

COMPARATIVE STUDY FOR THE ASSESSMENT OF HEAVY METAL MOBILITY IN MARINE SEDIMENTS

Ioanna DAMIKOUKA¹ and Alexandra KATSIRI²

¹ National School of Public Health, Department of Sanitary Engineering and Environmental Health, 196 Alexandras Avenue, 11521, Athens, Greece

² National Technical University of Athens, School of Civil Engineering, Division of Water Resources and Environmental Engineering, Athens, Greece
e-mail: idamikouka@esdy.edu.gr

EXTENDED ABSTRACT

For the assessment of metal mobility in marine sediments a modified version of the Tessier sequential extraction procedure (SEP) scheme is compared and correlated with a leaching test using dilute hydrochloric acid (HCl). The Tessier scheme employs five sequential extraction steps in which extraction solutions with increasing extractability are applied in sequence. This SEP is applied so as to determine five binding fractions of heavy metals in the sediments: the exchangeable fraction, the bound to carbonates fraction, the bound to manganese-oxides fraction, the bound to iron-oxides fraction and the bound to organic matter fraction of metals in sediment. All these fractions are considered potentially mobile and bioavailable. Whether mobilization will actually occur, depends on a large number of additional environmental factors. Leaching with dilute HCl can be applied for the assessment of metal mobility in sediments. The results from the leaching procedure are compared with the metal concentrations from the sum of the modified Tessier SEP. In this leaching test, the sample is stirred with 1 M HCl for one hour. The two procedures were applied to marine sediments excavated from the port of Piraeus in Greece and to a Certified Reference Material CRM BCR 701, which is certified as to the concentration of extractable trace elements in sediment following the BCR sequential extraction procedure.

For the CRM 701, the concentrations of metals in the dilute HCl leachant were similar to the sum of concentrations of each metal in the five binding fractions. However this similarity doesn't apply to the natural sediments, where there are differences between the concentrations of metals in the HCl leachant and the sum of concentrations of each metal in extractants from SEP. The correlation coefficient between the concentration of the metals in the acid extraction and the sum of the concentrations of the metals in the binding fractions, shows that there is a very good correlation between the concentrations in the case of copper, and a good correlation in the case of zinc and lead.

Both methods can be used for the assessment of potential bioavailability of elements. In some cases, the partial extraction with dilute HCl could be an alternative for the SEP, because it is simple, quick, economical, and therefore more easily applicable in the case of many samples, and targets the more mobile, labile and bioavailable phases of the metals in sediments. However, the differences in the characteristic of sediments and the fractionation analysis which is achieved with the SEP don't allow its general substitution with the leaching test.

Keywords: Marine sediments, heavy metals, sequential extraction, leaching test HCl

1. INTRODUCTION

Management of dredged contaminated sediments from coastal areas is a critical issue. Most management decisions are based on total pollutant concentrations, without taking into consideration any discrimination between the potential bioavailable and the non-mobile fractions of the metals in the sediments. The concentration of total or dissolved metals cannot be used for the prediction of bioavailability and acute toxicity, because not all of the metal appears to be bioavailable (Meyer, 2002). Furthermore, total metals should not be used for the assessment of environmental impact of metals, because in this case the knowledge of the relative available fraction of the metals in sediments is important (Smith, 2011). Several leaching tests and sequential extraction procedures have been designed and implemented with the aim of deducing information on the mobility and bioavailability of trace elements in soils and sediments.

SEPs employ different extractions steps, and are applied for the evaluation of the mobility of metal ions by fractionating into different mineralogical phases. Sequential extraction analysis can provide a decision-making tool for the evaluation of potential disposal options and the re-use of dredged sediments (Petrucci *et al.*, 2011). Although a large number of different protocols have been reported in the literature (Bacon and Davidson, 2008), the schemes proposed by Tessier *et al.* (Tessier *et al.*, 1979) and the protocol designed by the Commission of the European Communities Bureau of Reference BCR (Quevauviller *et al.*, 1994) are the most widely used.

However, little is known about the relationship between the labile phases removed by sequential extraction procedures and those liberated by single leaching tests (Sutherland, 2002). Furthermore, there is no correlation between the different protocols of SEPs or the leaching tests. The difficulties in the applications of SEPs, the lack of harmony between the different SEP methods, the cost, the significant long duration of the whole procedure as well as the difficulties in the chemical analysis of the extractants, motivate examination of alternative methods.

Partial extractions (Tessier and Campbell, 1987), and in particular the extraction with 1 N HCl (Bryan and Langston, 1992), have been shown to correlate better with the metal levels in benthic organisms than total metals. Dilute HCl is one of the most common extraction solutions and is used for the assessment of the mobility (Quevauviller *et al.*, 1996) and of the fraction of metals of anthropogenic origin (Abu-Rukan and Ghrefat, 2001). It has the ability to extract the most mobile phases of metals, without attacking silicates and the residual fraction (Agemian and Chau, 1976; Malo, 1977; Snape *et al.*, 2004; Sutherland, 2002). It can remove the adsorbed trace elements from the different mineral phases and decompose the carbonates, the ferromanganese minerals (Chester and Hughes, 1976; Cronan, 1976), the colloidal and labile organic phase of the sample (Agemian and Chau, 1977; Chester *et al.*, 1985; Luoma and Bryan, 1981), as well as the amorphous sulphide, which controls the bioavailability of metals in anoxic and suboxic sediments (Allen *et al.*, 1993; Ditoro *et al.*, 1990).

Some studies have been published and compare HCl single extraction and BCR SEPs in reference materials, soils (Ahumada *et al.*, 2004; Kubova *et al.*, 2004; Kubova *et al.*, 2008; Larner *et al.*, 2006; Larner *et al.*, 2008;) and sediments (Dassenakis *et al.*, 2003), and estimate the extractability of metals (Cu, Pb and Zn) by both methods (Madrid *et al.*, 2007).

The aim of this study was to compare and correlate a modified version of the Tessier SEP scheme, and total metal analysis with a leaching test using dilute HCl applied in marine sediments and in CRM 701.

2. MATERIALS AND METHODS

2.1. Sample Collection and Handling

Marine sediments were excavated from the port of Piraeus, Greece. Sediment samples were obtained using a stainless steel grab sampler from several stations in the port of Piraeus. The samples were collected in 2 different periods in 2007. After sampling, samples were placed in plastic containers fitted with a tight lid and transported to the laboratory for subsequent analyses. All sediments were kept in closed airtight containers under nitrogen atmosphere at 4°C.

2.2. Instrumentation and Reagents

The determination of metals—Cu, Zn, Pb – was performed by air/acetylene flame atomic absorption with a Perkin Elmer AA Analyst 100 atomic absorption spectrometer.

Nitric Acid (HNO₃) 70% and Hydrochloric Acid (HCl) 30%, used in the extraction and the leaching test were suprapur grade for trace analysis (Merck). Hydrogen peroxide (H₂O₂) solution 30% was TraceSelectUltra grade for Trace analysis (Fluka). All other chemicals were of analytical reagent grade. All glassware were pre-cleaned and acid-washed with 10% nitric acid before use and then rinsed with ultrapure water.

Working standard solutions of copper, lead, zinc, were prepared daily by dilution of certified stock standard solutions (1000 mg/L, CertiPUR, Merck). Quantification was achieved using matrix-matched standards. Relative standard deviations on triplicate analysis were below 5% for all elements. The concentrations of metals were reported on a dry mass basis, by drying a portion of sediment to constant weight at 105 °C for 24 hours.

2.3. Single Extraction Test

The leaching test with dilute HCl is performed for the assessment of metal mobility in sediments. In this leaching test, the sample, approximately 10g of wet sediment, is stirred with 120 ml of 1 M HCl, for one hour at room temperature (20±5 °C). At the end of the leaching cycle, the supernatant was collected, filtered through a 0.2 µm membrane filter (Pall), and stored at 4°C until analysis of metals by atomic absorption.

2.4. Sequential Extraction Procedure

Sequential extractions were performed using a modified version of the Tessier scheme (Tessier *et al.*, 1979; Belzile *et al.*, 1989). The phases and the reagents used are referred to in table 1.

Table 1. Reagents and conditions employed for the modified Tessier sequential extraction procedure

Phase	Reagent and conditions
Exchangeable metals	1 M MgCl ₂ , at pH 7.0, continuous agitation for 30 min at room temperature
Bound to carbonates	1 M sodium acetate (NaOAc), adjusted to a pH 5.0 with acetic acid (HOAc), continuous agitation for 5 h at room temperature
Bound to manganese-oxides	0.1 M hydroxylammonium chloride (NH ₂ OH.HCl) in 0.1 M HNO ₃ , with continuous agitation for 30 min, at room temperature
Bound to iron-oxides	0.04 M NH ₂ OH.HCl in 25% acetic acid, at 96±3 °C, for 6 h, with occasional agitation
Bound to organic matter and sulfides	0.02 M HNO ₃ and 10 mL of 30% hydrogen peroxide (H ₂ O ₂) adjusted to pH 2 with HNO ₃ for 2 h at 85°C with occasional agitation. A second 10 mL-aliquot of 30% H ₂ O ₂ (pH 2 with HNO ₃) was added and the sample was heated again at 85°C for 3h with intermittent agitation. After cooling, 15 mL of 3.2 M ammonium acetate in 20% HNO ₃ was added and agitated continuously for 30 min at room temperature.

Quality control was achieved by analysis of a certified reference material (sediment) for extractable metals, BCR 701, (Certified Reference Material, European Commission, Brussels) certified by the three step BCR sequential extraction procedure. A good agreement between measured and certified values was achieved.

3. RESULTS AND DISCUSSION

The table 2 presents the mean concentration of metals, Zn, Pb, Cu, in mg/kg dry sediment, in each fraction applying the SEP, and the mean concentration of metals applying the leaching test with 1 M HCl at the CRM 701 and the calculated extraction yield (%). Samples were run in triplicate. Results are compared with the results of a similar leaching test with 0.5 M HCl at the CRM 701 (Kubova *et al.*, 2008).

Table 2. Concentration values in each fraction applying the Tessier SEP scheme and the acid leaching test 1 M HCl, in CRM 701 (mean± standard deviation)

CRM 701	Zn (mg Zn/ kg dry sediment)	Cu (mg Cu/ kg dry sediment)	Pb (mg Pb/ kg dry sediment)
Exchangeable	18.4±1.1	4.7±0.2	12.3±1.4
Bound to carbonates	146.7±10.1	53.9±1.6	23.6±1.4
Bound to Mn-oxides	0.4±0.0	2.7±0.1	5.4±2.2
Bound to Fe-oxides	140.0±11.6	4.4±0.3	55.5±1.5
Bound to organic matter and sulphides	60.0±3.1	162.2±1.1	62.2±1.3
Calculated Sum	365.5±10.6	228.0±2.6	159.1±1.4
Total ^a	364.7	228.5	138.48
1 M HCl	264.0± 7.8	214.4±4.6	134.6±3.8
Extraction yield (%)	72	94	97
0.5 M HCl for 1 hour (Kubova <i>et al.</i> , 2008)	365±1	216±4	129±1

^a Certified values for CRM 701

In the case of marine sediments, a least-square correlation analysis was conducted, between the concentration of the metals in the acid extraction and the sum of the concentrations of metals in the 5 different binding fractions, presented in Figures 1a-c , and between total metals and the concentration of metals in the HCl leachant, presented in Figures 2a-c.

The concentrations of total metals have been published in a previous work (Damikouka and Katsiri, 2009).

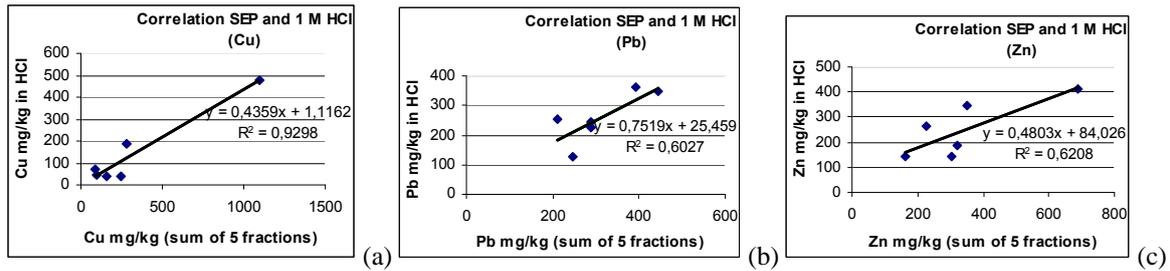


Figure 1: X-Y correlation plots comparing the acid leaching and the sequential extraction procedure for (a) copper, (b) lead, (c) zinc

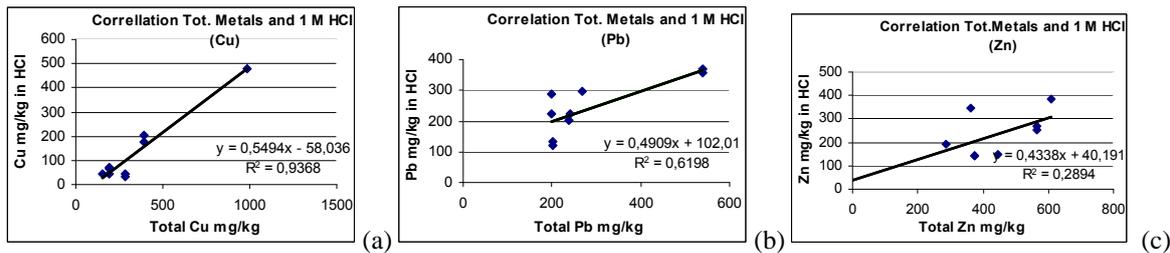


Figure 2: X-Y correlation plots comparing the acid leaching and the total metal analysis for (a) copper, (b) lead, (c) zinc

Correlation between the acid leaching procedure and total metal analysis is positive and very good for copper ($R^2=0.9368$) and good for lead ($R^2=0.6198$), but there is poor correlation in the case of zinc ($R^2=0.2894$). For CRM 701, the percentages of the extraction yield for each metal were higher than 70%, and the concentrations of metals in the leachant were similar to the sum of concentrations of each metal in the different binding fractions, except in the case of zinc. However this similarity doesn't apply to the natural sediments. Between the concentration of the metals in the acid extraction and the sum of the concentrations of the metal in the binding fractions, there is a positive and a very good correlation between the concentrations in the case of copper ($R^2=0.9298$), but the extraction yield ranges between the samples (17-78%). Cu is found mostly in the fraction bound to organic matter and sulphides (Damikouka and Katsiri, 2009). However, the extraction yields of dilute HCl aren't very satisfactory in all the samples, and this could be attributed to the ability of dilute HCl to decompose mainly the labile organic phase of the sample which is a portion of the organic matter, and not all the organic matter. In case of lead and zinc, there is a good correlation ($R^2=0.6027$) with a better range of extraction yields (50-105%), and $R^2=0.6208$, with a range of extraction yields (47-98%), respectively. The extraction with dilute HCl underestimates the amounts of elements extracted by SEP. Similar conclusions were reached by others researchers (Madrid et al., 2007). These differences between the concentrations of metals in the HCl leachant and in the sum of concentrations of each metal in extractants from SEP are attributed to differences in the composition of sediments which might demand changes in the duration of the leaching procedure or an increase in the strength of the leachant solution.

4. CONCLUSIONS

Both methods can be used for the assessment of potential bioavailability of elements. A leaching procedure with dilute HCl can be applied as a screening tool for environmental and management purposes. So, in some cases, partial extraction with dilute HCl could be an alternative for the SEP, because it is simple, quick, economical, and therefore more easily applicable in the case of many samples, and targets the more mobile, labile and bioavailable phases of the metals in sediments. However, the differences in the characteristics of sediments and the information from the fractionation analysis of metals achieved with the SEP which categorizes metals into

different chemical forms likely to be released under various environmental conditions, don't allow its general substitution with the acid leaching tests.

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