



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 km² 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 HNO₃ 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-H₂O) and in KCl (pH-KCl) by using a 1:2.5 soil or sediment/solution ratio. The total

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