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1 **COPPER CONTENT OF SOILS AND RIVER SEDIMENTS IN A WINEGROWING**  
2 **AREA, AND ITS DISTRIBUTION AMONG SOIL OR SEDIMENT COMPONENTS**

3  
4 **David Fernández-Calviño<sup>a</sup>, José Antonio Rodríguez-Suárez<sup>a</sup>, Eugenio López-Periago<sup>a</sup>,**

5 **Manuel Arias-Estévez<sup>a</sup>, and Jesús Simal-Gándara<sup>b,\*</sup>**

6  
7 <sup>a</sup>: Soil and Agricultural Science Group, Plant Biology and Soil Science Department.

8 <sup>b</sup>: Nutrition and Bromatology Group, Analytical and Food Chemistry Department.

9  
10 Faculty of Food Science and Technology, University of Vigo, Ourense Campus, 32004

11 Ourense, SPAIN.

12  
13 \* Author for correspondence (jsimal@uvigo.es)

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1 **Abstract.** This paper concerns copper levels in the components of soils and river  
2 sediments in a river basin partially devoted to vineyards that are regularly treated with  
3 copper-bearing grapevine fungicides. Copper concentrations were determined in 26 soil  
4 samples, 20 river sediment samples and 71 river water samples taken in a small basin  
5 with steep slopes suffering significant erosion. Mean total Cu concentration was  
6  $31 \text{ mg kg}^{-1}$  in woodland soils,  $30 \text{ mg kg}^{-1}$  in pasture soils, and eight times higher,  
7  $246 \text{ mg kg}^{-1}$  (range  $157\text{-}434 \text{ mg kg}^{-1}$ ), in productive vineyard soils. Total copper  
8 concentration in river sediments ranged from 18 to  $209 \text{ mg kg}^{-1}$  depending on the  
9 proportion of land under vineyard in the sub-basin drained via the sampling point  
10 ( $r=0.915, p<0.005$ ).

11         Soils differed relatively little as regards the distribution of Cu among various  
12 fractions; in particular, about 50% of total copper content was generally bound to soil  
13 organic matter. The distribution of Cu in sediments was more heterogeneous: sandy  
14 sediments had copper distributions similar to those observed in soils, but in silty  
15 sediments with large inorganic colloids fractions it was these amorphous colloids that  
16 bound the largest proportion of copper (mean 31.5%). The absence of significant  
17 differences among water-soluble Cu concentrations at the various water-sampling points  
18 suggests that winegrowing does not increase water-soluble Cu levels in the river under  
19 normal circumstances.

20

21 **Keywords:** copper fractionation; soil; river sediments; vineyards.

22

## 1 **1. Introduction**

2           The use of fertilizers, manure, cattle slurry and copper-based fungicides can  
3 markedly increase the Cu concentrations of cultivated soils (Kabata-Pendias and  
4 Pendias, 2001). In vineyards, fungal diseases such as downy mildew (*Plasmopara*  
5 *viticola*) have been fought since the late 19th century by intensive application of copper-  
6 based fungicides such as Bordeaux mixture ( $\text{Ca(OH)}_2 + \text{CuSO}_4$ ) and, more recently, Cu  
7 oxychloride. This has resulted in large accumulations of Cu in the surface layers of  
8 vineyard soils (see, for example, Pietrzak and McPhail (2004) regarding Australia;  
9 Magalhães *et al.* (1985) regarding Portugal; Arias *et al.* (2004, 2005) regarding Spain;  
10 and Flores-Vélez *et al.* (1996) regarding France, where levels exceeding  $1000 \text{ mg kg}^{-1}$   
11 have been recorded.

12           Rivers draining cultivated areas with high soil Cu concentrations can also have  
13 high Cu concentrations (Xue *et al.*, 2000). In the case of vineyard soils, which are the  
14 most easily eroded of cultivated soils (Kosmas *et al.*, 1997; Pardini and Gispert, 2006),  
15 applied Cu can reach waterbodies not only in water-soluble forms but also, through  
16 erosion, in colloid-bound forms that can accumulate below the waterbody in sediments.  
17 In winegrowing areas, evaluation of the risk to water quality posed by the use of  
18 copper-based fungicide therefore requires determination of Cu levels, and of the  
19 distribution of Cu among more and less bioavailable forms, not only in vineyard soils,  
20 but also in the sediments of local waterbodies.

21           In the work described here we studied the presence of Cu in a small river basin in  
22 Galicia (N.W. Spain) in which the most economically important crop is grapevine  
23 treated with Cu-based fungicides. We determined the concentration of copper in the  
24 surface layer of soils devoted to different uses (woodland, pasture and vineyard), and in  
25 samples of river water and river sediments collected at relevant sampling points; we  
26 investigated the relationship between land use and Cu concentrations in sediments; and  
27 to assess the risk of release into surface waters we examined the distribution of Cu

1 among relevant fractions of soils and sediments (Tessier *et al.*, 1979; Filgueiras *et al.*,  
2 2004).

## 3 4 **2. Material and methods**

### 5 **2.1. Study area**

6 The basin studied (Fig. 1) occupies an area of 1.73 km<sup>2</sup>, has a mean slope of  
7 19.5%, and is drained northwards by the Regato do Cecho, a tributary of the River Miño  
8 (northwest Iberian Peninsula). Geologically it consists mainly of schists, with granite  
9 appearing in the lower reaches, while climatically it lies within the middle Miño  
10 subregion, which is characterized by mild annual mean temperatures (14°C), mean  
11 annual rainfall of around 825 mm, and mean annual potential evapotranspiration of  
12 around 675 mm (Soto and Díaz-Fierros, 1996). Its soils are predominantly Cambisols  
13 and Regosols (FAO, 1998). Approximately 72% is occupied by woodland, 17% by  
14 natural pasture, 5% by productive vineyard, and 6% by abandoned vineyard that has  
15 been non-producing for > 10 years. Its vineyards are mostly > 30 years old and have an  
16 average area of only 0.15 ha. Bordeaux mixture is applied at a dosage of about 4 kg of  
17 Cu per hectare between four and six times a year.

### 18 19 **2.2. Sampling**

20 Soil samples were taken corresponding to each of the above land uses: 5 from  
21 woodland, 5 from pasture, 10 from productive vineyard, and 6 from abandoned  
22 vineyard. Each of the 26 samples comprised five replicate contributions that were  
23 collected within 0.5 m of each other and then pooled; in the vineyards, in which vine  
24 rows are separated by 1.0-1.2 m, two of the five replicates were taken from within a  
25 vine row and three from the adjoining between-rows area. Each total five-replicate  
26 sample consisted of 2 kg of soil collected from the top 20 cm of soil (the depth  
27 customarily affected by the use of rotary cultivators), and was transported in

1 polyethylene bags to the laboratory, where it was air-dried, passed through a 2-mm-  
2 mesh sieve, and stored in polyethylene jars.

3 For sediment and water sampling, six sampling points were defined along the  
4 course of the Regato do Cecho (points 1-6 in Fig. 1), and two further sampling points (7  
5 and 8) in tributary streams, just before their confluence with the Regato do Cecho. This  
6 set of points was chosen on the basis of their different upstream areas of vineyard,  
7 abandoned vineyard or non-vineyard land (Table 1). Surface sediment samples were  
8 taken by grabbing on one or more of three dates: June 12th, July 16th and  
9 September 26th 2002. At each sampling point, approximately 2 kg of sediment was  
10 collected, freeze-dried, passed through a 2-mm-mesh sieve, and stored in polyethylene  
11 jars. Water samples were collected between December 21st 2001 and September 26th  
12 2002 from sampling points 1 (21 times; twice a month), 4 (10 times; once a month), 5  
13 (10 times), 6 (10 times), 7 (10 times) and 8 (10 times). Water samples were collected in  
14 1 L polyethylene bottles and were immediately stored in a refrigerator. Once in the  
15 laboratory they were passed through 0.45  $\mu\text{m}$  pore membranes with a vacuum pump and  
16 stored at 4°C pending analysis.

### 18 **2.3. Physicochemical properties of soils and sediments**

19 The pH of 1:2.5 suspensions of soils and sediments in water was measured with a  
20 combined glass electrode. Nitrogen and carbon were determined by elemental analysis  
21 on a Thermo Finnigan Series 1112 NC instrument. The proportions of sand (2.000-  
22 0.050 mm), silt (0.050-0.002 mm) and clay (<0.002 mm) were determined by the  
23 standard pipette method after sieving (Gee and Bauder, 1986). Amorphous Fe ( $\text{Fe}_o$ ) was  
24 extracted with oxalic acid - ammonium oxalate (Schwertman, 1964).

## 2.4. Fractionation of Cu in soils and sediments

Soil and sediment Cu fractions were determined by non-sequential extractions followed by measurement of Cu in the extracts by atomic absorption spectrophotometry using a Thermo Solar M series spectrometer. The fractions extracted and the corresponding extraction procedures were as follows.

$Cu_a$ : 5 g of soil was shaken with 0.2 M ammonium acetate ( $5 \times 30$  mL, 5 min each time), and the pooled extracts were made up to 250 mL for spectrophotometry (Gupta and Chen, 1975).

$Cu_p$ : 1 g of soil was shaken for 16 h in 100 mL of 0.1 M sodium pyrophosphate at pH 10.1 (McKeague, 1967).

$Cu_o$ : 1 g of soil was shaken in darkness for 4 h in 50 mL of 0.2 M oxalic acid - ammonium oxalate buffer (Schwertman, 1964).

$Cu_{oa}$ : 1 g of soil was shaken for 30 min at 96 °C in 50 mL of 0.1 M oxalic acid - ammonium oxalate - ascorbic acid buffer (Shuman, 1982).

$Cu_t$  (total Cu concentration): 0.5 g of soil was digested in a microwave oven at 100 psi with 5 mL of  $HNO_3$ , 4 mL of HF, and 1 mL of HCl.

For quality assurance and control we used two reference materials certified by the European Community Bureau of Reference: CRM 141 (calcareous loam soil) and CRM 143 (sewage sludge amended soil). Triplicate samples of each reference material were digested and their  $Cu_t$  contents were determined as above. The  $Cu_t$  values so determined ( $32.7 \pm 1.1$  mg kg<sup>-1</sup> for CRM 141,  $229.7 \pm 3.2$  mg kg<sup>-1</sup> for CRM 143) were consistent with the certified values ( $32.6 \pm 1.4$  and  $236.5 \pm 8.2$  mg kg<sup>-1</sup>, respectively).

Copper fractions interpreted as associated with specific soil components were calculated from the above operationally defined fractions as follows.

$Cu_{EX}$  (exchangeable Cu):  $Cu_a$ .

$Cu_{OM}$  (Cu bound to organic matter):  $Cu_p - Cu_a$ .

$Cu_{IA}$  (Cu bound to amorphous inorganic materials):  $Cu_o - Cu_p$ .

1  $Cu_C$  (Cu bound to crystalline Fe and Al hydrous oxides):  $Cu_{oa} - Cu_o$ .

2  $Cu_R$  (residual Cu incorporated in the crystalline structure of minerals):  $Cu_t - Cu_{oa}$ .

3 When referred to total copper content, these symbols will be starred  
4 (e.g.  $Cu_C^* \equiv Cu_C/Cu_t$ , expressed as a percentage).

## 6 **2.5. Determination of copper in river water**

7 Cu was determined directly in filtered water samples by atomic absorption  
8 spectrophotometry using a Thermo Elemental M series spectrophotometer with a  
9 graphite furnace running under Solaar software.

## 11 **2.6. Statistical analyses**

12 Calculations of basic descriptive statistics and Pearson correlations, analyses of  
13 variance (ANOVA), least significant difference tests (at the 95% probability level),  
14 multiple linear regressions and *k*-means clustering were all performed using SPSS  
15 v.12.0 for Windows.

## 17 **3. Results and analysis**

### 18 **3.1. General soil and sediment characteristics**

19 The soil samples taken in this basin had large sand contents (24-75%; Table 2)  
20 and the loam or sandy loam textures that are typical of soils developed over granites and  
21 schists in Galicia (Sánchez-Rodríguez, 1995). The sediment samples had a similar range  
22 of sand contents (27-72%) but were more varied in texture (Table 3).

23 All soils were acid, but how acid they were depended on land use. On average,  
24 woodland soils were of pH 4.6, pasture soils of pH 5.5, productive vineyard soils of  
25 pH 5.1, and abandoned vineyard soils of pH 5.6 (Table 2), but vineyard soil pH varied  
26 considerably (SD 0.5, as against 0.2 for woodland and pasture), depending on whether it  
27 had been amended with calcium carbonate. Sediments had significantly higher pH than



1 soils ( $p < 0.05$ ), with an average value of 6.0 (range 5.1-6.4; see Table 3).

2 Soil organic matter contents were generally high (mean 86 g kg<sup>-1</sup>) but varied  
3 widely, ranging from 16 to 414 g kg<sup>-1</sup>. Woodland soils had a much larger average  
4 organic matter content than productive or abandoned vineyards (161 g kg<sup>-1</sup> as against 59  
5 and 65 g kg<sup>-1</sup>, respectively), while pasture soils had intermediate levels (mean 92 g kg<sup>-1</sup>).  
6 The organic matter contents of sediments were similar to those of woodland soils, with  
7 an average value of 135 g kg<sup>-1</sup>.

8 In soils, amorphous iron oxides content Fe<sub>o</sub> ranged from 1.1 to 8.9 g kg<sup>-1</sup>, but the  
9 average values associated with the various soil uses did not differ significantly  
10 (Table 2). Sediments had a larger average Fe<sub>o</sub> content than soils, 11.4 g kg<sup>-1</sup> (Table 3),  
11 which together with their generally higher pH suggests that they may have a greater  
12 capacity to retain copper.

### 14 **3.2. Total copper contents of soils and sediments**

15 Soil total copper contents Cu<sub>t</sub> ranged from 16 to 434 mg kg<sup>-1</sup> (Table 2). As  
16 expected, averages for given land uses differed markedly and significantly ( $p < 0.05$ ),  
17 ranging from 31 and 30 mg kg<sup>-1</sup> under woodland and pasture, respectively, to  
18 139 mg kg<sup>-1</sup> under abandoned vineyard and 246 mg kg<sup>-1</sup> under productive vineyard (see  
19 Table 2 and Fig. 2). The woodland and pasture values are at the upper extreme of the  
20 range found in natural soils over the same parent materials, 12-30 mg kg<sup>-1</sup> (Macías *et al.*,  
21 1993; Baker and Senft, 1995). The high Cu levels in vineyard soils are attributable to  
22 the use of copper-based fungicides, since increments due to fertilisers would be much  
23 lower (Gou *et al.*, 2007). The range of Cu levels found in productive vineyard, 157-  
24 434 mg kg<sup>-1</sup>, is higher than ranges recently reported for vineyards in certain areas of  
25 France and Spain: 31-251 mg kg<sup>-1</sup> in the Département de l'Hérault (Brun *et al.*, 1998),  
26 49-398 mg kg<sup>-1</sup> in the Montpellier area (Chaignon *et al.*, 2003), and 40-301 mg kg<sup>-1</sup>  
27 (Arias *et al.*, 2004) or 25-272 mg kg<sup>-1</sup> (Fernández-Calviño *et al.*, 2007a and 2007b) in

1 southern Galicia. The wide variability of Cu levels in vineyard soils is attributable  
2 mainly to differences in the time for which they were or have been used as vineyard,  
3 which in this study ranged from 30 to 100 years.

4 The total Cu concentrations of sediments varied considerably from one sampling  
5 point to another (Table 3), ranging from 18 mg kg<sup>-1</sup> at point 8 (which had no productive  
6 vineyard upstream) to 209 mg kg<sup>-1</sup> on July 16th at point 7 (which had proportionally the  
7 largest area of productive vineyard upstream, 18%). As these two extremes suggest, Cu<sub>t</sub>  
8 was significantly correlated with the proportion of the upstream area that was occupied  
9 by productive vineyard ( $r=0.915$ ,  $p<0.05$ ; see Fig. 3); and although this very high  $r$   
10 value was due mainly to the influence of the outlying data for sampling points 7 and 8, a  
11 similar trend held along the main watercourse, the average Cu<sub>t</sub> values in sediments  
12 extracted at sampling points 6, 5 and 4 decreasing in the same order as the proportion of  
13 productive or abandoned vineyard upstream, with averages over sampling dates of  
14 respectively 115, 44 and 34 mg kg<sup>-1</sup> (Fig. 3). At sampling point 3, which received  
15 sediment from both the main watercourse and from the sub-basins draining into it via  
16 points 7 and 8, Cu<sub>t</sub> rose to 63-79 mg kg<sup>-1</sup>, the influence of the vineyard-rich sub-basin  
17 possibly predominating due to greater soil exposure and erosion. That similar levels  
18 were maintained at the downstream sampling points 1 and 2, which lie within an area  
19 predominantly occupied by abandoned vineyard, is attributed to the vegetation cover of  
20 abandoned vineyard being sufficient to prevent marked erosion, so that sediments  
21 collected at these sampling points will for the main have originated in upstream  
22 locations. Multiple linear regression of sediment Cu<sub>t</sub> on the proportion of upstream  
23 basin occupied by productive vineyard (PV, %) and the organic matter content of the  
24 sediment (OM, %) afforded the expression

$$25 \quad \text{Cu}_t = 8.252 \text{ PV} + 0.216 \text{ OM} \quad (R^2 = 0.825; F = 49.581; p < 0.001)$$

26 To investigate whether the proportion of the upstream basin occupied by  
27 productive vineyard was also affecting the level of copper in river water, the latter was

1 also determined. Copper concentrations in water ranged from 10 to 117  $\mu\text{g L}^{-1}$  (Table 4),  
2 both these extremes being recorded at sampling point 1, where Cu concentration  
3 correlated with daily mean flow rate ( $r=0.603$ ,  $p<0.005$ ). These Cu concentrations in  
4 water are similar to those found in water with  $\text{pH}<7$  from agricultural areas in Turkey  
5 (Aydinalp *et al.*, 2005). In waters with  $\text{pH}>8$ , as in agricultural areas in Switzerland,  
6 much lower Cu levels are found (Xue *et al.*, 2000), probably due to precipitation of  
7 copper.

8 Unlike sediment samples, water samples showed no clear pattern of variation  
9 among sampling points, as analyzed by ANOVA. For example, there was no significant  
10 difference between sampling points 7 (with proportionally the largest area of productive  
11 vineyard upstream, 18%) and 8 (which had no productive vineyard upstream), which is  
12 in keeping with Nicolau *et al.*'s (2006) finding that Cu concentrations in water from  
13 winegrowing areas did not differ significantly from those found in water from areas  
14 devoted to other land uses. This may be due to Cu being tightly bound to particles,  
15 especially organic matter particles, since it has been reported that less than 8% of Cu  
16 added to northwest Spanish vineyard soil samples is readily desorbable (Arias *et al.*,  
17 2004). It must be borne in mind, however, that changes in pH due to pollution events  
18 might increase the solubility of bound Cu (Impelliteri *et al.*, 2002), so copper-rich  
19 sediments may still constitute a risk of Cu pollution.

20

### 21 **3.3. Copper fractions**

22 In woodland and pasture soils, exchangeable copper concentration  $\text{Cu}_{\text{EX}}$  ranged  
23 from 0.2  $\text{mg kg}^{-1}$  to only 0.6  $\text{mg kg}^{-1}$  (Table 5), a figure similar to that reported for other  
24 natural soils (McLaren and Crawford, 1973; Shuman, 1979). This amounts to an  
25 average of 1-2% of total copper content, suggesting that only a small fraction of the  
26 copper of woodland and pasture soils can reach the soil solution immediately. In most  
27 of the abandoned vineyard soils  $\text{Cu}_{\text{EX}}$  levels were similar to or only slightly higher than

1 those of woodland and pasture (the mean of  $3.4 \text{ mg kg}^{-1}$  is as high as it is due to a single  
2 outlying value of  $15.7 \text{ mg kg}^{-1}$ ), but in productive vineyard they were significantly  
3 higher ( $p < 0.05$ ), ranging from 2.3 to  $30.5 \text{ mg kg}^{-1}$ . These higher concentrations may  
4 imply phytotoxicity, exchangeable copper being in equilibrium with dissolved copper in  
5 the soil solution. That  $\text{Cu}_{\text{EX}}$  was so low in abandoned vineyards despite their high  $\text{Cu}_{\text{t}}$   
6 values may be the result of aging processes that slowly reduce copper availability (Ma  
7 *et al.*, 2006), copper-based fungicides not having been applied since the vineyards were  
8 abandoned.

9 In soils, copper bound to organic matter,  $\text{Cu}_{\text{OM}}$ , ranged from 8 to  $226 \text{ mg kg}^{-1}$ ;  
10 constituted 32-67% of total soil copper content; and like  $\text{Cu}_{\text{t}}$  was much higher in  
11 vineyard than in woodland or pasture (Table 5). The range of  $\text{Cu}_{\text{OM}}^* = \text{Cu}_{\text{OM}}/\text{Cu}_{\text{t}}$  ratios  
12 was somewhat higher than the range observed in previous studies, 25-52% (Piertzak and  
13 McPhail, 2004; Arias *et al.*, 2004; Fernández-Calviño *et al.*, 2007a and 2007b). Among  
14 the soil groups defined by land use, the lowest average  $\text{Cu}_{\text{OM}}^*$  value was that of  
15 woodland, 43% (the next lowest, 49%, was that of abandoned vineyard); but the other  
16 non-contaminated soil group, natural pasture, had an average  $\text{Cu}_{\text{OM}}^*$  of 56%, nearly as  
17 high as the 57% of productive vineyard. This difference between woodland and pasture  
18 may be due to their different amorphous iron oxide levels (Table 2), since  $\text{Cu}_{\text{OM}}^*$  was  
19 significantly correlated with  $\text{Fe}_o$  ( $r = 0.795$ ;  $p < 0.01$ ;  $n = 10$ ). Amorphous iron oxides can  
20 form organometal complexes increasing the capacity of the soil to adsorb Cu (Arias *et al.*,  
21 2002).

22 Woodland and pasture soils had low  $\text{Cu}_{\text{IA}}$  values of  $0\text{-}5 \text{ mg kg}^{-1}$ , with averages  
23 amounting to 3% and 6% of  $\text{Cu}_{\text{t}}$ , respectively (Table 5). Vineyard soils had higher  $\text{Cu}_{\text{IA}}$   
24 levels of  $2\text{-}61 \text{ mg kg}^{-1}$ , with averages amounting to 14% of  $\text{Cu}_{\text{t}}$  in productive vineyard  
25 and 15% in abandoned vineyard.

26 Copper bound to crystalline Fe and Al hydrous oxides ( $\text{Cu}_{\text{c}}$ ) ranged from  
27 undetectable levels to  $72 \text{ mg kg}^{-1}$ , and residual Cu incorporated in crystalline minerals

1 ( $Cu_R$ ) from 4 to 98 mg kg<sup>-1</sup> (Table 5). Although on average vineyard soils had  
2 considerably higher  $Cu_C$  and  $Cu_R$  levels than woodland or pasture, it was in woodland  
3 that these fractions constituted, on average, the largest proportion of total copper  
4 content, and in productive vineyard the least. The relatively minor contribution of  $Cu_C$   
5 and  $Cu_R$  to  $Cu_t$  in productive vineyard is in keeping with the copper content of these  
6 soils deriving largely from copper-based fungicides, since Cu added to soil binds mainly  
7 to organic matter and non-crystalline hydrous oxides of Al and Fe (Arias-Estévez *et al.*,  
8 2007).

9 Sediments were more varied than soils as regards their copper fraction profiles  
10 (Table 6), although  $Cu_{EX}$  values were generally similar to those of woodland and  
11 pasture soils, and much smaller than those of productive vineyard, being less than  
12 1 mg kg<sup>-1</sup> in most samples (all except two from sampling point 7) and accounting for no  
13 more than 1.1% of  $Cu_t$  (Table 6). By contrast,  $Cu_{OM}^*$  ranged from 16% to 59%,  $Cu_{IA}^*$   
14 from non-detectable levels to 48%,  $Cu_C^*$  from non-detectable levels to 31%, and  $Cu_R^*$   
15 from 14% to 61%.  $Cu_{IA}^*$  was positively correlated with silt and clay content ( $p < 0.01$ ;  
16 see Table 7), while  $Cu_{OM}^*$  was negatively correlated with these variables ( $p < 0.05$ ),  
17 suggesting that copper is mainly bound to amorphous inorganic colloids in fine-textured  
18 sediments and to organic matter in coarse-textured sediments.

19 K-means clustering of the 20 sediments into two clusters on the basis of their  
20  $Cu_{EX}^*$ ,  $Cu_{OM}^*$ ,  $Cu_{IA}^*$ ,  $Cu_C^*$  and  $Cu_R^*$  values identified two 10-sediment clusters with  
21 minimum within-cluster variance and maximum between-cluster variance (Table 8).  
22 These clusters, which did not differ significantly as regards  $Cu_{EX}^*$  or  $Cu_R^*$  ( $p > 0.05$ ),  
23 can be regarded as comprising in one case silty sediments and in the other sandy  
24 sediments, although the description is not perfect (three “silty” sediments had sand  
25 contents that were greater than the least in the “sandy” cluster, and three “sandy”  
26 sediments had sand contents that were smaller than the greatest in the “silty” cluster). In  
27 keeping with the correlations commented on in the previous paragraph, of the three

1 defining variables ( $Cu_{OM}^*$ ,  $Cu_{IA}^*$  and  $Cu_C^*$ ),  $Cu_{IA}^*$  had the largest average in the silty  
2 cluster and  $Cu_{OM}^*$  had much the largest average in the sandy cluster.

3 The average Cu fraction profile of sediments in the sandy cluster (Table 8) was  
4 similar to those found in soils (Table 5). This is attributable to relevant characteristics of  
5 these sediments being rather similar to those of the soils (see Tables 2 and 8). In the  
6 silty cluster, in which the average  $Cu_{OM}^*$  value was significantly smaller and the  
7 average  $Cu_{IA}^*$  value significantly larger than in the sandy cluster ( $p < 0.05$ ), the  
8 influence of the greater inorganic colloids (silt and clay) content (67.4% as against  
9 43.4% in the sandy cluster) evidently outweighed that of the greater organic matter  
10 content (16.3% as against 10.6%).

#### 12 **4. Discussion and conclusions**

13 The repeated use of copper-based fungicides in vineyards increases total Cu  
14 level in vineyard soils. In this study, the increase was eight-fold with respect to  
15 woodland and pasture soils, reaching concentrations that in principle pose a significant  
16 risk of environmental degradation for the vineyards and their surroundings. Although  
17 the threat is held at bay by most of the vineyard Cu being bound to organic matter, and  
18 therefore not immediately available for release into the soil solution (Bolan and  
19 Duraisamy, 2003; Bolan et al., 2003a), it would be made available by a sufficient rise in  
20 pH (Bolan et al., 2003b); in the present case, results on the dependence of copper  
21 desorption on soil pH (Arias *et al.*, 2006) suggest that it would suffice to increase pH to  
22 above 6.5 for copper release. Copper would also be released into the soil solution by a  
23 sufficient reduction in pH (in these soils, to values below pH 4.5; see Arias *et al.*, 2006),  
24 especially in abandoned vineyards (Hesterberg, 1993; Strobel et al., 2005).

25 In this study the concentration of copper in river water showed no relationship  
26 to the distribution of vineyards in the basin, but vineyard distribution *was* related to the  
27 concentration of copper in river sediments, which in river stretches under the influence

1 of productive vineyards constituted significant reservoirs of Cu. This difference  
2 between river water and sediments supports the notion that in this basin copper is  
3 transported from vineyards to rivers mainly in particulate form, as the result of soil  
4 erosion, rather than in soluble form.

5         The threat posed by sedimentary Cu is rather different from that posed by Cu in  
6 vineyard soils, in that these sediments generally have a higher pH (mean 6.0), which  
7 means that acid-induced Cu release would require a greater pH reduction than in soils,  
8 but release from organic matter a smaller pH increase. Relative phytotoxic risk will also  
9 be influenced both by differences between soils and sediments as regards the exposure  
10 of released Cu to dissolved organic matter, which can complexate  $\text{Cu}^{2+}$  (Bolan et al.,  
11 2003a), and by differences among sediments as regards their texture. In the more sandy  
12 sediments, the largest Cu fraction is bound to organic matter, and factors influencing the  
13 solubilization of organic matter will accordingly also influence the release of Cu into  
14 waters (Temminghoff et al., 1997); in sediments rich in finer fractions (silt and clay) the  
15 Cu fraction bound to organic matter, though considerable, is smaller than the fraction  
16 bound to amorphous inorganic colloids, from which Cu will be released by a reduction  
17 in pH (as due, for instance, to an acid spill) but not by a rise in pH (McBride et al.,  
18 1998).

19

1           In conclusion, the presence of productive vineyards treated with copper-  
2 bearing fungicides in a river basin can affect the total copper concentration in river  
3 sediments at least if the vineyards are subject to significant erosion, but does not  
4 significantly influence the copper concentration in river waters. The pH conditions  
5 under which the toxic risk posed by the polluted sediments may be realized will depend  
6 on the distribution of copper among various sediment fractions. In particular, in basins  
7 similar to the one studied in this work, toxic risk will depend on whether most  
8 releasable copper is bound to organic matter or to amorphous inorganic colloids, which  
9 in turn depends largely on the texture of the sediment,  $Cu_{OM}$  being larger than  $Cu_{IA}$  in  
10 sandy sediments and smaller in silty sediments.

11

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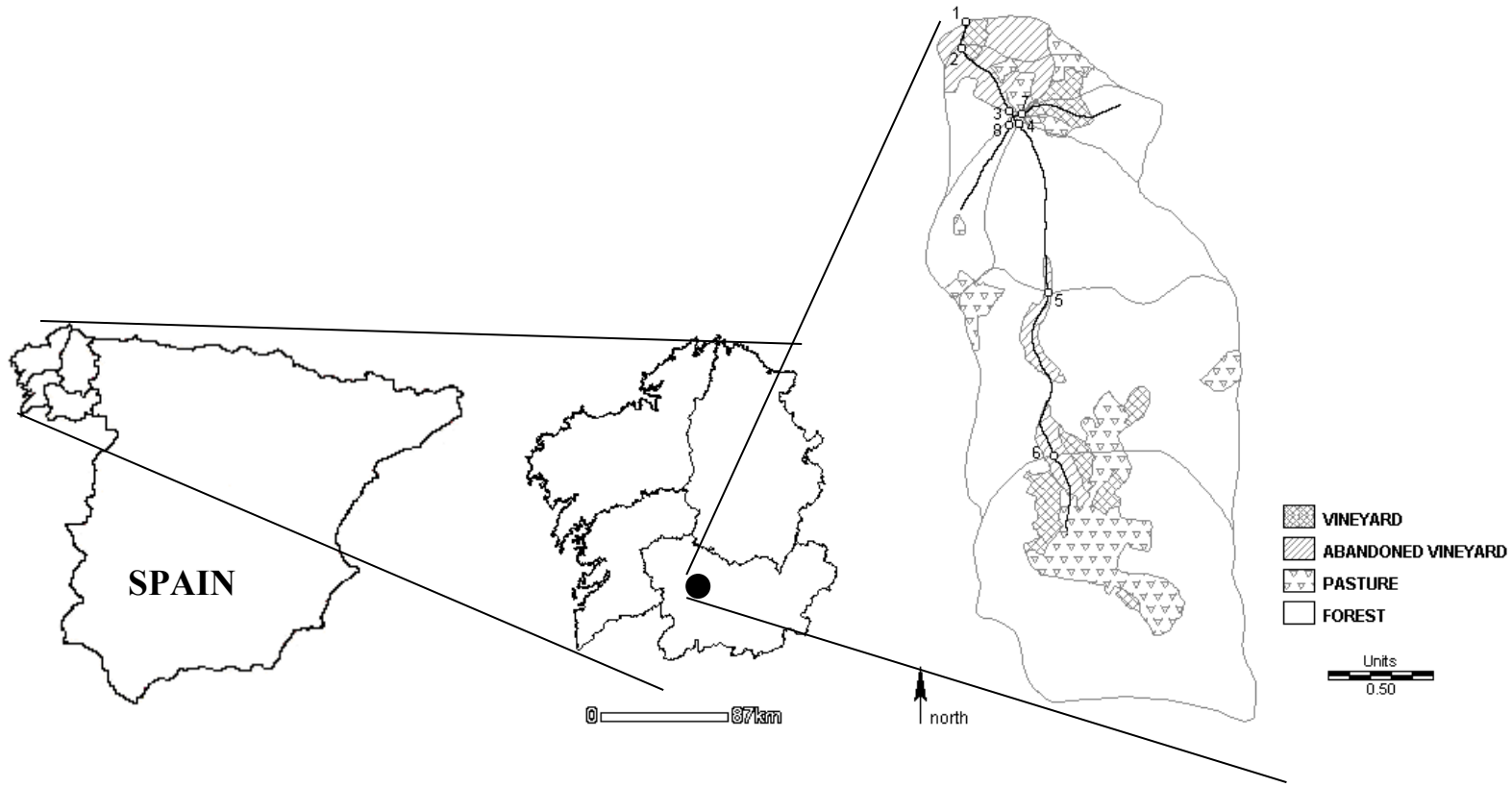
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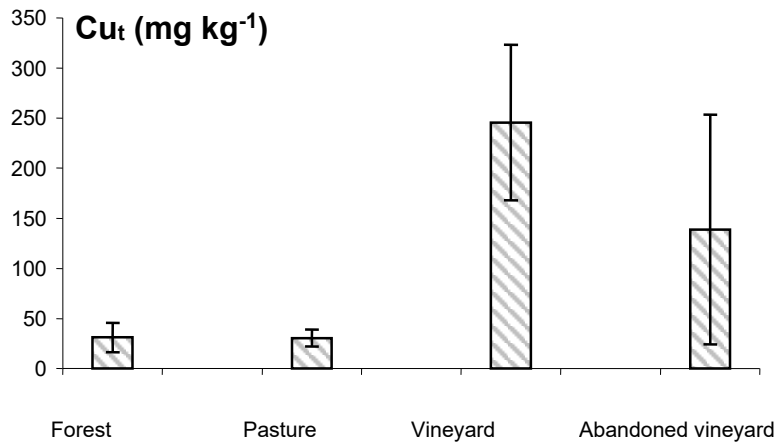
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**Figure 1.** Location of the basin studied (42° 19' 22" N, 8° 00' 40" W), and land uses therein. Numbers identify sediment and water sampling points.

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4 **Figure 2.** Total soil Cu concentration Cu<sub>t</sub> (means, with error bars indicating  
5 SDs) for each land use. Significant differences were found between vineyard  
6 use and forest or pasture use ( $p < 0.05$ ).

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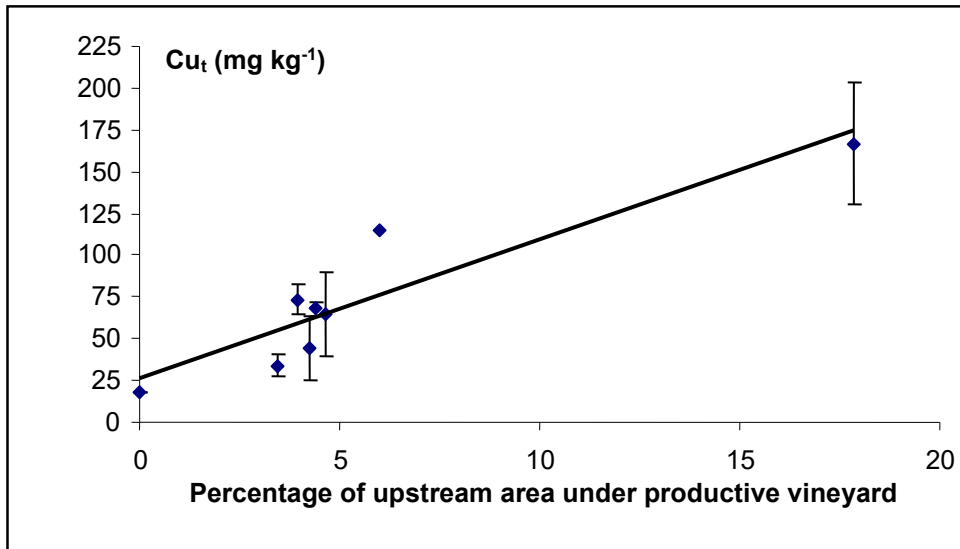
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**Figure 3.** Correlation between total Cu concentration in sediments at each sampling point ( $Cu_t$ ) and the proportion of the area upstream of that point that is occupied by productive vineyard ( $r=0.915$ ,  $p<0.005$ ).

1  
2 **Table 1.** Distribution of land use (%) upstream of each of the sampling points  
3 shown in Figure 1.

Sampling point	Land Use			
	Vineyard	Abandoned Vineyard	Pasture	Woodland
1	5	6	11	78
2	4	5	11	80
3	4	3	11	83
4	3	3	11	83
5	4	3	13	79
6	6	2	17	75
7	18	0	8	74
8	0	0	8	92

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1 **Table 2.** General characteristics of the soils studied.

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Use		Sand (%)	Silt (%)	Clay (%)	pH <sub>(H<sub>2</sub>O)</sub>	O.M	Fe <sub>o</sub>	Cu <sub>t</sub>
Woodland n = 5	Mean	50	34	16	4.6	161	2.7	31
	SD	9	9	3	0.2	150	1.2	15
	Maximum	63	44	20	4.8	414	3.9	54
	Minimum	40	22	13	4.3	31	1.1	16
Pasture n = 5	Mean	52	30	19	5.5	92	3.8	30
	SD	10	10	3	0,2	53	1.3	8
	Maximum	61	42	21	5.7	155	5.4	40
	Minimum	39	19	14	5.1	43	2.2	19
Productive Vineyard n = 10	Mean	59	26	15	5.1	59	2.2	246
	SD	13	9	4	0,5	48	0,9	78
	Maximum	75	38	22	6.0	178	3.9	434
	Minimum	41	15	9	4.5	19	1.2	157
Abandoned Vineyard n = 6	Mean	48	36	16	5.6	65	5.1	139
	SD	14	17	4	0,5	30	2,5	115
	Maximum	64	65	22	6.2	105	8.9	365
	Minimum	24	19	11	5.1	16	1.9	61

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4 O.M., organic matter (g kg<sup>-1</sup>); Fe<sub>o</sub>, iron extractable with ammonium oxalate-oxalic acid (g kg<sup>-1</sup>); Cu<sub>t</sub>, total Cu  
5 concentration (mg kg<sup>-1</sup>). Coefficients of variation were less than 10%.

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1 **Table 3.** General characteristics of the sediments studied.

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No.	Sampling Point	Date (dd/mm/yyyy)	Sand (%)	Silt (%)	Clay (%)	pH <sub>(H<sub>2</sub>O)</sub>	O.M.	Fe <sub>o</sub>	Cu <sub>t</sub>
1*	1	12/06/2002	27	51	22	5.6	198	10.3	94
2*	1	16/07/2002	51	31	18	5.1	100	7.7	52
3	1	26/09/2002	69	20	11	6.1	74	5.7	49
4*	2	12/06/2002	30	47	23	5.5	228	10.9	66
5*	2	16/07/2002	30	47	23	6.0	176	11.0	72
6	2	26/09/2002	44	40	16	6.3	162	10.1	65
7*	3	12/06/2002	23	53	24	6.2	193	11.8	78
8*	3	16/07/2002	48	34	18	6.1	147	7.7	63
9	3	26/09/2002	43	40	17	6.0	171	10.0	79
10	4	16/07/2002	57	28	15	5.9	116	5.8	29
11	4	26/09/2002	57	30	13	5.6	128	7.7	39
12*	5	12/06/2002	47	37	16	5.8	95	6.6	56
13*	5	16/07/2002	34	47	19	6.0	122	9.0	54
14	5	26/09/2002	43	42	15	5.7	91	10.8	22
15*	6	12/06/2002	14	58	28	6.1	178	10.3	115
16*	7	12/06/2002	22	46	32	6.4	195	38.4	148
17	7	16/07/2002	52	30	18	6.4	86	14.7	209
18	7	26/09/2002	62	25	13	6.2	59	15.1	143
19	8	12/06/2002	67	22	11	6.1	91	14.3	18
20	8	26/09/2002	72	18	10	6.3	86	9.8	18

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4 O.M., organic matter (g kg<sup>-1</sup>); Fe<sub>o</sub>, iron extractable with ammonium oxalate-oxalic acid (g kg<sup>-1</sup>); Cu<sub>t</sub>, total Cu  
 5 concentration (mg kg<sup>-1</sup>). Sampling points are shown in Fig. 1. Coefficients of variation were less than 10%. \* Sediments  
 6 assigned to the "silty" cluster identified by 2-means clustering (see Section 3.3).

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1 **Table 4.** Dissolved Cu concentration in water samples ( $\mu\text{g L}^{-1}$ ). Sampling  
2 points are shown in Fig. 1.

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	<b>Sampling point</b>					
	<b>1</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>7</b>	<b>8</b>
Mean <sup>*</sup>	40	47	44	53	39	27
SD	29	27	28	33	16	13
Maximum	117	113	84	90	68	51
Minimum	10	19	19	22	15	11

4 \* n = 10 at all sampling points except point 1, where n = 21.

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**Table 5.** Copper fractions in the soils studied, expressed in  $\text{mg kg}^{-1}$  and, in parentheses, as percentages of  $\text{Cu}_t$ .

Use		$\text{Cu}_{\text{EX}}$	$\text{Cu}_{\text{OM}}$	$\text{Cu}_{\text{IA}}$	$\text{Cu}_{\text{C}}$	$\text{Cu}_{\text{R}}$
Woodland n = 5	Mean	0.4 (1.2)	12 (43)	1 (3)	6 (18)	11 (35)
	Sd	0.2 (0.1)	4 (9)	1 (3)	6 (7)	6 (7)
	Maximum	0.6 (1.3)	17 (55)	2 (6)	16 (30)	20 (42)
	Minimum	0.2 (1.1)	8 (32)	0 (0)	3 (13)	4 (25)
Pasture n = 5	Mean	0.5 (1.5)	17 (56)	2 (6)	3 (9)	8 (28)
	Sd	0.2 (0.3)	6 (7)	2 (5)	3 (8)	2 (10)
	Maximum	0.6 (1.8)	22 (63)	5 (15)	6 (20)	10 (42)
	Minimum	0.2 (1.1)	10 (47)	1 (3)	0 (0)	5 (15)
Productive Vineyard n = 10	Mean	7.9 (2.8)	136 (57)	33 (14)	17 (7)	52 (20)
	Sd	8.4 (1.8)	35 (7)	15 (6)	11 (4)	24 (6)
	Maximum	30.5 (7.0)	226 (67)	61 (23)	36 (13)	98 (30)
	Minimum	2.3 (1.5)	105 (46)	2 (1)	2 (1)	13 (8)
Abandoned Vineyard n = 6	Mean	3.4 (1.5)	67 (49)	18 (15)	20 (11)	30 (24)
	Sd	6.0 (1.4)	53 (4)	10 (6)	28 (9)	25 (9)
	Maximum	15.7 (4.3)	172 (67)	28 (22)	72 (23)	80 (38)
	Minimum	0.5 (0.7)	31 (46)	6 (7)	0 (0)	15 (11)

$\text{Cu}_{\text{EX}}$ , exchangeable Cu;  $\text{Cu}_{\text{OM}}$ , Cu bound to organic matter;  $\text{Cu}_{\text{IA}}$ , Cu bound to amorphous inorganic materials;  $\text{Cu}_{\text{C}}$ , Cu bound to crystalline Fe and Al hydrous oxides;  $\text{Cu}_{\text{R}}$ , residual copper.

1 **Table 6.** Copper fractions in the sediments studied, expressed in mg kg<sup>-1</sup> and, in  
 2 parentheses, as percentages of Cu<sub>t</sub>. Sampling points are shown in Fig. 1.

No.	Sampling Point	Date (dd/mm/yyyy)	Cu <sub>EX</sub>	Cu <sub>OM</sub>	Cu <sub>IA</sub>	Cu <sub>C</sub>	Cu <sub>R</sub>
1	1	12/06/2002	0.6 (0.6)	26 (28)	33 (35)	3 (3)	31 (33)
2	1	16/07/2002	0.4 (0.8)	15 (28)	16 (31)	6 (12)	15 (29)
3	1	26/09/2002	0.3 (0.6)	29 (59)	1 (2)	8 (16)	11 (22)
4	2	12/06/2002	0.4 (0.6)	18 (27)	21 (32)	8 (12)	19 (29)
5	2	16/07/2002	0.4 (0.6)	19 (26)	20 (28)	6 (8)	27 (38)
6	2	26/09/2002	0.4 (0.6)	22 (33)	9 (14)	9 (14)	25 (38)
7	3	12/06/2002	0.4 (0.5)	16 (20)	30 (38)	1 (1)	31 (40)
8	3	16/07/2002	0.3 (0.5)	18 (28)	9 (14)	3 (5)	33 (52)
9	3	26/09/2002	0.3 (0.4)	29 (36)	11 (14)	11 (14)	28 (35)
10	4	16/07/2002	0.2 (0.7)	11 (37)	5 (17)	9 (31)	4 (14)
11	4	26/09/2002	0.2 (0.5)	12 (30)	1 (3)	8 (21)	18 (46)
12	5	12/06/2002	0.2 (0.4)	15 (26)	12 (21)	4 (7)	25 (45)
13	5	16/07/2002	0.2 (0.4)	13 (24)	15 (28)	2 (4)	24 (44)
14	5	26/09/2002	0.1 (0.5)	12 (54)	7 (32)	0 (0)	3 (14)
15	6	12/06/2002	0.5 (0.4)	19 (16)	55 (48)	1 (1)	40 (35)
16	7	12/06/2002	1.2 (0.8)	56 (38)	59 (40)	9 (6)	23 (16)
17	7	16/07/2002	1.2 (0.6)	90 (43)	18 (9)	50 (24)	50 (24)
18	7	26/09/2002	0.9 (0.6)	80 (56)	0 (0)	27 (19)	35 (24)
19	8	12/06/2002	0.2 (1.1)	8 (43)	2 (11)	0 (0)	8 (44)
20	8	26/09/2002	0.1 (0.6)	4 (22)	1 (6)	2 (11)	11 (61)

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 4 Cu<sub>EX</sub>, exchangeable Cu; Cu<sub>OM</sub>, Cu bound to organic matter; Cu<sub>IA</sub>, Cu bound to amorphous inorganic materials; Cu<sub>C</sub>, Cu  
 5 bound to crystalline Fe and Al hydrous oxides; Cu<sub>R</sub>, residual copper.

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1 **Table 7.** Coefficients of correlation between the chief sediment characteristics  
 2 and copper fractions  $Cu_X^* = 100 Cu_X/Cu_t$  (X = EX, OM, IA, C, R).

	Sand (%)	Silt (%)	Clay (%)	pH <sub>(H<sub>2</sub>O)</sub>	O.M.	Fe <sub>o</sub>	Cu <sub>t</sub>
<b>Cu<sub>EX</sub><sup>*</sup></b>	-0.289	-0.374	-0.086	0.012	-0.101	0.392	-0.047
<b>Cu<sub>OM</sub><sup>*</sup></b>	0.523*	-0.527*	-0.458*	0.152	<b>-0.567**</b>	0.146	0.109
<b>Cu<sub>IA</sub><sup>*</sup></b>	<b>-0.890**</b>	<b>0.864**</b>	<b>0.842**</b>	-0.236	<b>0.658**</b>	0.281	0.116
<b>Cu<sub>C</sub><sup>*</sup></b>	0.490*	-0.523*	-0.370	0.028	-0.309	-0.177	0.174
<b>Cu<sub>R</sub><sup>*</sup></b>	0.155	-0.101	-0.247	0.098	0.016	-0.333	-0.345

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4 Cu<sub>EX</sub>, exchangeable Cu; Cu<sub>OM</sub>, Cu bound to organic matter; Cu<sub>IA</sub>, Cu bound to amorphous inorganic materials; Cu<sub>C</sub>, Cu  
 5 bound to crystalline Fe and Al hydrous oxides; Cu<sub>R</sub>, residual copper.

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1 **Table 8.** K-means clustering of sediments (K = 2) in the space defined by the five copper fractions  $Cu_X^* = 100 Cu_X/Cu_t$  (X = EX, OM, IA, C, R).

Cluster		Sand (%)	Silt (%)	Clay (%)	pH <sub>(H<sub>2</sub>O)</sub>	O.M.	Fe <sub>o</sub>	Cu <sub>t</sub>	Cu <sub>EX</sub> *	Cu <sub>OM</sub> *	Cu <sub>IA</sub> *	Cu <sub>C</sub> *	Cu <sub>R</sub> *
1 (Silty sediments) n = 10 (1, 2, 4, 5, 7, 8, 12, 13, 15 & 16)	Mean	32.6	45.1	22.3	5.9	163.2	12.4	79.8	0.55	26.1	31.5	5.9	36.0
	SD	12.4	8.6	4.9	0.4	45.1	9.3	31.0	0.16	5.7	9.6	3.9	10.3
	Maximum	51.0	58.0	32.0	6.4	228.0	38.4	148.0	0.81	37.7	47.8	12.1	52.4
	Minimum	14.0	31.0	16.0	5.1	95.0	6.6	52.0	0.36	16.1	14.3	0.9	15.5
2 (Sandy sediments) n = 10 (3, 6, 9, 10, 11, 14, 17, 18, 19 & 20)	Mean	56.6	29.5	13.9	6.1	106.4	10.4	67.1	0.61	41.4	10.7	15.0	32.4
	SD	10.9	8.7	2.7	0.3	37.2	3.4	62.8	0.20	12.0	9.4	9.7	15.4
	Maximum	72.0	42.0	18.0	6.4	171.0	15.1	209.0	1.11	58.6	31.8	31.0	61.1
	Minimum	43.0	18.0	10.0	5.6	59.0	5.7	18.0	0.38	21.7	0.0	0.0	13.6

2

3