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ScienceDirect
Environmental Pollution 145 (2007) 1–6
ENVIRONMENTAL POLLUTION
www.elsevier.com/locate/envpol

Copper activity in soil solutions of calcareous soils

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Received 11 October 2005; received in revised form 8 April 2006; accepted 13 April 2006

Copper activity in contaminated calcareous soils is controlled by surface precipitated $CuCO_3$ with log ion activity product of −15.51.

Abstract

Copper partitioning was studied in seven calcareous soils at moisture content corresponding to 1.2 times the field moisture content (soil water potential 7.84 J kg^{-1}). Copper retention was accompanied by the release in soil solution of Ca^{2+}, Mg^{2+}, Na^{+}, and H^{+}, and the total amount of these cations released was 0.8 to 1.09 times the amount of Cu sorbed (mol_c:mol_c). The relationships between Cu activity and pH, and the balance of cations in soils correspond with the surface precipitation of $CuCO_3$ as the main mechanism of Cu retention. The values of ion activity product of surface precipitate were close for all studied soils with the average $\log(IAP_{CuCO_3}) = -15.51$. The relationship between copper activity in soil solutions and soil properties is well fit by a regression relating pCu (−log copper ion activity) with soil pH, total Cu, and carbonate content.

Keywords: Soil solutions; Calcareous soils; Copper activity

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1. Introduction

Soil carbonates may control mobility and bioavailability of copper in contaminated calcareous soils and in the soils ameliorated with limestone (Franklin and Morse, 1982; Compton and Pritchard, 1990; Elzinga and Reeder, 2002). However, the mechanisms influencing Cu retention in these soils remain unclear.

McBride and Bouldin (1984) found that in calcareous soil contaminated with $CuSO_4$ after about 50 years of aging soil solutions were undersaturated with respect to tenorite (CuO) and malachite ($Cu_2CO_3(OH)_2$). Only pieces of dolomitic limestone collected from the soil were coated with malachite, which was identified by infrared spectroscopy. The authors concluded that in the bulk soil, however, carbonates may have promoted the nucleation of Cu hydroxides or carbonates despite the undersaturation of soil solution with respect to pure mineral phases of Cu. Dudley et al. (1991), using X-ray diffraction, did not find tenorite (CuO) or any other specific Cu mineral in calcareous soils leached with mine waste extract contained Cu and suggested that the metal was retained by specific adsorption and not by precipitation. In freshly spiked calcareous soil horizons soil solutions were undersaturated with respect to $Cu(OH)_2$ (Cavallaro and McBride, 1978).

To clarify the mechanisms of Cu retention, detailed studies have been carried out on the interaction of Cu^{2+} with pure calcite. Schosseler et al. (1999), using continuous wave and pulse electron paramagnetic resonance, concluded that Cu^{2+} ions were retained on calcite by surface complexation. Upon recrystallization the Cu^{2+} ions are integrated into the calcite lattice. Elzinga and Reeder (2002) reported that extended x-ray absorption fine-structure (EXAFS) spectra of Cu/calcite samples were very different from that of malachite and were

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doi:10.1016/j.envpol.2006.04.010

consistent with Cu occupying Ca sites in the calcite structure forming dilute metal-calcite solid solutions (inner-sphere Cu^{2+} sorption complexes) at the calcite surface. Lee et al. (2005) using EXAFS also did not find malachite, CuO, or $Cu(OH)_2$ after interaction of Cu^{2+} with calcite, though calculations with the program PHREEQC showed that the initial suspensions were oversaturated with respect to these solids. This evidence was taken as an indication that Cu(II) adsorption on the calcite surface is kinetically favored over precipitation of the above phases. Papadopoulos and Rowell (1989), based on the relationships between Cu^{2+} activity calculated from measured Cu concentration and solution pH in calcite suspension, concluded that metal may be retained due to the surface precipitation of $CuCO_3$.

In soils copper retention may be influenced by the competition between calcite and soil organic matter (SOM) and by organic matter dissolved in soil solution. Copper(II) sorbed at the calcite surface apparently has a preference for surface carbonate ligands over sorbed humic acid (HA) ligands, whereas aqueous speciation results indicate that dissolved Cu(II) has a stronger preference for dissolved HA rather than for dissolved carbonate (Lee et al., 2005).

Sorption of Cu is a relatively fast process. About 80% of the Cu(II) was sorbed within the first 30 min and 87% within 24 h (Lee et al., 2005). Humic acid sorbed at the calcite surface or dissolved HA did not influence the rate of Cu(II) sorption (Lee et al., 2005). Observations of Cu uptake from solution onto calcite in distilled water and seawater carried out by Franklin and Morse (1982) also indicated similar rates of the processes.

Quantitative description of metal retention by calcite remains a challenging problem. Sorption of some trace metals (Cd, Mn, Zn, and Co) on calcite was described by the surface precipitation model (Comans and Middelburg, 1987), and retention of Cd (Papadopoulos and Rowell, 1988) and Cu (Papadopoulos and Rowell, 1989) by the model assuming formation of the surface solid solution.

The above data on Cu retention in calcareous soils (Cavallaro and McBride, 1978; Dhillon et al., 1981; Maftoun et al., 2002; Rodriguez-Rubio et al., 2003) are related to soil suspensions with relatively high solution to soil ratio. Metals speciation in soils at field moisture content may be different from that observed in suspensions. At low moisture content speciation could be influenced by relatively high concentration of dissolved organic matter, restricted interaction with atmospheric CO_2, and possibly some other factors.

The objective of this study was to determine the effect of soil carbonates on Cu^{2+} partitioning in soils at low moisture content.

2. Materials and methods

The study was carried out on seven calcareous soils from different regions of the European Union. Selected soil properties are presented in Table 1. Soil samples were spiked with $CuCl_2$ solution at amounts from 20 to 3700 mg Cu kg^{-1} and air-dried for 7 days. Sub-samples of spiked soils (60 g) in duplicate were placed into plastic 200-mL bottles, moistened with deionized water up to 1.2 times the field moisture content (corresponding to soil water potential 7.84 J kg^{-1}, $pF = 1.9$), and incubated at 20 ± 1 °C for 8 days. An 8-day period was found to be sufficient to obtain quasi-equilibrium between soil solid and solution phases. Then, soil solutions were separated from the samples using the centrifugation double chamber method. The design of the double chamber (Merckx et al., 2001) was similar to that suggested by Davies and Davies (1963) but the inner chamber was made of a cut 50-mL disposable syringe with a piece of quartz wool placed on the bottom. The solutions were filtered through a 0.45 μm nitrocellulose membrane filter and analyzed to determine dissolved organic carbon (DOC), being the measure of dissolved organic matter concentration, Cu, Ca, Mg, and Na concentrations, pH, and Cu^{2+} activity.

The pH values were measured with an Orion 370 pH meter with an Orion 91-55 combination pH electrode. Dissolved organic carbon was determined with a Rosemount (Dohrmann) DC-190 or Tekmar-Dohrmann Apollo 9000 TOC-analyser and Cu, Mg, Ca, and Na concentrations with a SPECTROFLAME ICP OES or Agilent 7500c ICP-MS. Copper activity, $\{Cu^{2+}\}$, was measured with a Weiss combination RCU 3001 Cu-ion selective electrode calibrated up to $pCu = 11$ just before each set of measurements according to the procedure suggested by Avdeef et al. (1983). To calibrate the electrode, 10^{-5} M Cu^{2+} standard in a 0.01 M KNO_3 background solution placed in a 100-mL Teflon beaker with a Teflon-covered stirring bar was titrated with 0.008 M ethylenediamine. After equilibration of the system, the electromotive force was measured with an Orion 370 meter. The pH was measured at the same time and copper activity at each step of the titration was calculated with the MINEQL+ speciation software (Schecher and McAvoy, 1992).

3. Results

The increase in the amount of Cu added resulted in an increase in $\{Cu^{2+}\}$ (decrease in pCu) (Fig. 1a,b) and a decrease in soil solution pH (Fig. 2a,b). The differences between pH values of soil solutions in different soils at the same Cu loading were generally within ±0.2 pH and only in the soil solutions of Brecy soil the pH was 0.4–0.5 pH units higher than in the rest of the soils. The relationships between dissolved Cu concentration and Cu loading plotted in a log vs log scale were close to linear for all the soils (Fig. 1c,d).

The highest DOC concentration was observed in soil solutions of Rots and Souli II soils with SOM 12.6 and 26.1 g C

Table 1
Selected soil properties

No.	Soil, location	Soil type	pH	SOM (g C kg^{-1})	CEC ($cmol_c$ kg^{-1})	Clay (%)	$CaCO_3$ (g kg^{-1})
1	Vault de Lugny (France)	Stagnic Luvisol	7.3	14.7	26.2	38	60.0
2	Rots (France)	Haplic Luvisol	7.4	12.6	20.0	27	149
3	Souli II (Greece)	Rendzic Leptosol	7.4	26.1	36.3	46	474
4	Marknesse (The Netherlands)	Calcaric Fluvisol	7.5	12.7	20.1	26	100
5	Barcelona (Spain)	Calcic Luvisol	7.5	14.8	14.3	21	72.0
6	Brécy (France)	Calcaric Cambisol	7.5	15.1	23.5	50	176
7	Guadalajara (Spain)	Calcic Cambisol	7.5	3.8	16.9	25	365