

Copper Speciation in Soil: Time Evolution and Effect of Clay Amendment

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Abstract Copper bioavailability, specially to plants, is strongly dependent on its chemical form, as for most metals. Copper-contaminated soil can be treated in situ by the addition of minerals such as Na-bentonite, which mixed with surface soil, can transform this pollutant to non-bioavailable forms. In this work, shelter experiments were conducted to study the time evolution of Cu speciation, in pristine soil as well as in amended one. A selective sequential extraction method was employed to determine the metal speciation in the samples. The results show that the major metal fraction is the organic matter-bound one, whereas the exchangeable fraction is very low, even the first day after Cu addition. The time evolution shows a slow decrease of the organic-bound Cu and a corresponding increase of the most stable

mineral fractions. With the addition of Na-bentonite to copper-contaminated soil, the most stable mineral fractions increase whereas the organic-bound one decreases, showing essentially similar time dependence of the several metal fractions. Sodium bentonite could be effectively used for remediation of soils polluted with Cu.

Keywords Sequential Selective Extraction · Availability · Bentonite · Heavy Metals · Soil Pollution

1 Introduction

Copper is a metal found naturally in the soil environment; the mean value in the earth's crust has been reported to be 50 mg kg^{-1} , whereas in soils the mean value is around $30\text{--}35 \text{ mg kg}^{-1}$ dry soil (Sparks 2002). It is found in a number of minerals, both primary and secondary (Alloway 2012). Trace levels of copper are necessary as a micronutrient for plants; however, it can be accumulated in the environment, due to anthropogenic processes, being toxic in high concentrations (Georgopoulos et al. 2001; Uriu-Adams and Keen 2005). In soil, copper can be bound to different fractions due to cation exchange, adsorption, or precipitation; the stability of most forms being pH dependent (Adriano 2001; Alloway 2012). Albeit bioavailability is dependent on the vegetal or animal species considered, in general, it is expected that labile forms, such as soluble and exchangeable Cu(II), will be bioavailable whereas more stable forms (e.g., precipitated) will not.

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Several studies have quantified the adsorption and bioavailability of Cu in different soils types (Covelo et al. 2008; Sipos et al. 2008; Fontes and dos Santos 2010; Soler-Rovira et al. 2010). However, the bioavailability is dependent on the Cu speciation in soil (Ryu et al. 2010; Soler-Rovira et al. 2010; Bourgeault et al. 2013). Thus, determination of the speciation of pollutants in soils, such as copper, is more relevant than a simple measurement of total metal contents. Among others, sequential selective extraction (SSE) methods have been proposed to assess speciation of sorbed species between different soil fractions (Tessier et al. 1979; McGrath and Cegarra 1992; Ma and Uren 1998; Hass and Fine 2010). The SSE methods are based on the exposure of a sample to a sequence of wet chemistry treatments. At each step of the sequence, the sample is treated with reactants of increasing reactivity, which are assumed to either selectively remove or dissolve a specific solid component that the sorbed species are associated with, or to desorb a specific adsorbate fraction. The successive steps are often assumed to remove the pollutant associated with a given soil component or fraction; however, due to the lack of complete knowledge on the soil composition, it is more appropriate to relate the fractions to the reactants employed giving an operational definition (Rao et al. 2008; Kabala et al. 2011). Furthermore, due to the nature and composition of soils, it is not possible to prevent that a fraction (expected to be small) of the analyte removed by a given reactant could be bound to more stable soil components. Thus, the different steps of SSE cannot be strictly taken as quantitative; nevertheless, SSEs are useful methods to study the speciation of pollutants, specially metals, in soil.

Soils contaminated by metal cations can be remediated in situ by adding organic and/or inorganic substances; mixing such substances with surface soil horizons can bring those pollutants to non-bioavailable forms (Soler-Rovira et al. 2010; Malandrino et al. 2011; Mallampati et al. 2012; Dhal et al. 2013). Clay minerals are good candidates for amendments as they are integral components of soil ecosystems and are widely available, non-toxic, and inexpensive. Bentonite (hydrated aluminosilicate composed primarily of montmorillonite) is, among others phyllosilicates, used for such purposes (Bergaya and Lagaly 2006). Their addition to soils can restore and enhance plant growth especially because they have a large specific area and a high cation exchange capacity (CEC) as well as water retention capacity.

Most of the physicochemical properties of clay minerals come from their laminar morphology and their small grain size ($<2\ \mu\text{m}$), as well as the electric charge originated by isomorphic substitutions in the layers. As a consequence, they can interact with heavy metals by different adsorption mechanisms, mainly ion exchange reactions and the formation of inner-sphere complexes (Celis et al. 2000). There is, however, little information on the immobilization of heavy metals from soils with the addition of clay minerals. Further studies on the remediation mechanisms and effectiveness of clay minerals for this purpose need to be done.

When a soil is polluted by addition of a trace metal in soluble form, the pollutant speciation undergoes an evolution from labile to stable forms, affected by soil water content, temperature, etc. (Ferreiro et al. 2014). In the present study, the time evolution of copper speciation in a Pampas soil was investigated, including the effect of Na-bentonite amendment. The speciation of copper is obtained experimentally using a SSE procedure; in a SSE, the different steps beyond the first are expected to selectively dissolve/destroy a particular solid (or groups of solids) fraction, with reactants of increasing strength, releasing the associated metal ions; it is in principle assumed that the metal is mainly incorporated into the solid, however surface-adsorbed species should also be removed in the course of the procedure. One of such methods is the Ma and Uren procedure (Ma and Uren 1998); this method was modified for the purposes of the present work (Ferreiro et al. 2014), giving an operational definition which can be better correlated with bioavailability or functional definition and provides a basis for the application of clays in remediation of contaminated soils.

2 Materials and Methods

2.1 Materials

2.1.1 Soil Samples

The studied soil was Typic Argiudoll (USDA Soil Taxonomy) taken nearby Solis town, Buenos Aires province, Argentina ($34^\circ\ 18'\ \text{S}$, $59^\circ\ 20'\ \text{W}$). The area is devoted to field crops and cattle husbandry and recognized as a non-polluted region (Lavado et al. 2004). In a $1,000\text{-m}^2$ plot, 20 soil subsamples were taken at 0–0.20 m, mixed manually thoroughly. From this

homogenized soil mass, the sample employed used in present research was obtained. This soil has been characterized previously (Ferreyroa et al. 2014), the main results being presented in Table 1. In short, it was found that this soil is moderately acid with predominance of silt plus clay and an important soil organic matter (SOM) content. The CEC indicates low clay mineral content, in agreement with the known top soil texture of the area (silty loam). The nitrates are predominant in the anions (432 mg NO₃⁻/kg soil). The copper content in the soil was 30 mg/kg, within typical soil values, both locally (Lavado et al. 2004) and in the world (Sparks 2002). XRD pattern analysis of the silt+clay fraction, using the Rita-Rista methodology (Ferrari and Lutterotti 1994; Wenk et al. 1994), is consistent with the presence of quartz (43 %), low T albite (7 %), high T albite (26 %), orthoclase (14 %), and small quantities of anhydrite, alunogen, biotite, and hematite. No evidence of carbonate minerals was found, which is consistent with the rather low pH values found.

2.1.2 Amendment

Sodium bentonite (SB), coming from the Allen Formation of North Patagonia, Argentina, was previously characterized (Musso et al. 2010) (SB was denoted as CATAE in that work), and was found to contain about 90 % smectite (montmorillonite), 1.5–2 % quartz, 2 % gypsum, 0.5–1 % feldspar, 0.4 % calcite, and 3–4 % zeolites. The silt+clay fraction of the sample amounted to 98 % v/v; the CEC was 105 cmol kg⁻¹; and chemical analysis did not found copper in its composition.

2.2 Methods

2.2.1 Chemical Analysis

All chemicals employed were analytical grade; ultrapure water from a Millipore MilliQ system was employed throughout.

The Cu contents were determined by flame atomic absorption spectrometry (FAAS) with a fuel lean air/acetylene flame after acid digestion (Wright and Stuczynski 1996) using a Shimadzu AA 6800. The instrumental parameters were those indicated by the manufacturer. The final residue of extraction was completely mineralized by microwave digestion in PTFE closed vessels (CEM, MDS 2000), running the program recommended by the manufacturer.

Table 1 Soil characterization

Property	Value
pH	
Water	5.21±0.02
0.01 M CaCl ₂	4.84±0.02
1.0 M KCl	4.40±0.02
Texture (volumetric fractions)	
Coarse sand $r > 500 \mu\text{m}$	10 %
Fine sand $500 \mu\text{m} > r > 62 \mu\text{m}$	25 %
Silt+clay $r < 62 \mu\text{m}$	65 %
Organic matter fraction (w/w)	10.9 %
CEC	9.3 cmol kg ⁻¹
Anions studied	mg anion/kg soil
Cl ⁻	55
NO ₃ ⁻	432
PO ₄ ³⁻	<1
SO ₄ ²⁻	69
Metals studied	mg metal/kg soil
Fe	15×10 ³
Mn	480
Cr	60
Zn	68
Cu	30
Pb	<10

r is the particle size (in the larger direction)

2.2.2 Microscopic Observation

To analyze the mineral composition, the soil mineral fractions (whole soil and silt+clay fraction) were examined under an optical microscope. Further observation was performed by scanning electron microscopy (SEM), using a Zeiss Supra 40 Gemini microscope. The samples were prepared by placing a small amount of solid on one side of a carbon tape.

2.2.3 Infrared Spectroscopy

Infrared (IR) spectroscopy was performed for the Na-bentonite, control, and contaminated samples using a Fourier transform IR (FTIR) Nicolet 8700 spectrometer, in the range 400–4,000 cm⁻¹. The samples were pressed into pellets prepared dispersing 1.0 mg of each one in 150 mg of KBr. For each sample, 32 scans were accumulated and averaged.

2.2.4 Cu Speciation Experiments

The study was conducted in 1-kg soil pots. There were control pots and Cu-polluted pots; to each one of these, 200 mL of a 0.0145 M $\text{Cu}(\text{NO}_3)_2$ solution were added at the start of the experiment and thoroughly mixed, so as to reach a fixed concentration of 200 mg kg^{-1} (value in the order of the average of typical polluted agricultural or residential soils; Environment Canada 1991; Gobierno Argentino 1993). Three types of Cu-polluted pots were set up: one without amendment, and the other two amended with bentonite (5 % w/w) at different times: initially and 90 days after Cu addition; SB was added in solid form followed by thorough homogenization. All pots were setup in triplicate. The pots were placed in a shelter and irrigated at 7-day intervals at 70 % field capacity. Samples from the pots were taken at intervals and analyzed with the SSE procedure described next; the whole experiment was run for a total of 160 days.

2.2.5 Sequential Selective Extraction Procedure

The modified method of Ma and Uren (Ferreyroa et al. 2014) was employed, which is shown in Table 2, where the steps are operationally defined. For the SSE procedure, the starting soil amount was 1.00 g. In each step, the soil was suspended in 10.0 mL of the corresponding extractant; the Cu contents of the respective fractions were determined by flame atomic absorption spectrometry as described above. The reproducibility was verified in a quintuplicate experiment and found to be satisfactory (the standard error was below 3 % for all fractions)

2.2.6 Speciation Calculations

The speciation of Cu(II) in several conditions was calculated with the aid of Visual Minteq program version 3.1 (Gustafsson 2011). Parameters for solution equilibria came from the internal (MINTEQA2) database; Freundlich isotherm parameters for adsorption calculations were taken from literature (Musso et al. 2014).

Table 2 Sequential selective extraction procedure employed

Step	Fraction description	Extractant
I	Water soluble/ exchangeable	MgCl_2 1.0 M, shaken 1 h
II	Associated to reducible components (e.g., Mn oxides).	Hydroquinone 0.2 %/1.0 M $\text{CH}_3\text{COONH}_4$, Shaken 1 h
III	Bound to oxidizable components (mainly organic matter)	30 % H_2O_2 (5 mL portions until end of reaction) in 0.5 M $\text{NaCH}_3\text{COO}/$ CH_3COOH at 80 °C, Shaken 1 additional hour
IV	Oxalate extractable (e.g., Fe/Al oxides or adsorbed to other minerals)	0.175 M $(\text{NH}_4)_2\text{C}_2\text{O}_4/0.1$ M $\text{H}_2\text{C}_2\text{O}_4$, Standing for 15 h and shaken for 2 more hours
V	Residue (mainly silicates)	Microwave digestion in H_2SO_4 (conc.) + HClO_4 (conc.) + HNO_3 (conc.) + HF (conc.)

3 Results and Discussion

3.1 Microscopical Observation

Figure 1 shows typical SEM images of the various samples investigated. In Fig. 1a, the Na-bentonite is observed; it is found to be mostly composed of particles in the micrometer range, with some larger, probably being agglomerates. Figure 1b shows a sample of the control soil; the minerals present (mostly quartz and plagioclases) are partially covered with SOM. In Fig. 1c, the soil with Cu (200 mg kg^{-1}) is observed; no significant differences with control soil are found; presumably the low level of Cu present did not affect the soil matrix. Finally, in Fig. 1d, the soil with 200 mg kg^{-1} Cu and 5 % SB is presented; the presence of some clay particles, presumably of bentonite, can be discerned here.

On the other hand, optical microscope observation shows mainly sedimentary clasts in the sand fractions, whereas in the finest fraction quartz, feldspars and some opaque minerals are observed; amorphous material was also found.

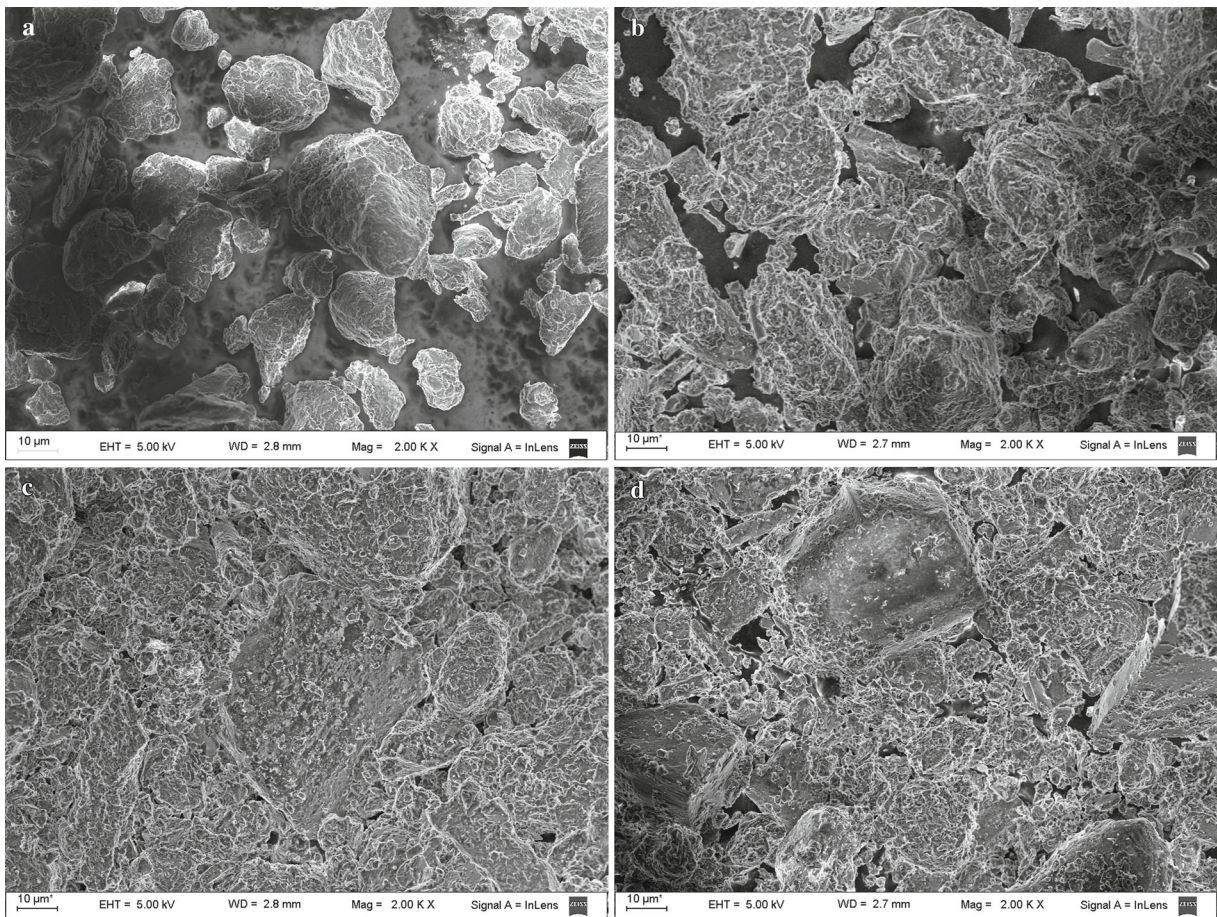


Fig. 1 Scanning electron microscopy images of **a** the bentonite used for amendment, **b** control soil sample, **c** soil with Cu (200 mg kg^{-1}), and **d** soil with Cu (200 mg kg^{-1}) and 5 % Na-bentonite

3.2 Cu(II) Speciation Experiments

The Cu(II) speciation results (fractions defined in Table 2) are presented, for the sake of clarity, distributed in two figures: Fig. 2 (all fractions, first 30 days) and Fig. 3 (fractions III–V, all experiments, including control experiment for the full run of 160 days). Figure 2a presents the results for the soil without amendment, whereas Fig. 2b shows the experiment with SB added at the beginning. The analysis of the control soil (Fig. 3) shows a small amount of Cu in fraction V and negligible contents in the other fractions, showing that the initial soil Cu is fully in stable mineral form, as expected. When Cu(II) is added to the soil, it is found that the metal is predominantly present in fractions III to V, indicating that the metal in soil evolves rapidly toward the more stable fractions. Fractions I and II (Fig. 2) contain in all cases below 3 % of metal, being nearly

constant throughout the study, thus were omitted in Fig. 3. The fact that at a short time after adding soluble Cu(II) almost no metal is found in the exchangeable fraction (I) indicates a fast fixation in stable forms; complexation with the organic fraction (III) appears to be the most probable way, as most metal is bound to that fraction. During the experiment time, there is an evolution toward more stable fractions (IV and V) with a concomitant decrease of fraction III, which nevertheless was the most important in all the experimental period.

The amendment with SB at the beginning of the experiment results in an increase of fractions IV (mostly) and V at the expense of fraction III; no increase of the exchangeable metal (fraction I) was found, indicating that Cu(II) was not bound in exchangeable form, despite the high CEC of the bentonite. Similar results (not shown) were found at the end of experiment (160 days) when SB is incorporated in soil 90 days after

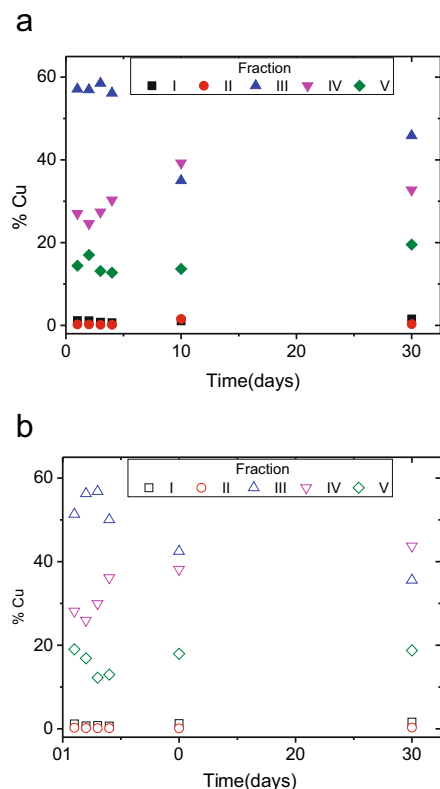


Fig. 2 Time evolution of Cu(II) speciation (first 30 days), expressed as percent of total Cu found in soil, in the pure soil sample (a) and soil amended with Na-bentonite (b)

pollution. This fact, and the observation on Fig. 3 that the lines for soil with and without amendment are essentially parallel, suggest that the SB-bound Cu(II) is

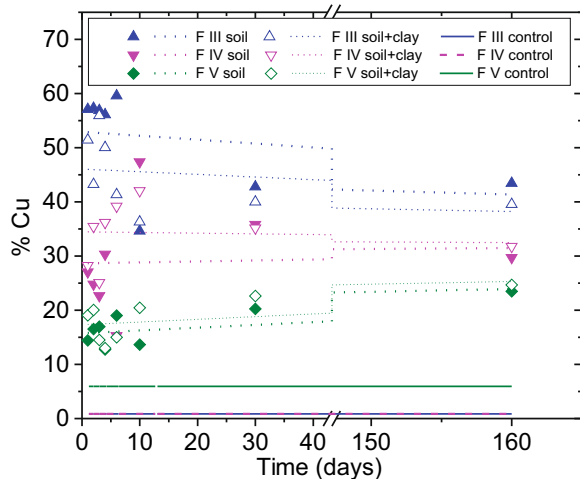


Fig. 3 Time evolution of the main Cu(II) fractions (III–V) during the full experiment time, compared with the control soil speciation (solid lines). Closed symbols correspond to unamended soil, whereas open symbols to the amended soil. Lines are linear fits

removed from fraction III, in a relatively fast process, compared with the experiment time span.

3.3 IR Spectroscopy

Figure 4 shows the IR spectra, from bottom to top: the pristine soil; pure SB; soil at day 3 with Cu (200 mg kg^{-1}); the same with SB added at experiment start; the soil with Cu at day 160; the same with SB added at day 1; and the soil with Cu, with SB added at day 90. The general features are typical of soil mainly composed of aluminosilicate minerals (Lerot 1976; Malhotra and Ogloza 1989; Bukka et al. 1992; Ostrooumov et al. 2005; Fonseca et al. 2009; Sdiri et al. 2011; Musso et al. 2014):

1. OH stretching vibrations are found at ca. $3,620 \text{ cm}^{-1}$ (internal hydroxyl groups in octahedral structures) and around $3,400 \text{ cm}^{-1}$, corresponding to surface OH groups and adsorbed/interlayer water.
2. The band at $1,620 \text{ cm}^{-1}$ due to water bending vibrations.
3. The intense bands at $1,090$ and $1,030 \text{ cm}^{-1}$ are attributed to shared apical O vibrations and tetrahedral Si-O stretching, respectively.
4. Organic matter, which is in relatively low proportion, is revealed by the C-H stretching bands in the range $3,000\text{--}2,800 \text{ cm}^{-1}$ and a broad band around $1,450 \text{ cm}^{-1}$.
5. The two bands at 800 and 780 cm^{-1} are due to quartz.
6. Finally, the lattice bands at 530 and 470 cm^{-1} are found in several silicate minerals.

Spectrum b in Fig. 4 corresponds to the pure SB. Most features are similar to the pure soil, as expected. The octahedral OH band at $3,620 \text{ cm}^{-1}$ is more intense here than in the soil, which is consistent with low phyllosilicate contents in the pure soil; obviously, the bands due to organic matter and quartz are absent, and the band at 530 cm^{-1} is enhanced in SB compared with soil.

In the presence of Cu, the mineral bands do not show noticeable changes (comparing Fig. 4c, d with Fig. 4a), neither in the SB spectrum (not shown); this is consistent with previous observations (Musso et al. 2014). Instead, a sharp band at $1,384 \text{ cm}^{-1}$ (marked in the figure) is noticed which is attributable to carboxylate

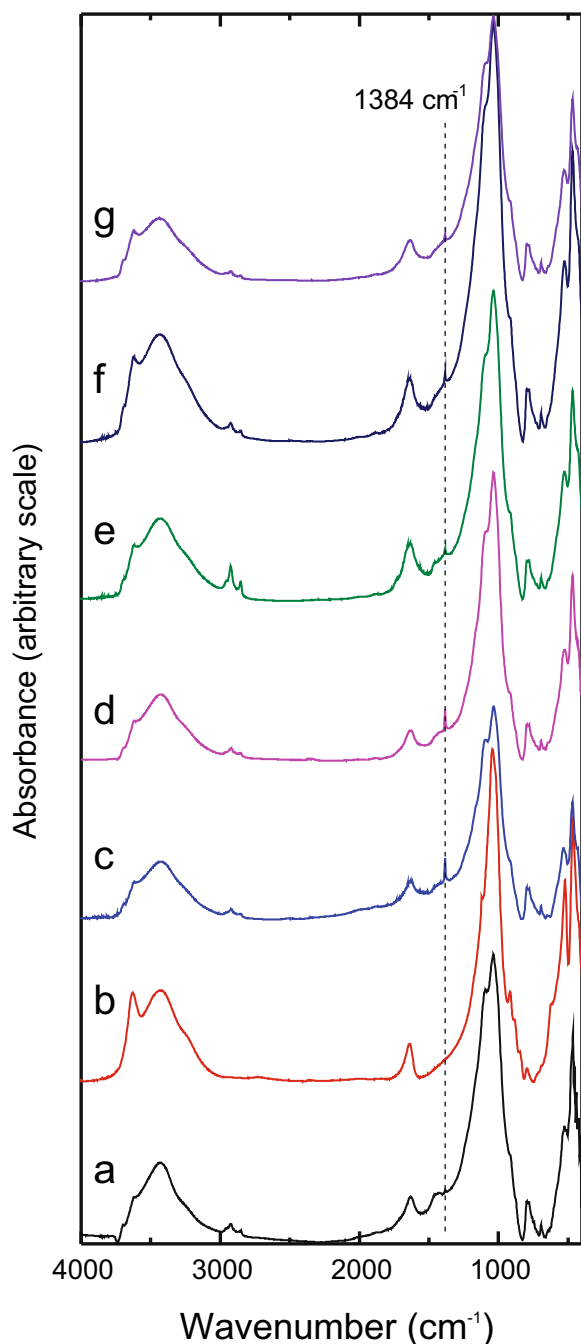


Fig. 4 FTIR spectra of **a** control soil sample; **b** pure Na-bentonite; **c** Cu-polluted soil, 3 days after pollution; **d** polluted and amended soil, 3 days after pollution; **e** Cu-polluted soil, end of experiment; **f** polluted and amended soil, end of experiment; **g** soil polluted at the start of experiment, amended at day 90, sample taken at end of experiment

stretching (Liu and Wang 2004); this band has been reported to increase sharply when heavy metals such

as Hg(II) or Pb(II) interact with carboxylate groups (Orsetti et al. 2006; Zhang et al. 2009; Ferreyroa et al. 2014). It should be noted that the band corresponding to nitrate anion (which is both present in the original soil and incorporated along Cu(II) in the experiment) also falls in this region and has been reported, in some cases, to appear at $1,385\text{ cm}^{-1}$ (Musić et al. 1999); however, the changes observed with time favor the attribution of the observed band to Cu-carboxylate interactions. On the other hand, the addition of SB to soil results in a small change in the relative intensities of the bands at $1,090$ and $1,030\text{ cm}^{-1}$ and those at 530 and 479 cm^{-1} . At the end of experiment (day 160, Fig. 4e–g), the intensity of the $1,384\text{ cm}^{-1}$ band is noticeably lower, which is qualitatively in agreement with the speciation results, but the decrease does not correlate quantitatively with the amount of metal in fraction III. It should be noted that the organic-bound Cu(II) should be itself distributed among different forms, namely singly coordinated, double coordinated, quelated, etc. with different stability (Senesi and Loffredo 2005), and those with lower stability will be removed first in the evolution toward mineral forms; thus, if the $1,384\text{ cm}^{-1}$ band is due to relatively low stability forms, its intensity will decrease faster than the total Cu in fraction III.

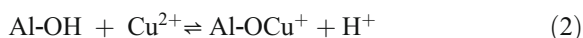
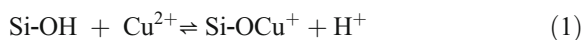
Comparing the spectrum in Fig. 4g (SB added at day 90) with Fig. 4f (SB added at day 0), very little differences are observed, which is consistent with the SSE results, where almost no differences were found between the two cases. Overall, the IR observations are in qualitative agreement with the speciation results.

3.4 Speciation Evolution and Bentonite Effect

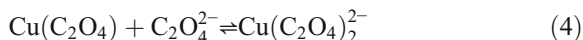
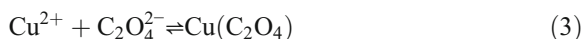
The speciation results show that Cu(II) is rapidly bound to the SOM, after that the speciation slowly evolves toward more stable fractions, i.e., fraction IV (oxalate extractable) and V (mineral). Albeit fraction IV was originally formulated as iron and aluminum oxide bound metal (Ma and Uren 1998), it has been shown to include metal adsorbed onto minerals such as aluminosilicates (Ferreyroa et al. 2014); thus, the time evolution of copper in the soil under study can be summarized as organic-bound \rightarrow strongly adsorbed \rightarrow mineral form.

The effect of Na-bentonite addition is mainly the increase of fraction IV at the expense of fraction III, that is SB removes part of the Cu(II) bound to SOM. This fact, along with the observation that fraction I Cu contents does not change in the presence of SB, indicates

that this mineral interacts strongly with the metal, presumably through specific adsorption. As all smectites, SB has a high CEC, thus a high capacity to bind cations electrostatically, but it is also capable of binding metal cations specifically through edge OH groups; this has been verified by several authors (Stadler and Schindler 1993; Undabeytia et al. 2002; Furnare et al. 2005). The metal cations can bind to surface silanol or aluminol groups:



The adsorption of Cu(II) has been studied in the SB employed in present paper (Musso et al. 2014), finding that the adsorption capacity is higher than the CEC, indicating a contribution of specific adsorption at edge sites. In similar montmorillonites, specific adsorption has been reported (Undabeytia et al. 2002; Gu et al. 2010). If Cu is (partially) adsorbed onto the clay and this metal is recovered in fraction IV, it must be desorbed by the oxalate reactant, which forms stable complexes with Cu(II):



Reactions (3) and (4) have high equilibrium constants, $10^{5.72}$ and $10^{4.51}$, respectively, suggesting that oxalate is able to remove specifically adsorbed Cu. To get some more insight into this aspect, the Cu speciation during the SSE stage IV was estimated using Freundlich isotherm parameters found in literature (Musso et al. 2014) at pH=5; total Cu(II) concentration was 3×10^{-4} M (as $\text{Cu}(\text{NO}_3)_2$), corresponding 200 mg kg⁻¹ in soil in the SSE conditions. Cu speciation was computed for three cases:

1. Cu(II) in the presence of bentonite alone: 99.4 % of Cu was adsorbed to bentonite.
2. Cu(II) in the presence of bentonite and organic ligands (all 0.01 M) to model SOM: acetate, benzoate, and phthalate. The results show 91.6 % of Cu adsorbed onto bentonite, consistent with the fact that adding SB to soil removes part of organic-bound Cu.

3. Cu(II) in the presence of bentonite and the oxalate buffer reactant of step IV (Table 2), resulting in 99.9 % complexed with oxalate, consistent with bentonite-bound Cu being removed in step IV.

Thus, it is proposed that the incorporation of cupric ion in the soil under study results in the following processes:

1. In the absence of SB, Cu(II) is rapidly (less than one day) bound to SOM, after that evolves to more stable forms, namely strongly adsorbed to mineral colloids and finally incorporated in minerals.
2. In the presence of SB, Cu(II) is strongly adsorbed onto this mineral removing, at least partially, SOM-bound Cu. The fact that only a partial removal is observed can be attributed to the relatively low proportion of SB (5 %) compared to SOM contents (>10 %); however, it is conceivable that some SOM compounds could quela strongly the metal ions. The SB-bound Cu (adsorbed) is removed by the strongly complexing capability of the oxalate reactant.

The effect of use of SB as an amendment for remediation, in the case of the studied soil, was limited, mainly because the SOM contents, in high proportion, rapidly complexes the pollutant metal, contributing to its fixation. However, for soils with low organic matter content, SB as amendment could be an effective way to limit the pollutant bioavailability.

4 Conclusions

The results show that in soil contaminated with copper ion, the metal is bound to the organic fraction in a few days, but over time it is displaced to more stable soil fractions. The addition of bentonite causes a decrease of organic-bound metal, but does not affect substantially the time evolution of Cu speciation toward less soluble fractions. Sodium bentonite could be effectively used for remediation of low organic mater soils polluted with Cu(II).

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