

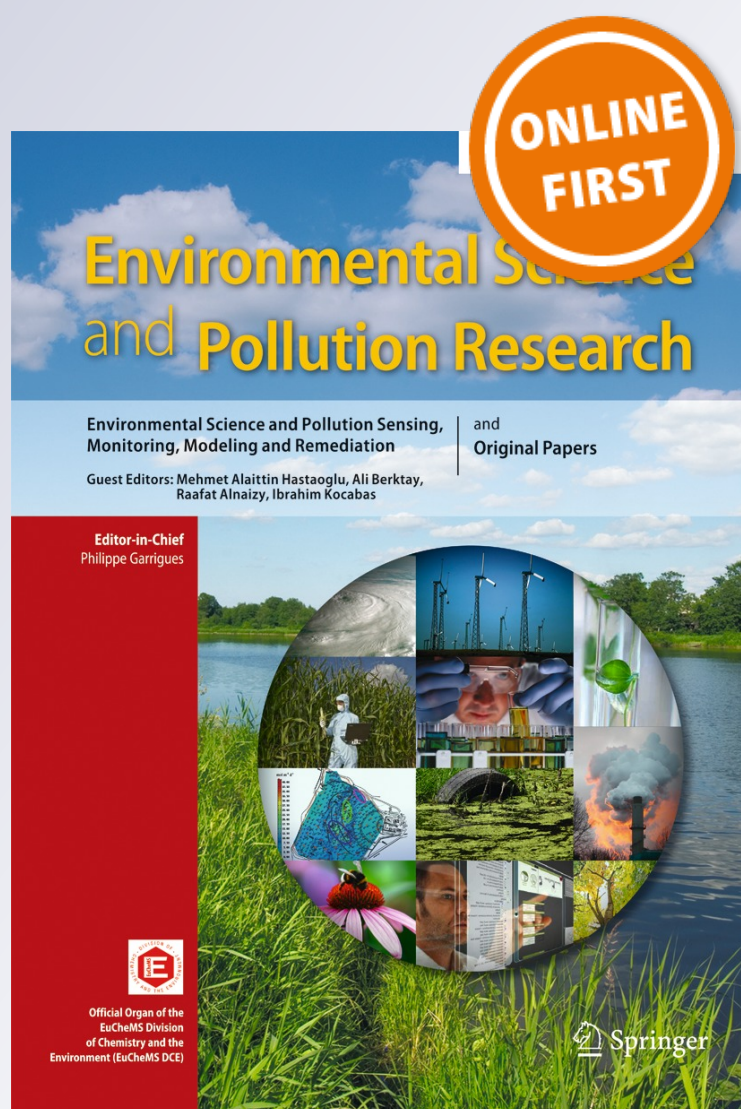
# *Effects of time, soil organic matter, and iron oxides on the relative retention and redistribution of lead, cadmium, and copper on soils*

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# Effects of time, soil organic matter, and iron oxides on the relative retention and redistribution of lead, cadmium, and copper on soils

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**Abstract** In order to predict the bioavailability of toxic metals in soils undergoing degradation of organic matter (OM) and iron oxides (IOs), it is vital to understand the roles of these soil components in relation to metal retention and redistribution with time. In this present work, batch competitive sorptions of Pb(II), Cu(II), and Cd(II) were investigated between 1 and 90 days. Results showed that competition affected Cd(II) sorption more than Cu(II) and Pb(II). The sorption followed the trend  $Pb(II) \gg Cu(II) > Cd(II)$ , irrespective of aging, and this high preference for Pb(II) ions in soils reduced with time. Removal of OM led to reduction in distribution coefficient ( $K_d$ ) values of  $\approx 33\%$  for all cations within the first day. However,  $K_d$  increased nearly 100% after 7 days and over 1000% after 90-day period. The enhanced  $K_d$  values indicated that sorptions occurred on the long run on surfaces which were masked by OM. Removal of IO caused selective increases in the  $K_d$  values, but this was dependent on the dominant soil constituent(s) in the absence of IO. The  $K_d$  values of the IO-degraded samples nearly remained constant irrespective of aging indicating that sorptions on soil components other than the IO are nearly instantaneous while iron oxides played greater role than other constituents with time. Hence, in the soils studied, organic matter content determines the immediate relative metal retention while iron oxides determine the redistribution of metals with time.

**Keywords** Soil organic matter · Iron oxides · Relative metal retention · Bioavailability

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## Introduction

Aquifer contamination depends on several factors and conditions and can be predicted using models such as DRASTIC (Aller et al. 1987). Such models assume that bioavailability depends on soil texture, hydrological conditions, hydrogeological settings, and climatic conditions. However, the effects of soil properties are not accounted for when using these models. It is well documented that soil constituents such as organic matter (OM) and iron oxides (IOs) play important roles in the sorption of contaminants in soil (Pérez-Novo et al. 2008; Agbenin 2010; Agbenin and Olojo 2004; Mustafa et al. 2004; Olu-Owolabi et al. 2014), but the effects of degradation of soil OM/IO and contaminant/soil contact time on redistribution of contaminants within the soil constituents are hardly known.

Contaminants of priority concern in soils include heavy metal cations such as Pb(II), Cd(II), and Cu(II). The fate of these metals in soils is dependent on their specific sorption reactions with soil constituents (Arias et al. 2002; Pérez-Novo et al. 2008; Agbenin 2010) which determine their bioavailability and the severity of the harm they cause in the environment (Olu-Owolabi et al. 2012). OM and IOs in soils are major natural sinks for metals. OM in soils are either bound or coated onto other soil mineral fractions. They possess high molecular weights, exhibit low mobility in soil, and have various functional groups endowing them with a high capacity to immobilize potentially toxic metals (Pérez-Novo et al. 2008). Tropical soils are especially rich in hydrous IO minerals (hematite, goethite, and ferrihydrite). The surface chemistry of these oxides is responsible for the adsorption, remobilization, and distribution of toxic metals (Mustafa et al. 2004; Spathariotis and Kallianou 2001). Studies have reported non-competitive and competitive sorptions of heavy metals on soils in relation to its OM or IO contents (Agbenin 2010; Pérez-Novo et al. 2008; Arias et al. 2002; Juang and Chung 2004;

Lai et al. 2002; Serrano et al. 2005; Shaato 1996). However, in the environmental water solution, metals occur as cocktail and the redistribution of the adsorbed metals is unknown especially for soils prone to environmental degradation.

Although the roles of soil OM and IO constituents are well established for short-time metal adsorptions from single-metal solutions, there is lack of information on the relative retention of metals as soil constituents degrade, as well as the effect of time on redistribution during such a scenario. Hence, the aim of this work was to study the effects of time, soil organic matter, and iron oxides on the relative retention and redistribution of Pb(II), Cd(II), and Cu(II) on tropical soils.

## Materials and methods

### Sampling and soil characterization

Four tropical surface soils (0–30 cm) with contrasting physical and chemical properties were obtained from different agro-ecological zones (AEZs) of Nigeria (Table 1 and 2). Prior to sorption experiments, the soil samples were air-dried, crushed gently, and sieved through a 230-mesh-size sieve and the fine fractions ( $\leq 70 \mu\text{m}$ ) retained for the study. The soils' pH, particle size determination, OM, and metals (oxides, exchangeable and trace) were determined following standard analytical methods (Olu-Owolabi et al. 2014). The cation exchange capacity (CEC) values were determined from the exchangeable bases and the exchange acidity. Exchangeable bases (Na, K, Ca, and Mg) were determined by the 1.0 M ammonium acetate ( $\text{NH}_4\text{OAC}$ ) method at pH 7.0 while the exchange acidities were determined by titration method (Benton 2001). Metals and metal oxides in this study were determined using inductively coupled plasma optical emission spectrometry (ICP-

OES, Optima 5300DV), except for Cd which was by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7500).

### Soil organic matter and iron oxide removal

Soil OM and IOs in the samples were removed using hot hydrogen peroxide (30 %) and sodium dithionite in citrate-bicarbonate buffer, respectively, following the procedure described by McKeague (1978). Complete removal of OM and IOs was indicated by the color of the samples which turned reddish/brown and gray, respectively. The treated soil samples were washed five times, dried, sieved as above, and labeled as organic-matter-degraded (OMD) and iron-oxide-degraded (IOD), respectively.

### Noncompetitive sorptions of lead, copper, and cadmium

Solution-sample mixtures for Pb(II), Cu(II), and Cd(II) adsorptions were obtained by weighing 1.0 g of each soil and equilibrating with 20 mL nitrate solution (200 mg/L) of the individual metals over varying pH range (3–7) and time (30–1440 min) and at  $26 \pm 2 \text{ }^\circ\text{C}$  using 0.01 M  $\text{NaNO}_3$  as background electrolyte (Olu-Owolabi et al. 2014). The mixtures were incubated in corked polyethylene bottles by shaking in a thermostat ( $25 \text{ }^\circ\text{C}$ ) shaker for 1440 min (except for the effect of time experiments) at the ambient soil pH except for the effect of pH. The pH values of these solutions were monitored during the incubation periods to ensure that they remained within the ambient soil pH values (Table 1). At the end of the incubations, the mixtures were centrifuged at 4000 rpm for 20 min and then analyzed (as described in the "Sampling and soil characterization" Section) to determine the concentration of Pb(II), Cu(II), or Cd(II) left in each solution. All experiments were done in duplicate.

**Table 1** Physico-chemical properties of the soil samples

Soil	pH water	pH KCl	CEC (cmolc/kg)	OM (%)	Particle size analysis (%)			Oxides (wt%)		Trace elements/heavy metals (mg/kg)					
					Sand <sup>a</sup>	Silt <sup>b</sup>	Clay <sup>c</sup>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	Cd	Cu	Mn	Pb	Zn	Ni
Lokoja (LF)	6.73	5.86	8.29	6.25	48.28	31.07	20.64	0.16	1.69	0.02	7.64	220.70	16.84	24.62	0.91
Gembu (GSF)	5.14	4.25	2.37	2.80	13.88	79.75	6.36	3.90	15.75	0.00	20.15	126.30	29.52	23.24	11.22
Jos (JB)	5.17	4.08	2.98	3.57	42.26	57.11	0.63	3.13	9.12	1.02	33.10	134.20	119.80	165.70	9.85
Maiduguri (MA)	6.67	5.21	4.25	1.67	70.44	28.89	0.67	0.99	2.23	0.10	13.60	123.50	45.85	6.57	0.00

CEC cation exchange capacity, OM organic matter

<sup>a</sup> % sand ( $> 50 \mu\text{m}$ )

<sup>b</sup> % silt (2–50  $\mu\text{m}$ )

<sup>c</sup> % clay ( $< 2 \mu\text{m}$ )

**Table 2** The mineralogical composition of the soils

Soil	Mineral (%)										
	Aragonite	Calcite	Dolomite	Gibbsite	Goethite	Hematite	Illite	Kaolinite	Montmorillonite	Quartz	Siderite
LF	11.77	0.29	16.21	–	18.26	1.51	15.41	11.52	–	25.03	–
GSF	3.84	2.17	3.42	6.06	–	1.87	–	3.97	–	78.67	–
JB	7.86	1.14	11.83	57.13	–	1.47	4.41	5.96	0.59	9.61	–
MA	9.89	2.37	11.72	3.48	–	2.19	–	4.62	0.14	63.21	2.38

LF Lokoja, GSF Gembu, JB Jos, MA Maiduguri

**Competitive sorption of lead, copper, and cadmium on untreated and treated samples**

Competitive adsorption experiments were conducted on the untreated samples (RS) and OMD and IOD soils. Sorptions from mixed solutions containing Pb(II), Cu(II), and Cd(II) ions were assessed like the noncompetitive sorptions above with similar soil–solution ratio but with solutions containing Pb(II), Cu(II), and Cd(II) in ratios (mg/L) of A (100:100:100), B (50:200:50), C (50:50:200), and D (200:50:50). The total cation concentrations used in these ratios did not exceed 300 mg/L since metal concentrations of most polluted soils usually do not exceed 300 mg/L. The soil/metal solution mixtures were stirred intermittently throughout the incubation period. The pH values of the soil/metal solution mixtures were adjusted to 6.0±0.2, and then the mixtures were incubated for 1, 7, and 90 days. After the incubation periods, the mixtures were centrifuged and then analyzed as described above to determine the metal concentrations of solution. These experiments were done in triplicate.

**Data treatment**

The amounts of various metals removed from solution were calculated from the initial ( $C_o$ ) and final ( $C_e$ ) concentrations in solutions using the Eq. 1:

$$q_e = \frac{(C_o - C_e)V}{M} \tag{1}$$

where  $q_e$ ,  $V$ , and  $M$  are the amount of metal sorbed (mg/g), volume of the solution (mL), and mass (g) of sample, respectively.

The distribution coefficients ( $K_d$ ) were calculated from Eq. 2:

$$K_d = \frac{C_{ads}}{C_e} \tag{2}$$

where  $C_{ads}$  and  $C_e$  are the metal amount adsorbed per unit mass of soil (mg/g) and the final concentration of solutions.

The Langmuir (1916) (Eq. 3) and Freundlich (1906) (Eq. 4) adsorption isotherm models were employed in describing the noncompetitive metal adsorptions:

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \tag{3}$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{4}$$

where  $Q_o$  ( $\mu\text{g/g}$ ) is the soil maximum adsorption capacity,  $b$  the binding energy constant, and  $K_f$  and  $n$  are Freundlich isotherm constants.

The data were also described using the Lagergren (1898) pseudo-first-order (PFO) (Eq. 5) and pseudo-second-order (PSO) (Eq. 6) models:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{5}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{6}$$

where  $q_e$  and  $q_t$  are amount sorbed ( $\text{mg g}^{-1}$ ) at equilibrium and at time  $t$ , respectively, and  $k_1$  ( $\text{min}^{-1}$ ) and  $k_2$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ) are the rate constants of PFO and PSO, respectively. The  $q_e$  and rate constants were calculated from the slope and intercept of the plots of  $\log(q_e - q_t)$  versus  $t$ , and  $t/q_t$  versus  $t$  for PFO and PSO, respectively.

**Results and discussion**

**Soil properties**

The soil physicochemical properties are shown in Tables 1 and 2. By correlating the soil physicochemical properties (Tables 1 and 2) with the classification system of the FAO-UNESCO-ISRIC (1988), the soils were classified as Eutric Fluvisols (GSF and LF), Ferric Acrisols (JB), and Ferralic Cambisols (MA). Table 1 shows that the pH values of the LF and MA soils are

neutral while those of GSF and JB are slightly acidic. The CEC values of the soils were low and majorly contributed by the exchangeable cations. Soil OM values were high except for GSF and MA which had medium values. LF had the highest CEC and OM contents. The granulometric measurements showed that the soil textural classes were loamy in nature (soil survey staff, 2006), but percentage of loam and metal oxide contents varied with soil type. GSF and JB had the highest percent of Fe and Al oxides, while heavy/trace metals were within concentration ranges found in soils (Sparks 2003). XRD data analyzed by the PANalytical X Pert HighScore software showed varying mineralogical compositions (Table 2) for the soils; quartz was the most common; GSF and MA had over 60 % quartz, while LF and JB had  $\leq 25$  %. Kaolinite clay (a 1:1 inexpandive clay mineral) and the carbonate minerals (aragonite, calcite, siderite, and dolomite) were common features of these soils. Gibbsite was present in all soils except LF while goethite and hematite were present as minor minerals. Montmorillonite (a 2:1 expansive clay mineral) was found in JB and MA, while Illite, another 2:1 expansive clay mineral, was present in LF and JB.

CEC and soil pH of the whole and treated soils were compared (Table 3) to quantify the changes associated with the respective treatments. It was observed that removal of OM lowered the soils' pH as well as caused a reduction in the CEC values of LF OMD and GSF OMD soils. However, CEC in JB OMD increased significantly (29 %). The decrease in CEC of LF OMD and GSF OMD was an indication that exchangeable cations that contribute to the CEC of these soils are associated with the OM components; thus, removal of the OM led to reduction in CEC values. The CEC increase in JB OMD was attributed to the masking effect of OM on other soil components. OM coated these soil components (especially the

expansive clays minerals—illite and montmorillonite) and masked the contributory exchangeable cations from such components; removal of OM unmasked this effect resulting in the observed increase. This result also showed that the CEC contribution from other components was greater than that from OM in the JB soil. Removal of IO on the other hand resulted in increases in pH and CEC (>100 %). This increase in CEC was attributed to the increases in exchangeable bases (predominantly  $\text{Na}^+$  ions) associated with soil components other than IO, and this may not be unconnected to similar masking effect of IO as described earlier.

#### Cation sorption study

##### *Noncompetitive sorption of lead, copper, and cadmium*

Understanding the sorption characteristics of each separate metal in this study is vital for better comprehension of the behavior of these metals in cocktail solutions. Results of the preliminary non-competitive sorption experiments (Fig. 1) showed that the LF soil had the fastest equilibrium sorption time (60 min) for all three metal ions. The trend is LF (60 min) < GSF (720 min)  $\leq$  JB (720 min) < MA (1440 min). Since the rate of metal sorption in soils may be related to its bioavailability (Lu et al. 2005), it means that these metals will be more available in the MA soil. It was also observed that the sorption trend for the metals were the same in all soils: Pb(II) > Cu(II) > Cd(II).

Fittings of the effect of time data to the PFO, PSO, and IPD kinetics models (Table 4) gave information on the possible mechanism(s) involved in these sorptions (Olu-Owolabi et al. 2014). Comparisons of the correlation coefficients ( $r^2$ ) and the estimated sorption capacities ( $q_e$ ) of the PFO and PSO showed that the data were better described by the PSO; the  $r^2$  values of the PSO were close to unity and the  $q_e$  values were better correlated to the experimentally obtained results. This implied that these sorptions involved sharing or exchange of valence electrons (Diagboya et al. 2014a; Olu-Owolabi et al. 2015).

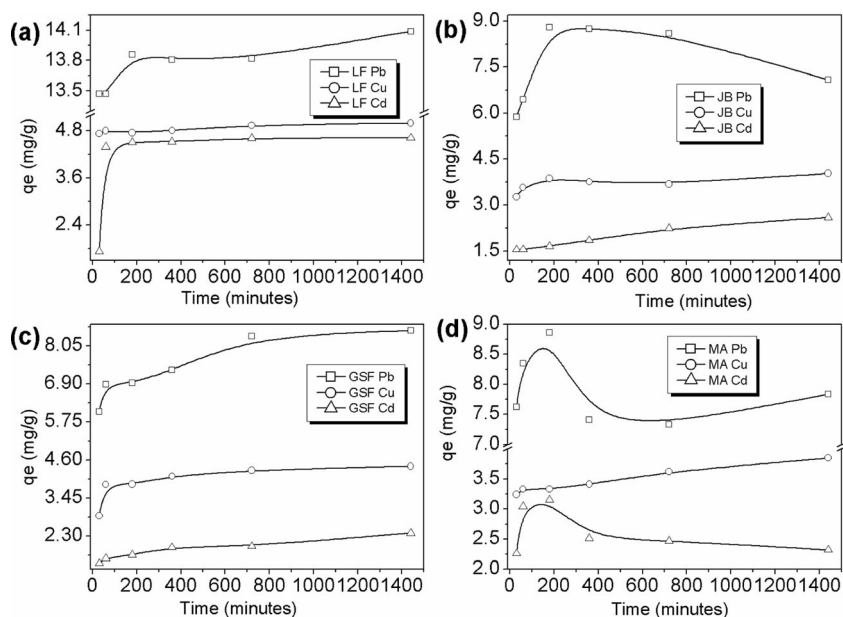
Fitting of the equilibrium sorption data to the Langmuir and Freundlich adsorption isotherm models (Table 5) showed that the sorptions of Pb(II) and Cu(II) on these soils were better described by the Langmuir adsorption isotherm, indicating sorptions on similar sites of nearly equal adsorption energies, and a monolayer adsorption at equilibrium. However, Cd(II) sorption on these soils was better fitted to the Freundlich adsorption isotherm ( $r^2 \geq 0.75$ ) than to the Langmuir, indicating probably multi-layer adsorptions on heterogeneous sites (Diagboya et al. 2014b). In addition, comparing the  $Q_0$  or  $q_e$  (similar) to  $r^2$  ( $\geq 0.75$ ) values for Pb(II) and Cu(II) sorption on LF and JB soils (Table 3) suggests that these data may be described simultaneously by the Langmuir and Freundlich isotherms, suggesting that the final isotherms were combinations of several Langmuir-type isotherm (Weber et al. 1992).

**Table 3** Comparison of selected physico-chemical characteristics of three whole and treated soils

	pH H <sub>2</sub> O	pH KCl	CEC (cmol kg <sup>-1</sup> )	Exchangeable cations (cmol kg <sup>-1</sup> )			
				Ca	Mg	K	Na
LF	6.73	5.86	8.29	6.03	1.15	0.21	0.75
GSF	5.14	4.25	2.37	1.35	0.07	0.10	0.71
JB	5.17	4.08	2.98	1.84	0.38	0.23	0.09
LF OMD	6.08	5.57	3.26	0.41	2.18	0.30	0.33
GSF OMD	4.38	3.98	2.14	0.44	0.26	0.14	0.24
JB OMD	4.14	3.63	3.87	2.14	0.52	0.31	0.15
LF IOD	7.79	7.01	17.91	1.88	0.49	0.15	15.35
GSF IOD	8.06	7.26	24.77	2.87	0.14	0.42	21.26
JB IOD	8.00	6.98	37.94	1.31	0.30	0.38	35.87

LF Lokoja, GSF Gembu, JB Jos, OMD organic-matter-degraded, IOD iron-oxide-degraded

**Fig. 1** Effect of time on metal sorptions on **a** LF, **b** JB, **c** GSF, and **d** MA soils



Weber et al. (1992) has shown that combination of several Langmuir-type isotherms results in a Freundlich-type isotherm.

*Competitive sorptions of Pb(II), Cu(II), and Cd(II) ions on untreated and treated soils*

Distribution coefficients ( $K_d$ ) of the competitive sorptions studies are shown in Figs. 2, 3, 4 and Tables 6, 7, 8 for the various soils and incubation periods. It was observed that  $K_d$  values for the LF whole soil (Fig. 2) were higher than other whole soils; this was attributed to the high OM content and CEC of the LF soil. Competition had the least effect on Pb(II) sorptions while the highest effect was on Cd(II). The  $K_d$  values increased with time; however, depending on the solution concentration ratios, there were both  $K_d$  reductions and increments after 7- and 90-day periods.

Competitive sorption (at equal cation ratios) showed that  $K_d$  values for Pb(II) increased continuously while those of Cu(II) and Cd(II) increased in the first 7 days and then decreased afterward. This  $K_d$  increase in the first 7 days was regarded as “superficial” because  $K_d$  values of metal ions decreased with time (90 days), and this was attributed to the superficial nature of the sorption which resulted in easy metal desorption from the surfaces with time. This argument is in line with the IPD model parameter  $C$  described above which showed that sorptions on these whole soils were mainly a surface phenomenon. These high  $K_d$  values or preference for Pb(II) ions implied that these soils had higher affinity for Pb(II) ions.

Higher solution Cu(II) ratio in cocktail ratio  $B$  did not lead to higher Cu(II)  $K_d$  values but to reduction in Pb(II) and Cd(II)  $K_d$  values within the 7-day period. This implied that increased competition led to higher disorder in the soil solution system but with no concomitant rise in the sorption of the ion with

**Table 4** Adsorption kinetics model parameters for Pb(II), Cu(II), and Cd(II)

		LF			JB			GSF			MA		
		Pb(II)	Cu(II)	Cd(II)	Pb(II)	Cu(II)	Cd(II)	Pb(II)	Cu(II)	Cd(II)	Pb(II)	Cu(II)	Cd(II)
PFO	$q_e$ (mg g <sup>-1</sup> )	1.43	1.76	1.09	1.50	5.41	7.40	2.45	0.90	0.79	1.04	1.13	1.85
	$K_1$ (min <sup>-1</sup> )	0.000	0.000	0.001	0.000	0.000	0.000	0.001	0.001	0.001	0.000	0.001	0.001
	$r^2$	0.746	0.917	0.304	0.003	0.531	0.976	0.898	0.757	0.956	0.104	0.999	0.229
PSO	$q_e$ (mg g <sup>-1</sup> )	14.08	5.03	4.69	7.19	4.02	2.67	8.70	4.46	2.40	7.75	3.88	2.30
	$K_2$ (g mg <sup>-1</sup> min <sup>-1</sup> )	0.015	0.026	0.011	0.005	0.014	0.004	0.004	0.011	0.007	0.052	0.010	0.017
	$r^2$	0.999	0.999	0.999	0.990	0.997	0.988	0.998	0.999	0.990	0.998	0.998	0.998

PFO pseudo-first-order, PSO pseudo-second-order, LF Lokoja, GSF Gembu, JB Jos, MA Maiduguri

**Table 5** Isotherm model parameters

Adsorption isotherm	Isotherm parameters	LF			JB			GSF			MA		
		Pb(II)	Cu(II)	Cd(II)	Pb(II)	Cu(II)	Cd(II)	Pb(II)	Cu(II)	Cd(II)	Pb(II)	Cu(II)	Cd(II)
Langmuir	$Q_0$ (mg g <sup>-1</sup> )	14.93	4.59	4.42	7.81	3.23	0.26	8.40	2.86	0.10	10.99	3.17	0.10
	$b$	0.918	0.445	0.005	0.011	0.095	0.004	0.01	0.074	0.005	0.011	0.033	0.005
	$r^2$	0.996	0.987	0.289	0.95	0.96	0.462	0.764	0.948	0.604	0.883	0.903	0.438
Freundlich	$q_c$ (mg g <sup>-1</sup> )	15.16	4.77	2.29	6.37	3.07	1.80	6.64	3.04	3.08	9.02	2.48	3.13
	$n$	0.16	0.22	0.68	0.25	0.24	2.09	0.30	0.31	3.06	0.35	0.27	2.91
	$r^2$	0.766	0.917	0.753	0.871	0.816	0.808	0.575	0.69	0.845	0.781	0.919	0.858
	$k_f$	8.11	1.89	0.06	1.41	0.96	0.00	1.12	0.63	0.00	1.14	0.65	0.00
Experimental	$q_e$ (mg g <sup>-1</sup> )	14.91	4.56	2.01	6.88	3.12	1.02	8.82	2.63	1.42	8.85	2.92	1.60

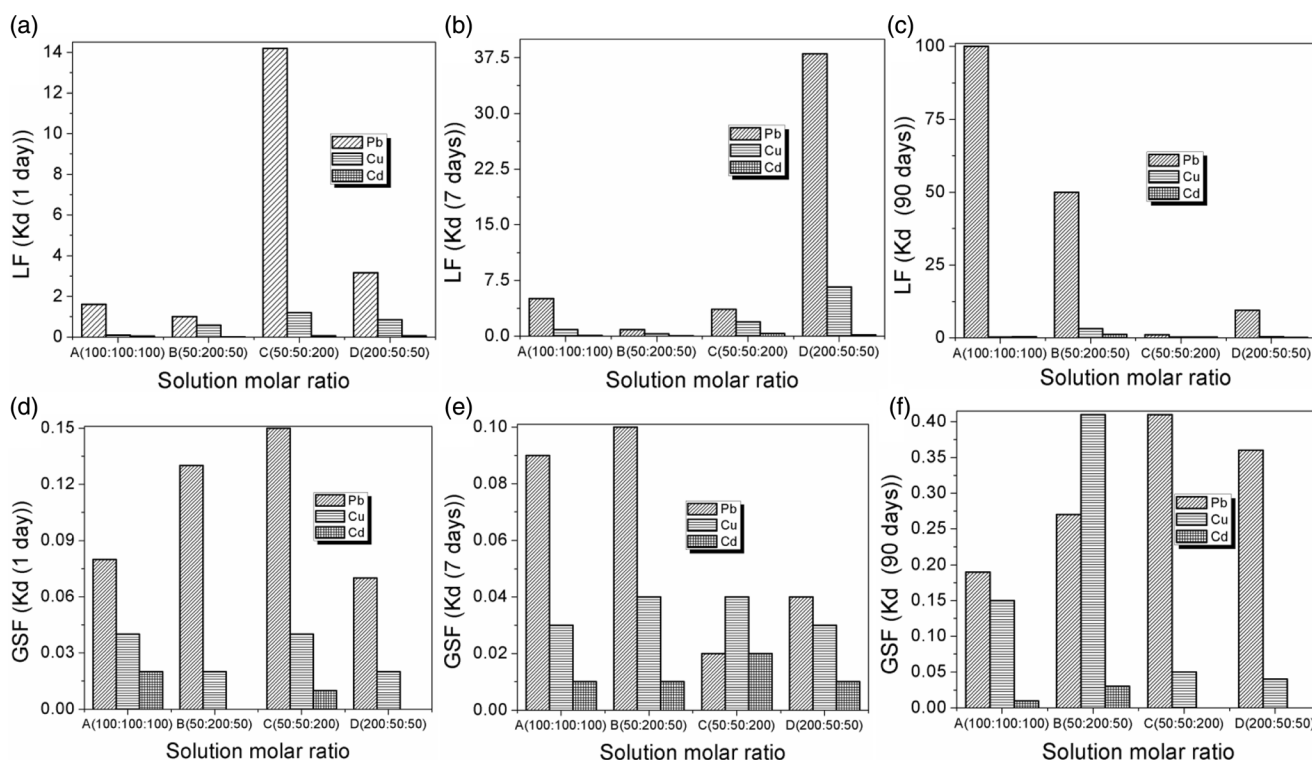
LF Lokoja, GSF Gembu, JB Jos, MA Maiduguri

higher concentration (Cu(II)) or higher sorption for the usually preferred cation (in this case Pb(II)).

Increasing Cd(II) concentration in cocktail ratio C led to increase in  $K_d$  values of Cu(II) and Cd(II) but a decrease for Pb(II) within the first 7 days. After the 90-day period, there was a threefold reduction in  $K_d$  values for Pb(II) and a sixfold reduction for Cu(II), while no changed was observed for Cd(II). Increasing the ratio of solution Pb(II) in cocktail ratio D increased the Pb(II)  $K_d$  value only within the first 7 days while Cd(II)  $K_d$  values increased gradually with time. This could mean that the binding of Pb(II) ions has some kind of co-operative binding effect on Cd(II) ions, and this is in

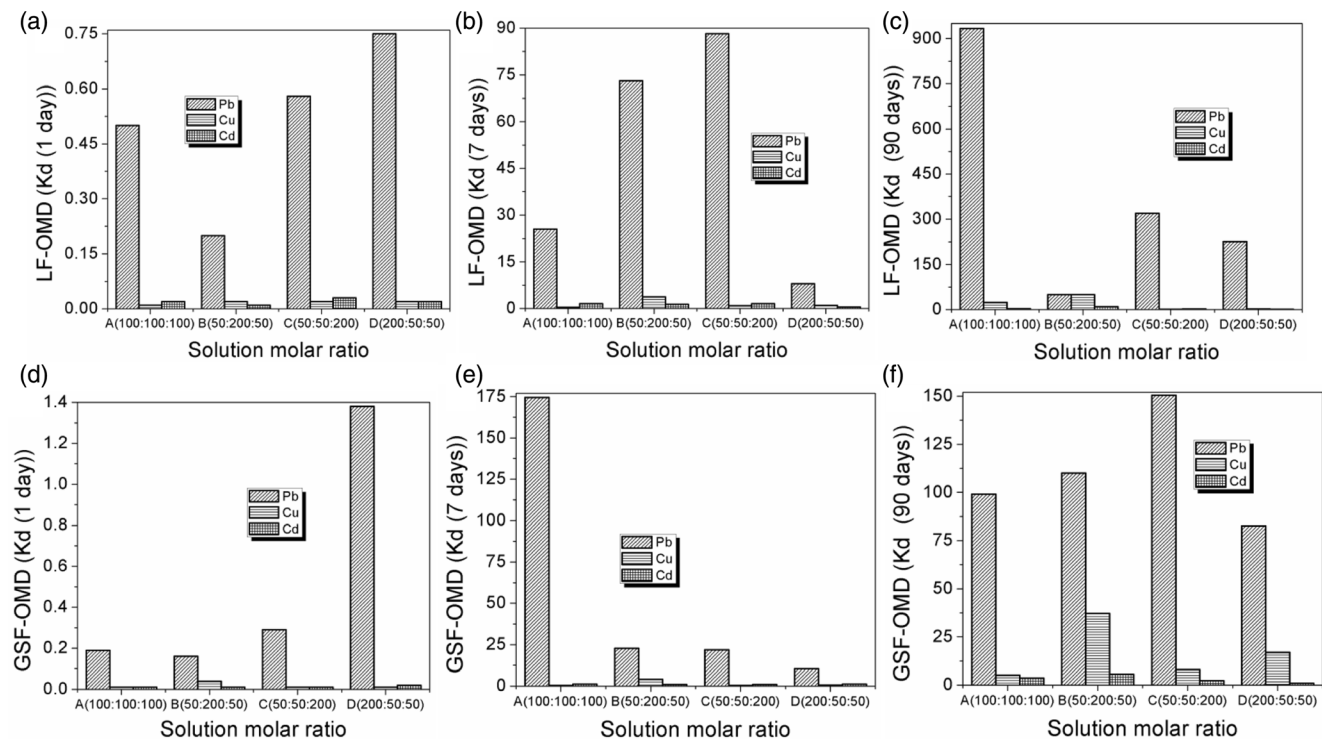
agreement with the fitting of the non-competitive Cd(II) sorption data to the Freundlich adsorption isotherm implying sorption on heterogeneous sites of unequal energies. However, the Cu(II)  $K_d$  values showed increase (7-fold) and decrease (14-fold) after the 7 and 90 days, respectively.

The sorption trends in the GSF whole and treated soils (OMD and IOD) were similar to those of MA and JB whole and treated soils (Figs. 2, 3, 4 and Tables 6, 7, 8); this may not be unrelated to their similar physicochemical characteristics in terms of low clay, CEC, and OM contents of these soils. Hence, the explanation of the GSF whole and treated soils will suffice for these soils too. Comparing the  $K_d$  values of these



**Fig. 2** Distribution coefficients ( $K_d$ ) for Pb(II), Cu(II), and Cd(II) ions on LF and GSF whole soils

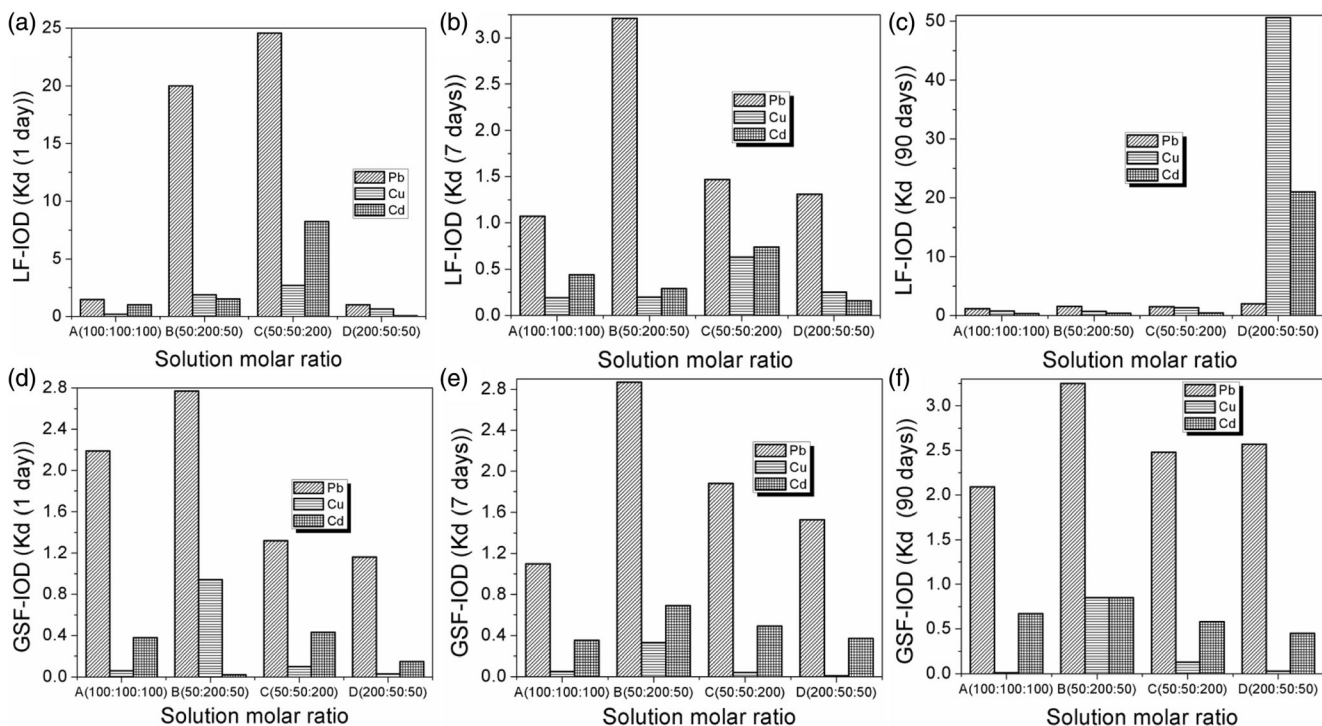




**Fig. 3** Distribution coefficients ( $K_d$ ) for Pb(II), Cu(II), and Cd(II) ions on LF OMD and GSF OMD soils

cations for the JB, GSF, and MA soils, it was observed that Pb(II) also had higher  $K_d$  values than Cu(II) and Cd(II), but in general, there was no significant increase in  $K_d$  values of these soils with time. In this study, competition was observed to be greater for Cd(II) than for Cu(II) and Pb(II); the sorption trend

of the metal cations in all soils followed the same trend as in the single sorption: Pb(II)>Cu(II)>Cd(II). This trend was attributed to the fact that Cd(II) is basically retained in the soil by exchange reactions, while Cu(II) and Pb(II) form inner sphere complexes with OM, Fe, Al, and Mn oxides. Hence,



**Fig. 4** Distribution coefficients ( $K_d$ ) for Pb(II), Cu(II), and Cd(II) ions on LF IOD and GSF IOD soils

**Table 6** Competitive adsorptions distribution coefficients ( $K_d$ ) for the untreated JB and MA soils at the various molar concentrations of metals

Solution molar ratio	$K_d$ (1 day)			$K_d$ (7 days)			$K_d$ (90 days)		
	Pb	Cu	Cd	Pb	Cu	Cd	Pb	Cu	Cd
JB A <sup>a</sup>	0.03	0.01	0.01	0.08	0.04	0.01	0.31	0.04	0.01
JB B <sup>b</sup>	0.05	0.02	0.01	0.09	0.03	0.00	0.53	0.17	0.01
JB C <sup>c</sup>	0.09	0.03	0.01	0.13	0.04	0.02	0.08	0.03	0.00
JB D <sup>d</sup>	0.06	0.02	0.01	0.08	0.04	0.01	0.04	0.01	0.00
MA A <sup>a</sup>	0.05	0.04	0.01	0.06	0.02	0.01	0.13	0.03	0.00
MA B <sup>b</sup>	0.04	0.02	0.01	0.05	0.01	0.01	0.07	0.03	0.00
MA C <sup>c</sup>	0.08	0.02	0.01	0.08	0.07	0.01	0.20	0.13	0.01
MA D <sup>d</sup>	0.06	0.07	0.01	0.08	0.04	0.01	0.25	0.08	0.00

<sup>a</sup>A=(1:1:1); <sup>b</sup>B=(1:4:1); <sup>c</sup>C=(1:1:4); <sup>d</sup>D=(4:1:1)—the figures in parentheses represent the ratio of Pb(II), Cu(II), and Cd(II) in aqueous solutions, respectively

in competitive adsorption, Cu(II) and Pb(II) maintain their strong affinity on the surface sites, while Cd(II) is displaced from the surface sorption sites. A similar trend has been reported by Lu and Xu (2009) for some Chinese soils.

The preference for Pb(II) over Cu(II) and Cd(II) is not new because it has been recognized that Pb(II) can compete effectively with Cu(II) or other cations for similar adsorption sites (Heidmann et al. 2005; Lu and Xu 2009); however, the observed reduced affinity (which led to lower  $K_d$  values) with longer incubation time is interesting. The implication of this is that competition among metal ions in solution for similar adsorption sites tends to suppress the strength and magnitude of some other metals retention.

The  $K_d$  values obtained for competitive sorptions on the treated soils (Figs. 3 and 4, and Tables 7 and 8) showed similar

**Table 7** Competitive adsorptions distribution coefficients ( $K_d$ ) for the JB OMD and MA OMD soils at the various molar concentrations of metals

Conc. ratio	OMD, 1 day			OMD, 7 days			OMD, 90 days		
	Pb	Cu	Cd	Pb	Cu	Cd	Pb	Cu	Cd
JB A <sup>a</sup>	0.07	0.01	0.03	5.40	1.38	0.93	26.97	4.61	0.97
JB B <sup>b</sup>	0.09	0.02	0.03	3.14	1.62	0.83	75.92	131.93	3.48
JB C <sup>c</sup>	0.10	0.01	0.01	9.04	1.64	1.20	51.91	64.19	1.18
JB D <sup>d</sup>	0.17	0.01	0.01	53.57	99.81	0.49	11.21	22.93	0.41
MA A <sup>a</sup>	0.03	0.01	0.01	2.08	0.68	0.72	3.39	1.45	0.28
MA B <sup>b</sup>	0.02	0.02	0.01	1.30	0.93	0.22	1.61	1.08	0.09
MA C <sup>c</sup>	0.05	0.02	0.15	0.28	0.44	0.64	20.83	1.83	0.82
MA D <sup>d</sup>	0.04	0.02	0.01	1.90	0.58	0.34	4.87	2.60	0.10

<sup>a</sup>A=(1:1:1); <sup>b</sup>B=(1:4:1); <sup>c</sup>C=(1:1:4); <sup>d</sup>D=(4:1:1)—the figures in parentheses represent the ratio of Pb(II), Cu(II), and Cd(II) in aqueous solutions, respectively

**Table 8** Competitive adsorptions distribution coefficients ( $K_d$ ) for the JB IOD and MA IOD soils at the various molar concentrations of metals

Conc. ratio	IOD, 1 days			IOD, 7 days			IOD, 90 days		
	Pb	Cu	Cd	Pb	Cu	Cd	Pb	Cu	Cd
JB A <sup>a</sup>	0.81	0.34	1.42	0.21	0.01	0.11	0.39	0.05	0.04
JB B <sup>b</sup>	0.87	0.24	0.10	0.05	0.02	0.01	1.70	0.00	0.25
JB C <sup>c</sup>	0.52	0.10	0.23	0.47	0.02	0.05	0.97	0.07	0.07
JB D <sup>d</sup>	0.57	0.24	0.06	0.24	0.01	0.01	0.55	0.03	0.00
MA A <sup>a</sup>	0.27	0.15	0.13	0.28	0.01	0.08	0.15	0.04	0.01
MA B <sup>b</sup>	0.52	0.36	0.02	0.64	8.33	0.01	0.25	0.67	0.01
MA C <sup>c</sup>	0.67	0.27	1.85	0.63	0.06	0.10	0.33	0.15	0.01
MA D <sup>d</sup>	0.34	0.08	0.03	0.53	0.23	0.01	0.14	0.35	0.01

<sup>a</sup>A=(1:1:1); <sup>b</sup>B=(1:4:1); <sup>c</sup>C=(1:1:4); <sup>d</sup>D=(4:1:1)—the figures in parentheses represent the ratio of Pb(II), Cu(II), and Cd(II) in aqueous solutions, respectively

sorption trend as the whole soils (Pb(II)>Cu(II)>Cd(II)) irrespective of the solution cation ratio and incubation time. Removal of OM in the LF soil (LF OMD) led to drastic reductions in  $K_d$  values (Fig. 3 and Table 7) for all cations when compared to the whole soils (1-day incubation). The  $K_d$  values were, however, nearly 100 % higher than after 7 days of incubation, and over 1000 % after the 90-day incubation. The drastic reduction in cation sorption for 1-day incubation of the OMD soils implied that the sorptions on the OM components of the soils were nearly instantaneous, while the enhanced  $K_d$  values observed for the same soil samples after the 7- and 90-day incubations indicated that with longer incubation periods, sorptions occurred on surfaces which (i) have been masked by SOM and thus prevented sorption on the whole samples, and (ii) become available with longer incubation in aqueous solution such as the expansive clays—montmorillonite and illite (Table 2).

Removal of the iron oxides in the LF sample (LF IOD) led to higher  $K_d$  values (Fig. 4 and Table 8) in the 1-day incubations. These  $K_d$  values were higher than those observed in the whole soil after corresponding incubation periods; these high  $K_d$  values were attributed to metal ions that were weakly sorbed (physisorbed) because longer incubation time led to lower  $K_d$  values. These physisorbed metal ions may be related to the good fit of the sorption data to the Freundlich adsorption isotherm observed in the non-competitive sorption. Such fitting implies multi-layer adsorptions which can easily be desorbed with time and, hence, the lower  $K_d$  values with longer incubation.

The IOD soil samples with low OM contents (GSF, JB, and MA) showed no significant change in  $K_d$  values with time. This confirmed that apart from the OM components of these soils, the iron oxide components played significant roles in metal sorption.

## Conclusion

The metal distribution and redistribution patterns for untreated and treated soil showed that soils with high organic matter content retained more metal ions than those with high iron oxides content in the short term. In the long term, however, high organic matter contents led to reduced metals retention and increased desorption with time, while iron oxides enhanced retention and retarded desorption with time. Hence, soil organic matter played significant role in the short-time (less than 7 days) sorptions of metals while iron oxides at longer times. The high metal sorption capacity of some soils implied a risk of future environmental re-contamination because these metals become desorbed with time. Irrespective of solution concentration, metals retained by inner sphere complexation are preferentially sorbed; however, there is reduction in this preference with time in the presence of high concentrations of other metals not retained by this mechanism. Thus, time and competition among metal ions in solution for similar adsorption sites are vital parameters needed for prediction of the retention, redistribution, and bioavailability of metals in soils undergoing degradation of organic matter and iron oxides.

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