

Citation for published version:

Fernández-Calviño, D., Pateiro-Moure, M., López-Periago, E., Arias-Estévez, M. and Nóvoa-Muñoz, J.C. (2008), Copper distribution and acid-base mobilization in vineyard soils and sediments from Galicia (NW Spain). *European Journal of Soil Science*, 59: 315-326.
<https://doi.org/10.1111/j.1365-2389.2007.01004.x>

Peer reviewed version

Link to published version: <https://doi.org/10.1111/j.1365-2389.2007.01004.x>

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1 **Copper distribution and acid-base mobilization in vineyard soils and sediments**
2 **from Galicia (NW Spain)**

3

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11

12 Running head title: Copper distribution and mobilization in vineyards

13

1 **Summary**

2

3 In northern Spain and elsewhere in the world, many vineyards are located on steep
4 slopes and are susceptible to accelerated soil erosion. Contaminants, notably Cu,
5 originating from repeated application of copper-based fungicides to the vines to prevent
6 mildew, are transported and stored in the sediments deposited close to valley bottoms.

7 In this study, the contents and distribution of Cu in 17 soil samples and 21 sediment
8 samples collected from vineyard stands were determined. In addition, the effect of pH
9 on Cu release from vineyard soils and sediments was quantified. The total Cu content
10 (Cu_T) in the soils varied between 96 and 583 mg kg⁻¹, and was between 1.2 and 5.6
11 times greater in sediment samples. The mean concentration of potentially bioavailable
12 Cu (Cu_{EDTA}) in the sediments was 199 mg kg⁻¹ (46% of Cu_T), and was 80 mg kg⁻¹ (36%
13 of Cu_T) in the soils. Copper bound to soil organic matter (Cu_{OM}) was the dominant
14 fraction in the soils (on average, 53% of the Cu_T), while in sediment samples Cu_{OM}
15 values varied between 37 and 712 mg kg⁻¹ and were significantly greater ($P<0.01$) than
16 in the soils. Copper associated with non-crystalline inorganic components (Cu_{IA}) was
17 the second most important fraction in the sediments, in which it was 3.4 times greater
18 than in the soils. Release of Cu due to changes in the pH followed a U-shaped pattern in
19 soils and sediments. The release of Cu increased when the pH decreased below 5.5 due
20 to the increased solubility of the metal at this pH. When the pH increased above 7.5, Cu
21 and organic matter were released simultaneously.

22

23 **Introduction**

24

1 A large fraction (45%) of the total area of land in the world dedicated to vine growing
2 (3.4 million ha) is concentrated in Europe, where this activity generates €4500 million
3 annually.

4 Since ancient times, vines have been grown on shallow soils located on steep
5 slopes where exposure to sunlight improves grape ripening. These topographic and
6 pedologic conditions favour growth of vines in Mediterranean countries such as Italy,
7 France, Greece and Spain, but also in other European countries (Germany and Bulgaria)
8 in South America (e.g., Chile and Argentina), in western United States (California and
9 Oregon), and in Oceania (Australia and New Zealand).

10 During the last few decades, vineyards growing in steep soils in Europe have been
11 progressively abandoned due to social and economical change. The soil lost through
12 erosion, as a result of the land use change, has raised serious environmental concerns
13 (Dunjó *et al.*, 2003; Martínez-Casasnovas & Ramos, 2006; Koulouri & Giourga, 2007).
14 Sediment alone is a pollutant, but it also has the ability to transport a variety of sorbed
15 contaminants. For example, the intensive use of copper-based fungicides, mainly as
16 Bordeaux mixture [$\text{Ca}(\text{OH})_2 + \text{CuSO}_4$], since of the the end 19th century has resulted in
17 a large Cu accumulation in surface layers of vineyard soils. Bordeaux mixture and,
18 more recently, Cu oxychloride (Blitox, Coppesan), are used to prevent and treat fungal
19 diseases such as downy mildew (*Plasmopara viticola*), and Cu-fungicides are also
20 applied to orchards (Li *et al.*, 2005). Several studies have reported Cu_T concentrations
21 of approximately 500 mg kg^{-1} in vineyard soils in France (Flores-Vélez *et al.*, 1996;
22 Brun *et al.*, 1998; Chaignon *et al.*, 2003), Portugal (Magalães *et al.*, 1985) and Spain
23 (Arias *et al.*, 2004; Nóvoa-Muñoz *et al.*, 2007).

24 The combination of large levels of Cu in soil and the high rates of erosion lead
25 to the transport and deposition of Cu-enriched sediments (Ribolzi *et al.*, 2002). This is

1 of particular concern since vineyard soils have been identified as the most erodible
2 agricultural soils (Kosmas *et al.*, 1997). Thus, the mobilization and transport of Cu-
3 enriched soil particles may generate environmental problems downslope and
4 downstream of vineyards. Until now this issue has received little attention because the
5 mobilization of Cu-enriched particles occurs slowly and is less apparent than the mass
6 movements of soil due to erosion.

7 The aim of this study was to examine the fate of Cu in sediments derived from
8 erosion of vineyard soil. Since measurement of Cu_T provides little information about the
9 possible environmental impacts caused by this metal (Flores-Vélez *et al.*, 1996; Pietrzak
10 & McPhail, 2004) or about its bioavailability, soils and sediments were studied by a
11 non-sequential extraction procedure. Along with soil organic matter content and type,
12 concentrations of Fe and Mn, clay content and mineralogy (Yu *et al.*, 2002), pH is one
13 of the soil parameters that has the greatest effect on Cu mobility, and an additional aim
14 of this work was to assess the effect of pH on the release of Cu present in soil and
15 sediment samples.

16

17 **Material and methods**

18

19 *Soil and sediment samples*

20

21 Seventeen soil samples (0-5 cm) were obtained from vineyards in two wine regions in
22 NW Spain (Denomination of Origin, Ribeiro and Valdeorras). At each sampling
23 location, 10 subsamples were collected from the rows of vines and combined to form a
24 composite sample. The sampled soils have developed from diverse parent rocks,
25 including granite (S1-S7), schists (S8-S12) and slate (S13-S17). Cambisols and

1 Regosols are the predominant soil type in both wine producing areas, and clay size
2 fraction mineralogy is commonly dominated by 1:1 dioctaedral phyllosilicates (mainly
3 halloysite), vermiculites (usually interlayered Al hydroxide) and gibbsite.

4 All of the soils have been used for vine cultivation for at least 50 years, with the
5 exception of soils S9 and S10, which have only been under cultivation for 8 years.

6 In order to establish the “baseline” values of Cu_T , A-horizons were sampled in two
7 forest soils for each parent material and study area (n=12).

8 In addition to soil samples, sedimentary material (Sd) was also collected from
9 different hillslope zones, such as mid slope (Sd_m for sampling sites 1, 2, 5 and 6) and at
10 the foot of slopes (Sd_f) in all sites. Each sedimentary sample was combined from
11 approximately 10 subsamples collected 0-5 cm above the buried soil.

12 Prior to the analytical determinations, the soil and sediment samples were air-
13 dried and sieved (mesh size 2 mm). The particle-size distribution was determined in the
14 <2 mm fraction by the internationally-recognised pipette method, the pH of the soil was
15 measured in water and in 0.1 M KCl (ratio of soil:solution 1:2.5); the total contents of
16 organic C and N were determined in finely-milled samples in an agate mortar (Retsch
17 RM100; Retsch GmbH, Hann, Germany), with a soil analyzer (Thermo Finnigan 1112
18 Series NC; Thermo Fisher Scientific Inc., Madrid, Spain). The cation exchange capacity
19 (CEC) was estimated as the sum of base cations (BS) displaced with 1 M NH_4Ac at pH
20 7 (Gupta & Chen, 1975) and the Al extracted with 1 M KCl (Al_E). The distribution of Fe
21 and Al in the soils and sediments was studied by the selective extraction methods
22 usually used for acid soils: with 0.1 M Na-pyrophosphate, pH 10 (Fe and Al bound to
23 organic matter, Al_p and Fe_p), 0.2 M oxalic acid-ammonium oxalate at pH 3 (Fe and Al
24 bound to organic matter and non-crystalline inorganic forms, Al_o and Fe_o), 0.5 M
25 dithionite-citrate (total free Fe, Fe_d) and 0.5 M NaOH (total free Al, Al_n ; Borggaard,

1 1985). Base cations (Na, K, Ca and Mg), and Al and Fe were determined by emission or
2 flame atomic absorption spectrophotometry, with a Thermo Solaar M Series
3 spectrophotometer (Thermo Fisher Scientific Inc., Madrid, Spain).

4 5 *Copper distribution in soil and sediments*

6
7 The distribution of Cu in the solid phase of the soils and sediments was determined in
8 triplicate, by the methods applied by Arias *et al.* (2004):

9
10 **Exchangeable Cu (Cu_E):** 50 ml of 1 M NH₄Ac (pH 7) was added to 10 g of soil or
11 sediment and the resulting suspension was shaken for 1 hour. The copper displaced by
12 this reagent is assumed to provide an estimate of the amount of metal adsorbed to
13 exchangeable sites.

14 **Pyrophosphate-extracted Cu (Cu_p):** 100 ml of 0.1 M Na-pyrophosphate was added to
15 1 g of soil or sediment and the resulting suspension was shaken for 16 hours. Sodium
16 pyrophosphate is known to be a highly effective extractant for metal-humus complexes
17 and is assumed to recover organically bound Cu.

18 **Oxalic-oxalate-extracted Cu (Cu_o):** 50 ml of 0.2 M oxalic acid-ammonium oxalate (pH
19 3) was added to 1 g of soil or sediment and shaken in the dark for 4 hours. In addition to
20 Cu bound to soil organic matter, oxalic acid-ammonium oxalate can also dissolve non-
21 crystalline hydrous oxides of Al and Fe, and release Cu bound to these soil components.

22 **Ascorbic-oxalic-oxalate-extracted Cu (Cu_{as}):** 50 ml of a solution of 0.2 M oxalic acid-
23 ammonium oxalate + 0.1 M ascorbic acid (pH 3.25) was added to 1 g of soil or sediment
24 and shaken for 30 minutes in a water bath at 96°C. In addition to Cu bound to both

1 organic and inorganic non-crystalline soil components, this reagent extracts Cu
2 associated with crystalline Al and Fe hydrous oxides.

3 After the period of incubation, the different extracts obtained were centrifuged (700 g
4 for 15 minutes) and then filtered through acid washed filter paper (2-5 μm pore size).

5 **Total-extracted Cu (Cu_T):** 5 ml of HNO₃, 4 ml of HF and 1 ml of HCl were added to
6 0.5 g of soil or milled sediment and digested in a microwave oven at 700 kPa. Copper
7 recovery by this method provides an estimate of the total Cu content of soil. For quality
8 assurance and control (QA/QC) purposes, we used two certified reference materials
9 endorsed by the Community Bureau of Reference, Commission of the European
10 Communities (*viz.* CRM 141 calcareous loam soil and CRM 143 sewage sludge
11 amended soil). Samples of each reference standard material were digested in triplicate
12 and analysed by the above-described method for total Cu. The copper recoveries
13 obtained for both materials (*viz.* $32.7 \pm 1.1 \text{ mg kg}^{-1}$ for CRM 141 and $229.7 \pm 3.2 \text{ mg}$
14 kg^{-1} for CRM 143) were consistent with the certified values (32.6 ± 1.4 and 236.5 ± 8.2
15 mg kg^{-1} , respectively).

16 As regards the suitability of the aforementioned methods to assess Cu
17 distribution, it is recognized that no extractant can remove all targeted solid-phase
18 components, and no selective dissolution scheme can be considered to be wholly
19 accurate in distinguishing between different forms of an element. Despite shortcomings
20 such as potential overlaps between consecutive, non-sequentially applied reagents, or
21 metal re-adsorption during extractions, previously used methods for selective
22 dissolution still provide useful information on Cu binding, mobility and bioavailability.

23 Thus, in addition to Cu_E, the following operationally-defined fractions were determined:

24 Cu_{OM} = Cu bound to soil organic matter (Cu_p-Cu_E).

25 Cu_{AM} = Cu associated with non-crystalline inorganic components (Cu_o-Cu_p).

1 Cu_{CR} = Cu associated with crystalline compounds of Fe and Al ($Cu_{as}-Cu_o$).

2 Cu_R = residual Cu (Cu_T-Cu_{as}).

3

4 In addition to the above-described extractions, the potentially bioavailable Cu
5 (Cu_{EDTA}) was determined after addition of 0.02 M Na_2 -EDTA + 0.5 M NH_4Ac (pH 4.65)
6 to the soil or sediment samples.

7

8 *pH-dependent release of copper from soil and sediments*

9

10 The effect of pH on the release of Cu from soils and sediments was determined in a
11 batch type experiment. To examine a wide range of pH values (approximately 2-12), 20
12 ml of one of various solutions of HNO_3 (0.02; 0.0125; 0.0075; 0.0025 M), 0 (no acid or
13 base addition) and $NaOH$ (0.005; 0.01; 0.02 or 0.04 M) were added to 2 g of material (n
14 = 9). Background electrolyte (0.05 M $NaNO_3$) was added to all solutions. The
15 suspensions were shaken for 24 hours, then centrifuged (700 g for 15 minutes) and
16 filtered through acid washed paper (2-5 μm pore size). All determinations were carried
17 out in triplicate. The pH, the concentration of Cu (by flame atomic absorption) and the
18 concentrations of dissolved organic carbon (DOC) were measured by visible
19 spectrophotometry at 400 nm, with the values obtained during calibration with a
20 solution of humic acids used as reference values. Extraction and characterization of
21 humic acid are described by Arias *et al.* (1996).

22

23 *Statistical analysis*

24

1 The distribution of the data was tested for normality by the Kolmogorov–Smirnov (K–
2 S) test and then all data (except particle-size fractions) were log-transformed to
3 normalise their distribution. Non-parametric statistical tests (Kruskal-Wallis and Mann-
4 Whitney) were used to assess the effect of parent material on particle-size distribution,
5 whereas Wilcoxon’s test was applied to compare differences between soil and sediment
6 samples from each location. For log-transformed data, one-way analysis of variance
7 (ANOVA) was used to test for differences between mean values of the soil and
8 sediment parameters, with parent material as a factor. A paired two-sample test was
9 used to compare soil and sediments (mean values for mid-slope, m, and foot, f, samples)
10 from the same location. A step-wise multiple regression analysis was carried out to
11 investigate the relationships between Cu released under acid (0.02 M HNO₃), neutral
12 (0.05 M NaNO₃) and basic (0.02 M NaOH) conditions, as a function of several soil and
13 sediment parameters. For all these analyses, the results were considered significant at a
14 probability level of $P=0.05$. Summary statistics were used to obtain the mean,
15 maximum, minimum and standard deviation of all studied parameters except
16 soil/sediment enrichment values, the mean value of which was accompanied by 95%
17 confidence intervals (CI). All statistical analyses were carried out with Statistical
18 Package for the Social Sciences (SPSS), version 14.0, for Windows (www.spss.com).

19

20 **Results and discussion**

21

22 *Chemical characterization of soils and sediments*

23

24 The granulometric distribution of the soil samples by mass was dominated by the sand
25 fraction (0.05-2 mm) which was up to 66% in the granite soils (Table 1). Mean values

1 of the sum of fine and coarse silt (0.002-0.05 mm) ranged from 21 to 38 %, whereas the
2 clay fraction varied from 13 to 20 % (Table 1). The Kruskal-Wallis test revealed
3 significant differences in sand, silt and clay on the basis of parent material ($P=0.005$;
4 $P=0.009$ and $P=0.031$, respectively). The results of the Mann-Whitney test revealed that
5 the sand fraction of granite soils was significantly larger than in schist and slate soils
6 ($P=0.003$ and $P=0.010$ respectively), whereas the opposite trend was found for the silt
7 fraction ($P=0.010$ and $P=0.005$). The clay fraction was significantly greater ($P=0.010$)
8 in schist than in granite soils. The results of this statistical test did not show any
9 significant differences in the granulometric fractions in schist and slate soils. As result
10 of the granulometric distribution, the texture of the soils studied varied from sandy loam
11 (characteristic of granite soils) to loam, which is more common in soils derived from
12 schist or slate. The mean value of the pH in water (pH_w) varied between 5.3 and 5.8, but
13 in granite soils the mean pH in KCl solution (pH_k) was <4.0 (Table 1). The differences
14 in soil pH in H_2O and 0.1 M KCl (ΔpH) ranged from 0.3 for slate soils to 1.4 for granite
15 soils (Table 1). In all cases this difference was due to the increase in the concentration
16 of H^+ after hydrolysis of aluminium displaced by potassium.

17 The total content of C was less than 30 g kg^{-1} (Table 1) and did not differ
18 significantly on the basis of the parent material (ANOVA, $F= 1.2$; $P=0.327$). The
19 concentration of total N did not exceed 3 g kg^{-1} , and was significantly greater in slate
20 than in granite or schist soils ($F= 5.6$; $p=0.015$). The mean value of the CEC of these
21 soils was rather small ($4.0\text{-}4.6 \text{ cmol}_c \text{ kg}^{-1}$), with Ca being the dominant base cation,
22 representing up to 54 % of the total base cations. This suggests that the soils have been
23 treated with a liming agent, which is common practice in vineyard soils as it reduces the
24 damaging effects of the soil acidity. Mean levels of exchangeable Al were less than 0.7
25 $\text{cmol}_c \text{ kg}^{-1}$ of soil (Table 1).

1 The distribution of aluminium in the solid phase was dominated by the total free
2 Al (Al_n), with mean values between 1.5 and 3.2 g kg⁻¹ (Table 2), whereas most of the
3 non crystalline Al was bound to the soil organic matter ($Al_p/Al_o \geq 1$). The distribution of
4 Fe was also characterized by a predominance of crystalline Fe (calculated as $Fe_d - Fe_o$),
5 for which mean values of between 7 and 33 g kg⁻¹ were obtained (Table 2), whereas the
6 Fe-humus complexes (Fe_p) accounted for 47-74% of the total non crystalline Fe. The
7 application of a Kruskal-Wallis test showed that there were significant differences in the
8 contents of Fe_p and Fe_d ($P=0.021$ and $P=0.002$, respectively) according to the soil
9 parent material.

10 In sediment samples, the mean percentage of sand fraction was significantly
11 lower than in the soils, as revealed by the Wilcoxon test ($Z=3.6$, $P=0.000$), but there
12 was a noteworthy increase in the silt fraction (37-55%; $Z=3.6$, $P=0.000$). The proportion
13 of clay was similar in soils and sediments (Table 1).

14 Sand and silt fractions in sediment samples reflected significant differences in
15 relation to parent material (Kruskal-Wallis test, $P=0.001$ for both). The results of the
16 Mann-Whitney test showed that granite sediments had a greater content of sand and a
17 lower content of silt than schist or slate sediments ($P<0.002$ in all cases), whereas there
18 were no differences between schist and slate sediments in the sand and silt-sized
19 particles. Thus, sediment samples originating from erosion of the vineyard soils are
20 enriched in silt-sized particles and depleted in sand-sized particles. Typically, fine-
21 grained materials show greater chemical reactivity, and thus the observed enrichment
22 would affect the other properties of these sediments.

23 The mean pH_w and pH_k of the sediments was 0.2-0.7 units higher than in the
24 soils, and these differences were statistically significant for pH_w ($Z= 3.6$, $P=0.000$) and
25 pH_k ($Z= 3.6$, $P=0.001$). As with the pH, sediment samples showed significantly more

1 total C and N contents than soils ($t=6.6$, $P=0.000$ and $t=6.2$, $P=0.000$ respectively),
2 especially in the case of sediments derived from granite soils, in which the mean
3 concentrations of total C and N were approximately three times those observed in soils
4 (Table 1).

5 The mean values of sum of bases (BS) and CEC in sediments samples were also
6 significantly greater ($Z=3.2$, $P=0.001$ for both parameters) than those obtained for the
7 soils (Table 1). The increase is mainly due to exchangeable Ca (the amounts of which
8 were up to twice as great in the granitic materials) whereas the amount of exchangeable
9 Al (Al_E) decreased. Carbon and silt enrichment in sediment samples would be expected
10 to provide a greater number of exchange sites, explaining the observed increase in CEC
11 and pH values.

12 The distribution of Fe and Al in the solid phase of the sediments was similar to
13 those observed in soil samples (Table 3), and significantly greater values were observed
14 in sediments than soils in the Fe and Al extracted with Na-pyrophosphate ($Z=2.7$,
15 $P=0.006$ and $Z=3.5$, $P=0.001$) and oxalic acid-ammonium oxalate ($Z=3.3$, $P=0.001$ and
16 $Z=3.5$, $P=0.000$).

17

18 *Total Cu content in soils and sediments*

19

20 The concentrations of Cu_T in the established vineyard soils (over 50 years) varied
21 between 96 and 583 mg kg⁻¹ (Table 2); smaller values were obtained in the youngest
22 vineyards (S9 and S10) (<50 mg kg⁻¹). Excluding the latter two soils, the concentration
23 of Cu_T in the vineyard soils was much greater than in surface horizons of forest soils in
24 the surrounding area (24-43 mg kg⁻¹), which showed similar concentrations to those

1 observed in C-horizons of soils from the study area (10-25 mg kg⁻¹) (Guitián Ojea,
2 1992).

3 The concentrations of Cu_T (excluding soils S9 and S10) did not differ
4 significantly (F=1.8, P=0.268) on the basis of parent material. In addition, a step-wise
5 regression analysis showed that 46 % of the variability in Cu_T was associated with Al_p
6 and CEC (F=7.1, P=0.009). This suggests that the intense application of copper-based
7 fungicides provides large amounts of Cu to the soil, which may mask possible
8 differences derived from the native content of this metal in the parent material.
9 Therefore, hereafter the results obtained in the complete set of samples analysed will be
10 evaluated.

11 Most of the soil samples (88%) contained levels of Cu_T between 2 and 11 times
12 larger than the maximum concentration allowed by the European Union for sewage
13 sludge application on acid agricultural soils (50 mg kg⁻¹) (86/278/CEE). Total Cu
14 concentrations as great as those obtained in the present study (up to 600 mg kg⁻¹
15 maximum value) are relatively common in areas characterized by a high level of
16 humidity throughout the grape growing season, because of the frequent and intensive
17 use of copper-based fungicides.

18 Maximum concentrations of Cu_T similar to or greater than those determined in
19 the present study have been reported for vineyards in northern France (300-500 mg kg⁻¹;
20 Drouineau & Mazoyer, 1962) and western France (800 mg kg⁻¹; Delas, 1963). Brun *et al.*
21 (1998) have also suggested that climatic conditions may account for the differences
22 between the maximum concentrations of Cu_T in vine-growing areas in the north and
23 west of France and in Mediterranean areas. Deluisa *et al.* (1996) also observed higher
24 levels of Cu_T in vineyards in humid mountain areas in northern Italy than in vineyards
25 in a dry zone in the south of the country.

1 Traditionally, each application of Bordeaux mixture introduces 3-5 kg of Cu per
2 ha of soil (Geoffrion, 1975), and the treatment is repeated on average up to 6 times a
3 year in the study area. Taking into account that these vineyards have been established
4 for more than 50 years, the amount of Cu that the upper 5 cm of the soils have received
5 during this period will vary between 1.8 and 3.0 g Cu kg⁻¹ soil, which represents three
6 times the mean concentration of Cu_T observed in the present study and is above the limit
7 of the absorption capacity of 1.8 g Cu kg⁻¹ soil, estimated for vineyard soils in the area
8 by Arias *et al.* (2004). These findings appear to indicate that a large part of the Cu
9 added to the soils may have been exported by soil erosion, as demonstrated in previous
10 studies (Besnard *et al.*, 2001; Ribolzi *et al.*, 2002), although in a field-scale study in
11 Florida, dissolved Cu was found in runoff from agricultural land (He *et al.*, 2004).
12 Similarly, Bennett *et al.* (2000) already pointed out the potential negative effects that
13 large Cu concentrations observed in some cultivated soils could have on soil
14 productivity and on human health.

15 The total concentration of Cu in sediment samples ranged between 74 and 947
16 mg kg⁻¹ (Table 3), whereas mean value was 423±248 mg kg⁻¹. The average Cu_T values
17 at mid slope “m” and foot of the slope “f” were compared to soils by a two-sampled
18 paired test, which showed that Cu_T in the sediments was significantly more ($t=22.7$,
19 $P=0.000$) than in the soils. To compare the concentrations of Cu_T in the sediments with
20 those in the original soils, an enrichment factor was calculated as X_{Sed}/X_{Soil} , where X_{Sed}
21 and X_{Soil} are the concentrations of Cu (mg kg⁻¹) in the sediment and soil respectively.

22 The mean value of Cu_T enrichment factor was 2.6±0.7 in sediments originating
23 from vineyards on granite soils (Table 4), whereas in sediments from vineyards on
24 schist or slate the mean values were somewhat less (1.7±0.4 and 1.5±0.3, respectively).
25 Values of Cu_T enrichment factors obtained for sediment samples in this study were less

1 than those recently reported by Quinton & Catt (2007) in sediments derived from
2 agricultural soils (i.e. approximately 4.0, but reaching up to 13.5 after some erosion
3 events).

4 The apparent differences between sediments samples in Cu_T enrichment as a
5 function of lithology contrast with the absence of significant differences in the total
6 content of Cu in the soils from which the sediments originated.

7 One possible explanation for these differences may be the significantly greater
8 enrichment of total C in the granitic sediments (3.5 ± 0.9 ; Table 4) in comparison to the
9 schist sediments (2.3 ± 0.7) whereas the enrichment in slate was not significant (1.8 ± 0.8)
10 sediments.

11 When sample $Sd1_f$ was excluded (since it is an outlier), a close correlation
12 between EF_{Carbon} and EF_{Cu_T} ($r=0.849$; $P=0.000$) was observed, which suggests the
13 importance of organic matter in copper retention. Such a role for organic matter has
14 been demonstrated in several studies carried out in vineyards soils (Flores-Vélez *et al.*,
15 1996; Parat *et al.*, 2002; Arias *et al.*, 2004; Pietrzak & McPhail, 2004). Furthermore,
16 Besnard *et al.* (2001) indicated that the high levels of Cu in the silt and clay fractions
17 are related to large contents of total C.

18 As regards the clay enrichment factor (EF_{Clay}), the mean values for sediment
19 samples derived from granite soils were 1.5 ± 0.2 (Table 4), whereas for sediments
20 derived from schist and slate soils they were 1.0 ± 0.2 and 1.1 ± 0.4 , respectively. These
21 results reveal that there were no significant differences in the EF_{Clay} in relation to the
22 parent material, although a significant difference has been previously observed for the
23 silt fraction in soil samples. Moreover, only the clay-sized fraction was significantly
24 enriched in the sediments from the granite derived soils, since EF_{Clay} values for schist

1 and slate sediments did not differ significantly from a value of 1.0, i.e., the clay content
2 in sediments is similar to that in soil.

3 Results from studies of soil erosion have identified lower intensity rainfall
4 events as the main cause of preferential transport of fine-sized particles, such as clay or
5 silt, and organic matter (Quinton & Catt, 2007). Such fine mineral particles generally
6 have greater surface areas and greater number of sorption sites which would contribute
7 to the observed Cu accumulation, mainly in granite derived sediments. Previous studies
8 have reported that Cu tends to accumulate in fine fractions such as silt and clay (Flores-
9 Vélez *et al.*, 1996; Besnard *et al.*, 2001; Parat *et al.*, 2002; Arias *et al.*, 2005) and this
10 accumulation was attributed to greater reactivity of the constituent minerals and to the
11 organic matter-mineral associations in these fractions (Essington & Mattigod, 1990).
12 These arguments could explain the greater amounts of Cu_t in the granitic sediments.

13

14 *Cu distribution in soils and sediments*

15

16 The concentrations of Cu extracted from soil and sediments samples are shown in
17 Tables 2 and 3, whereas Cu distribution is illustrated in Figure 1. The concentrations of
18 Cu in the exchangeable fraction (Cu_E) varied from 0.4 mg kg⁻¹ in the youngest
19 vineyards soils (S9 and S10) to 23.3 mg kg⁻¹ in soil S3 (Table 2). The mean soil Cu_E
20 concentration was 5.0±5.7 mg kg⁻¹ whereas for sediments it was 9.7±9.7 mg kg⁻¹
21 (Figure 1). However, this fraction accounts for <4% of the Cu_T for soil and sediments.
22 The concentrations of Cu_E suggest that the metal supplied tends to be irreversibly bound
23 to soil components (Arias *et al.*, 2004), thereby reducing its potential impact on the
24 natural environment as this is usually considered as the most mobile metal fraction in
25 soils (Kabata-Pendias, 2001).

1 Copper extracted with EDTA salts (Cu_{EDTA}) provides an estimate of bioavailable
2 Cu (Brun *et al.*, 2001; Pietrzak & McPhail, 2004). The mean value of Cu_{EDTA} in soils
3 samples was $80 \pm 54 \text{ mg kg}^{-1}$ (range 6-213 mg kg^{-1} ; Table 2), i.e. 2.6 ± 0.6 times lower
4 than the mean value for sediments ($199 \pm 127 \text{ mg kg}^{-1}$; Table 3), which gives rise to
5 significant differences between soils and sediments (paired two-sample test, $t=8.4$,
6 $P=0.000$). The concentrations of Cu_{EDTA} in soil samples were highly correlated
7 ($r=0.986$, $P=0.000$) with those of the Cu extracted with Na-pyrophosphate (Cu_p),
8 suggesting that Na_2 -EDTA may overestimate the bioavailable Cu in acid vineyard soils
9 in NW Spain (Arias *et al.*, 2004; Nóvoa-Muñoz *et al.*, 2007) since this EDTA salt is
10 capable of dissolving high molecular weight organic compounds and of sequestering the
11 Cu from the organic matter binding sites (McBride *et al.*, 1998).

12 The concentrations of both Cu_E and Cu_{EDTA} are similar to those reported for
13 other vineyard soils in Europe and Australia (Brun *et al.*, 1998, 2001; Chaignon *et al.*,
14 2003; Arias *et al.*, 2004; Pietrzak & McPhail, 2004; Nóvoa-Muñoz *et al.*, 2007).

15 The Cu associated with the organic matter (Cu_{OM}), calculated as $Cu_p - Cu_E$
16 (Tables 2 and 3), was the most abundant fraction in soils and sediments. Mean values of
17 Cu_{OM} in soils was $116 \pm 83 \text{ mg kg}^{-1}$ (range 13-352 mg kg^{-1} ; Figure 1) and represented, on
18 average, $53 \pm 11\%$ of the Cu_T , which is slightly smaller than the values up to 77%
19 reported by Chaignon *et al.* (2003) for vineyards soils in the south of France. The mean
20 concentration of the Cu_{OM} fraction in sediments was $257 \pm 174 \text{ mg kg}^{-1}$ (range 37-712
21 mg kg^{-1} ; Table 3), and the results of the paired two-sample test revealed a significantly
22 higher ($t=8.9$, $P=0.000$) concentration of Cu_{OM} in sediments (where “m” and “f”
23 samples for Sd1, Sd2, Sd5 and Sd6 were averaged for each location) than in soils
24 (Figure 1). The strong affinity of Cu for organic matter (Senesi *et al.*, 1989), accounts

1 for the importance of Cu_{OM} in vineyard soils and sediments analyzed in the present
2 study.

3 The mean value of Cu associated with non crystalline inorganic compounds
4 (Cu_{AM}) for soils, estimated as $\text{Cu}_o\text{-Cu}_p$, was $22\pm 14 \text{ mg kg}^{-1}$ (range 3-47 mg kg^{-1} ; Figure
5 1) and only represented on average $12\pm 6\%$ of the Cu_T . The low importance of this
6 fraction in vineyard soils may be due to the greater affinity of Cu for organic matter and
7 the paucity of non-crystalline inorganic components, since the ratios of Al_p/Al_o and
8 Fe_p/Fe_o were equal or close to 1 (Table 2). The mean value of Cu_{AM} for sediment
9 samples was $71\pm 76 \text{ mg kg}^{-1}$ (4.9 ± 2.8 times more than the soils; Table 3) and this
10 difference was statistically significant ($t=4.9, P=0.000$). In sediments samples, the Cu_{AM}
11 fraction was the most enriched with respect to the soils, becoming the second most
12 predominant fraction (after Cu_{OM}) in the distribution of Cu which contrasts with its
13 lower relevance in the soils.

14 The mean concentration of Cu associated with the crystalline components in the
15 soil (Cu_{CR}), estimated as $\text{Cu}_{\text{ao}}\text{-Cu}_o$, was $32\pm 29 \text{ mg kg}^{-1}$ (range 7-122 mg kg^{-1} ; Figure 1)
16 and only accounted for between 4 and 32% of the Cu_T (mean, $16\pm 8\%$). The scarcity of
17 crystalline compounds of Al (estimated as Al_o/Al_n ; Table 2) suggests that the Cu
18 incorporated in this fraction is predominantly associated with the crystalline Fe
19 (estimated as Fe_o/Fe_d).

20 In sediment samples, the mean concentration of Cu_{CR} was $42\pm 8 \text{ mg kg}^{-1}$ (range,
21 1-183 mg kg^{-1} ; Table 3), which was 1.3 ± 0.6 times more than in the soils. The mean
22 concentrations of the residual Cu (Cu_R), estimated as $\text{Cu}_T\text{-Cu}_{\text{ao}}$ (Table 2 and 3), were 31
23 mg kg^{-1} (range 1-87 mg kg^{-1}) and 43 mg kg^{-1} (range 9-92 mg kg^{-1}) for soils and
24 sediments respectively (Figure 1). Although the mean value of Cu_R in sediments was
25 2.2 ± 1.7 times more than in the soils, this fraction represents 13% of the Cu_T whereas in

1 the case of soils this value reached 18%. The decrease in the Cu_R fraction in sediments
2 samples is not unexpected given that they are enriched in the finest and geochemically
3 most reactive particles (silt and clay), which leads to an increase in the levels of Cu in
4 the Cu_{EX} , Cu_{OM} and Cu_{AM} fractions.

5 The small amounts of residual Cu in vineyards soils contrasts with the large
6 amounts found in natural soils from the study areas (10-50% Cu_T), which is clear
7 evidence of the anthropogenic addition of Cu since the conversion of active forms of Cu
8 (exchangeable, bound to organic matter) into inactive forms (residual) takes decades or
9 even centuries (Pietrzak & McPhail, 2004). However, recent studies have shown that
10 changes in residual Cu can be observed within 2 years, which suggests strengthening of
11 the bonds between Cu and soil colloids (Arias-Estévez *et al.*, 2007).

12

13 *pH-dependent release of copper from soil and sediments*

14

15 The accumulation of Cu observed in the solid fraction of soils and sediments may result
16 in the appearance of environmental problems associated with the mobilization of the
17 metal to the soil solution or to surface waters. As with most metals, the solubility and
18 therefore the mobility of Cu are strongly affected by pH. Traditional agricultural
19 practices carried out in NW Spain to maintain or treat vineyard soils may alter the pH
20 and lead to either a decrease in pH, due to over-fertilization or the addition of Cu
21 sulphate, or to an increase in pH due to liming.

22 Soils and sediments had different buffering capacities. Sediments were more
23 strongly buffered than soils both above and below their initial pH. On average,
24 sediments had pH values 0.6 ± 0.3 greater than soils after acidification and pH values
25 1.5 ± 1.0 lower than soils after alkalisation (Figure 2). These differences were

1 statistically significant (two-sample paired test, $t=6.7$, $P=0.000$ for acidification and
 2 $t=6.2$, $P=0.000$ for alkalisation). Typical titration curves for soil and corresponding
 3 sediment samples are shown in Figure 2 (m and f samples of sediments 1 and 5 were
 4 averaged).

5 The release of Cu in soils and sediments with regard to their total contents (Cu_T)
 6 varied as a function of pH and followed a U-shaped pattern (selected samples are shown
 7 in Figure 3), with the greatest release of Cu occurring at the most acid (*c.a.*, 2.0) or
 8 basic (approximately 12.0) pH-values applied. The release of Cu intensified when the
 9 pH of the solution decreased below 5.5 as a result of the increase in the solubility of this
 10 metal under acid conditions (Figure 3). The amount of Cu released with respect to Cu_T
 11 after acidification ranged between 11 to 48% for soils and from 3 to 43% for sediments,
 12 although there were no significant differences between soils and sediments ($t=0.8$,
 13 $P=0.439$).

14 A stepwise multiple regression analysis, with the concentration of Cu released after
 15 acidification as the dependent variable (Cu_{HNO_3}) and clay, pH_k , C, BS, CEC, Al_o , Fe_o ,
 16 Cu_E , Cu_p , Cu_T and DOC_{HNO_3} (dissolved organic carbon released following acidification)
 17 as independent variables, resulted in the following significant regression

18

$$19 \text{ Log } Cu_{HNO_3} = -1.6 \pm 0.2 - 0.3 \pm 0.1 \text{ Log } Al_o - 0.6 \pm 0.2 \text{ Log } CEC + 1.6 \pm 0.1 \text{ Log } Cu_T$$

$$20 \quad -0.6 \pm 0.1 \text{ Log } C. \quad (1)$$

$$21 \quad F=162.9 \quad P=0.000 \quad R^2=0.952$$

22

23 Non-crystalline inorganic Al (Al_o), cation exchange capacity, total Cu (Cu_T) and carbon
 24 content (C) explained 95% of the variance of Cu released as a result of the addition of
 25 acid. The negative effect of Al_o , CEC and C on Cu release may be explained by the fact

1 that these parameters are closely related to buffering capacity of acid soils (Nóvoa-
 2 Muñoz & García-Rodeja, 2007), which prevents a decrease in pH and thus diminishes
 3 the amount of Cu released mainly as a result of metal decomplexation of organic matter.
 4 The lesser release of DOC under acid than under basic conditions could be due to
 5 protonation of soil/sediment organic matter, which was found to be a major mechanism
 6 contributing to the stabilization of organic matter in extremely acidified soils (Berggren
 7 *et al.*, 1998).

8 For near neutral conditions (no acid or base added), the amount of dissolved Cu
 9 in sediments and soils represented less than 1.5 % of Cu_T , although sediment samples
 10 released more Cu than soils ($t=2.7$, $P=0.025$). In this case, the results of a stepwise
 11 multiple regression analysis (2) in which the concentration of Cu released after addition
 12 of neutral salt was the dependent variable (Cu_{NaNO_3}) and the parameters mentioned
 13 above (except DOC_{NaNO_3}) were the independent variables, showed that Cu_p , DOC_{NaNO_3}
 14 and pH_K explained 60% of the variation of released Cu for all samples (soils plus
 15 sediments):

16
 17
$$\text{Log } Cu_{NaNO_3} = -1.9 \pm 0.7 + 0.7 \pm 0.2 \text{ Log } Cu_p + 0.8 \pm 0.2 \text{ Log } DOC_{NaNO_3} - 0.3 \pm 0.1 \text{ pH}_K.$$

 18 (2)

19
$$F=12.6 \quad P=0.000 \quad R^2=0.602$$

20
 21 For soil samples, Cu release is only related to Cu_p , which explained 49% of the variance
 22 of mobilized Cu (3), whereas for sediment samples DOC_{NaNO_3} and Cu_E explained 54%
 23 of the variance in Cu_{NaNO_3} (4).

24
 25
$$\text{Log } Cu_{NaNO_3} = -2.1 \pm 0.6 + 0.9 \pm 0.3 \text{ Log } Cu_p,$$
 (3)

1 $F=9.7$ $P=0.014$ $R^2=0.491$

2

3 $\text{Log Cu}_{\text{NaNO}_3} = -2.4 \pm 0.6 + 0.9 \pm 0.2 \text{ Log DOC} + 0.6 \pm 0.2 \text{ Log Cu}_E$. (4)

4 $F=8.6$ $P=0.006$ $R^2=0.538$

5

6 As revealed by the addition of NaNO₃ solution, release of Cu from soils depends on the
 7 concentration of Cu_p (i.e., Cu bound to soil organic matter). However, for sediment
 8 samples, the amount of Cu released is more closely related to DOC_{NaNO₃} and readily
 9 mobilized Cu (Cu_E).

10 As pH was increased beyond 7.5, the release of Cu followed the same trend as
 11 the increasing release of organic carbon (Figure 3). The percentage of Cu released with
 12 respect to Cu_T after alkalisation ranged between 19 to 44% for soils and from 5 to
 13 30% for sediments (the absolute values were significantly higher in sediments than in
 14 soils: $t=3.0$, $P=0.008$). After alkalisation of soil and sediment samples, the stepwise
 15 multiple regression analysis revealed that Cu_p, CEC, C and pH_K explained 95% of the
 16 variance of released Cu:

17

18 $\text{Log Cu}_{\text{NaOH}} = 0.1 \pm 0.1 + 0.9 \pm 0.0 \text{ Log Cu}_p - 0.5 \pm 0.1 \text{ Log CEC} - 0.3 \pm 0.1 \text{ Log C} +$
 19 $0.1 \pm 0.0 \text{ pH}_K$. (5)

20 $F=173.6$ $P=0.000$ $R^2=0.954$

21

22 For soil samples (6), 98% of the variance of released Cu depended on Cu_p, CEC and
 23 Fe_o. However, for sediment samples (7), 96% of the released Cu was explained by Cu_p,
 24 C and DOC_{NaOH}.

25

1 $\text{Log Cu}_{\text{NaOH}} = 0.3 \pm 0.1 + 0.8 \pm 0.0 \text{ Log Cu}_p - 0.6 \pm 0.1 \text{ Log CEC} - 0.2 \pm 0.1 \text{ Log Fe}_o$, (6)

2 $F=222.6$ $P=0.000$ $R^2=0.977$

3

4 $\text{Log Cu}_{\text{NaOH}} = -1.5 \pm 0.6 + 0.9 \pm 0.0 \text{ Log Cu}_p - 0.5 \pm 0.1 \text{ Log C} + 0.4 \pm 0.1 \text{ Log DOC}_{\text{NaOH}}$.

5 (7)

6 $F=119.0$ $P=0.000$ $R^2=0.957$

7

8 Equations 5, 6 and 7 reveal that the release of Cu after alkalisation was mainly related
9 to Cu content and variables such as C, CEC and DOC. The presence of Cu_p in all
10 equations is consistent with its role as the major Cu fraction in soils and sediments (see
11 Table 2 and 3). In addition, the increase in pH observed after addition of alkaline
12 solutions (Figure 2) promoted organic matter solubilization and hence the release of
13 complexed Cu from soils and sediments (Figure 3). Carbon, CEC and DOC are directly
14 or indirectly associated with soil or sediment organic matter, solubilization of which
15 appears to be responsible for the release of Cu, as previously suggested.

16

17 **Conclusions**

18 We found that:

19 1) Sediment samples mobilized from vineyard soils on steep slopes (>15%) were
20 enriched in Cu. The degree of enrichment was related to the levels of total organic
21 carbon and finest size particles (silt and clay), which were subject to preferential
22 transport and deposition, especially in sediments originating from granite soils.

23 2) Copper bound to soil organic matter (Cu_{OM}) was the most abundant fraction in both
24 soils and sediments, although it was significantly greater in the latter. In sediment
25 samples, Cu associated with non-crystalline inorganic compounds (Cu_{AM}) was the most

1 enriched fraction with respect to the soils, whereas the smaller mean value of residual
2 Cu (Cu_R) was related to enrichment of organic carbon and fine particles (silt and clay)
3 in the soils.

4 3) The amount of Cu released in response to changes in pH was variable, as it largely
5 depended on Cu_T . The pattern of Cu liberation on addition of acid or alkali was usually
6 almost identical in soils and sediments if differences in the buffer capacity were
7 considered. Release of Cu was enhanced at pH below 5.5, as result of the increase in the
8 solubility of this metal under acid conditions, and at pH above 7.5 when Cu is mobilized
9 due to soil organic matter solubilization.

10

11 **Acknowledgements**

12

13 This work was funded by PGIDIT program (PDIDIT05PXIB38302PR, Xunta de
14 Galicia) and by the Spanish Ministry of Education and Science, contract AGL2006-
15 04231/AGR. M. Arias-Estévez and E. López-Periago are funded by Ramón y Cajal
16 contracts (Spanish MCyT). J.C. Nóvoa-Muñoz and D. Fernández-Calviño were funded
17 respectively by Parga Pondal and María Barbeito contracts from the Galician Council of
18 Innovation and Industry. Two anonymous reviewers, S. Staunton and P. Loveland, are
19 thanked for helpful comments which substantially improved the manuscript.

20

21

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23

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- 25

26 Table 1. Mean, standard deviation, maximum and minimum values of selected properties of the soil and sediment samples.

Sample	Parent material	n		Sand /%	Silt /%	Clay /%	C / g kg ⁻¹	N / g kg ⁻¹	pH _w ^a	pH _k ^a	Exchangeable cations					CEC ^b	
											Na	K	Ca	Mg	Al		
Soil	Granite	7	mean	66	21	13	15.3	1.4	5.3	3.9	0.6	0.7	1.8	0.5	0.7	4.3	
			sd	10	7	3	4.8	0.3				0.3	0.3	0.7	0.3	0.5	1.5
			max	73	36	19	21.0	1.7	5.5	4.3	1.2	1.3	3.1	1.0	1.4	7.1	
			min	45	15	11	8.0	0.8	5.1	3.7	0.5	0.3	0.8	0.3	0.1	3.1	
	Schist	5	mean	42	38	20	16.6	1.6	5.8	4.9	0.5	0.7	2.3	0.8	0.6	4.6	
			sd	2	4	5	3.6	0.5				0.1	0.1	0.6	0.3	0.1	0.6
			max	44	42	27	20.0	22.0	6.5	5.6	0.6	0.8	2.9	1.1	0.6	5.1	
			min	40	33	14	11.0	1.0	4.9	3.9	0.5	0.6	1.3	0.4	0.5	3.7	
	Slate	5	mean	46	38	17	19.8	2.2	5.5	5.2	0.5	0.8	2.1	0.6	0.2	4.0	
			sd	6	3	4	6.3	0.5				0.0	0.3	0.7	0.2	0.2	0.9
			max	53	42	21	28.0	3.0	6.1	5.6	0.6	1.1	2.8	0.8	0.3	4.8	
			min	38	35	12	12.0	1.7	5.0	4.7	0.5	0.5	1.1	0.3	0.1	2.7	
Sediment	Granite	11	mean	43	37	20	50.1	4.1	5.9	4.6	0.6	1.7	4.3	1.0	0.5	7.9	
			sd	8	6	3	20.5	1.4				0.1	1.2	2.3	0.4	0.6	2.5
			max	56	47	24	88.0	6.3	6.4	5.2	0.7	4.8	7.1	1.6	1.7	10.5	
			min	32	28	16	24.0	1.9	5.4	3.7	0.4	0.9	1.5	0.6	0.1	4.7	
	Schist	5	mean	27	53	19	38.0	2.9	6.4	5.5	0.5	0.9	4.0	1.2	0.3	6.7	
			sd	3	6	3	16.2	1.3				0.2	0.2	1.7	0.6	0.0	2.3
			max	31	60	25	63.0	4.9	7.5	6.6	0.9	1.3	6.4	1.8	0.3	10.0	
			min	23	44	17	21.0	1.7	5.6	4.7	0.4	0.7	1.7	0.6	0.3	3.9	
	Slate	5	mean	27	55	18	34.4	3.2	6.0	5.4	0.5	0.9	2.5	0.7	0.0	4.6	
			sd	8	9	2	10.4	0.7				0.0	0.2	0.4	0.1	0.0	0.6
			max	33	69	20	45.0	3.9	6.5	6.0	0.5	1.2	3.0	0.8	0.0	5.4	
			min	14	46	14	22.0	2.2	5.7	5.0	0.5	0.6	1.8	0.5	0.0	3.8	

27 ^a pH_w, pH_k: pH in water and in 0.1 M KCl

28 ^b CEC: cation exchange capacity estimated as the sum of exchangeable cations (Na+K+Ca+Mg+Al)

29 Table 2. Selective extractions of Al, Fe and Cu in the soil samples under study.

Sample	Parent Material	Al _p	Al _o	Al _n	Fe _p	Fe _o	Fe _d	Cu _E	Cu _{EDTA}	Cu _p	Cu _o	Cu _{as}	Cu _T
		/ g kg ⁻¹							/ mg kg ⁻¹				
S1	Granite	0.6	0.8	2.6	0.5	1.3	3.7	2.9	35.9	52.5	57.9	77.0	97.0
S2		1.3	1.2	2.6	0.5	1.1	5.0	14.3	156.9	237.0	281.5	332.6	359.4
S3		1.8	2.3	4.9	1.0	2.6	9.1	23.3	212.6	375.0	408.4	529.9	583.1
S4		0.8	1.2	2.3	0.3	0.6	6.6	6.1	81.9	112.8	133.2	144.5	231.1
S5		1.7	1.5	4.3	0.9	1.5	7.2	5.4	69.9	133.7	142.4	160.3	200.4
S6		1.5	1.4	2.8	1.2	2.8	9.8	3.6	85.6	148.1	159.2	173.8	205.3
S7		1.7	1.6	2.8	1.2	2.1	9.1	4.4	93.8	170.2	183.7	210.4	240.6
S8	Schist	0.6	0.7	1.3	1.5	1.4	27.0	2.5	62.7	81.1	101.2	125.2	146.4
S9		2.1	2.1	4.1	1.9	2.0	22.0	0.4	6.3	13.7	19.2	28.8	41.5
S10		1.9	1.4	2.2	1.3	1.1	24.0	0.4	10.5	15.8	26.8	36.2	48.9
S11		0.5	0.5	1.1	0.9	2.9	36.0	2.4	89.9	91.5	127.1	133.6	170.3
S12		0.9	0.8	1.9	1.6	2.2	32.0	1.1	19.6	43.2	46.6	69.5	95.8
S13	Slate	0.9	0.7	1.7	0.8	2.1	30.0	6.0	92.8	156.3	185.1	209.7	250.5
S14		0.8	0.5	1.3	0.7	1.2	32.0	3.4	98.7	128.7	156.3	231.4	232.6
S15		0.8	0.5	1.4	0.8	1.3	30.0	4.6	145.9	149.8	196.7	235.9	279.8
S16		0.6	0.6	1.4	0.8	1.7	34.0	2.9	59.8	87.0	107.3	153.4	166.1
S17		0.7	0.7	1.9	0.9	1.6	36.0	1.9	41.9	55.8	84.5	107.7	133.3
	mean	1.1	1.1	2.4	1.0	1.7	20.8	5.0	80.3	120.7	142.2	174.1	204.8
	sd	0.5	0.6	1.1	0.4	0.6	12.3	5.7	54.1	88.3	96.3	120.4	128.3
	max	2.1	2.3	4.9	1.9	2.9	36.0	23.3	212.6	375	408.4	529.9	583.1
	min	0.5	0.5	1.1	0.3	0.6	3.7	0.4	6.3	13.7	19.2	28.8	41.5

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34 Table 3. Selective extractions of Al, Fe and Cu in the sediment samples under study.

Sample	Parent Material	Al _p	Al _o	Al _n	Fe _p	Fe _o	Fe _d	Cu _E	Cu _{EDTA}	Cu _p	Cu _o	Cu _{as}	Cu _T	
		/ g kg ⁻¹							/ mg kg ⁻¹					
Sd1 _m ^a	Granite	1.3	1.7	3.7	0.9	2.2	6.8	4.8	88.8	145.1	166.0	188.9	232.8	
Sd1 _f		1.2	2.1	2.9	0.9	3.0	5.9	24.1	209.5	392.5	422.1	487.5	541.9	
Sd2 _m		2.1	2.4	4.9	1.0	2.4	7.2	34.2	379.4	746.3	823.4	930.2	947.0	
Sd2 _f		1.9	2.0	3.5	0.9	3.6	7.9	26.0	378.1	578.3	656.1	839.4	848.4	
Sd3 _f		2.2	2.7	4.2	1.6	3.4	11.0	27.1	372.4	498.8	597.3	708.6	784.6	
Sd4 _f		1.4	2.7	4.9	0.4	1.1	9.0	11.1	378.0	220.3	593.8	651.7	694.4	
Sd5 _m		2.0	2.7	4.3	0.9	2.2	7.4	8.1	142.6	243.7	316.6	320.4	403.6	
Sd5 _f		2.5	2.8	4.9	1.1	2.4	8.7	9.1	442.5	393.1	532.3	588.6	629.1	
Sd6 _m		2.3	2.3	4.3	1.6	4.8	13.0	6.7	206.3	274.3	325.5	336.3	428.6	
Sd6 _f		1.9	1.7	3.8	1.3	3.5	12.0	7.0	184.8	271.9	300.9	338.0	406.9	
Sd7 _f		2.4	2.4	4.0	1.3	3.0	11.0	7.0	305.8	395.4	501.7	513.7	528.2	
Sd8 _f		Schist	0.6	0.6	1.5	1.6	2.0	23.0	2.7	113.6	122.2	142.9	149.7	209.0
Sd9 _f			3.2	2.5	4.1	2.5	2.5	24.0	0.7	16.5	37.7	50.7	59.3	78.8
Sd10 _f	3.4		3.1	3.4	2.2	2.3	25.0	0.8	34.9	38.6	57.1	58.0	73.9	
Sd11 _f	0.7		0.6	1.3	1.0	2.2	28.0	2.5	145.9	153.9	207.7	216.7	255.7	
Sd12 _f	1.4		1.1	2.3	1.3	2.4	25.0	1.6	91.8	102.3	155.1	159.5	199.1	
Sd13 _f	Slate	1.2	1.0	2.2	1.0	2.4	24.0	8.3	193.2	294.2	346.3	376.1	451.6	
Sd14 _f		1.1	0.9	1.9	0.9	1.9	27.0	6.5	158.4	226.3	284.8	342.5	360.7	
Sd15 _f		0.7	1.0	1.4	0.7	2.6	29.0	10.7	158.9	245.4	276.4	313.8	357.1	
Sd16 _f		1.3	0.9	1.7	1.3	2.7	23.0	2.2	120.9	162.5	223.6	265.7	288.6	
Sd17 _f		0.9	0.8	1.7	0.8	1.7	27.0	1.6	60.0	61.1	117.1	139.6	156.7	
	mean	1.7	1.8	3.2	1.2	2.6	16.9	9.7	199.2	266.9	338.0	380.2	422.7	
	sd	0.8	0.8	1.3	0.5	0.8	8.7	9.7	127.2	182.8	211.1	247.4	247.7	
	max	3.4	3.1	4.9	2.5	4.8	29.0	34.2	442.5	746.3	823.4	930.2	947.0	
	min	0.6	0.6	1.3	0.4	1.1	5.9	0.7	16.5	37.7	50.7	58.0	73.9	

35 ^a m and f denote sediment sample collected at mid slope and at the foot of the slope

36 respectively.

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38 Table 4. Enrichment factor values (EF) for clay, carbon and total Cu in the sediment
 39 samples. CI is the confidence interval at 95%.

Parent Material	Sediment	EF _{Clay}	EF _{Carbon}	EF _{Cu_T}
Granite	Sd1 _m ^a	1.5	3.0	2.4
	Sd1 _f	1.5	3.0	5.6
	Sd2 _m	1.5	3.0	2.6
	Sd2 _f	1.6	2.9	2.4
	Sd3 _f	1.2	2.3	1.3
	Sd4 _f	2.0	4.9	3.0
	Sd5 _m	1.3	2.6	2.0
	Sd5 _f	1.5	6.8	3.1
	Sd6 _m	1.7	3.7	2.1
	Sd6 _f	1.4	2.8	2.0
	Sd7 _f	1.3	3.4	2.2
	mean	1.5	3.5	2.6
95% CI	0.2	0.9	0.8	
Schist	Sd8 _f	0.8	1.9	1.4
	Sd9 _f	1.1	1.6	1.9
	Sd10 _f	1.2	2.3	1.5
	Sd11 _f	0.9	2.0	1.5
	Sd12 _f	0.9	3.5	2.1
	mean	1.0	2.3	2.0
	95% CI	0.2	0.9	0.4
Slate	Sd13 _f	1.4	2.5	1.8
	Sd14 _f	1.4	1.5	1.6
	Sd15 _f	1.1	0.9	1.3
	Sd16 _f	0.9	2.5	1.7
	Sd17 _f	0.7	1.8	1.2
	mean	1.1	1.8	1.5
	95% CI	0.4	0.9	0.3

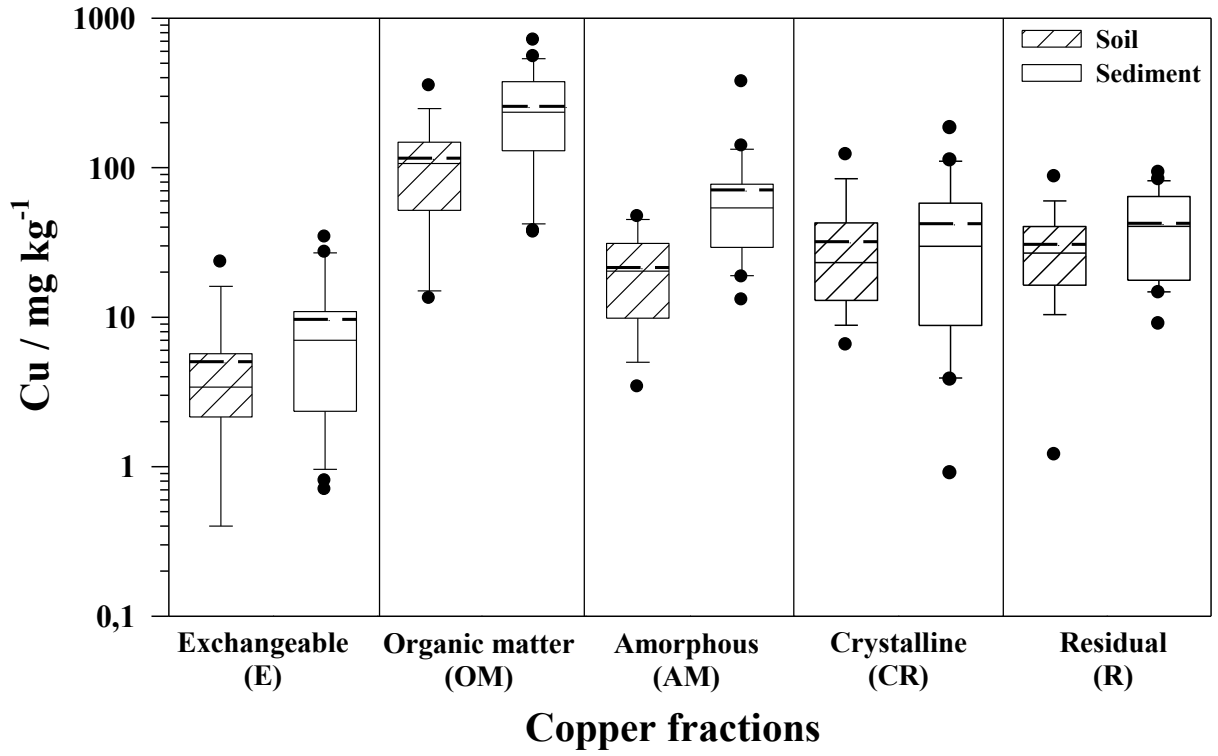
40 ^a m and f denote sediment sample collected at mid slope and at the foot of the slope
 41 respectively.

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43 **Figure 1**

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67 **Figure 2**

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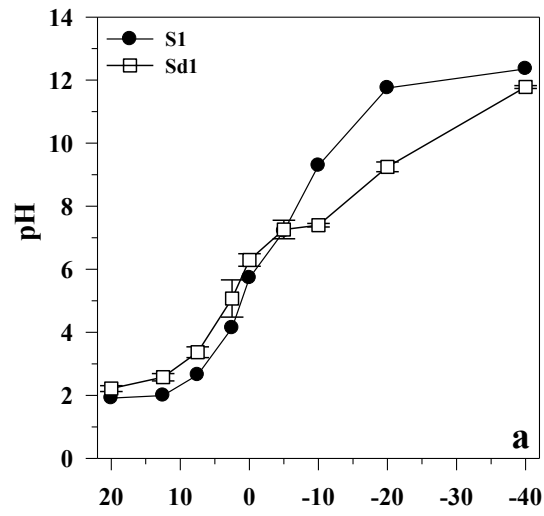
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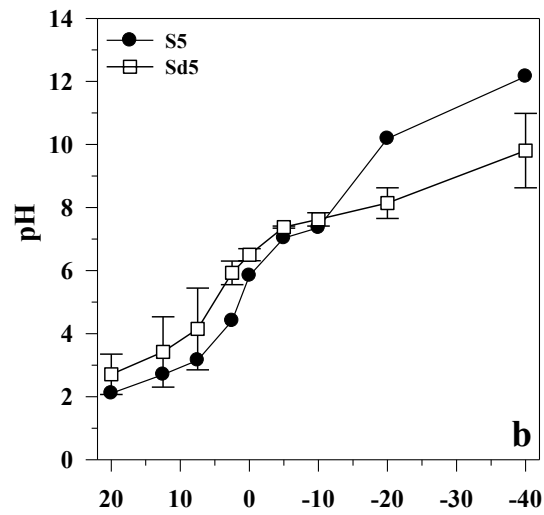
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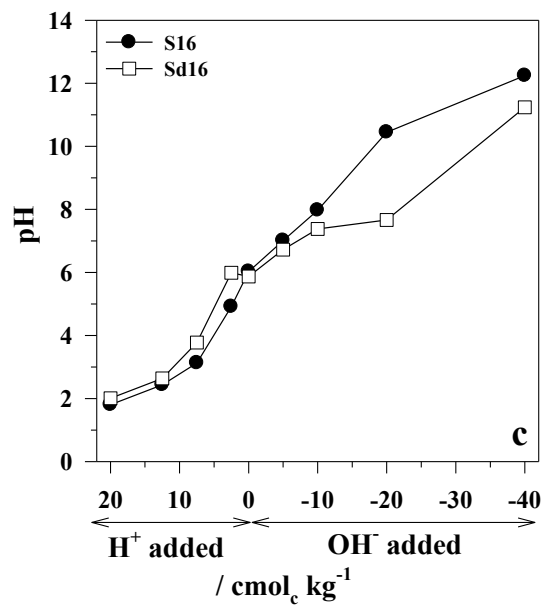
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92 **Figure 3**

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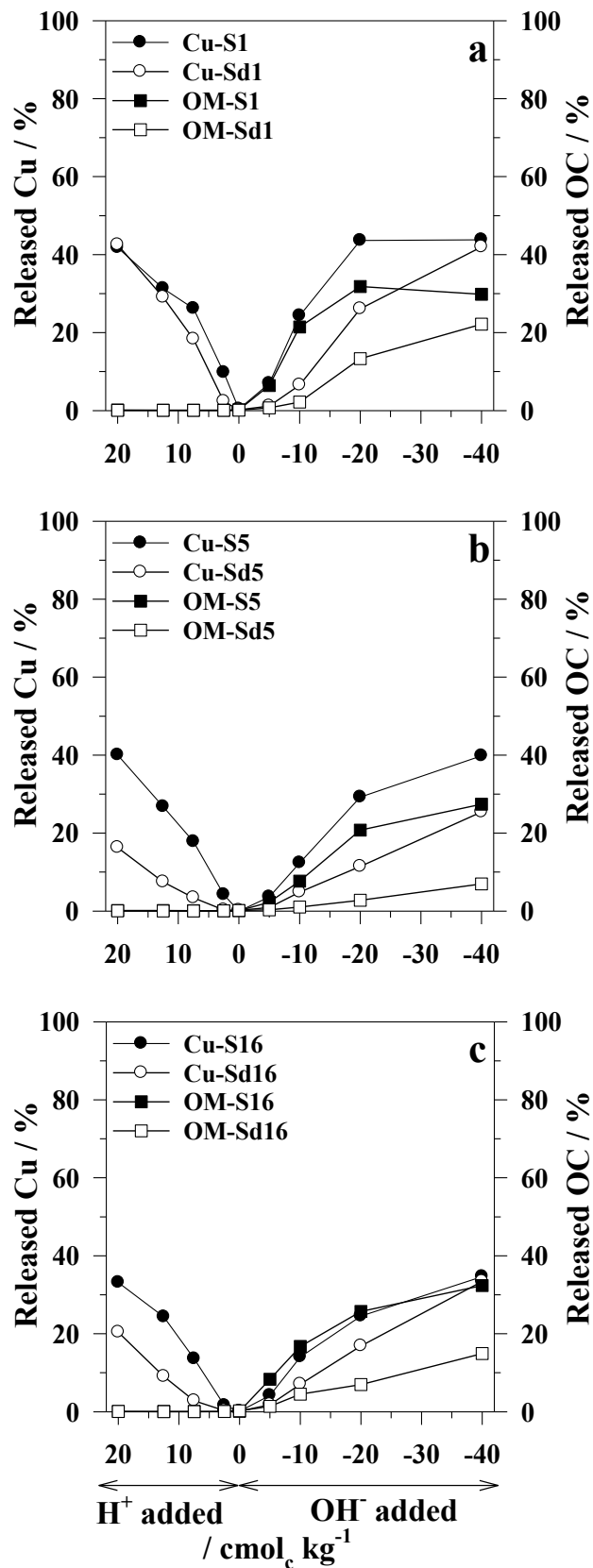
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117 **Figure captions**

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119 Figure 1. Box and whisker plot for copper fractions of soil and sediment samples. The
120 lower and the upper boundaries of the box represent the 25th and 75th percentiles.
121 Whiskers above and below the box indicate the 90th and 10th percentiles. The solid and
122 dashed lines inside the boxes represent medians and means, respectively. Filled symbols
123 represent anomalous values.

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126 Figure 2. Changes in pH after the addition of acid or base to a selection of soil and
127 sediment samples derived from granite (a and b) and slate (c). Symbols represent mean
128 values (averaged for “m” and “f” samples of Sd1 and Sd5) and error bars show the
129 standard deviations.

130

131 Figure 3. Release of Cu and organic carbon as percentage of total Cu and total organic
132 carbon for selected soils and sediments derived from granite (a and b) and slate (c).
133 Symbols represent mean values (averaged for “m” and “f” samples of Sd1 and Sd5).

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