueous phase were effectively competing with the surface functional groups for the metal cation until the complexation capacity of that component was exceeded and at which point the slope

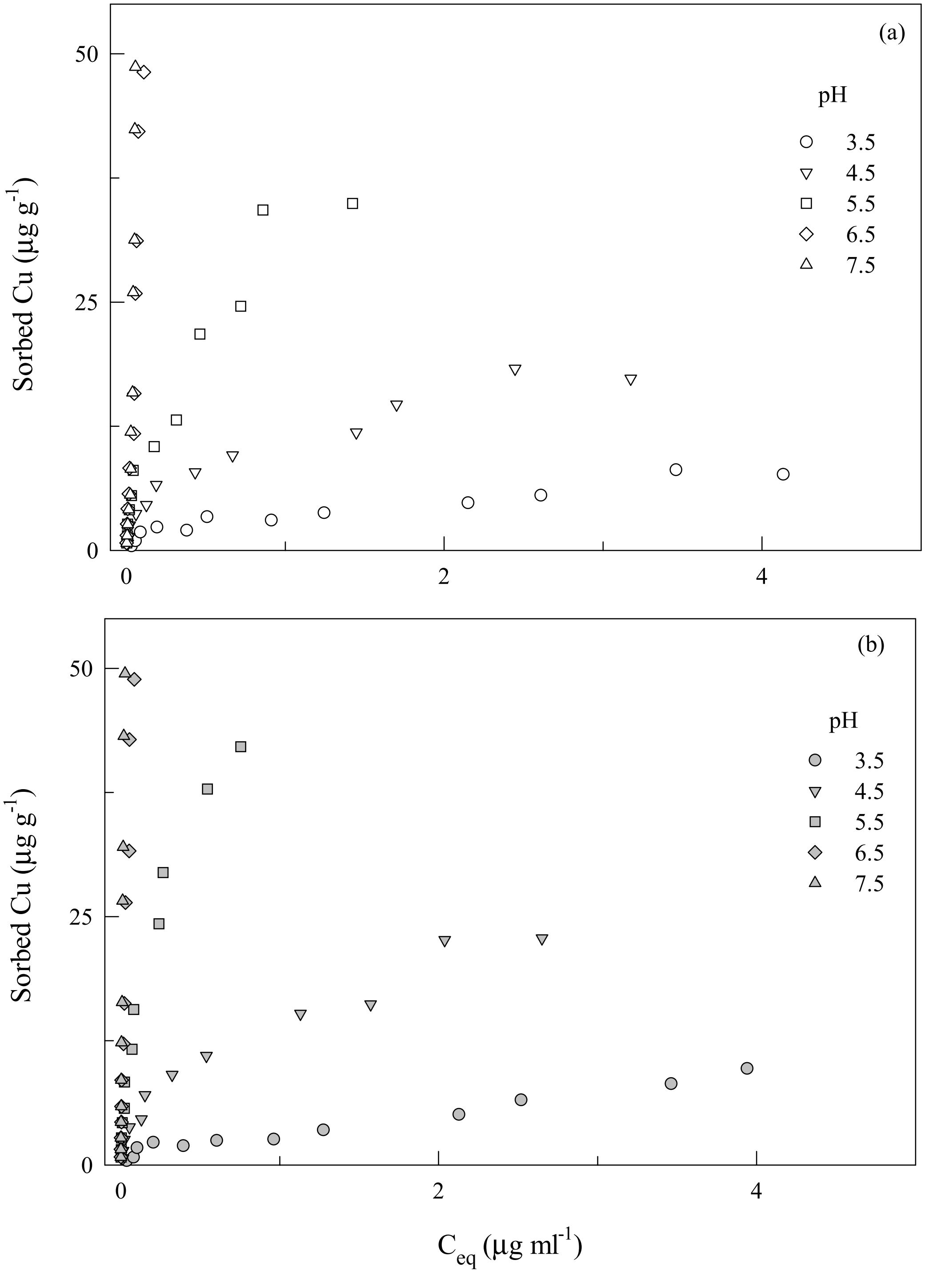

Fig.3.7. Adsorption isotherms of Cu in Bertie sandy (a) and Starr-Dyke clay (b) soils at six different pH levels.

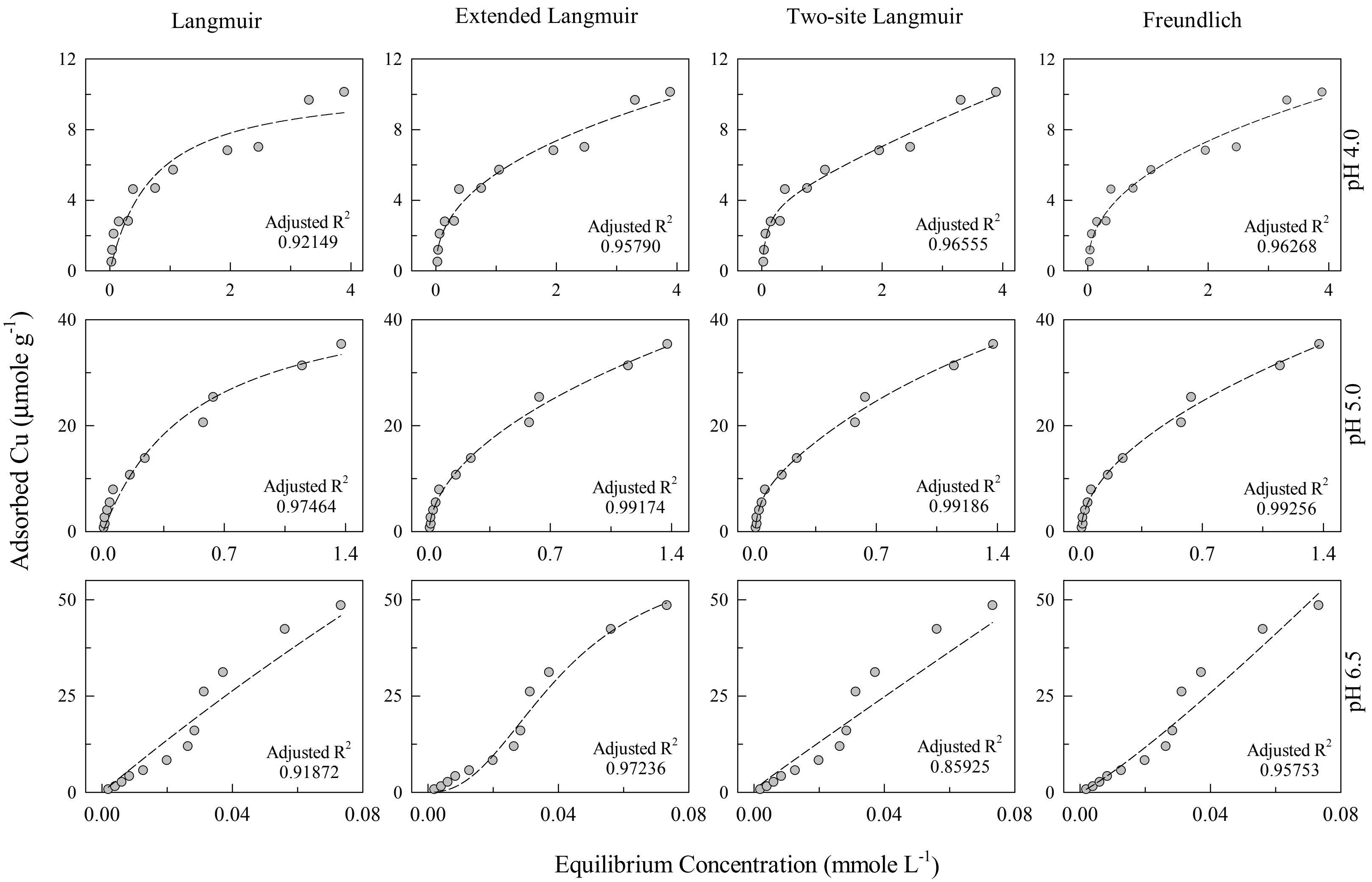

Fig. 3.8. Comparison of four different sorption isotherm equations (Langmuir, Extended Langmuir, Two-site Langmuir, and Freundlich) for Cu adsorbed by Bertie soil at pH 4.0, pH 5.0, and pH 6.5. Initial concentration of $Cu(ClO_4)_2$ was from 0.1 mM to 6.0 mM.

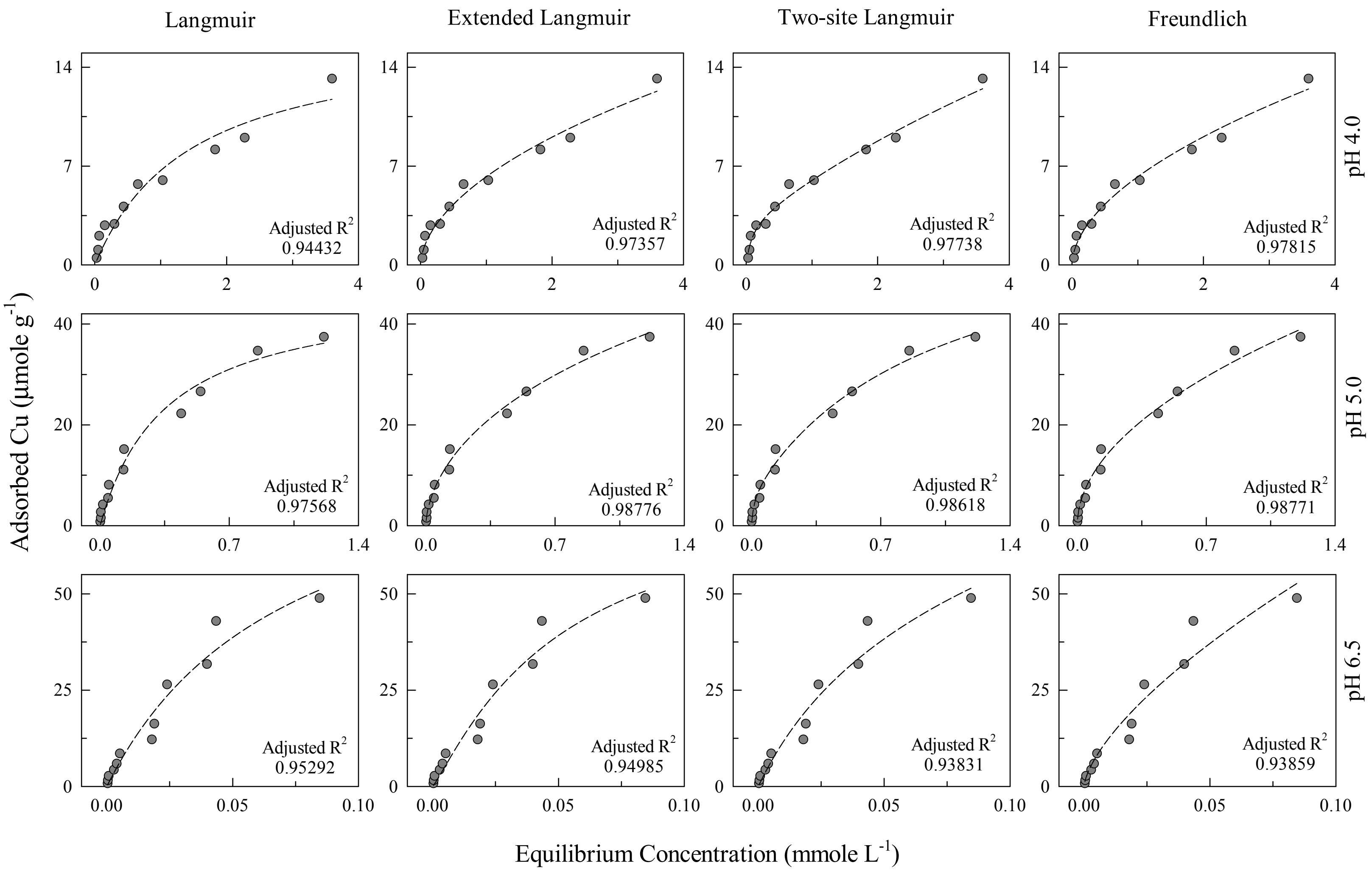

Fig. 3.9. Comparison of four different sorption isotherm equations (Langmuir, Extended Langmuir, Two-site Langmuir, and Freundlich) for Cu adsorbed by Starr-Dyke soil at pH 4.0, pH 5.0, and pH 6.5. Initial concentration of $Cu(ClO_4)_2$ was from 0.1 mM to 6.0 mM.

of the isotherm increased. Isotherms for Starr-Dyke soil began to display sigmoid character at pH 6.5 and higher, though this shape was less distinguishable than with the Bertie soil. Takahashi and Imai (1983) also presented adsorption isotherms for Cu at pH 4 through 7. Their adsorption curve at pH 6 showed an inflection point at concentration of 0.11 μmole ml^{-1}, but L-type curves were observed at pH values below 5. In both soils the best fit across all models (Langmuir, extended Langmuir, two-site Langmuir, and Freundlich) was observed at pH 5.0. The extended Langmuir equation can fit a sigmoid-type curve to the data, which is suitable for Bertie soil at pH 6.5.

Copper sorption isotherm parameters with varying pH and ranges from 0.1 mM to 6.0 mM of initial concentrations in Bertie and Starr-Dyke soils are presented in Table 3.2. Though the parameter values are possibly imprecise due to dependency of one parameter on another, important information can be obtained from the relative values of the calculated adsorption capacities. In most cases, Cu adsorption was successfully explained by Freundlich equations across the range of pH, while the Langmuir equation fit better below pH 5.5. In contrast, the extended Langmuir equation was more suitable at higher pH levels. The "b" term of the Langmuir was much less affected by differences in pH than by varying ionic strength and composition of the background solution (Table 2.6). With the Langmuir equation, increasing pH resulted in increased "b" and "Γ_m". The "Γ_m" values of the extended Langmuir equation were less affected by pH. With the Freundlich equation, "k" values were increased with increasing pH while "n" values generally decreased. It was not possible to determine adsorption maxima for Bertie soil at pH > 5.5 because the adsorption isotherm curve did not follow an L-type curve. Others have pointed out that using the Langmuir equation to describe the soil systems is not appropriate because the equation cannot differentiate between adsorption and secondary precipitation (Veith and Sposito, 1977).

Sorption isotherm patterns were similar for both soils when they were treated with pig manure at pH 6.5 (Fig. 3.10). The Bertie soil that received pig manure sorbed less Cu than soil without pig manure across all equilibrium concentrations. The Starr-Dyke soil followed a similar pattern until 2.0 mM of initial Cu concentration was added to the soil,

Table 3.2. Comparison of different Cu sorption isotherm parameters for Bertie and Starr-Dyke soils at various pH levels.

Sorption Isotherms†

A. Bertie soil		--- Langmuir ---		--- Freundlich ---		--------- Two-site Langmuir ---------				--- Extended Langmuir ---		
		b	Γ_m	k	n	b_1	Γ_{m1}	b_2	Γ_{m2}	b	Γ_m	d ‡
pH	4.0	0.022^{***}	675^{***}	59.5^{***}	2.35^{***}	0.19^{NS}	243^{*}	0.01^{NS}	3150^{NS}	0.007^{NS}	8417^{NS}	0.557^{**}
	4.5	0.028^{***}	1249^{***}	122.6^{***}	2.34^{***}	0.32^{NS}	380^{***}	0.01^{NS}	2121^{*}	0.019^{NS}	5994^{NS}	0.524^{***}
	5.0	0.030^{***}	2949^{***}	212.0^{***}	1.90^{***}	0.56^{NS}	486^{**}	0.01^{NS}	4576^{**}	0.009^{NS}	24318^{NS}	0.447^{***}
	5.5	0.041^{NS}	12448^{NS}	497.9^{***}	1.13^{***}	0.04^{NS}	924^{NS}	0.04^{NS}	11518^{NS}	0.074^{**}	3529^{***}	-1.058^{NS}
	6.5	0.027^{NS}	26327^{NS}	564.0^{***}	0.87^{***}	21.23^{NS}	68^{NS}	0.01^{NS}	115424^{NS}	0.104^{***}	3951^{***}	-1.336^{*}
	7.0	0.012^{NS}	90180^{NS}	870.0^{***}	0.77^{***}	0.48^{NS}	71^{NS}	0.01^{NS}	117873^{NS}	0.025^{*}	3152^{***}	-12.280^{***}

B. Starr-Dyke soil		--- Langmuir ---		--- Freundlich ---		--------- Two-site Langmuir ---------				--- Extended Langmuir ---		
		b	Γ_m	k	n	b_1	Γ_{m1}	b_2	Γ_{m2}	b	Γ_m	d
pH	4.0	0.011^{***}	1050^{***}	42.4^{***}	1.86^{***}	0.17^{NS}	206^{**}	0.01^{NS}	3031^{NS}	0.004^{NS}	10360^{NS}	0.441^{***}
	4.5	0.024^{***}	1716^{***}	125.1^{***}	2.07^{***}	0.21^{NS}	492^{*}	0.01^{NS}	4153^{NS}	0.012^{NS}	9963^{NS}	0.478^{***}
	5.0	0.044^{***}	2978^{***}	276.9^{***}	1.98^{***}	1.16^{NS}	403^{*}	0.02^{NS}	3712^{***}	0.027^{NS}	9510^{NS}	0.415^{***}
	5.5	0.164^{***}	4137^{***}	751.8^{***}	1.99^{***}	0.15^{NS}	1307^{NS}	0.02^{NS}	2824^{NS}	0.161^{***}	3943^{***}	-0.073^{NS}
	6.5	0.217^{**}	6023^{***}	1089.9^{***}	1.50^{***}	0.37^{NS}	2686^{NS}	0.06^{NS}	5778^{NS}	0.261^{*}	5055^{**}	-0.136^{NS}
	7.0	0.493^{**}	7400^{***}	2363.2^{***}	1.34^{***}	0.50^{NS}	3715^{NS}	0.49^{NS}	3685^{NS}	1.685^{NS}	4105^{***}	-0.596^{NS}

† Treatment concentrations for adsorption isotherms ranged from 0.1 mM to 6.0 mM of $Cu(ClO_4)_2$.

‡ Units of parameters are as follows: b, ml μg^{-1}; Γ_m, $\mu g\ g^{-1}$; k, ml g^{-1}, and d, n are dimensionless.

*** Significant at the 0.01 level, ** Significant at the 0.05 level, * Significant at the 0.1 level of probability.

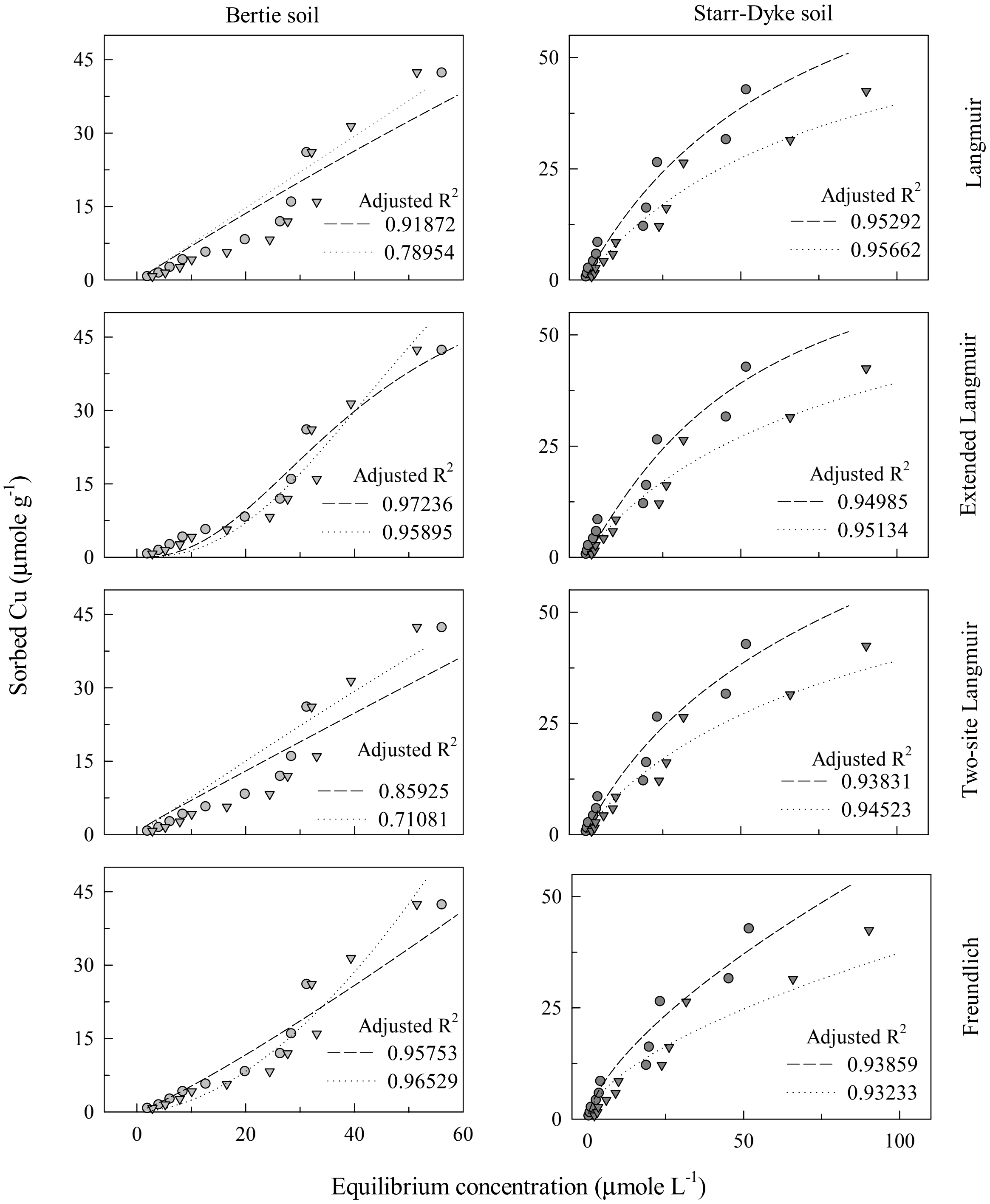

Fig. 3.10. Comparison of four different adsorption isotherm equations for Cu adsorbed by Bertie and Starr-Dyke soils treated without (○ , ● ; ———) or with (▽ , ▼ ; ········) Cu-enriched pig manure at pH 6.5. The light and dark colored symbols represent Bertie and Starr-Dyke soils, respectively.

but when initial concentration was greater than 2.0 mM, pig manure-treated soil had a much greater reduction in Cu sorption than the control soil. For Bertie soil with or without pig manure, the extended Langmuir and Freundlich equations fit well with high correlation coefficients, while the Langmuir equation fit results for Starr-Dyke soils. The adsorption isotherm parameters for both soils treated with Cu-rich pig manure were compared in Table 3.3. Most parameters of model equations except Freundlich were not significant for the Bertie soil. Pig manure application reduced the adsorption maximum in Starr-Dyke soil.

Numerous investigators have reported that Cu sorption patterns were L-type (McLaren and Crawford, 1973b; Harter, 1979; McKenzie, 1980; Dhillon et al., 1981; Petruzzelli et al., 1985) or linear (Jarvis, 1981; McLaren et al., 1981) depending on the initial metal concentration. Copper adsorption isotherms had different shaped curves regardless of whether pH was held constant or was not controlled (Fig. 3.11). Without pH control, adsorption isotherms had a greater degree of plateau (L-type) than when pH was controlled. As initial Cu concentration increased, soil pH decreased (Appendix, Table C.1), and had less sorption when pH was not controlled.

Soil individual components or soil minerals (McLaren et al, 1981; Gerritse and van Driel, 1984; Backes, 1995), soil separates following removal of soil fractions (Zachara et al., 1992; Cavallaro and McBride, 1984; Bibak, 1997), or sequential extraction procedures (Miller et al., 1986; Narwal e al., 1999; McLaren and Crawford, 1973a) have been used to evaluate the effects of soil components on metals sorption. In this study, Cu adsorption of Bertie sandy and Starr-Dyke clay soils was compared with kaolinite (KGa-2; Fig. 3.12). Whole soils had much greater adsorption capacity than kaolinite mineral because soil contains organic matter, amorphous oxides of Al-, Fe-, and Mn oxides, and other clay minerals. Both soils treated with $NH_2OH{\cdot}HCl$ had greater sorption capacity than with any other treatment (Fig. 3.13). Organic matter and free MnO_2 have been reported as main factors for Cu adsorption (McLaren and Crawford, 1973a; Ma and Rao, 1997). However, those results were derived using the sequential extraction technique. Bibak (1997) observed a negligible effect on Cu sorption after

Table 3.3. Copper adsorption isotherm parameters of Bertie and Starr-Dyke soils at pH 6.5 and treated without or with Cu-enriched pig manure (PM).

Sorption Isotherms†	--- Langmuir ---		--- Freundlich ---		--- Two-site Langmuir ---				--- Extended Langmuir ---		
‡	b	Γ_m	k	n	b_1	Γ_{m1}	b_2	Γ_{m2}	b	Γ_m	d
Soils											
Bertie	0.027^{NS}	26327^{NS}	564.0^{***}	0.87^{***}	21.23^{NS}	68^{NS}	0.01^{NS}	115424^{NS}	0.104^{***}	3951^{***}	-1.336^{*}
Bertie+PM	0.002^{NS}	321401^{NS}	344.7^{***}	0.56^{***}	0.02^{NS}	19161^{NS}	0.02^{NS}	19161^{NS}	0.038^{NS}	7062^{NS}	-1.429^{NS}
Starr-Dyke	0.217^{**}	6023^{***}	1089.9^{***}	1.50^{***}	0.37^{NS}	2686^{NS}	0.06^{NS}	5778^{NS}	0.261^{*}	5055^{**}	-0.136^{NS}
Starr-Dyke+PM	0.200^{***}	4485^{***}	788.5^{***}	1.68^{***}	1.44^{NS}	282^{NS}	0.15^{NS}	4539^{NS}	0.185^{*}	4877^{**}	0.064^{NS}

† Treatment concentrations for adsorption isotherms ranged from 0.1 mM to 6.0 mM of $Cu(ClO_4)_2$.

‡ Units of parameters are as follows: b, ml μg^{-1}; Γ_m, $\mu g\ g^{-1}$; k, ml g^{-1}, and d, n are dimensionless.

*** Significant at the 0.01 level, ** Significant at the 0.05 level, * Significant at the 0.1 level of probability.

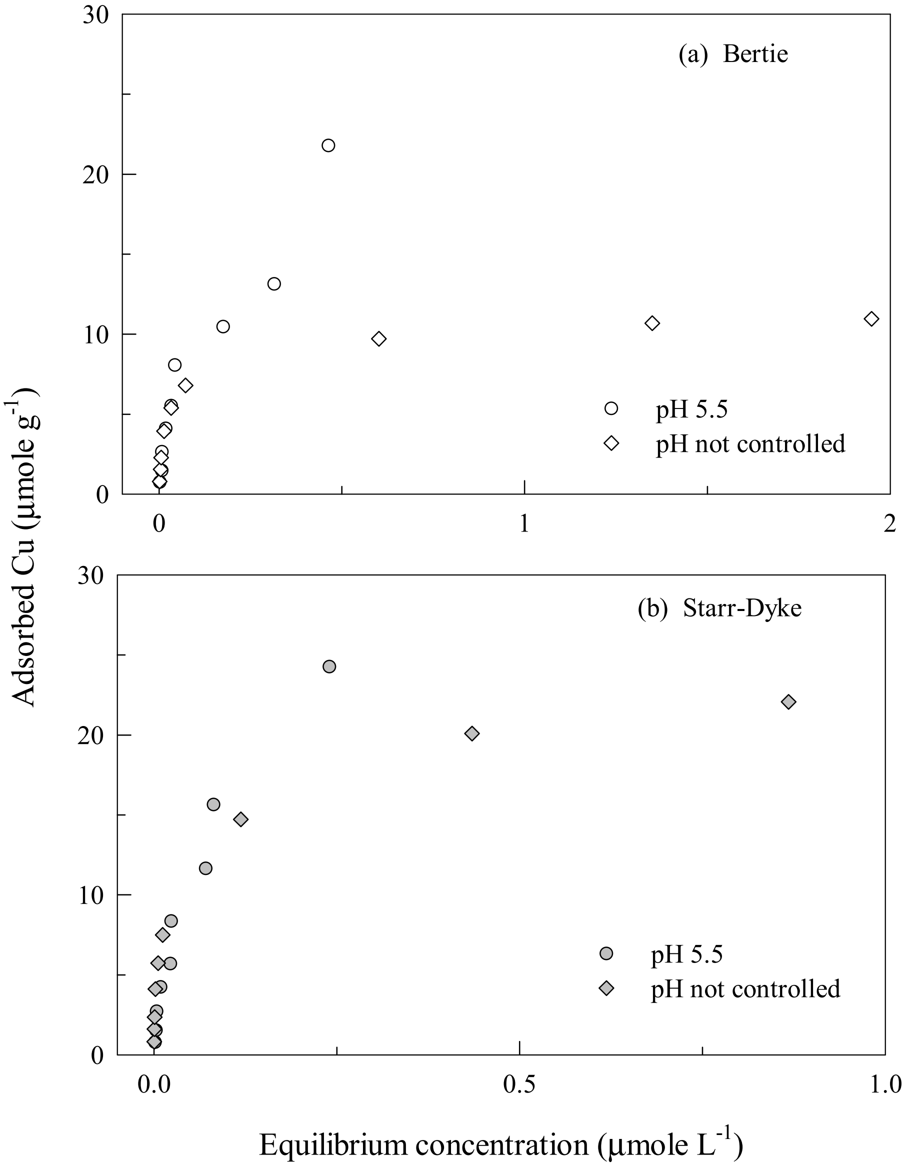

Fig. 3.11. Adsorption isotherms of Cu adsorbed by Bertie (a; open) and Starr-Dyke (b; filled) soils at pH 5.5 (○ , ●) or with pH not controlled (◇ , ◆).

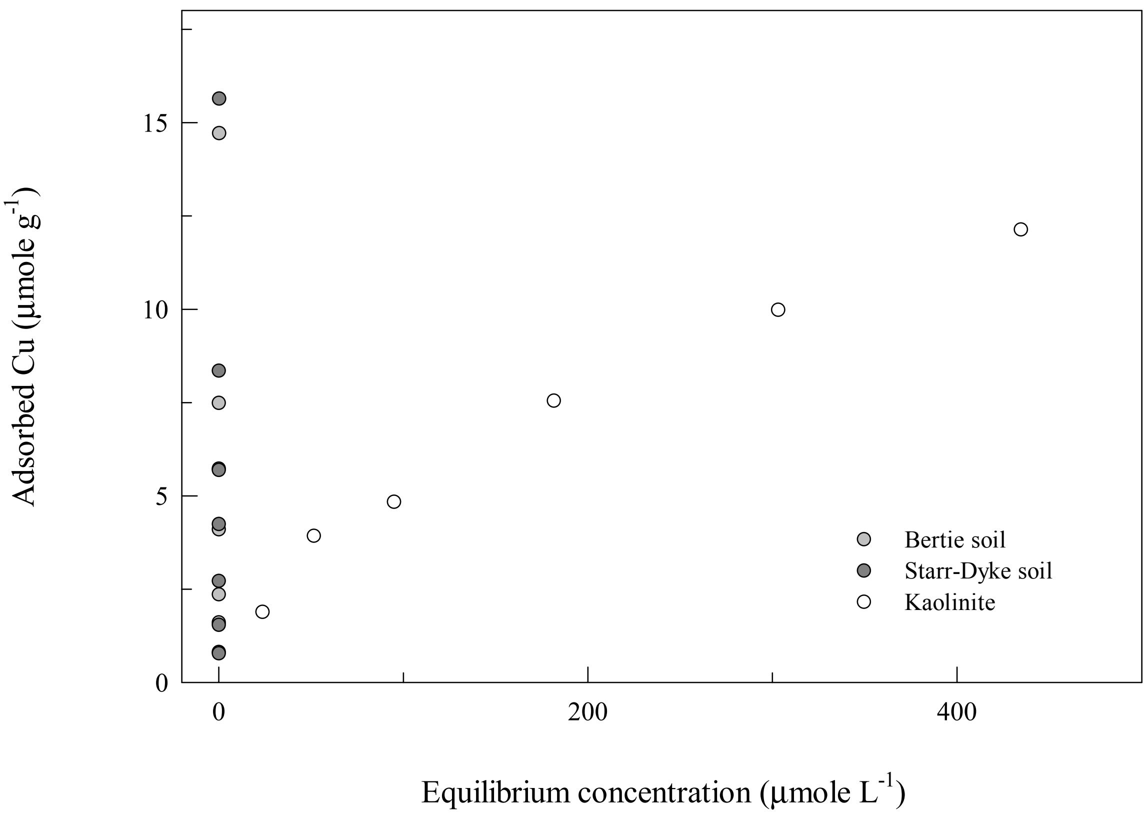

Fig. 3.12. Adsorption isotherms for Cu adsorbed by Bertie soil, Starr-Dyke soil, and kaolinite at pH 5.5.

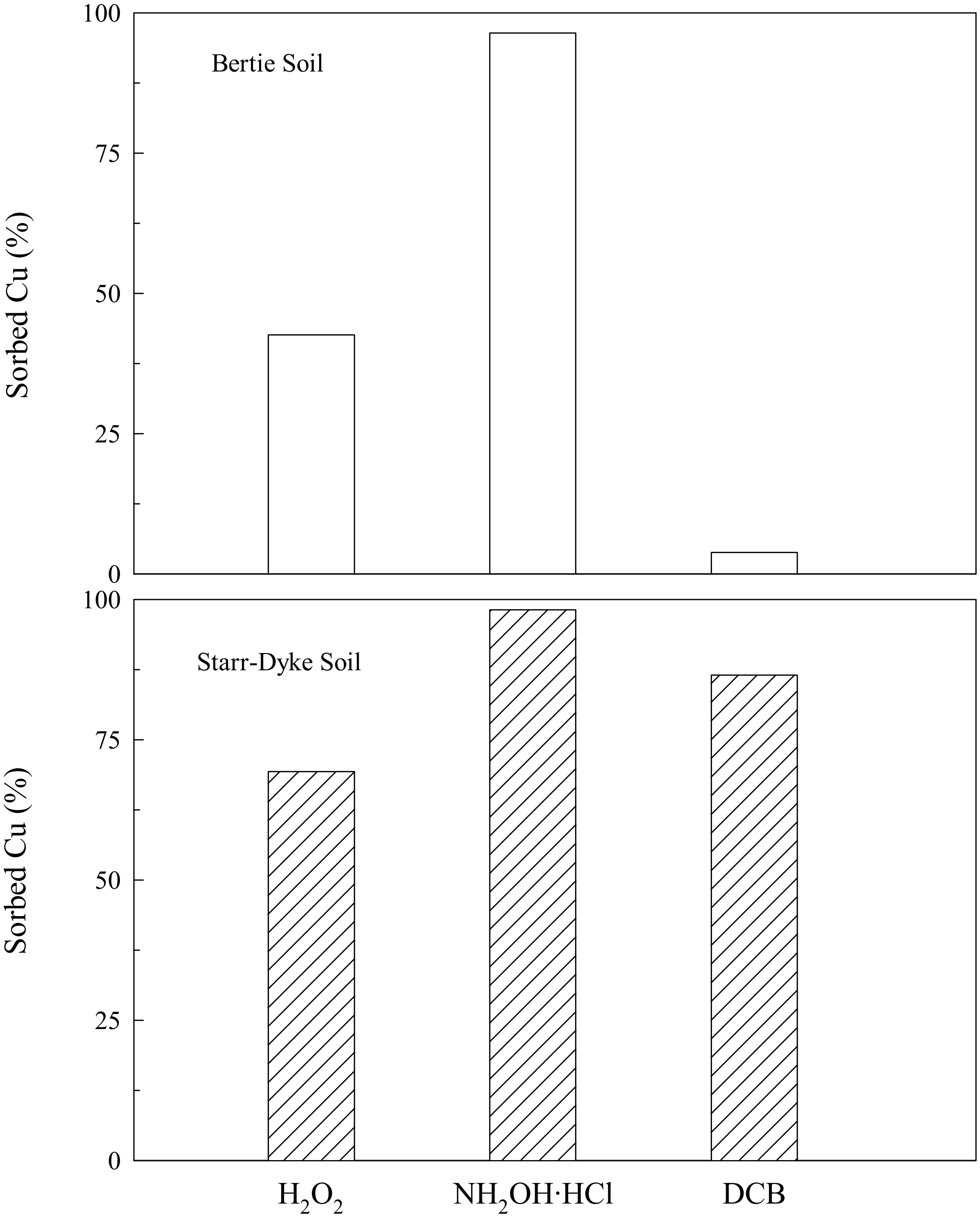

Fig. 3.13. Adsorption of Cu in Bertie and Starr-Dyke soil separates at pH 5.5. Soil separates were treated with H_2O_2, $NH_2OH·HCl$, and DCB.

removal of Mn oxides with $NH_2OH{\cdot}HCl$ treatment and suggested that this was due to their low concentration in his soils. However, Cu sorption also was less affected by $NH_2OH{\cdot}HCl$ treatment in Starr-Dyke soil, which has large amounts of MnO_2 (3900 mg L^{-1}; Table 2.1). In sequential extraction procedure, acid oxalate has been used for extraction of free oxides, which was correlated significantly with free iron suggesting that this constituent is the dominant factor affecting this fraction (McLaren and Crawford, 1973a). However, oxalate-extracted Cu is related to MnO_2 by general agreement since the soil oxide fraction is described by; Cu-Ox (μg g^{-1}) = 0.93 + 0.62%Fe + 24.8%Mn (Le Reiche and Weir, 1963; Crawford, 1969). Therefore, they concluded that the MnO_2 has a significant effect on Cu sorption. Copper sorption was highly depressed in the DCB-treated Bertie soil, while sorption in Starr-Dyke soil samples treated with DCB were less affected than those of Bertie soil. However, the large amount of DCB required removing Fe_2O_3 in Starr-Dyke soil resulted in increased pH (9.72) and as a consequence masked the effect of Fe_2O_3 removal. The sorption isotherms of soil samples treated with $NH_2OH{\cdot}HCl$ had L-type curve characteristics (Fig. 3.14). However, Cu sorption isotherms of H_2O_2-, and DCB-treated sample were linear. These chemical treatments could change the percentage of clay and surface area but with less destruction of clay minerals (Zelazny and Quresh, 1973).

CONCLUSIONS

Copper is bound tightly with soil materials, so added Cu primarily sorbed at low concentrations regardless of pH, but at high concentrations Cu sorption was strongly related to solution pH. Increases in pH resulted in greater Cu sorption due to the pH-dependent negative charges and precipitation. Also, the addition of OH^- causes successive displacement of water molecules from the hydration sheath and stepwise formation of Cu complexes. The USEPA suggested that soil pH be maintained above 6.5 where high concentrations of metals are land applied because of the impact of soil pH on metal sorption. However, pig manure applications to Bertie soil resulted in greater Cu in soil solution than in control (no manure) soil at pH > 6.5 due to soluble organic matter.

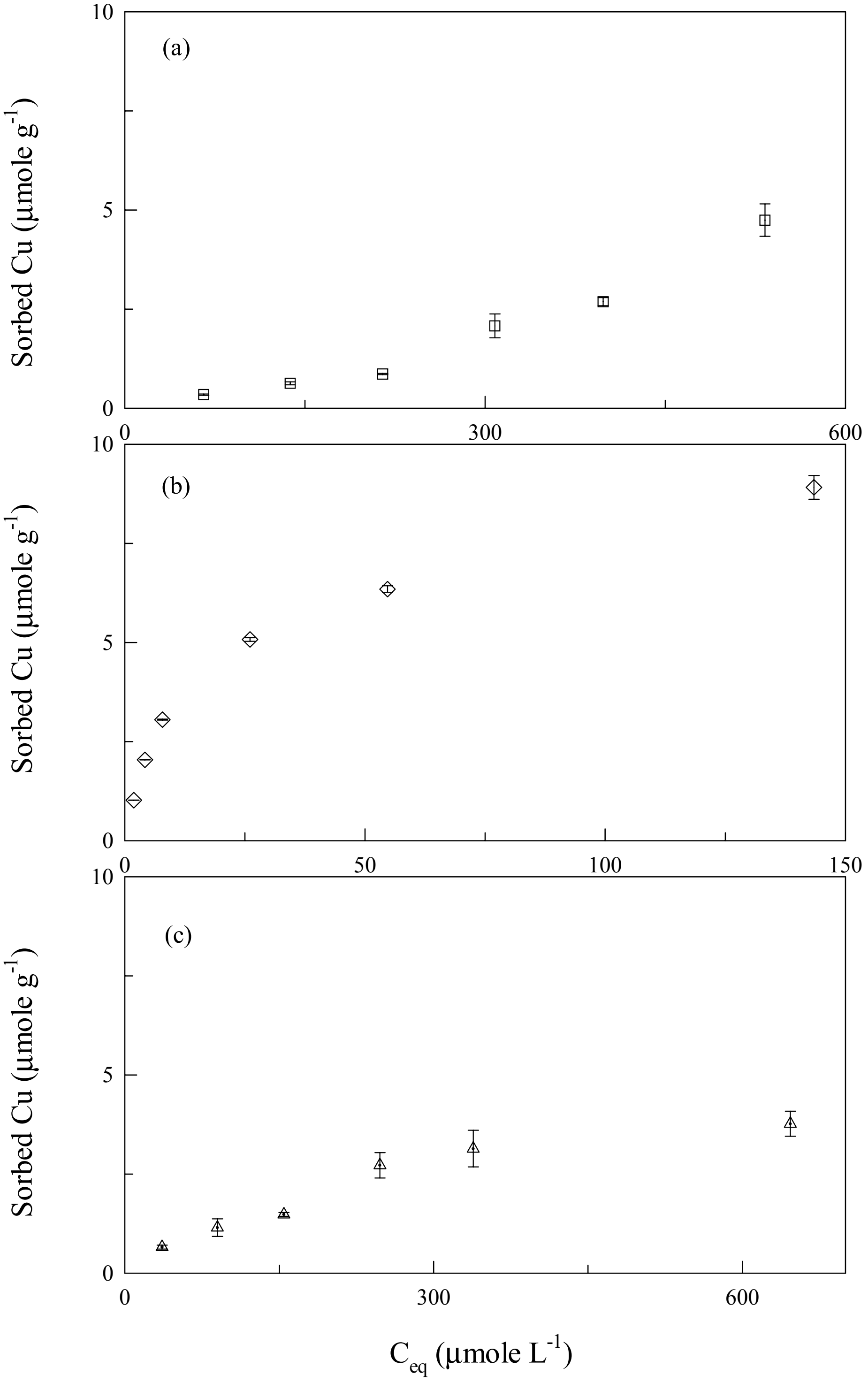

Fig. 3.14. Adsorption isotherms of Cu in Bertie soil when treated with a) H_2O_2, b) $NH_2OH \cdot HCl$, and c) DCB (Dithinite-Citrate-Bicarbonate) at pH 5.5.

The Bertie soil solution was yellowish brown at high pH, and Stevenson (1991) reported that a large part of heavy metals present in soil solution and in surface waters appears to be linked in a yellowish compound with fulvic acid. In the laboratory, pH was adjusted with NaOH, which might increase the solubility of alkaline soluble organic matter such as fulvic and humic acids.

Copper sorption was dependent on pH. To obtain less than 1 mg L^{-1} in soil solution when 0.1 mM, 0.2 mM, 0.3 mM, and 0.5 mM of Cu were added to Bertie soil, pH values should be raised above 4.24, 4.64, 4.71, and 5.77. When 0.75 mM of Cu were added to Bertie soil, concentrations of soil solution were less than 1 mg Cu L^{-1} in the pH range between 6.60 and 7.19. Regardless of pH, no Bertie soil solution had Cu concentration < 1 mg Cu L^{-1} when 1.0 mM of Cu was added. However, in Starr-Dyke soil the same solution concentrations can be attained at lower pH levels. Sigmoid shaped curves were observed in the Bertie soil at the pH > 5.5 and at pH > 6.5 in the Starr-Dyke soil. These curves could be due to soluble organic matter, precipitation with inorganic ions or both. Therefore, determination of adsorption maxima for Bertie soil at pH > 5.5 was not possible because the adsorption curves did not follow the L-type. In both soils the best fit across all models (Langmuir, extended Langmuir, two-site Langmuir, and Freundlich) was observed at pH 5.0. This research found that soils are not a factor for fitting model equations but that soil conditions such as pH have strong influence on the goodness of fit of the models. With increasing concentration, Cu sorption was more linear when pH was maintained at 5.5 than when pH was not controlled. When pH was not controlled, increased Cu concentration reduced solution pH, resulting in decreased Cu sorption. This is important to note because of how results are affected by pH management in experiments. The free MnO_2 effect on Cu sorption had a contradictory result between sequential extraction procedure and soil separates after removal of free Mn oxides with $NH_2OH{\cdot}HCl$ treatment. Further research needs to be conducted to elucidate the effects of chemical reagents on soil components.

REFERENCES

Alloway, B. 1990. Cadmium. p. 100-124. *In* B. J. Alloway (ed.) Heavy metals in soils. Blackie, Glasgow.

Anderson, P.R., and T.H. Christensen. 1988. Distribution coefficients of Cd, Co, Ni, and Zn in soils. J. Soil Sci. 39: 15-22.

Backes, C.A., R.G. McLaren, A.W. Rate, and R.S. Swift. 1995. Kinetics of cadmium and cobalt desorption from iron and manganese oxides. Soil Sci. Soc. Am. J. 59: 778-785.

Baldwin, A., T.A. Brown, P.H.T. Beckett, and G.E.P. Elliott. 1983. The forms of combination of Cu and Zn in digested sewage sludge. Water Res. 17: 1935-1944.

Bell, P.F., B.R. James, and R.L. Chaney. 1991. Heavy metal extractability in long-term sewage sludge and metal salt-amended soils. J. Environ. Qual. 20: 481-486.

Bibak, A. 1997. Copper retention by Danish Spodosols in relation to contents of organic matter and aluminum, iron, and manganese oxides. Commun. Soil Sci. Plant Anal. 28: 939-948.

Bidwell, A.M., and R.H. Dowdy. 1987. Cadmium and zinc availability to corn following termination of sewage sludge applications. J. Environ. Qual. 16: 438-442.

Bingham, F.T., A.L. Page, and J.R. Sims. 1964. Retention of Cu and Zn by H-montmorillonite. Soil Sci. Soc. Am. Proc. 28: 351-354.

Cabrera, F., E. Diaz, and L. Madrid. 1989. Effect of using urban composts as manure on soil contents of some nutrients and heavy metals. J. Sci. Food Agric. 47: 159-169.

Campbell, D.J., and P.H.T. Beckett. 1988. The soil solution in a soil treated with digested sewage sludge. J. Soil Sci. 39: 283-298.

Cavallaro, N., and M.B. McBride. 1984. Zinc and copper sorption and fixation by an acid soil clay: Effect of selective dissolutions. Soil Sci. Soc. Am. J. 48: 1050-1054.

Chaney, R. L., and J. A. Ryan. 1993. Heavy metals and toxic organic pollutants in MSW-composts: Research results on phytoavailability, bioavailability, fate, etc. p. 451-506. *In* H.A.J. Hoitink and H.M. Keener (ed.) Science and engineering of composting: design, environmental, microbiological and utilization aspects. Renaissance Publ., Worthington, Ohio.

Chang, A.C., J.D. Hinesly, T.E. Bates, H.E. Doner, R.H. Dowdy, and J.A. Ryan. 1987. Effects of long-term sludge application on accumulation of trace elements by crops. p.

53-66. *In* A.L. Page et al. (ed.) Land application of sludge: Food chain implications. Lewis Publ., Chelsea, MI.

Chao, T.T. 1972. Selective dissolution of manganese oxides from soils and sediments with acidified hydroxylamine hydrochloride. Soil Sci. Soc. Am. Proc. 36: 764-768.

Crawford, D.V. 1969. Studies on the growth of ferro-manganese concretions. Rep. Welsh Soils Discuss. Group. 10: 25-32.

Davis, J.A. 1977. Adsorption of trace metals and complexing ligands at oxide/water interface. Ph.D. Dissertation. Standford Univ., Standford, CA.

Douglas, L.A., and F. Fiessinger. 1971. Degradation of clay minerals by H_2O_2 treatments to oxidize organic matter. Clay and Clay Miner. 19: 67-68.

Dhillon, S.K., P.S. Sidhu, M.K. Sinha. 1981. Copper adsorption by alkaline soils. J. Soil Sci. 32: 571-578.

Elliott, H.A. 1983. Adsorption behavior of cadmium in response to soil surface charge. Soil Sci. 136: 317-321.

Farrah, H., and W.F. Pickering. 1976. The sorption of copper species by clays. II. Illite and montmorillonite. Aust. J. Chem. 29: 1174-1184.

Farrah, H., D. Hatton, and W.F. Pickering. 1980. The affinity of metal ions for clay surfaces. Chem. Geol. 28: 55-56.

Gerritse, R.G., and W. van Driel. 1984. The relationship between adsorption of trace metals, organic matter, and pH in temperate soils. J. Environ. Qual. 13: 197-204.

Harter, R.D. 1979. Adsorption of copper and lead by A_p and B_2 horizons of several northeastern United States soils. Soil Sci. Soc. Am. J. 43: 679-683.

Harter, R.D. 1983. Effect of soil pH on adsorption of lead, copper, zinc, and nickel. Soil Sci. Soc. Am. J. 47: 47-51.

Hodgson, J.F., H.R. Geering, and W.A. Norvell. 1965. Micronutrient cation complexes in soil solution: I. Partition between complexed and uncomplexed forms by solvent extraction. Soil Sci. Soc. Pro. 29: 665-669.

Hodgson, J.F., W.L. Lindsay, and J.F. Trierweiler. 1966. Micronutrient cation complexes in soil solution: II. Complexing of zinc and copper in displaced solution from calcareous soils. Soil Sci. Soc. Pro. 30: 723-726.

Kiekens, L. 1983. Behavior of heavy metals in soil. p. 126-134. *In* Berglund, S. Davis, R.D., and L'Hermite, P. (ed.) Utilisation of sewage sludge on land: Rates of application and long-term effects of metals. D. Reidel Publishing Company.

Kishk, F.M., and M.N. Hassan. 1973. Sorption and desorption of copper by and from clay minerals. Plant Soil. 39: 497-505.

Kononova, M.M. 1966. Soil organic matter: Its nature, its role in soil formation and in soil fertility. Pergamon Press. p. 317-376.

Koppelman, M.H., and J.G. Dillard. 1977. A study of the adsorption of Ni (II) and Cu (II) by clay minerals. Clays and Clay Miner. 25: 457-462.

Kunze, G.W., and J.D. Dixon. 1982. Pretreatment for mineralogical analysis. p. 91-100. *In* A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. Agronomy 9(1). American Society of Agronomy, Inc., and Soil Science Society of America, Inc. Madison, WI

Kornegay, E.T., J.D. Hedges, D.C. Martens, and C.Y. Kramer. 1974. Effect on soil and plant mineral levels following application of manures of different copper contents. Plant and Soil. 45: 151-162.

Kuo, S., and A.S. Baker. 1980. Sorption of copper, zinc, and cadmium by some acid soils. Soil Sci. Soc. Am. J. 44: 969-974.

James, R.O., and M.G. MacNaughton. 1977. The adsorption of aqueous heavy metals on inorganic minerals. Geochim. Cosmochim. Acta. 41: 1549-1555.

Jarvis, S.C. 1981. Copper sorption by soils at low concentrations and relation to uptake by plants. J. Soil Sci. 32: 257-269.

LeClaire, J.P. 1985. Adsorption of copper and cadmium onto soils: Influence of organic matter. Ph. D. Dissertation. University of California, Riverside. Riverside, CA.

LeRiche, H.H., and A.H. Weir. 1963. A method of studying trace elements in soil fractions. J. Soil Sci. 14: 225-235.

Levesque, M.P., and S.P. Mathur. 1986. Soil tests for copper, iron, manganese, and zinc in Histosols: 1. The influence of soil properties, iron, manganese, and zinc on the level and distribution of copper. Soil Sci. 142: 153-163.

Mattigod, S.V., and G. Sposito. 1977. Estimated association constants for some complexes of trace metals with inorganic ligands. Soil Sci. Soc. Am. J. 41: 1092-1097.

McBride, M.B. 1976. Origin and position of exchange sites in kaolinite. An ESR study. Clays and Clay Miner. 24: 88-92.

McBride, M.B. 1978. Retention of Cu^{2+}, Ca^{2+}, Mg^{2+}, and Mn^{2+} by amorphous alumina. Soil Sci. Soc. Am. J. 42: 27-31.

McBride, M.B. 1981. Forms and distribution of copper in solid and solution phases of soil. p. 25-45. *In* Loneragan, J.F., A.D. Robson, and R.D. Graham. (ed.) Copper in soil and plants. Academic Press, New York.

McBride, M.B. 1995. Toxic metal accumulation from agricultural use of sludge: Are USEPA regulations protective? J. Environ. Qual. 24: 5-18.

McGrath, S.P., and J. Cegarra. 1992. Chemical extractability of heavy metals during and after long-term applications of sewage sludge to soil. J. Soil Sci. 43: 313-321.

McKenzie, R.M. 1980. The adsorption of lead and other heavy metals on oxides of manganese and iron. Aust. J. Soil Res. 18: 61-73.

McLaren, R.G., and D.V. Crawford. 1973a. Studies on soil copper. I. The fractionation of copper in soils. J. Soil Sci. 24: 172-181.

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

McLaren, R.G., R.S. Swift, and J.G. Williams. 1981. The adsorption of copper by soil materials at low equilibrium solution concentrations. J. Soil Sci. 32: 247-256.

Mehra, O.P., and M.L. Jackson. 1960. Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. *In* Clays and Clay Minerals Pro. 7th Conf., p. 317-327. Natl. Acad. Sci.-Natl. Res. Council Publ., Washington, DC.

Miller, W.P., D.C. Martens, and L.W. Zelazny. 1986. Effect of sequence of trace metals from soils. Soil Sci. Soc. Am. J. 50: 598-601.

Mullins, G.L., D.C. Martens, W.P. Miller, E.T. Kornegay, and D.L. Hallock. 1982. Copper availability, form, and mobility in soils from three annual copper-enriched hog manure applications. J. Environ. Qual. 11: 316-320.

Narwal, R.P., B.R. Singh, and B. Salbu. 1999. Association of cadmium, zinc, copper, and nickel with components in naturally heavy metal rich soil studied by parallel and sequential extractions. Commun. Soil. Sci. Plant Anal. 30: 1209-1230.

Page, A.L., R.H. Miller, and D.R. Keeney (eds.). 1982. Methods of soil analyses. Part 2. Chemical and microbiological properties. 2nd ed. American Society of Agronomy. Madison, WI., USA.

Parfitt, R.L. 1980. Chemical properties of variable charge soils. p. 167-194. *In* B.K.G. Theng (ed.) Soil with variable charge. N.Z. Soc. Soil Sci., Palmerston, N.Z.

Petruzzelli, G., G. Guidi, and L. Lubrano. 1985. Ionic strength effect on heavy metal adsorption by soil. Commun. Soil Sci. Plant Anal. 16: 971-986.

Sanders, J.R., and C. Bloomfield. 1980. The influence of pH, ionic strength and reactant concentrations on copper complexing by humidified organic matter. J. Soil Sci. 31: 53-63.

Sposito, G. 1981. The thermodynamics of soil solutions. Clarendon Press. Oxford.

Sposito, G. 1984. The surface chemistry of soils. Clarendon Press. Oxford.

Sposito, G., and K. M. Holtzclaw. 1979. Copper(II) complexation by fulvic acid extracted from sewage sludges as influenced by nitrate versus perchlorate background ionic media. Soil Sci. Soc. Am. J. 43:47-51.

Sposito, G., and A.L. Page. 1984. Cycling of metals in the soil environment. p. 287-332. *In* Sigel, H. (ed.) Metal ions in biological systems. vol. 18. Circulation of metals in the environment. Marcel dekker, Inc. New York.

Stevenson, F.J. 1991. Organic matter- micronutrient reactions in soil. p. 145-186. *In* J.J. Mortvedt (ed.) Micronutrients in agriculture. SSSA book series: 4. Soil Sci. Soc. Am. Inc., Madison, WI.

Stevenson, F., and M.S. Ardakani. 1972. Organic matter reactions involving micronutrients in soils. p. 79-114. *In* J.J. Mortvedt (ed.) Micronutrients in agriculture. Soil Sci. Soc. Am. Inc., Madison, WI.

Takahashi, Y., and H. Imai. 1983. Adsorption of heavy metal cations in montmorillonite. Soil Sci. Plant Nutr. 29: 111-122.

Terry, R.E., D.W. Nelson, and L.E. Sommers. 1979. Carbon cycling during sewage sludge decomposition in soils. Soil Sci. Soc. Am. J. 43:494-499.

U.S. Environmental Protection Agency. 1993. Clean water act. Section 503. Vol. 58.

No. 32. USEPA, Washington, DC.

Van Olphen, H., J.J. Fripiat. 1979. Data handbook for clay materials and other non-metallic minerals. Pergamon Press, New York.

Veith, J.A., and G. Sposito. 1977. On the use of the Langmuir equation in the interpretation of "Adsorption" phenomena. Soil Sci. Soc. Am. J. 41: 697-702.

Zachara, J.M., S.C. Smith, C.T. Resch, and C.E. Cowan. 1992. Cadmium sorption to soil separates containing layer silicates and iron and aluminum oxides. Soil Sci. Soc. Am. J. 56: 1074-1084.

Zelazny, L.W., and J.N. Qureshi. 1973. Chemical pretreatment effects on clay separation and mineralogical analyses of selected Florida soils. Soil Crop Sci. Soc. Fl. 32: 117-121.

CHAPTER IV
SUMMARY

Adsorption of Cd, Cu, Pb and Zn was affected by concentration of background electrolytes [$NaClO_4$, $Ca(ClO_4)_2$, and $Al(ClO_4)_3$]. The degree of adsorption depended upon metal species and soil type. Also, the adsorption isotherm parameters varied with ionic strength and composition of the background solution. Therefore, background electrolytes used in laboratory analysis should be considered when making simulations of real situations.

Copper adsorption changed little with increasing ionic strength of Na^+ for Bertie sandy and Starr-Dyke clayey soils. Increasing ionic strength of Ca^{2+} in background solutions had minimal effect on Cu adsorption in Starr-Dyke soil, which contains a large amount of Fe_2O_3 and MnO_2. In the presence of Na^+, Cd and Zn adsorption decreased with increasing ionic strength, while Pb adsorption was unaffected by ionic strength in any of the soils. Fewer differences in metals adsorption existed at different ionic strengths in Starr-Dyke soil than in Bertie soil. Soils with applied Cu-rich pig manure exhibited less difference in metals adsorption than the control soils at different background ionic strengths. Enhanced adsorption of metals in those soils was attributed to preferential bonding of the metals by organic material.

Adsorption isotherms often were dependent upon the concentration range over which the experiments were conducted and a sufficiently large concentration range was not likely to have a C-curve characteristic (linear form). Apparent success of Freundlich or Langmuir equations might depend on the concentration range of adsorbent, the adsorption capacity of the adsorbent, and the $C_{geomedia}$ (solid concentration) (Jenne, 1998).

Numerous researchers have used the Langmuir equation to determine adsorption maxima for soil systems. In most cases the Langmuir and Freundlich equations can successfully explain the adsorption of metals with various background electrolytes, but despite the good fits obtained between experimental data and adsorption plots, some parameters in the model equations may not be reliable because of their dependency on other parameters. Even when using the same set of experimental data, the equation values are often variable and dependent upon the method of fitting the regression model equation.

Researchers have tried to determine adsorption maxima primarily to estimate the maximum levels of metals that soil systems can retain without harmful consequences for the environment. One approach to understanding the potential for environmental contamination is to determine the metal concentration in soil solution provided a given set of environmental factors. Application of Cd, Cu, Pb, and Zn should be 0.21 mM, 0.7 mM, 0.78 mM, and 0.27 mM for Bertie soil in the presence of 0.02 mol_c Ca L^{-1} to obtain metal concentrations of < 10 mg L^{-1} based on concentration isolines. With 1 mM treatment of each metal, Cd, Cu, Pb, and Zn remained below 10 mg L^{-1} in soil solution at pH values of 5.25, 4.5, 4.25, and 5.3 for Bertie soil, and 5.0, 4.5, 4.0, and 5.0 for Starr-Dyke soil, respectively. Using isolines, metal-loading rates could be estimated to give the desired metal concentration in soil solution dependent upon background electrolytes, soil type, pH, and possibly other factors.

Soil conditions such as pH and composition and concentration of background electrolytes had a strong influence on the goodness of fit to the models for Cu sorption data. With increasing concentration, Cu sorption was more linear when pH was maintained at 5.5 than when pH was not controlled. Without controlling pH, increased Cu concentration reduced solution pH, resulting in decreased Cu sorption. This is important to note because the impact of pH on Cu sorption in such experiments.

Sigmoid shaped curves were observed in the Bertie soil at the pH > 5.5 and at pH > 6.5 in the Starr-Dyke soil. These curves could be due to soluble organic matter, precipitation with inorganic ions or both. Determination of adsorption maxima for Bertie soil at pH > 5.5 was not possible because the adsorption curves did not follow the L-type curve. In both soils the best fit across all models (Langmuir, extended Langmuir, two-site Langmuir, and Freundlich) was observed at pH 5.0.

Studies of pH the effects on Cu sorption indicate that added Cu was mostly sorbed at low concentrations regardless of pH, but at high concentrations Cu sorption was strongly related to solution pH. Increases in pH resulted in greater Cu sorption due to the pH-dependent negative charges and precipitation. Also, the addition of OH^- causes successive displacement of water molecules from the hydration sheath and stepwise formation of Cu complexes.

To obtain less than 1 mg L^{-1} of Cu in soil solution, when 0.1 mM, 0.2 mM, 0.3 mM, and 0.5 mM of Cu were added to Bertie soil, pH values should be raised above 4.24, 4.64, 4.71, and 5.77. When 0.75 mM of Cu was added to Bertie soil, Cu concentrations in soil solution < 1 mg L^{-1} in the pH range between 6.60 and 7.19. Regardless of pH, no Bertie soil solution had Cu concentration < 1 mg Cu L^{-1} when 1.0 mM of Cu was added. In Starr-Dyke soil, however, the same solution concentrations can be attained at lower pH levels.

The USEPA suggested that soil pH be maintained above 6.5 where high concentrations of metals are land applied because of the impact of soil pH on metal sorption. However, pig manure applications to Bertie soil resulted in greater Cu in soil solution than in control (no manure) soil at pH > 6.5 due to soluble organic matter. The Bertie soil solution was yellowish brown at high pH, and Stevenson (1991) reported that a large part of heavy metals present in soil solution and in surface waters appears to be linked in a yellowish compound containing fulvic acid. In the laboratory, pH was adjusted with NaOH, which might increase the solubility of alkaline soluble organic matter such as fulvic and humic acids.

Sequential extraction procedure and soil separates, after removal of free Mn oxides with $NH_2OH{\cdot}HCl$ treatment, did not agree on the impact of free MnO_2 on Cu sorption. Thus, further research is needed to elucidate the effects of chemical reagents on soil components.

Table A.1. Average macro- and micro-element concentrations in pig manure over a 13-year period.*

Elements	Concentration
	----------- % -----------
Ca	4.1
K	1.7
Mg	0.82
N	4.5
Na	0.45
P	2.3
	--------- mg Kg^{-1} ---------
B	20
Cu	1322
Fe	1184
Mn	288
Zn	420

* cited from Annual Report ICA project No 292(M) (Martens et al., 1992).

Table A.2. Comparison of concentration between saturated soil solution and sodium perchlorate solution. Information used to select concentration of background solution.

Soils		Electrical conductivity (mS/cm)	Saturated soil solution concentration comparing as $NaClO_4$ concentration
Betie	Control	0.97	0.009 M of $NaClO_4$
	Receiving pig manure	2.04	0.0197 M of $NaClO_4$
Starr-Dyke	Control	1.79	0.017 M of $NaClO_4$
	Receiving pig manure	3.04	0.033 M of $NaClO_4$

Table A.3. Solution pH after metal adsorption with different background electrolytes (concentration = 0.02 mol_c L^{-1}).

Metals Species	Bertie soil			Bertie + pig manure		
	$NaClO_4$	$Ca(ClO_4)_2$	$Al(ClO_4)_3$	$NaClO_4$	$Ca(ClO_4)_2$	$Al(ClO_4)_3$
Cd	5.50 (0.045)*	4.70 (0.041)	3.38 (0.025)	5.50 (0.008)	4.87 (0.045)	3.41 (0.000)
Cu	5.06 (0.029)	4.18 (0.042)	3.58 (0.021)	5.33 (0.012)	4.20 (0.014)	3.62 (0.048)
Pb	5.05 (0.029)	4.68 (0.070)	3.43 (0.069)	5.44 (0.053)	4.73 (0.053)	3.35 (0.024)
Zn	5.12 (0.014)	4.74 (0.063)	3.44 (0.064)	5.19 (0.026)	4.93 (0.057)	3.39 (0.062)

Metals Species	Starr-Dyke soil			Starr-Dyke + pig manure		
	$NaClO_4$	$Ca(ClO_4)_2$	$Al(ClO_4)_3$	$NaClO_4$	$Ca(ClO_4)_2$	$Al(ClO_4)_3$
Cd	5.81 (0.062)	5.09 (0.071)	3.55 (0.031)	5.96 (0.073)	5.78 (0.045)	3.58 (0.037)
Cu	5.38 (0.014)	4.72 (0.090)	3.76 (0.024)	6.09 (0.298)	5.25 (0.194)	3.94 (0.000)
Pb	5.89 (0.088)	4.82 (0.090)	3.51 (0.016)	6.25 (0.090)	5.73 (0.242)	3.50 (0.026)
Zn	6.01 (0.102)	5.02 (0.008)	3.51 (0.041)	6.10 (0.071)	5.59 (0.019)	3.60 (0.040)

* (   ) shows standard deviation

Table A.4. Electrical conductivity (mS cm^{-1}) after metal adsorption with different background electrolytes (concentration = 0.02 mol$_c$ L^{-1}).

Metals	Bertie soil			Bertie + pig manure		
Species	$NaClO_4$	$Ca(ClO_4)_2$	$Al(ClO_4)_3$	$NaClO_4$	$Ca(ClO_4)_2$	$Al(ClO_4)_3$
Cd	0.233	0.234	0.227	0.235	0.239	0.232
Cu	0.235	0.307	0.187	0.237	0.312	0.187
Pb	0.232	0.237	0.232	0.234	0.239	0.238
Zn	0.229	0.240	0.232	0.232	0.241	0.236

Metals	Starr-Dyke soil			Starr-Dyke + pig manure		
Species	$NaClO_4$	$Ca(ClO_4)_2$	$Al(ClO_4)_3$	$NaClO_4$	$Ca(ClO_4)_2$	$Al(ClO_4)_3$
Cd	0.235	0.237	0.228	0.243	0.245	0.239
Cu	0..237	0.309	0.184	0.245	0.317	0.194
Pb	0.234	0.237	0.232	0.241	0.244	0.244
Zn	0.233	0.241	0.232	0.239	0.250	0.241

* Standard deviation is from 0.000047 to 0.000602.

Table B.1. Comparison Langmuir constant "b" using nonlinear regression least squares analyses and using linear regression analyses with different ionic strengths and cations in background electrolytes on Bertie and Starr- Dyke soils.

Langmuir constant "b"

A. Bertie soil

Background Electrolytes§		Cadmium		Copper (low) †		Copper (high) ‡		Lead		Zinc	
		Nonlinear	Linear	Nonlinear	Linear	Nonlinear	Linear	Nonlinear	Linear	Nonlinear	Linear
$NaClO_4$	0.02	0.210	0.264	0.993	0.970	0.538	0.451	1.612	1.697	0.164	0.189
$Ca(ClO_4)_2$	0.01	0.037	0.045	0.506	0.552	0.156	0.160	0.704	0.968	0.035	0.037
	0.02	0.026	0.031	0.332	0.365	0.077	0.095	0.386	0.491	0.019	0.020
	0.05	0.013	0.019	0.109	0.131	0.026	0.037	0.159	0.185	0.010	0.011
$Al(ClO_4)_3$	0.02	0.017	0.020	0.054	0.061	0.019	0.024	0.028	0.035	0.001	-0.043

B. Starr-Dyke soil

Background Electrolytes§		Cadmium		Copper (low) †		Copper (high) ‡		Lead		Zinc	
		Nonlinear	Linear	Nonlinear	Linear	Nonlinear	Linear	Nonlinear	Linear	Nonlinear	Linear
$NaClO_4$	0.02	0.345	0.468	7.626	8.123	0.880	0.853	6.104	22.955	0.582	0.778
$Ca(ClO_4)_2$	0.01	0.103	0.134	3.055	3.538	0.383	0.430	10.780	12.608	0.261	0.316
	0.02	0.077	0.093	1.968	2.582	0.223	0.301	3.609	7.253	0.157	0.195
	0.05	0.047	0.060	0.831	0.940	0.108	0.157	1.733	2.115	0.135	0.165
$Al(ClO_4)_3$	0.02	0.014	0.018	0.062	0.069	0.022	0.027	0.081	0.108	0.001	-0.046

† The concentration range of adsorption isotherms ranges from 0.1mM to 1.0mM of $Cu(ClO_4)_2$.

‡ The concentration range of adsorption isotherms ranges from 0.1mM to 4.0mM of $Cu(ClO_4)_2$.

§ Unit of background electrolytes are $mol_c\ L^{-1}$.

Table B.2. Comparison Langmuir constant “Γ_m” using nonlinear regression least square analyses and using linear regression analyses with different ionic strengths and cations in background electrolytes on Bertie and Starr- Dyke soils.

Langmuir constant “Γ_m”

A. Bertie soil

Background Electrolytes§		Cadmium		Copper (low) †		Copper (high) ‡		Lead		Zinc	
		Nonlinear	Linear	Nonlinear	Linear	Nonlinear	Linear	Nonlinear	Linear	Nonlinear	Linear
$NaClO_4$	0.02	881	831	521	526	675	702	1926	1894	519	504
$Ca(ClO_4)_2$	0.01	841	766	563	567	864	904	1954	1920	421	412
	0.02	701	633	469	472	810	825	1914	1858	413	397
	0.05	607	486	395	380	779	736	2004	1949	377	337
$Al(ClO_4)_3$	0.02	108	100	256	247	444	425	1540	1439	1418	5

B. Starr-Dyke soil

Background Electrolytes§		Cadmium		Copper (low) †		Copper (high) ‡		Lead		Zinc	
		Nonlinear	Linear	Nonlinear	Linear	Nonlinear	Linear	Nonlinear	Linear	Nonlinear	Linear
$NaClO_4$	0.02	1184	1052	538	541	1300	1403	2910	1764	730	681
$Ca(ClO_4)_2$	0.01	1249	1106	746	735	1717	1837	2025	2048	650	617
	0.02	1057	968	667	649	1616	1675	2152	1907	646	601
	0.05	918	816	613	617	1364	1377	2279	2184	532	507
$Al(ClO_4)_3$	0.02	276	236	403	389	699	670	2023	1909	4404	17

† The concentration range of adsorption isotherms ranges from 0.1mM to 1.0mM of $Cu(ClO_4)_2$.

‡ The concentration range of adsorption isotherms ranges from 0.1mM to 4.0mM of $Cu(ClO_4)_2$.

§ Unit of background electrolytes are $mol_c\ L^{-1}$.

Table C.1. Solution pH after Cu adsorption with increasing metal treatments for Bertie and Starr-Dyke soils.

Treatment (mM)	Bertie soil	Starr-Dyke soil
0.10	5.45	5.49
0.20	5.43	5.38
0.30	5.15	5.33
0.50	5.08	5.11
0.75	4.93	5.05
1.00	4.72	4.98

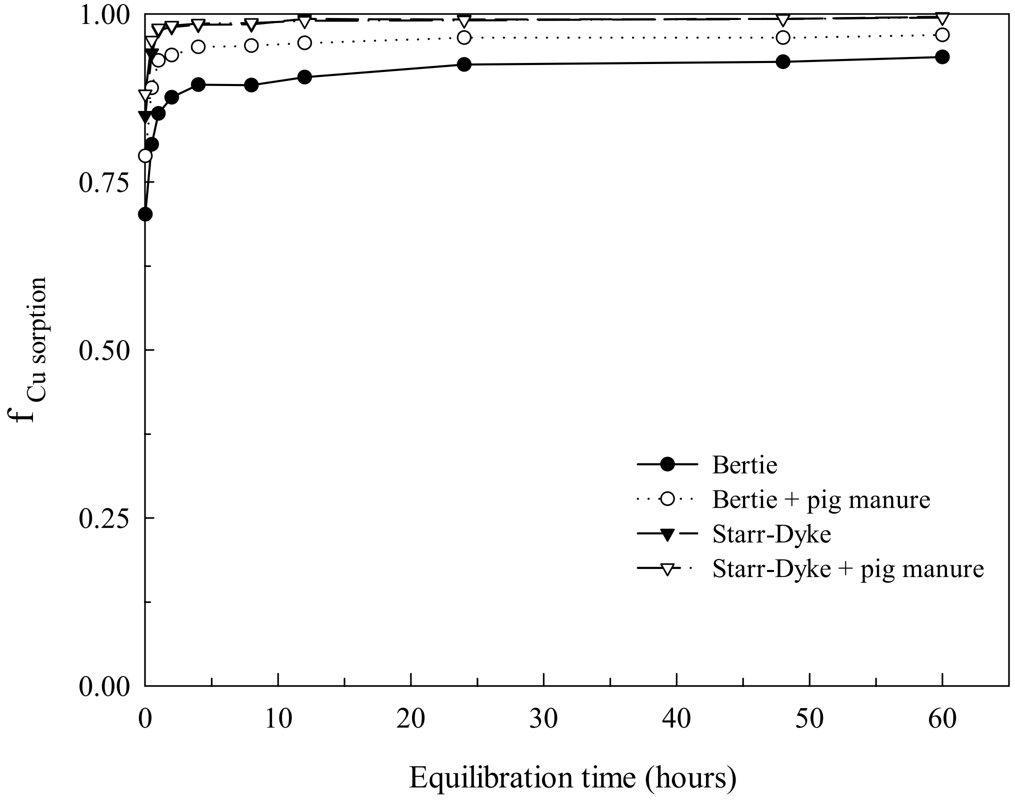

Fig. A.1. Kinetics of copper sorption by Bertie and Starr-Dyke soils, with and without pig manure. $f_{\mathrm{Cu\ sorption}}$ is a fraction of Cu sorbed by soil particles. Electrolyte solution is 0.02 $\mathrm{mol_c}$ $NaClO_4$ L^{-1}.

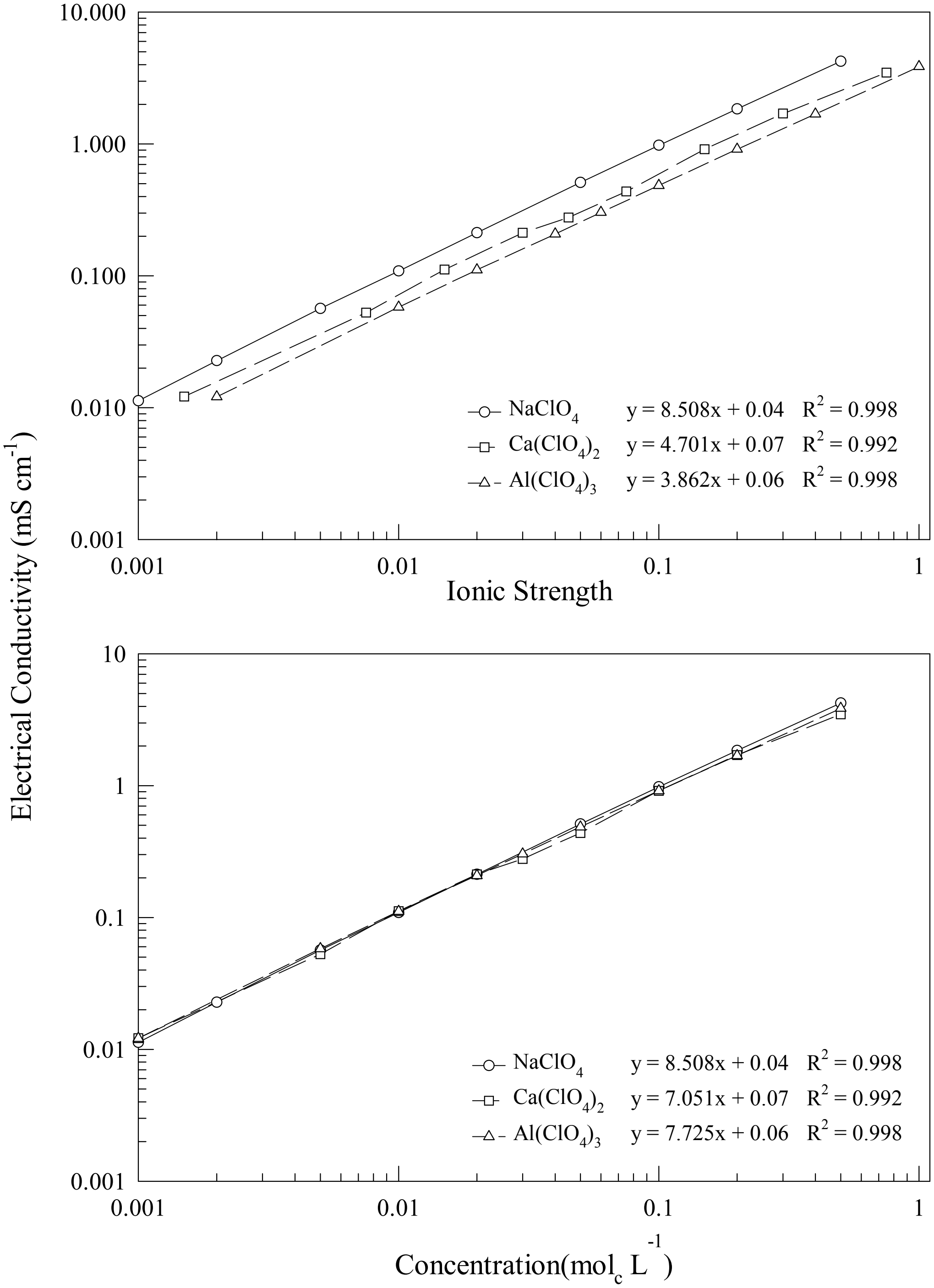

Fig. A.2. Relationships between electrical conductivity and ionic strength or concentration under three different background electrolytes.

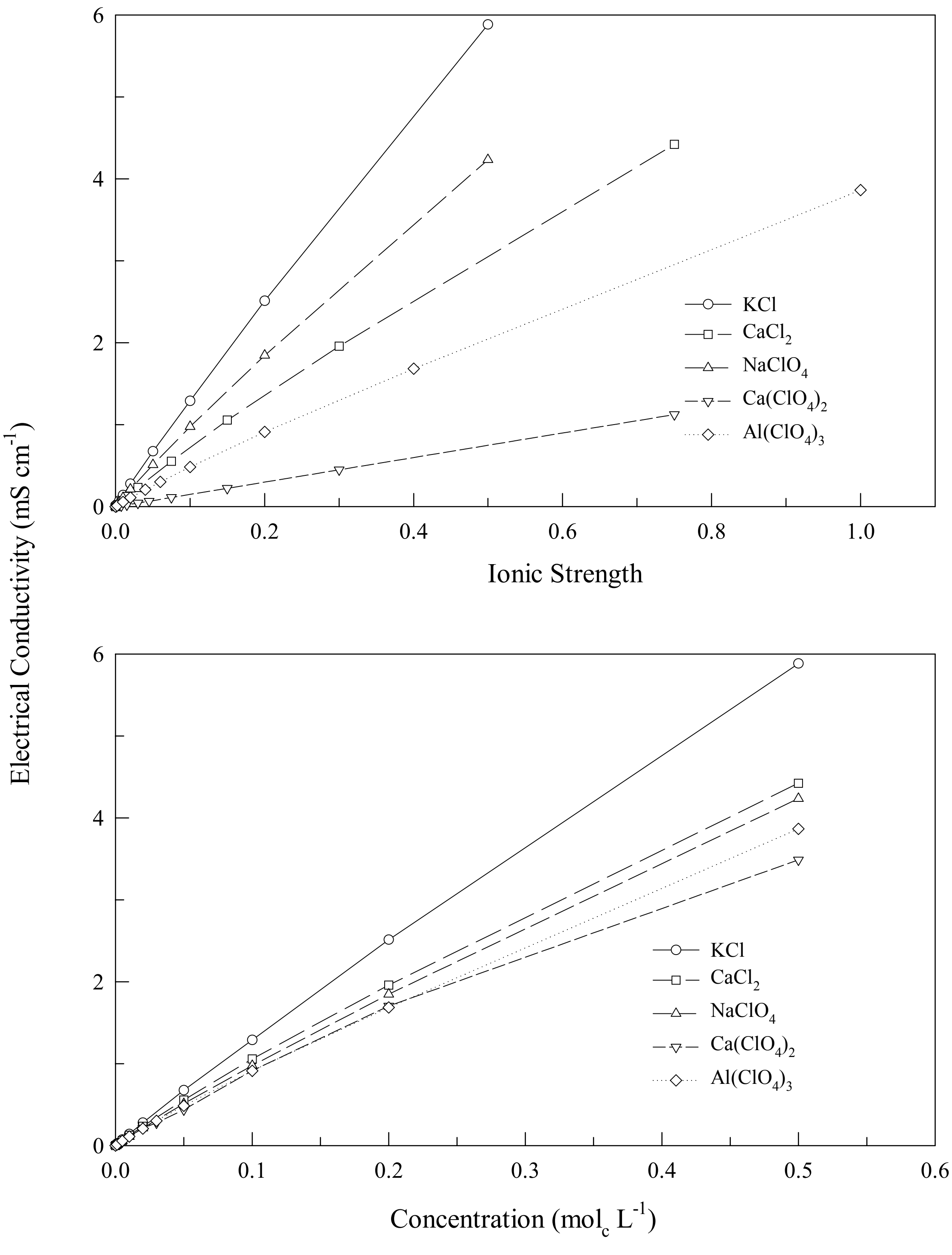

Fig. A.3. Comparison of relationship between electrical conductivity against normality and ionic strength.

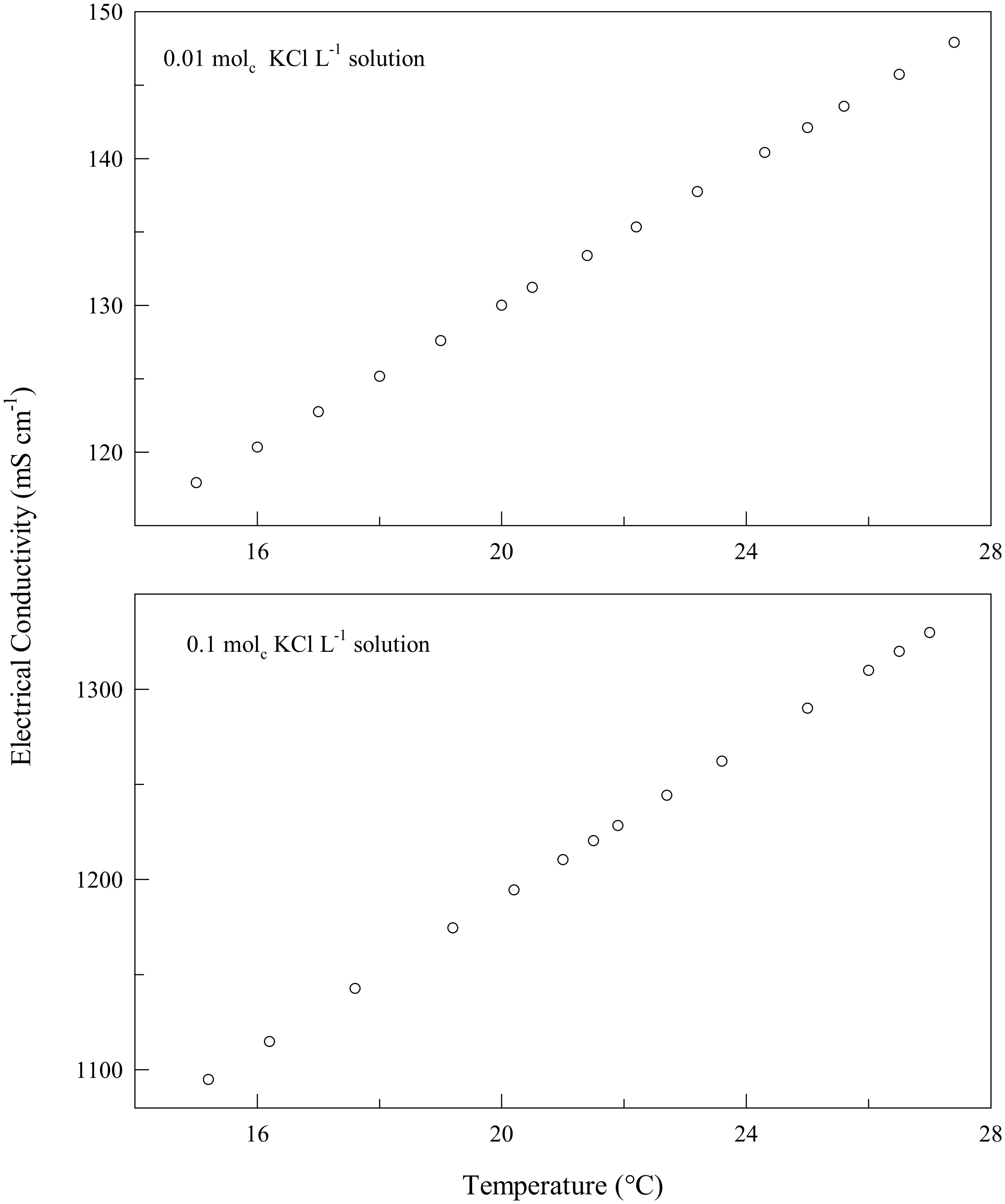

Fig. A.4. Relationship between temperature of solution and measured electrical conductivity at two different concentrations.

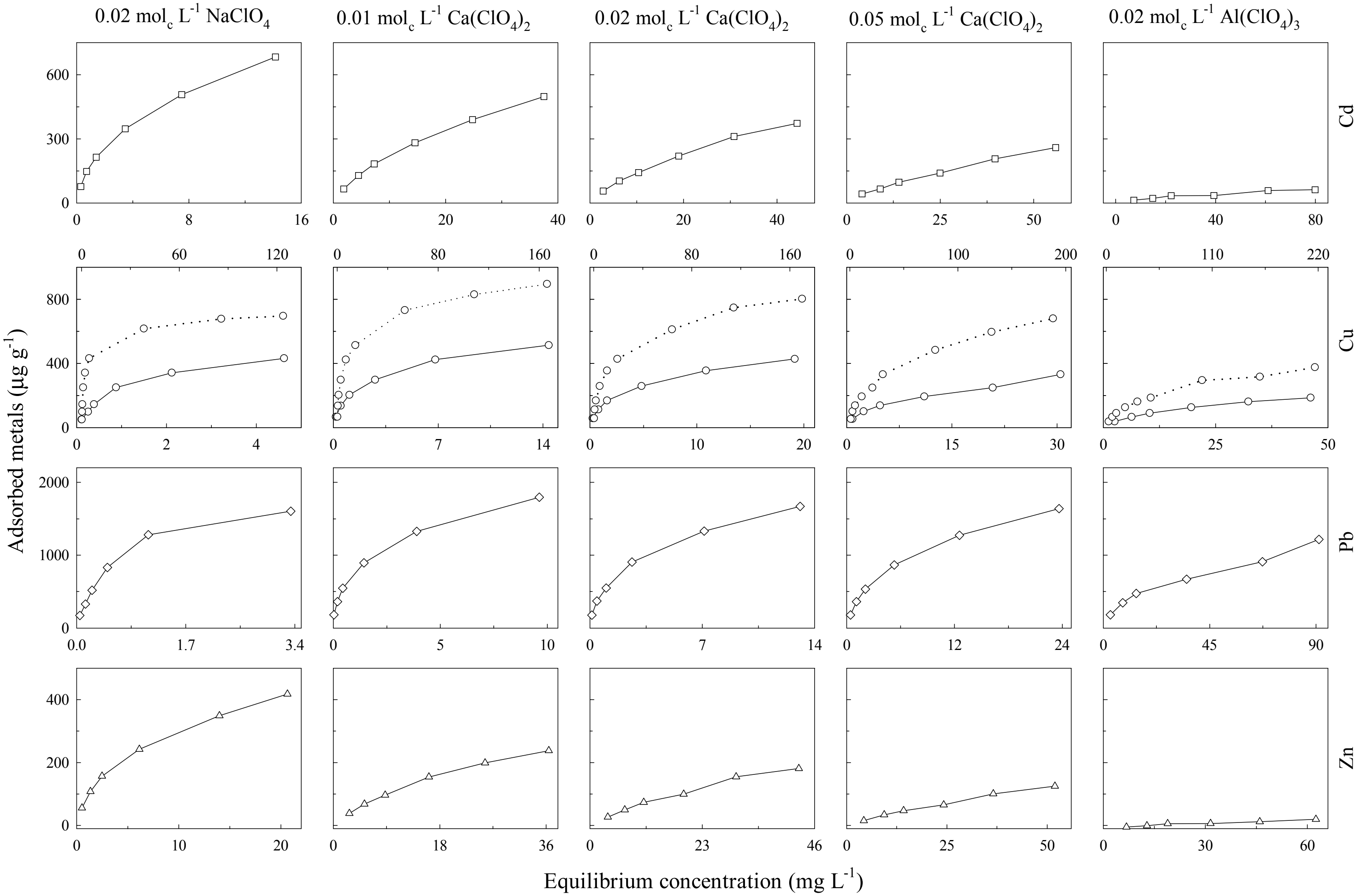

Fig. B.1. Comparison of curve characteristics for Cd, Cu, Pb, and Zn adsorption isotherms by Bertie soil in presence of various background electrolytes. Intial concentration ranged from 0.1 mM to 1.0 mM of Me(ClO$_4$)$_2$ (solid line) and from 0.1 mM to 4.0 mM of Cu(ClO$_4$)$_2$ (dotted line).

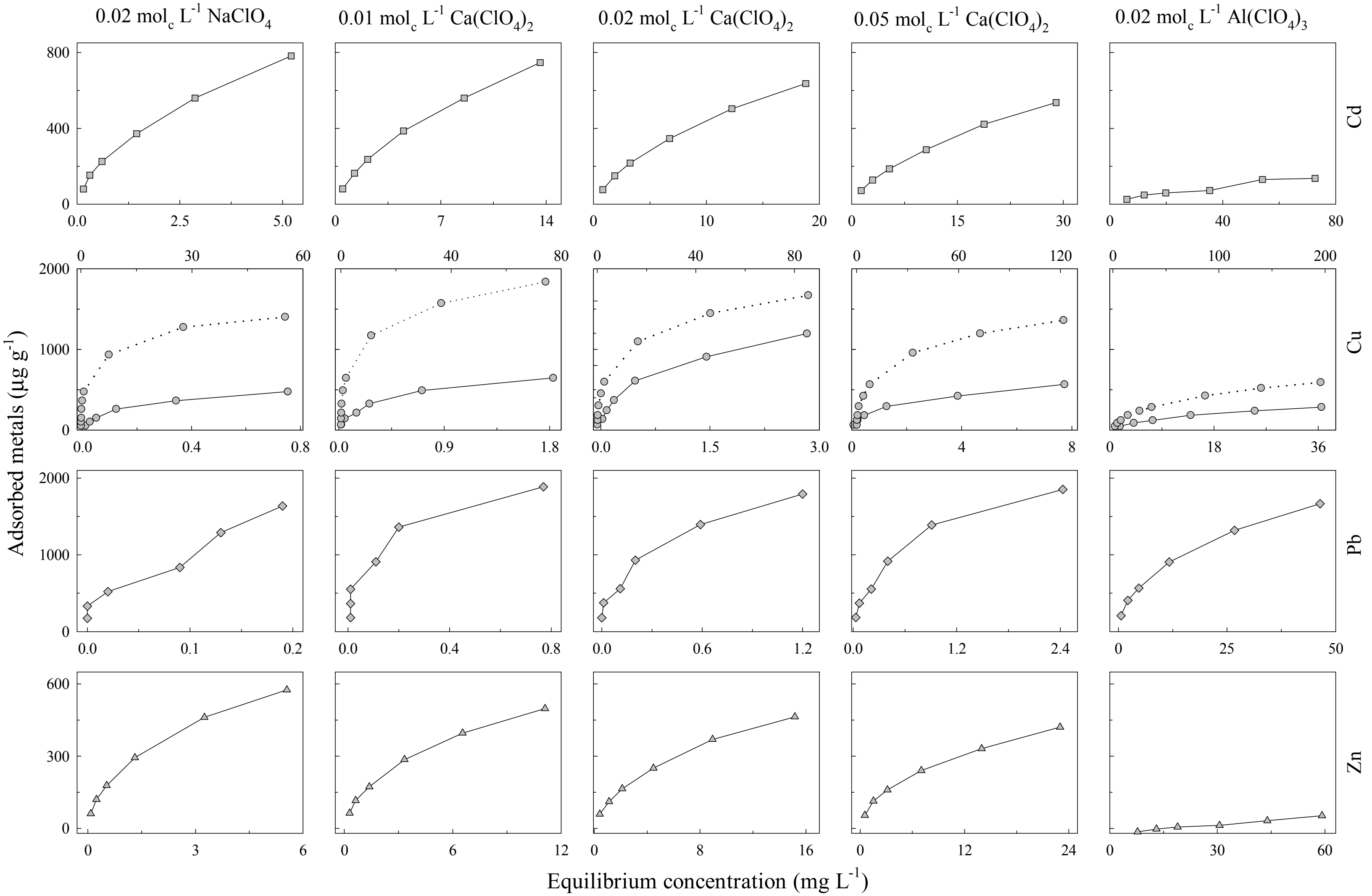

Fig. B.2. Comparison of curve characteristics for Cd, Cu, Pb, and Zn adsorption isotherms by Starr-Dyke soil by Starr-Dyke soil in presence of various background electrolytes. Intial concentration ranged from 0.1 mM to 1.0 mM of Me(ClO$_4$)$_2$ (solid line) and from 0.1 mM to 4.0 mM of Cu(ClO$_4$)$_2$ (dotted line).

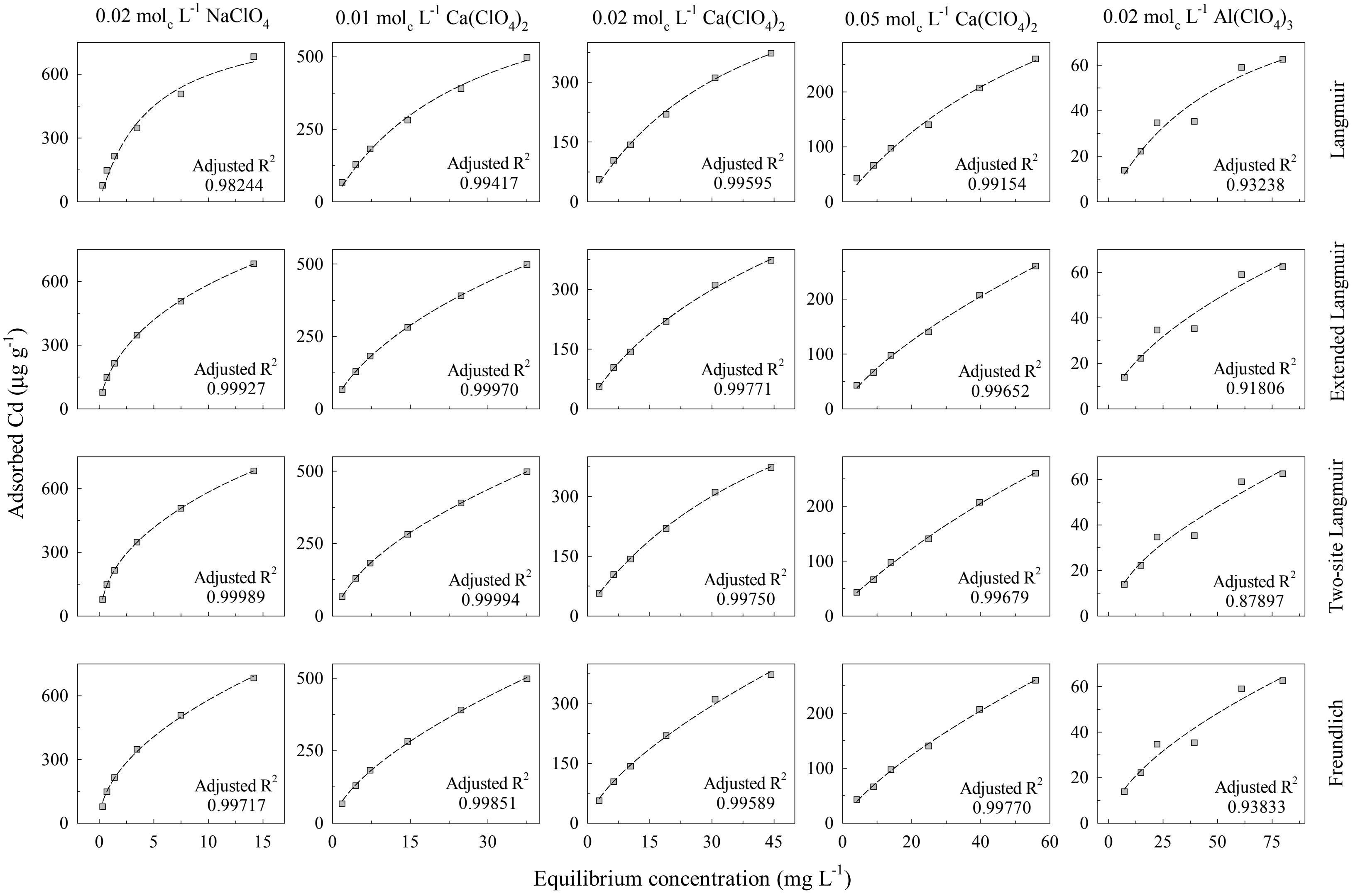

Fig. B.3. Comparison of four different adsorption isotherm equations (Langmuir, Extended Langmuir, Two-site Langmuir, and Freundlich) for Cd adsorbed by Bertie soil in presence of various background electrolytes. Intial concentration ranged from 0.1 mM to 1.0 mM of Cd(ClO$_4$)$_2$.

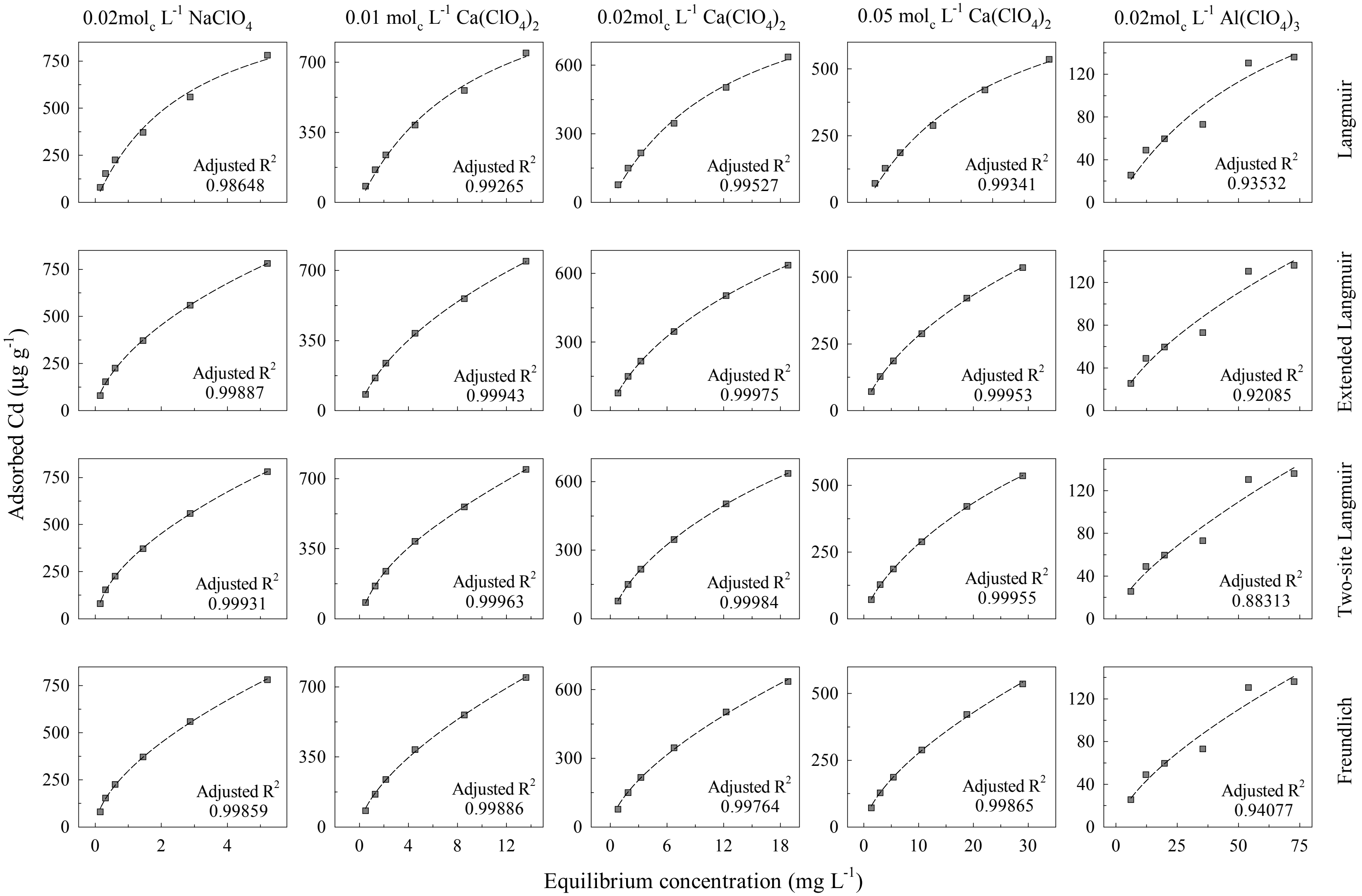

Fig. B.4. Comparison of four different adsorption isotherm equations (Langmuir, Extended Langmuir, Two-site Langmuir, and Freundlich) for Cd adsorbed by Starr-Dyke soil in the presence of various background electrolytes . Intial concentration ranged from 0.1 mM to 1.0 mM of Cd(ClO$_4$)$_2$.

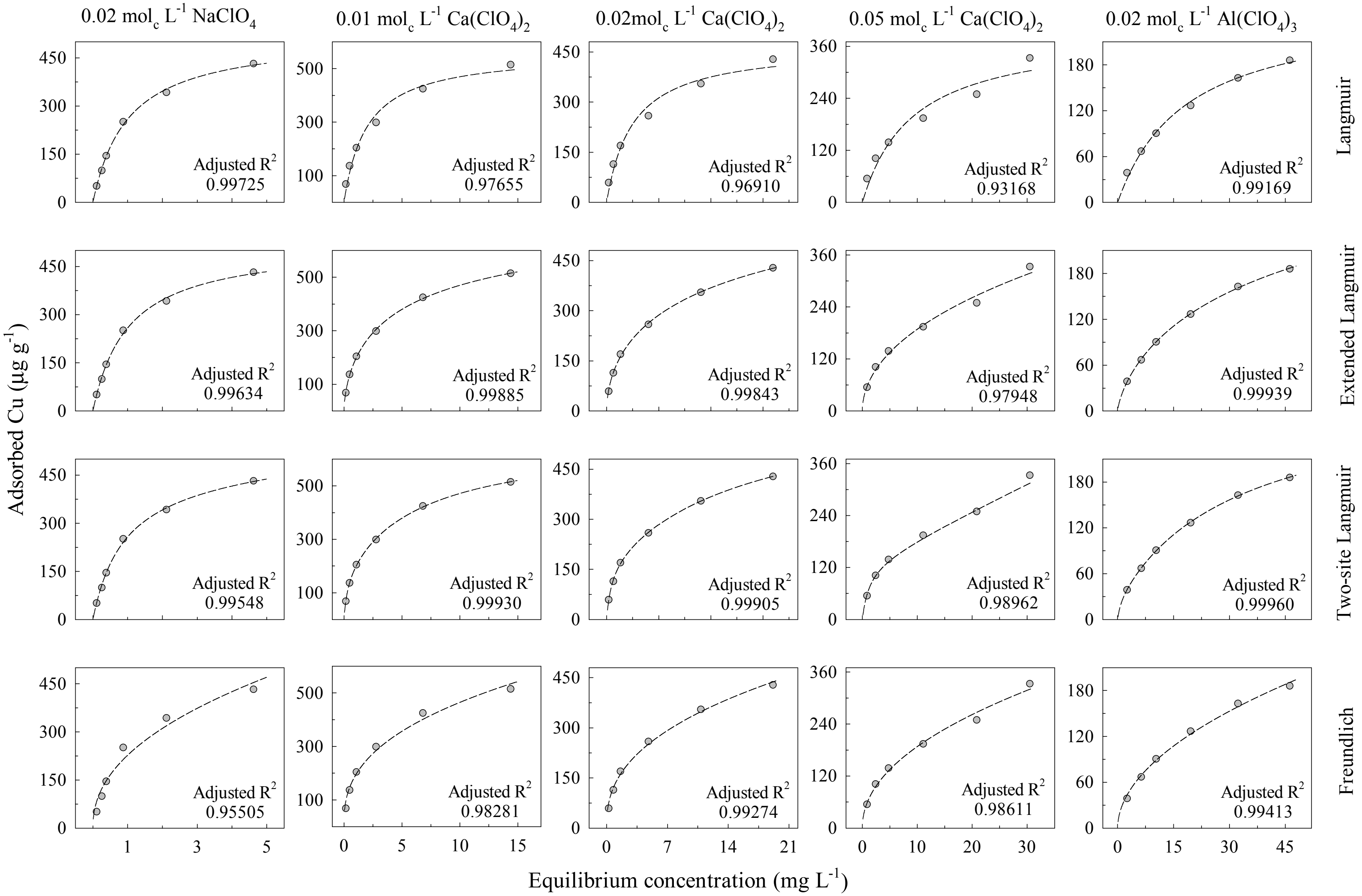

Fig. B.5. Comparison of four different adsorption isotherm equations (Langmuir, Extended Langmuir, Two-site Langmuir, and Freundlich) for Cu adsorbed by Bertie soil in the presence of various background electrolytes . Initial concentration ranged from 0.1 mM to 1.0 mM of Cu (ClO$_4$)$_2$.

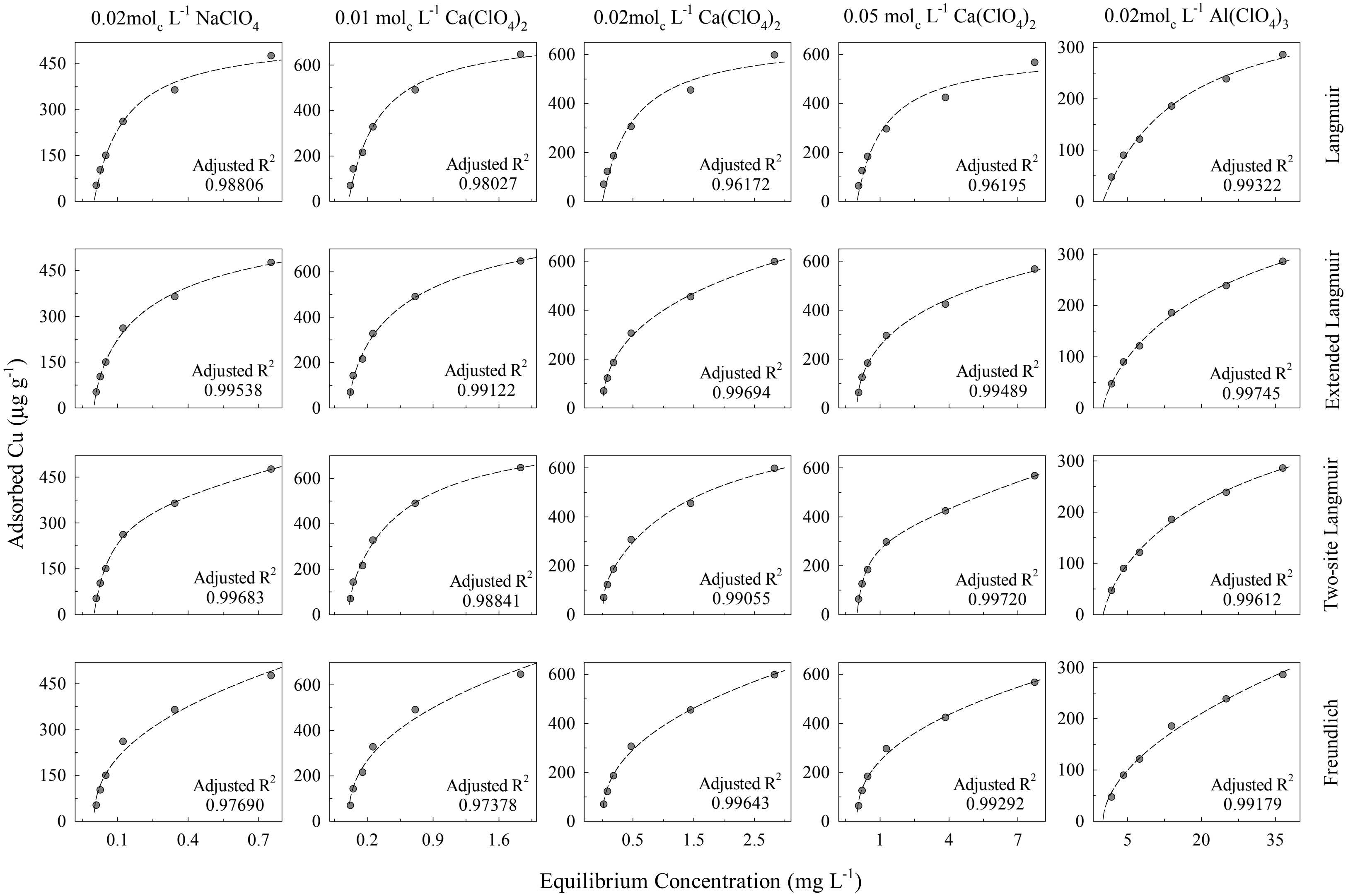

Fig. B.6. Comparison of four different adsorption isotherm equations (Langmuir, Extended Langmuir, Two-site Langmuir, and Freundlich) for Cu adsorbed by Starr-Dyke soil in the presence of various background electrolytes. Initial concentration ranged from 0.1 mM to 1.0 mM of Cu $(ClO_4)_2$.

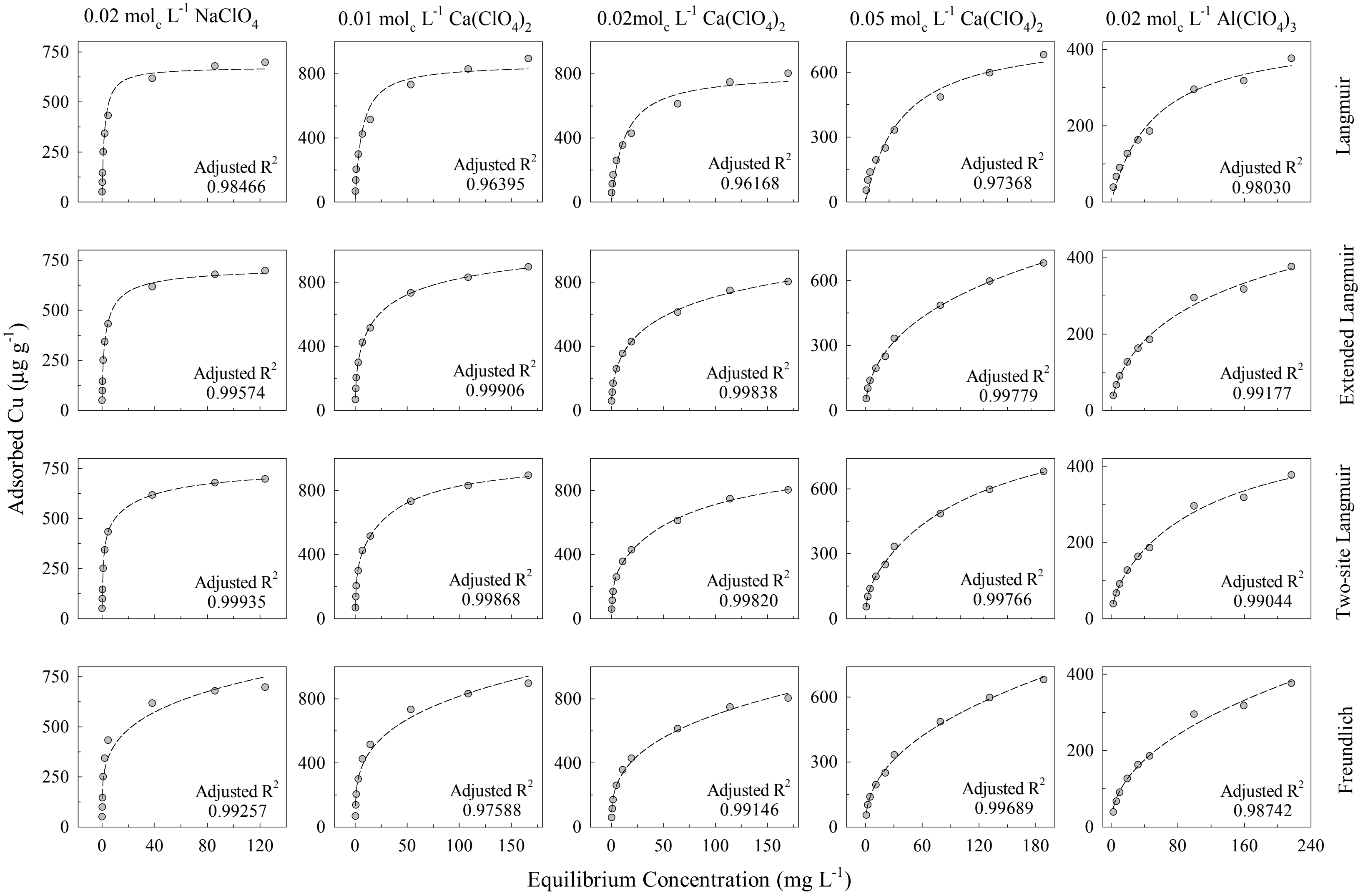

Fig. B.7. Comparison of four different adsorption isotherm equations (Langmuir, Extended Langmuir, Two-site Langmuir, and Freundlich) for Cu adsorbed by Bertie soil in presence of various background electrolytes. Initial concentration ranged from 0.1 mM to 4.0 mM of Cu $(ClO_4)_2$.

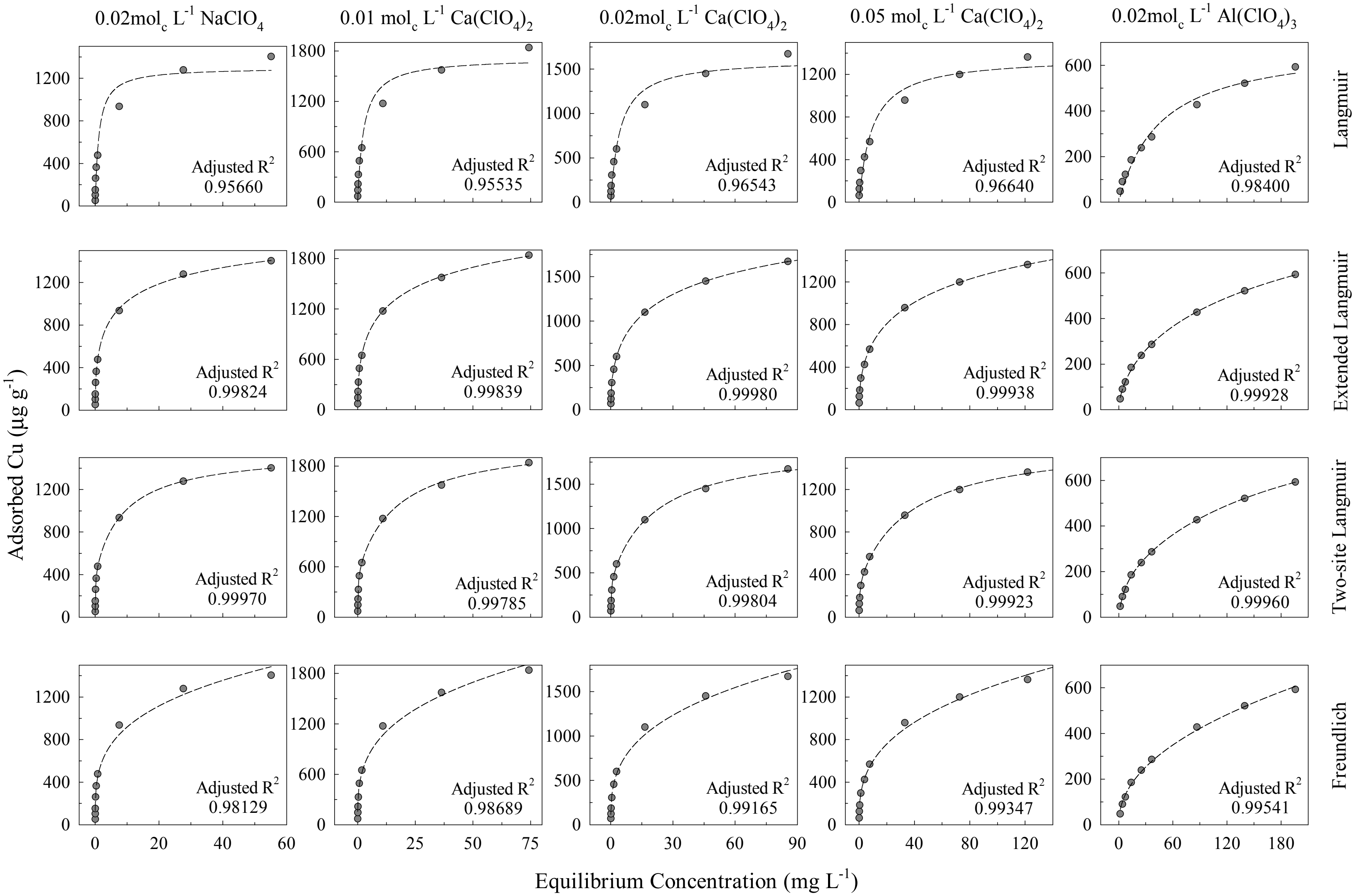

Fig. B.8. Comparison of four different adsorption isotherm equations (Langmuir, Extended Langmuir, Two-site Langmuir, and Freundlich) for Cu adsorbed by Starr-Dyke soil in presence of various background electrolytes. Initial concentration ranged from 0.1 mM to 4.0 mM of Cu $(ClO_4)_2$.

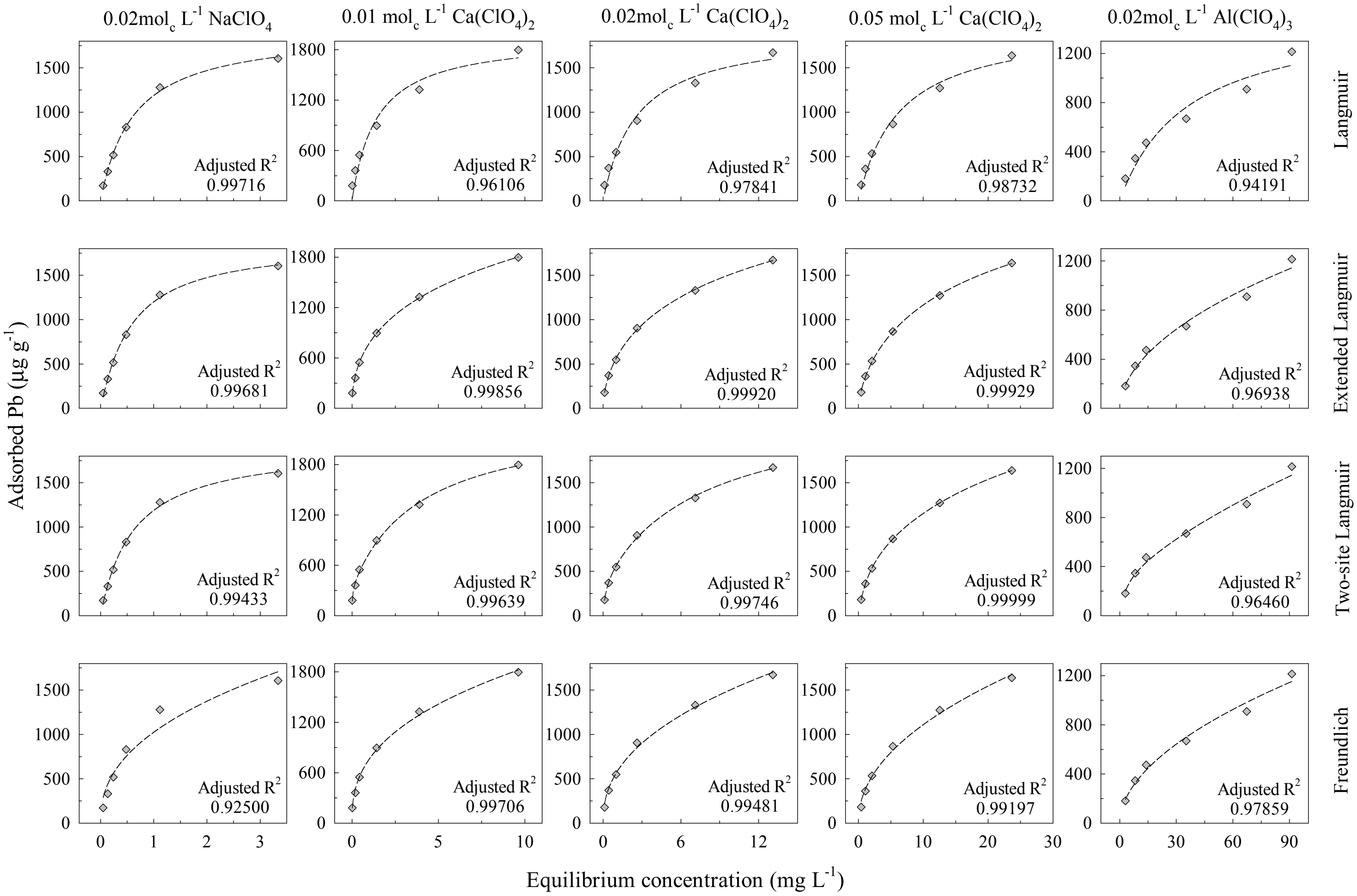

Fig. B.9. Comparison of four different adsorption isotherm equations (Langmuir, Extended Langmuir, Two-site Langmuir, and Freundlich) for Pb adsorbed by Bertie soil in presence of various background electrolytes. Initial concentration ranged from 0.1 mM to 1.0 mM of Pb(ClO$_4$)$_2$.

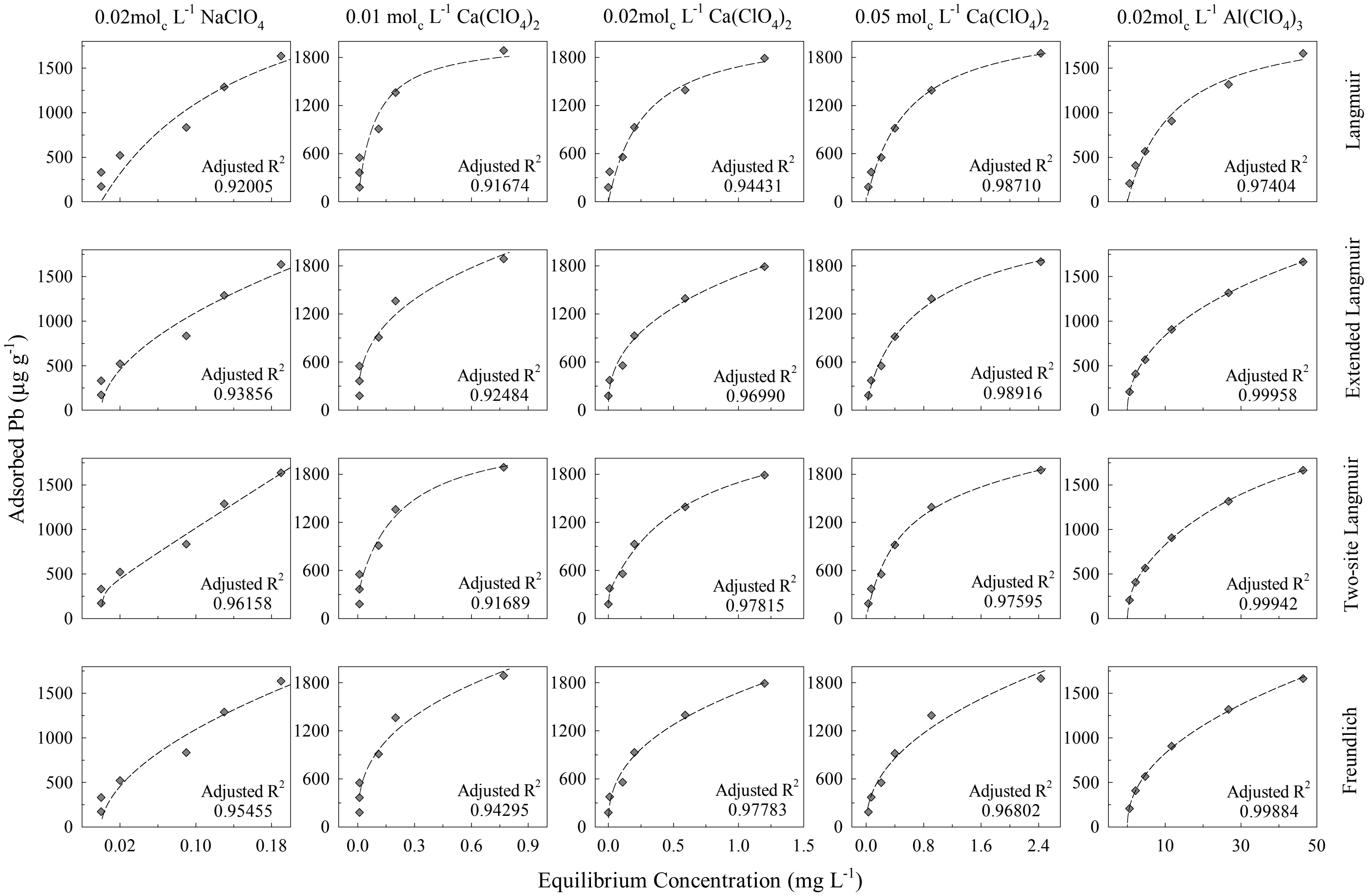

Fig. B.10. Comparison of four different adsorption isotherm equations (Langmuir, Extended Langmuir, Two-site Langmuir, and Freundlich) for Pb adsorbed by Starr-Dyke soil in presence of various background electrolytes. Initial concentration ranged from 0.1 mM to 1.0 mM of Pb(ClO$_4$)$_2$.

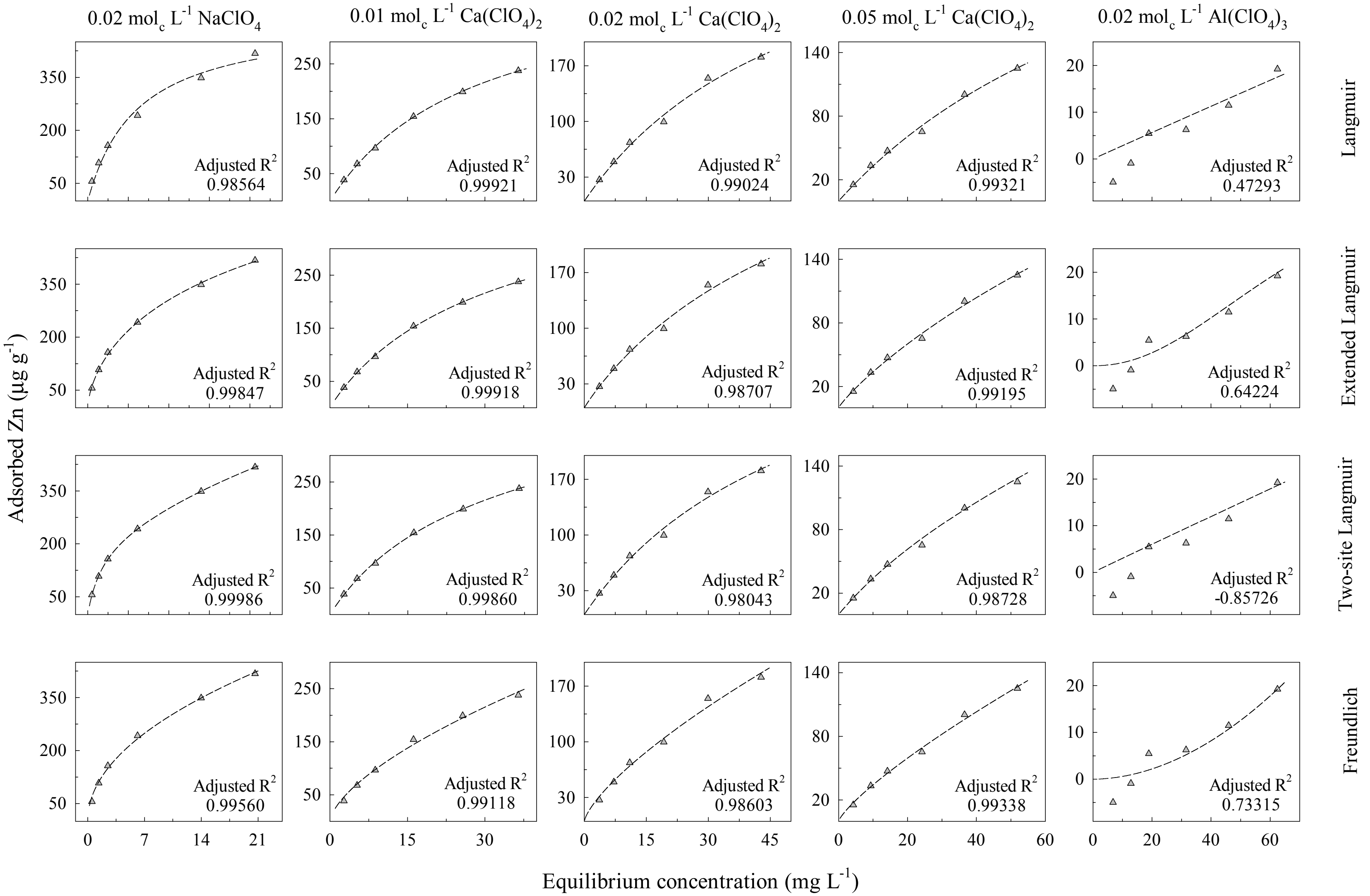

Fig. B.11. Comparison of four different adsorption isotherm equations (Langmuir, Extended Langmuir, Two-site Langmuir, and Freundlich) for Zn adsorbed by Bertie soil in rpresence of various background electrolytes. Initial concentration ranged from 0.1 mM to 1.0 mM of Zn(ClO$_4$)$_2$.

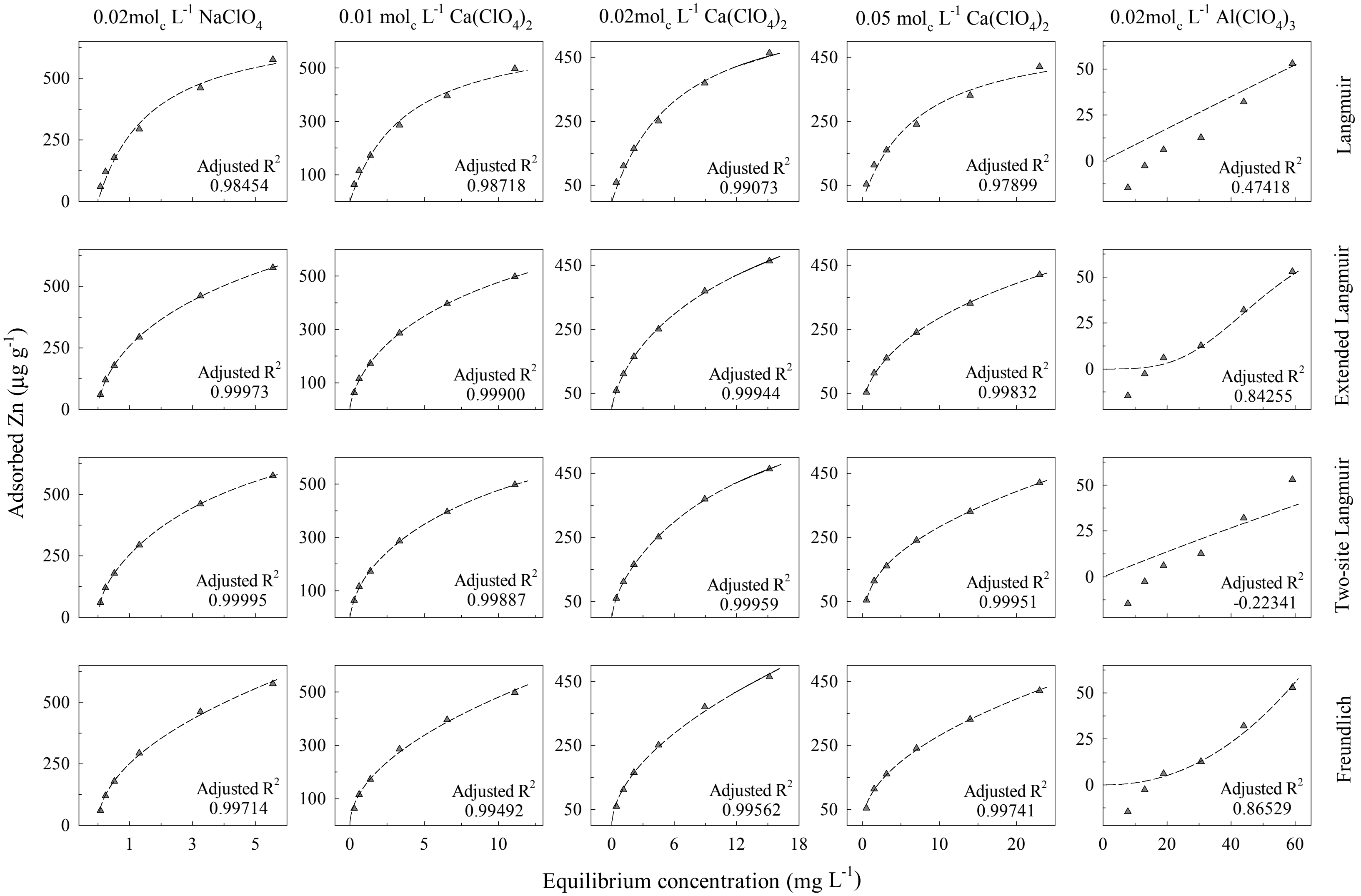

Fig. B.12. Comparison of four different adsorption isotherm equations (Langmuir, Extended Langmuir, Two-site Langmuir, and Freundlich) for Zn adsorbed by Starr-Dyke soil in presence of various background electrolytes. Initial concentration ranged from 0.1 mM to 1.0 mM of Zn(ClO$_4$)$_2$.

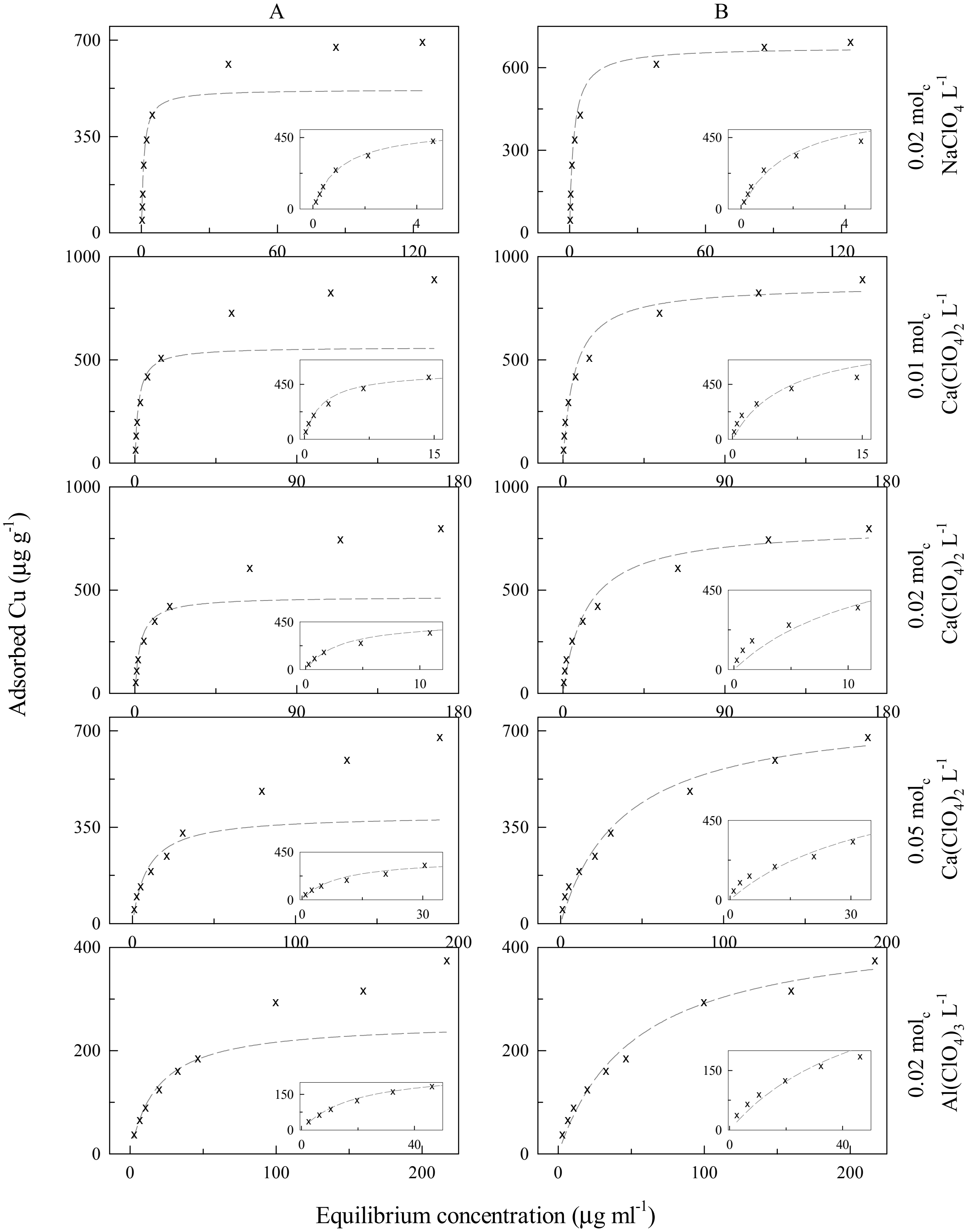

Fig. C.1. Comparison of fit of the nonlinear Langmuir equation using different initial concentration ranges (A; 0.1 mM ~ 1.0 mM; and B, 0.1 mM ~ 4.0 mM) of Cu adsorption in Bertie soil.

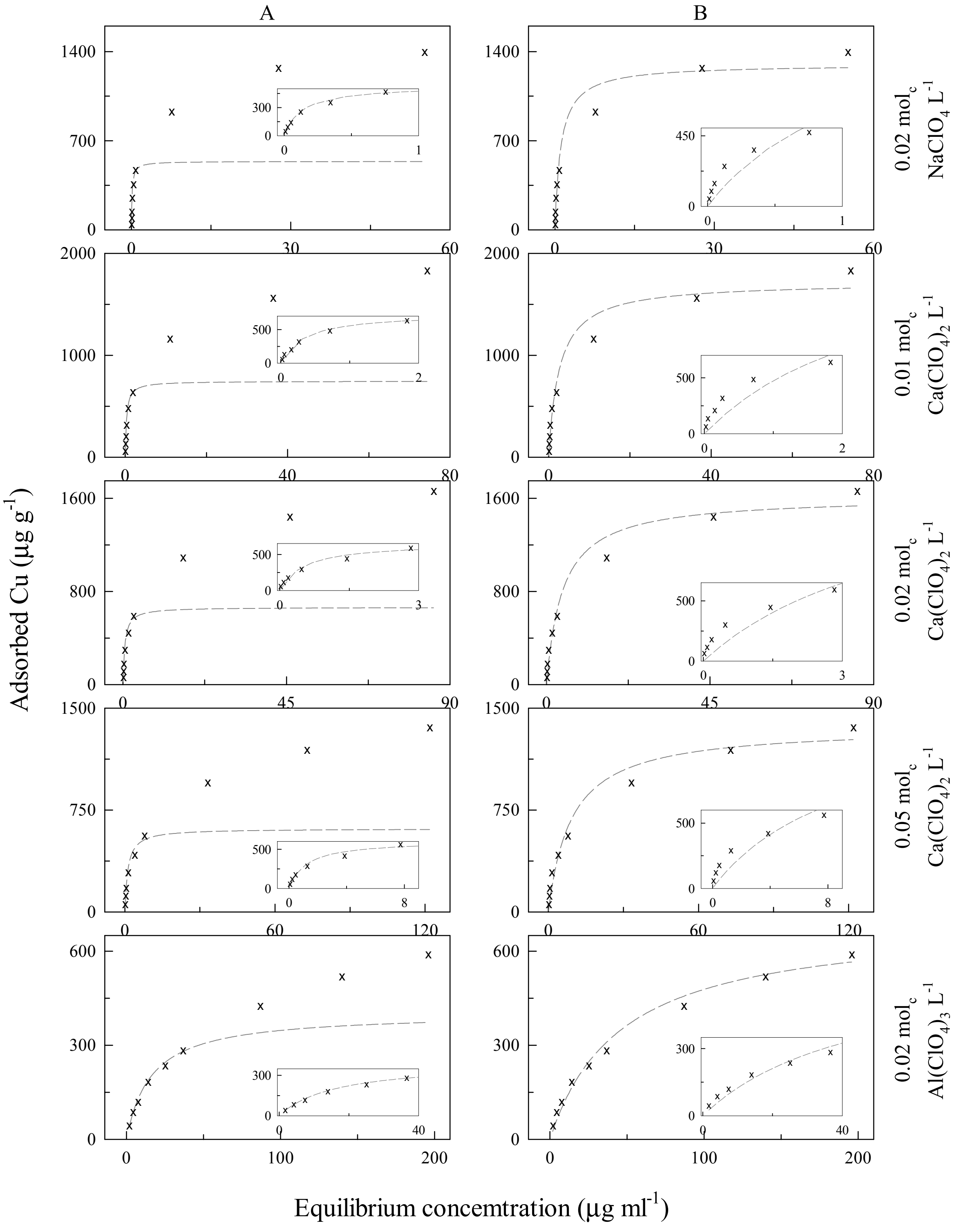

Fig. C.2. Comparison of fit of the nonlinear Langmuir equation using different initial concentration ranges (A; 0.1 mM ~ 1.0 mM, and B; 0.1 mM ~ 4.0 mM) of Cu adsorption in Starr-Dyke soil.

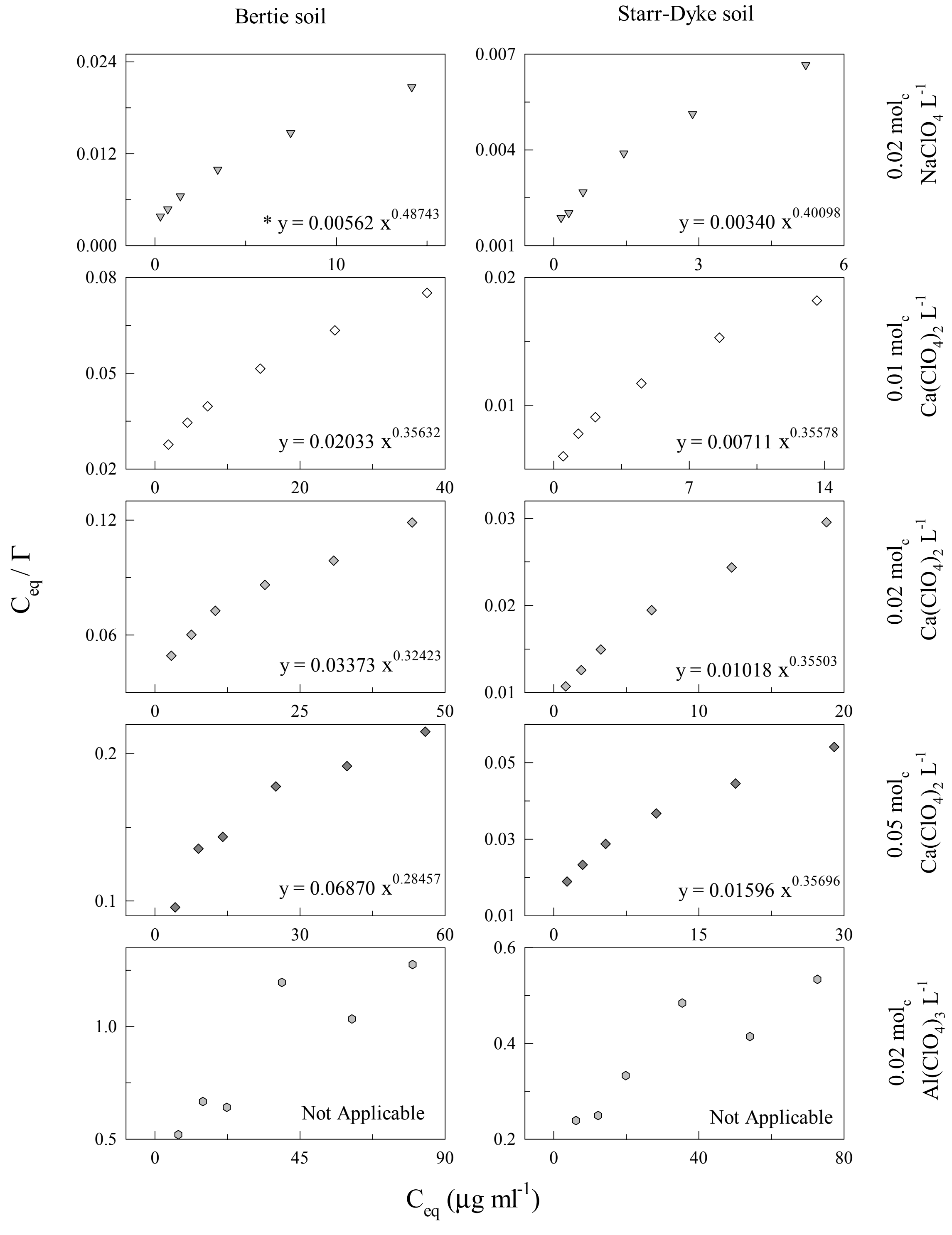

Fig. C.3. Cadmium adsorption with linear transformation of the Langmuir equation in Bertie and Starr-Dyke soils. Initial concentration of $Cd(ClO_4)_2$ ranged from 0.1 mM to 1.0 mM.

* Equations in each plot show the general exponential form for fitting the curve, where y = ax^b.

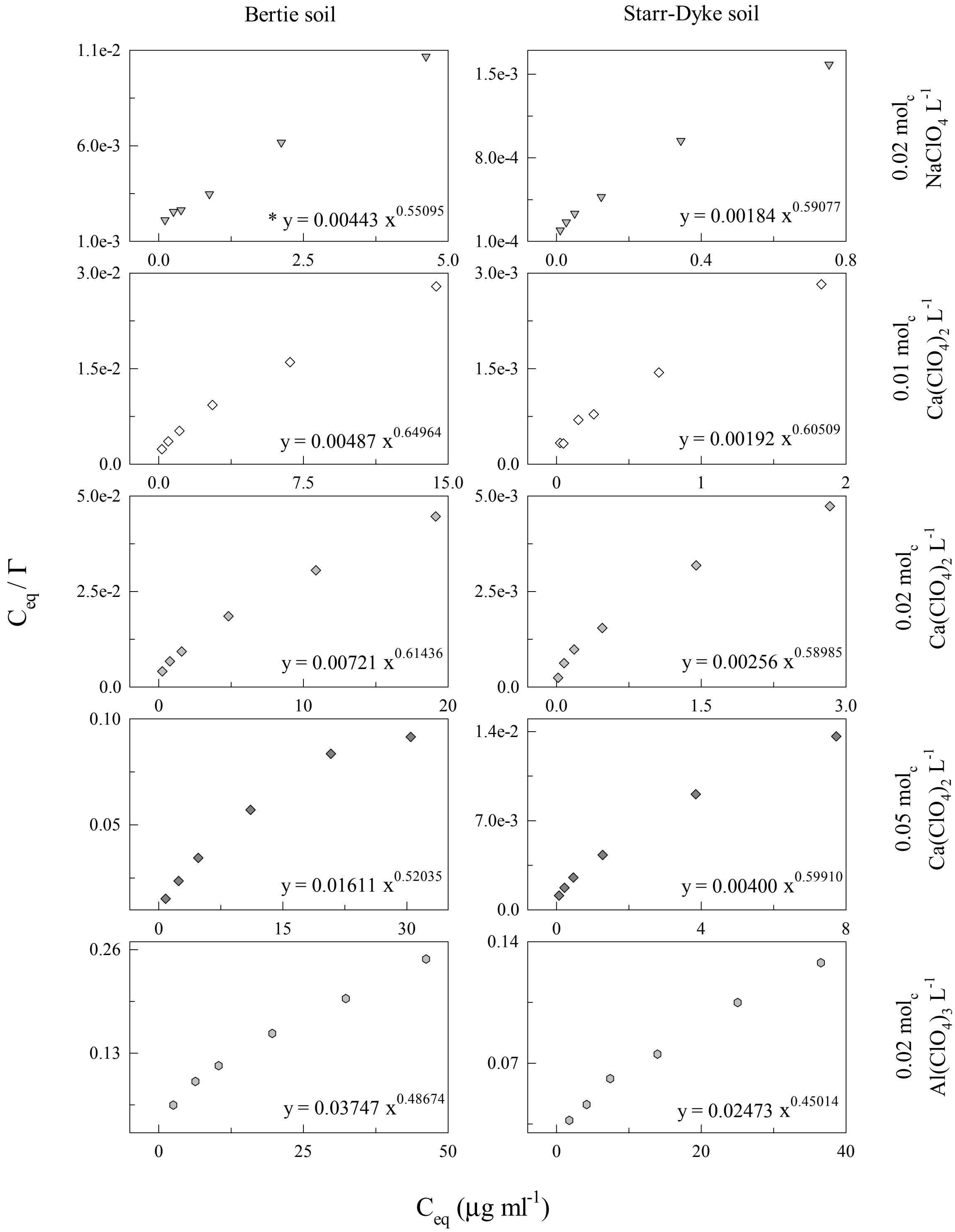

Fig. C.4. Copper adsorption with linear transformation of Langmuir equation in Bertie and Starr-Dyke soil. Initial concentration of $Cu(ClO_4)_2$ is from 0.1 mM to 1.0 mM.

* Equations in each plot show the general exponential form for fitting the curve, where y = ax^b.

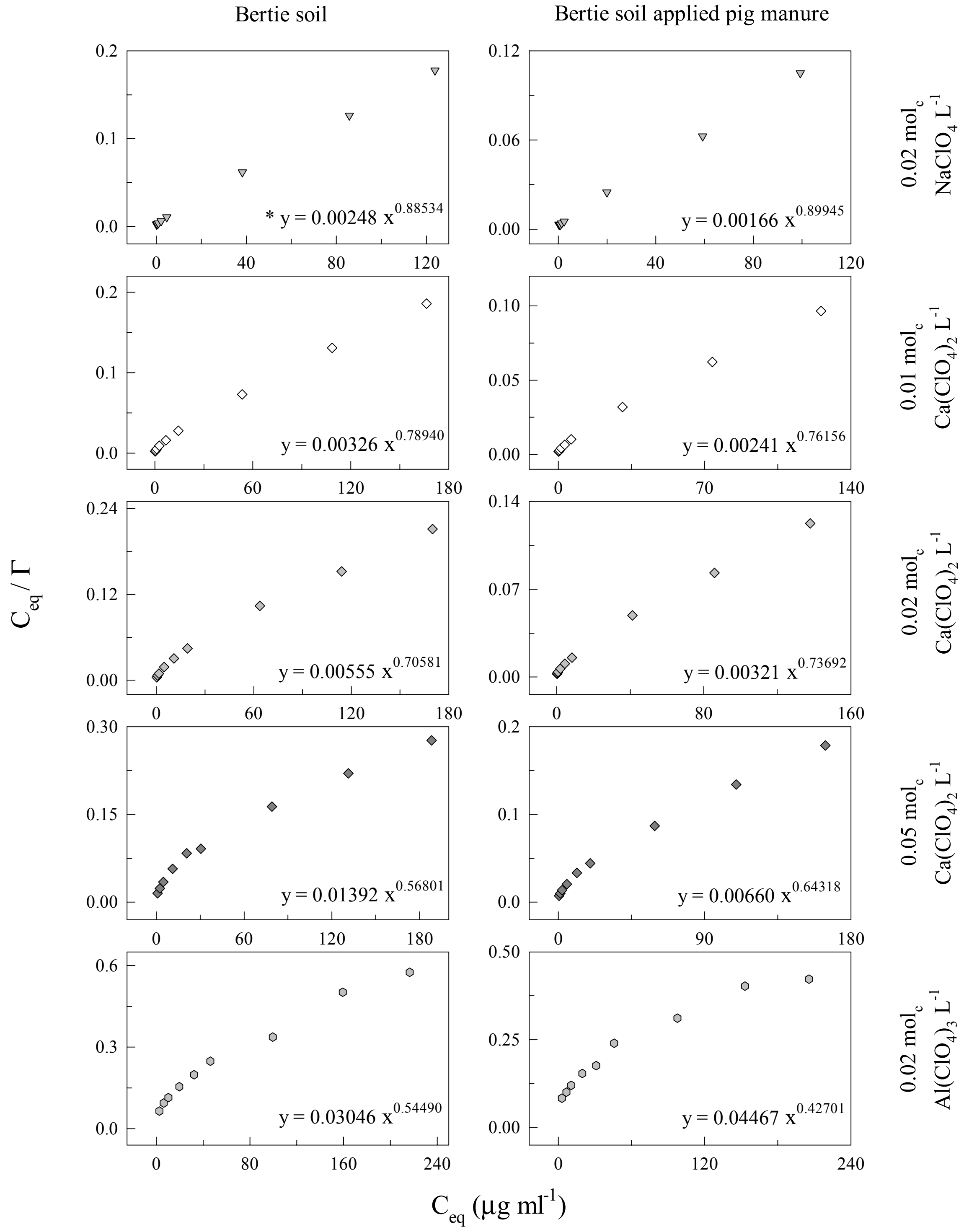

Fig. C.5. Copper adsorption with linear transformation of the Langmuir equation in Bertie soil with or without applied pig manure. Initial concentration of $Cu(ClO_4)_2$ ranged from 0.1 mM to 4.0 mM.

* Equations in each plot show the general exponential form for fitting the curve, where y = ax^b.

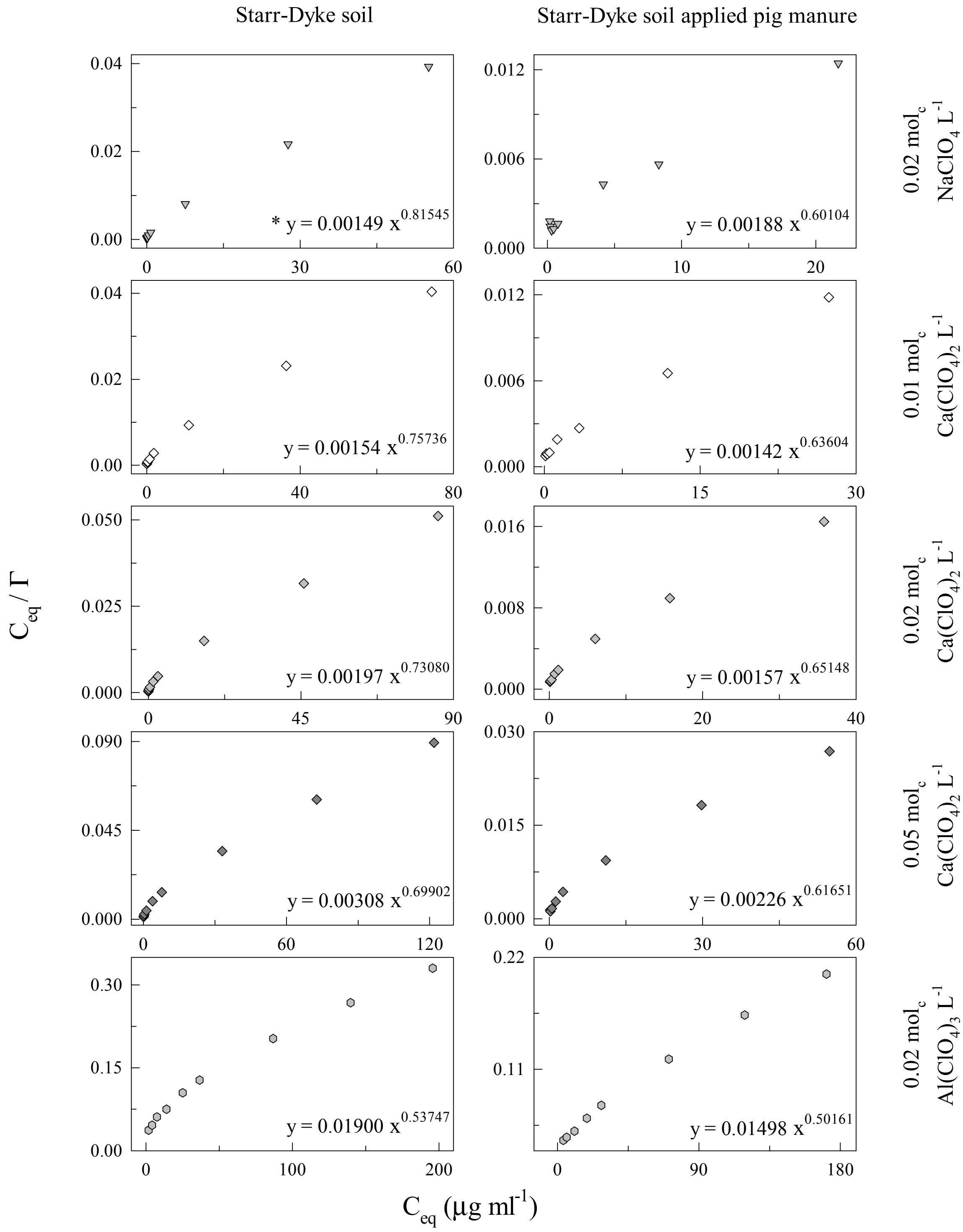

Fig. C.6. Copper adsorption with linear transformation of the Langmuir equation in Starr-Dyke soil with or without applied pig manure. Initial concentration of $Cu(ClO_4)_2$ ranged from 0.1 mM to 4.0 mM.

* Equations in each plot show the general exponential form for fitting the curve, where y = ax^b.

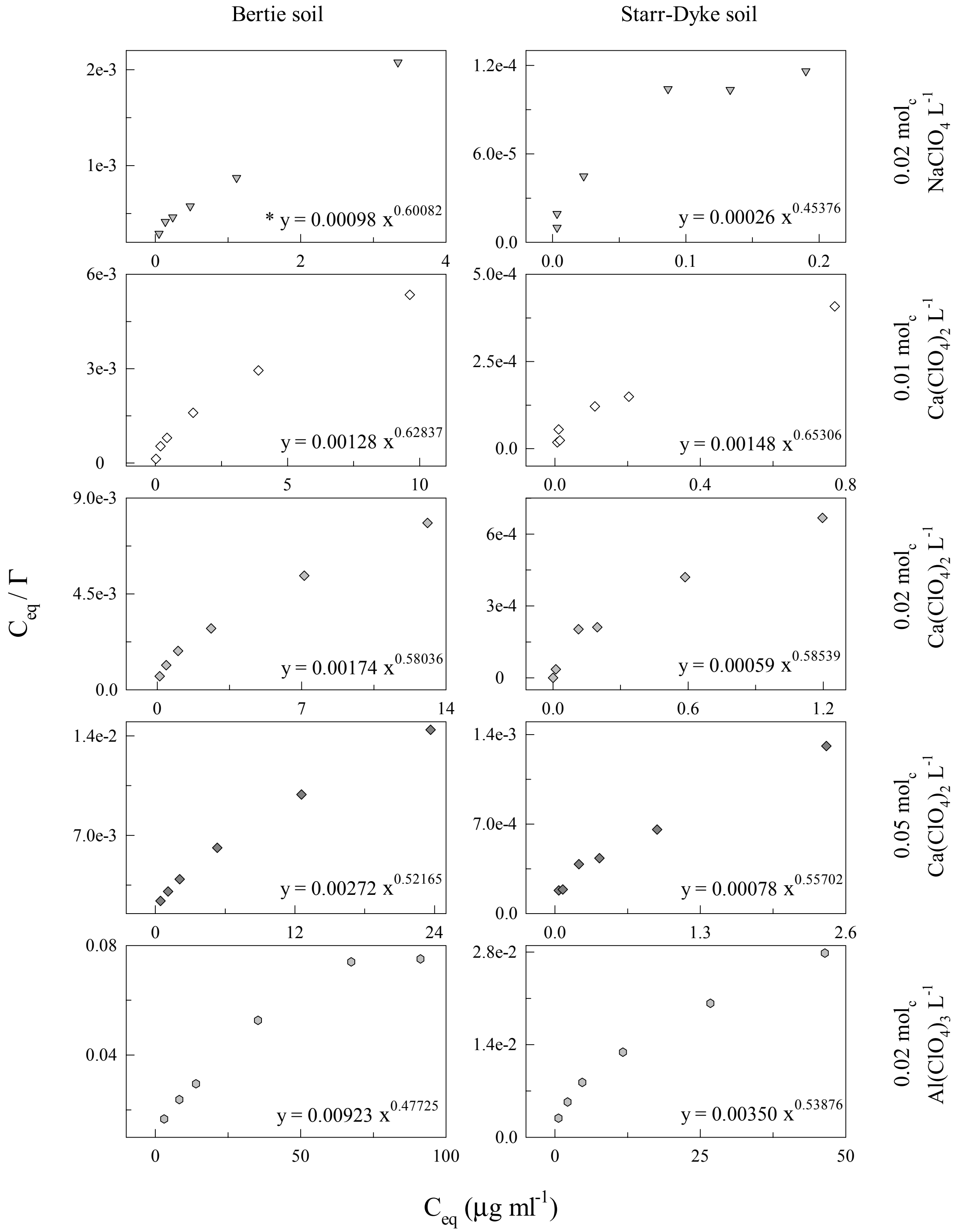

Fig. C.7. Lead adsorption with linear transformation of the Langmuir equation in Bertie and Starr-Dyke soils. Initial concentration of $Pb(ClO_4)_2$ ranged from 0.1 mM to 1.0 mM.

* Equations in each plot show the general exponential form for fitting the curve, where y = ax^b.

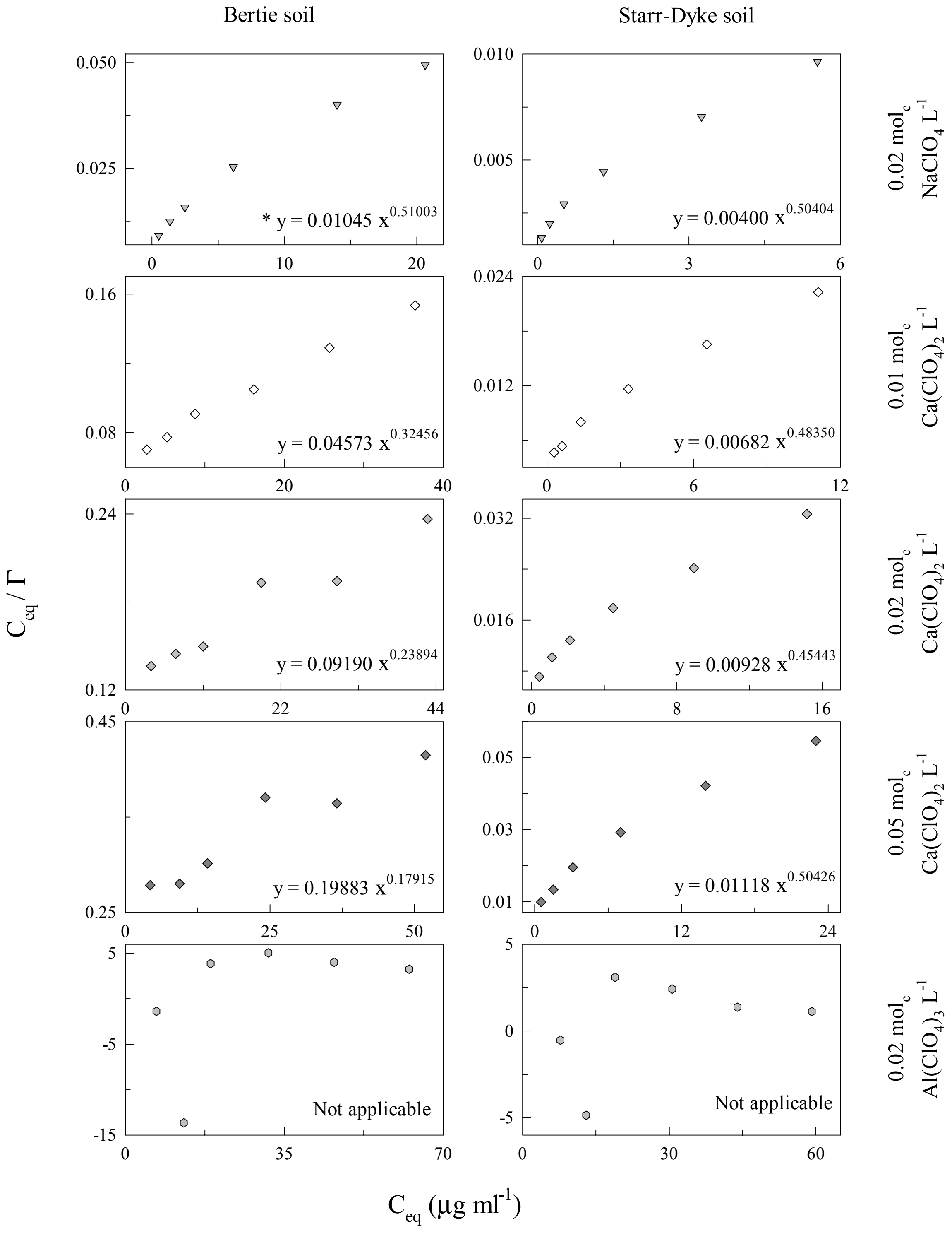

Fig. C.8. Zinc adsorption with linear transformation of the Langmuir equation in Bertie and Starr-Dyke soils. Initial concentration of $Zn(ClO_4)_2$ ranged from 0.1 mM to 1.0 mM.

* Equations in each plot show the general exponential form for fitting the curve, where y = ax^b.

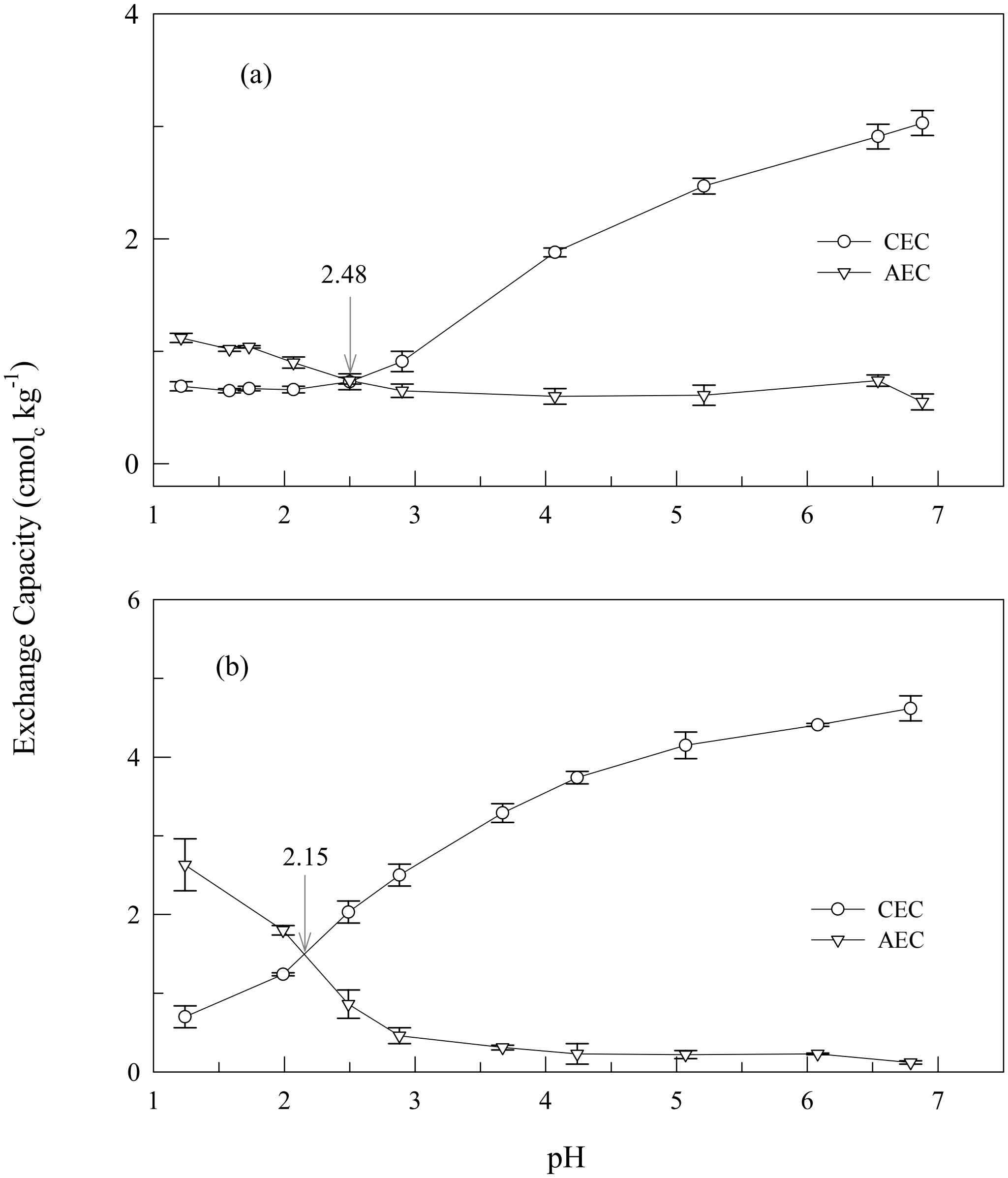

Fig. D.1. Point of zero net charge (PZNC) for Bertie (a) and Starr-Dyke (b) soils.

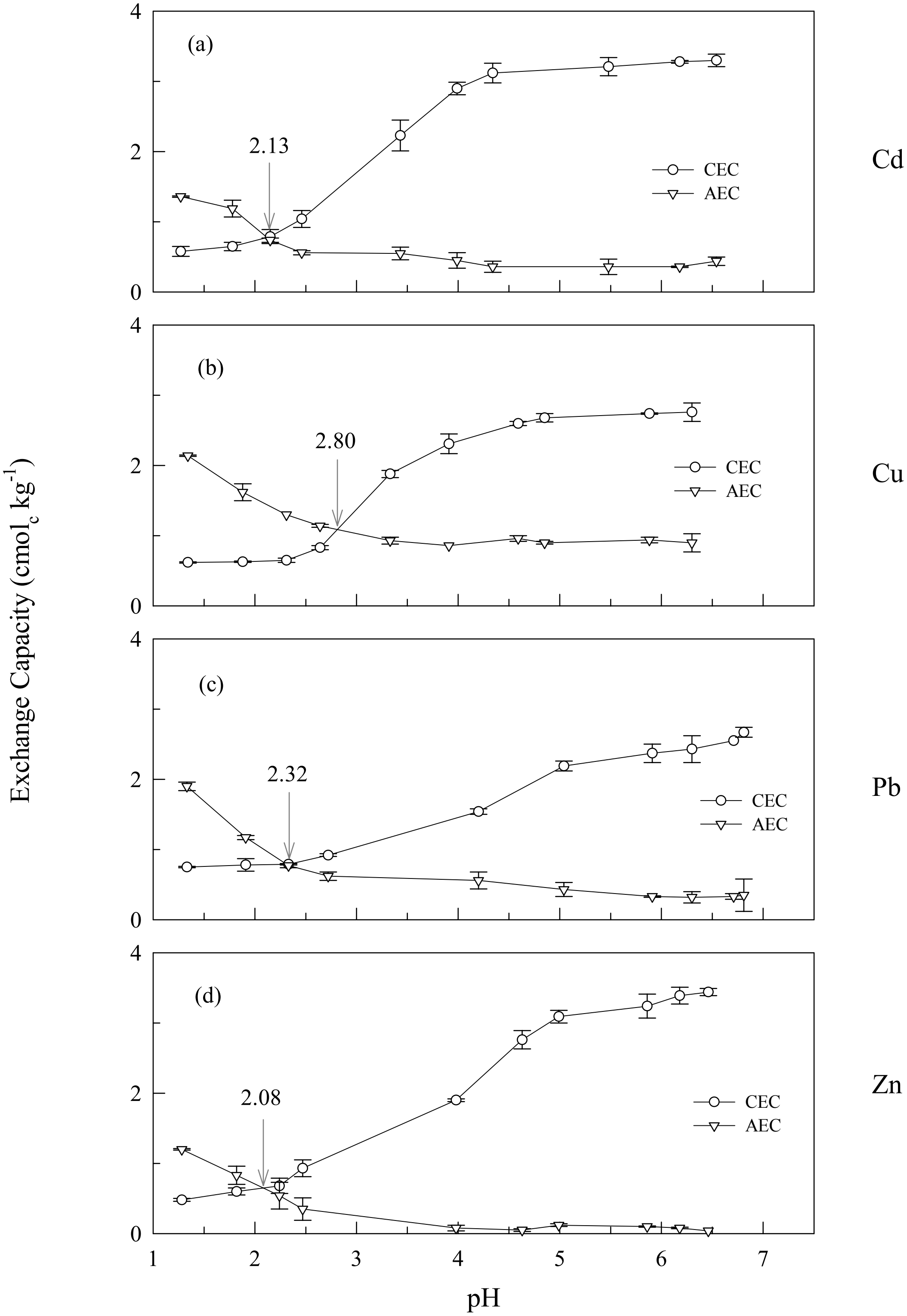

Fig. D.2. Point of zero net charge (PZNC) for Berti soil after Cd adsorption(a), after Cu adsorption(b), after Pb adsorption(c), and after Zn adsorption(d).

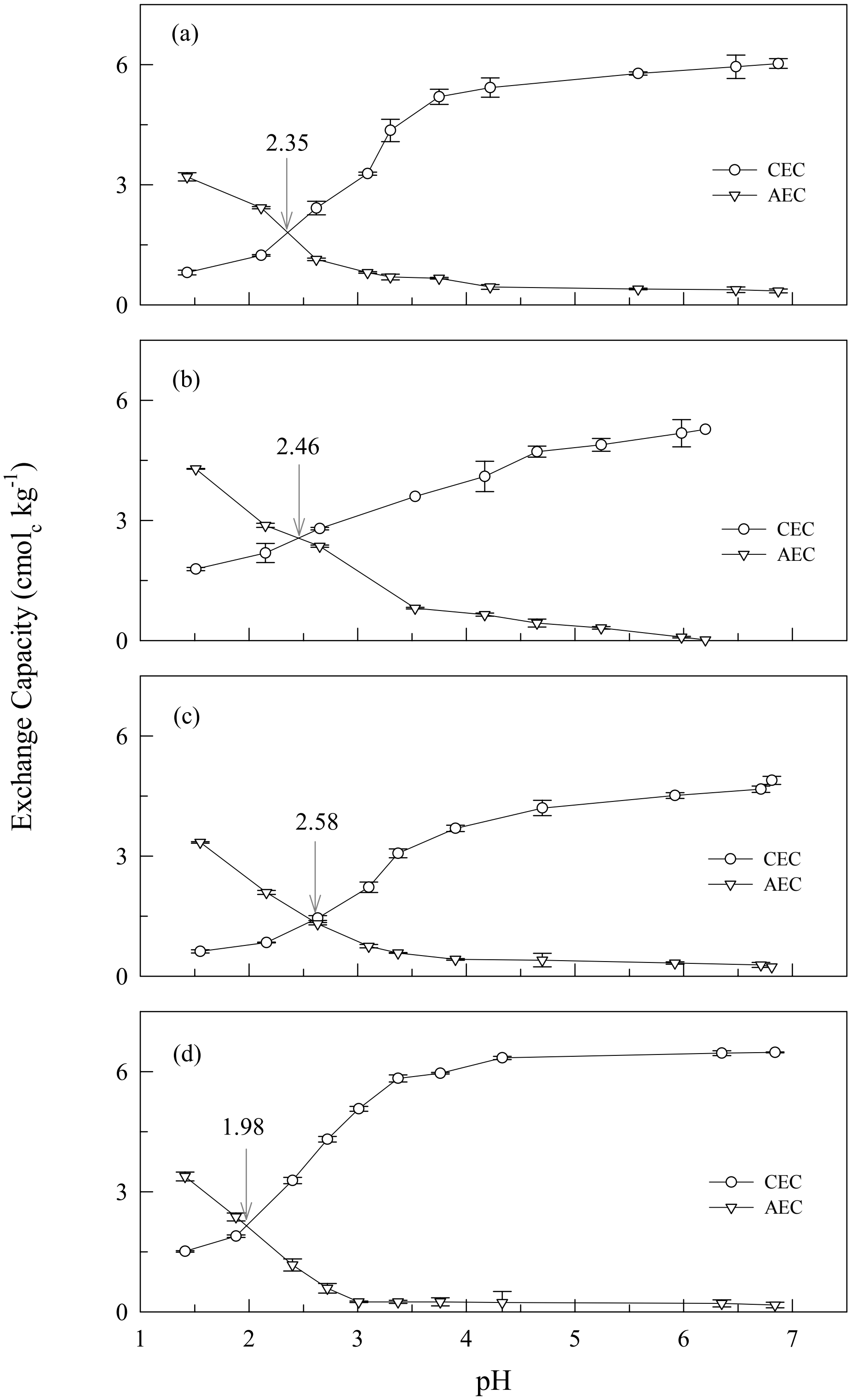

Fig. D.3. Point of zero net charge (PZNC) for Starr-Dyke soil after Cd adsorption (a), after Cu adsorption (b), after Pb adsorption (c), and after Zn adsorption (d).

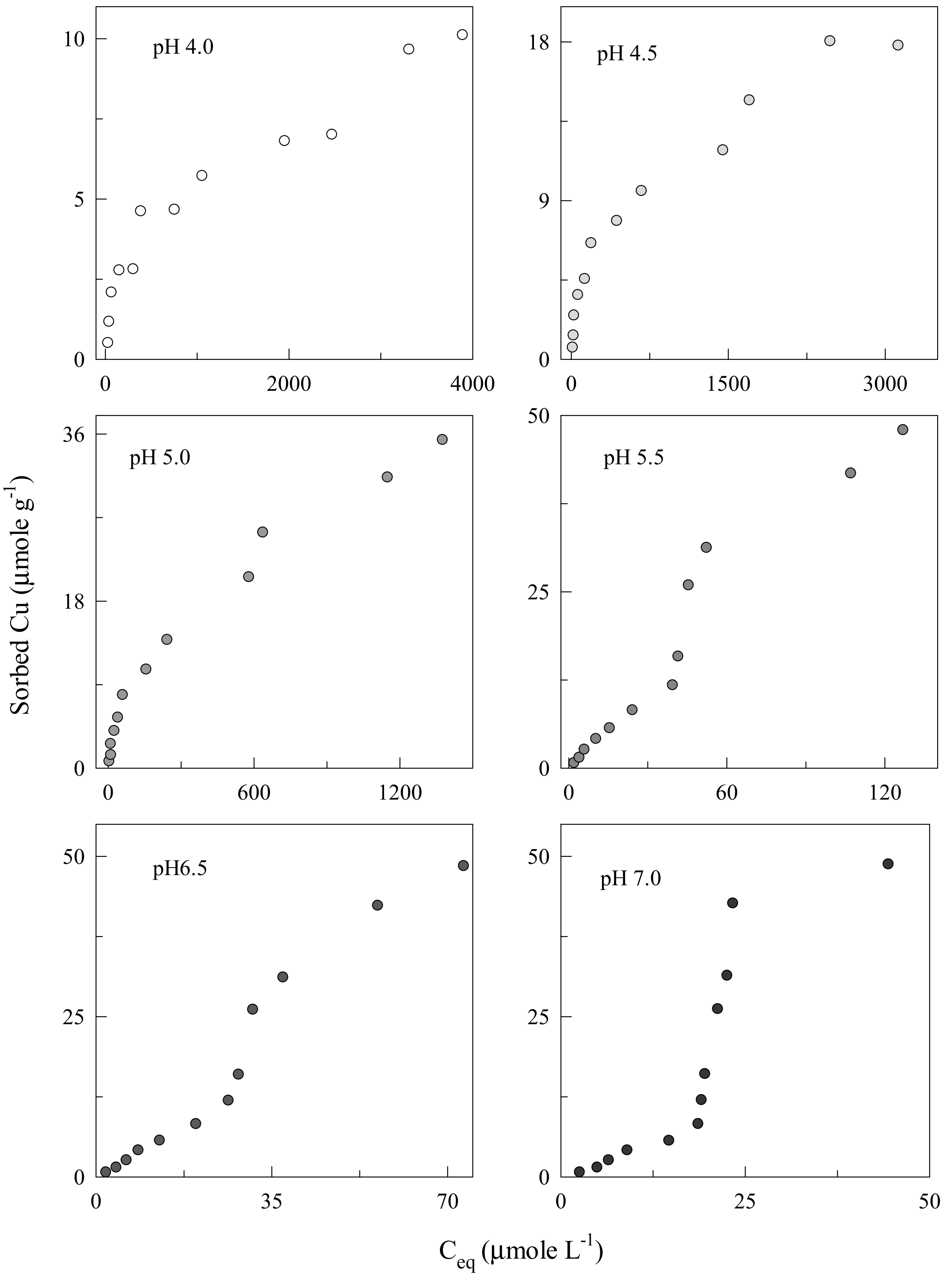

Fig. E.1. Adsorption isotherms for Bertie soil at different pH levels.

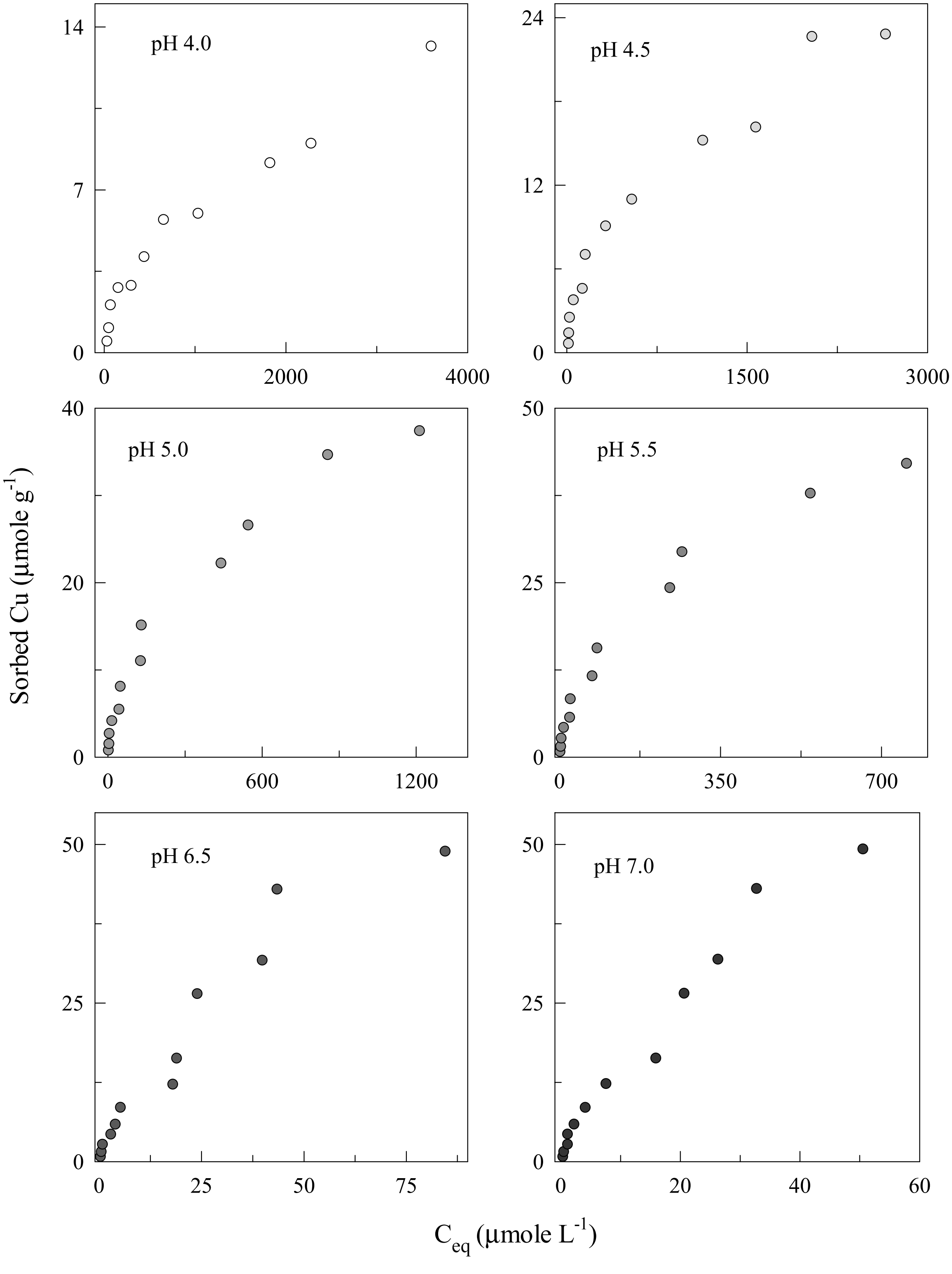

Fig. E.2. Adsorption isotherms for Starr-Dyke soil at different pH levels.

VITA

Wonae Bong Fike was born Wonae Bong in Seoul, Republic of Korea. She attended Korea University studying in the Department of Agricultural Chemistry and was one of only three women in her class. She received her B.S. in 1982. She returned to Korea University for her M.S. degree in 1986.

From 1987 to 191 she held the position of Junior Researcher in the Soil Chemistry Division of the Agricultural Science Institute, in Korea. Her research focused on organic matter in soil systems. In 1992 she began efforts on her Ph.D. at Virginia Polytechnic Institute and State University.

During her academic career she has received numerous awards including: he Un-Jung Fellowship (a full scholarship), the Hankuk Foundation Fellowship, and the AAUW Educational Foundation Scholarship.

In 1996 she married John Hershcel Fike and in 1998 became the proud mother of Jonah Paul Bong Fike.