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ORIGINAL PAPER

pH-dependent copper release in acid soils treated with crushed mussel shell

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Abstract The aim of this study was to assess the influence of pH on copper mobilization in two copper-rich acid soils (from vineyard and mine) amended with crushed mussel shell. Crushed mussel shell amended soils (0–48 Mg ha^{-1}) were subjected to the effect of several acid and alkali solutions in a batch experiment in order to study their copper release. Copper distribution was studied in decanted soils from batch experiments using a sequential extraction procedure, whereas the effect of crushed mussel shell on copper release kinetics was studied using a stirred flow reactor. When soils were treated with acid solutions, the copper mobilization from non-amended soils was significantly higher than from the amended samples. Major changes in copper fractionation were an increase of the acid soluble fraction in acid-treated vineyard soil samples with shell dose. For the mine soil, the oxidable fraction showed a relevant diminution in acid-treated samples at the highest crushed mussel shell dose. For both soils, copper desorption rates diminished up to 86 % at pH 3 when crushed mussel shell was added. At pH 5, copper release rate was very slow for both soils decreasing up to 98 % for the mine soil amended with the highest shell dose, whereas no differences were observed at pH 7 between amended and non-amended soils. Thus, crushed mussel shell addition could contribute to reduce potential hazard of copper-enriched soils under acidification events.

Keywords Copper fractionation · Mine soil · Release kinetics · Vineyard

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Introduction

As a result of using fungicides with high copper (Cu) content, this metal usually accumulates in the upper layers of vineyard soils, a process which was favoured by its low mobility (Fernández-Calviño et al. 2008, 2009a). This fact may cause damage to the soil quality and could produce environmental deterioration. Other environments where high Cu levels can be detected are Cu-exploited mine tailings. The pollution potential of these areas is high, mostly due to the risk of leaching pollutants to the watercourses in the nearby zone. These leachates may contain high Cu levels, as well as high acidity (Álvarez et al. 2011).

In recent years, low-cost materials were used as sustainable bioadsorbent for the removal of toxic metals (Bailey et al. 1999; Zvinowanda et al. 2009; Dizadji et al. 2011); however, the mussel shell was scarcely tested.

Galicia (NW Spain) is one of the most important producers of mussel (*Mytilus galloprovincialis*) in the world (Caballero et al. 2009). Most of this mussel production is processed by the cannery industry generating great amounts of wastes (mainly mussel shells), which will vary between 65,682 and 93,541 tonnes per year depending on mussel production (Barros et al. 2009; Peña-Rodríguez et al. 2010). In coastal areas, it is traditional that farmers helped to the direct recycling of untreated shell using it to increase the pH of acid soils. However, in the last decades some factories have implemented industrial processes leading to the treatment of waste shells, in order to transform it into products rich in carbonates and oxides with an appropriate particle size and without residual organic matter. These factories are engaged in different processes including particularly washing, crushing (and also calcination in some factories) and finally sieving of the treated shells.

Regarding the effects of mussel shell on the retention and releasing of certain substances, it was shown that the degree of retention of divalent cations in the shell is higher when it contains more aragonite than calcite (Prieto et al. 2003; Cubillas et al. 2005a; Köhler et al. 2007; Sakulkhaemaruethai et al. 2010). The shell of some species is mainly constituted by aragonite, and only after calcination it showed a higher percentage of calcite (Currie et al. 2007; Abeynaike et al. 2011). Other species may have shells that originally contain higher percentage of calcite, or even high levels of both $CaCO_3$ polymorphs (Cubillas et al. 2005a, b). The adsorption of dissolved Cu and Zn was studied by Kitano et al. (1976) showing clear differences between calcite and aragonite. Focusing on other divalent cations, Prieto et al. (2003) showed positive results as regards Cd^{2+} retention in aragonite by means of cockle shell showing as well that retention was clearly lower when using calcite. The same higher retention of Cd^{2+} in aragonite was reported by Cubillas et al. (2005b), this time using mussel shell and also shell from other bivalves. The high efficacy of aragonite in the retention of dissolved Cd^{2+}, Pb^{2+} and Zn^{2+} was reported by Köhler et al. (2007), whereas high levels of Hg^{2+} could be retained using calcined mussel shell, but this material contained 7 % of aragonite even after calcination (Peña-Rodríguez et al. 2010).

The aims of this study were to assess the effects of the amendment of two Cu-enriched soils, a vineyard soil and a soil from a Cu-mine tailing, with crushed mussel shell (CMS) on the pH-dependent release and the kinetic characteristics of copper release. In addition, changes in Cu distribution in soil residues amended and non-amended with CMS after acid and alkali treatments were also assessed. Since CMS contains 44 % aragonite, a high potential for Cu^{2+} retention could be expected. This research was conducted at the laboratories of soil science of the universities of Vigo and Santiago de Compostela and in the laboratory of soil biochemistry of the Agrobiological Research Institute of Galicia (Spain) during 2010.

Materials and methods

Soil characteristics

The surface layer of two soil types (0–20 cm) was sampled in a vineyard area (A) and in a copper mine tailing (B), both located in NW Spain. Both soil samples were air-dried, sieved through 2-mm sieve and then stored until being analysed.

The pH in water and in 0.1 M KCl was measured with a combined glass electrode using a 1:2.5 (soil:water) ratio. Total carbon and nitrogen contents were determined by elemental analysis using a Thermo Finnigan 1112 Series NC elemental analyser. The particle size distribution was determined by the wet sieving and pipette methods according to Gee and Bauder (1986). The effective cation exchange capacity (eCEC) was estimated as the sum of base cations (Na, K, Ca, Mg) extracted with 0.2 M NH_4Cl (Sumner and Miller 1996) and Al extracted with 1 M KCl (Bertsch and Bloom 1996). Base cations and Al were determined by emission (Na and K) or flame atomic absorption spectrophotometry, with a Thermo Solaar M Series spectrophotometer. The total contents of Ca (Ca_T) and Al (Al_T) were determined by ICP-OES after digestion of 0.5 g of finely ground soil sample with a mixture of concentrated strong acids (5 mL HNO_3 + 4 mL HF + 1 mL HCl) in a microwave oven (ETHOS 900 Microwave Labstation). General characteristics of both soils are shown in Table 1.

Crushed mussel shell (CMS) and soil/CMS mixtures

The crushed mussel shell samples were from Abonomar S.L. (Illa de Arousa, Pontevedra, Spain), and its general characteristics are shown in Table 1. The aragonite and calcite contents of the shells used in this study were determined by X-ray diffraction analysis (Philips PW1710 Difractometer), being 44 and 48 %, respectively. The content of both polymorphs is high.

To carry out the present study, various mixtures of CMS and soils (soil A or soil B) were performed. Considering an effective soil depth of 20 cm and a soil bulk density of 1 g cm^{-3}, 400 g of soil A or soil B was mixed with different amounts of CMS to obtain final doses of 0, 12, 24 and 48 Mg ha^{-1} of CMS (which correspond to the addition of 0, 6, 12 and 24 g of CMS per kg of soil, respectively).

Table 1 General characteristics of the vineyard soil (soil A), the mine soil (soil B) and the crushed mussel shell (CMS)

Sample	Sand (%)	Silt (%)	Clay (%)	pH (H_2O)	pH (KCl)	C_T (%)	N (%)	eCEC (cmol kg^{-1})	Cu_T (mg kg^{-1})	Ca_T (%)	Al_T (%)
Soil A	73.4	12.0	14.6	4.5	3.5	2.6	0.17	5.30	361	0.06	2.21
Soil B	67.4	14.0	18.6	3.8	3.0	0.3	0.04	3.89	651	0.06	0.96
CMS	99.5	0.3	0.1	9.4	9.0	12.4	0.08	30.30	9	36.4	0.3

In order to facilitate a better homogenization of the mixtures, they were shaken end-over-end for 72 h in 2 L polypropylene bottles. After shaking, all mixtures were passed at least five times for a Retsch homogenizer, and then they were stored until further use.

pH-dependent Cu, Ca and Al release

The following experiment was performed to assess the effect of CMS addition on Cu release in a wide range of pH values. Thus, 10 mL of various HNO_3 solutions (0.02, 0.015, 0.01, 0.0075 and 0.005 M) or NaOH solutions (0.02, 0.015, 0.01, 0.0075 and 0.005 M) were added to a 1 g of mixture. All solutions (acid and alkali) contained 0.05 M $NaNO_3$ as background electrolyte. In addition, 0.05 M $NaNO_3$ solution was also used as a control (no acid or base added). The resulting suspensions were shaken for 24 h and afterwards centrifuged at 4,000 rpm for 5 min. The supernatant was filtered through acid washed paper and then pH was measured by means of a glass electrode, whereas Cu, Ca and Al concentrations were determined by atomic absorption spectrophotometry, with a Thermo Solaar M Series spectrophotometer.

Copper fractionation

Soil residues precipitated after centrifuging from 0.02 M HNO_3, no acid or base added (0.05 M $NaNO_3$) and 0.02 M NaOH treatments were selected to asses the effects of pH treatments and CMS addition in Cu distribution. Soil residues were washed with 30 mL of 0.05 M $NaNO_3$ solution and then centrifuged at 4,000 rpm for 5 min to remove the excess acid or base. This wash step was repeated twice and afterwards soil residues were oven dried at 30–35° C and homogenized. Copper distribution was studied in soil residues according to the BCR method (Ure et al. 1993; Rauret et al. 1999). BCR method is a sequential extraction procedure consisting in four steps in which the following reagents are used: 0.11 M acetic acid, hydroxylamine chlorhydrate solution (acidified to pH 2 with HNO_3), 30 % H_2O_2 solution and 3 mL HNO_3^{+} 9 mL HCl digestion in a microwave oven. After the application of each reagent a washing step, consisting in washing the soil residue with 30 mL of 0.05 M $NaNO_3$ solution, then centrifuging (4,000 rpm for 5 min) and finally removing the supernatant, was carried out in triplicate. This sequential extraction procedure gives the following Cu fractions: acid soluble fraction (ASF), reducible fraction (RF), oxidable fraction (OF) and the residual fraction (REF). Thus, Cu in ASF fraction is assumed to be derived from cationic exchange sites of soil colloids, as well as Cu associated with carbonates. Copper in RF is assumed to be associated with Fe and Al oxides and oxyhydroxides, whereas OF estimates Cu bound to soil organic matter and its presence as sulphides. Finally, REF is supposedly a mixture of the most recalcitrant Cu forms in the soil.

In all soil extracts, copper was measured by atomic absorption spectrophotometry, with a Thermo Solaar M Series spectrophotometer.

Kinetics of Cu release

We performed stirred flow reactor experiments in order to study the effect of the addition of CMS on Cu releasing kinetics. We carried out experiments with samples from both soils without CMS addition (control) and with a CMS addition of 48 Mg ha^{-1}. The experiments were performed at three different pH values of the inflow solution (3, 5 and 7). The polypropylene stirred flow reactor (1.5 cm^3) was the same used in a previous study by Fernández-Calviño et al. (2010a), based on that reported by López-Periago et al. (2008). Tests were performed in a cabinet thermostated at 25.0 ± 0.1 °C, the flow rate was 0.6 mL min^{-1} and one vial was collected each 2.5 min during 200 min.

The experiments were carried out as follows: 0.2 g of sample was placed together with a magnetic stirring bar in the reaction chamber. Solutions with different pH values (3, 5 and 7) were circulated at the selected flow rate with 0.01 M $NaNO_3$ solution as background electrolyte. In total, 80 samples of 1.5 mL were collected in different vials (all filled in 2.5 min each) in which Cu was determined by atomic absorption spectrophotometry, with a Thermo Solaar M Series spectrophotometer.

The Cu released from the soil samples ($q(i)$) at time $i\Delta t$ (where Δt is the time taken to collect each effluent sample) was calculated, following Yin et al. (1997), from

$$q(i) = \left\{ \sum_{j=1}^{i} \left[\frac{(C_1(j) - C_2(j))\Delta t J_{\mathrm{w}}}{\mathrm{Ve}} \right] + [C_1(i+1) - C_2(i+1)] \right\} \frac{\mathrm{Ve}}{m} \quad (1)$$

where $C_1(i)$ and $C_2(i)$ are the concentrations of metal in the ith effluent sample in the absence and presence of sample, respectively, Ve is the effective volume of solution in the reactor, J_{w} is the flow rate (0.6 mL min^{-1}) and m is the mass of the soil sample. Cu released rates ($V(i)$) were calculated as follows:

$$V(i) = \frac{q(i + \Delta t) - q(i)}{\Delta t} \quad (2)$$

Results and discussion

Effects of CMS addition on pH and on Ca, Cu and Al release from amended soils

Figure 1 showed the variation of pH values as a function of the amount of acid or base added to the soil/CMS mixtures. This figure indicates that the buffer potential of the soils increases with the CMS dose. Under near-neutral pH conditions (no acid or alkali addition), the buffer effect promoted by CMS addition to the vineyard soil (A) caused a pH increase that ranges from 4.8 (no CMS addition) to 7.5 when 48 Mg ha^{-1} CMS was added (Fig. 1). In the mine soil, the addition of 48 Mg ha^{-1} CMS resulted in a pH increase from 4.0 (no acid or alkali addition) to 7.3 (Fig. 1). However, the buffer effects associated with CMS addition are higher after the application of acid solutions than after applying alkali solutions. Thus, after the treatment of vineyard soil samples with 0.02 M $\mathrm{HNO_3}$ solution, the pH value changed in 4.5 units comparing to no CMS addition and to 48 Mg ha^{-1} CMS amendment (2.6–7.1), while this difference was only 0.4 units (8.5–8.9) when the treatment was 0.02 M NaOH (Fig. 1). The behaviour of the mine soil (B) is similar to soil A at the 0.02 M $\mathrm{HNO_3}$ treatment, showing the same variation in terms of pH units (4.4) but a different range of pH values, from 2.2 without CMS addition to 6.6 after the addition of 48 Mg ha^{-1} CMS (Fig. 1). Nevertheless, the buffer potential of soil B is higher than that of soil A at basic pH values, since pH difference was only 1.3 units between the control sample (6.7) and the sample with the highest CMS dose (8.0) as was shown in Fig. 1.

These results mean that CMS is suitable to reduce the acidity of these soils, being this application very interesting especially due to its low cost. Thus, CMS addition provides buffer potential to acid soils which avoid drastic pH changes. As shown in Fig. 1, pH changes were less pronounced after the addition of the highest CMS dose. These changes in soil pH, as an effect of the buffer capacity supplied by CMS addition, are narrowly associated to a marked Ca release due to dissolution of calcium carbonates present in the mussel shell.

The changes in Ca release as function of the amount of acid or alkali added are shown in Fig. 2. When no CMS was added (control), Ca release was always higher in soil A than in soil B. Under a near-neutral pH conditions (0.05 M $\mathrm{NaNO_3}$ treatment) soil A released more Ca (280 ± 5 mg kg^{-1}) than soil B (128 ± 2 mg kg^{-1}). However, under the treatment with acid solutions, the release of Ca increases greatly in both soils (Fig. 2) being higher in soil A (up to 900 mg kg^{-1}) than in soil B (200 mg kg^{-1}). In the soil/CMS mixtures, Ca release increased as a function of CMS dose (Fig. 2). Thus, at the highest acid addition (20 cmol H+ kg^{-1}), Ca release was lower in soil A than in soil B (5,077 mg kg^{-1} vs. 5,687 mg kg^{-1}) when CMS dose was 48 Mg ha^{-1}. Taking into consideration the difference

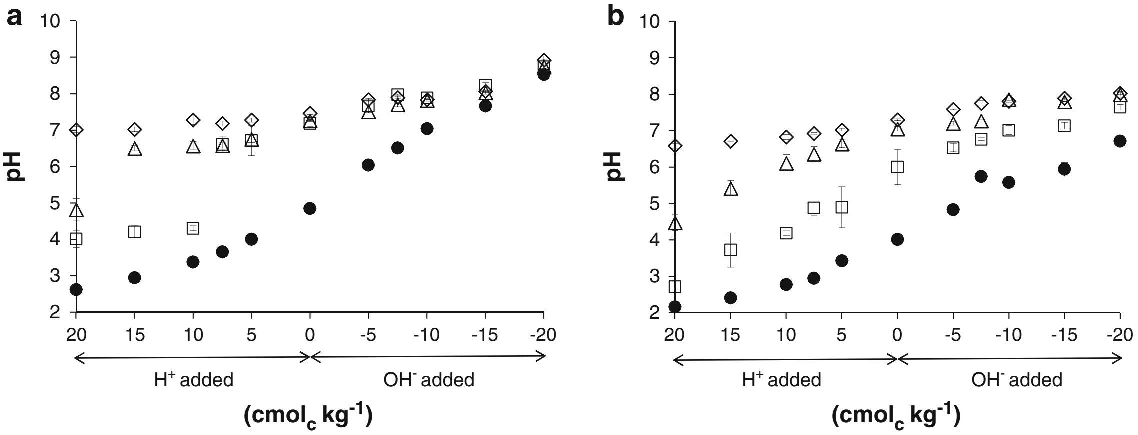

Fig. 1 Changes in pH values due to the addition of $\mathrm{HNO_3}$ or NaOH solutions to samples of a vineyard soil (**a**) and mine soil (**b**) non-amended (*filled circles*) and amended with 12 (*squares*), 24 (*triangles*) and 48 (*diamonds*) Mg ha^{-1} of CMS

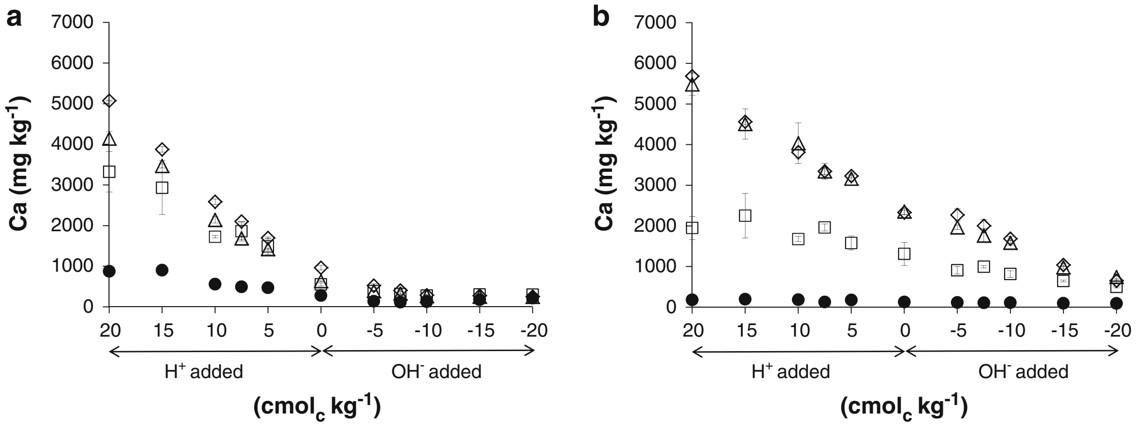

Fig. 2 Changes in Ca release as a function of the addition of HNO_3 or NaOH solutions to samples of a vineyard soil (**a**) and mine soil (**b**) non-amended (*filled circles*) and amended with 12 (*squares*), 24 (*triangles*) and 48 (*diamonds*) Mg ha^{-1} of CMS

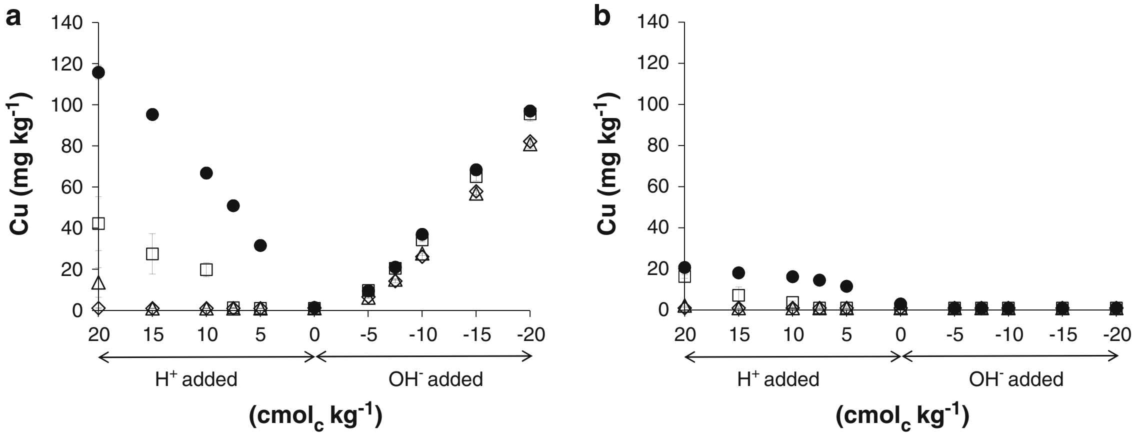

Fig. 3 Changes in Cu release as a function of the addition of HNO_3 or NaOH solutions to samples of a vineyard soil (**a**) and mine soil (**b**) non-amended (*filled circles*) and amended with 12 (*squares*), 24 (*triangles*) and 48 (*diamonds*) Mg ha^{-1} of CMS

between Ca released from the control soil samples and from soils amended with the highest CMS dose, soil A released 4,202 mg kg^{-1} (48 % of the Ca added with CMS) while soil B released 5,505 mg kg^{-1} (63 % of the Ca added with CMS). Under treatment with highest alkali dose (20 cmol OH− kg^{-1}), a comparison between the amount of Ca released from control samples and from samples amended with 48 Mg ha^{-1} of CMS resulted in a lower increase in Ca released at basic pH values from soil A (38 mg kg^{-1}, approximately 0.4 % of the Ca added with CMS) than for soil B (560 mg kg^{-1}, equivalent to 6.4 % of the Ca added with CMS) (Fig. 2).

The differences in Ca release from CMS/soil A and CMS/soil B mixtures could depend on their different soil mineralogical composition, with several cations that would interact with calcite and aragonite forming mineral coatings, resulting in contrasting calcite and aragonite dissolution rates (Cubillas et al. 2005a). In this sense, Cubillas et al. (2005b), studying the effect of Cd on calcium carbonate dissolution rates, reported that thin coatings on mineral surfaces can reduce significantly their dissolution rates.

Since both vineyard and mine soils here studied had a considerably high Cu content, the changes in its release depending on the amount of acid or alkali added and CMS addition was shown in Fig. 3. The results obtained revealed that Cu mobility is highly affected by pH and thus non-amended vineyard soil samples (A) showed a Cu release for all pH range experimented as a U-shaped curve, while control samples of the mine soil (B) only released Cu at most acid pH values (Fig. 3). Copper release was higher in soil A (achieving above 100 mg kg^{-1} as result of the addition of more acid or alkali solutions) than in soil B (up to 21 mg kg^{-1} of Cu at the highest acid treatment, but only 1 mg kg^{-1} Cu at the highest alkali treatment). These amounts of Cu released, referred as percentages of total Cu

Table 2 Mean and standard error values of percentages of Cu (referred to total Cu) and dissolved organic matter (OM$_d$, mg kg^{-1}) released for vineyard soil (A) and mine soil (B) as a function of the amount of acid or base added and the CMS dose (A$_0$ and B$_0$: no CMS; A$_{12}$ and B$_{12}$: 12 Mg ha^{-1} of CMS; A$_{24}$ and B$_{24}$: 24 Mg ha^{-1} of CMS; A$_{48}$ and B$_{48}$: 48 Mg ha^{-1} of CMS)

Sample	Acid or base added					
	0.02 M HNO$_3$		None		0.02 M NaOH	
	Cu (%)	OM$_d$	Cu (%)	OM$_d$	Cu (%)	OM$_d$
A						
A$_0$	32.1 ± 0.8	303 ± 1	0.4 ± 0.0	138 ± 2	26.9 ± 0.6	14942 ± 40
A$_{12}$	11.7 ± 2.9	166 ± 9	0.3 ± 0.0	183 ± 2	26.5 ± 0.8	14118 ± 119
A$_{24}$	3.8 ± 1.6	36 ± 2	0.3 ± 0.1	43 ± 2	22.4 ± 0.5	4494 ± 210
A$_{48}$	0.3 ± 0.1	54 ± 3	0.3 ± 0.0	73 ± 9	22.8 ± 0.3	4309 ± 83
B						
B$_0$	3.5 ± 0.1	27 ± 6	0.5 ± 0.0	14 ± 1	0.2 ± 0.0	19 ± 4
B$_{12}$	2.8 ± 0.1	25 ± 1	0.2 ± 0.0	15 ± 2	0.2 ± 0.0	19 ± 2
B$_{24}$	0.4 ± 0.1	8 ± 2	0.2 ± 0.0	7 ± 0	0.2 ± 0.0	21 ± 1
B$_{48}$	0.2 ± 0.0	11 ± 1	0.2 ± 0.0	14 ± 1	0.2 ± 0.0	25 ± 1

(CuT) are shown in Table 2. The percentage of Cu releases was one order of magnitude higher in soil A (32 and 27 % of CuT when 0.02 M of HNO$_3$ or NaOH solutions were added, respectively) than in soil B (3.5 and 0.2 % of CuT when 0.02 M of HNO$_3$ or NaOH solutions were added, respectively).

The increase in Cu liberation, both at acid and basic pH values (U-shaped curve) was due to an increased Cu solubility at acid pH values and to the dissolution of organically bound Cu at basic pH values (Fernández-Calviño et al. 2008). This last hypothesis is consistent with the observed increase in the liberation of dissolved organic matter (OMd) at basic pH (Table 2).

Regarding the differences in Cu release from both soils, Fernández-Calviño et al. (2009b) found a similar response when compared vineyard soils and corn-cropping soils, with U-shaped Cu release curves in the vineyard soils, and with the corn-cropping soils behaving as the mine soil in this study. These authors attributed this different behaviour to the different origin of the copper in both soils, being mainly anthropogenic in the vineyard soils and derived from lithology in the corn-cropping soils. This explanation could be also applied in the present study, being the Cu from the vineyard soil mainly anthropogenic (due to application of copper-based fungicides), while the Cu in the mine soil is attributed to the presence of minerals with high copper content inherited from the parent material (mainly chalcopyrite).

Crushed mussel shell additions diminished clearly the amount of Cu released from both soils under acid conditions (Fig. 3). Thus, when 0.02 M HNO$_3$ solution was added, Cu liberation diminished from 100 mg kg^{-1} in non-amended soil A to about 1 mg kg^{-1} when soil A was mixed with CMS at dose of 48 Mg ha^{-1}. Under the same acid treatment, Cu liberation from soil B diminished from 21 mg kg^{-1} when no CMS was added till near 1 mg kg^{-1} after the addition of 48 Mg ha^{-1} CMS. These values of diminution of Cu release, expressed as percentage of CuT, were shown in Table 2. As opposite to acid treatments, when soils were treated with alkali solutions, the effect of CMS addition in the diminution of Cu liberation was very low in both soils (Fig. 3).

The results of Cu liberation revealed that the addition of CMS may be used to immobilize Cu in a broad range of pH values. However, the CMS addition drastically diminished Cu release in both soils even when they were exposed to high acid loads, especially at the highest CMS doses (Fig. 3). This diminution in Cu release was mainly due to the additional buffer potential provided by CMS to the soils, but also due to its expected faster dissolution rate, when compared with typical soil compounds responsible for neutralization in acid soils, such as alumino-silicates and metal (Al, Fe)-humus complexes (Simonsson and Berggern 1998; Yagasaki et al. 2006; Nóvoa-Muñoz and García-Rodeja 2007). The effect of the CMS dose on Cu release would be partially related to its aragonite/calcite contents (44 and 48 %, respectively). Kitano et al. (1976), studying the adsorption of copper ions on calcite and aragonite, reported that Cu ions were removed completely through its adsorption on aragonite.

Aluminium release showed a similar behaviour to that of Cu, with a U-shaped curve for its liberation from non-amended samples of soil A, suggesting that Al release increased when acid or alkali solutions were added. In non-

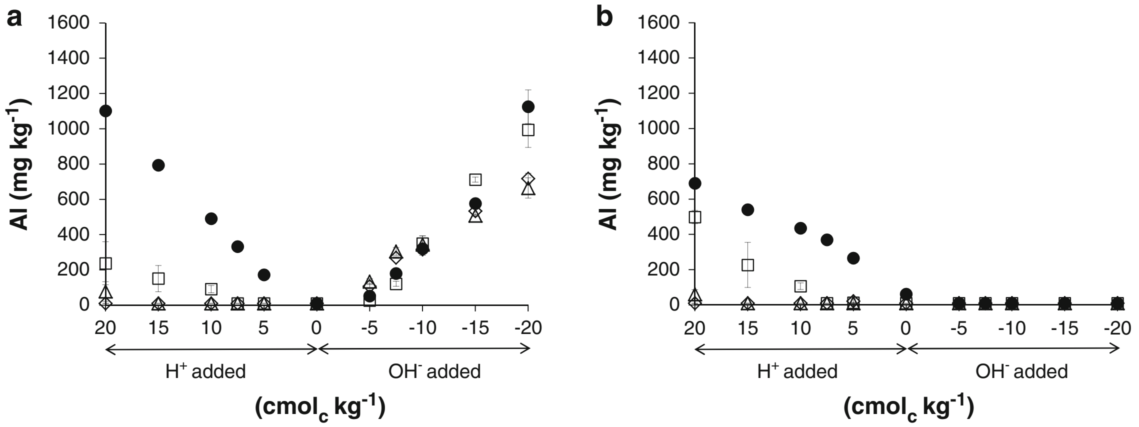

Fig. 4 Changes in Al release as a function of the addition of HNO_3 or NaOH solutions to samples of a vineyard soil (**a**) and mine soil (**b**) non-amended (*filled circles*) and amended with 12 (*squares*), 24 (*triangles*) and 48 (*diamonds*) Mg ha^{-1} of CMS

amended soil B, Al only was released when soil samples were treated with acid solutions (Fig. 4). The release of Al observed in both soils after acid treatments is consistent with the well-known role of Al compounds in soil solid phase as dominant source of buffering capacity in acid soils (Mulder and Stein 1994; Lazerte and Findeis 1995). The different behaviour observed after alkali treatments could be related to the different pH values reached in soil A or B after application of basic solutions. Thus, soil A reached pH 8 when 0.02 M NaOH solution was added being seven in the case of soil B. Since Al precipitates at pH between 5 and 7, pH values should be higher than seven to be released by dissolution of Al-bearing solid phases, which could occur in soil A but not in soil B. Crushed mussel shell additions also diminished clearly the amount of Al released from both soils under acid conditions (Fig. 4) and thus, the average of Al liberated when both soils were treated with the most acid solution was about 10 mg kg^{-1} for CMS additions of 48 Mg ha^{-1} for both soils (Fig. 4). No effects of CMS addition were observed in Al released from soil B when control or soil/CMS mixtures were treated with alkali solutions. However, Al liberation was slightly lower in CMS amended samples at such pH values (Fig. 4). The liberation of Al from soil under alkali treatments was also accompanied by the release of OMd (see Table 2), suggesting that Al-humus complexes could be dissolved due to the action of alkali solutions. This hypothesis is consistent with findings of Takahashi et al. (2006), who observed a significant reduction in organically complexed Al after liming in acid soils.

Copper fractionation

The results of Cu fractionation for the various residues of soil/CMS mixtures treated with acid (0.02 M HNO_3), base (0.02 M NaOH) and without acid or base (0.05 M NaNO3) were shown in Table 3. Non-amended samples of soil A showed a significant decrease in Cu content of the ASF fraction (LSD, $p < 0.001$) from values of 72 ± 3 mg kg^{-1} for samples without acid or base treatment to 31 ± 3 mg kg^{-1} for those treated with acid. However, the decrease in Cu content from ASF fractions was less pronounced (and not significant, LSD, $p < 0.065$) for alkali-treated samples which showed a mean value of 62 ± 1 mg kg^{-1} (Table 3). A similar behaviour was observed for Cu content in the RF fraction, which showed a significant decrease from 43 ± 2 mg kg^{-1} for the untreated samples (0.05 M $NaNO_3$) to 27 ± 2 mg kg^{-1} for the acid-treated samples (LSD, $p < 0.039$), although Cu diminution in RF fraction treated with alkali solution (30 ± 1 mg kg^{-1}) did not differ significantly from untreated samples (LSD, $p < 0.080$). As regards Cu content in the OF fraction, there were no significant differences (LSD) between the untreated and the acid-treated samples (33 ± 2 vs. 37 ± 4 mg kg^{-1}), whereas significant differences between the not treated and the alkali-treated samples (LSD, $p < 0.022$) were observed (Table 3). Regarding the most abundant Cu fraction, REF, there were no significant differences between the untreated and the acid-treated samples (LSD, $p < 0.199$) which could be due to the high variability observed within samples. However, a significant decrease in Cu content in REF fraction was shown by alkali treated samples of soil A, whose Cu average in this fraction was significantly lower than for not treated samples (LSD, $p < 0.046$). These results suggest that for non-amended samples of A soil treated with 0.02 M HNO_3 solution, the Cu release took place mainly from labile fractions such as ASF and RF fractions. This may be inferred taking into consideration the decrease of Cu content observed in these fractions when they were

Table 3 Mean and standard error values (in mg kg^{-1}) of Cu distribution in amended and non-amended samples (A_0 and B_0: no CMS; A_{12} and B_{12}: 12 Mg ha^{-1} of CMS; A_{24} and B_{24}: 24 Mg ha^{-1} of CMS; A_{48} and B_{48}: 48 Mg ha^{-1} of CMS) for vineyard soil (A) and mine soil (B) as a function of the amount of acid or base added

Sample	Acid or base added											
	0.02 M HNO_3				None				0.02 M NaOH			
	ASF	RF	OF	REF	ASF	RF	OF	REF	ASF	RF	OF	REF
A												
A_0	31 ± 3	27 ± 2	37 ± 4	138 ± 18	72 ± 3	43 ± 2	33 ± 2	162 ± 13	62 ± 1	30 ± 1	23 ± 1	89 ± 2
A_{12}	56 ± 5*	36 ± 2	30 ± 3	128 ± 20	75 ± 3	46 ± 0	37 ± 3	166 ± 2	66 ± 2	35 ± 3	29 ± 4	114 ± 12
A_{24}	69 ± 3*	38 ± 2	27 ± 1	156 ± 13	78 ± 2	51 ± 1*	42 ± 3	190 ± 8*	65 ± 5	40 ± 1	28 ± 5	122 ± 23
A_{48}	67 ± 3*	51 ± 5*	39 ± 3	160 ± 14	68 ± 1	53 ± 0*	45 ± 1	188 ± 1*	55 ± 1	38 ± 1	18 ± 1	115 ± 1
B												
B_0	4 ± 0	4 ± 0	114 ± 10	338 ± 11	7 ± 0	6 ± 0	128 ± 2	342 ± 4	5 ± 0	8 ± 0	88 ± 7	433 ± 16
B_{12}	4 ± 0	4 ± 0	120 ± 2	379 ± 23	5 ± 1	7 ± 0	108 ± 18	407 ± 16	4 ± 0	8 ± 0	113 ± 16	419 ± 12
B_{24}	5 ± 0	5 ± 1	118 ± 6	360 ± 17	5 ± 0	7 ± 0	92 ± 10	396 ± 14	4 ± 0	8 ± 0	113 ± 10	383 ± 5
B_{48}	4 ± 0	8 ± 0	70 ± 2*	445 ± 8*	4 ± 0	7 ± 0	76 ± 21	449 ± 16	4 ± 0	8 ± 0	47 ± 1	436 ± 14

* Significant differences with the control sample (A0 and B0), as per Dunnet test ($p < 0.05$)

compared to those samples non-acid or alkali treated (0.05 M $NaNO_3$). However in the case of soil A non-amended samples treated with 0.02 M NaOH, the Cu liberation seemed to derive from the less mobile fractions such as OF and REF.

The statistic test of Dunnet was used to compare non-amended soils and amended soils with the various CMS doses. In soil A, regarding the ASF fraction in the acid-treated samples, the addition of all CMS doses resulted in a significant increase ($p < 0.05$) of Cu content in this fraction (from 31 ± 3 mg kg^{-1} till values ranged from 56 to 69 mg kg^{-1}; Table 3). The Cu content in RF fraction of samples treated with acid also showed significant differences, but only at the highest CMS dose. Copper content in OF and REF fractions did not show significant differences for samples treated with acid at any CMS dose (Table 3). For samples of soil A treated with 0.05 M $NaNO_3$ (no acid or base added), only Cu contents for RF and REF fractions showed a significant increase regarding non-amended samples when CMS addition was 24 or 48 Mg ha^{-1} (Table 3). Samples of A soil treated with alkali solutions did not show significant differences for any Cu fraction or CMS dose.

In samples from soil B, either for untreated, acid and alkali treated, Cu content in ASF and RF fractions showed low values that ranged from 4 to 8 mg kg^{-1} (Table 3). This suggests that pH treatments and CMS addition did not influence Cu distribution in these fractions. However, Cu content in OF decreased significantly in acid treated samples amended with the highest CMS dose (70 ± 2 mg kg^{-1}) comparing to non-amended samples (114 ± 10 mg kg^{-1}; Table 3). On the contrary, a significant increase in Cu content of the REF fraction was observed after comparing the Cu values in non-amended soil (338 ± 11 mg kg^{-1}) and that amended with 48 Mg ha^{-1} CMA (445 ± 8 mg kg^{-1}). Although it was not statistically significant, for untreated samples (0.05 M $NaNO_3$ solution) there is an apparent trend to diminution of Cu contents in the OF fraction with the increase in the CMS dose (from 128 ± 2 mg kg^{-1} at no CMS addition to 76 ± 21 mg kg^{-1} at 48 Mg ha^{-1} CMS, Table 3). A similar result was found for alkali-treated samples, although in this case the highest values of Cu in the OF fraction occurred in samples amended with 12 and 24 Mg ha^{-1} (Table 3). The addition of CMS did not constitute a significant factor of variation in Cu content for the REF fractions, ranging from 342 to 449 mg kg^{-1} for untreated samples and from 383 to 436 mg kg^{-1} for alkali treated samples (Table 3).

The results from Cu fractionation in soil B revealed that Cu distribution was very similar in all cases. This was an expected result bearing in mind that Cu release was limited to acid pH values, either in control samples (no CMS added) or in samples amended with low-CMS doses. In all cases, dissolved Cu was always lower than 5 % of the total Cu content in the control sample.

Cu desorption kinetics

Figure 5 shows the results of Cu release kinetics for the control samples (A0, without CMS addition) compared with those treated with the highest CMS dose (A48,

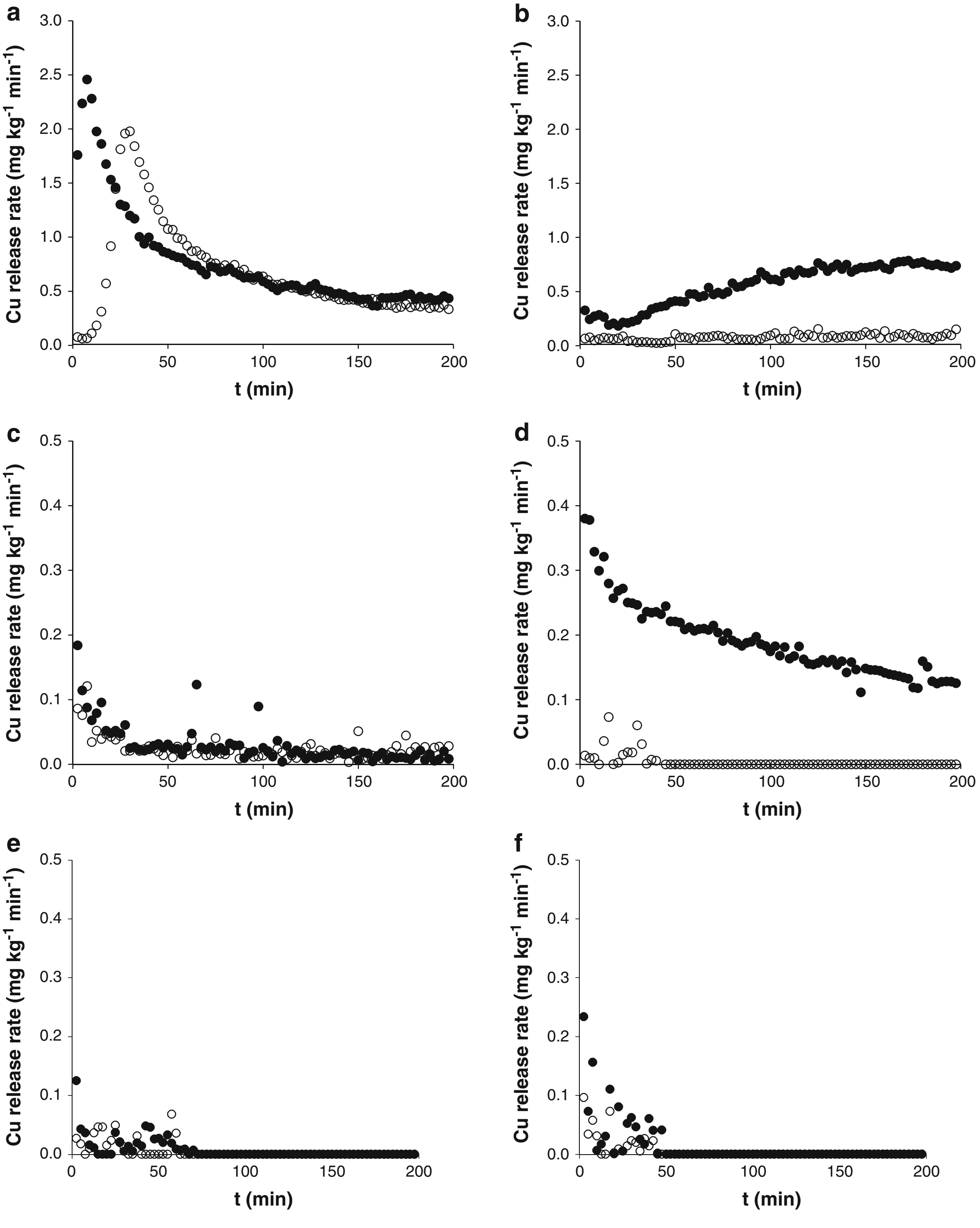

Fig. 5 Changes in Cu release rates in vineyard soil samples (**a**, **c**, **e**) and mine soil samples (**b**, **d**, **f**) without CMS addition (*filled circles*) and with 48 Mg ha^{-1} of CMS (*empty circles*) at inflow solution pH 3 (*top*); pH 5 (*middle*) and pH 7 (*bottom*)

48 Mg ha^{-1} of CMS). These results showed that the Cu release rates were highly affected by pH values, and diminished as the pH of the inflow solution increased. Referred to the vineyard soil at pH 3, A0 soil sample showed a value of 2.46 mg kg^{-1} min^{-1} as maximum release velocity, while the amended sample (A48) showed a value of 1.98 mg kg^{-1} min^{-1}. The A0 sample reached its maximum release velocity faster (7.5 min) than the

A48 (30 min). The addition of CMS to soil A resulted in a decrease of 12 % in the average Cu release velocity during the experiment, whereas the maximum Cu release velocity measured during the experiments suffered a 19 % diminution. The Cu release velocities vary notably with time. Between the beginning of the experiment and 22.5 min, Cu release velocities are much higher when CMS is absent than in its presence, while between 22.5 and 75 min Cu release velocities are higher in the presence of CMS than in its absence and, finally, since 75 min until the end of the experiment, Cu release velocities are very similar with or without CMS addition. This means that the addition of CMS was very effective diminishing Cu release during first 22.5 min of the experiment (Cu release diminishes 86 % in this lag), while for times over 22.5 min the percentage reduction was lower. When this experiment was carried out with mine soil (B), the results obtained were very different. The B0 sample (no CMS addition) showed a slight increase in the Cu release velocity with time, reaching 0.80 mg kg^{-1} min^{-1} as a maximum, while the Cu release velocity was very low for the B48 sample, reaching 0.15 mg kg^{-1} min^{-1} as a maximum (Fig. 5), meaning a 86 % of Cu desorption rate reduction. These differences between soil A and B in Cu release rates would be explained by the particular Cu distribution in each one. Although the mine soil (B) has more total Cu, the vineyard soil (A) had higher Cu contents in the most labile fractions (ASF and RF) which favoured its release as a response to the addition of an acid solution (pH 3). Furthermore, the different mineral composition of both soils could affect the potential Cu retention due to the aragonite into the shell, as was suggested by the study of Köhler et al. (2007) on the removal of cadmium by aragonite shells and the influence of other divalent cations.

At pH 5, the Cu release velocities were very low in both soils. In soil A, the maximum velocities reached 0.18 and 0.12 mg kg^{-1} min^{-1} for the A0 and A48 samples, respectively. In soil B, the Cu release velocity diminished with time from 0.38 to 0.15 mg kg^{-1} min^{-1} in the B0 sample, whereas the velocity decreased up to 98 % in the B48 sample with B0 being very low during the whole experiment (Fig. 5). When the pH of inflow solution was five, the differences in soil A and soil B would be explained by soil pH. The vineyard soil had an average pH value of 5.0 in the outflow solution, while this value was 4.0 in the case of the mine soil due to its higher natural acidity. Consequently in the absence of high acid load, the mine soil will release more Cu than the vineyard soil (38 and 7 mg kg^{-1}, respectively). It is well known that Cu retention in the soil increased as soil pH decreased (Fernández-Calviño et al. 2010b).

At pH 7, the Cu release velocities were very low for all samples without CMS addition (0.00–0.13 mg kg^{-1} min^{-1} for soil A and 0.00–0.23 mg kg^{-1} min^{-1} for soil B), and there were no significant differences between control samples and those amended with 48 Mg ha^{-1} (Fig. 5). The Cu bonds to the soil particles could be very high at this pH value, resulting in a high Cu retention in the soil. However, this pH value is not enough to release Cu from the soil by means of organic matter dissolution in high proportions (Fernández-Calviño et al. 2008).

Conclusion

The addition of crushed mussel shell to Cu-rich acid soils provides them with a substantial buffer capacity which keeps pH values near neutrality even after extreme acid events. This makes CMS a suitable material to reduce the acidity of acid soils, being this application very interesting especially due to its low cost. This buffer capacity supplied by CMS is mainly due to the dissolution of Ca carbonates from mussel shell. Moreover, the addition of CMS to both vineyard and mine soils caused a significant decrease in Cu release when they were experimentally acidified. However, under alkali treatments, Cu liberation increased in CMS amended soil A (vineyard) whereas the level of this metal released by CMS amended soil B (mine) remains near the detection limit. This difference was narrowly associated to the distinct Cu distribution in the solid phase of both soils, mainly in terms of organically complexed Cu.

Copper released after acid treatment of non-amended samples of soil A derived from ASF and RF fractions. In the case of samples treated with alkali solutions, mobilized Cu is originated from OF and REF fractions. An increase in Cu content corresponding to ASF and FR fractions was found for acid treated CMS amended samples of soil A. No influences of pH treatment and CMS addition in ASF and RF Cu fractions were found for soil B, although a decrease in the OF fraction was observed for acid treated samples amended with 48 Mg ha^{-1}.

The presence of CMS significantly diminished the mean and maximum Cu release rate values at acid pH in both soils. When the inflow solution pH was 5, the mine soil showed a drastic Cu release rate reduction upon CMS addition, whereas no significant effects of CMS addition were found in Cu release rates in the vineyard soil. When pH of inflow solution was seven, Cu released rates were very low, and no significant effects of CMS addition were found.

The obtained results revealed that, the addition of CMS to the soils as amended would diminish the risks of environmental damage (namely those related to Cu) when an acidification or an acid pollution event takes place. Particularly on acid vineyard soils, widely spread in Galicia, the addition of CMS in order to prevent an excessive Cu uptake by plants would be recommended.

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