Journal of Soil Contamination, 8(3):343–364 (1999)

Copper, Lead, Cadmium, and Zinc Sorption By Waterlogged and Air-Dry Soil

I. R. Phillips

School of Environmental Engineering, Griffith University, Nathan, Qld 4111, Australia

Competitive sorption of copper (Cu), lead (Pb), cadmium (Cd), and zinc (Zn) was studied in three soils of contrasting chemical and physical properties under air-dry and waterlogged conditions. Competitive sorption was determined using the standard batch technique using six solutions, each with Cu, Pb, Cd, and Zn concentrations of approximately 0, 2.5, 5, 10, 20, and 50 mg L^{-1}*. Waterlogged soils tended to sorb higher amounts of added Cu, Pb, Zn and Cd relative to soils in the air-dry condition; however, this increase in sorption was generally not statistically (*$p < 0.05$*) significant. The magnitude of sorption under both waterlogged and air-dry conditions was affected by the type and amount of soil materials involved in metal sorption processes, and competition between other metals for the sorption sites. Metal sorption was closely correlated with soil properties such as cation exchange capacity, organic carbon, and Fe and Mn hydrous oxides. Exchangeable Al may have markedly reduced metal sorption due to its strong affinity for the sorption sites, while increases in exchangeable Mn may have enhanced Zn and Cd sorption. Heavy metal sorption was best described as a combination of both specific and nonspecific interactions. The extractability of Cu, Pb, Cd, and Zn under waterlogged and air-dry conditions was also studied. Three solutions containing these metals were mixed with each soil to achieve a final concentration of 0, 50, and 500 mg* kg^{-1}*. Each soil was extracted every 7 days using 1 M* $MgCl_2$ *(pH 7) to determine metal extractability. Metal extractability initially decreased then increased due to waterlogging. The increased extractability of added metals was closely related to increased solubility of Fe and Mn suggesting that dissolution of Fe and Mn, oxides under reducing conditions caused a release of previously sorbed Cu, Pb, Cd, and Zn.*

KEY WORDS: *competitive sorption, copper, lead, cadmium, zinc, cation exchange capacity, metal extractability.*

INTRODUCTION

Increasing demand is being placed on soil for treating heavy metal bearing wastes such as agricultural and urban runoff, industrial wastewater, sewage sludge, chemical spills, and acid mine drainage. Soils have a finite capacity to sorb heavy metals, and once this capacity has been exceeded, the potential for loss of added metals through leaching and in surface water runoff increases dramatically (Gambrell, 1994). Recently, there has been considerable interest in developing management strategies which enhance the ability of soils to retain heavy metals (Phillips, 1998a), one of these being the use of constructed wetlands to treat heavy metal-rich wastewater prior to land disposal or discharge to surface water bodies (e.g., QDPI, 1995; Tarutis and Unz, 1996).

The sorption of heavy metals by soil materials is highly dependant on pH and redox conditions and involves adsorption by nonspecific and specific interactions (Kinniburgh *et al*., 1976; Huang *et al*., 1977; Schulthess and Huang, 1990; Naidu *et al*., 1994), and precipitation reactions with carbonates, phosphates, sulfates, and sulfides (Tiller *et al.*, 1984). Nonspecific sorption involves retention of heavy metals by relatively weak (electrostatic) forces of attraction due to the negative surface charge of soil colloids. Specific sorption involves the exchange of heavy metal cations with surface ligands to form partly covalent bonds with lattice ions and has been used to explain why soil colloids can sorb heavy metals in concentrations greater than their cation exchange capacity (Alloway, 1995). The proportion of heavy metals involved in specific (and nonspecific) interactions increases with increasing pH (e.g., Kinniburgh *et al*., 1976; Huang *et al*., 1977; Schulthess and Huang, 1990; Naidu *et al*., 1994). This phenomenon has been explained by various chemical processes such as metal hydrolysis (e.g., Basta and Tabatabai, 1992), the hard-soft Lewis acid-base (HSAB) principle (e.g., Puls and Bohn, 1988), changes in pH-dependant surface charge and electrostatic potential in the plane of adsorption (e.g., Naidu *et al*., 1994), and complexation of heavy metals with deprotonated surface OH and COOH groups (e.g., Abd-Elfattah and Wada, 1981). These chemical processes have been used to describe the heavy metal affinity sequences observed for soil materials such as Fe and Al gels, clay minerals and organic matter, and whole soils (Kinniburgh *et al*., 1976; Abd-Elfattah and Wada, 1981; Puls and Bohn, 1988; Schulthess and Huang, 1990; Basta and Tabatabai, 1992).

Soils in wetland systems often experience extended periods of inundation. Under these waterlogged conditions, soil redox potential (Eh) can be reduced to very low positive or negative values, and soil pH shifts to a value near neutrality (Ponnamperuma, 1972). Changes in pH and/or Eh can have a significant impact on the properties of those soil colloids responsible for heavy metal sorption (i.e., organic matter, clay minerals, and sesquioxides). Recently, Phillips and Greenway (1998) showed that waterlogging increased the cation exchange capacity (CEC) of soils with variably charged colloids (e.g., organic matter) due to increases in soil solution pH and ionic strength. While increases in CEC may encourage heavy metal retention by wetland soils, the magnitude of sorption may still be governed by competition between the added and resident metals for the sorption sites, and preferential sorption of individual metals by soil colloids (Tiller *et al.*, 1979; Tyler and McBride, 1982; Miller *et al.* 1983; Christensen, 1987; Basta and Tabatabai, 1992; Naidu *et al*., 1994; Paalman *et al.*, 1994).

While considerable information is available on heavy metal sorption for air-dried soils (Alloway, 1995), little published information is available on the sorption behavior of waterlogged soils or how the time of waterlogging affects the extractability of added heavy metals (Sims and Patrick, 1978; Mandal *et al.,* 1992; Gambrell, 1994). The primary objective of this study was to determine the effect of waterlogging on heavy metal sorption and extractability using a range of soils with contrasting physical and chemical properties.

MATERIALS AND METHODS

Soils Used

Three soils exhibiting contrasting chemical and physical properties were used in this study: the A and B horizon of a krasnozem soil; the A and B horizon of a sandy loam soil; and the highly organic surface material from a *Melaleuca* wetland. Detailed information on the soil classifications, sampling locations, sampling depths, and basic properties of these soils were presented in Phillips and Greenway (1998). All soils were air-dried and passed through a 2-mm sieve. All experimental work was undertaken using the <2-mm-size fraction. Some initial properties of the soils in the air-dry and waterlogged condition are presented in Table 1. For simplicity, the krasnozem A, and B horizon, sandy loam A and B horizon and wetland soils will be referred to throughout the text as Kras A, Kras B, Sand A, Sand B, and wetland, respectively.

Experiment 1: Heavy Metal Sorption Isotherms

Heavy metal sorption isotherms were determined by the standard batch technique using mixed solutions of Cu (as $CuCl_2$), Pb (as $Pb(NO_3)_2$), Cd (as $Cd(NO_3)_2$), and Zn (as $ZnCl_2$). Six equilibrating solutions were used to determine the isotherms, and the concentration of each metal in each solution was approximately 0, 2.5, 5, 10, 20, and 50 mg L^{-1}. Mixed metal solutions were used rather than single metal solutions to simulate competition between metals for the sorption sites because metal-bearing wastes commonly contain a range of heavy metals. Isotherms were determined for two soil moisture conditions: (1) air-dry (AD); and (2) waterlogged (WL).

TABLE 1
Selected Properties of Each Soil in the Air-Dry (AD) and Waterlogged Condition (WL)

Property	Kras A		Kras B		Sand A		Sand B		Wetland	
	AD	WL	AD	WL	AD	WL	AD	WL	AD	WL
SOC (mg L^{-1}	18.9(0.14)	433.83(2.18)	1.36(0.45)	5.96(0.72)	10.67(1.31)	87.25(2.98)	1.01(0.11)	3.04(0.02)	20.56(1.11)	169.11(3.55)
pH	6.41(0.03)	6.90(0.01)	5.85(0.04)	6.31(0.04)	5.11(0.06)	6.19(0.02)	4.42(0.01)	4.64(0.11)	4.36(0.02)	5.74(0.03)
Eh (mV)	+264(9)	-261(5)	+248(12)	-42(15)	+205(6)	-210(11)	+408(12)	+149	+270	-189(28)
CEC (cmol kg^{-1}	9.99(0.11)	15.18(0.25)	1.66(0.03)	3.09(0.22)	1.47(0.09)	2.68(0.15)	1.11(0.01)	1.67(0.01)	25.46(0.21)	76.95(3.57)
Org C (%)	5.6(0.13)	ND	2.6(0.05)	ND	1.7(0.24)	ND	0.9	ND	35(3.26)	ND
Sand (%)	37(5)	ND	34(5)	ND	80(3)	ND	84(7)	ND	ND	ND
Silt (%)	18(2)	ND	15(4)	ND	7(1)	ND	8(1)	ND	ND	ND
Clay(%)	45(6)	ND	51(8)	ND	13(4)	ND	8(2)	ND	ND	ND
Exchangeable cations (% of CEC)										
Ca	38(2)	49(4)	52(3)	51(9)	19(5)	14(3)	10(1)	14(5)	48(13)	30(8)
Mg	16(2)	20(3)	18(3)	18(4)	10(1)	6(1)	5(<1)	5(2)	6(1)	38(11)
K	5(1)	4(2)	14(1)	11(5)	14(1)	6(2)	6(<1)	4(1)	4(2)	2(<1)
Na	<1(<1)	<1(<1)	1(<1)	31)	4(<1)	3(<1)	5(<1)	4(2)	35(8)	15(4)
NH_4	40(7)	7(1)	13(4)	6(3)	11(2)	9(2)	6(<1)	1(<1)	1(<1)	<1(<1)
Al	<1(<1)	<1(<1)	<1(<1)	<1(<1)	35(6)	7(3)	64(16)	71(19)	4(<1)	<1(<1)
Fe	<1(<1)	12(2)	<1(<1)	<1(<1)	3(<1)	51(11)	2(<1)	<1(<1)	<1(<1)	13(3)
Mn	<1(<1)	7(1)	1(<1)	12(2)	4(<1)	6(2)	<1(<1)	2(<1)	<1(<1)	3(<1)
Total metal (mmol kg^{-1})										
Cu	1.55(0.21)	ND	1.44(0.15)	ND	0.16(0.03)	ND	0.18(0.03)	ND	0.59(0.12)	ND
Pb	0.08(<0.01)	ND	0.08(0.01)	ND	0.09(0.02)	ND	0.1(0.02)	ND	0.13(0.06)	ND
Cd	0.002(<0.01)	ND	0.008(<0.01)	ND	0.003(0.001)	ND	0.013(<0.01)	ND	0.008(<0.01)	ND
Zn	1.53(0.14)	ND	1.19(0.13)	ND	0.32(0.02)	ND	0.45(0.08)	ND	1.51(0.11)	ND
Fe	1763(34)	ND	1776(64)	ND	90.3(10.1)	ND	3(0.02)	ND	2.7(0.06)	ND
Mn	18.6(1.2)	ND	17(4)	ND	2.4(0.24)	ND	3.1(0.09)	ND	2.8(0.03)	ND

Note: ND = not determined; values represent the mean of two replicates followed by standard error in parenthesis.

Phillips and Greenway, 1998.

For the AD treatment, approximately 5 g (oven-dry weight basis) of air-dry soil were weighed into a series of six 50-mL polypropylene centrifuge tubes, and 24 mL of Milli-Q deionised water (>18 MΩ) accurately added. One mL of mixed metal solution was then added to the centrifuge tubes to give a final volume of 25 mL, and the soil suspension shaken end-over-end for 24 h. After shaking, the suspensions were centrifuged at 3000 rpm for 0.5 h. The supernatant was removed, passed through a 0.45 μm filter, acidified to pH < 2 with HNO_3, and stored at 4°C in acid-washed polycarbonate containers prior to analysis. The concentrations of Cu, Pb, Cd, and Zn in the initial and final solutions were measured by atomic absorption spectrometry (AAS; Varian SpectrAA Atomic Absorption Spectrometer), and the difference between the amount of metal added initially and that in the final solution was considered to have been sorbed by the soil. The concentration of Cu, Pb, Cd, and Zn initially present in the soil was taken into account when calculating sorbed metal concentrations.

Copper, Pb, Cd, and Zn sorption isotherms under waterlogged conditions were determined following the same procedure as for AD samples, except that the 24 mL of Milli-Q deionized water was initially mixed with the soil then the soil suspension allowed to stand for a period of 21 days. During this period the centrifuge lids were loosely fitted and the samples stored in the dark at room temperature (≈25°C). After this period, 1 mL of each metal solution was added and sorption isotherms determined as described above. Changes in the pH and redox potential (Eh) of these soils due to waterlogging were presented in Phillips (1998b).

The Freundlich equation (Equation 1) was fitted to each isotherm (Table 2), and the concentration of each metal sorbed at an equilibrium solution concentration of 0.005 and 0.05 mmol L^{-1} predicted (Table 3). These concentrations were selected to simulate the higher solution metal concentrations in many wastewaters (mine drainage, industrial chemical liquid wastes) relative to those normally encountered in, for example, agricultural situations. Multiple regression analysis was carried out using these sorbed concentrations and various soil properties to identify which properties were largely responsible for Cu, Pb, Cd, and Zn sorption. The Freundlich equation is

$$S = k\,c^{n}$$

where S is the amount of sorbed metal per unit weight of soil (mmol kg^{-1}), c is the equilibrium metal solution concentration (mmol L^{-1}), k and n are constants.

Experiment 2: Cu, Pb, Cd and Zn Extractability

The effect of waterlogging on the extractability of Cu, Pb, Cd and Zn was determined using the same procedure described in Phillips (1998b). A solution containing copper chloride ($CuCl_2$), lead nitrate ($Pb(NO_3)_2$), cadmium nitrate

TABLE 2
Values of “*k*”, “*n*”, and r^2 For Each Soil, Metal, and Moisture Condition Obtained by Fitting the Freundlich Equation to the Isotherm Data

Soil		**Fitted Freundlich Parameters**											
		Cu			**Pb**			**Cd**			**Zn**		
		k	*n*	r^2	*k*	*n*	r^2	*k*	*n*	r^2	*k*	*n*	r^2
Kras A	**AD**[a]	93.77	0.75	0.97	126.25	0.86	0.99	320.61	1.02	0.99	48.53	0.58	0.99
	WL[b]	76.96	0.70	0.92	255.11	1.00	0.97	1699.35	1.33	0.99	114.75	0.68	0.81
Kras B	**AD**	10.18	0.17	0.99	85.16	0.71	0.99	1.68	0.27	0.97	3.74	0.13	0.99
	WL	18.20	0.26	0.97	38.43	0.49	0.97	2.04	0.27	0.97	4.56	0.12	0.99
Sand A	**AD**	3.44	0.32	0.98	4.41	0.37	0.97	0.61	0.21	0.91	1.09	0.13	0.93
	WL	4.71	0.33	0.94	14.69	0.64	0.98	0.56	0.17	0.84	1.11	0.12	0.85
Sand B	**AD**	1.10	0.21	0.98	1.35	0.26	0.98	0.27	0.21	0.98	0.85	0.09	0.99
	WL	0.98	0.20	0.97	1.30	0.26	0.98	0.21	0.17	0.94	0.86	0.10	0.96
Wetland	**AD**	932.10	0.87	0.99	1164.10	0.81	0.99	29.56	0.67	0.99	31.95	0.56	0.94
	WL	1374.60	1.21	0.99	1035.50	0.79	0.99	33.77	0.66	0.99	30.68	0.49	0.97

[a] Air dry treatment.

[b] Waterlogged treatment.

TABLE 3

Sorbed Metal Concentrations Calculated at Equilibrium Solution Concentrations of 0.005 and 0.05 mmol L^{-1} using the Freundlich Equation, and the Sum of Sorbed Metal Concentrations Expressed as a Percentage of CEC

	Sorbed metal concentration (mmol kg^{-1})									
	Cu		Pb		Cd		Zn		Sum/CEC (%)	
Soil	**AD**	**WL**	**AD**	**WL**	**AD**	**WL**	**AD**	**WL**	**AD**	**WL**
c = 0.005 mmol L^{-1}										
Kras A	1.726	1.855	1.309	1.274	1.442	1.434	2.178	3.042	7	5
Kras B	3.546	4.146	2.033	2.819	0.392	0.502	1.917	2.361	48	32
Sand A	0.622	0.823	0.616	0.488	0.208	0.228	0.537	0.603	13	8
Sand B	0.359	0.338	0.338	0.328	0.089	0.084	0.523	0.514	12	8
Wetland	9.376	22.476	15.716	15.522	0.864	1.013	1.686	2.309	11	5
lsd ($p < 0.05$)		2.309								
c = 0.05 mmol L^{-1}										
Kras A	9.796	9.362	9.576	12.745	15.101	31.072	8.393	14.733	43	45
Kras B	6.126	8.422	10.305	8.774	0.737	0.921	2.562	3.141	109	69
Sand A	1.308	1.756	1.448	2.143	0.333	0.338	0.731	0.786	26	19
Sand B	0.583	0.535	0.616	0.597	0.144	0.125	0.644	0.642	18	12
Wetland	69.198	361.004	102.063	96.323	4.01	4.651	6.055	7.106	71	61
lsd ($p < 0.05$)		34.408								

(Cd(NO_3)$_2$, and zinc chloride ($ZnCl_2$) was thoroughly mixed with each soil to achieve a final metal concentration of approximately 0, 50, and 500 mg kg^{-1} (M0, M50, and M500). These rates were selected to reflect metal concentrations in soil that have received low (M50, e.g., sewage wastewater, urban and agricultural runoff) and high (M500 mg kg^{-1}, e.g., mine drainage, industrial wastewater) metal loadings over time. Following metal addition, approximately 100 g of each soil were placed in a 250-mL glass jar, and 150 mL of Milli-Q deionized water (>18 MΩ) added. This volume of water maintained a ponded depth of water above the soil of about 5 cm. The soil and water were stirred to obtain an initially homogeneous suspension, the lids loosely placed on the jars, and the waterlogged samples stored in the dark (to minimize algal growth) for a period of 21 days.

Metal extractability was monitored on a weekly basis as follows. One gram (oven-dry weight basis) of waterlogged soil was shaken end-over-end with 10 mL of 1 *M* $MgCl_2$ (pH 7) for 1 h at 25°C (Tessier *et al*., 1979). Following shaking, the suspension was centrifuged at 3000 rpm for 0.25 h, the supernatant filtered (0.45 μm), placed in an acid-washed polycarbonate container and acidified (pH <2) with HNO_3. When extracting the waterlogged soils, the 1 *M* $MgCl_2$ solution was made up using deaired, deoxygenated water, and shaking was carried out under a N_2 atmosphere. Total metal concentrations for each soil treatment on Day 0 were determined by digesting 1 g (oven-dry weight basis) of each soil with concentrated HF-$HClO_4$-HCl as described by Tessier *et al*. (1979). All extracted solutions were analyzed for Cu, Pb, Cd, Zn, Fe, and Mn using inductively coupled plasma–mass spectrometry (ICP-MS).

Statistical Analysis

Results presented are the mean of two replicates (n = 2), and were statistically analyzed by simple linear and multiple regression analysis, analysis of variance (ANOVA), and comparison of means (LSD) procedures using the statistical analytical software package *Statistix* (Analytical Software, 1994).

RESULTS AND DISCUSSION

Experiment 1: Cu, Pb, Cd, and Zn Sorption Isotherms

Copper, Pb, Cd, and Zn sorption isotherms for Kras A, Kras B, Sand A, and B and wetland soils for AD and WL treatments are presented in Figures 1 and 2. These isotherms were adequately described by the Freundlich equation (Equation 1), and values of “*k*”, “*n*”, and r^2 are presented in Table 2. Metal sorption was higher in Kras A and wetland soils irrespective of moisture condition, as shown by the higher values of the slope term (*k*) of the Freundlich equation. The very steep

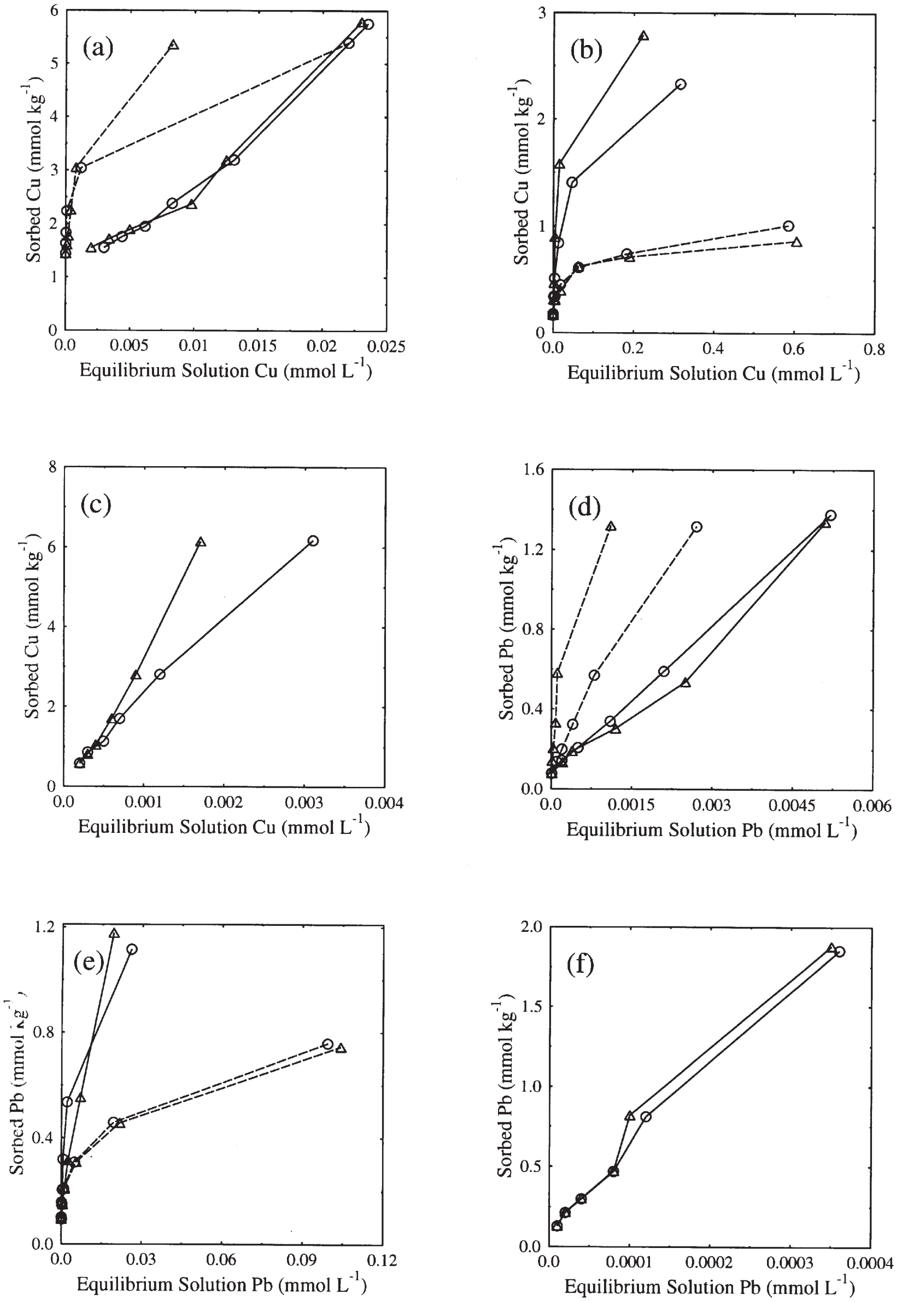

FIGURE 1

Effects of waterlogging on Cu sorption for (a) Kras A and Kras B, (b) Sand A and Sand B, and (c) wetland soil, and on Pb sorption for (d) Kras A and Kras B, (e) Sand A and Sand B, and (f) wetland soil. AD (○) and WL (△) . Solid lines represent A horizon soils, dashed lines represent B horizon soils.

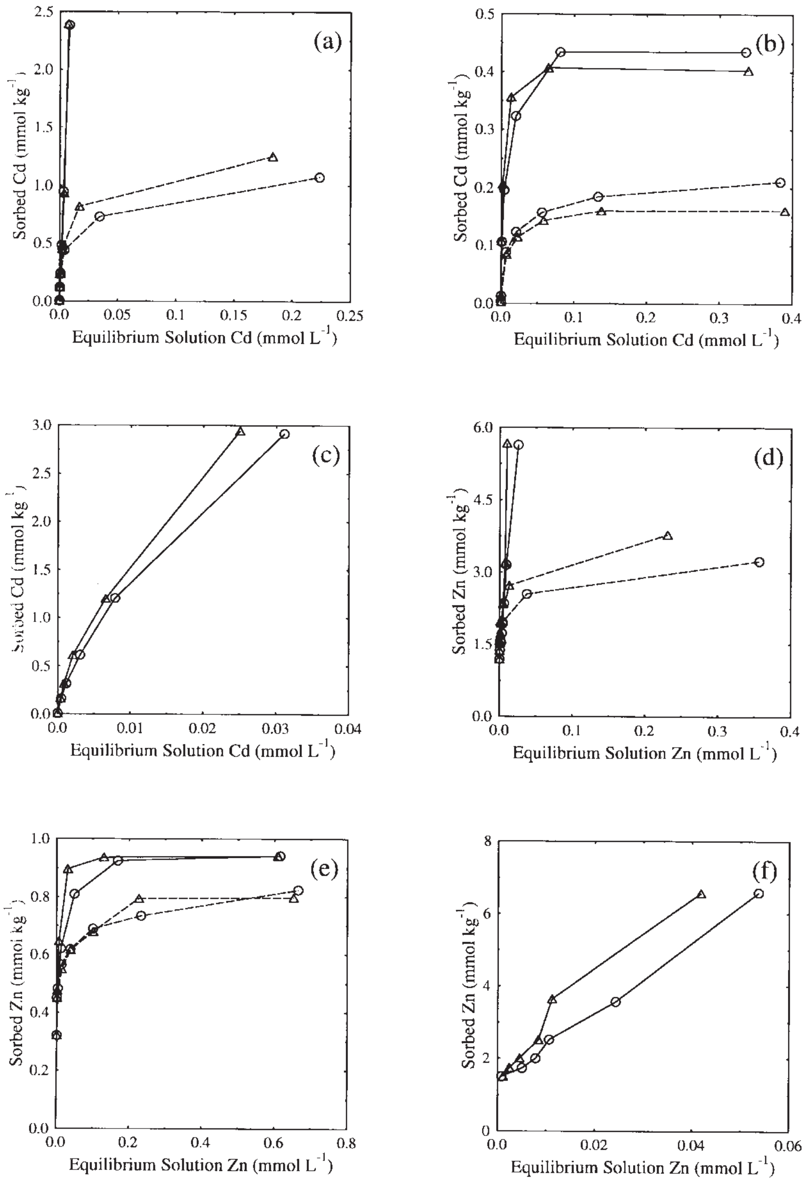

FIGURE 2

Effects of waterlogging on Cd sorption for (a) Kras A and Kras B, (b) Sand A and Sand B, and (c) wetland soil, and on Zn sorption for (d) Kras A and Kras B, (e) Sand A and Sand B, and (f) wetland soil. AD (○) and WL (△). Solid lines represent A horizon soils, dashed lines represent B horizon soils.

curvature of the isotherms for the Kras A and wetland soils can be attributed to the very high proportion of the applied metals that removed from the solution phase due to sorption mechanisms.

These isotherms highlight two important points. First, the amounts of metals sorbed varied considerably between soils, and, second, waterlogging tended to increase Cu, Pb, Cd and Zn sorption by Kras B, Cu sorption by Sand A, and Cu, Cd, and Zn sorption by the wetland soils only when compared with the AD treatment.

Metal Sorption between Soils. The amounts of Cu, Pb, Cd, and Zn sorbed at an equilibrium solution concentration of 0.005 and 0.05 mmol L^{-1} are presented in Table 3. Least significant differences (LSD) between the calculated sorbed metal concentrations for all soils and moisture conditions were determined for each equilibrium solution concentration (i.e., 0.005 and 0.05 mmol L^{-1}). Generally, it was found that the wetland soil sorbed the highest amount of metal while the sandy loam soil sorbed the least, with the magnitude of variation between soils being more pronounced at the higher solution metal concentrations. To identify which soil properties were possibly responsible for this variation in metal sorption, multiple regression analysis for each soil and horizon was conducted using sorbed Cu, Pb, Cd, and Zn concentrations (Table 3) and values for the soil properties pH, Eh, CEC, percent base saturation, organic carbon, amorphous Fe and Mn hydrous oxides, exchangeable Fe and exchangeable Mn. Multiple regression analysis showed significant ($p < 0.05$) positive correlations with a number of these properties; however, the strongest correlations for Cu and Pb sorption were with CEC ($r^2 = 0.68$ to 0.95), organic carbon percentage ($r^2 = 0.75$ to 0.98) and exchangeable Fe ($r^2 = 0.62$ to 0.96), and weaker correlations with percent base saturation and amorphous Fe content ($r^2 \approx 0.54$). Cadmium and Zn sorption were significantly ($p < 0.05$) correlated with exchangeable Mn ($r^2 = 0.68$ to 0.83), organic carbon percentage ($r^2 \approx 0.45$), percent base saturation ($r^2 = 0.44$ to 0.66), and amorphous Fe and Mn ($r^2 = 0.62$ to 0.96).

Regression analysis highlighted the importance of CEC for Cu and Pb sorption and was found to explain over 95% of the variation in Cu and Pb sorption between all of the soils. Because much of the CEC generated in these soils originates from the presence of organic matter and/or amorphous Fe and Mn, it is not surprising a significant relationship between metal sorption and these soil components was observed. Furthermore, it is well documented that Cu and Pb have a strong affinity for organic matter and Fe and Mn hydrous oxides (Kinniburgh et al., 1976; Abd-Elfattah and Wada, 1981; Alloway, 1995; Phillips and Greenway, 1997). Reasons for the weak correlation between Cd and Zn sorption and CEC are discussed below.

Effects of Waterlogging on Sorption. Increased metal sorption by Kras B, Sand A, and wetland soils due to waterlogging suggests (1) the number of sites available for heavy metal sorption have increased, (2) the concentration of other cations in the soil that have a higher affinity for the sorption sites have decreased, or (3) chemical conditions favorable to specific sorption and/or precipitation of the heavy metals have been generated. It has been reported that the CEC represents a major proportion of the sites available for metal sorption in soil (e.g., Naidu *et al*., 1994), particularly at high metal loading rates. Although waterlogging did increase the CEC of all soils (Table 1), this increase in CEC did not appear to markedly increase metal sorption for all soils. This may be because, with the exception of Kras B, the summation of sorbed metal concentrations never exceeded the CEC of any soil for both the AD or WL treatments (Table 3). Because the number of exchange sites always exceeded the amounts of metals added, the number of potential sorption sites was never a limiting factor. This was probably the main reason why waterlogging had little effect on metal sorption by Kras A.

The lack of a relationship between increased CEC and increased metal sorption suggests other factors were controlling the magnitude of sorption. One possible reason may be due to the resident cation composition initially balancing the exchange sites. Regression analysis showed a strong correlation existed between Cu, Pb, Cd, and Zn sorption and amorphous Fe and Mn hydrous oxides, and this finding is consistent with previous workers (e.g., Abd-Elfattah and Wada, 1981; Zasoski and Burau, 1988; Stahl and James, 1991a and b; Zhu and Alva, 1993). The order of sorption of heavy metals by Fe and Mn oxides has been reported to be: Cu > Pb > Zn > Cd > Mn, and Pb > Cu > Mn > Zn, respectively (Schwertmann and Taylor, 1989; McKenzie, 1980), while kaolinite (present in Kras A and Kras B) exhibits a preference for Pb, Cu, and Ca relative to Cd and Zn (Alloway, 1995). This shows that Cu and Pb are commonly sorbed in preference to Cd and Zn; however, Mn is less strongly sorbed by Fe oxides than by Mn oxides. In most soils, waterlogging increased the concentration of exchangeable Fe and/or Mn due to the solubilization of Fe and Mn oxides under reducing conditions and their subsequent retention by newly created CEC sites (Table 1). Where exchangeable Mn increases to a greater extent than exchangeable Fe, such as in Kras B, then Cu and Pb sorption may be expected to increase due to their greater ability to displace Mn from the exchange sites. The increased sorption of Zn and Cd by this soil may indicate that sorption of the heavy metals occurred primarily on Fe oxides rather than on Mn oxides.

The curvilinear nature of the Cu, Pb, Cd, and Zn sorption isotherms for Sand A and Sand B (Figure 1b and e and Figure 2b and e) suggests that heavy metal sorption (Cd and Zn in particular) may have been limited by exchangeable cations other than Fe and/or Mn. Exchangeable Al comprised nearly 35% and 64% of the CEC in the air-dry moisture condition (Table 1), and this trivalent cation is more strongly sorbed relative to divalent cations (John, 1972; Lagerwerff and Brower, 1972; Cavallaro and McBride, 1978). It is possible that the added metals could not displace significant amounts of exchangeable Al thereby severely limiting the amount of Cu, Pb, Cd, and Zn sorption. Waterlogging, however, significantly decreased exchangeable Al in Sand A with a concomitant increase in exchangeable

Fe. The replacement of trivalent Al by (ferrous) Fe may therefore have favored sorption of Cu and Pb. This effect was not observed in Sand B because waterlogging had no effect on exchangeable Al concentrations (Table 1).

Specific Sorption of Metals. Metal sorption processes can be broadly divided into two groups: specific and nonspecific sorption. Nonspecific sorption refers to metal cations bound by weak coulombic forces to balance the negative charges on soil colloids (similar to exchangeable cations). In a separate experiment investigating the effects of waterlogging on heavy metal extractability (Experiment 2), it was found that following the addition of Cu, Pb, Cd, and Zn to these soils (particularly at the highest rate) a significant proportion was present in the exchangeable fraction (Table 4). For example, much of the applied Cd and Zn was present in an exchangeable form in all soils (generally >80% of that added), whereas Cu and Pb tended to exist in both exchangeable and nonexchangeable forms, particularly for Kras A, Kras B, and wetland soils. Thus, it appears that for Cd and Zn in all soils, and for Cu and Pb in Sand A and Sand B, the added metals were largely retained through electrostatic forces as balancing cations for the exchange sites. Similar findings have been reported by previous workers (Tiller *et al.*, 1984; Naidu *et al.*, 1994).

The tendency for Cu and Pb to be held by additional forces, which render them nonexchangeable with simple salt solutions suggests a proportion of the added metals were also retained by specific sorption processes. Various mechanisms have been forwarded to explain specific sorption of metals by soil colloids. These include sorption of the metal in a hydrolyzed form as pH increases, and metal complexation with surface OH groups. In this study the maximum pH obtained for any soil (Table 1) was well below the metal hydrolysis constants of all metals (e.g., Kinniburgh *et al*., 1976; Basta and Tabatabai, 1992). For example, the maximum pH in this study was 6.9 for Kras A WL treatment, whereas hydrolysis constants for Pb, Cu, Zn, and Cd are 7.8, 8.0, 9.0, and 10.1, respectively (Basta and Tabatabai, 1992). Consequently, only a very small proportion of the added metals would have been in the hydrolyzed form. The possible explanation may be that the metals may have undergone specific interaction with surface OH^- (i.e., OH^- -M^{2+}) groups as suggested by Kinniburgh *et al*. (1976)

Experiment 2: Cu, Pb, Cd, and Zn Extractability

A consistent pattern in Cu, Pb, Cd, and Zn extractability under waterlogged conditions was observed among these soils (Figures 3 and 4*a,b,c,d,e,f*). Initially (Day 0), metal extractability was relatively high, and declined over the following 7 to 14 days, and again increased between Days 14 to 21. The extent of metal extractability varied considerably between soils and was consistently found to be greater in Sand A and Sand B than in the other soils for all treatments. Also, the

TABLE 4
Proportion of Cu, Pb, Cd, and Zn Present in the Exchangeable Fraction Following Metal Additions of 50 and 500 mg kg^{-1}

Soil	Sorbed metal concentration (% of added)[a]							
	Cu		Pb		Cd		Zn	
	50	500	50	500	50	500	50	500
Kras A	12	17	28	61	84	96	25	73
Kras B	13	12	17	62	78	96	30	72
Sand A	66	88	70	92	96	99	93	97
Sand B	77	96	64	91	97	99	72	96
Wetland	15	31	48	67	92	97	46	83

[a] Exchangeable metals extracted using 1 *M* $MgCl_2$ at a soil to solution ratio of 1:8 (Tessier *et al.*, 1979).

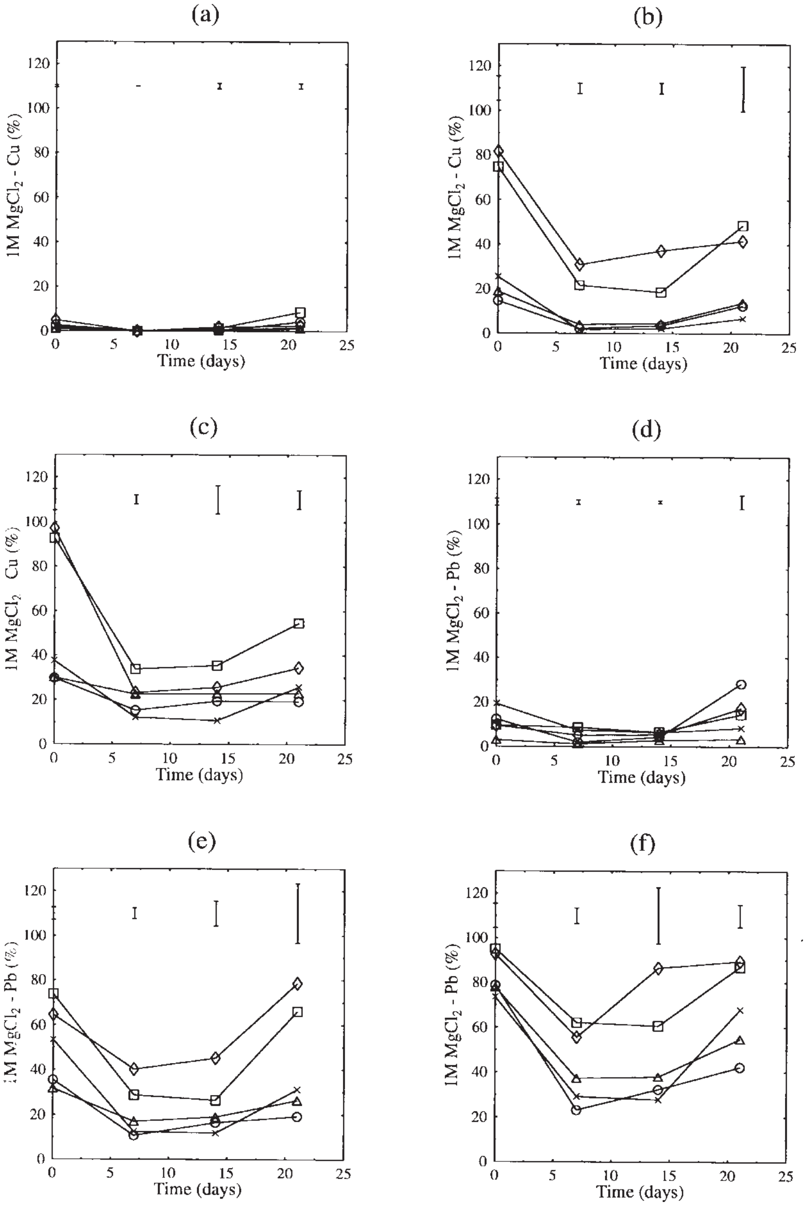

FIGURE 3

Effects of waterlogging on 1 M $MgCl_2$ extractable Cu for treatments (a) M0, (b) M50, and (c) M500, and 1 M $MgCl_2$ Pb for treatments (d) M0, (e) M50 and (f) M500. ○ Kras A, △ Kras B, □ Sand A, ◇ Sand B, and x wetland soils. Vertical bars denote LSD ($p < 0.05$).

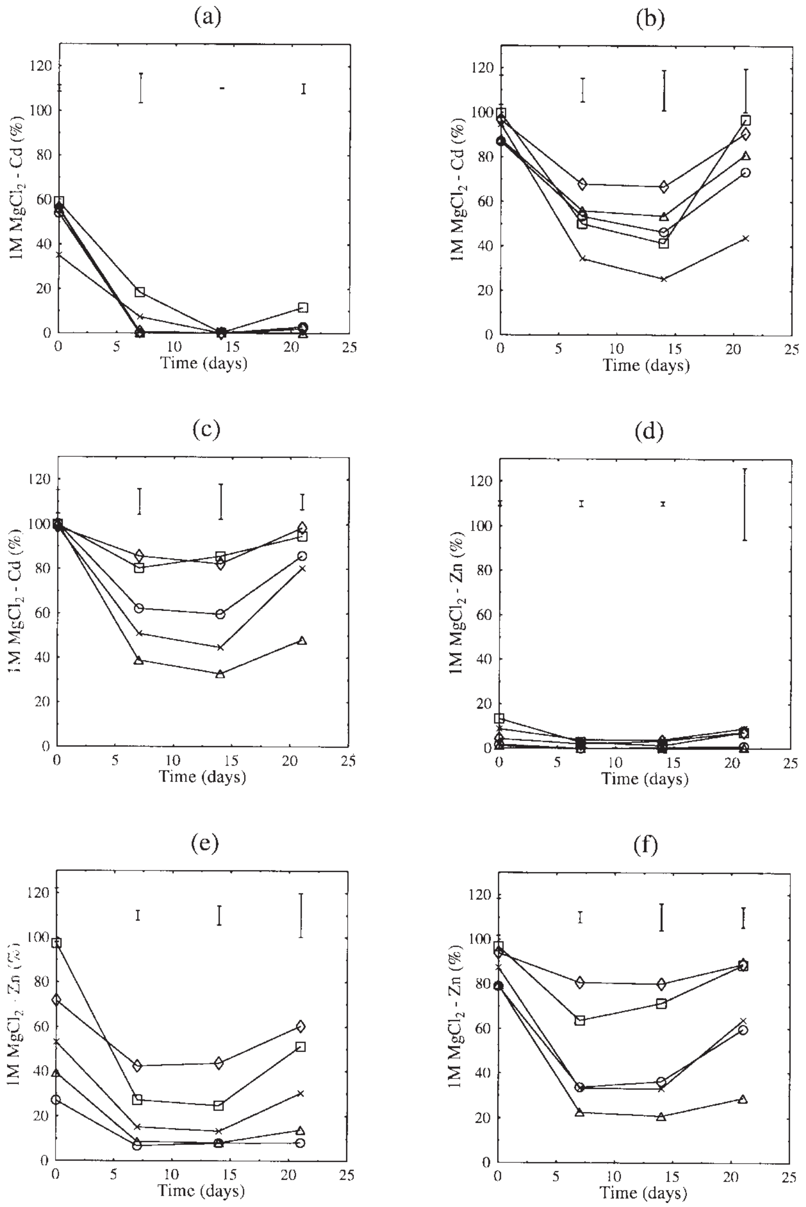

FIGURE 4

Effects of waterlogging on 1 M $MgCl_2$ extractable Cd for treatments (a) M0, (b) M50, and (c) M500, and 1 M $MgCl_2$ extractable Zn for treatments (d) M0, (e) M50, and (f) M500. ○ Kras A, △ Kras B, □ Sand A, ◇ Sand B, and x wetland soils. Vertical bars denote LSD ($p < 0.05$).

extractability of all metals was found to increase with increasing loading rate (M500 > M50 3 M0). For example, Cu extractability (1 *M* $MgCl_2$ extractable) in the control soils (M0) remained very low throughout the experiment and commonly represented <5% of Total Cu (Cu_{tot}). At the 50 mg kg^{-1} loading rate (M50), Cu extractability in Kras A, Kras B, and wetland soils never exceeded 25% of Cu_{tot}, and consistently fell below <10%. In the sandy loam, however, extractability often exceeded 20% and 30% of Cu_{tot} in Sand A and Sand B, respectively. At the 500 mg kg^{-1} loading rate (M500), Cu extractability in Kras A, Kras B, and wetland soils consistently remained <30% of Cu_{tot}, while in Sand A and Sand B Cu extractability often exceeded 30% of Cu_{tot}.

Extractable (1 *M* $MgCl_2$) Fe remained extremely low throughout the experiment with the maximum concentration (<20% of Fe_{tot}) observed on Day 21 for all soils (Figure 5). Over the waterlogged period, extractable Mn concentrations were greatest in Kras A M0 treatment (approximately 80% of Mn_{tot}) and least in Sand B (approximately 5% of Mn_{tot}), and ranged between 20% to 40% of Mn_{tot} for the other soils.

Effect of Waterlogging on Extractability. Under waterlogged conditions, a relatively high proportion of the added metals initially (Day 0) remained in readily available forms (i.e., water soluble and exchangeable), suggesting metal retention by predominantly nonspecific (coulombic attraction) sorption mechanisms. This finding may largely be attributed to the high metal loadings employed in this study as discussed previously in Experiment 1 of this paper. Subsequent decreases in metal extractability (Day 7 to 14) suggests these metals may have become progressively redistributed into less-available fractions (i.e., bound to Fe/Mn hydrous oxides, bound to organic matter and present in residual fractions such as clay mineral lattices). Metal fractionation (Phillips and Greenway, 1997) revealed that following waterlogging these soils for 21 days, metal (Pb and Cd) concentrations in the exchangeable fraction decreased, with a corresponding increase in the oxide and organic fractions. Thus, the decrease in extractability of the added metals may be due to (1) specific sorption by the hydrous Fe and Mn oxides, and organic matter (e.g., Phillips and Greenway, 1997); (2) diffusion of the metals into soil colloids (e.g., Tiller *et al.*, 1984; McLaren and Ritchie, 1993; Mann and Ritchie, 1994); and/or (3) precipitation as metal sulfides and metal hydroxides. To what extent any or all of these processes were occurring in this study is unknown. Mann and Ritchie (1994) investigated the effects of time on Cd sorption using four Western Australian soils (a yellow earth, a lateritic podzolic, a peaty sand and a siliceous sand). Following an incubation period of 8 days, they reported a decrease in water-soluble and exchangeable forms of added Cd and a corresponding increase in Cd bound to oxides and that present in the residual fraction. These changes in water-soluble and exchangeable Cd were greatest in the Fe oxide-rich yellow earth and least in the relatively inert siliceous sand, and are consistent with the findings of the study reported here. The redistribution of applied heavy metals throughout the various

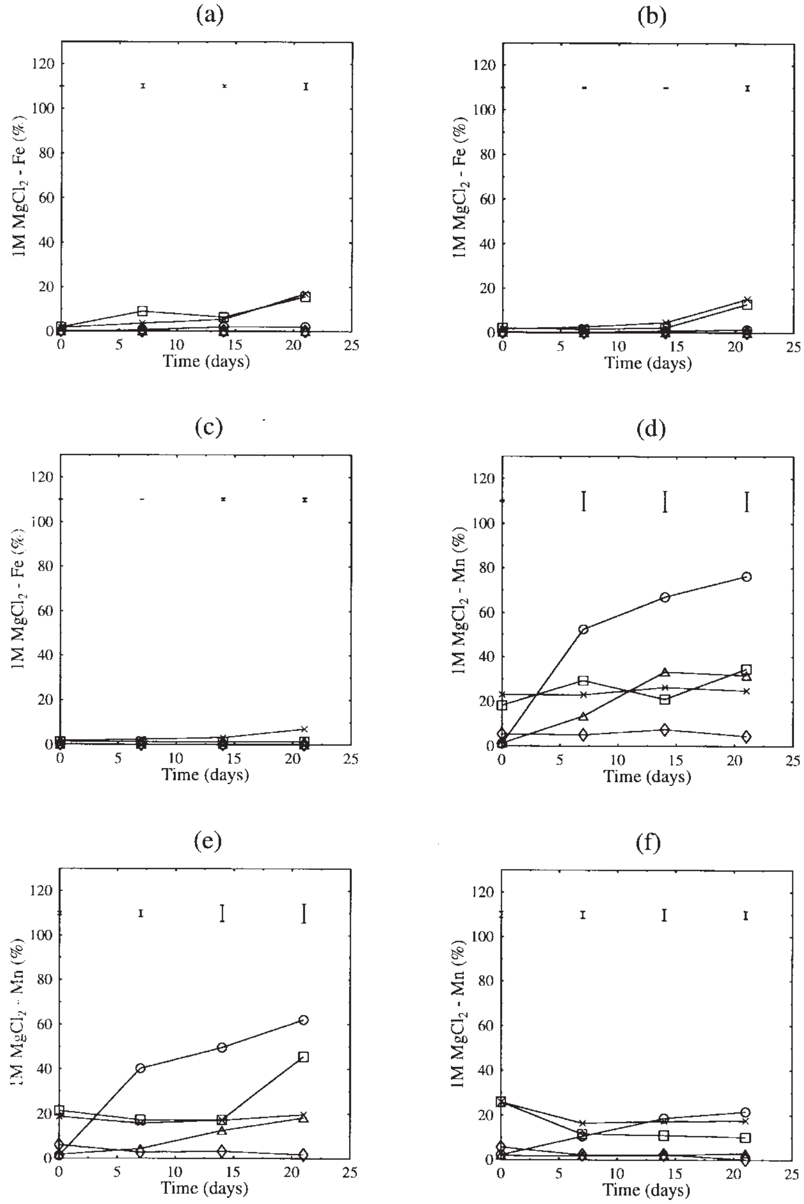

FIGURE 5

Effects of waterlogging on 1 M $MgCl_2$ extractable Fe for treatments (a) M0, (b) M50, and (c) M500, and 1 M $MgCl_2$ extractable Mn for treatments (d) M0, (e) M50, and (f) M500. ○ Kras A, △ Kras B, □ Sand A, ◇ Sand B, and x wetland soils. Vertical bars denote LSD ($p < 0.05$).

soil fractions with time has been reported by various workers (e.g., McLaren and Ritchie, 1993).

The increased extractability of all added metals after waterlogging (Day 21) was accompanied by increases in the extractability of Fe and Mn (due to solubilization of Fe and Mn hydrous oxides), and increased soluble organic carbon ([SOC] Table 1). These results suggest that following initial sorption by the soil Fe and Mn hydrous oxides and organic matter, subsequent solubilisation of these materials under reducing conditions transferred the sorbed Cu, Pb, Cd, and Zn into more readily available fractions such as the water-soluble (either in ionic form or complexed with SOC) and exchangeable (after displacement of initial resident cations) fractions. The increased solution Fe and/or Mn concentrations would further increase competition for the CEC sites, thereby displacing those metals of lower affinity into the soil solution (Experiment 1). Sims and Patrick (1978) found that waterlogging caused increased extractability of Cu, Zn, Fe, and Mn, and that a high proportion of these metals were associated with the exchangeable fraction or complexed with SOC. Their results indicated that Cu tended to be retained by the CEC sites and complexed with SOC to a greater extent compared with Zn, the latter metal remaining primarily as the divalent cation Cd^{2+}.

Effect of Metal Loading on Extractability. The effect of metal loading rate on Cu, Pb, Cd, and Zn, Fe, and Mn extractability may be largely explained by the variation in Eh between treatments. For example, after 21 days of waterlogged conditions, the Eh for Kras A was -299mV, -250mV and +124mV for M0, M50, and M500, respectively. The higher Eh with increasing metal loading can be attributed to increasing concentrations of nitrate in the added metal solutions, which therefore act as electron acceptors following oxygen depletion (Phillips, 1998b). Under less-severe chemically reducing conditions, Fe and Mn hydrous oxides would have been less soluble, which would have limited the associated release of metals sorbed by these materials.

CONCLUSIONS

Waterlogging caused small but often nonsignificant increases in Cu, Pb, Cd, and Zn sorption by three soils of contrasting chemical and physical properties. The strong relationship between CEC, coupled with the high proportion of these metals in an exchangeable form, suggests that much of the added metals were retained by nonspecific interactions. This finding was attributed to the high metal loading rates employed in this study. Competitive sorption was observed in soils where the number of sorption sites was limiting, and/or where the soil colloids had a higher affinity for particular cations relative to others (e.g., $Al^{3+} > Cd^{2+}$).

After the addition of Cu, Pb, Cd, and Zn there was an initial rapid sorption of these metals, followed by their redistribution from available fractions (water-soluble and exchangeable) to nonexchangeable fractions (e.g., bound to Fe and Mn oxides and bound to organic matter). The increased extractability of the metals under waterlogged conditions was closely related to Fe and Mn solubility and soluble organic carbon concentrations, suggesting that solubilization of Fe and Mn oxides and soil organic matter caused a concomitant release of previously sorbed metals. More importantly, however, these results show that a significant proportion of the added metals remained in a readily extractable form over the 21-day period, and these amounts increased with increasing loading rate.

From these results it appears that waterlogged soils have a similar ability to sorb heavy metals to that of freely drained soils where high metal loading rates are employed. In a wetland system, soils should be selected which exhibit a moderate to high CEC (>15 cmol kg^{-1}), and whose exchange sites are initially balanced by cations with a weaker affinity for the sorption sites. However, because a major proportion of the sorbed metals may be retained by nonspecific forces they will be susceptible to desorption via cation exchange processes and via solubilization of Fe and Mn hydrous oxides, and, consequently, have the potential for contaminating receiving waters. More detailed work is currently being undertaken regarding the application of the findings from these laboratory-based experiments to a fully operational wetland system under field conditions.

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