

Studies on Heavy Metal Ion Adsorption by Soils.

(Part 1) PH and phosphate effects on the adsorption of Cd, Cu, Ni and Zn by mineral soils with low CEC and low organic carbon content.

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(Received Aug. 4, 1977)

重金屬 이온의 土壤 흡착에 관한 연구

(제1보) CEC 및 유기탄소 함량이 낮은 광물토양에의 Cd, Cu, Ni, 및 Zn의 흡착과 이에 미치는 pH 및 인산의 효과

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(1977년 8월 4일 수리)

ABSTRACT

The information related to the heavy metal pollution in the environment was obtained from studies on the effects of pH, phosphate and soil properties on the adsorption of metal ions (Cd, Cu, Ni, and Zn) by soils. Three soil materials; soil 1 with low CEC (8.2 me/100g) and low organic carbon content (0.34%); soil 2 with high CEC (36.4 me/100g) and low organic carbon content (1.8%) and soil 3 with high CEC (49.9 me/100 g) and high organic carbon content (14.7%) were used. Soils were adjusted to several pH's and equilibrated with metal ion mixtures of 4 different concentrations, each having equal equivalents of each metal ion (0.63, 1.88, 3.12 and 4.38 micromoles per one gram soil with and without 10 micromoles of phosphate per one gram soil).

Reported here are the results of the equilibrium study on soil I. The rest of the results on soil 2 and soil 3 will be reported subsequently. Generally higher metal ion concentration solution resulted in higher final metal ion concentrations in the equilibrated solution and phosphate had minimal effect except it tended to enhance removal of cadmium and zinc from equilibrated solutions while it tended to decrease the removal of copper and nickel.

In soil 1, percentages of added metal ions removed at pH 5.10 were; Cu 97, Ni 69, Cd 63, and Zn 55, while increasing pH to 6.40, they were increased to Cu 90.9, Zn 99, Ni 96, and Cd 92 per

As initial metal ion concentration increased, final metal ion concentrations in the equilibrated solution showed a relationship with pH of the system as they fit to the equation $p[M^{++}] = a \text{ pH} + b$ where $p[M^{++}] = -\log[\text{metal ion concentration in Mol/liter}]$. The magnitude of pH and soil effects were reflected in slope (a) of the equation, and were different among metal ions and soils. Slopes (a) for metal ions in the aqueous system are all 2. In soil 1 they were; Zn 1.23, Cu 0.99, Ni 0.69 and Cd 0.59 at highest concentration. The adsorption of Cd, Ni, and Zn in soil 1 could be represented by the Langmuir isotherm. However, construction of the Langmuir isotherm required the correction for pH differences.

INTRODUCTION

Growing concern over possible heavy metal pollution of the environment has been widely expressed as research reports on the hazardous effect of heavy metals on plants, animals and man accumulate in increasing numbers. The location of heavy metal contaminations range from the direct vicinity of man's residence to the animal and plant habitat, because of the transportation of these metals in the air, and water. Perhaps the most obvious sources of these heavy metals in the environment would be the ever increasing industrial products or byproducts containing these heavy metals. One of the major byproducts of industrial activities are waste materials, and depending on the waste disposal practices, air, water and soils are subject to the possible pollution by these metals.

If these metals are released to the air, they will eventually settle to water, soil or plant surfaces to further react in the water system, soil system, soil system or plant system. In the water system, they will go through subsequent reactions with aquatic plants, animals or bottom sediments. Heavy metals introduced to the soil system will also go through adsorption, desorption, precipitation and other reactions in the soil matrix and uptake and assimilation by soil organisms and higher plants. Further possibilities are the accumulation and concentration of these

metals through the food chain thus giving hazardous influences to animal and human health.

Among the waste disposal practices, spreading waste on agricultural land has been one of the common practices. According to Chaney (1973) the philosophy of land application is "to use land to contain toxic metals, to prevent pollution of air and water; manage to prevent injury to food chain." suggesting the capability of soil to immobilize heavy metals in such a way as to reduce their availability to plants, animals, and man, or their possibility to concentrate through the food chain. There are many reports supporting this philosophy as long as the condition of soils is favorable for "containing" these metals, however, these conditions are still being investigated due to their complicated inter-relationships with various plant species and their interaction among one another and between them and soil components of various properties.

The kinds abundance of elements vary from one waste material to another depending on their source materials, locality and so on. According to Chaney (1973), Page (1974) Leeper (1973) and Lihdsay (1973) Potentially hazardous elements are generally As, B, Ba, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, P, Pb, Se, Zn, and V in the sewage wastes. Not all of them are essential "heavy metal ions" in a chemical sense (Leeper 1973).

Among these elements, Cu, Ni, Zn and Cd (hereafter, heavy metal ions) have been getting considerable attention since these four metals are

not normally found in soils in large quantities while their amounts in sewage wastes are quite higher (Chaney 1973, Lindsay 1973, and Page 1974). Leeper (1973) grouped these heavy metal ions together as potentially hazardous heavy metals added to soil as foreign elements. These metal ions have some properties in common. They are bivalent, hydrolyzed and are potentially toxic. Except Cd, they are linked together in England where a "Zn equivalent" of waste is computed from the formula $Zn+2Cu+8Ni$, suggesting that Cu is twice as toxic as Zn and Ni is 4 times as toxic as Cu to plants. Even though the Cd content is low compared to the others, this element is considered hazardous to the food chain at low levels due to its adverse effect on human health.

Cu and Zn have been extensively studied on their solubility in soils, uptake by plants and many factors that control, since they are essential micronutrients to plants. (Reuther and Smith, 1954, McBride and Mortland, 1974, Chapman, 1966, Bingham et al. 1964). Ni also has been subject to considerable research work due to its toxicity to plants and its abundance in serpentine soils. ⁽⁹⁾ ⁽¹⁰⁾ Recent discoveries on the adverse effect of Cd on human health has led to concentrated studies on the behavior of Cd in the environment.

In judging the possibility of "containing" the metal ions in soils, reactions of these metal ions with soils such as adsorption, desorption, precipitation, and reversion to less extractable forms should be well understood.

Among many factors that influence those reactions mentioned above, pH, cation exchange capacity, clay minerals, organic matter, Fe and Mn oxides and phosphates of the soils are the major ones studied intensively (Leeper 1973, Crooke 1956).

It has been confirmed that pH plays an important role on the solubility of these metal ions, and also many reports suggest that phosphate interaction with these metal ions are substantial (Leeper 1973, Chapman 1966, Crooke 1956, Hodgson 1963). Since these metal ions are introduced to soils together as the result of waste disposal on land, studying them simultaneously becomes desirable. Therefore metal ion mixture were reacted with soils of different properties adjusted to different pH and phosphate levels in order to investigate the effect of their variables on the adsorption of the metals by soils.

Materials and Methods

1. Materials.

Soil material with low CEC, low organic carbon content was collected from the 6-12 inch layer of a Freehold sandy loam soil at the Rutgers Soils and Crops Research Farm, Adelphia, New Jersey, U.S.A.

New Jersey. Some general characteristics of the three soil materials pertinent to this study are shown in Table. 1

2. Methods

Preparation of Soil material

Table 1. General Characteristics of Soils for the Equilibrium study

Soil	pH	CEC (m.e./100gm)	Exch. Cations (m.e./100g)				organic carbon (%)	Mechanical Analysis		
			Ca	Mg	K	Na		Sand (%)	Silt(%)	Clay(%)
Freehold Sandy loam	5.85	8.22	1.85	0.25	0.15	0.15	0.34	61	12	27
Extractable Metal Ions (ppm) of Freehold SandS Loam			Cd	Cu	Ni	Zn				
1N-NH ₄ OAL			ND*	0.5	ND	0.5				
DTPA			ND	1.6	ND	5.3				
0.1N-HCl			ND	2.2	0.6	7.0	*not detected.			

To investigate the adsorption of metal ions, the soils were treated so as to have different initial pH and phosphorus levels. The pH adjustment was made by adding amounts of CaCO₃ selected from the lime requirement curve to produce pH's between the original soil pH and pH 7 and by incubating. Slightly excess amounts of CaCO₃ were added to account for the acidity in the metal ion solution. The amounts of CaCO₃ added in lime treatments 0, 1, 2 and 3 were 0, 108, 215 and 324mg per 100gm of soil. Soils were then brought to nearly saturation and incubated for one month at room temperature. After one month, each CaCO₃ treated soil was air dried and ground

to pass a 2mm screen.

The phosphorus treatment (31mg P/100gm soil) was made when the metal ion solutions were added.

3. Preparation of mixed metal ion solutions

Stock solutions were prepared for each metal ion and by mixing and diluting appropriate amounts, four different concentrations of mixed metal ion solutions were made. In each of these solutions there was an equal equivalent concentration of the four metal ions as described in Table 2. For the phosphorus treatment, these concentrations were prepared in solutions containing 0.002M P as KH₂PO₄.

Table 2. Concentrations of Mixed Metal Ion Solutions

Solution	Total Conc. (mMol)	Conc. of Each Metal Ion (mMol)	Conc. (ppm) of Each Metal Ion			
			Cd	Cu	Ni	Zn
1	0.5	.125	15.5	7.75	7.38	8.25
2	1.5	.375	46.5	23.25	22.13	24.75
3	2.5	.625	77.5	38.75	36.88	41.25
4	3.5	.875	108.5	54.25	51.63	57.75

4. Procedure

Fifty ml of the mixed metal ion solution of each concentration level and phosphorus level was added to duplicate 10gm samples of each treated soil in a 100ml plastic bottle. The bottles were then closed and equilibrated for one week in room temperature. During this period, the bottles were shaken for 10-20 seconds once a day. After one week of equilibration, a portion of each sample was filtered through Whatman No. 42 filter paper and the filtrates were subject to analysis for Cd, Cu, Ni and Zn by Atomic Absorption Spectrophotometer (Jarrell-Ash model 810) with background correction with non-absorbing lines.

RESULTS AND DISCUSSION

As shown in Table 3 and Figure 1 and 2, the results indicates that pH, phosphate and initial metal ion concentrations affected the final concentrations of metal ions.

Generally increasing pH reduced final concentrations of metal ions although degrees to which each metal ion were affected by pH were different from one another. Phosphate seemed to enhance the removal of cadmium and zinc from solution at concentrations 2, 3 and 4, and depress the removal of nickel and copper. At concentrations 3 and 4, when no phosphate was added, cadmium was the least removed, then nickel which was less removed than zinc. Copper adsorption was the most at a constant pH. As pH was increased, the differences between metal ions were more pronounced. But when phosphate was added, nickel was removed less than cadmium as shown in Figure 2. At concentration 1 and 2, the order of removal found was not similar to that of higher concentrations probably due to low final concentrations of all metal ions which was in the range of the limit of detection by atomic absorption spectrophotometry.

1. Solubility concept

Removal of metal ions from equilibrated solution

Table 3. Percent of Metal Ions Removed from Solutions Equilibrated with Soils
A. Freehold Sandy Clay Loam

Treatment		No Phosphate Added					Phosphate Added				
Metal	Lime Conc.	pH	Cd	Cu	Ni	Zn	pH	Cd	Cu	Ni	Zn
0	1	6.25	97.7	99.5	96.8	98.4	5.87	96.8	97.9	94.2	97.8
	2	5.60	86.6	99.3	86.7	86.9	5.50	88.5	98.3	86.0	89.7
	3	5.40	77.5	98.2	76.0	72.4	5.22	79.9	97.4	74.2	80.1
	4	5.10	62.6	96.8	68.9	54.9	5.07	68.2	95.8	63.6	54.9
1	1	6.60	99.2	99.6	98.1	99.5	6.62	98.9	98.5	96.9	99.4
	2	6.40	96.4	99.7	96.9	99.2	6.25	96.3	99.0	93.2	98.7
	3	6.22	89.4	99.7	91.5	96.6	6.00	91.4	99.2	86.4	95.6
	4	5.90	82.3	99.6	83.2	90.0	5.75	85.2	98.9	76.8	87.9
2	1	6.90	99.9	99.6	98.8	99.6	7.05	99.4	98.7	98.2	99.6
	2	6.80	99.0	99.7	99.2	99.8	6.67	98.0	99.2	96.8	99.4
	3	6.50	96.0	99.9	98.4	99.6	6.32	94.5	99.3	92.4	98.3
	4	6.40	92.1	99.9	95.8	98.9	6.10	90.3	99.3	85.7	95.7
3	1	7.35	99.8	99.4	98.6	99.8	7.36	99.5	98.9	98.6	99.6
	2	7.20	99.2	99.8	99.3	99.9	6.82	98.4	99.3	97.7	99.7
	3	7.00	97.2	99.9	98.6	99.7	6.55	96.1	99.4	95.0	99.1
	4	6.60	93.3	99.9	96.9	99.2	6.25	91.9	99.4	88.9	97.1

with soils of different properties revealed several aspects on its characteristic with respect to the effects of pH and other soil properties. At high pH a distinctive order of removal among metal ions in mineral soils (copper zinc nickel cadmium) was inversely related to the solubility products of their hydroxide compounds (Sillen and Martell, 1964). However, the absolute amount of metal ions in the final solution was far below that predicated by the solubility products of metal ion hydroxides suggesting adsorption and chelation in addition to hydroxide formation as suggested by Lindsay (1972). Since it is quite obvious that numerous kind of reactions may have occurred during the equilibrium period, and since equilibrium in its true sense may not have been reached in this short period of time (Lindsay, 1972), total dependence on solubility concept may not give full explanation.

In the Freehold soil, when the pH was low, the distinct order of removal was not followed, except much higher removal of copper, indicating soil properties exceeds the pH and solubility

products. On the other hand, when pH was higher, the distinct order of removal was more clearly observed indicating the pH effect exceeded the effect of soil properties such as cation exchange capacity.

When phosphate was added, the order of removal changed from that without phosphate addition. In the Freehold sandyloam soil the altered order was inversely related to the solubility products of metal ion phosphate (Sillen and Martell, 1964) with nickel showing highest solubility.

The solubility of metal ion hydroxides in aqueous solution is represented by $p[M^{#}] = 2pH - 2pK_w + pK_{sp}$ where $p[M^{#}] = -\log[M^{#}]$, or by combining K_{sp} and K_w , $p[M^{#}] = 2pH + K$ is obtained. This then is a linear relationship with a slope of 2.

This solubility line for each metal ion hydroxide could not be included in the Figures presented in the result section because of the much lower concentration of metal ions in the solutions equilibrated with soils and the solubility lines

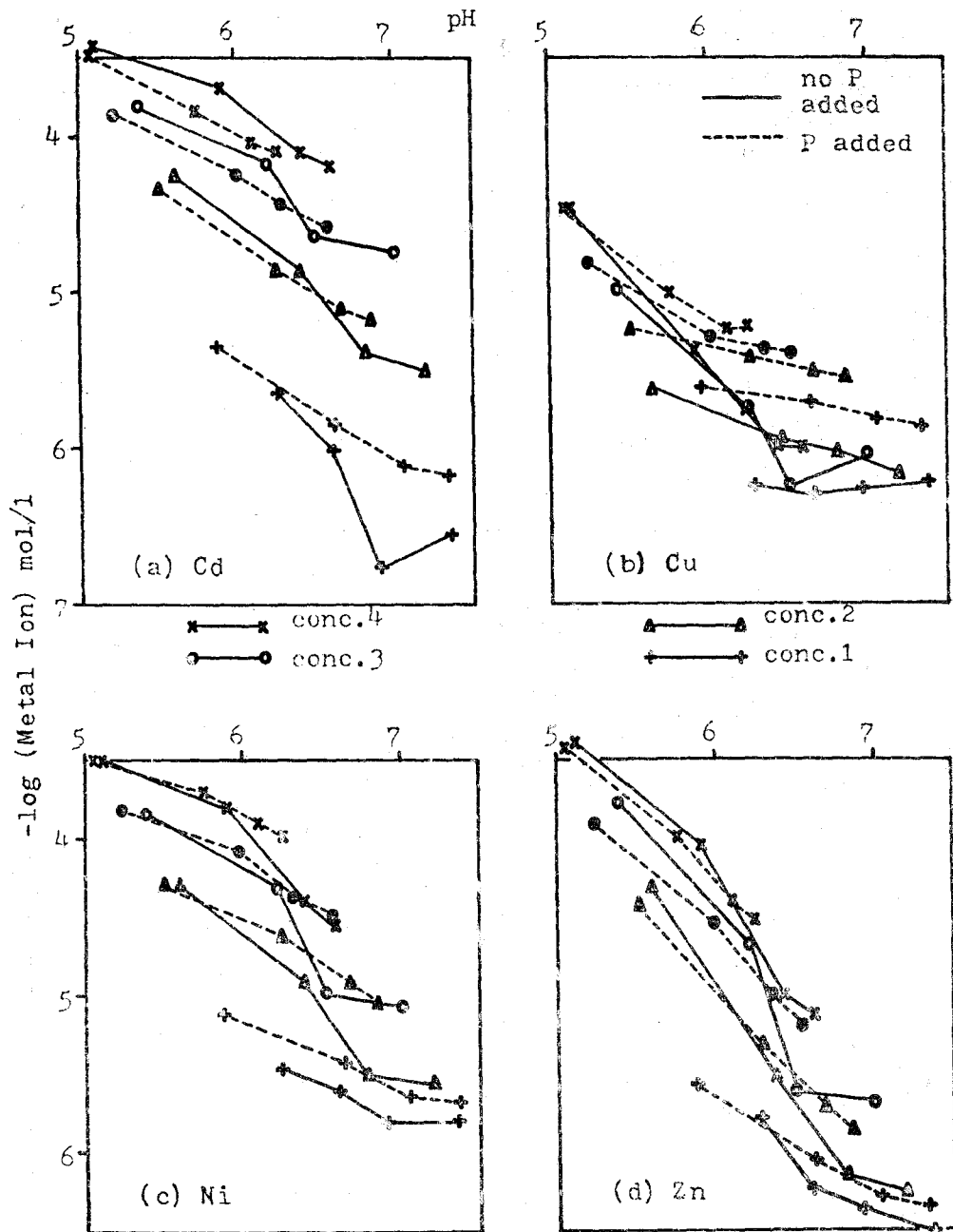


Fig. 1. Effects of pH and initial metal ion concentrations on their final concentrations in solutions equilibrated with freehold sandy clayloam.

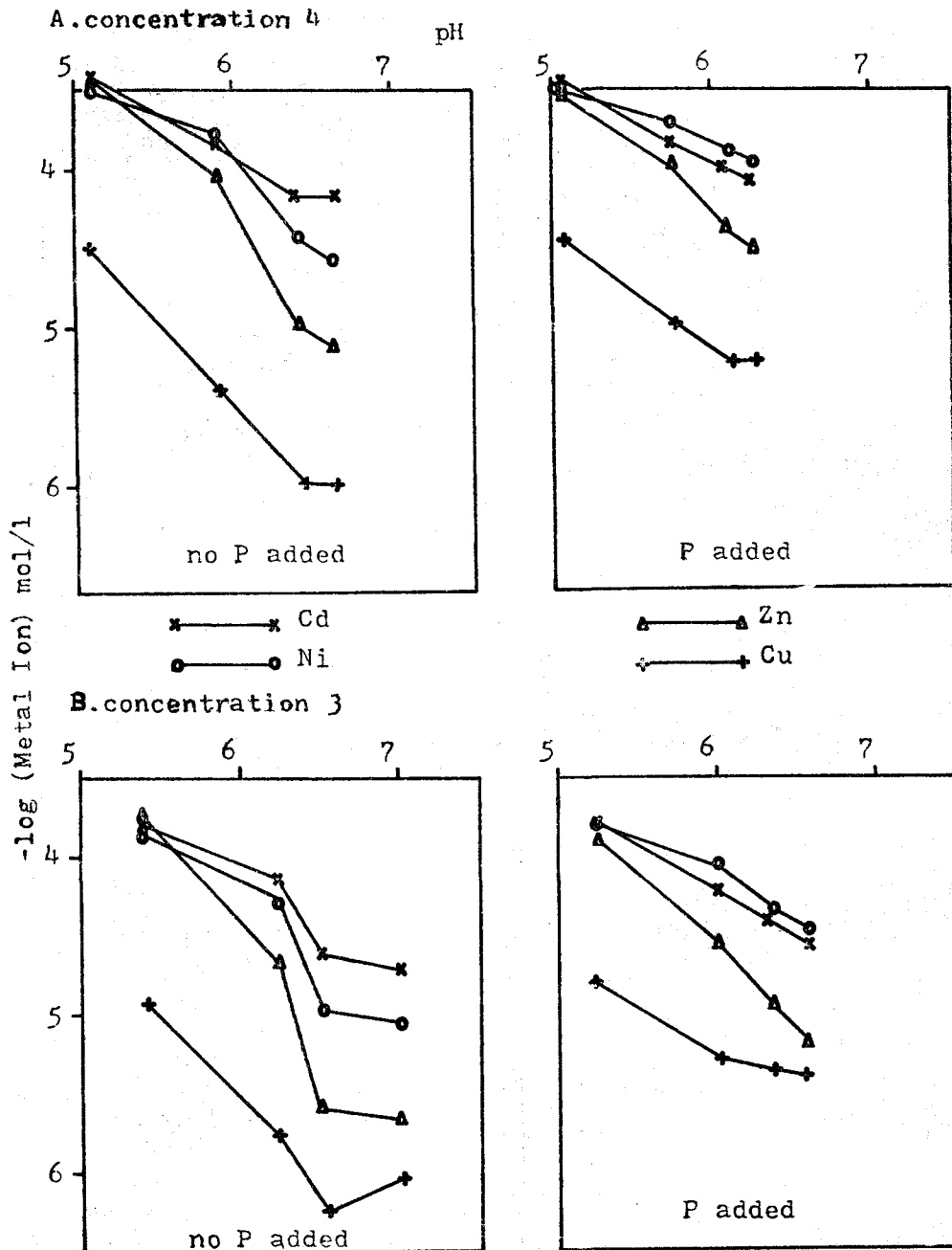


Fig. 2. Effect of pH on the final concentrations of each metal ion in solution equilibrated with freehold sandy clay loam.

of metal ion hydroxides were outside of the area of the Figures presenting the results. The results from the equilibrium study were subject to calculation to see if they fit to the equation $p[M^{#}] = apH + b$. The results generally fit to this from of equation which shows linear relationship between metal ion concentration and pH as in the case of aqueous system. The equations shown in Table 4 all indicate that cadmium, nickel, and zinc solubilities are significantly related to pH. Copper solubility is only related to pH at the higher concentration in the Freehold soil. However, slopes indicate that the final metal ion

concentration was less affected by pH than in a pure water system.

Lindsay (1972) reported that zinc-soil and copper-soil solubility lines are parallel to those of zinc and copper hydroxide with the former being lower than the latter, suggesting two unit increase of $p[\text{Metal ion}]$ by one unit pH increase, and also suggesting a uniform pH effect on solubility of metal ions in soil solutions at equilibrium.

Generally the calculated slopes suggest that phosphate treatment tend to reduce the effect of pH on the metal ion adsorption. As indicated

Table 4. Parameters of the Solubility Equation ($p[M^{#}] = apH + b$) for Metal Ions Equilibrated with Soils Calculated by Least Square Methods

Conc. of initial metal ion	Metal ions	Slope (a)		Intercept (b)		Simple Correlation coefficient	
		no P added	P added	no P added	P added	no P added	P added
		r: 1% .834 5% .707					
Conc. 1	Cd	.97	.54	-.38	2.20	.797	.990
	Cu	-.04	.19	.52	4.48	.257	.995
	Ni	.30	.43	3.61	2.59	.475	.995
	Zn	.58	.52	2.26	2.55	.768	.964
Conc. 2	Cd	.81	.65	-.31	.76	.984	.999
	Cu	.37	.27	3.49	3.72	.963	.992
	Ni	.85	.58	-.47	1.02	.972	.982
	Zn	1.30	1.09	2.89	-1.58	.979	.997
Conc. 3	Cd	.61	.53	.51	1.06	.939	.997
	Cu	.75	.48	1.04	2.33	.901	.979
	Ni	.84	.52	.71	1.02	.931	.977
	Zn	1.30	.99	3.20	-1.30	.949	.994
Conc. 4	Cd	.51	.50	.80	.94	.991	.999
	Cu	.99	.72	.46	.81	.995	.988
	Ni	.69	.42	.04	1.29	.960	.976
	Zn	1.23	1.02	2.95	-1.80	.978	.994

earlier, slopes obtained also suggest that cadmium and zinc are more affected by pH than copper and nickel. The non-significant correlations of copper with pH at the low concentrations are probably due to the high degree of adsorption.

2. Adsorption Isotherm Concept

In describing the adsorption of metal ions, effort has been made to utilize the adsorption isotherm equation to describe adsorption pheno-

mena in quantitative mathematical terms. Two adsorption isotherms, the Freundlich and the Langmuir isotherms have been widely applied to the adsorption of plant nutrients by soils (Chao et. al., 1962;

Among the two isotherms, the Langmuir isotherm was derived from the kinetic theory of gas adsorption on solids and enables one to calculate maximum adsorption (Langmuir, 1918). According

to Ellis and Knezek (1972) $\frac{c}{x/m} = \frac{1}{Kb} + \frac{c}{b}$ is the general form of Langmuir isotherm equation where c =final solution concentration of adsorbate, x/m =amount of adsorbate adsorbed per unit of adsorbent, b =adsorption maximum and K =a constant related to the bonding energy of the adsorbent for the adsorbate. For adsorption data fitted to the linear form of Langmuir equation, a plot of the ratio $\frac{c}{x/m}$ against c should yield a straight line with slope $=\frac{1}{b}$ and intercept $=\frac{1}{Kb}$. A computer program was used to calculate the ratio $\frac{c}{x/m}$ for each metal ion concentration of each metal ion, lime level and soil where c =final concentration of each metal ion (ppm) and x/m =metal ions adsorbed by soils (mg per gram soil). For each soil of each lime level, these paired data for the four different concentrations of each metal ion was used to calculate the best fitting straight line. The maximum adsorption, b , was derived from the relationship

$b = \frac{1}{\text{slope}}$. Table 5 shows the correlation coefficients and adsorption maxima. As shown in Table 5, cadmium Nickel and zinc adsorptions conformed to the Langmuir isotherm equation in the Freehold soil for all phosphate and lime treatments. However, copper adsorption only fit a Langmuir isotherm in the original Freehold soil without lime application.

At each lime rate, equilibration with metal ion solutions of lower concentration resulted in higher pH than with higher concentration. Therefore the Langmuir isotherm equation constructed for each soil of each lime rate contained a pH variation due to different concentration of metal ion solutions added. The Langmuir isotherm calculated may not represent the correct adsorption maxima due to a pH effect. An attempt has been made to construct Langmuir isotherm equations at constant pH's.

Using percent adsorption curve for each metal

Table 5. Correlation Coefficients (r) and Adsorption Maxima (b) of Langmuir Equations

		Freehold sandy clay loam							
		Cadmium		Copper		Nickel		Zinc	
Lime		r	b	r	b	r	b	r	b
1	no P	.996	.36	.995	.30	.986	.19	.999	.16
	P	.996	.40	.962	.43	.997	.18	.999	.16
2	no P	.993	.47	.184	2.25	.998	.23	.999	.27
	P	.994	.50	-.481	-.72	.998	.22	.995	.27
3	no P	.995	.52	-.420	-.15	.987	.30	.973	.36
	P	.993	.53	-.854	-.23	.998	.25	.998	.30
4	no P	.996	.53	-.405	-.06	.952	.34	.985	.35
	P	.995	.54	-.827	-.27	.990	.29	.999	.31

r: 1% .834
5% .707
b=mg/gm

Table 6. Correlation Coefficients (r) and Adsorption Maxima (b) of Langmuir Equation at Constant pH.

		Freehold sandy clay loam							
		Cadmium		Copper		Nickel		Zinc	
pH		r	b	r	b	r	b	r	b
6	no P	.989	.59	—	—	.982	.28	.948	.33
	P	.983	.61	—	—	.990	.30	.977	.37
6.5	no P	.987	.58	—	—	.947	.52	—	—
	P	.986	.68	—	—	.991	.45	—	—
7.0	no P	.978	.59	—	—	—	—	—	—
	P	.980	.72	—	—	—	—	—	—

r: 1% .990
5% .950
b: mg/gm

ion solution of different concentrations vs. pH of the equilibrated solution, percent adsorptions of each metal ions at a constant pH was obtained. This data at constant pH were subject to subsequent calculations as described previously for the construction of Langmuir equation. Results are tabulated in Table⁶.

In their adsorption studies using Langmuir equation neither John (1972) nor Shuman (1975) discussed the possible pH changes of equilibrated system due to metal ion concentration and consequent effect of pH change on the construction of Langmuir isotherm and calculation of maximum adsorption. However, the result obtained here clearly suggest the effect of pH changes due to metal ion concentration and subsequent calculation of Langmuir isotherm parameter as described in the Table 5 and 6.

Shuman (1975) found two types of adsorption isotherm for zinc in one soil. Uncorrected pH of the equilibrated soil water system between low and high metal ion solution may be one cause of these two types of adsorption isotherm in addition to what he attributed them to.

The validity of using a Langmuir isotherm equation for the adsorption of metal ions and using its parameters in explaining metal ion status in soils are still debatable Ellis and Knezek (1972). However, the necessity of constructing a Langmuir isotherm at a constant pH could be pointed out based on the observation explained so far.

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