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In Book Chapter   1995   WWRC-95-15

In Plant Soil Interaction at Low pH
R.A. Date et al. (eds.), Kluwer Academic
Publishers. pp 141-146.

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1995

Solubility and mobility of copper, zinc and lead in acidic environments

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Abstract

Understanding the chemical speciation of metals in solution is necessary for evaluating their toxicity and mobility in soils. Soil samples from the Powder River Basin, Wyoming were extracted with distilled deionised H_2O. Soil water extracts were subjected to chemical speciation to determine the relative distribution and chemical forms of copper (Cu), zinc (Zn) and lead (Pb) in acidic environments. As pyrite oxidised, the pH decreased from 6.6 to 2.4, concentration of dissolved sulfate (S_T) increased from 259 to 4,388 mg L^{-1} and concentration of dissolved organic carbon (DOC) decreased from 56.9 to 14.4 mg L^{-1}. Dissolved Cu concentrations ranged from 0.06 to 0.42 mg L^{-1} and dissolved Zn concentrations ranged from 0.084 to 4.60 mg L^{-1}. Dissolved concentrations of Pb were found to be 0.003 to 0.046 mg L^{-1}. Chemical speciation indicated that at near neutral pH, dissolved metal concentration in soil water extracts was dominated by DOC- metal complexes. At low pH, dissolved metal concentration in soil water extracts was dominated by free ionic forms (e.g. Cu^{2+}, Zn^{2+}, Pb^{2+}) followed by ion pairs (e.g. $CuSO_4^0$, $ZnSO_4^0$, $PbSO_4^0$). Results obtained in this study suggest that as soil pH decreased, the availability and mobility of metal ions increased due to the chemical form in which these metal ions are present in soil solutions.

Introduction

Acidic conditions in soil often enhance the solubility of heavy metals (e.g. Cu, Zn, Pb). An increase in the dissolved concentration of heavy metals may represent toxicity and contamination problems in soils. The behaviour of heavy metals in plant-soil environments is dependent on the chemical speciation and the relative distribution of chemical forms of metals in soil solutions. These, in turn, will influence the availability and mobility of these metals in soils (Adriano, 1986; Senesi, 1992).

Oxidation of pyrite (FeS_2) is considered as one of the main sources of acidity in acid soils (Van Breeman, 1973). As FeS_2 oxidises, the pH of soil decreases and concentration of dissolved sulfate (SO_4^{2-}) increases. Such conditions significantly modify the chemical speciation and relative distribution of chemical forms of the Cu, Zn and Pb in soils. Additionally, studies have shown that organic metal complexes in soil solution play an important role in the availability of these metals to plants (Stevenson, 1982). However, very little is known regarding the chemical speciation of dissolved Cu, Zn and Pb concentrations in acidic environments. Thus, the objectives of our study were to examine the chemical speciation of dissolved Cu, Zn and Pb in water extracts of soils and to determine the importance of dissolved organic carbon (DOC) and SO_4^{2-} concentrations in chemical speciation of Cu^{2+}, Zn^{2+} and Pb^{2+} in soil solutions at low pH.

Materials and methods

Samples of surface soil were collected from the Glenrock region of the southern edge of the Powder River Basin, Wyoming, USA. These soils are classified as sandy, mixed, Ustic Torriorthents. The samples are representative of materials that are widespread in the USA as well as in other parts of the world (Kennedy, 1986).

The climate of the Power River Basin is temperate and semiarid. Average daily temperature varies from a low of -15°C in winter to 32°C in July. Precipita-

tion ranges from 30 cm in the southern part of the study area to 45 cm in the north (Martin et al., 1988). The Powder River Basin is part of the Fort Union and Wasatch geological formations of early tertiary age and consists of continental-type sediments deposited in fluvial, lacustrine and swampy environments. Strata in these formations are lenticular and consist of alternating sandstone, siltstone and claystone, with occasional coal beds (Naftz and Rice, 1989).

Samples were sieved through a 2 mm screen and analysed for organic matter (OM), $CaCO_3$ content and pyritic sulfur. Fifty grams of each sample, in triplicate, were suspended in 150 mL of distilled-deionised H_2O for solubility measurements. Four drops of toluene were added to each sample suspension which was then closed tightly with a rubber stopper to minimise the microbial oxidation of FeS_2. Sample suspensions were agitated on a rotary shaker at 200 rpm at $25 \pm 1°C$.

After reacting for 14, 21 and 28 d, sample suspensions were centrifuged and filtered through a 0.45 μm Millipore filter. Each extract was divided into two subsamples. One was acidified with HCl to pH 4.0–4.5 and the other one was left unacidified and analysed for pH, Eh, total carbonate species, sulfate, fluoride and chloride. Acidified extracts were analysed for cations, anions and DOC.

The pH was measured with an Orion combination electrode before and after each reaction period to determine the oxidation of FeS_2. The Eh was measured with an Orion platinum (Pt) electrode and a $Ag/AgCl_2$ reference electrode. The Eh readings were taken over a period of 0.5 to two hours until the drift was less than three mV. Stable readings were always obtained within two hours. Stability of the readings was confirmed in selected extracts by monitoring the readings over a period of 24 hours. The pe ($-\log e^-$ activity) was calculated from Eh measurements.

Carbonate species were measured by titrating extracts with standardised HCl to pH 4.5 end point. Copper, Zn and Pb were determined with atomic absorption (AA) using a graphite furnace to achieve lower detection limits. Calcium, Mg, Si, Al, Fe, Mn and B were measured by inductively coupled plasma optical emission spectrometry (ICP-OES) (Soltanpour et al., 1982). Potassium and Na were measured by atomic emission (Baker and Suhr, 1982). Ion chromatography was used to measure the concentration of sulfate, fluoride and chloride. The DOC was analysed with carbon analyser.

The speciation model GEOCHEM (Sposito and Mattigod, 1980) was used to calculate chemical spe-

Table 1. Selected chemical data of soil water extracts

Reaction time (days)	pH	Total dissolved ions[a] ($-\log mol\ L^{-1}$)			
		Cu_T	Zn_T	Pb_T	S_T
Sample 1					
14	6.6	5.95	5.89	6.67	2.60
21	6.5	6.03	5.84	6.67	2.57
28	6.6	6.03	5.89	6.66	2.57
Sample 2					
14	5.5	6.10	5.32	7.07	2.04
21	5.6	6.61	5.32	7.36	2.06
28	5.6	6.76	5.22	7.14	2.07
Sample 3					
14	5.6	6.14	5.83	6.78	2.36
21	5.4	6.59	5.97	5.73	2.37
28	5.4	6.48	5.90	6.93	2.38
Sample 4					
14	5.3	7.19	5.57	6.66	2.39
21	5.1	7.19	5.61	6.65	2.38
28	5.1	7.05	5.68	6.63	2.41
Sample 5					
14	2.5	5.21	4.40	7.71	1.38
21	2.5	5.17	4.28	7.94	1.38
28	2.5	5.19	4.28	7.91	1.37
Sample 6					
14	2.4	5.12	4.13	7.61	1.33
21	2.4	5.12	4.13	7.61	1.34
28	2.4	5.18	4.15	7.83	1.34

[a]Cu_T, Zn_T, Pb_T and S_T respectively total dissolved Cu, Zn, Pb and SO_4^{2-} in soil water extracts. Values are mean triplicate analyses.

ciation. This model uses total elemental concentration and pH of soil water extracts to calculate ion activities. From ion activities, ion activity products (IAPs) were calculated and compared with solubility products (K_{sp}s) to evaluate potential solid phases controlling the concentrations of Cu^{2+}, Zn^{2+} and Pb^{2+} in soil water extracts.

We assumed that IAPs within ± 0.50 log units of $K_{sp}S$ of solid phases represented near saturation with respect to that solid phase. The variation within that range is accounted for by the uncertainty of IAP estimations and K_{sp} measurements (Stumm and Morgan, 1981).

Table 2. Effect of DOC-Cu^{2+} complexation on Cu^{2+} activities in soil water extracts

Sample No.	pH	DOC (mg L^{-1})	Cu^{2+} activity (-log)[a]		%DOC-Cu^{2+} Complex
			with DOC	without DOC	
1	6.6	56.9	7.74	6.38	95
2	5.6	26.2	7.67	7.20	66
3	5.4	37.2	7.73	6.83	87
4	5.1	12.7	7.87	7.41	65
5	2.5	11.4	6.09	5.93	32
6	2.4	14.4	6.12	5.92	37

[a] Calculated with GEOCHEM (Sposito and Mattigod, 1980).

Table 3. Effect of DOC-Zn^{2+} complexation on Zn^{2+} activity in soil water extracts

Sample No.	pH	DOC (mg L^{-1})	Zn^{2+} activity (-log)[a]		%DOC-Zn^{2+} Complex
			with DOC	without DOC	
1	6.6	56.9	7.32	6.18	93
2	5.6	26.2	5.91	5.61	50
3	5.4	37.2	6.64	5.96	79
4	5.1	12.7	6.30	6.01	48
5	2.5	11.4	5.13	5.04	19
6	2.4	14.4	5.02	4.91	23

[a] Calculated with GEOCHEM (Sposito and Mattigod, 1980).

Results and discussion

Selected properties of the soil samples suggest that OM content varied from 0.4 to 1.6% and $CaCO_3$ content was below 0.2%. The pH measurements before and after solubility experiments suggest that FeS_2 did not oxidise during the reaction time (i.e. 14–28 d). Selected chemical data of water extracts of the soils (Table 1) suggest that Cu, Zn and Pb concentrations approached nearly steady state within the 28 d of the reaction period. Therefore, day 28 data were selected for chemical speciation calculations.

Dissolved organic carbon in natural waters usually consists of fulvic and humic acids. Fulvic acid is known to complex Cu^{2+}, Zn^{2+} and Pb^{2+} in soil solutions (Gamble, 1970; Reuter and Perdue, 1977; Sposito et al., 1981; Stevenson and Welch, 1979; Truitt and Weber, 1979). Determination of these metals in soil water extracts with ICP-OES or AA probably included both inorganic and organic species. Thus, Cu^{2+}, Zn^{2+} and Pb^{2+} activities would be overestimated using the concentration of dissolved Cu, Zn and Pb in these extracts, without correcting for organic complexes.

The concentration of DOC for soil water extracts ranged from 56.9 to 11.4 mg L^{-1} (Table 2) and decreased as pH was reduced. Determination of the concentration of individual organic compounds in natural waters is very difficult because they are complex to analyse. Studies have shown that fulvic acid usually dominates (75 to 95%) in the DOC of natural waters (Oliver et al., 1983). Furthermore, fulvic acid has greater affinity for binding Cu^{2+}, Zn^{2+} and Pb^{2+} than humic acid in soils (Sarr and Webber, 1980; Schnitzer and Skinner, 1966, 1967). Therefore, we assumed DOC concentrations as fulvic acid for chemical speciation of Cu^{2+}, Zn^{2+} and Pb^{2+} in soil water extracts.

Calculation, with and without considering fulvic acid as an input to the GEOCHEM model (Mattigod and Sposito, 1979), were made to determine the effect of fulvic acid on the chemical speciation of dissolved Cu^{2+}, Zn^{2+} and Pb^{2+} in soil water extracts.

The activity of Cu^{2+} (Table 2), Zn^{2+} (Table 3) and Pb^{2+} (Table 4) in soil water extracts decreased significantly when DOC was considered for chemical speciation calculations. The percent of Cu^{2+}, Zn^{2+} and Pb^{2+} complexed with DOC also is summarised in these

Table 4. Effect of DOC-Pb^{2+} complexation of Pb^{2+} activity in soil water extracts

Sample No.	pH	DOC (mg L^{-1})	Pb^{2+} activity (-log)[a] with DOC	Pb^{2+} activity (-log)[a] without DOC	%DOC-Pb^{2+} Complex
1	6.60	56.9	8.80	7.06	98
2	5.61	26.2	8.81	7.47	78
3	5.43	37.2	8.47	7.23	79
4	5.13	12.7	7.79	7.07	80
5	2.50	11.4	9.09	8.84	43
6	2.40	14.4	9.06	8.76	49

[a] Calculated with GEOCHEM (Sposito and Mattigod, 1980).

Table 5. Activity of selected elements in soil water extracts

Sample No.	Pyritic Sulfur (%)	pH	Activity (-log) of Cu^{2+}	Activity (-log) of Zn^{2+}	Activity (-log) of Pb^{2+}	Activity (-log) of SO_4^{2-}
1	0.08	6.6	7.74	7.32	8.80	2.76
2	0.07	5.6	7.67	5.91	8.18	2.41
3	0.02	5.4	7.73	6.64	8.47	2.62
4	0.03	5.1	7.87	6.30	7.79	2.68
5	ND	2.5	6.09	5.13	9.09	1.99
6	ND	2.4	6.12	5.02	9.06	1.91

ND=<0.01%

tables. Results suggest that percent of total dissolved Cu, Zn and Pb in soil water extracts bound with DOC was greater than 50% for all samples except soils 5 and 6. Based on these findings, we selected chemical speciation calculations with DOC for the following discussion.

Activities of Cu^{2+}, Zn^{2+}, Pb^{2+} and SO_4^{2-} in soil water extracts, as well as content of pyritic sulfur and pH, are summarised in Table 5. Pyritic sulfur content ranged from 0.08 to below 0.01% and the pH ranged from 6.6 to 2.4. These conditions represented somewhat neutral to highly acidic environments. A comparison between the pH of samples suggests that as FeS_2 oxidised, pH decreased from 6.6 to 2.4. Furthermore, as pH decreased activities of Cu^{2+}, Zn^{2+} and Pb^{2+} increased and then decreased in soil water extracts. However, SO_4^{2-} activity increased in soil water extracts.

Results from chemical speciation of soil water extracts for 28 d reaction time are summarised in Figure 1. Only results for Cu and Zn at pH 6.6, 5.4 and 2.4 are shown in Figure 1 because other samples produced similar results. As pyrite oxidised, the pH decreased from 6.6 to 2.4 and the DOC concentration decreased

from 57 to 14.4 mg L^{-1}. Furthermore, the reduction in the pH increased the concentration of Cu_T (from 0.06 to 0.42 mg L^{-1}), Zn_T (from 0.084 to 4.60 mg L^{-1}) and S_T (from 259 to 4,388 mg L^{-1}) in soil water extracts.

For Cu, as pH decreased the proportion present as Cu^{2+} ion in soil water extract increased from 3 to 29%. Concentration of the $CuSO_4^0$ ion pair increased from < 1 to 33%. However, the concentration of Cu^{2+}-DOC complex decreased from 95 to 37%. Similarly, for Zn, a reduction in pH increased Zn^{2+} ion from 5 to 35% in soil water extract. The concentration of $ZnSO_4^0$ ion pair increased from < 1 to 41% and the concentration of Cu^{2+}-DOC complex decreased from 93 to 23%. These results suggest that an increase in the dissolved concentration of ionic forms (e.g. Cu^{2+} or Zn^{2+}) due to the oxidation of FeS_2 may increase the availability of these elements to plants because plants usually absorb charged ionic forms from soil solutions. The increase in the concentration of neutral species such as $CuSO_4^0$ and $ZnSO_4^0$ may represent a potential for leaching problems because these neutral species may not be sorbed onto Fe and Al oxides and/or hydroxides as a
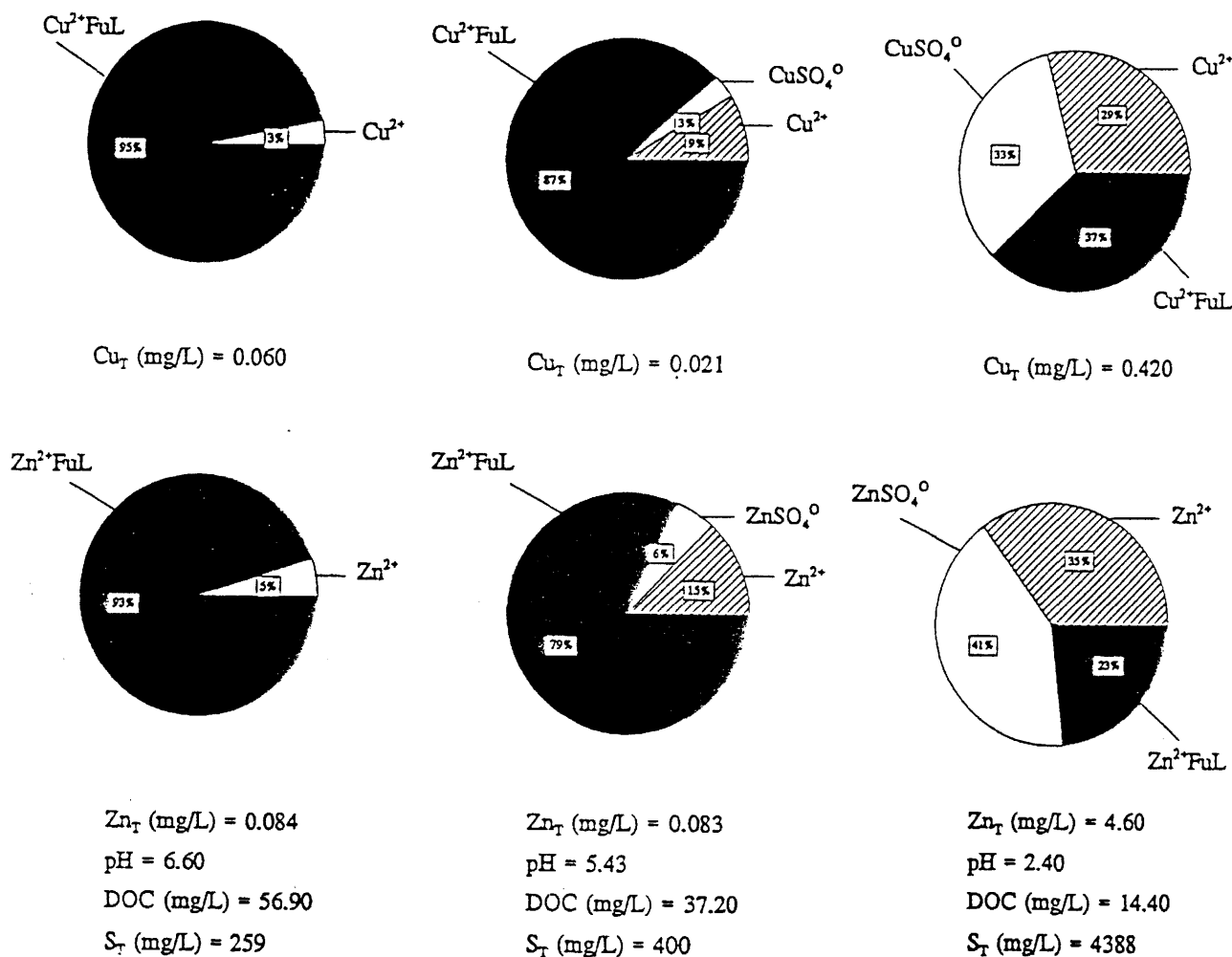
Fig. 1. Effects of pH, DOC and SO_4^{2-} on the chemical speciation of Cu and Zn in soil water extracts.

charged species and are therefore subject to leaching (Reddy and Gloss, 1993).

Lindsay (1979) developed an empirical reaction for soil-Cu to explain the solubility Cu^{2+} concentrations in soils. Based on the thermodynamic calculations, he also predicted that secondary minerals such as $ZnFe_2O_4(c)$ and $Pb_5(PO_4)_3Cl(c)$ may control Zn^{2+} and Pb^{2+} concentrations, respectively in soils. In this study, we explored all these possibilities except phosphate mineral because phosphate concentrations were very low.

Our evaluations suggest that soil-Cu and $ZnFe_2O_4(c)$ were not controlling the concentrations of Cu^{2+} and Zn^{2+}, respectively, in the soils examined. However, we should not rule out that Cu, Zn and Pb secondary minerals, which still need to be discovered, may control Cu^{2+}, Zn^{2+} and Pb^{2+} concentrations in soils at low pH.

Conclusions

Soil water extracts were subjected to chemical speciation to determine the effects of DOC and SO_4^{2-} concentrations on the relative distribution of chemical forms of Cu, Zn and Pb. As pH decreased, the dissolved concentrations of Cu and Zn were increased and the dissolved concentration of Pb increased and then decreased. Chemical speciation suggests that at near neutral pH, metal DOC complexes were predominant in the soil water extracts. At very low pH, metal ionic forms (e. g. Cu^{2+} or Zn^{2+}) and metal ion pairs (e.g. $CuSO_4^0$ and $ZnSO_4^0$) were predominant. The availability and mobility of Cu, Zn and Pb will increase in low pH environments due to the chemical form in which these metals are present in the soil solutions. Although soil solution chemical speciation does not prove or disprove the presence of different species, it is a convenient method for evaluating the relative distribution

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and importance of chemical forms contributing to the availability and mobility of metals in soils.

Acknowledgements

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