Adsorption-solubility equilibria and speciation of Pb, Cd, and Zn in a savanna soil

Equilibrios de adsorción-solubilidad y especiación de Pb, Cd y Zn en un suelo de sabana
Equilíbrio de adsorção-solubilidade e especiação de Pb, Cd e Zn num solo de savana

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ABSTRACT

Emission of contaminants into the environment is a common feature of industrialization. The danger of these substances has generated interest in their solubility and speciation. In this study, the nature of adsorption, solubility and speciation of Pb, Cd and Zn under high levels of accumulation were evaluated through a model sorption-solubility experiment. Equilibrium concentrations of metals and other soil characteristics were used as input parameters in a metal speciation model. The solubility controls of metal activities were evaluated through the use of activity/stability diagrams. The solubility of Pb, Cd and Zn was enhanced between pH 4.8 and 6.6. Increased solubility at this pH range indicates higher bioavailability and toxicity. Speciation results showed a predominance of free metal species in the soil solution. The activity diagrams used to test the stability of possible mineral bearing compounds in the soils did not show any particular solid phase as possible control of the activities of Pb, Cd and Zn in solution. This suggests that solubility controls might be due to the formation of metastable minerals which are not well crystallized.

RESUMEN

La emisión de contaminantes al medio ambiente es una práctica común como consecuencia del proceso de industrialización. El peligro que estas sustancias genera ha despertado el interés por el estudio de su solubilidad y especiación. En este trabajo se evalúa la naturaleza de la adsorción, solubilidad y especiación de Pb, Cd y Zn en condiciones de elevada acumulación a través de un modelo de sorción-solubilidad. Como parámetros de entrada del modelo se utilizaron las concentraciones en equilibrio de los metales y otras características del suelo. Los controles de solubilidad de las actividades de los metales se evaluaron mediante diagramas de actividad/estabilidad. Las solubilidades de Pb, Cd y Zn fueron más elevadas a pH entre 4,8 y 6,6. El incremento de la solubilidad dentro de este rango de pH indica una mayor biodisponibilidad y toxicidad. Los resultados de la especiación mostraron un predominio de las especies metálicas libres en la solución del suelo. Los diagramas de actividad utilizados para evaluar la estabilidad de posibles compuestos minerales en los suelos no mostraron ninguna fase sólida en particular como posible control de las actividades de Pb, Cd y Zn en solución. Esto sugiere que su solubilidad podría estar controlada por la formación de minerales metaestables mal cristalizados.

RESUMO

A emissão para o ambiente de contaminantes é uma caraterística comum da industrialização. O perigo deste tipo de substâncias tem vindo a despertar interesse no que se refere à sua solubilidade e especiação. Neste estudo avaliou-se num ensaio recorrendo a um modelo sorção-solubilidade, a natureza da adsorção, solubilidade e especiação do Pb, Cd e Zn em condições de elevada acumulação. No modelo de especiação de metais utilizaram-se como parâmetros de entrada as concentrações de equilíbrio dos metais bem como outras caraterístícas do solo. O controlo da solubilidade das atividades dos metais foram avaliadas recorrendo ao uso de diagramas atividade/estabilidade. A solubilidade do Pb, Cd e Zn aumentou para valores de pH entre 4,8 e 6,6. O aumento da solubilidade nesta gama de pH é indicativo de maior biodisponibilidade e toxicidade. Os resultados da especiação revelaram uma predominância de espécies de metais na forma livre na solução do solo. Os diagramas de atividade usados para testar a estabilidade de possíveis compostos minerais perigosos no solo não revelaram nenhuma fase sólida em particular suscetível de controlar as atividades do Pb, Cd e Zn em solução. Este facto sugere que o controlo da solubidade deve ser devida a minerais metastizados que não ese encontram ainda perfeitamente cristalizados.

1. Introduction

Several studies have been conducted on heavy metal retention, adsorption and solubility as a result of their potential toxicities to biota and humans and possible food chain contamination (Martínez and Motto 2000). The form of sorption reaction between metal contaminants and the soil solid determines the extent to which an element can be re-mobilized to the ground water, where it causes pollution to aquatic life and, eventually, humans.

To evaluate the extent of a metal's retention by the soil, sorption studies involving either a batch or a column technique are normally employed. Sorption studies have found application in evaluating the effect that changing a soil solution parameter have on metal retention (McLean and Bledsoe 1992). Such studies have also been used to suggest the type of sorption reaction involved in the retention of Cd on two different types of soils (McLean and Bledsoe 1992). In principle, the metal retention capacity of a soil could be a useful tool in the design of remediation techniques that utilizes the soil as a natural sorbent for contaminants in free water bodies. However, the laboratory procedures employed in these studies suffer from a major limitation in that they do not allow enough reaction time to attain equilibrium (Martínez and Motto 2000). Although several authors have reported in the influence of pH on metal sorption (Saeki and Kunito 2009; Silber et al. 2012; Najafi and Jalali 2016), there is also a dearth of information on the pH at which solubility of added metals increases (Martínez and Motto 2000) especially for tropical savanna soils that differ considerably in reactions.

In cases where very high levels of heavy metals accumulate in soils, the formation of compounds that controls the activity of the metal in solution is a possibility (Santillan-Medrano and Jurinak 1975). The extent of this process is influenced by soil conditions such as pH, redox condition, ionic strength, etc. In temperate soils where climatic processes suffer less seasonality, mineral solubility principles have found wider applications. Thus, the objectives of the present study were: 1) to use mineral solubility principles to predict the formation of trace element bearing minerals in tropical savanna soils, using the addition of heavy metals to soils to levels attainable under heavy contamination and aging of the system; 2) to study the solubility and speciation of the added heavy metals at varying pH levels in order to observe the points of maximum and minimum solubilities and species distribution in solution.

2. Material and methods

2.1. Sampling and soil analysis

The soils for this study were collected from farmlands around a lead contaminated goldmine in Dareta village, Anka local government area (LGA) of Zamfara State, northern Nigeria. Anka is located at 12º 06' 30" N, 5º 56' 00" E and has an area of 2,746 km^2 and a population of 142,280 at the time of the 2006 census (Mohammed and Abdu 2014). The climate of Zamfara is a Sudan savannah with a mean annual rainfall of 579 mm. The dominant soil type is a Typic Haplustalf, according to the USDA classification (Soil Survey Staff 2010). Soil samples were taken at 0-20 cm depth. on a grid at distances of 10, 30, 50, 150, 300, 500, and 1000 m. The soil samples were air dried and screened through a 2-mm sieve. The particle size distribution of the soils was determined by the hydrometer method (Gee and Or 2002). The pH of the soil samples was determined in 1:2.5 soil:water ratio. The cation exchange capacity (CEC) was determined by ammonium acetate (NH4OAC) saturation (Rhoades 1982). Organic carbon (OC) was determined by the acid-dichromate wet oxidation as described by Nelson and Sommers (1982).

2.2. Determination of Pb, Cd and Zn in soils

About 0.2 g of air-dried and finely ground soil was weighed into a glass beaker and digested with a 10:3:2 mixture of HNO_3, HF, and HCl, respectively following the procedure of Lim and Jackson (1986). The beaker was swirled gently and digested on a digestion block until brown fumes appeared which subsequently turned white (indicating full digestion). The digested soil sample was set aside to cool and then filtered through Whatman No. 42 filter paper and diluted to 50 ml with distilled water in a clean plastic vial prior to analysis. Concentrations of Pb, Cd, and Zn in the filtrate were determined by atomic absorption spectrometery (AAS; Model AA 500, PG Instrument, U.K). The available concentrations of Pb, Cd, and Zn were extracted by saturating 10 g soil with 20 mL of 0.01 M $CaCl_2$, and shaking the mixture for 16 hrs. The soil suspension was filtered through Whatman No. 42 filter paper. The concentrations of Pb,

Cd, and Zn in the filtrate were analyzed with AAS (Model AA 500, PG Instrument, U.K).

2.3. Sorption and solubility study of added Pb, Cd, and Zn

Sorption/solubility experiment was carried out following the procedure modified from Egwu and Agbenin (2012). The soils from 0-20 cm depth were treated with stock solution of $Pb(NO_3)_2$, $Zn(NO_3)_2 \cdot 6H_2O$, and $Cd(NO_3)_2 \cdot 4H_2O$ solution in 0.01 M KNO_3 and left for 12 days (d). The stock solutions were prepared by dissolving 1.1 g of Pb as $Pb(NO_3)_2$, 0.6 g of Cd as $Cd(NO_3)_2 \cdot 4H_2O$, and 1.8 g of Zn as $Zn(NO_3)_2 \cdot 6H_2O$ in 0.01 M KNO_3 to give concentrations of 700 ppm Pb, 200 ppm Cd and 500 ppm Zn. One hundred grams of the air-dried soil was weighed into plastic containers and replicated twice. The soils were incubated with the individual metals from the stock solutions at a soil: solution ratio of 1:1 to achieve an application rate of 700 mg kg^{-1} soil Pb, 200 mg kg^{-1} soil Cd, and 500 mg kg^{-1} Zn. The pH of the soil suspension was adjusted to between 4 and 9 by adding appropriate amounts of different concentrations of either NaOH or HNO_3. The pH of the soil suspensions was occasionally measured with a pH meter until the desired pH values were obtained. The soil suspensions were agitated and allowed to equilibrate for 12 d. After 12 d equilibration, aliquots of the soil suspension were taken with the aid of syringes to determine pH; concentrations of Pb, Cd, Zn, Ca, and Mg, were determined by atomic absorption spectrometry (Model AA 500, PG Instrument, U.K); K and Fe were determined by flame emission photometery (Model PL 902, PG Instrument, U.K). Inorganic ligands such as SO_4^{2-}, PO_4^{2-}, HCO_3^-, and Cl$^-$ were also determined. Sulfate was determined by the turbidity method (Rhoades 1982), phosphate by the method of Murphy and Riley (1962), bicarbonate (HCO_3^-) was determined by titration with standard HCl (Rhoades 1982), and chloride by direct potentiometric titration with $AgNO_3$ as described by Rhoades (1982). The metal sorbed by the soil was calculated as the difference between metal added to the soil and metal remaining in the equilibrium soil solution (Lo et al. 2009):

$$M_{\text{adsorbed}(\%)} = \frac{M_{\text{total}} - M_{\text{solubility}}}{M_{\text{total}}} \times 100$$

where $M_{adsorbed}$ (%) is the adsorbed metal, M_{total} is the total metal content added to the soil, and $M_{solubility}$ is the equilibrium metal concentration in solution.

Soil solution speciation calculations were performed using PHREEQC Version 2 (Parkhurst and Appelo 1999). Input data for the model include concentration of cations and ligands, pH, temperature, alkalinity, and density of water. Output data consist of free Pb^{2+}, Cd^{2+} and Zn^{2+} concentrations and their complexes in the soil solution. From the metal sorption and free metal ions concentration, the partitioning of the heavy metal between the solid and the solution phases of the soil was measured and assessed in terms of the partitioning coefficient Kd (L kg^{-1}) (Degryse et al. 2009).

$$K_d = [M]_S / [M]_L$$

where $[M]_S$ is the amount of metal sorbed per unit weight of soil in mg kg^{-1} and $[M]_L$ is the equilibrium concentration of metal solubilized in mg L^{-1}

3. Results and discussion

3.1. Soil physicochemical properties

The mean physicochemical properties of the soil are presented in **Tables 1 and 2**.

Table 1. Mean physicochemical properties of the soil of Dareta village, Northern Nigeria

Sampling Direction	Clay (g kg^{-1})	Sand (g kg^{-1})	pH	OC (g kg^{-1})	CEC (cmol$_{(c)}$$kg^{-1}$)
Dareta North	259 (19.1)	428 (69.4)	6.14 (0.1)	9.92 (1.19)	10.6 (1.53)
Dareta South	255 (26.2)	460 (104)	6.47 (0.23)	7.34 (0.48)	8.72 (0.78)
Dareta East	251 (30.2)	532 (75.5)	6.23 (0.30)	8.32 (1.13)	9.68 (0.51)
Dareta West	285 (117.6)	463 (133.4)	6.39 (0.16)	5.28 (2.70)	8.04 (0.75)

Values in parenthesis are standard deviations; OC, Organic carbon; CEC, Cation exchange capacity.

Table 2. Averages of total and available metal concentration of soil of Dareta village, Northern Nigeria

Sampling Direction	Total Metal (mg kg^{-1})			Available Metal (mg kg^{-1})		
	Pb	Cd	Zn	Pb	Cd	Zn
Dareta North	381 (262.5)	27.8 (18.7)	172.8 (62.6)	3.3 (0.99)	0.134 (0.07)	0.5 (0.3)
Dareta South	424.2 (218.6)	40.7 (19.4)	194 (87.6)	3.2 (0.9)	0.6 (0.4)	0.6 (0.3)
Dareta East	578.9 (489)	39.5 (18.8)	154.6 (83.1)	2.4 (0.5)	1.3 (0.6)	0.5 (0.3)
Dareta West	555.7 (182)	15.9 (6.0)	145.5 (54.1)	1.7 (0.4)	1.8 (0.3)	0.4 (0.2)

Values in parenthesis are standard deviations.

3.2. Sorption of Pb, Cd, and Zn added to the soil

As typical for all cationic metals, the adsorption of Pb, Cd, and Zn for the soils of this study increased with pH. Between pH 4.8 and 5.8, the percentage of Pb sorbed increased until it reached 99% around pH 5.8 (**Figure 1**); after this point only relatively slight increase in adsorption was observed. A peculiar feature of adsorption of metals in these soils was the observed convergence of the adsorption lines of Cd and Zn from pH 7.3 onwards (**Figure 1**).
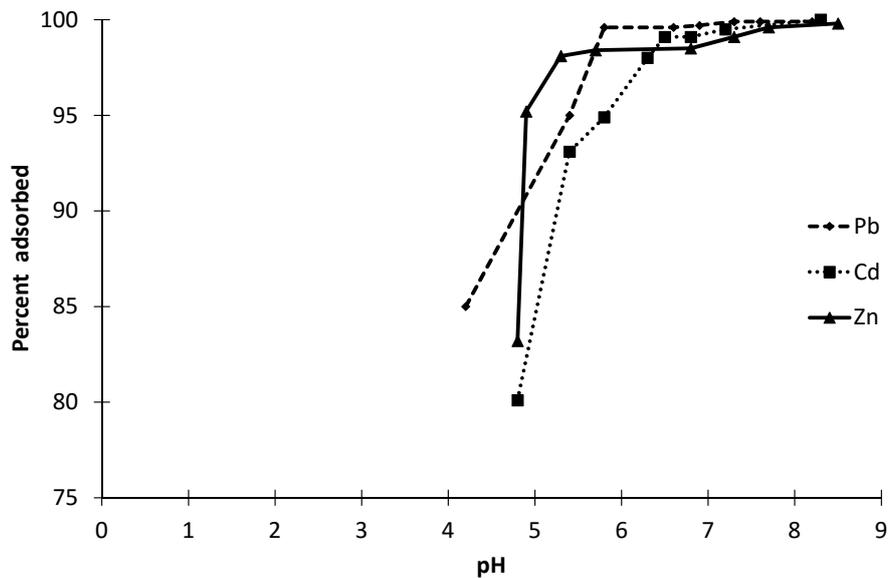
Figure 1. Sorption of Pb, Cd, and Zn as a function of pH on the soil of Dareta village, Northern Nigeria incubated with for 12 days.

The adsorption pattern for Cd and Zn were similar to that of Pb however, the order of adsorption was Pb > Zn > Cd, across the entire pH range. Mclean and Bledsoe (1992) reported from Biddappa et al. (1981) and Tiller et al. (1984) the following order of relative affinity of soils for metals: Pb > Cu > Zn > Cd > Ni (Biddappa et al. 1981); Zn > Ni > Cd (Tiller et al. 1984). Both observations are similar to the observations for this study. McBride and Blasiak (1979) showed increase retention of Zn with increasing pH, however McLean and Bledsoe (1992) reported that maximum retention of cationic metals generally occur at pH > 7. In the present study, maximum adsorption was observed just after pH 7. Many adsorption sites in soils, especially the highly weathered tropical soils which are the predominant soil type in the study area, are pH dependent; hence metal sorption is controlled largely by changes in soil pH. The pH dependence of adsorption reactions of cationic metals is partly due to the preferential adsorption of the hydrolyzed metal species relative to the free metal ion (James and Healy 1972; Davis and Leckie 1978; Cavallaro and McBride 1980); and probably due to the effect of deprotonation of potential determining ions thereby creating additional sorption sites onto which cations can adsorb. Lagerweff and Bower (1972) and Bittel and Miller (1974) observed preferential adsorption of Pb^{2+} to Cd^{2+} at pH > 5. The observed disparity in the pH at which maximum adsorption was attained by Pb, Cd, and Zn probably reflect differences in the first hydrolysis

constants (pK1) of the metals (Egwu 2010) which is about 7.71 for Pb^{2+}, 8.96 for Zn^{2+} and 10.08 for Cd^{2+} (Essington 2004). The chemistry of metals, especially in terms of their adsorption and exchange behavior is altered by hydrolysis. Since the hydrolysis species of metals are positively charged, it implies that these species would adsorb readily to the negatively charged solid matrix. Where hydrolysis occurs at a relatively lower pH, maximum adsorption would be attained quickly compared to a metal that hydrolyses at a relatively higher pH. It therefore follows that a high pH value for hydrolysis implies low adsorption affinity whereas metals that hydrolyze at a low pH adsorbs strongly (Sposito 2008). However, the pH at which maximum adsorption was attained by Cd was lower than its first hydrolysis constant (pK1) given as 10.08 (Essington (2004). This wide disparity suggests an increasing organic matter (OM) complexation of Cd because of the increased surface area and charge density, and also the solubility of OM at high pH (Egwu and Agbenin 2012). Several authors (Almas et al. 2000; Suave et al. 2000; and Krishnamurti and Naidu 2003) extensively demonstrated the role of OM in Cd complexation and this might explain the observed disparity. Similarly, ionic potential and ionic radii may alter the sequence of adsorption of metal cations. Metal cations with a larger ionic radius will create a smaller electronic field and thus less likely to remain solvated during complexation by surface functional groups. A larger ionic radius implies a more labile electron configuration, a general tendency for metal cations to polarize in response to electrical field of a charged surface functional group (Sposito 2008). However, the observed sequence of Pb > Zn > Cd contradicts the metal adsorption predictions based on ionic potential and ionic radii. The manner of adsorption of Pb, Cd, and Zn demonstrated by the soils of the study limits the risk of heavy metal leachability from long-term accumulation of heavy metals. Therefore, in the non-arable soils around the goldmine significant metal pollution control can be achieved by simply maintaining the soil reaction at above neutral.

3.3. Metal solubility as a function of pH

The relationship between the soluble metal concentrations and pH after 12 days of equilibration (aging) are represented in **Figure 2**. The solubility of Pb, Cd, and Zn increased with decreasing pH (**Figure 2**), almost linearly, up to pH of about 6. However there was disparity on the pH at which solubility increased for Pb, Cd, and Zn. For Pb, this was between pH 4.8 and 5.4 while for Zn it was between pH 5.4 and 5.8. Similar observation was made for Cd between pH 4.8 and 6.6.

The pH range at which solubility of metals increased corresponds to the pH range of optimum crop growth. It therefore implies that over long period of metal accumulation from aerial enrichment especially in the form of "harmattan" dust as well as from irrigation of farmlands, the risk of metal accumulation in the food chain due to increased plant uptake and also the pollution of ground water due to metal leaching are very high. The differences among the pH values of maximum adsorption indicate different affinities for the metals in soils and suggest a weaker reaction of Cd with soil constituents than Pb and Zn (Martínez and Motto 2000). Hence there is a higher risk of Cd accumulation in the food chain. A number of researches have reported worrisome amounts of Cd in plants grown on arable fields with no problem of metal contamination (Kirkham 2006). This stresses the importance of monitoring metal input into the soil. The nature of the solubility for Pb, Cd, and Zn observed in this study corresponds with several other studies on metal interactions with soil solid (Martínez and Motto 2000; Cavallaro and McBride 1980; García-Miragaya 1984; Agbenin and Olojo 2004; Egwu 2010). Given the nature of soils of this region, highly weathered and dominated by low activity clays and variably charged surfaces, the decreasing metal solubility with increasing pH is usually a consequence of the increasing charge density and the hydrolysis of metal cations.

3.4. Heavy metals partitioning

Lead showed the highest metal partitioning coefficient (Kd) compared to the other heavy metals studied (**Figure 3**). Metal partitioning coefficient of Pb had a maximum value of 4995 L kg^{-1}. Also, the metal partitioning of the three elements studied increased as pH increased, particularly at pH values higher than 7 (**Figure 3**).
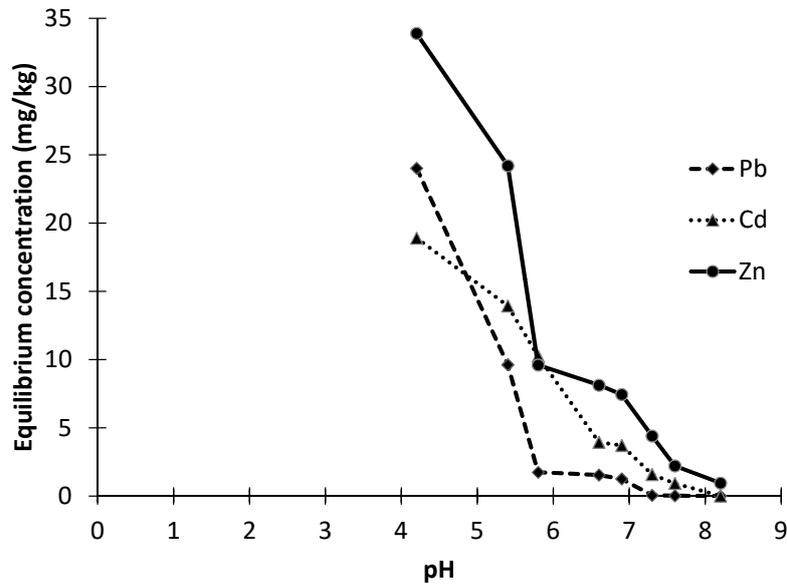
Figure 2. Solubility of Pb, Cd, and Zn added to the soil of Dareta village as a function of pH.
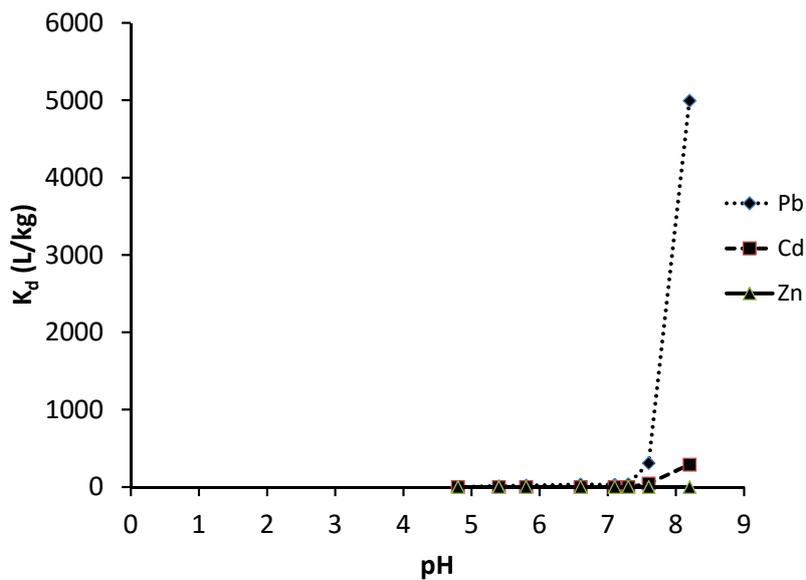
Figure 3. Partition coefficients (Kd) for Pb, Cd, and Zn under varying pH in soil of Dareta village, Northern Nigeria.

Metal adsorption versus metal solubility showed the different distribution patterns for Pb, Cd, and Zn. Lead and Cd showed similar distribution patterns with slightly wider adsorption versus lower solubility while that of Zn was narrower (**Figure 3**). Zinc showed an almost uniform distribution pattern across the pH range of the study. Although calculated Kd values reflects adsorption, the values of soluble concentrations of the metals studied suggest the occurrence of other sorption reactions such as precipitation. Some researchers (Rickard and Nriagu 1978) have suggested the possibility of precipitation of metals when soluble concentration exceeds 4 mg L^{-1} at pH 4.

3.5. Solubility controls of Pb, Cd, and Zn added to the soil

3.5.1. Lead solid-solution equilibria

The solubility of Pb added to the soils is indicated by the scatter data-points in **Figure 4**. The possible solubility controls of the activities of Pb^{2+} in solution are represented by the lines of $Pb(SO_4)$ (anglesite), $PbCO_3$ (cerrusite), and $Pb_5(PO_4)_3Cl$ (chloropyromorphite).

The relative distribution of data points for Pb^{2+} activity with respect to pure minerals (**Figure 4**) does not suggest the formation of a pure mineral compound as controls of the solubility of Pb, as it has been widely suggested by some researchers (Nriagu 1973; Lindsay 1979). There was no apparent equilibrium between the free Pb^{2+} activities in solution and the pure mineral compounds considered. The distribution of data points (**Figure 4**) indicates that below pH 6 the soil solution was under-saturated with respect to $PbCO_3$. As pH increased towards 8, activity data points showed that the free Pb^{2+} in the soil solution was super-saturated with respect to cerrusite ($PbCO_3$).
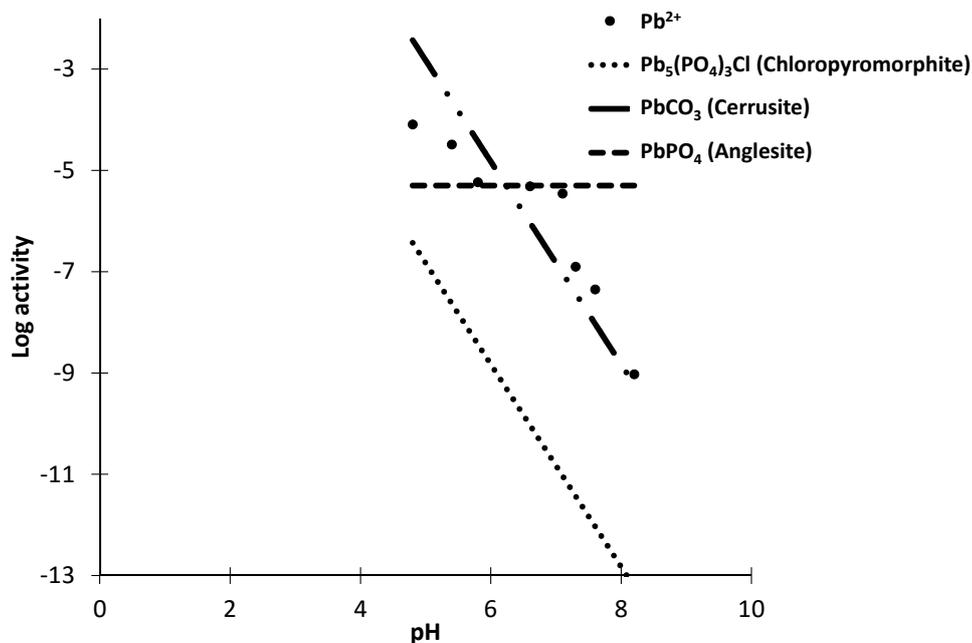
Figure 4. Logarithm (base 10) of soluble Pb from the amended soil of Dareta and from various pure compounds. Stability lines for minerals were calculated based on log K values reported by Lindsay (1979).

However, the increased solubility of Pb with decrease in pH could suggest the possibility of Pb^{2+} activities controlled by $PbCO_3$. When soils of high pH become more acidic in reaction, they may release fixed Pb especially when $PbCO_3$ is involved (Bolt and Bruggenwert 1978) due to the high dependence of carbonate on pH. The control of above threshold concentration of Pb by the formation of relatively insoluble compounds such as $PbCO_3$, $Pb_3(PO_4)_2$, and $PbSO_4$ has been described by Singer and Hansen (1969).

3.5.2. Zinc solid-solution equilibria

The solubility of the added Zn to the soils of the study is indicated by the scatter data-points in **Figure 5**. Similar to the observation for Pb, no apparent equilibrium between the activities of Zn^{2+} in solution and the pure minerals considered could be seen from the results.

At pH 8.3, activity data point for Zn^{2+} was slightly above the solubility line of hopeite (**Figure 5**), indicating super-saturation. However, at lower pH values, activity data points for the soils fell below the solubility line of hopeite. The relative positions of soil-Zn and franklinite ($ZnFe_2O_4$) render both mineral unlikely controls of Zn activities in solution.
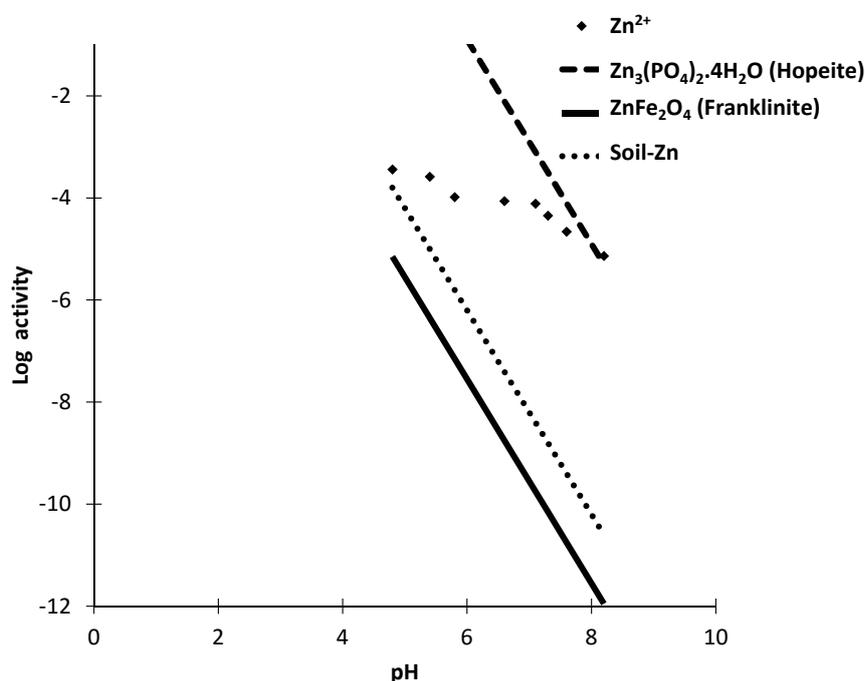
Figure 5. Logarithm (base 10) of soluble Zn from the amended soil of Dareta and from various pure compounds. Stability lines for minerals were calculated based on log K values reported by Lindsay (1979).

3.5.3. Cadmium solid-solution equilibria

Three Cd minerals, including free soil-Cd, were considered as likely controls of Cd activities in solution. Although high levels of Cd were added to the soil in order to simulate Cd pollution from dust deposition and irrigation water over time, there was no clear evidence to suggest the formation of either of $CdCO_3$ and $Cd_3(PO_4)_2$. Therefore, the observation from this study suggests mechanism(s) other than formation of pure minerals as likely control of Cd activities in the soil solution.

The activity of Cd^{2+} in the soil solution has been shown to be limited by $CdCO_3$ (otavite) depending on the CO_2 (g) concentration. Hence an atmospheric CO_2 pressure of 0.003 atm was assumed in constructing the $CdCO_3$ line (**Figure 6**), since the CO_2 in soils is generally higher than that of the atmosphere.

The relative distribution of the activity data points of Cd^{2+} with respect to the stability lines of the pure minerals makes it tenuous to suggest the formation of any mineral as the controlling mechanism of Cd^{2+} activity in the soil solution.
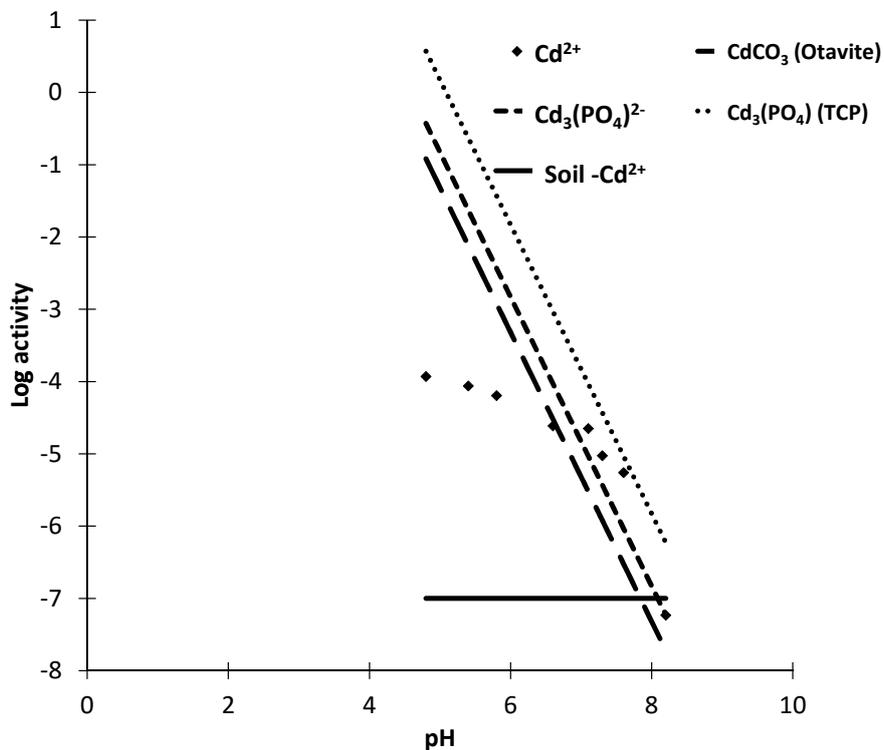
Figure 6. Logarithm (base 10) of soluble Cd from the amended soil of Dareta and from various pure compounds. Stability lines for minerals were calculated based on log K values reported by Lindsay (1979).

Despite the various assumptions made while constructing the solubility lines of the pure Cd minerals, no apparent equilibrium between Cd in solution and the solid phase was discerned. Although McBride (1980), on the chemisorption of Cd^{2+} on calcite surfaces, concluded that $CdCO_3$ could precipitate at high pH values, and Santillan-Medrano and Jurinak (1975) suggested that the formation of $CdCO_3$ and $Cd_3(PO_4)_2$ were possible in Cd-contaminated soils, the distribution of the data points of the added Cd did not suggest the attainment of any sort of equilibrium between the Cd^{2+} activities in solution and the pure minerals.

3.6. Soil solution speciation

3.6.1. Inorganic complexes of Pb

The distribution of inorganic complexes of Pb is shown in **Figure 7**. The soil solution is dominated by positively charged and neutral complexes of SO_4^{2-}, Cl^-, and OH^-. Across the pH range considered in this study, free Pb (Pb^{2+}) accounted for most of the Pb in solution until around pH 7.6, after which $PbOH^+$ was the most dominant Pb species in the soil solution. The activities of $PbOH^+$ increased with pH, similar to that of $Pb(OH)_2$. Generally, the order of magnitude observed for the distribution of inorganic complexes of Pb in the soil solution was: $PbOH^+ > PbSO_4 > PbCl^+ > Pb(OH)_2$. The general trend for these complexes was a downward curve after pH 6.6. In comparison to $PbOH^+$ and $Pb(OH)_2$, $PbSO_4$ and $PbCl^+$ showed a similar trend although $PbSO_4$ was more dominant. In total, the inorganic species of Pb accounted for just 1.3% (**Table 3**) of the total Pb in solution while Pb^{2+} accounted for 70.24%. The remaining 28.46% represents Pb-organic complexes. The percentage of these organic complexes reduced to 28.26% and 27.47% as pH dropped to 6.6 and 7.1 respectively. At pH 7.1, $PbOH^+$ accounted for 14.13% of the total dissolved Pb in solution.
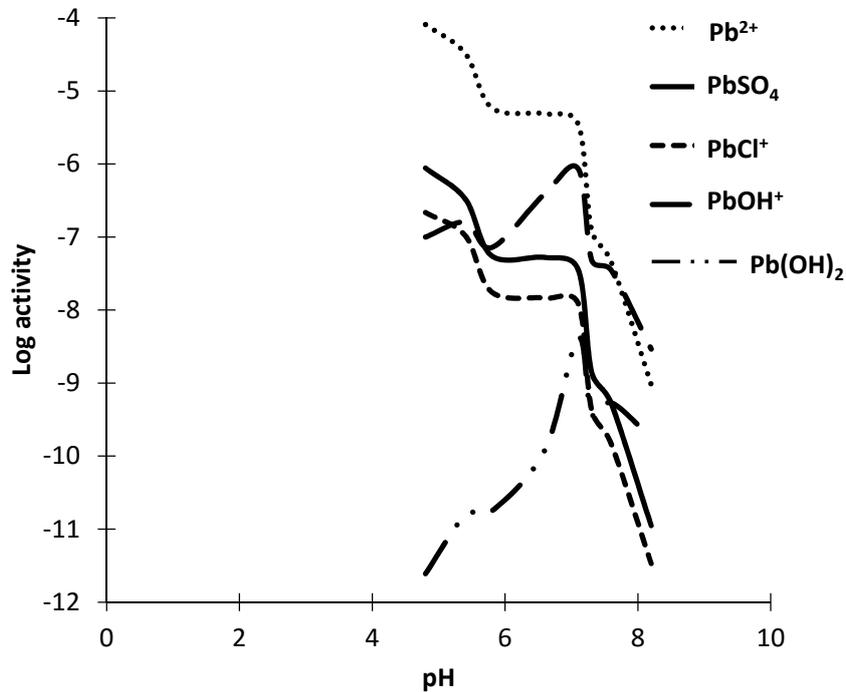
Figure 7. The distribution of the inorganic complexes of Pb in the soil solution of Dareta, Northern Nigeria.

The high proportion of organic complexes corresponds with the high stability constants of organic ligands relative to inorganic ligands, resulting in the predominance of organic complexes under the soil conditions of this experiment.

3.6.2. Inorganic complexes of Cd

The trend and differences in the distribution of the various inorganic complexes of Cd (**Figure 8**) are more striking compared to those of Pb. For all the inorganic species (including free Cd^{2+}) the trend appears relatively more uniform with a generally downward trend after pH 7.4. The order of distribution of these complexes was: $CdCl^+$ > $CdSO_4$ > $CdOH^+$ > $CdCl_2$. The observed dominance of $CdCl^+$ is consistent with the high affinity of chloride for Cd as well as the higher stability constant of $CdCl^+$ complexes compared to other metal chloride complexes

such as ZnCl and PbCl (Egwu and Agbenin 2012). The complexation of Cd with hydroxide and chloride ions may enhance the mobility of Cd in the environment (Hahne and Kroontje 1973).

The inorganic species of Cd accounted for just 0.89% of the total Cd in solution at pH 5.4 (**Table 4**), and this increased to 0.90% and 0.99% as pH increased from 6.6 to 7.1, respectively. Summation of calculated inorganic species plus free Cd concentration in solution added up to 71.12%, 70.38% and 69.01% at pH 5.4, 6.6, and 7.1 respectively. The organic Cd complexes accounted for 28.88%, 29.62%, and 30.99% at the same pH. The formation of significant Cd–organic complexes in the solutions of several soils has also been reported in several other works (Almas et al. 2000; Suave et al. 2000; Krishnamurti and Naidu 2003). The Cd organic complexes in solution have been attributed to

Table 3. The activities of dominant inorganic complexes of Pb in soil solution of Dareta village, Northern Nigeria, expressed as percentages of total Pb (PbT) in soil solution at different pH

pH	Metal complex	Activity	%
5.4	Pb_T	$4.64E^{-05}$	
	Pb^{2+}	$3.26E^{-05}$	70.24
	$PbSO_4$	$3.31E^{-07}$	0.71
	$PbOH^+$	$1.60E^{-07}$	0.34
	$PbCl^+$	$1.04E^{-07}$	0.25
	Pb-OM*	$1.32E^{-05}$	28.46
6.6	Pb_T	$7.44E^{-06}$	
	Pb^{2+}	$4.87E^{-06}$	65.5
	$PbOH^+$	$3.96E^{-07}$	5.32
	$PbSO_4$	$5.27E^{-08}$	0.71
	$PbCl^+$	$1.46E^{-08}$	0.2
	$Pb(OH)_2$	$6.42E^{-10}$	0.01
	Pb-OM	$2.11E^{-06}$	28.26
7.1	Pb_T	$6.083E^{-06}$	
	Pb^{2+}	$3.501E^{-06}$	57.55
	$PbOH^+$	$8.594E^{-07}$	14.13
	$PbSO_4$	$3.55E^{-08}$	0.58
	$PbCl^+$	$1.22E^{-08}$	0.2
	$Pb(OH)_2$	$4.21E^{-09}$	0.07
	Pb-OM	$1.67E^{-06}$	14.13

*Pb-OM: Pb-organic complexes.
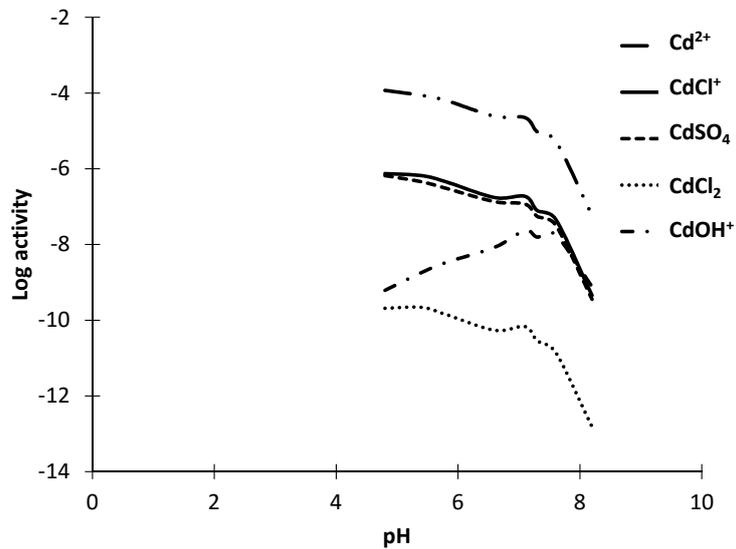
Figure 8. Distribution of inorganic complexes of Cd in the soil solution of Dareta village, Northern Nigeria

the formation of Cd-fulvate (Egwu and Agbenin 2012).

3.6.3. Inorganic complexes of Zn

The graphical relationship among the various inorganic complexes of Zn observed for the heavy metal amended soils of Dareta is presented in **Figure 9**. The Zn complexes show a dual-trend in distribution, in the sense that there was an upward trend for the hydrolysis species ($ZnOH^+$ and $Zn(OH)_2$) while the trend was downward for $ZnCl^+$ and $ZnSO_4$ as the pH increased. The order of distribution for these complexes was: $ZnSO_4 > ZnCl^+ > ZnOH^+ > Zn(OH)_2$. The dominant species of a metal in solution is a strong indication of mobility and potential toxicity of the metal. Inert complexes are least harmful while the free metal species are most toxic. The $ZnCl^+$ implies high mobility of the metal especially in a net-negatively charged soil, while the rate of adsorption will increase with increase in hydrolysis species. The inorganic complexes of Zn together with the free Zn only accounted for 69.48% of total Zn dissolved in solution at

pH 8.2 (**Table 5**). Inorganic complexes alone accounted for 1.4% of the total; hence the organic complexes of Zn accounted for 30.52%. It was reported by Egwu (2010) that dissolved organic carbon (DOC) contributed more significantly to total Zn in several soils through the formation of Zn-fulvate complexes. This possibility, together with the higher stability values of organic ligands in comparison to inorganic ligands explains the high proportion of the Zn organic complexes.

3.6.4. Mechanism(s) controlling Pb, Cd, and Zn activities in the metal amended soils

A number of equilibrium studies have suggested the precipitation of pure minerals as controls of metal activities in the soil solution, especially under conditions of high contamination. However, precipitation as a mechanism controlling mineral solubility in soils has been rejected by other researchers (McBride and Blasiak 1979; Cavallaro and McBride 1980; Basta et al. 1993). This is because solubility diagrams of pure compounds show a uniform pH effect on metal solubility, which is not the case under field condition.

Table 4. The activities of dominant inorganic complexes of Cd in soil solution of Dareta village, Northern Nigeria, expressed as percentages of total Cd (Cd_T) in soil solution at different pH

pH	Metal complex	Activity	%
5.4	Cd_T	$1.24E^{-04}$	
	Cd^{+2}	$8.71E^{-05}$	70.23
	$CdCl^+$	$6.61E^{-07}$	0.53
	$CdSO_4$	$4.51E^{-07}$	0.36
	Cd-OM*	$3.58E^{-05}$	28.88
6.6	Cd_T	$3.51E^{-05}$	
	Cd^{2+}	$2.44E^{-05}$	69.48
	$CdCl^+$	$1.74E^{-07}$	0.50
	$CdSO_4$	$1.35E^{-07}$	0.38
	$CdOH^+$	$8.45E^{-09}$	0.02
	Cd-OM	$1.04E^{-05}$	29.62
7.1	Cd_T	$3.30E^{-05}$	
	Cd^{2+}	$2.25E^{-05}$	68.02
	$CdCl^+$	$1.87E^{-07}$	0.57
	$CdSO_4$	$1.17E^{-07}$	0.35
	$CdOH^+$	$2.35E^{-08}$	0.07
	Cd-OM	$1.02E^{-05}$	30.99

*Cd-OM: Cd-organic complexes.
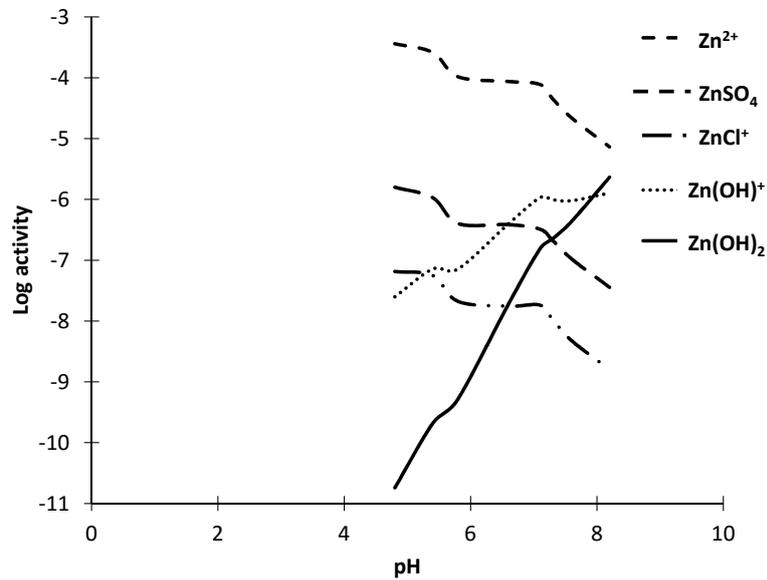
Figure 9. The distribution of inorganic complexes of Zn in the soil solution at Dareta village, Northern Nigeria.

Table 5. The activities of dominant inorganic complexes of Zn in soil solution of Dareta village, Northern Nigeria, expressed as percentages of total Zn (Zn_T) in solution at different pH

pH	Metal complex	Activity	%
5.4	Zn_T	3.70E^{-04}	
	Zn^{2+}	2.61E^{-04}	70.4
	$ZnSO_4$	1.07E^{-06}	0.29
	$ZnOH^+$	7.18E^{-08}	0.02
	$ZnCl^+$	5.61E^{-08}	0.02
	Zn-OM*	9.82E^{-05}	29.27
6.6	Zn_T	1.24E^{-04}	
	Zn^{2+}	8.69E^{-05}	69.93
	$ZnOH^+$	3.97E^{-07}	0.32
	$ZnSO_4$	3.86E^{-07}	0.31
	$ZnCl^+$	1.75E^{-08}	0.01
	$Zn(OH)_2$	1.90E^{-08}	0.02
	Zn-OM	3.62E^{-05}	29.41
7.1	Zn_T	1.14E^{-04}	
	Zn^{2+}	7.75E^{-05}	68.08
	$ZnOH^+$	1.07E^{-06}	0.94
	$ZnSO_4$	3.23E^{-07}	0.28
	$Zn(OH)_2$	1.55E^{-07}	0.14
	ZnCl+	1.82E^{-08}	0.02
	$Zn(SO_4)_2^{2-}$	4.68E^{-11}	0.02
	Zn-OM	3.49E^{-05}	30.52

*Zn-OM: Zn-organic complexes.

Also the solubility lines of pure minerals should usually have a slope of 2 (Martínez and Motto 2000). The slopes of experimental data are mostly far below this value, and for the soils of this study it was only Pb that gave slope above unity (1.29) (**Table 6**). Slopes were 0.7 and 0.4 for Cd and Zn, respectively. The divergence of calculated slopes of these soils from 2 indicates that the slopes are lower than those for pure compounds, and therefore only a slim likelihood of metal precipitation exist. Despite their limitations, Santillan-Medrano and Jurinak (1975) as well as El-Falaky et al. (1991) still argued for the use of solubility diagrams and the precipitation of minerals at high metal concentrations and high pH values. However, Catlett et al. (2002) showed that extremely low slopes could mean that the control for a metal is likely dominated by cation exchange reactions, but Martínez and Motto (2000) argued that solubility studies cannot differentiate between ion exchange, specific adsorption, and precipitation reaction.

Although the soils in this study were amended with very high concentrations of Pb, Cd, and Zn in order to simulate high level soil contamination, the data generated from this experiment is not sufficient to establish the actual mechanism controlling metal activities in the soil solution. However, the lack of observance of any equilibrium between ions in solution and the pure (well-crystallized) mineral phases considered in the activity diagram suggest the formation of metastable minerals (poorly crystalline) as likely controls of metal activity in solution.

Table 6. The slopes and coefficient of determination of -log Me^{2+} - pH relationship of soils from the lead polluted farms of Dareta village, Northern Nigeria

Me^{2+}	Slope	r^2
Pb^{2+}	1.29	0.84
Cd^{2+}	0.766	0.718
Zn^{2+}	0.447	0.718

4. Conclusions

From this experiment, the following conclusions were drawn:

1. The rate of solubility of Pb, Cd, and Zn at pH ranges within that of optimum crop growth shows a high risk of metal uptake by plants, especially Cd, and the accumulation of heavy metals in the food chain.

2. The predominance of free species of Pb, Cd, and Zn in the soil solution and the high proportion of organic metal complexes would enhance plant uptake and the mobility of metal contaminants in the environment.

3. The lack of observance of any equilibrium between ions in solution and the pure (well-crystallized) mineral phases considered in the activity diagrams suggest the formation of metastable minerals which are not well crystallized. The formation of amorphous, metastable mineral phases is favored in terrestrial environment.

4. The absence of an apparent equilibrium between solution species and the pure mineral phases could also suggest that the progression of the chemical reactions may be limited by kinetic processes; this is fairly indicated by the value of the ΔGr of the solid species.

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