

# Comparison of three procedures (single, sequential and kinetic extraction) for mobility assessment of Cu, Pb and Zn in harbour sediments

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## Abstract

The mobility of Cu, Pb and Zn in harbour sediments was investigated using single, sequential and kinetic extraction techniques. Each type of extraction provides different information on the mobility of these elements in the environment. The single HCl extraction assesses general mobility, the sequential extraction assesses geochemical partitioning and kinetic extraction allows quickly and slowly mobilized elements to be identified. Kinetic extraction also allows the influence of extraction duration to be assessed. The results presented in this paper highlight the complementary information provided by different types of mobility study.

## 1. Introduction

Marine and estuarine harbour sediments are often subject to anthropogenic impact including elevated concentrations of potentially toxic metals such as Cu, Pb and Zn. The degree of metal association with the distinct geochemical phases in a sediment depends on the binding capacity and physico-chemical characteristics of those phases. Lability studies are conducted order to estimate the mobile metal fraction. These use various chemical extractions to assess metal mobility which is equated to the potential bioavailability of those metals (Da Silva *et al.*, 2002 ; Giancoli Barreto *et al.*, 2004 ; Gismera *et al.*, 2004 ; El Azim et El-Moselhy, 2005 ; Singh *et al.*, 2005). Chemical extraction procedures follow two approaches: the thermodynamic approach and the kinetic approach. Unlike the thermodynamic approach, the kinetic approach uses different extraction times to assess the time frame of element mobilisation.

Extraction using a single reagent is a simple and cost-effective way to investigate the labile metals in soils and sediments. Numerous reactants may be used for single extractions, these generally fall into three categories: acids, unbuffered salts and complexing reagents. Single or mixed dilute acids are often used to estimate the mobility of elements (e.g. 0.10 mol.L<sup>-1</sup> CH<sub>3</sub>COOH (Lebourg *et al.*, 1996), 1.00 mol.L<sup>-1</sup> HCl or a mixture such as 0.05 mol.L<sup>-1</sup> HCl and 0.0125 mol.L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> (Mulchi *et al.*, 1992). HCl is assumed to extract metals due to its acidic properties and the chelant property of Cl<sup>-</sup>. HCl has been studied extensively in lability studies and is recommended by many authors (Duinker *et al.*, 1974, Scouller *et al.*, 2006, Doherty *et al.*, 2000), a concentration of 1.00 mol.L<sup>-1</sup> is suggested for harbour sediments (Szefer *et al.*, 1995; Burton *et al.*, 2005; Santos *et al.*, 2010; Larner *et al.*, 2008; Leleyter *et al.*, 2012).

Sequential extractions are widely used to investigate the association between heavy metals and the different mineral and organic phases in sediments. Results can be used to predict the mobility and potential bioavailability of the metals. The technique uses reagents to carry out successive leaching of specific geochemical fractions and several different protocols are proposed in the literature. The first, developed by Tessier *et al.* (1979), proposed a five-step extraction to establish the different fractions to which the elements are sorbed. Subsequent authors including Ure *et al.* (1993, Rauret *et al.* (1998) and Leleyter and Probst (1999) have adapted this protocol by using other reagents or by adding or

reducing the number of steps in order to improve the efficiency and selectivity of the protocol. However, the sequential extraction protocols are criticized about the lack of selectivity and re-adsorption phenomena of the elements (Gomez-Ariza, 1999; Gleyzes, 2002). Moreover, the element mobility is assessed in specific physicochemical conditions imposed by the chemical reagents used.

The optimum contact time between sediment and reagent corresponds to the time taken for maximum extraction of the elements and is determined using kinetic extraction (Yu and Klarup (1994), Lin and Chen (1998), Fangueiro *et al.* (2002), Gismera *et al.* (2004), Labanowski *et al.* (2004). Single and sequential extractions assume that the reaction equilibrium is reached by the end of the extraction period; however optimum contact times determined by kinetic extraction can be longer than those recommended for single and sequential extractions (Abi Ghanem, 2008). Moreover, kinetic extractions allow fast and slow metal mobilisation to be distinguished (Bordas and Bourg, 1998; Bermond *et al.*, 2005). Several kinetic models that differentiate this temporal mobilisation have been proposed in the literature, including the Elovich equation, the two-compartment model, the diffusion model and an equation with two constants (Abi Ghanem, 2008). Fangueiro *et al.* (2005) assert that the two-compartment model has the advantage of separating the elements into three distinct categories; Q1: quickly mobilised, Q2: slowly mobilised and Q3: not mobilised. Gismera *et al.* (2004) and Labanowski *et al.* (2008) use EDTA as an extractant because it is non-specific (only cations) and can therefore mobilise a large number of elements, it is also capable of extracting metal bound to organic matter, carbonate and Fe and Mn oxides providing good long-term prediction of metal bioaccessibility from these different sediment phases. Cornu *et al.* (2004) and Gismera *et al.* (2004) consider that the kinetic approach is complementary to sequential extractions and helps to expand understanding of the geochemical speciation of elements.

The objective of this study is to compare different procedures in order to assess the mobility of Cu, Pb and Zn in marine harbour sediments collected in the English Channel. These metals are often present at elevated levels in harbor sediments due to pre-industrial deposition (Chiffolleau *et al.*, 1999; Pirrie *et al.*, 2002; Hamdoun, 2013). The mobility will be studied using thermodynamic and kinetic extraction techniques.

## **2. Materials and methods**

### **2.1 Sample collection**

Marine sediment samples were taken from the harbours of Ouistreham, France (S1), Concarneau, France (S2) and Pool, UK (S3) harbours between March 2010 and June 2011. Each harbour was sampled at one GPS point using a grab or a suction dredger, water depths ranged from 4 to 11 meters. On return to the laboratory, samples were homogenised, air-dried for 4 days, sieved at 500  $\mu\text{m}$  using a nylon sieve and ground with an agate pestle and a mortar.

### **2.2 Total concentrations**

To determine the pseudo-total metal content present in the samples, a microwave assisted aqua regia acid digestion was performed on 0.2 g of dry sediment (3.33 mL of HNO<sub>3</sub> NORMAPUR 65% and 6.66 mL of HCl technical 35% VWR) (Alloway, 1995). Hereafter pseudo-total metal concentrations will be referred to as total metal concentrations. Each acid digestion was performed in triplicate. Analysis of standard certified material HR-1 (Canada Centre for Inland Waters National Laboratory for Environmental) showed satisfactory recovery for the elements of interest, the values obtained are shown in Table 1 after microwave-assisted (Berghof Speedwave MWS-2) acid digestion (Table 2).

Table 1.

Element recovery for certified sediment HR-1 after microwave-assisted (Berghof Speedwave MWS-2) acid digestion (Cu, Pb and Zn in mg.kg<sup>-1</sup>)

|                                   | Cu          | Pb          | Zn        |
|-----------------------------------|-------------|-------------|-----------|
| HR-1 certified values             | 81.2        | 134         | 1136      |
| Acid digestion (three replicates) | 68.4 ± 12.8 | 113.6 ± 9.2 | 1003 ± 88 |

Table 2.

Program mineralization (Power: 1000w)

| Step | Power | Temperature | Time   |
|------|-------|-------------|--------|
| 1    | 80%   | 175°C       | 20 min |
| 2    | 40%   | 100°C       | 20 min |
| 3    | 40%   | 80°C        | 10 min |

## 2.3 Mobility determination

### 2.3.1 Single extractions

The single extractions were performed as batch extractions. 1 mol.L<sup>-1</sup> HCl was used with a ratio of 10:1 (liquid: solid), shaken for 1h at room temperature. After filtration (0.45 µm HVLP with syringes), the solution were stored at 4 °C (acidified with 5 % of HNO<sub>3</sub>) until chemical analyses. Each extraction step was performed in triplicate.

### 2.3.2 Sequential extraction

The procedure used (Leleyter and Probst, 1999; Leleyter and Baraud, 2005) allows seven mineralogical fractions to be distinguished successively. The sum of these seven fractions represents the operationally defined “labile fraction” for this technique. Operating conditions for the sequential extraction are summarised in Table 3. Each extraction step was performed in triplicate.

Table 3.

Sequential extractions procedure (order: F1 to F5)

| Fraction                  | reagent  | pH   | Time    |         |
|---------------------------|--|--|---------|---------|
| <b>F1 : water soluble</b> | Water  | 5.7  | 30 min  |         |
| <b>F2 : exchangeable</b>  | 1 M Mg(NO <sub>3</sub> ) <sub>2</sub>  | 5.0  | 120 min |         |
| <b>F3 : acid soluble</b>  | 1 M NaOAc/HOAc   | 4.5  | 300 min |         |
|                           | Manganese oxides   | 0.1 M NH <sub>2</sub> OH HCl   | 3.5     | 30 min  |
| <b>F4 : reducible</b>     | Amorphous iron oxides  | 0.2 M (NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> +<br>0.2 M H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>  | 3.0     | 240 min |
|                           | Crystalline iron oxides  | 0.2 M (NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> +<br>0.2 M H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> +<br>0.1M C <sub>6</sub> H <sub>8</sub> O <sub>6</sub> | 2.3     | 30 min  |
| <b>F5 : oxidisable</b>    | 35% H <sub>2</sub> O <sub>2</sub> /0,02 M HNO <sub>3</sub><br>(8 ml/3 ml), then 3.2 M<br>NH <sub>4</sub> OAc | 2.0  | 300 min |         |

M: mol.L<sup>-1</sup> ; pH can be adjusted with NaOH or HNO<sub>3</sub> solutions (1 M)

### 2.3.3 Kinetic extraction

Kinetic extraction was achieved using 0.05 mol.L<sup>-1</sup> EDTA solution at 13 contact times (using 13 sacrificial batch) ranging from 15 min to 24 h and a solid/liquid ratio of 1:10. After filtration (0.45 µm HVLP), the solutions were stored at 4 °C (addition of 5 % of HNO<sub>3</sub>) until chemical analysis.

Experimental kinetic curves resulting from extraction with EDTA were modeled using two first-order reaction models as recommended by Cornu *et al.* (2004) and Gismera *et al.* (2004). The two first-order extraction reactions may take place simultaneously, having rates that are assumed to be independent on each other. This allowed three compartments to be defined: quickly mobilised, slowly mobilised and not mobilised. Each extraction was performed in triplicate.

### 3. Chemical analysis

Reagents were used in all experiments. Deionised water with a resistivity of 18.2 M $\Omega$ .cm produced by a Milli-Q water system (MAXIMA, Millipore) was used throughout. Standard stock solutions of 1000 mg.L<sup>-1</sup> for major metallic elements and 100 mg.L<sup>-1</sup> for trace metallic elements (VARIAN, PLASMACAL, ULTRA scientific) were used for calibration. All glassware and plastic materials were soaked for 24 h in 10% nitric acid and rinsed with deionised water prior to use. 50 mL polyethylene vessels were used for the storage of leachates. All leachate solutions were analysed using ICP-AES (inductively coupled plasma-atomic emission Spectrometry, Varian, Vista MPX)

## 4. Results and discussion

### 4.1 Total concentrations

Characteristics of the three sediments are presented in Table 4. Metal concentrations are reported as mg.kg<sup>-1</sup> of dry sediment. Inorganic carbon and TOC (total organic carbon) are reported as percentage of dry sediment. Sediments S1 and S2 have similar concentrations of Cu, Pb and Zn. Likewise S3 has similar concentrations of Cu and Zn to S1 and S2, however it has a lower concentration of Pb. The metal concentrations in all three sediments are within ranges previously reported for harbour sediments in the English Channel area (Pirrie *et al.*, 2002; Dubrulle, 2007; Hamdoun, 2013). The TOC contents measured in these sediments range from 1.9 to 6.0%; these values are within the range of 2 and 10% previously reported in marine sediments (Hamdoun (2013); Tack *et al.*, 1999; Isaure, 2001; Schneider, 2008). The CaCO<sub>3</sub> values for the three sediments in this study range from 11 and 20%, also falling within the previously reported range of 10% to 40% (Dubrulle, 2007, Hamdoun, 2013).

Table 4.  
Sediment characteristics

|                           | S1           | S2           | S3           | English Channel sediments* | French harbour sediments** |
|---------------------------|--------------|--------------|--------------|----------------------------|----------------------------|
| CaCO <sub>3</sub> (%)     | 15.0 ± 1.3   | 11.5 ± 1.1   | 19.2 ± 2.1   | 11.5 to 25.1               |                            |
| TOC (%)                   | 3.8 ± 0.3    | 6.0 ± 0.2    | 1.9 ± 0.2    | 1.4 to 6.0                 |                            |
| Cu (mg.kg <sup>-1</sup> ) | 58.9 ± 8.7   | 59.7 ± 8.1   | 62.0 ± 5.9   | 12 to 393                  | 41.3                       |
| Pb (mg.kg <sup>-1</sup> ) | 133.5 ± 17.3 | 135.1 ± 5.6  | 42.4 ± 9.4   | 11 to 190                  | 41.0                       |
| Zn (mg.kg <sup>-1</sup> ) | 285.8 ± 21.1 | 209.1 ± 18.6 | 233.2 ± 13.1 | 53 to 1226                 | 1 500                      |

\*Hamdoun, 2013; \*\*Padox *et al.*, 2010

### 4.2 Single extraction

The metal mobility expressed as the percentage of the total content of a metal leached by 1 mol.L<sup>-1</sup> HCl is displayed for each sediment in Figure 1. The mobilities of Cu, Pb and Zn are very similar in S1 and S3 and the mobility of Zn is similar in all samples. However, Cu and Pb have a significantly lower mobility in S2 than in S1 and S3. The mobility of Cu is only 24% in S2 compared with 48% in S1, despite the fact that Cu total contents are virtually identical in all three sediments, ranging from 59 to 62 mg.kg<sup>-1</sup>. The sediment matrix plays an important role in binding and immobilising contaminants, these functions are affected by both the geochemical composition and the local environmental

conditions. Extraction using 1M HCl demonstrates that S2 has a greater capacity to bind Cu and Pb than S1 and S3 as a lower mobile fraction is reported for S2 for both these elements.

Sediment S2 contains the most organic matter (6%) and has the lowest liabilities of Cu, Pb and Zn. Results presented here do not show a direct link between CaCO<sub>3</sub> content and liability; S1 and S3 sediment have a similar Pb mobility whilst having different CaCO<sub>3</sub> contents (15 and 19% respectively).

This lack of correlation between element mobility and total metal concentration emphasises the inadequacy of using total metal concentrations in risk assessment.

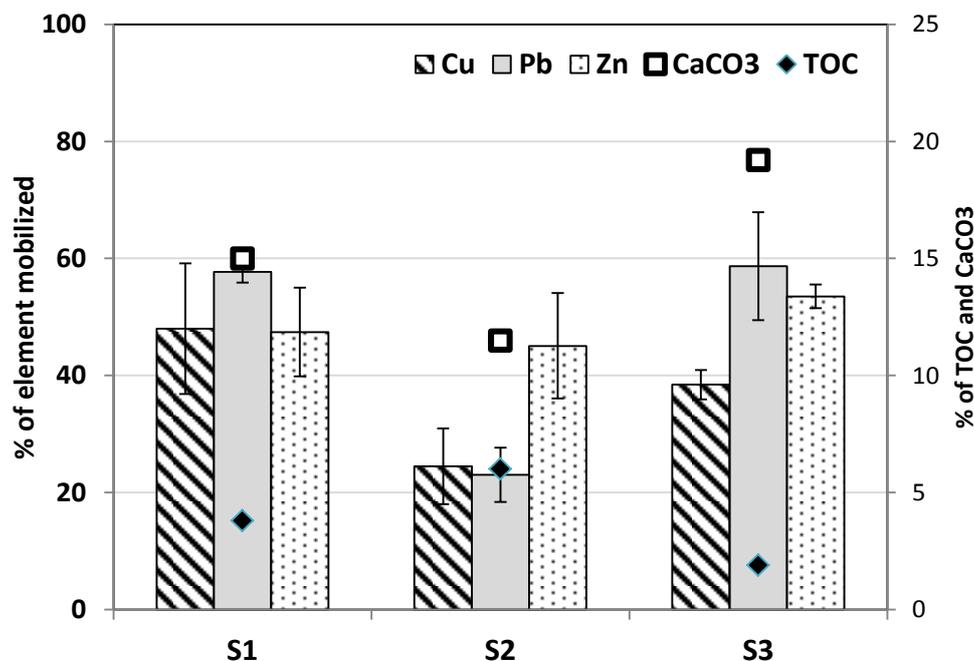


Figure 1. Percentage of Cu, Pb and Zn mobilised by 1 mol L<sup>-1</sup> HCl for sediment samples S1, S2 and S3

### 4.3 Sequential extractions

The metal distribution expressed as the percentage of total metal which is present in each of the five sequential extraction fractions (F1-F5) is displayed in Figure 2. The geochemical distribution of Cu, Pb and Zn in the three samples showed some differences:

- Cu is mainly located in the acid-soluble fraction for S2 and S3 (35 and 49% respectively), however in S1 it is mainly associated with the reducible and oxidisable fractions (32 and 10% respectively). Thus S1 and S3 both have a large proportion of Cu associated with the reducible fraction (32 and 20% respectively). This distribution of Cu is unexpected as Cu is often reported to be associated with the oxidisable fraction (Span, 1984; Ramos *et al.*, 1994; Azzawi *et al.*, 1998; Algan *et al.*, 2004).
- Pb is mainly associated with the reducible fraction in all three sediments. The oxidisable fraction, which is the fraction thought to contain organic matter, does not have a high affinity with Pb in these samples (1 to 8%). Similar observations were made by Span (1984), Illou (1999) and Morillo *et al.* (2004) for marine sediments.
- Zn in sediment S1 is distributed in the acid-soluble, reducible and oxidisable fractions (18, 12 and 15% respectively). Zn in S2, which has the lowest percentage CaCO<sub>3</sub>, has a similar distribution to Cu; i.e. it is mainly located in the acid-soluble fraction (37%), whereas in S3 Zn is mainly associated with the reducible fraction (25%). Pempkowiak *et al.* (1999), Baize and

Tercé (2002) have previously also demonstrated the important role of oxidisable and reducible fractions, in the retention of zinc in sediments.

The geochemical distribution of Cu, Pb and Zn varies greatly between the samples reflecting the heterogeneity of the sediments and the complexity of the various parameters involved.

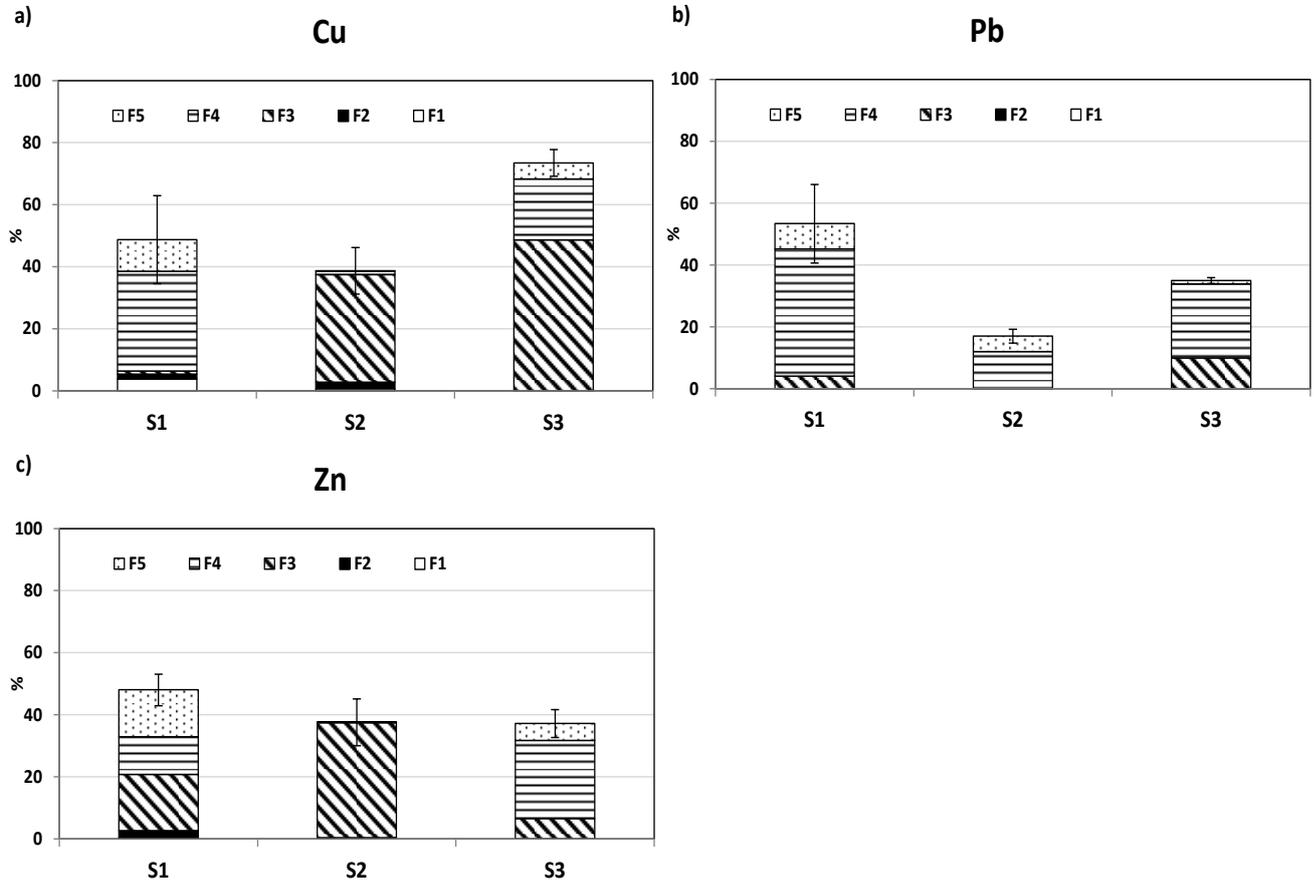


Figure 2. Percentages of Cu (a), Pb (b) and Zn (c) mobilised by sequential extractions for the three sediment samples

#### 4.4 Kinetic extraction

Kinetic extraction has the advantage of allowing differentiation between the quickly and slowly mobilized fraction of an element present in the sediment. Figure 3 presents the metal mobility expressed as the percentage of element leached quickly (Q1) or slowly (Q2) by 0.05 mol.L<sup>-1</sup> EDTA relative to its total content. For the three elements in the three sediments:

- The behaviors of Pb and Zn are similar. In S1 and S3 mobile Pb and Zn are evenly divided in the “rapid Q1” and “slow Q2” compartments. By contrast in S2, Q1 is more important than Q2 for both elements.
- The behavior of Cu is different to that of Pb and Zn. The mobile Cu is mainly present in Q1 for both S1 and S2 with a similar percentage value observed in both sediments. However most of the mobile Cu present in S3 is slowly mobilised.

Previously, Abi Ghanem (2008) found amounts Pb in the Q1 compartment to be systematically higher than those mobilised in the Q2 compartment in marine sediments. The amount of element associated with the Q1 or Q2 compartment is linked to the interaction of the sedimentary matrix with elements.

Kinetic fractionation shows the strength binding of the sediment matrix for each of these elements and provides information on the time frame of the environmental risk posed by elevated metal concentrations. The mobility of Pb and Zn is equivalent for Q1 and Q2 in both S1 and S3. For Cu the results of kinetic extraction show differences in the time frame of the potential environmental risk. The global mobility of Cu (Q1 + Q2) remains close for S1, S2 and S3: 73, 67 and 79% respectively. However, the kinetic mobilisation of Cu in S3 is very different: 28% in Q1 (58 and 53% for S1 and S2) and 51% in Q2 (15 and 14% for S1 and S2). This indicates that the short-term risk posed by mobile Cu in S3 is much lower than in S1 and S2. This phenomenon is linked to the strength of the interaction between the sediment matrix and the elements concerned.

These results show the importance of assessing short (45 min) and long term (1440 min) metal mobility. In a scenario where the sample was exposed to elevated concentrations of complexing ligands, long contact times will cause maximum dissolution of the elements. However, the Q1 compartment helps to differentiate samples. Moreover, a feature of the EDTA is an ability to dissolve some iron oxides (Sigg *et al.*, 2000). This slow reaction, may explain some the element mobility in the Q2 compartment for S3.

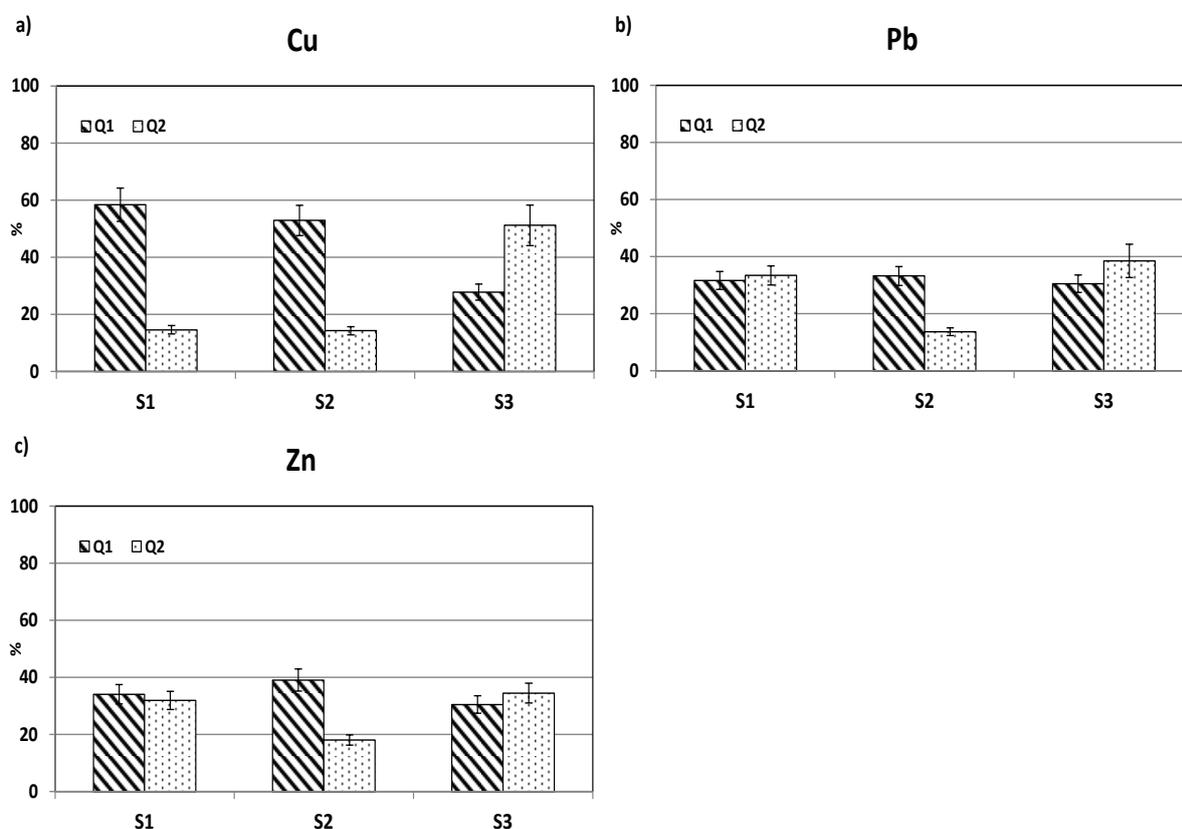


Figure 3. Percentage of Cu (a), Pb (b) and Zn (c) mobilised by kinetic extraction for the three samples (3 replicates were analysed for each extraction) in the two compartments Q1 and Q2

#### 4.5 Comparison

The global mobility (%) estimated by single, sequential (F6: sum of fractions F1 to F5) and kinetic (Q1+Q2) extractions is shown in Figure 4. Comparison of the two thermodynamic approaches (HCl and F6), indicates that the global mobility of Cu, Pb and Zn is similar for S1 and S2. This is surprising as sequential extractions are usually expected to be more aggressive than single reagent extraction using HCl (Larner *et al.*, 2006). It is possible that a potentially labile fraction (e.g sulfides) was not leached during the sequential extractions (Aranguren, 2008), perhaps due to the relatively short

extraction of the oxidisable phases, but that  $\text{Cl}^-$  and EDTA ligands were able to desorb cations from this fraction by complexation. Cu, Pb and Zn are chalcophile (Goldschmidt, 1954) therefore in an anoxic environment it is possible that Zn is trapped in sulfide mineral phases (Morin, 2010). In this study the oxidation state of the sediments was changed by removing them from the anoxic environment on the sea floor to the oxic environment in the laboratory. This may have influenced the speciation of the metals with a redistribution into the geochemical fraction.

Aranguren (2008) suggest a modification to the sequential extraction procedure of Leleyter and Probst (1999). They use a solution of 8N nitric acid to extract the trace metals bound by the recalcitrant sulphide phases in the sediments. Quantification of the fraction of metals bound to the sulphide phase may help to explain findings for sediments which have similar Cu total concentration and variable mobilities.

The comparison between the three extractions shows a higher percentage of Cu, Pb and Zn mobilised by the kinetic extraction for the three samples studied. This result suggests that the thermodynamic approaches do not reach reaction equilibrium:

- It generally accepted that the metals associated with the water-soluble, exchangeable and acid-soluble fractions are easily mobilised (Sundaray *et al.*, 2011). For Cu, Pb and Zn, there is no obvious relationship between Q1 (“rapid” compartment) and the sum the first three fractions of the sequential extraction analysis (F1+F2+F3).
- Reaction equilibrium is reached for the sequential and single extraction, but they do not extract the entire labile fraction from the sediment. EDTA is a stronger ligand than the chloride ion and as such may complex metals hosted in the sulphide phases.

Cornu *et al.* (2004) and Gismera *et al.* (2004) show that certain sequential and kinetic extractions are consistent and complementary for Cu, Pb and Zn. For example, in river sediments Gismera *et al.* (2004) found correlations between the mobility of Cu, Pb and Zn between the exchangeable and carbonate bound fraction and the fraction which was quickly leached by EDTA.

For improved assessment of the environmental risk associated with the sediment, a kinetic approach should be considered.

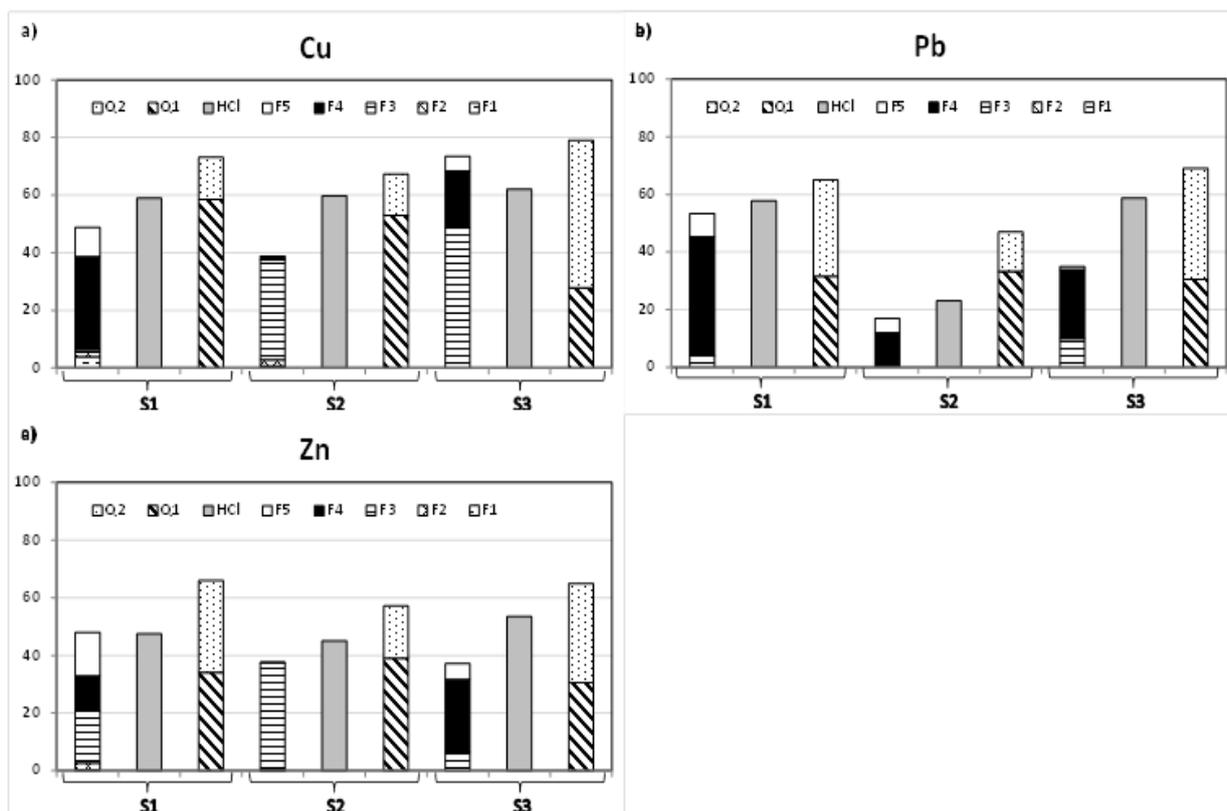


Figure.4 Percentage of Cu (a), Pb (b) and Zn (c) mobilised by HCl, sequential (F1 to F5) and kinetic (Q1+Q2) extraction for the three sediments.

## 8. Conclusion

The aim of this work was to compare several procedures for the environmental risk assessment. Metal mobility was scrutinized using single, sequential and kinetic extractions; each method provided different information on the sediment. Key findings of this research are that:

- The mobility of Cu, Pb and Zn varied from sediment sample to another and was dependent on the binding nature of phases present in the sediment matrix.
- Of the five sediment fractions distinguished by the sequential extraction, only the acid soluble, oxidisable and reducible fractions appeared to be involved in the process of retention and release of metals, suggesting that the remobilization of elements in marine sediments will be highly dependent on local pH and redox conditions.
- Simplification of the sequential extraction method by starting at step 3 is justified in marine sediments since the first two fractions, water soluble and exchangeable, will have already been dissolved in-situ.
- A specific step in the sequential extraction procedure to estimate the sulfide fraction would provide further information on the labile metals present in the sediments. This would involve a modification of the current extraction for the oxidisable fraction.
- The time frame of one hour for single extractions may be too short. Results presented here for kinetic extraction using EDTA raise the possibility that risk is underestimated (for a time contact exceeding 60 min) if only the quickly mobilised fraction is considered.

- Kinetic fractionation provides additional information showing a possible underestimation of the quantities of element potentially released and thus of the potentially elevated long-term risk. The mobility of Cu, Pb and Zn assessed by kinetic extraction were higher than by thermodynamic approaches (single and sequential), although a different extractant was used in each case.

Numerous studies conducted on metal mobility from harbour sediments focus on thermodynamic aspect of mobility and ignore the kinetic aspect. However, even if results comparing the three protocols: single, sequential and kinetics are not always consistent, it is important to consider kinetic extraction in addition to methods with a fixed extraction time to ensure that the equilibrium has been achieved and long term risk can be effectively predicted.

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