Metal fractionation in topsoils and bed sediments in the Mero River rural basin: Bioavailability and relationship with soil and sediment properties

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ABSTRACT

Comprehensive studies that examine the transfer of metals across soil-river bed sediment systems at the basin scale are scarce. An understanding of the distribution of metals among various fractions of soils and sediments within a basin is fundamental to understand their environmental behavior and, thus, to define watershed management plans. This study aims to determine the distribution of metals (Fe, Mn, Cu, and Zn) in topsoils under different land uses (cultivation, pastures, and forests) and river surface sediments in the upper Mero River basin (NW Spain) and to assess these metals' mobility and bioavailability in both environmental compartments to detect potential threats to crops and the water quality. Sequential extraction is used to fractionate the four metals into six fractions: soluble/exchangeable/specifically adsorbed, metals that are bound to Mn oxides, amorphous compounds, metals that are bound to organic matter, crystalline Al and Fe oxides, and residual metals (metals within the crystal lattices of minerals). The fractionation results for both soils and sediment indicate an abundance of metals in the residual fraction (except for Mn in soils) followed by relatively high percentages of oxide-bound fractions (mostly crystalline Fe oxides for both Fe and Zn, amorphous for Cu, and Mn oxides for Mn). On average, the Mn residual fraction in soils (30.2%) is only slightly exceeded by the Mn oxide fraction (34.7%). The land uses do not affect the sequence of metal-binding phases in soils, except for Mn, which is only slightly altered. The results also suggest that Fe, Mn, Cu and Zn in both soils and sediments are not readily mobile under current environmental condition and hence pose no threat to crops or the water quality. In overall terms, the mobility and bioavailability of the four metals (considering the sum of the three least mobile fractions, namely, organic matter, crystalline Al and Fe oxides, and residual) in the soils decrease in the following order: Mn > Cu > Fe > Zn. The same sequence occurs in the sediments, but the order between Fe and Zn is reversed. The soils and sediments that are studied cannot be considered polluted in terms of these metals because of their low levels and prevalence in the residual fraction, which is typical of contributions from natural sources and indicates the pedogenic/lithologic origin of these metals.

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1. Introduction

The concentration and distribution of metals in soils are influenced by several factors, such as the texture, organic matter content, drainage, soil horizons, and vegetation (Adriano, 2001). The overall content of metals in soils also depends on the geochemical nature of the parent material because soil inherits a certain quantity of elements from its parent rock that is then redistributed by pedological processes (Kabala and Szerszen, 2002). Elevated concentrations of metals in soils pose potential hazards to human health because of their toxicity and persistence in the environment (Nagajyoti et al., 2010; Sheng et al., 2012). Metals that enter aquatic environments become part of the water-sediment system, and their distribution processes are controlled by a dynamic set of physicochemical interactions and equilibria. Knowledge

of the total contents of metals in soils and sediments provides limited information regarding their potential behavior and bioavailability (Maiz et al., 2000; Gleyzes et al., 2002; Gao and Chen, 2012). Metals are associated with various soil and sediment components in different ways, and these associations determine their mobility and availability. Thus, metals can exist as water-soluble and exchangeable forms; precipitate in carbonates; occlude in Mn, Fe or Al oxides; bind to organic matter; or appear in residual phases (Tessier et al., 1979; Salomons and Förstner, 1980; Bradl, 2004; He et al., 2004). Water-soluble and exchangeable forms are considered readily mobile and available to biota, while metals that are incorporated into the crystalline lattices of clays appear relatively inactive. The other forms (precipitated in carbonates; occluded in Fe, Mn, and Al oxides; or complexed with organic matter) could be considered relatively active or firmly bound depending on the actual combination of physical and chemical properties of the soil or sediment (Shuman, 1985; Kersten and Förstner, 1989). Thus, the pH, texture, organic matter, clay mineralogy, and Fe-Mn oxides have

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been found to be the most important soil and sediment properties and components that influence the lability and biological uptake of metals (Salomons and Förstner, 1984; Ma and Rao, 1997). Some of these properties can be altered by tillage (Cattani et al., 2006; Lair et al., 2007). Shuman and Hargrove (1985) found that tillage had a greater effect on the distribution of Mn and Fe among soil fractions than on the distribution of Zn and Cu. These authors also reported that no tillage lowered the Mn in the exchangeable and amorphous Fe oxide fractions and raised Mn in the organic fraction compared to minimum tillage or conventional tillage. Generally, only a small fraction of metals is present in biota-available form under natural conditions (Kabata-Pendias, 2011). Changes in environmental conditions, such as the temperature, pH, redox potential and organic ligand concentrations, can cause the release of metals from the solid phase to the liquid phase and sometimes cause the contamination of surrounding waters (Sahuquillo et al., 2003).

Sequential extraction can provide information regarding the association degree of metals with different geochemical phases in soils and sediments and both mobile and stable fractions of metals, allowing us to assess their actual and potential mobility (Filgueiras et al., 2002; Sundaray et al., 2011). Fractionation is also useful to distinguish the metals' origin (lithogenic or anthropogenic); anthropogenic metals mainly occur as liable extractable fractions, whereas those from lithogenic sources are present in the residual fraction (Salomons and Förstner, 1980; Hooda and Alloway, 1994; Madrid et al., 2004).

Numerous fractionation techniques have been used for the sequential extraction of metals in soils and sediments, which varied in the number of fractions that were extracted (three to seven) and in the order and type of reagents that were used (Tessier et al., 1979; Shuman, 1985; Ure et al., 1993; Campanella et al., 1995; Cardoso Fonseca and Ferreira da Silva, 1998). Although commonly used chemical sequential extraction procedures are reasonably specific for most metals from soil and sediment, whether the soil use can modify the metal fractionation remains unclear, even though the land use is known to modify the total metal concentrations in soils and in aquatic systems (Xue et al., 2003; Das et al., 2009).

This study was conducted in the headwater of the Mero River basin (NW Spain) to (i) assess the concentrations and distributions of metals (Fe, Mn, Cu, and Zn) in the topsoil under different land uses (cultivation, pastures, and forests); (ii) investigate the relationship between soil properties and the geochemical fractions of metals; (iii) assess the concentrations and distributions of Fe, Mn, Cu, and Zn in river bed surface sediments; and (iv) identify the origin of these metals and assess their potential mobility and availability in both environmental compartments.

Fe and Mn were selected as indicators of natural processes and for their potential to influence the distribution of trace metals in the geochemical phases of soils and sediments, although enrichment in such metals may occur because of both natural processes and anthropogenic activities. Cu and Zn were investigated because they are trace metals, which usually have an anthropogenic origin. Although the headwater of the Mero River Basin is a rural area that is free from industrial activities, animal manures (cattle and pig slurries) and chemical fertilizers are frequently applied to agricultural soils. These products are known to include a variable proportion of metals (Cu and Zn, especially in pig slurry) as constituents or impurities (L'Herroux et al., 1997; Xue et al., 2003).

Notably, most of the published studies analyzed soils and sediments from different areas. However, analyzing the soils and sediments of water bodies within the same basin should enhance the interest of this study. Previous studies on this basin have shown that the transfer of metals from soils to surface waters is mostly mediated by association with suspended particulates (Palleiro et al., 2014a,b), with soil erosion processes being primarily responsible for sediment transport to the water course. However, the total contents and chemical forms in which these metals are associated with the bed sediments have not been studied. Sediments are generally considered to behave as a sink for metals in aquatic environments and frequently act as a source for their presence in waters, creating implications for basin management. On the other hand, this topic is important to study because the headwaters of both the

Mero River and Barcés River feed the Abegondo-Cecebre reservoir, which constitutes the only drinking water source of the city of A Coruña and its metropolitan area (approximately 400,000 inhabitants). In addition, this reservoir was declared a Special Area of Conservation and Site of Community Importance in the Natura 2000 Network. Possible degradation in the water and sediment quality in the headwater of the Mero River Basin will impact the drinking water quality and the entire ecosystem of Abegondo-Cecebre.

2. Materials and methods

2.1. Study area

This study was conducted in the headwater of the Mero River Basin, which is a rural basin of 65 km^2 that is located in the northeastern A Coruña province (A Coruña, Galicia, NW Spain; Fig. 1). The geology of the drainage area is dominated by basic metamorphic schists from the Órdenes Complex (IGME, 1981), which formed from easily alterable minerals such as biotite (sometimes chlorite), plagioclase and amphiboles. The main soil types are classified as Umbrisols and Cambisols (IUSS Working Group WRB, 2015), which are usually deep because of intense weathering. The land uses include forests (53%), which mainly contain pine and eucalyptus; pastures (38%); cultivation (4%); and impervious areas (5%), which consist of streets, roads and single family homes that are not always connected to sewers, with their wastewaters being potential pollutants. Organic and inorganic fertilizers are commonly applied to 42% of the basin (agricultural area) throughout the year. Information on the load and distribution of metals in the waters of the Mero River can be found in Palleiro et al. (2014a) and Soto-Varela et al. (2014). The study area is located in a typical Atlantic (humid oceanic) climate zone with a mean annual rainfall of 1194 mm (historic series: 1983–2013) and mean annual temperature of 13 °C.

2.2. Sample collection of soils and sediments

Twelve topsoil samples (0–20 cm depth) were collected (after removing the litter layer and O-horizons in the forest soils), four for each land use (forests, pastures and cultivation) within the basin, so differences in the metals' distributions as a function of the soil use may be evaluated. The sampling sites for each land use were selected based on the proximity to the river (Fig. 1). This approach was adopted because previous studies of the Corbeira Basin, which is adjacent to the Mero Basin, have shown that zones that are close or well connected to the river are the dominant sediment source areas (Rodríguez-Blanco et al., 2010a). This phenomenon could likely occur in the Mero basin because both basins have similar characteristics. Around 4 to 6 representative subsamples were collected at each site and thoroughly mixed to obtain a composite sample for analysis.

River bed sediments were sampled at 4 points that were distributed along the upper course of the Mero River between the headwater of the river and the basin outlet, covering a distance of approximately 27 km (Fig. 1). Samples were collected under high flow conditions and labeled from S1 to S4; S1 was collected in the headwater and S4 at the basin outlet. The sediment samples were collected from the top 5 cm of the river bed with a small plastic shovel and taken to the laboratory in plastic containers. Around 4 to 6 representative subsamples were collected from each site and mixed to compose a unique sample.

Both the soil and sediment samples were air dried, mixed and sieved through a 2-mm nylon sieve. Special care was taken to avoid metal contamination. All the material was pre-cleaned with 0.01 M HNO$_3$ and rinsed with double-distilled water.

2.3. Soil and sediment physicochemical analysis and metal fractionation

The pH of each sample was measured in water (pH-H$_2$O) and in KCl (pH-KCl) by using a 1:2.5 soil or sediment/solution ratio. The total
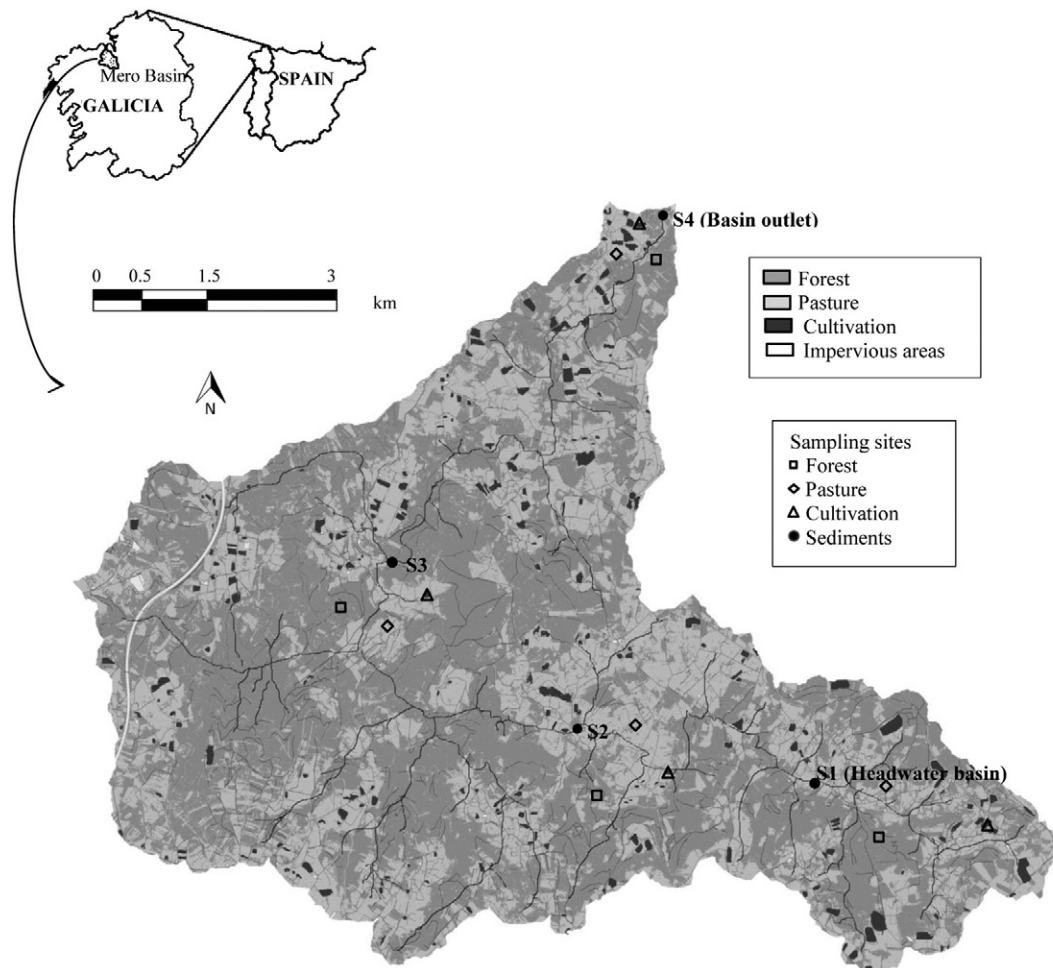
Fig. 1. Localization of the Mero River basin and types of land uses. The sampling sites in the basin are indicated.

organic carbon content (determined by oxidation with a mixture of $K_2Cr_2O_7$ and H_2SO_4 and titration with Mohr Salt), the nitrogen content (determined by wet digestion with H_2SO_4 by the Kjeldhal method), and the grain size distribution were determined as per Guitián and Carballas (1976).

Metal fractionation was performed by using a six-step sequential extraction procedure called SEP, which was discussed by Cardoso Fonseca and Ferreira da Silva (1998). The following reagents were used: a) F1–ammonium acetate (1 mol L^{-1} NH_4Ac, pH of 4.5, continuous agitation for 600 min, room temperature) for water-soluble, exchangeable, specifically adsorbed and some carbonate-bound ions; b) F2–hydroxylamine hydrochloride (0.1 mol L^{-1} NH_2OH - HCl in 0.01 mol L^{-1} HNO_3, pH of 2, continuous agitation for 600 min, room temperature) for metals in Mn oxides; c) F3–ammonium oxalate in darkness (0.175 mol L^{-1} $(NH_4)_2C_2O_4$–0.1 mol L^{-1} $H_2C_2O_4$, pH 3.3, continuous agitation for 600 min, room temperature) for metals that were linked to amorphous compounds (organic amorphous compounds and non-crystalline hydrous oxides of Al and Fe); d) F4–hydrogen peroxide 35% for metals that were associated with oxidizable organic matter (shaking at 60 °C until reaction stopped); e) F5–ammonium oxalate under ultraviolet radiation (0.175 mol L^{-1} $(NH_4)_2C_2O_4$–0.1 mol L^{-1} $H_2C_2O_4$, pH of 3.3, continuous agitation for 600 min) for metals that were associated with crystalline Al and Fe oxides; and f) F6–hot mixed acid (HCl + HNO_3 + HF) for metals that were embedded in the crystal lattices of minerals (residual fraction). The metal contents were measured by atomic absorption spectrophotometry with a GBC 906 AA apparatus, which involved the direct aspiration of the aqueous solution into an air-acetylene flame. The elements that solubilized

during the first step (F1) were considered to be in soluble, exchangeable and specifically adsorbed forms as the presence of carbonates is unlikely because of the acidic nature of the soils. This SEP was selected over other more widely used methods such as the Tessier scheme (Tessier et al., 1979), standard BCR (Ure et al., 1993) or Campanella et al.'s (1995) procedure because this process enables more detailed partitioning of metals, particularly among reducible fractions. This technique separates metals that are (i) easily reducible (bound to Mn oxides), (ii) bound to amorphous Fe oxides, and (iii) bound to crystalline Fe oxides, which may provide useful information regarding the soil/sediment under changing redox conditions (Naumeister et al., 1997) and in geochemical soil studies (Lair et al., 2007; Reis et al., 2012). Iron and manganese oxides, which can be present in soils and sediments as concretions, cement between particles or coatings on particles, are excellent substrates with large surface areas for adsorbing trace metals. The reduction of Fe (III) and Mn (IV) under anoxic conditions and their subsequent dissolution could release adsorbed trace metals. Another methodological advantage of the Cardoso Fonseca and Ferreira da Silva (1998) procedure compared to the method of Campanella et al. (1995) or the BCR is the extraction of residual fractions (not considered in the other two). Such extraction is performed with a mixture of aqua regia and HF, which provides the total metal concentration (not the pseudo-total) in the residual fraction. This procedure is necessary to ensure the complete decomposition of silicates (Agemian and Chau, 1975).

The accuracy and analytical precision in the determination of the total metal content in soils and sediments were examined by analyzing a reference material (NCS ZC 73004) and duplicate samples in each analytical set. The coefficients of variation for the various elements were as

follows: Fe – 4%, Mn – 2%, Cu – 2%, and Zn – 3%. The total concentrations of Fe, Mn, Cu and Zn were determined in separate soil/sediment samples, with 1 g of each digested in hot mixed acid ($HCl + HNO_3 + HF$), to verify the accuracy of the sequential treatment (sum of the sequential extractions). The overall recovery rates (sum of the six fractions/independent total concentrations) ranged from 80 to 110%, which indicates good agreement between the sum of all the fractions and the total concentration of a particular metal, which was measured directly.

The total content of metals (presented in the tables, figures and text) in both topsoil and sediments was considered as the sum of the six fractions that were extracted according to the ESP method (total concentration was not considered as a directly obtained value).

2.4. Data analysis

ANOVA was performed to examine the effect of soil use on the mean concentrations of the total metals in the soils and mean concentrations of fractionated metals. In cases where the ANOVA results were significant, the mean values were compared by using the Tukey test. Pearson correlation analysis was applied to assess the relationship between the total metals and the physicochemical properties and between the mean concentrations of the metal fractions and the physicochemical properties.

3. Results and discussion

3.1. General soil characteristics

Table 1 shows data for some soil properties under different land uses. The soil pH was moderately acidic in the all soils, but the mean pH (in both water and KCl) was almost 0.9 units higher in the pastures and 0.6 units higher in the cultivated soils than in the forest soils, i.e., a statistically significant ($p < 0.05$) difference, possibly because liming agricultural soils is a common management practice in the area. However, vegetation plays an important role in determining the acidification of soil. Certain species, mainly conifers, have been reported to acidify soil and, therefore, are associated with degrading processes, particularly in cold regions as reported by Augusto et al. (1998) and others. In Galicia, Calvo and Díaz-Fierros (1981) and Gómez-Rey and Calvo de Anta (2002) found that through-fall and stem-flow waters were more acidic in pine forests than in eucalyptus or oak stands. On the contrary, Molina et al. (1991), among others, ascertained that eucalyptus is a more acidifying species because of the high content of phenolic compounds in its leaves. In our case, the acidification of forest soils with pine and eucalyptus could also be the cause of the lower pH of forest soils compared to agricultural soils and especially pastures. The increase in pH (pH_{H_2O}-pH_{KCl}) ranged from 0.9 to 1.2, indicating the predominance of negative electric charges. The organic matter content was high in all the soils, independent of their use (Table 1). Despite the range of variations, this range was significantly higher ($p < 0.05$) in the forest soils (mean: 14.3%) than in the cultivated soils (4.1%) because forest use favors the accumulation of organic matter, whereas pasture soils had intermediate levels (8.7%) despite the high input of organic matter (widespread use of cattle and pig slurry as fertilizers) and the almost total absence of tillage. These observations agree with the findings of Troitiño et al. (2008) for similar circumstances in the same region, which were attributed to the higher biological activity that occurs in these ecosystems. These results also seemed to occur in our case as

inferred from the lower C/N ratio of pasture soils compared to forest soils. The total nitrogen (N) content followed a similar pattern to that of organic matter (Table 1) representing an average of 93% and 65%, respectively, of the N content from forest soils in pasture soils and cultivation. The C/N ratio is considered an indicator of the quality of soil organic matter; the higher the value of said ratio, the more recalcitrant the soil (Parr and Papendick, 1978). The C/N ratio decreased in this order: forest soils (19) > pasture (13) > cultivation soils (10). This sequence indicates that the organic matter in forest soils is poorly decomposed and promotes accumulation, while the decomposition rate in agricultural soils (lower C/N than in forest soils) and particularly in cultivation soils is higher than that in forest soils, which promotes degradation. The texture was quite similar for all three uses and mainly in silt and silty-loam, which was expected because schist was the soil parent material in the study area.

3.2. Total metal contents of the soils and relationship with soil properties

Table 2 shows the metal concentrations in the topsoil of the Mero River and the values for the C-horizon soils in the basin, surface horizons of natural soils over the schists in the "Órdenes Complex" in the surrounding area, and world data. The average abundance order of the metal contents in the topsoil was (mg kg^{-1}) Fe (36,976) >>> Mn (876.1) >>> Zn (76.4) > Cu (23.6). A similar pattern was found in the C-horizon of catchment soils (Guitián et al., 1992). The predominance of ferromagnesian minerals (biotite, chlorite and amphiboles) in the parent material (biotite schists) of the catchment soils justifies the presence of these metals in the soil. No significant differences existed between the mean concentrations of both Fe and Cu among the three land use types (Table 3). However, Mn and Zn were significantly higher ($p < 0.05$) in cultivation (1055 and 87.7 mg kg^{-1}) and pasture soils (933 and 80.5 mg kg^{-1}) than in forest soils (624.8 and 57.8 mg kg^{-1}). In any case, the mean value of each metal in the topsoil of the Mero catchment soils was lower than the mean that was proposed for the world's soils and the mean concentrations that were reported in the Geochemical Atlas of Galicia (Guitián et al., 1992) for the C-horizon of the soils in the study area (Table 2), except for Mn and Cu, which very slightly exceeded (approximately 1.2 times higher) the C-horizon values. The discrepancies that occur for Mn and Cu may be explained by the effects of pedogenesis or could also indicate that these elements partly originate from a source that is not lithogenic. The latter seems unlikely because, in both cases, the mean and upper extreme of the range are within the range that is found in the surface horizons of natural soils over the same parent materials in the surrounding area; the Mn range is 105–2325 mg kg^{-1} and the Cu range is 3–89 mg kg^{-1} (Macías et al., 1993).

A correlation analysis among the total metals only revealed significant correlations between Fe and Zn ($r = 0.68$, $p < 0.01$), which could indicate an analogous origin for these metals.

An analysis of the correlations between the total metals and soil properties indicated that the soil pH, which has a strong influence on metal adsorption, retention and movement in soil profiles (Harter, 1983), was positively correlated with Zn ($r = 0.67$; $p < 0.01$), which suggests that an increase in the soil pH favors Zn retention within the soil. Apart from Zn, no other elements showed significant correlations with the pH. Fe, Cu and Zn were negatively correlated ($p < 0.01$) with the sand content ($r = -0.92$, -0.66, and -0.74, respectively) and

Table 1
Mean ± standard deviation of the main topsoil characteristics in the study area according to land use. Different letters within the columns correspond to significant differences ($p < 0.05$) among the land uses. The number of samples per land use was 4.

Land use	pH-H$_2$O	pH-KCl	Organic matter %	N%	C/N	Sand (2 mm–50 μm) %	Silt (50–2 μm) %	Clay (< 2 μm) %
Cultivation	5.7b ± 0.5	4.5b ± 0.4	4.1b ± 1.2	0.3a ± 0.19	10a ± 5	31a ± 4	47a ± 3	22a ± 3
Pasture	6.0b ± 0.4	5.0b ± 0.4	8.7ab ± 4.0	0.43a ± 0.25	13a ± 6	29a ± 3	48a ± 4	23a ± 4
Forest	5.1a ± 0.3	4.1a ± 0.2	14.3a ± 4.4	0.46a ± 0.12	19a ± 9	31a ± 2	41a ± 7	28a ± 6

Table 2
Metal concentrations in the topsoil, suspended sediments, and bed sediments of the Mero River. The values for the C-horizon soils of the basin, surface horizons of natural soils over the schists in the "Órdenes Complex" in the surrounding area, and world data are also shown for comparison. The values are means, with their ranges in parentheses. The units are in mg kg^{-1}.

	Fe	Mn	Cu	Zn
Mero River topsoil	36,976	876.1	23.6	76.4
	(27,762–45,049)	(327–1271)	(16.1–30.7)	(52.7–101.3)
C-horizon soils[a]	52,500	750	20	300
Surface horizons of natural soils in the surrounding area[b]	–	535	26	58
		(105–2325)	(3–89)	(22−132)
World soils[c]	40,000	10,000	30	90
Mero River suspended sediment (flow-weighted)[d]	59,850	4050	191	1365
Mero River bed sediment	27,737	756	15.7	61.2

[a] Guitián et al. (1992).
[b] Macías et al. (1993).
[c] Martin and Whitfield (1983).
[d] Palleiro et al. (2013).

positively correlated (p < 0.01) with the sum of the clay and silt (r = 0.92, 0.66, and 0.74), which indicates that the major fractions that were associated with these metals were the finest fractions of the soil. Mn followed the same trend as Fe, Cu and Zn with respect to the grain size, although the correlations were not statistically significant. Fine particulate fractions have been reported to exhibit a strong correlation with metals because of their large surface area and high absorption capacity (Horowitz and Elrick, 1987; Hu et al., 2013). No significant relationship between the total metals and organic matter content was observed.

3.3. Sequential extraction of metals in soils

The metal contents for the three soil uses and for each fraction of the sequential extraction are listed in Table 3 and as percentages of the total elements in Fig. 2. The metal distributions in the different phases of the sequential extraction varied for each element and for each land use, although some general tendencies could be observed. A relatively wide range of concentrations for each metal and each land use could also be seen (Table 3). These results can be explained by local variations in the general properties of the sampling area.

3.3.1. Iron

Fe exhibited distributions over all the analyzed geochemical phases, with the highest proportions in the residual fraction (58.9% on average), assuming that this element mainly occurs in the inner lattice positions of the minerals and clay mineral matrices. Its non-residual fraction was markedly dominated by crystalline forms (23.4%; 8625 mg kg^{-1}) and, to a lesser extent, by amorphous forms (14%; 5175 mg kg^{-1}); the Fe that was associated with Mn-oxides was very low (2% of total Fe content). Very small contributions from both the soluble/exchangeable/specifically adsorbed fraction (1.2%, 408 mg kg^{-1}) and the fraction that was bound to oxidizable organic matter (0.5%, 183 mg kg^{-1}) was recorded. The distribution pattern of Fe was similar among all the land uses. However, forest soils had a significantly lower contribution of residual fraction (51.3%) to the total Fe concentration compared to the other uses (pastures: 60.3%; cultivation: 65.1%). This result indicates the higher liberation of Fe to non-residual fractions in the forest soils (particularly to the crystalline fraction: 28.9% for forests and approximately 21% for the other uses) than for the remaining uses, probably because the more acidic conditions and higher production of organic acids in forest soils favor the weathering of ferromagnesian minerals and release Fe (Adriano, 2001). The other fractions showed no significant differences among the uses.

The organic fraction that is released during the oxidizable step is not considered to be bioavailable because this fraction is thought to be associated with stable high-molecular-weight humic substances that slowly release small amounts of metals (Singh et al., 1998). The negligible presence of Fe in the oxidizable organic matter fraction (Table 3; Fig. 2) revealed the poor formation of stable Fe-organic matter complexes

despite the relatively high content of organic matter in these soils (Table 1). This result occurred because not all organic matter fractions are similarly active in their retention of metals. A correlation analysis showed that the oxidizable organic matter fraction did not practically correlate with the organic matter content, while the F1 fraction (water-soluble/exchangeable/specifically adsorbed) was correlated with this soil component (r = 0.66, p < 0.01). Despite the limited effect of organic matter on the retention of Fe in all the soils in this study, these results suggest a greater influence of organic matter on binding Fe, either by providing ionic exchange sites (labile bonds) or specific adsorption sites (some stability bonds) against the formation of highly stable complexes with this metal. In fact, the highest amounts of the F1 fraction were found in forest soils (507 mg kg^{-1}; 1.5%), which agrees with their higher organic matter content, followed by pasture (454 mg kg^{-1}; 1.3%) and cultivation soils (263 mg kg^{-1}; 0.7%). In a previous study that involved the same soils, Palleiro et al. (2016) found a greater proportion of Al than Fe in the water-soluble/exchangeable/specifically adsorbed, amorphous and oxidizable organic matter fractions. These authors also found significant and positive correlations between both these Al fractions and the total Al and organic matter contents. The greater trend of Al to combine with soil organic matter (Oades, 1989) was probably the cause of the low presence of Fe that was bound to organic matter in the surface soil horizons of the Mero catchment.

From a mobility standpoint, the first fraction can release its metal loads by lowering the pH, so this fraction is the most mobile and potentially the most dangerous of all the fractions. The last three fractions of the SEP (F4 + F5 + F6) are considered more immobile than the first three (F1 + F2 + F3). Fe mainly occurred in the most resistant phases (F4 + F5 + F6: 82.8% average for all soils), such as silicates and crystalline Fe-oxides. Fe in so-called more soluble soil phases only constituted 17.2% of the total Fe on average and was always higher in forest soils than in the other two soil types. Some significant correlations were found, particularly for the residual fraction, when the relationships among the different Fe fractions and the relationships between these and the total Fe amounts were analyzed. As expected, this fraction was positively correlated with the total Fe (r = 0.80; p < 0.01), confirming the natural source of Fe in these soils. The residual fraction was also inversely correlated with the amorphous-Fe fraction (r = −0.81; p < 0.01) and with the oxidizable organic matter fraction (r = −0.71; p < 0.01).

3.3.2. Manganese

Mn was distributed over all the phases except in the oxidizable organic matter fraction (Table 3; Fig. 2). The lack of Mn in this last fraction is not surprising because the literature states that Mn is less readily complexed by organic ligands than Fe and Al (Laxen et al., 1984; Adriano, 2001). On average, the highest proportions of Mn were extracted with NH$_2$OH·HCl (F2) and associated with the Mn-oxide fraction (34.7% on average; 308 mg kg^{-1}). This result is consistent with those by Rico et al. (2009) and Obrador et al. (2007) for acidic

Table 3
Mean and ranges of metal contents (mg kg⁻¹) for each soil use, which were extracted from each step of sequential extraction, and the sum of the metal concentrations from all steps. For each element, different letters within each row correspond to significant differences (p < 0.05) among uses. The number of samples per land use was 4.

Fractions	Fe Cultivation	Fe Pasture	Fe Forest	Mn Cultivation	Mn Pasture	Mn Forest	Cu Cultivation	Cu Pasture	Cu Forest	Zn Cultivation	Zn Pasture	Zn Forest
F1	263a (203–325)	454a (211–706)	507a (475–543)	36.6a (33.8–41.9)	65.5a (30.4–41.9)	59.5a (32.7–90.69)	< DL	< DL	< DL	2.3a (1.7–3.4)	2.7a (1.6–4.3)	2.1a (1.7–2.7)
F2	583a (464–700)	805a (579–1268)	747a (610–909)	394.2a (327.4–485.1)	341.9ab (251.7–483.9)	188.2b (52.6–340)	< DL	< DL	< DL	< DL	< DL	< DL
F3	4578a (3813–5794)	5334a (3518–7546)	5614a (3766–6483)	261.4a (167.9–370.9)	217.1a (95.9–388.3)	113.6a (28.0–244.4)	6.6a (2.7–11.4)	5.8a (5.2–8.8)	5.6a (3.7–7.1)	4.1a (2.5–6.6)	6.0a (2.6–11.4)	6.9a (5.0–11.3)
F4	124a (112–127)	247a (104–408)	179a (97–265)	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL
F5	8299a (631–12,220)	7269a (794–10,231)	10,308a (8150–11,476)	42.9a (28.1–51.6)	56.8a (29–127.1)	55.6a (27.8–96.5)	19.0a (12.7–19.3)	17.9a (15.7–20.2)	16.0a (12.4–20.7)	9.3a (6.2–10.5)	10.6a (8.7–13.2)	9.1a (7.7–10.2)
F6	25,824a (24,657–27,390)	21,498ab (10,254–29,514)	18,295b (13,811–26,087)	320a (250.1–418.6)	251.8a (167.6–362.5)	207.9a (125.9–274.3)	25.6a (19.7–30.7)	23.7a (21.2–25.7)	21.6a (16.1–26.8)	72.0a (53.1–83.1)	61.2ab (34.8–87.6)	39.7b (35.2–44.9)
Sum of fractions	39,671a (31,983–45,049)	35,607a (27,762–44,953)	35,650a (32,460–42,579)	1055.1a (928–1182)	933.1a (696–1271)	624.8b (327–951)				87.7a (65.8–97.8)	80.5a (57.7–101.3)	57.8b (52.7–61.2)

F1: soluble/exchangeable/specifically adsorbed; F2: Mn oxides; F3: amorphous compounds; F4: oxidizable organic matter; F5: crystalline compounds; F6: residual; DL: detection limit.

agricultural soils from Central Spain, where the contribution of the Mn-oxide fraction comprised 30.9% on average (ranging from 13 to 51%) of the total content. Next to the Mn-oxide fraction, residual phases (30% on average; 259.9 mg kg⁻¹) were the phases with the largest share of Mn in the studied soils, followed by the amorphous Fe-oxide fraction (22.1% on average; 197 mg kg⁻¹). The water-soluble/exchangeable/specifically adsorbed and crystalline Fe oxide fractions, which were present in similar proportions (approximately 6.5% on average), had limited contributions to the total Mn. Therefore, the general trend for the Mn fractions in the topsoil was as follows: Mn bound to Mn oxides > residual amorphous Fe oxides > soluble/exchangeable/specifically adsorbed ≈ crystalline Fe oxides, except for the forest soils, in which the Mn-oxide fraction (30%, 188 mg kg⁻¹) was slightly lower than the residual fraction (33%, 207.9 mg kg⁻¹). On the other hand, the Mn-oxide fraction showed significantly higher values in cultivated soils (mean: 37.4%; 394.2 mg kg⁻¹) than in forest soils (mean: 30%, 188 mg kg⁻¹) and higher values, although not statistically significant, in cultivated soils than in pasture soils (mean: 36.6%; 341.9 mg kg⁻¹) and in pasture soils versus forest soils. The differences between forest use and cultivation could be explained by the differences in the pH and organic matter values between both land uses because the most acidic pH and the largest organic matter content of the forest soils probably facilitate Mn mobilization to other more mobile forms. The larger proportion of soluble/exchangeable/specifically adsorbed fractions in the forest soils (mean: 9.5%, 59.5 mg kg⁻¹) compared to cultivation (mean: 3.5%, 36.6 mg kg⁻¹) could support this hypothesis. However, other processes cannot be excluded. Shuman and Hargrove (1985) showed that soil tillage causes the transformation of soil Mn from exchangeable forms to less mobile oxide and residual forms by increasing aeration. The addition of fertilizers to agricultural soils could also increase the amount of easily reducible forms (Mn oxides).

Simple linear correlation analysis between the Mn fractions and soil components showed a positive relationship between the F1 fraction of Mn (soluble/exchangeable/specifically adsorbed) (r = 0.60, p < 0.05) and clay content in the soil, indicating that clay minerals could retain Mn in the form of exchange cations and/or specific adsorption, while the organic matter content was negatively correlated with the residual fraction (r = −0.58; p < 0.05). On the other hand, Mn that was associated with the amorphous fraction was also negatively correlated with the organic matter content (r = −0.53; p < 0.05). Because the oxalic acid-ammonium oxalate (in the dark) that was used in phase F3 could dissolve both amorphous organic forms and non-crystalline hydrous oxides of Al and Fe (inorganic amorphous compounds) (Shuman, 1982) and release Mn and other metals that are bound to these soil components, the relationship between the amorphous fraction and organic matter could suggest that Mn is preferably associated with amorphous inorganic compounds instead of amorphous organic compounds. A comparison of soil uses revealed that the highest proportions of this fraction were found in cultivated soils (24.8% on average), which agrees with their lower organic matter content, followed by pasture (23.3% on average) and forest soils (18.2% on average).

The presence of up to a mean proportion (for all soils) of 63.5% (559.2 mg kg⁻¹) of total Mn in the first three extracted fractions (in more labile forms) indicates that most of the Mn in the topsoil of the Mero basin was potentially phytoavailable and bioavailable and therefore more likely to be solubilized than the Mn that was associated with the most resistant fractions (F5 + F6). However, only 6.7% of the total Mn content was present in extremely labile forms (F1 fraction). Mn compounds are known for their rapid oxidation and reduction under variable soil environments, so oxidizing conditions may greatly reduce the availability of Mn and associated metals, whereas reducing conditions may facilitate the availability of these elements even up to the toxic range (Kabata-Pendias, 2011). Although the solubilization of potentially bioavailable forms of Mn under current conditions seems unlikely, environmental conditions that induce important changes in redox processes or in acid-
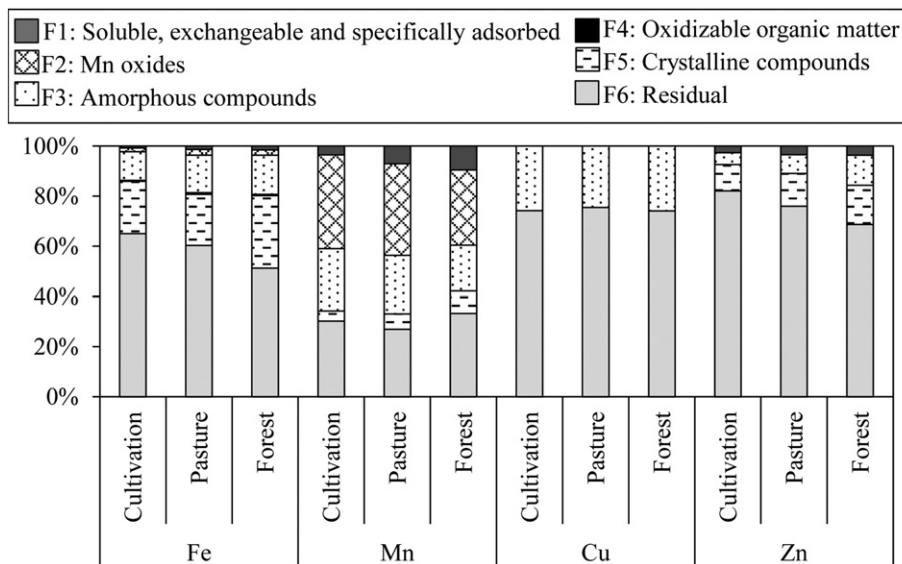
Fig. 2. Mean percentages of the metal forms that were obtained from successive stages of the sequential extraction for different land uses.

base conditions will therefore influence the liberation of this metal into the surroundings (Watmough et al., 2007).

3.3.3. Copper

Cu was only present in the residual and amorphous phases, with a noticeable preference for residual forms (mean for all soils: 74.6%, 17.6 mg kg^{-1}), which accumulate from soil minerals. However, Cu that was associated with amorphous fractions (mean: 25.4%; 6 mg kg^{-1}), which represents the reactive Cu pool and the fraction of potentially more mobile Cu in these soils, still had a noticeable contribution to the total Cu content. The land use did not appear to significantly affect this sequence in terms of the concentration and proportion (Table 3). High Cu contents in residual fractions are often described in soils (McLaren and Crawford, 1973; Ramos et al., 1994). On the other hand, McLaren and Crawford (1973) indicated that the adsorption of Cu to Fe oxides may be an important control of Cu levels. The high surface area and adsorbing capacity of Fe oxides and the ability of Cu to replace Fe (II) in some Fe oxides may be responsible for such adsorption (Taylor, 1965).

The Cu that was extracted in the F3 phase was not correlated with the organic matter and only correlated positively with silt (r = 0.53; p < 0.05), which could suggest that the Cu in the F3 fraction was associated with amorphous inorganic materials. The contribution of this fraction to the total Cu content was comparable to that in the surface horizons of uncontaminated cultivation soils (33%) from other areas of the Galician region (Graña et al., 1991). The relative importance of Cu that is bound to inorganic amorphous fractions compared to the absence of Cu in crystalline fractions can be explained by the lower affinity of crystalline colloids for Cu compared to inorganic amorphous materials (Adriano, 2001; Agbenin and Olojo, 2004). This fact was also reported for uncontaminated cultivation soils in Galicia (Graña et al., 1991), although the differences between the two fractions were less pronounced than those in our soils.

The residual fraction was positively correlated with the total Cu (r = 0.81, p < 0.01), which could indicate a lithological source for the Cu in these soils. The amorphous fraction was significantly correlated with the total Cu (r = 0.60, p < 0.05). This result was expected because noncrystalline hydrous oxides of Al and Fe (together with soil organic matter) were the most active components of the soils in terms of Cu retention. Although numerous authors have described the pronounced tendency of Cu to form highly stable organic complexes (McLaren and Crawford, 1973; Senesi et al., 1989; Barona et al., 1999; Kabata-Pendias, 2011), the Cu distribution in these soils contrasted with the general trend because the distribution was not detectable in the oxidizable

organic matter fraction. The lack of Cu that was bound to organic matter in these soils is consistent with the low values that were reported by Graña et al. (1991) for uncontaminated cultivation soils in Galicia, in which the Cu that was bound to the organic fraction (extracted with sodium pyrophosphate) only reached 5%.

The Cu fractionation results indicate that the residual fraction was predominant and could hardly be mobilized from soil. However, iron oxides in soil can alter Cu mobility (McBride et al., 1998), so one should bear in mind the potential influence of the amorphous fraction, which constitutes the second most abundant Cu fraction in these soils, on the distribution of this metal, especially under more acidic or strongly reducing conditions.

3.3.4. Zinc

Zn followed a similar sequential pattern to Fe but was not detected in the oxidizable and Mn-oxide phases (Table 3), although oxides of Mn, Fe and, to a lesser extent, Al are traditionally considered excellent metal scavengers as either strong adsorbents or co-precipitating matrices (Kabata-Pendias, 2011). Zn was concentrated in the residual fraction (75.6% on average), which suggests that this metal was strongly fixed within crystalline silicate lattices and was not easily mobilized; these results match those of Graña et al. (1991) for uncontaminated cultivation soils in Galicia (66% of total Zn). Other authors such as Ma and Rao (1997) also highlighted the importance of this fraction in uncontaminated soils, measuring up to 98% of its total content. Among the non-residual forms, the crystalline fraction (13.1%) (Al and/or Fe oxides), which is also essentially considered a poorly reactive fraction, and, to a lesser extent, the amorphous fraction (8.1%) prevailed, both with similar values to those from uncontaminated cultivation soils (Graña et al., 1991). The scarcity of crystalline Al compounds in these soils (9.6% of the total Al, estimated by using the same SEP as that in this work) (Palleiro et al., 2016) compared to Fe crystalline forms (23.4% of the total Fe) suggests that the Zn that was incorporated in the crystalline fraction was predominantly associated with crystalline Fe. Other investigators have also reported the dominance of Fe oxide-bound Zn in non-residual forms (Ramos et al., 1994; Nachtegaal and Sparks, 2004; Kabala et al., 2011). Shuman (1976) showed that Fe oxides adsorb considerable quantities of Zn; these oxides may also occlude Zn in the lattice structures. On the other hand, the relative abundance of Zn that is bound to Fe oxides and its absence in Mn oxides, as indicated above, may be explained by the greater abundance of Fe versus Mn in these soils (Table 2). The water-soluble/exchangeable/specifically adsorbed fraction was the smallest fraction of Zn and did not exceed 3.5% (2.4 mg kg^{-1}) of the total Zn on average.

Such a low proportion suggests that only a small fraction of Zn was present in the soils as extremely labile forms, which are the most likely to reach the soil solution in the short term. Even when considering the sum of the most and moderately labile fractions (F1 + F3), the potentially bioavailable fraction of Zn remained low (11%, corresponding to 8.1 mg kg^{-1} of Zn). In contrast, more stable fractions (residual and crystalline Fe oxides) remained high. According to Stanton and Burger (1967), the Fe oxides in soils play a predominant role in limiting Zn availability to plants that grow directly in soil, partially because of the high stability constants of Zn oxides.

The sequence of the Zn distribution was the same for all land uses: residual $\ggg$ crystalline oxides > amorphous compounds > water-soluble/exchangeable/specifically adsorbed. The only significant variation (p < 0.05) between land uses was with the residual fraction, which was lower in forest soils (68.7%; 39.7 mg kg^{-1}) compared to cultivated soils (82.1%; 72 mg kg^{-1}), suggesting a higher liberation of Zn to non-residual fractions in the first because of compensation from a higher proportion of amorphous forms (12% in forests vs. 4.7% in cultivation) and, to a lesser extent, crystalline forms (15.7% versus 10.6%) (Table 3; Fig. 2).

Some correlations were found with respect to the relationship between the Zn fractions and soil properties. Thus, positive and significant correlations between the amorphous fraction and organic matter (r = 0.71, p < 0.01) and negative correlations between the residual fraction and organic matter (r = −0.65, p < 0.05) were observed, which suggests that increases in the organic matter decreased the residual Zn and increased the Zn that was bound to the amorphous fraction. Residual Zn, similar to the total Zn as mentioned in Section 3.2, was also positively correlated with pH (r = 0.73; p < 0.01), which occurred because high pH favors the immobilization of this metal in soil (Sims and Patrick, 1978). An inverse correlation between Zn that was associated with crystalline Fe oxide fractions and the sand content (r = −0.60, p < 0.05) and a positive correlation between this Zn fraction and the silt + clay contents (r = 0.60, p < 0.05) were obtained. These results indicate that the crystalline Fe oxide scavengers of Zn in these soils were among the fractions with fine grain sizes.

In overall terms, the metal fractionation results suggest that the mobility and bioavailability of the four metals (considering the last three fractions) decreased in the following order: Mn (36.5%) > Cu (74.6%) > Fe (82.8%) > Zn (88.7%), which indicates that Mn was potentially more bioavailable than the other metals. The relatively low total metal concentrations and higher percentages of metals in the residual fractions indicate their lithogenic origin and do not generally constitute an environmental risk. The stable nature of these mineralogical compounds and the fact that the metals were bonded firmly within mineral lattices restricted the bioavailability of these metals (Tessier et al., 1979).

3.4. General sediment characteristics

The general characteristics of the river bed sediments are shown in Table 4. The sediments had higher pH than the soils, with an average value of 6.64 (range 6.4–6.8), i.e., close to neutral, with increases in the pH (pHH$_2$O-pHKCl ranged from 1.5 to 2 units) also being greater. The mean organic matter content (9.5%; range: 4.5–19.3%) and mean N content (0.27%) were similar to the mean value of the soils. The C/N ratio was high (mean: 19) and similar to that for the forest soils in the basin. The dominant grain size fraction was the sand fraction (> 60% on average, ranging from 57.4–73.3%), followed by the silt fraction (20.1% on average) and the clay fraction (15.0% on average), providing sandy loam texture that contrasted with silt and silty-loam texture of the soils (Table 1).

3.5. Total metal concentrations in the sediments

The average contents of the total metals in the river bed sediments followed the same order of abundance as in the catchment soils (mg kg^{-1}): Fe (27,737) $\ggg$ Mn (756) $\ggg$ Zn (61.2) > Cu (15.7). However, the metals' concentrations were slightly lower with respect to

Table 4
Summary of the selected properties for the bed sediments.

Sampling points	pH (H$_2$O)	pH (KCl)	Organic matter (%)	Total nitrogen (%)	C/N	Sand (%)	Silt (%)	Clay (%)
S1	6.41	4.86	4.54	0.16	16	69.73	16.8	13.42
S2	6.71	4.68	9.17	0.25	21	73.34	13.80	12.86
S3	6.81	5.02	5.19	0.17	18	59.28	23.90	16.82
S4	6.61	5.12	19.26	0.49	23	57.41	25.72	16.87
Mean	6.64	4.92	9.54	0.27	20	64.94	20.06	14.99

their corresponding average values in both the topsoils (reductions of 25%, 14%, 20% and 33% for Fe, Mn, Cu and Zn, respectively, relative to those of the soils) and C-horizons (Table 2). The coarse texture of the bed sediments may have contributed to the lower retention of metals with respect to the soils (silt and silty-loam textures) because coarse particles are less efficient than fine particles at retaining metals (Horowitz and Elrick, 1987). This phenomenon is attributed to the high specific surface areas of the finest fractions, which consequently favor adsorption processes. Moreover, the average concentrations of metals in the sediments were considerably lower than the flow-weighted mean metal concentrations in the suspended sediment of the Mero River (reductions of 53%, 81%, 95%, and 92% for Fe, Mn, Cu and Zn) (Table 2). The metals showed a concentration factor in the suspended sediments of the Mero River of more than 150% (162% for Fe, 362% for Mn, 709% for Cu and 1687% for Zn) relative to the soils. These results occurred because soil erosion mainly transports finer particles, which contain relatively high concentrations of metals, as has been previously inferred from the positive correlations between the total metal concentrations and the fine fractions of soils. Several studies have shown the importance of suspended particulate matter as a carrier for Fe, Mn and other trace metals in both the Mero Basin (Palleiro et al., 2012, 2014b; Soto-Varela et al., 2014) and other areas (Shafer et al., 1997; Ollivier et al., 2011). No consistent variations in the metal concentrations of the bed sediments were observed along the watercourse (Fe ranged between 24,245 and 33,790 mg kg^{-1}, Mn between 607 and 900 mg kg^{-1}, Cu between 14.9 and 16.4, and Zn between 57.9 and 68.5; Table 5). This fact may indicate a natural origin for these metals, which were mainly derived from erosion, transport, and sediment processes, as is typical in a drainage basin and as reported by Delgado et al. (2010) for another basin in the Iberian Peninsula. The small differences between sampling points could be explained by the greater management of the adjacent lands than the upstream land uses because the basin's landscape is a mosaic of different land uses and because the Mero River has a low transport capacity for suspended sediments, as denoted by the in situ visualization of angular grains. In this basin, the major transfer of metals to the river occurs during flood events, particularly when combined with moments of turbulence in the waters (Palleiro et al., 2014a, b). Similar patterns were observed for nutrients (Rodríguez-Blanco et al., 2010b, 2013, 2015) and metals (Soto-Varela et al., 2015) in the Corbeira catchment.

The total concentrations of Fe, Mn, and Zn in the bed sediments were positively correlated among each other (r Fe-Mn: 0.81, p < 0.01; r Fe-Zn: 0.99, p < 0.01; r Mn-Zn: 0.79, p < 0.05). These correlations may suggest a common origin or a similar geochemical behavior for these metals. In addition, the origins of these relationships can be explained by the interactions or reactions that occur between these metals in soils. The total metal concentrations in the studied bed sediment did not indicate any significant dependence on the pH, grain size or organic matter content, probably because of the insufficient number of cases, although the concentrations of the metals could have also been affected by other components or sediment properties beyond those that were addressed here.

3.6. Sequential extraction of metals in the sediments

The ranges and mean concentrations for each metal fraction are summarized in Table 5, and the average percentages of the fractions

Table 5
Mean and ranges of the metal contents (mg kg^{-1}) for the different fractions from the sequential extraction in the bed sediments. The number of samples was 4.

Fractions	Fe	Mn	Cu	Zn
F1	783	158	< DL	4.3
	522–823	131–201		3.7–5.8
F2	619	170	< DL	2.8
	571–641	61–312		2.5–3.0
F3	2792	45	3.4	4.2
	2656–3016	26–63	2.5–4.3	3.3–5.0
F4	127	< DL	< DL	< DL
	101–164			
F5	4693	23	< DL	7.5
	3494–5895	17–28		6.5–8.9
F6	18,723	360	12.3	42.4
	15,114–23,826	224–561	11.1–13.1	37.5–51.1
Sum of fractions	27,737	756	15.7	61.2

F1: soluble/exchangeable/specifically adsorbed; F2: Mn oxides; F3: amorphous compounds; F4: oxidizable organic matter; F5: crystalline compounds; F6: residual; DL: detection limit.

for each metal are shown in Fig. 3. The metals' distributions in the different geochemical phases of the sediments follow a similar pattern to the soils for Fe, Cu and, to a lesser extent, Zn, both in terms of the order of abundance and the contribution to the total content, while Mn exhibited some differences. Thus, Fe, Cu and Zn were characterized by the predominance of the residual fraction in all the sampling points (Fe: 67.5%, 18,723 mg kg^{-1}; Cu: 78.3%, 12.3 mg kg^{-1}; Zn: 69.3%, 42.4 mg kg^{-1}, on average) and the fraction that was associated with Fe oxides, with crystalline and/or amorphous phases (mainly the crystalline fraction for Fe and Zn and only the amorphous fraction for Cu) being the second most important in the binding of these metals in the sediments, in accordance with the results for the soils. On the contrary, the fraction that was associated with Mn oxides, i.e., with easily reducible oxides, was irrelevant for Fe and Zn and absent for Cu. These findings again show the relative importance of Fe oxides versus Mn oxides in the retention processes of these metals, probably because of the greater abundance of Fe versus Mn in these sediments. The importance of Fe oxides as scavengers of Zn in freshwater sediments was also highlighted by Whitney (1975), among others. A low contribution from the extremely labile fraction (water-soluble/exchangeable/specifically adsorbed) for Fe (2.8%, 783 mg kg^{-1} on average) and a slightly higher contribution from Zn (7%, 4.3 mg kg^{-1}) were observed.

In summary, the distributions of Fe, Cu and Zn were as follows: (Fe): residual > crystalline > amorphous > water-soluble/exchangeable/specifically adsorbed ≈ Mn oxides > oxidizable organic matter; (Cu): residual > amorphous; and (Zn): residual > crystalline > water-soluble/exchangeable/specifically adsorbed ≈ amorphous > Mn oxides.

The distribution of Mn in the sediments exhibited the following sequence: residual (47.5%, 360 mg kg^{-1}) > Mn oxides (22.5%, 170 mg kg^{-1}) > water-soluble/exchangeable/specifically adsorbed (21%, 158 mg kg^{-1}) > amorphous (6%, 45 mg kg^{-1}) > crystalline

(3%, 23 mg kg^{-1}). The most prominent changes in Mn in the sediments with respect to the soils were the considerable decrease in Mn that was associated with amorphous compounds (16% less than in the soil) and, to a lesser extent, Mn oxides (8% less than in soil) and the increase in Mn in the water-soluble/exchangeable/specifically adsorbed fraction. The increase in extremely labile forms of Mn in the sediment may be understood as a result of Mn mobilization in the sediments (Kersten and Förstner, 1989). The Mn was probably solubilized as a result of the reduction of Mn oxides and amorphous compounds, which were subjected to continuous changes in their redox state because of water flow changes and organic matter decomposition. Subsequently, the soluble Mn could have bound to the sediments by ion exchange processes and/or specific adsorption, increasing the levels of Mn in the water-soluble/exchangeable/specifically adsorbed fraction. The solubilization processes of Mn compounds in bed sediments were also reported by Devesa-Rey et al. (2010) for the Anllóns River (NW Spain), where Mn was mainly associated with the exchangeable fraction (obtained by the BCR sequential extraction procedure). Although Fe is also sensitive to reducing conditions, this metal is less susceptible to reduction than Mn (Stumm and Morgan, 1981), which would explain the different behaviors of these two metals in these superficial sediments. The sum of the most mobile fractions (F1 + F2 + F3) for Mn was 49.5% (average 373 mg kg^{-1}) versus 50.5% of the most resistant fractions (residual + crystalline in this case); specifically, approximately half of the Mn in the sediments appeared in potentially bioavailable forms among the extremely labile fraction (water-soluble/exchangeable/specifically adsorbed), which represented a relatively high proportion of the total Mn (21%).

The results of the sequential extraction for the sediments suggest that the mobility and bioavailability of the four metals (considering the last three fractions) decreased in the following order: Mn (50.5%) > Cu (78.3%) > Zn (81.5%) > Fe (84.9%). Thus, Mn was potentially more
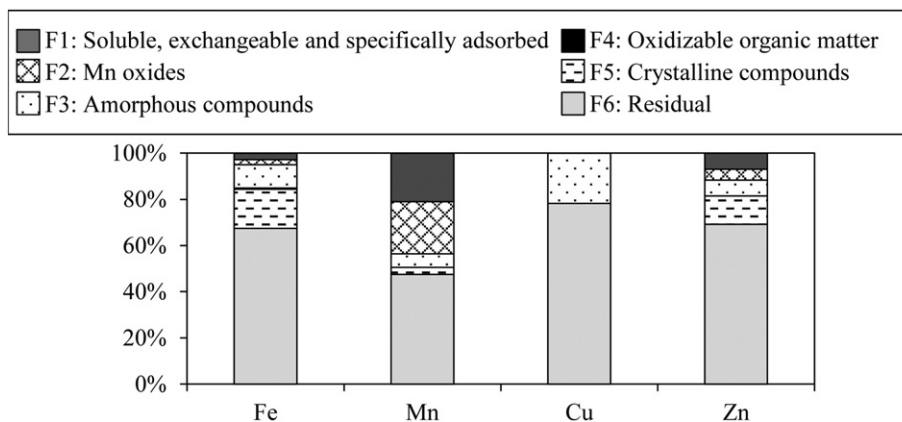

Fig. 3. Fractionation of metals in bed sediments.

bioavailable in the bed sediments (just as in soils) than the other metals and, therefore, more easily available in the water column. Nevertheless, the residual fraction, which was predominant for all these metals, is considered to be more stable, less reactive, and less bioavailable compared to the other solid phase fractions because associated metals are thought to be occluded within the crystal lattices of layer silicates. Trace metals that are tied up in silicate phases or poorly soluble mineral phases such as crystalline Fe oxides are only released after the complete destruction of the matrix. Under the current environmental conditions, these residual phases would not likely be severely attacked even over the long term. Therefore, the presented data suggest that these metals pose no threat to the water quality under the current environmental conditions. Salomons and Forstner (1980) showed that the lithogenous fraction of heavy metals increased in less polluted rivers. The relatively low total metal concentrations and higher percentages of metals in the residual fraction, which are representative of contributions from natural sources, indicate their pedogenic/lithogenic origin.

4. Conclusions

The results from the present study showed that the land uses did not affect the distribution of Fe, Cu and Zn in various geochemical phases in terms of the order of abundance, with Mn only slightly affected. The total metal concentrations were slightly lower in the sediments compared to the soils. The metals' distributions' in the sediments followed a similar pattern to that in the soils, except for Mn. In both cases, the metals were mainly associated with less reactive phases (residual), except for Mn (similarly represented by the residual and Mn-oxide fractions), which is a symptom of the high stability of these metals. Thus, these metals are not readily mobile under the current environmental conditions and hence pose no threat to crops or the water quality. After the residual fraction, Fe oxides were the most important geochemical phase in the transport of Fe, Zn, and Cu, while Mn oxides accumulated a large proportion of Mn. Mn was potentially more bioavailable than the other metals that were examined. The soils and sediments that were studied here cannot be considered polluted in terms of these heavy metals because the prevalence of the residual fraction shows that the metal content was controlled by lithogenic and pedogenic sources. This finding was supported by the relatively low mean levels of these metals in the topsoil versus the mean levels in the C-horizon of the catchment soils.

Acknowledgments

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