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## Fast assessment of bioaccessible metallic contamination in marine sediments

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## ABSTRACT

A fast (16 min) procedure to assess the bioaccessible metallic fraction of Cd, Cr, Cu, Ni, Pb and Zn simultaneously extracted (SEM) from marine sediments plus an indirect approach to determine acid volatile sulfides (AVS) are presented. For the extraction process magnetic agitation was compared with ultrasonic stirring (using a bath and a probe), and several stirring times were assayed. The proposed SEM procedure uses an ultrasonic probe and 1 mL of HCl. It dramatically minimizes the turnaround time and the residues. AVS were evaluated as the difference between the amounts of sulphur in the solid residue after the extraction and total sulphur in the original sample. These procedures are fast, easy to implement and cost-effective to assess the potential risk posed by metals in marine sediments. They were tested using several CRMs and applied to sediments from two Galician Rias (NW Spain); their SEM-AVS differences indicated no biological risk.

## 1. Introduction

The total content of metals in sediments should not be the unique criterion to set their potential risks to the aquatic ecosystems as the levels of toxicity and bioaccessibility might not coincide with it. Quantifying the accessible (or labile) metal fraction in sediments is a better indication on their quality (Larner et al., 2008). There were recent attempts to clarify what bioavailability of a compound is. The so many viewpoints yielded a ‘semantic stumbling block’ communication across sciences (Semple et al., 2004). Recently, IUPAC defines bioaccessibility (i.e., the potential for a substance to come in contact with a living organism and then interact with it) and bioavailability (i.e., the extent of absorption of a substance by a living organism compared to a standard system). Both terms depend on chemical fractionation and biological properties of the substance (Nordberg et al., 2010) and are particularly important in relation to substances present in soils, sediments, aerosols, and other particulate matter to which humans may be exposed.

So far, there is not a uniform, broadly accepted methodology to measure the fraction of metals implied in such definitions despite relevant institutions, such as USEPA or ICMM (Environmental Protection Agency US, 2005; Parkman, 2007; Tarazona et al., 2014), tried to establish sediment quality guidelines (SQGs) (MacDonald et al., 2000). Several analytical procedures have been applied to evaluate the accessible metallic fraction in sediments, including sequential and partial (single) extractions (Villanueva et al., 2013). The first sequential extraction proposed by Tessier (Tessier et al., 1979) is still used (Anju and

Banerjee, 2010). Nevertheless, a lot of modifications have been proposed and thus sequential extraction schemes vary widely in number of steps, reagents and extraction conditions (Rao et al., 2008). For this reason it is very difficult to establish meaningful comparisons between results obtained in different laboratories. Worst, a detailed interpretation of the data generated in the studies is unusual and only the amount of metal associated with a certain phase is given (Bacon et al., 2008).

In addition, the level of harmonization across different regional monitoring marine frameworks in the European Union is rather low (Tornero and Hanke, 2016). In response to the need for standardization, the Standards, Measurements and Testing Programme, SM & T (formerly BCR) of the European Commission developed a sequential extraction protocol (Quevauviller et al., 1994) for sediments which was amended later (Rauret et al., 1999). Nevertheless the overall sequential extraction protocols are labor-demanding and time-consuming, usually about 50 h are required to extract three or four individual phases, being its application to a large number of samples lengthy and costly (Madrid et al., 2007) and, worst, the fractions extracted are only defined operationally (Hlavay et al., 2004).

Partial (single) extractions constitute a simple and cost-effective approach to determine the labile metals in sediments, which make them suitable for incorporation into routine assessment programs. A variety of reagents were reported although they can be classified into three groups: dilute solutions of strong mineral acids, weak acids and solutions of complexing agents or reducing agents (Sutherland and Tack, 2008; Larner et al., 2006). Among them, diluted HCl outstand to solubilize the metallic accessible fraction from the more resistant phases

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in sediments (Snape et al., 2004). Several concentrations, agitation modes and times were proposed, although their validation is cumbersome because no reference material exists with certified values for such a procedure and, so, several strategies were undertaken.

Sutherland et al. (Sutherland, 2002) compared first time the single HCl procedure to the BCR sequential extraction concluding that the latter was no advantageous for quantitation purposes. They set that HCl-extraction was useful as a screening technique to monitor metals in disturbed environments (Sutherland and Tack, 2008). Similar results were reported by Larner et al. (Larner et al., 2006) when analyzing the NIST 2711 CRM and they highlighted the applicability of their method to large sample sets (Larner et al., 2008). Several authors found that the extraction efficiency of the HCl single extraction depends on the composition of the samples and on the nature of the elements (Choi et al., 2012).

Diluted HCl was proposed to generate the acid volatile sulfides (AVS) and to lixiviate the so-called simultaneously extractable metals (SEM) in order to evaluate the bioaccessibility of some divalent metals in aquatic sediments. The AVS is an operational concept defined as the sulfide that evolved from a sediment sample after its treatment with diluted HCl. A large variety of SEM-AVS extraction techniques have been developed employing cold (Brumbaugh and Arms, 1996; Machado et al., 2004) and hot HCl (Zhuang and Gao, 2013), at different concentrations (Rickard and Morse, 2005). Sulfides have been determined by gravimetry (Di Toro et al., 1990), ion-selective electrodes (Leonard et al., 1996) and spectrometry (Silva et al., 2001). Nowadays, the U.S. Environmental Protection Agency (US-EPA) and the European Union established sediment quality guidelines in accordance to the SEM-AVS subtraction (Environmental Protection Agency US, 2005; Environmental Protection Agency US, 1991). Disappointingly, Hammerschmidt and Burton (Hammerschmidt and Burton, 2010) verified the irreproducibility of the results among laboratories for both parameters using an interlaboratory study, highlighting the need for improving quality control and standardization.

The aim of this study is, first, to propose a fast and reliable procedure to assess the bioaccessible SEM fraction of Cd, Cu, Cr, Ni, Pb and Zn leached by diluted HCl ( $1 \text{ mol L}^{-1}$ ) in marine sediments; and, second, to evaluate AVS with a fast approach by comparing the sulphur contents in both the solid residue after the extraction and the original sample. To account for the first objective, magnetic agitation was compared with ultrasonic stirring (using both a bath and a probe), and several stirring times were assayed. The metals were quantified by inductively coupled plasma-mass spectrometry (ICP-MS). The leached fraction was correlated with the sum of the 3-step sequential extraction procedure of the SM & T, analyzing the BCR-701 sediment to validate the method. In addition, two reference sediments with certified total metal contents were analysed. As a practical case study, sediments from two economically relevant Galician Rias (Rias of Arousa and Vigo, NW of Spain), were analysed and toxicologically evaluated using the SEM-AVS criterion.

## 2. Materials and method

### 2.1. Field sampling

Sediments were collected in 2011 in two economically relevant Galician estuaries (Northwest Spain), namely the Rias of Arousa and Vigo (Fig. 1). They were freeze-dried, sieved through a 2 mm mesh and kept in dark bottles until analysis. The Galician Rias were defined (Evans and Prego, 2003) as incised valleys where the estuarine zone can fluctuate according to climatic changes. These sites are particularly suitable for evaluation of coastal contamination because they are exposed to increasingly dense population as well as industrial and aquaculture activities (Prego and Cobelo-García, 2003). The samples were provided by the Spanish Institute of Oceanography (IEO).

### 2.2. Single-step extraction procedures

The agitation of the slurry (sediment plus diluted acid) favors the lixiviation of the available metals and reduces the extraction time. Here, magnetic and ultrasonic agitation (bath and probe) were compared considering different stirring times usually reported in literature (Larner et al., 2008; Sutherland and Tack, 2008; Duzgoren-Aydin et al., 2011). For magnetic and ultrasonic bath the times assayed were 20 min, 1 h, 2 h, 3 h and 4 h; and for ultrasonic probe agitation they were 0.5, 2, 4, 8 and 12 min. All assays were quadruplicated. For the first, 'magnetic stirring-assisted extraction' procedure -MSEP-, 0.250 g of sediment were accurately weighted directly in a glass beaker (50 mL) and 10 mL of  $1 \text{ mol L}^{-1}$  HCl were added. Up to twelve samples were treated simultaneously in a Multipoint Magnetic Stirrer system model ANM-10112 (Science Basic Solution, Barcelona, Spain). For the second procedure 'ultrasound bath assisted extraction' (UBEP), 0.250 g of sediment were weighted into glass test tubes (20 mL), 10 mL of  $1 \text{ mol L}^{-1}$  HCl were added and, then, a rack with 12 tubes was introduced into the ultrasound bath (model 3,000,513 of Selecta Barcelona, Spain) refrigerated with tap water. The final slurries were filtered and stored in polyethylene bottles at  $4 \text{ }^\circ\text{C}$  until their analysis.

For the third procedure, the 'ultrasound probe assisted extraction' (UPEP), 0.025 g of sediments were weighted directly into polyethylene cups (1.2 mL) and 1 mL of  $1 \text{ mol L}^{-1}$  HCl was added. The cups were closed, the titanium probe (VC 50-1, Sonic Materials) was introduced through a cap hole and the slurries were sonicated at 40% power (maximum 50 W) for 0.5 to 20 min. The supernatant was filtered and the extracts were stored in polyethylene cups at  $4 \text{ }^\circ\text{C}$  until analysis. The extracts of the samples were diluted (to 4 mL) for analysis.

All procedures were tested with the 3-step BCR-701 CRM. Procedural blanks were obtained following the whole protocol. The method selected finally was applied also to analyze two additional sediment CRMs (with certified total metal contents): New York/New Jersey waterway sediment SRM-1944 (National Institute of Standards & Technology, USA) and harbour sediment PACS-2 (National Research Council of Canada). In addition, the 3052 USEPA method (Environmental Protection Agency US, 1999) was used to determine the total metal contents of the BCR-701, which had not been reported in the certificate.

### 2.3. Acid volatile sulfides procedure

The acid volatile sulfides in sediments were indirectly estimated as the difference between total sulphur and non-volatile sulphur. Total sulphur was measured directly in lyophilized sediments whereas non-volatile sulphur was determined in the solid residue obtained after the HCl extraction, drying it at  $40 \text{ }^\circ\text{C}$  during 48 h. Both sulphur determinations were performed on an EA 1112 Thermo Finnigan Flash analyser (2 mg aliquots). The method was validated using the BCSS-1 and PACS-2 CRMs.

### 2.4. ICP-MS measurements

A Thermo Scientific XSERIES 2 Quadrupole ICP-MS was employed for metal determination. The operating conditions are given in Table 1. The following atomic masses were selected for quantitation by ICP-MS: 52Cr, 60Ni, 65Cu, 66Zn, 111Cd and 208Pb. The internal standards used were: 45Sc for Cr, Cu and Zn; 72Ge for Ni; 103Rh for Cd; and 209Bi for Pb. The linearity (straight line behavior) of the response was evaluated for each metal. For Cd and Ni good linearity was achieved up to  $200 \text{ } \mu\text{g L}^{-1}$  while for Cr, Cu and Pb it extended up to  $2000 \text{ } \mu\text{g L}^{-1}$ . The quantitation methodology was evaluated comparing direct calibration and the standard addition methods. For the target metals, the slopes did

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