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Comparison of EDTA, HCl and sequential extraction procedures, for selected metals (Cu, Mn, Pb, Zn), in soils, riverine and marine sediments

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ABSTRACT

Knowledge of the total concentration of metals in soils and sediments is frequently insufficient to ascertain environmental risk. Simple and sequential extractions are useful tools for estimating the mobility of metals. Many chemical extraction procedures have been proposed in the literature. This study compares the efficiency of three chemical extractions (two single procedures, using EDTA or HCl as reactant, and a sequential chemical extraction) on soils, riverine, estuarine and marine sediments. In the case of riverine sediments and soils, similar results are observed with 0.05 mol.L^{-1} EDTA or 0.2 mol.L^{-1} HCl extractions, whereas 0.2 mol.L^{-1} HCl is inefficient for marine or estuarine samples. Comparison of the results obtained for the various samples, suggests that it is necessary to use a unique procedure for all the samples. The use of 0.05 mol.L^{-1} EDTA rather than 0.2 mol.L^{-1} HCl, as reactant for the single extractions is recommended. The applied sequential extraction procedure is more aggressive than EDTA (except to evaluate Pb mobility for some samples). Assuming that the metal enrichments are mainly of anthropogenic origin and that these metals are of higher mobility, compared to native metals, it is concluded that, for estimation of metal mobility, EDTA leaching is better adapted for Pb, whereas the sequential extraction procedure is better suited for Zn and Cu.

1. Introduction

The occurrence of metals in soils or sediments results from natural weathering processes affecting soils and rocks, also potentially additional anthropogenic inputs. The fate of these metals in the environment depends on several factors, such as soils or sediments properties, (e.g., metal source, loading rate, soil pH, redox potential, texture, organic matter and mineral composition), as well as external factors, such as chemical and biological processes. The metals can be bound in various ways. For example, they may be adsorbed on clay surfaces, or iron and manganese oxyhydroxides, and or, also present in the lattice of residual primary mineral phases (e.g., silicates) and or, secondary mineral phases, such as carbonates, sulphates and oxides. The metals may also be bound in amorphous materials, such as iron and manganese oxyhydroxides, or complexed with organic matter (Gismera et al., 2004; Tessier et al., 1979). Depending on the partitioning of the metal, the labile fraction may be dissolved, due to changes in environmental physico-chemical conditions, or reactions resulting from biological activities, related to microorganisms or plants roots (Abollino et al., 2002; Bourg, 1995; Forstner, 1993; Forstner and Kersten, 1988; Leleyter and Probst, 1999). That means that the mobile metals (in sediments) is concerned metals which could be solubilise due to changes in the physico-chemical properties of the aquatic environment and, on the contrary, residual (or no mobile) metals are associated with very stable fractions of sediments, which can never be solubilised in the natural environment. Hence, knowledge of total metal concentration is not sufficient to evaluate elemental mobility. Determination of their solid fractionation is known to be useful to predict their actual mobility and their fate in the environment (Giancoli Barreto et al., 2004).

Many chemical extraction (leaches) procedures have been proposed in the literature, to estimate the mobility of metals in soil and sediments, or their bioavailability defined as, the capacity of an element to be transferred from a soil fraction, to a living organism, regardless of mechanism (Baize, 1997). Despite the fact that the transfer of metals from soils or sediments to plants represents a major pathway of human exposure to contamination, there is still no agreement as to which extractant most accurately estimates the lability, or the bioavailability, of the metals. The various extractions procedures described in the literature mainly differ by the number of steps of operation. The single leaches (one step) provide inexpensive and rapid assessment methods. Depending on the nature of the reactant used, they fall into three categories (Lebourg et al., 1996; Sutherland, 2002). Firstly, those which employ salts as $CaCl_2$ or $Ca(NO_3)_2$ (e.g., An and Kampbell, 2003; Fang et al., 2007), in order to leach cations adsorbed onto solid materials, due to permanent

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structural charges (phyllosilicates, phyllomanganates and sometimes organic matter). Secondly, techniques which employ acid solutions, in order to simulate the effect of an acid input (e.g. through acid rain or an accidental spill), because low pH favours the dissociation of the existing complexes. The third category consists of those techniques which employ complexing or reducing agents, such as EDTA, (Alvarez et al., 2006; Chao, 1984; Gismera et al., 2004; Madrid et al., 2007; McCready et al., 2003; Sahuquillo et al., 2003).

Dilute HCl is one of the most widely used reagents, in techniques which employ acid solutions to isolate the non-residual phase, in a variety of solid environmental media. HCl is assumed to extract metals on exchange sites, due to its acidic properties, that dissolve calcareous materials, combined to the chelatant property of Cl^- which is a strong ligand. The HCl concentration employed differs within separate studies. Giancoli Barreto et al. (2004) study of metal availability in sediments from Lake Ipê, Brazil, employed 0.1 $mol.L^{-1}$ HCl. The study concluded that HCl extraction might lead to erroneous conclusions about metal associations and lability. Similarly, Wei et al. (2005) concluded that estimating the level of metals taken-up by plants, with 0.1 $mol.L^{-1}$ HCl, can underestimate the intake of lead, because Pb^{2+} readily reacts with chloride, to form a $PbCl_2$ precipitate, that is only slightly soluble in dilute acids or water. In a further study, *Yu* et al. (2004) concluded that 0.1 $mol.L^{-1}$ HCl overestimates soil available Cu, because it releases some Fe/Mn oxide-bound Cu that may not be bioavailable under field conditions. Menzies et al. (2007) conclude that 0.1 $mol.L^{-1}$ HCl extraction is generally poorly correlated to metals plant uptake. Sutherland (2002) indicates that the dilute 0.5 $mol.L^{-1}$ HCl leach is slightly more aggressive than a three steps sequential procedure and that a dilute HCl leach is a valuable, rapid, and cost-effective analytical tool in contamination assessment. Kubová et al. (2008) also propose that 0.5 $mol.L^{-1}$ HCl offers a good reactant concentration, to estimate metal phytoavailability on contaminated soil. In a separate study of marine sediments from Antartica, Snape et al. (2004) recommend a 1 $mol.L^{-1}$ HCl acid extraction as a standard method for assessing metal contamination.

EDTA is one of the most widely used complexing agents because of his high extraction capacity (Sahuquillo et al., 2003). EDTA is assumed to extract metals on exchange sites of both inorganic and organic complexes. Additionally, it can dissolve calcareous materials through complexation of calcium and magnesium (Chao, 1984; Gismera et al., 2004; Sahuquillo et al., 2003). The EDTA leaching seems less questioned than HCl leaching, most of the authors using the same EDTA concentration value (0.05 $mol.L^{-1}$ ETDA), even if 0.02 $mol.L^{-1}$ EDTA is also sometimes reported (Gismera et al., 2004).

Sequential extraction procedures (several steps) do not give direct information about mineralogy but also enable the differentiation of mobile and residual fractions, with the advantage of characterizing the different labile fractions (Leleyter and Baraud, 2006; Leleyter and Probst, 1999; Shuman, 1985; Tessier et al., 1979; Ure et al., 1995). Generally three to height extractants are used in a sequence, the earlier ones are the least aggressive and the more specific, subsequent extractants are progressively more destructive. These sequential extraction procedures are a useful tool for solid speciation of particulate elements, to study the origin, the fate, the biological and physicochemical availability and transport of sorbed elements. As many chemical extraction procedures have been proposed in the literature (Alvarez et al., 2006; Giancoli Barreto et al., 2004; Gismera et al., 2004; Sahuquillo et al., 2003; Sutherland, 2002), the aim of this work is to compare the mobility of Cu, Mn, Zn and Pb, determined by two single leaches (HCl and EDTA) and one sequential extraction procedure (developed by Leleyter and Probst, 1999), applied to soils, riverine, estuarine and marine sediments; thus, to compare three chemical procedures, to estimate the metals mobility, on four surficial deposit types.

2. Experimental

2.1. Sampling

Soils and sediments were collected from various localities in France (Fig. 1). The sampled materials fall into four categories: riverine sediments (RS), estuarine sediments (ES), marine sediments (MS) and soils (S). All the samples were air-dried, then passed through a 2 mm sieve before analysis and stored at 4 °C in polypropylene bottles. The use of air dried materials in this study, does not present a problem, because the sediment samples were collected in oxic conditions (Kersten and Forstner, 1986; Rapin et al., 1986).

2.1.1. Riverine and estuarine sediments

The Vire and Orne rivers and their tributaries drain an area of 3500 km^2 each, (Fig. 1). Five river sediment (RS) samples were collected from the upper basins (water depth about 30 cm). Three estuarine sediments were collected, from the Orne (ES1), Aure (ES2) and Vire (ES3) (water depth about 30 cm).

2.1.2. Marine sediments

One marine sediment (MS-1) obtained from the seawater settling (49°18 N; 00°21 W), was collected in Luc-sur-Mer (Normandie) in the North of France (Fig. 1). Two marine sediments were collected in the Thau lagoon (water depth 8 m) (Fig. 1). This Mediterranean shallow coastal lagoon, a total surface 75 km^2, is a site of an intense shell fish production. The two sampling stations were chosen in contrasting areas. MS-2 was sampled in the middle of the lagoon (43°24 N; 3°36E), MS-3 was sampled from the oyster bank zone (43°25 N, 3°39E).

2.1.3. Soils

Two local soils (S1, S2) submitted to different anthropic pressure were selected. Soil S1 (48°48 N; 00°54 W) was a private garden soil from a rural area. S2 (49°18 N; 00°35 W) was an agricultural soil, periodically amended and/or treated. These surface soils samples were collected from the top 10 cm.

2.2. Extractions procedures

2.2.1. Single extractions

To evaluate the mobile fraction, representative aliquots of each sample were leached by two different chemical reagents. 1 g of dry sediment was leached with 10 mL of extractant solution 0.2 $mol.L^{-1}$ HCl (Kuo et al., 2006) or 0.05 $mol.L^{-1}$ EDTA (Chao, 1984; Sahuquillo et al., 2003), at room temperature and shaken for 1 h. The resulting mixture was filtered at 0.45 μm and the filtrate was analysed using ICP-AES.

2.2.2. Sequential extraction

The samples were also leached by an optimized sequential chemical extraction procedure. This method was chosen among several procedures because it was checked for selectivity, reproducibility, and repeatability of the different steps (for details, see Leleyter, 1998, and Leleyter and Probst, 1999) and it was commonly used in literature (Bur et al., 2009; Cecchi et al., 2008; N'guessan et al., 2009; Salvarredy-Aranguren et al., 2008). This procedure selectively and efficiently dissolves all the chemical constituents of the sediments, in the following fractions $[F_x]$. The water soluble fraction $[F_0]$ is released by ultrapure water. The $[F_1]$ exchangeable fraction is extracted with a magnesium nitrate solution. The acido-soluble $[F_2]$ fraction is leached by an acid/acetate buffer. The reducible fraction $[F_3]$ is extracted with hydroxyl ammonium, oxalic acid and ascorbic acid. The oxidable fraction $[F_4]$ is released by hydrogen peroxide–