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**Title: Characterization of harbor sediments from the English Channel:  
assessment of heavy metal enrichment, biological effect and mobility**

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## Abstract

For a full assessment of the environmental risk posed by dredged sediments not only the anthropogenic enrichment of contaminants, but also their mobility and biological impact should be considered. This study reports on the enrichment factor (EF), mobility, and Adverse Effect Index (AEI) of metals and metalloids in nine dredged sediments. Significant enrichment of As, Cd, Pb and Zn with respect to background values is detected, and calculated AEI values for these elements suggest that it is possible that a corresponding biological effect may be observed. Correlation coefficients also reveal a link between mobility in HCl and enrichment for Cd, Cr, Ni, Pb and Zn, however As and Cu do not display such a link, possibly suggesting that the source of contamination for these elements is less recent. Mobility and enrichment are two parameters which are often studied separately; however this paper shows that in some cases strong correlations occur.

## 1. Introduction

The accumulation of heavy metals in dredged sediments is based upon a range of key factors including the mineralogical texture of the sediment, natural background levels of heavy metals, recent and historical anthropogenic inputs, dredging activities and port development. Metal toxicity and bioavailability are influenced by various physical and chemical characteristics including metal speciation; pH and redox potential of the sediment, degree of organic chelation, salinity and temperature. The determination of the total concentration of heavy metals in sediments is not sufficient to predict the potential adverse effect of those metals on the environment. Many studies focus on an evaluation of anthropogenic inputs (Muniz et al., 2004; Chen et al., 2007); others focus on the potential bioavailability of elements in dredged sediments (Guevara-Riba et al., 2004; Di Palma and Mecozzi, 2007). For a comprehensive environmental risk assessment, both approaches are essential in order to fully characterize the sediments. Methods used to determine the total metal concentration of a sample include (i) microwave assisted acid digestion (HNO<sub>3</sub> and HCl), (ii) alkaline fusion and (iii) tri-acid attack (HNO<sub>3</sub>–HCl–HF).

However, alkaline fusion can cause the loss of volatile elements (As and Pb) and the tri-acid attack does not give the total concentration of Si due to the formation of SiF<sub>4</sub> gas. Despite

the fact that microwave assisted digestion provides only a pseudo-total concentration of the major elements (Al and Si), it allows a good estimation of volatile elements and Cu, Pb and Zn.

Various indices have been developed to assess the contamination level of heavy metals in soils and sediments. These indexes, outlined in Table 1, rely on a geochemical background value for an element in order to calculate an enrichment/contamination factor for that element. The background value chosen can either be a feature of the area of interest (for example a measurement taken upstream of a contamination point source), the value from the sample with the lowest concentration, the concentration value at the base of a core sample or an accepted background value. For the most accurate estimate, the best approach is to establish a background value for the area of interest. The index chosen will require different input variables which can restrict its use. For example, Allen and Rae (1986) use Rb concentration (as internal reference), and Dickinson et al. (1996) require a core sampling.

Many authors (Audry, 2003; Leleyter and Baraud, 2005; Dubrulle et al., 2007; Meybeck et al., 2007; Leleyter et al., 2012) use the enrichment factor (EF) approach to easily visualize atypical enrichment which may be anthropogenic. The EF formula (Covelli and Fantolan, 1997) uses an internal reference, known as a normalizer, to moderate the deviations produced by heterogeneous sediments (Magesh et al., 2011). In the absence of geochemical background data of the area studied, the average shale values reported by Turekian and Wedephol (1961) are often used as background reference values (Dubrulle et al., 2007; Christophoridis et al., 2009; Magesh et al., 2011). These shale reference values correspond to the theoretical geochemical composition of particular material likely to be exported to the ocean (Turekian and Wedephol, 1961). Calculated enrichment factors cannot be used to evaluate the probability of adverse effects on benthic biota. In the absence of toxicity studies, Muñoz-Barbosa et al. (2012) suggest that element concentrations can be compared with Threshold Effect Level (TEL) sediment quality guidelines (SQG) developed by Long et al. (1995) in order to assess an Adverse Effect Index (AEI). TEL SQGs were developed in order to interpret metal concentrations in sediments in the context of their potential biological effect. Lability studies are usually conducted using chemical extractions to determine the fraction of total metal in a sample which is mobile under the conditions of the extraction procedure; this value is then used as a proxy for potential metal bioavailability in a sample. Such extractions may be sequential or single reagent and assume that leached metal concentration corresponds to non-residual metal content in a sample. Whilst sequential extractions allow a more detailed understanding of which phase is hosting the metals of interest in the sample, single extractions are a simple and cost-effective way to investigate the labile metal fraction of soils and sediments. Although there are numerous reagents that may be used for single extractions, they generally fall into three categories: acids, unbuffered salts and complexing reagents.

Acids are often used to determine the total element composition of soils and sediments. However, dilute acids (e.g.; CH<sub>3</sub>COOH 0.10 mol L<sup>-1</sup>; HCl 0.10 mol L<sup>-1</sup> or a mixture; HCl 0.05 mol L<sup>-1</sup> and H<sub>2</sub>SO<sub>4</sub> 0.0125 mol L<sup>-1</sup> (Mulchi et al., 1992)) can also be used to estimate the mobile fraction of an element. HCl 1.00 mol L<sup>-1</sup> is assumed to extract metals due to its acidic properties combined with the chelant property of Cl<sup>-</sup>. Hydrochloric acid has been used extensively as a reagent in this type of study and is recommended by many authors (Duinker et al., 1974; Scouller et al., 2006; Doherty et al., 2000); for harbor sediments 1.00 mol L<sup>-1</sup> is often suggested (Szefer et al., 1995; Burton et al., 2005; Larner et al., 2008; Leleyter et al., 2012). The phyto-available fraction of the element is often estimated by extractions performed using complexing agents which are assumed to extract elements present in the sample on the exchange sites of both the carbonate and organic fractions. The most widely used chelating agents for bioavailability assessment are ethylene diamine tetra-acetic acid (EDTA) and diethylene triamine penta-acetic acid (DTPA)

(Fangueiro et al., 2002; Di Palma et al., 2005; Leleyter et al., 2012). Unbuffered salt extractants are rarely used for marine samples because they are not adapted to the high ionic strength of these samples (Leleyter et al., 2012).

The objective of the study is to investigate the both (i) the relationship between metal enrichment (based on geochemical background) and biological effect (based on sediment quality guidelines) and (ii) the relationship between metal enrichment and mobility (assess through chemical extraction); in nine harbour dredged sediments from the UK and French sides of the English Channel.

## 2. Materials and methods

### 2.1. Sediment sampling and pre-treatment

This study forms part of a European project on the sustainable, environmental treatment and re-use of marine sediments (SETARMS), the project aims to find treatment and re-use options for marine dredged sediment. The studied samples are coded Sed1 to Sed9 and were sampled from nine harbors from both the UK and French sides of the English Channel (Fig. 1). Samples were collected using a grab, a diver or a suction dredger depending on locally available techniques. Sediment samples were collected between March 2010 and June 2011 at a single GPS point from each harbor. The water depth during sampling varied between 4 and 11 m. The sediment samples were homogenized, and then air-dried for 4 days, sieved at 500  $\mu$ m using a nylon sieve, and ground manually using an agate pestle and mortar.

### 2.2. Geoaccumulation index

#### 2.2.1. Enrichment factor (EF)

The enrichment factors were calculated using the method outlined in Table 1 (Covelli and Fantolan, 1997). The calculation used total element concentrations obtained after acid digestion as the [X]<sub>sediment</sub> value, the value for shales as reported by Turekian and Wedepohl (1961) was used as [X]<sub>background</sub>, and Al was chosen as the normalizer (Y). According to Dubrulle et al. (2007), if EF = 1 element X is representative of the shale reference value, if EF < 1 element X is depleted with respect to the shale reference and if EF > 1 element X is enriched with respect to the shale reference.

All reference values can be found in Table 3.

**Table 1**  
Example of index used to assess contamination or adverse biological effects.

Index	Variable	References
Im = nondimensional metal index	$Im = (C_{si} - Y_{si})/C_{si}$	$C_{si}$ = metal concentration in sample $Y_{si}$ = metal concentration in sediment at zero Rb content
Concentration factor through the core (EF core)	$CF (core) = C_{top}/C_{bottom}$	$C_{top}$ = average concentration of metal upper 50 cm of core $C_{bottom}$ = average concentration of metal below 100 cm in core
Enrichment factor (EF)	$EF = ([X]/[Y]_{sediment})/[X]/[Y]_{background}$ <i>reference value</i>	X = concentration of metal Y = concentration of normalizer
Adverse Effect Index	$AEI = [X]/[TEL]$	AEI = Adverse Effects Index [X] = Metal concentration TEL = Threshold Effect Level

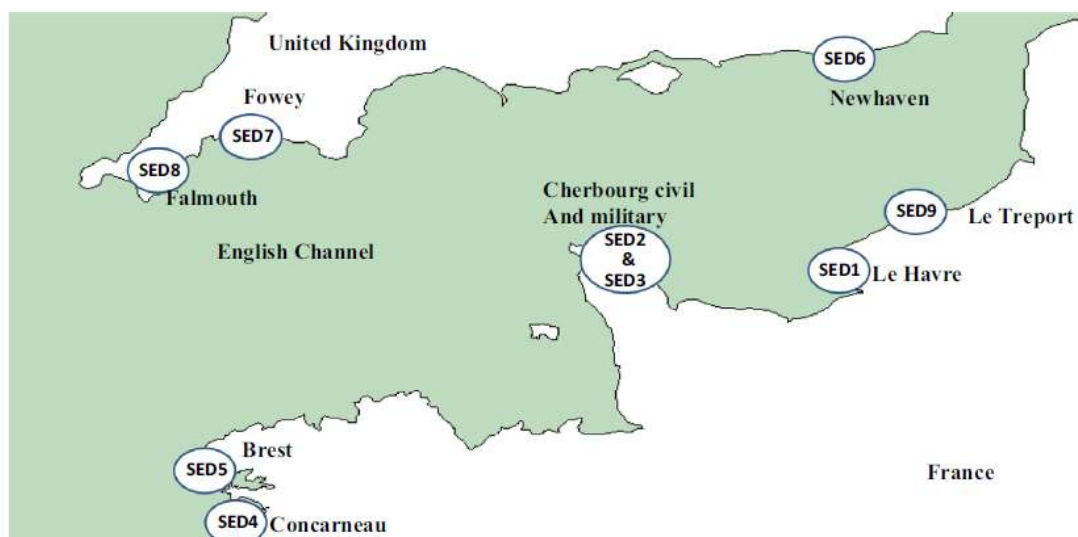


Fig. 1. Harbor and sample locations.

**Table 2**

Element recovery for certified sediment HR-1 after microwave-assisted acid digestion (As, Cd, Cr, Cu, Ni, Pb, and Zn in  $\text{mg kg}^{-1}$ ) and alkaline digestion (Al and Si in  $\text{g kg}^{-1}$ ).

	Element	Certified values	Measured values
Alkaline digestion	Al	$59.2 \pm 23.0$	$50.3 \pm 3.7$
	Si	Not certified	$240 \pm 72$
Acid digestion	As	$6.0 \pm 1.0$	$7.8 \pm 2.7$
	Cd	$4.0 \pm 1.0$	$3.3 \pm 1.6$
	Cr	$126 \pm 45$	$90 \pm 10$
	Cu	$80.0 \pm 11.0$	$68.4 \pm 12.8$
	Ni	$39.0 \pm 15.0$	$31.1 \pm 3.4$
	Pb	$139.0 \pm 37.0$	$113.6 \pm 9.2$
	Zn	$\pm 0.1$	$1.12 \pm 0.03$

### 2.2.2. Adverse Effect Index (AEI)

AEI values were calculated as suggested by Muñoz-Barbosa et al. (2012), using the equation outlined in Table 1 (in his article, he used ERL instead of TEL to calculate the AEI). The Threshold Effect Levels (TELs) used in the calculation of AEI values were derived by Long et al (1995). According to Muñoz-Barbosa et al. (2012), if  $AEI \geq 1$  the metal concentration in the sample is not high enough to produce adverse effects in biota, however if  $AEI < 1$  the metal concentration in the sample could produce adverse effects.

### 2.3. Total metal concentration determination

Both alkaline fusion (for Al) and microwave assisted acid digestion (for As, Cd, Cr, Cu, Ni, Pb and Zn) were used to determine the total metal and metalloid concentrations in the

sediments (performed in triplicate). Alkaline fusion based on NF ISO 14869- 2 was undertaken on 0.2 g of ground sample which was oven heated in a platinum crucible at 450 °C for 3 h. After cooling, the calcined sample was mixed thoroughly with 0.2 g of lithium tetraborate (Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>) and 0.8 g of lithium metaborate (LiBO<sub>2</sub>).

The mixture was heated to 1100 °C for 30 min, and then recovered in to an acid solution (HNO<sub>3</sub> 1.0 mol L<sup>-1</sup>). Microwave assisted acid digestion was undertaken on 0.2 g of dry sediment using aqua regia digest (3.33 mL of HNO<sub>3</sub> and 6.66 mL of HCl) (Alloway, 1995) and a Berghof speedwave MWS-2 microwave.

#### 2.4. Mobility determination

Two separate single extractions were performed in triplicate as batch extractions. The sediment samples were shaken using a ratio of 10:1 (liquid/solid), with either 1.00 mol L<sup>-1</sup> HCl or 0.05 mol L<sup>-1</sup> EDTA, for 1 h at room temperature. Following filtration at 0.45 μm, the solutions were stored at 4 °C until chemical analyses.

#### 2.5. Analytical technique and data validation

High-purity reagents were used in all experiments. Deionized water with a resistivity of 18.2 M Ω cm, produced by a Milli-Q water system (MAXIMA) was used throughout. Standard stock solutions of 1000 mg L<sup>-1</sup> for major elements and 100 mg L<sup>-1</sup> for trace elements (VARIAN, PLASMACAL, ULTRA scientific) were used for calibration. Glassware and plastic materials were pre-soaked for 24 h in 10% nitric acid and rinsed with deionized water; including the 50 ml polyethylene vessels used for storage of extractants.

All leachate solutions were analyzed by ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometry, Varian, Vista MPX, results are expressed on the average of 5 analysis). The analytical quality of the chemical data was controlled using standard certified materials HR-1 (Canada Center for Inland Waters National Laboratory for Environmental). As can be seen in Table 2; the recovery was satisfactory for all the elements of interest.

### 3. Results and discussion

#### 3.1. Total metal concentrations

Concentrations values determined in the sediments for Al, As, Cd, Cr, Cu, Ni, Pb, Si and Zn are reported in Table 3 where each concentration value is the mean of three extraction replicates and the standard deviation. Total concentrations reported in this study fall within the range reported in the literature by other authors for dredged sediment around the world (Table 4), including data from French harbor sediments from the Atlantic, Mediterranean and English Channel coast (Padox et al. (2010)). The concentrations reported in the literature show a wide concentration range for these elements both within and between harbors on a national and international level.

Data from other studies are highly variable and therefore cannot be relied upon to assess the quality of the sediments analysed in this study. This variability can either be explained by the natural background inhomogeneity of the sampling areas or by anthropogenic inputs related to specific activities. The interpretation of total concentrations must therefore be based on the geological context and the use of enrichment factors (using the geochemical background) is in order to evaluate sediment quality.

**Table 3**

Background reference values for Shales, TEL values, and total metal concentrations obtained after acid digestion (As, Cd, Co, Cr, Cu, Ni, Pb, and Zn in  $\text{mg kg}^{-1}$ ) and alkaline fusion (Al and Si in  $\text{g kg}^{-1}$ ) (average of three replicates).

	Al	As	Cd	Cr	Cu	Ni	Pb	Si	Zn
Shales <sup>a</sup>	80	13	0.3	90	45	68	20	n.r	95
TEL <sup>b</sup>	/	7.2	0.7	52.3	18.7	15.9	30.2	n.r	124
Sed1	24.6 ± 0.3	42 ± 3	4.1 ± 0.1	74.4 ± 0.4	10.3 ± 0.4	27.1 ± 0.3	37.2 ± 0.2	114 ± 18	194.4 ± 0.4
Sed2	17 ± 2	10 ± 2	1.2 ± 0.1	18.5 ± 0.3	18.6 ± 0.2	9.1 ± 0.1	32 ± 1	73 ± 2	97 ± 1
Sed3	20 ± 3	17 ± 1	1.8 ± 0.1	28 ± 1	59 ± 1	14.1 ± 0.5	263 ± 6	160 ± 21	316 ± 9
Sed4	25 ± 3	16.2 ± 0.2	2.6 ± 0.2	45.5 ± 0.2	112.9 ± 0.2	21.0 ± 0.2	75.5 ± 0.2	73 ± 1	327.1 ± 0.4
Sed5	15 ± 1	27 ± 1	1.6 ± 0.1	18 ± 2	254 ± 23	9.6 ± 0.5	57 ± 5	60 ± 7	241 ± 21
Sed6	13 ± 1	37 ± 2	2.3 ± 0.3	9 ± 1	31 ± 4	12 ± 1	36 ± 5	80 ± 5	109 ± 14
Sed7	21 ± 1	6.5 ± 0.2	2.2 ± 0.1	17 ± 1	15.3 ± 0.5	14 ± 1	9.0 ± 0.3	10 ± 1	24 ± 1
Sed8	15.4 ± 0.8	21 ± 1	3.9 ± 0.1	38 ± 1	101 ± 2	23 ± 1	39 ± 1	37 ± 2	123 ± 4
Sed9	20 ± 1	6 ± 3	1.5 ± 0.2	27 ± 1	54 ± 2	18 ± 0	51 ± 1	71 ± 2	226 ± 3
Mean	19	20	2	31	73	16	67	75	184
Maximum	25	42	4	74	254	27	263	160	327
Minimum	13	6	1	9	10	9	9	37	24

(± Standard deviation); n.r: not reported.

<sup>a</sup> Shales, Turekian and Wedephol (1981).

<sup>b</sup> TEL = Threshold Effect Level (Long et al. 1995).

**Table 4**

Concentration ranges in marine sediments from harbor areas ( $\text{mg kg}^{-1}$ ).

Authors	Location	As	Cd	Cr	Cu	Ni	Pb	Zn
Goerra-García and García-Gómez (2005)	Ceuta harbor	4-42	n.r	14-381	5-865	8-671	10-516	29-695
Sprovieri et al. (2007)	Naples harbor	1-1121	0.01-3	7-1798	12-5743	4-362	19-3083	17-7234
Sorensen and Måne (2009)	Porirua harbor	2.4-8.7	0.06-0.19	7.7-17	8.5-30	4.9-10	14-34	130-410
Padoux et al. (2010)	French harbors	0.1-196	0.0-8.6	1-636	2-2651	1-214	5-1340	1.5-3493

n.r: Not reported.

**Table 5**

EF values for the studied sediments based on shales content.

	As	Cd	Cr	Cu	Ni	Pb	Zn
Sed1	10	44	3	0.7	1.3	6	7
Sed2	4	15	1	2	0.6	7	5
Sed3	5	24	1	5	0.8	53	13
Sed4	4	28	2	8	1	12	11
Sed5	11	27	1	29	0.7	15	13
Sed6	17	47	0.6	4	1	11	7
Sed7	2	28	0.7	1	0.8	2	0.9
Sed8	8	69	2	12	2	10	7
Sed9	2	20	1	5	1	10	10
	1 < EF < 2			EF > 2			

### 3.2. Indices of contamination

#### 3.2.1. Enrichment factor (EF) assessment

The calculated EF values suggest important anthropogenic inputs for As, Cd, Cu, Pb and Zn (2–17; 15–69; 0.7–29; 2–53; and 0.9–13 respectively) and low anthropogenic inputs for Cr (0.6–3) Ni (0.6–2) (Table 5). Enrichment factors reported in the literature for other sediments can be seen in Table 6 and show that the level of enrichment found in this study is characteristic of marine sediments in dredging areas. Port areas are subject to important anthropogenic inputs which could explain these relatively high EFs. Comparing EFs of the nine samples with those in Table 6, it appears that the samples in this study have particularly high levels of Cd and Pb.

Previous authors (Hughes, 1999; Pirrie et al., 1997, 2002, 2003) reported the presence of As, Cu, Hg, Pb and Zn in estuarine areas of Falmouth and Fowey due to mining activities. Sediments from estuaries of the Thames, Stour and Orwell also present significant enrichments of Cd, Cu, Hg, Pb and Zn (Wright and Mason, 1999). Chiffolleau et al. (1999) argues that the Seine is an important source of contaminant for the sediments in the Bay of Seine.

**Table 6**  
EF values in marine sediments from harbor areas (based on shales content).

Authors	Location	Internal reference	Geochemical background	Cd	Cr	Cu	Ni	Pb	Zn
Christophoridis et al., 2009	Thermaikos Gulf	Fe	Shale	n.r	2-7	2-5	n.r	2-10	0.9-2
Chen et al., 2007	Kaohsiung Harbor	Al	Talor, 1994	3-36	0.3-8.4	0.6-7.1	n.r	2.4-13.6	3-138
Idris (2006)	Sawakin harbor	Fe	Reference material	n.r	n.r	1-5	n.r	0.2-5	1-5
Reddy et al. (2004)	Indiana harbor	Fe	Shale	n.r	2-3	2-4	1-3	3-5	3-5
Huerta-Diaz et al. (2008)	El Sauzal and Ensenada harbor	Al	Shale	10	n.r	1.2	0.6	2.3	1.7
Dubrulle et al., 2007	Bay of Seine	Al	Shale	3-9	2	0.5-2	0.5-2	2-8	1-3

n.r: Not reported.

**Table 7**

AEI values for As, Cd, Cr, Cu, Ni, Pb and Zn (based on Threshold Effect Level).

	As	Cd	Cr	Cu	Ni	Pb	Zn
<b>Sed1</b>	5,8	6,1	1,4	0,6	1,7	1,2	1,6
<b>Sed2</b>	1,4	1,4	0,4	1,0	0,6	1,1	0,8
<b>Sed3</b>	2,4	2,6	0,5	3,1	0,9	8,7	2,5
<b>Sed4</b>	2,2	3,8	0,9	6,0	1,3	2,5	2,6
<b>Sed5</b>	3,8	2,4	0,3	13,6	0,6	1,9	1,9
<b>Sed6</b>	5,1	3,5	0,2	1,7	0,7	1,2	0,9
<b>Sed7</b>	0,9	3,2	0,3	0,8	0,9	0,3	0,2
<b>Sed8</b>	2,9	5,8	0,7	5,4	1,5	1,3	1,0
<b>Sed9</b>	0,9	2,2	0,5	2,9	1,1	1,7	1,8

### 3.2.2. Adverse Effect Index (AEI)

These results shown in Table 7 suggest adverse biological effect for at least one element. Conclusions drawn from a consideration of the calculated EF values are not always consistent with those drawn from the calculated AEI values. For example, the EF for Ni is 1 for Sed4 and Sed9 but the AEI is greater than 1 for these sediments. To better elucidate possible links between these different indices, correlations are made and can be seen in Fig. 2.

### 3.3. Relationship between enrichment and AEI

The correlations between AEI values and EF values are displayed in Fig. 2. The linear regression between EF and AEI is significant for each element with  $r^2$  values ranging from 0.61 to 0.98. These values show significant relationships (from  $R^2 = 0.6$ ) exist between EFs and AEIs for As, Cd, Cr, Cu, Ni, Pb and Zn. Despite a confirmed link between AEI and EF observed phenomena are sometimes different from one element to another. In the case of Cr and Ni, a sediment with a moderate EF may produce biological effects. For Ni,

enrichment factors below 2, could often associated with an AEI values exceeding 1. In the case of Cr, the AEI predicts that samples are not expected to generate an adverse biological effect despite the fact that the EFP1 (1–3) for six of the sediments. In contrast, Cd, Pb and Zn have calculated EF values which are very high and are associated with high AEI values. The interpretation of the relationship between AEI and EF can be very different from one element to another. Muñoz-Barbosa et al. (2012) found an adverse effect for Cd, Cu, Ni and Zn for different values of enrichment factor ( 6, 1, 1 and 2 respectively). EFs calculated were different in this study because Muñoz- Barbosa et al. (2012) use Fe as internal reference.

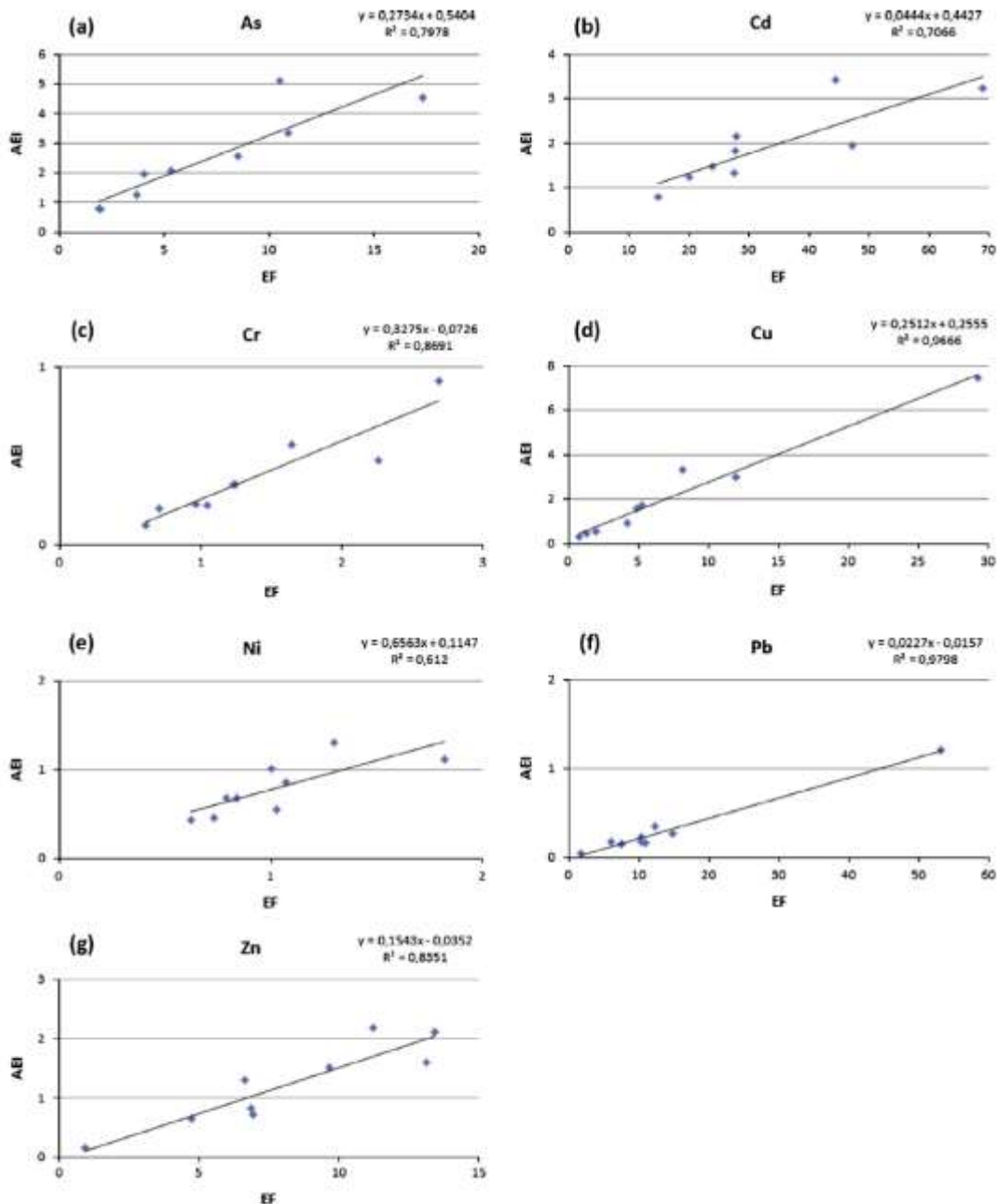


Fig. 2. Adverse effect index versus enrichment factor (significant relationships from  $R^2 = 0,6$ ).



### 3.4. mobility determination

The percentage each element relative to the total concentration recovered by both HCl and EDTA are presented in Fig. 3 and Table 9 for each sample. From these results HCl (1.00 mol L<sup>-1</sup>) appears more aggressive than EDTA (0.05 mol L<sup>-1</sup>) and release more As, Cd, Cr, Cu, Ni, Pb and Zn. Nevertheless, Leleyter et al (2012) show that EDTA is suitable for estimating Pb mobility and sequential extraction for Cu and Zn.

According to Sahuquillo et al. 2003, the mobility of Cu and Pb with EDTA can be attributed to two processes: first, Cu and Pb have high complexation constants with EDTA (log KPb-EDTA = 18.03, log KCu-EDTA = 17.08); second, Cu and Pb are highly associated with Fe oxides and hydroxides, and they may be remobilized due to the complexation of Fe with EDTA (log KFe-EDTA = 25.1). The differences between the extraction efficiency of HCl and EDTA for the mobilization of Pb can be explained by the proportion of calcium carbonate in sediments. According to Di Palma et al. (2007) EDTA extraction can cause an increase in pH and thus a dramatic reduction in Ca<sup>2+</sup> content and the development of exchange reactions between the EDTA-metal complexes previously formed with Ca<sup>2+</sup>.

Mobility of an element varies greatly from one sediment to another for the two types of extraction. Baize et al. (2009) argues that extractants suitable for one element is not necessarily good for another. Nevertheless, the nature of sediments can be an important parameter in the choice of extractant. So, as recommended by Sahuquillo et al. (2003) an appropriate extractant must be selected as a function of the trace element target and the total concentration of the element.

Al is poorly mobilized by the two extractants (<9%), probably because Al is widely present in the residual fraction. The calculated EF show that enrichment is suspected in the sediments characterized in this study for As, Cd, Cu, Pb and Zn. The mobile fractions for these elements also have a range with the mobile fractions reported as As (4–33%), Cd (5–22%), Cu (3–70%), Pb (10–56%); and Zn (17–39%). There is clearly an increased environmental risk where elements have both a high EF value and a high labile or mobile fraction.

**Table 8**

Correlation coefficient matrix of element mobility (by HCl and EDTA) and enrichment factor for the nine samples.

	HCl (mg kg <sup>-1</sup> ) versus EF	EDTA (mg kg <sup>-1</sup> ) versus EF
As	0.16	0.10
Cd	<b>0.60</b>	0.30
Cr	<b>0.91</b>	<b>0.65</b>
Cu	0.10	0.16
Ni	<b>0.79</b>	0.51
Pb	<b>0.65</b>	<b>0.96</b>
Zn	<b>0.79</b>	<b>0.62</b>

Strong correlation for a transitive correlation between 8.0 and 1.0.

Affinity for a transitive correlation between 0.6 and 0.8.

Fairly good correlation for a transitive correlation between 0.5 and 0.6.

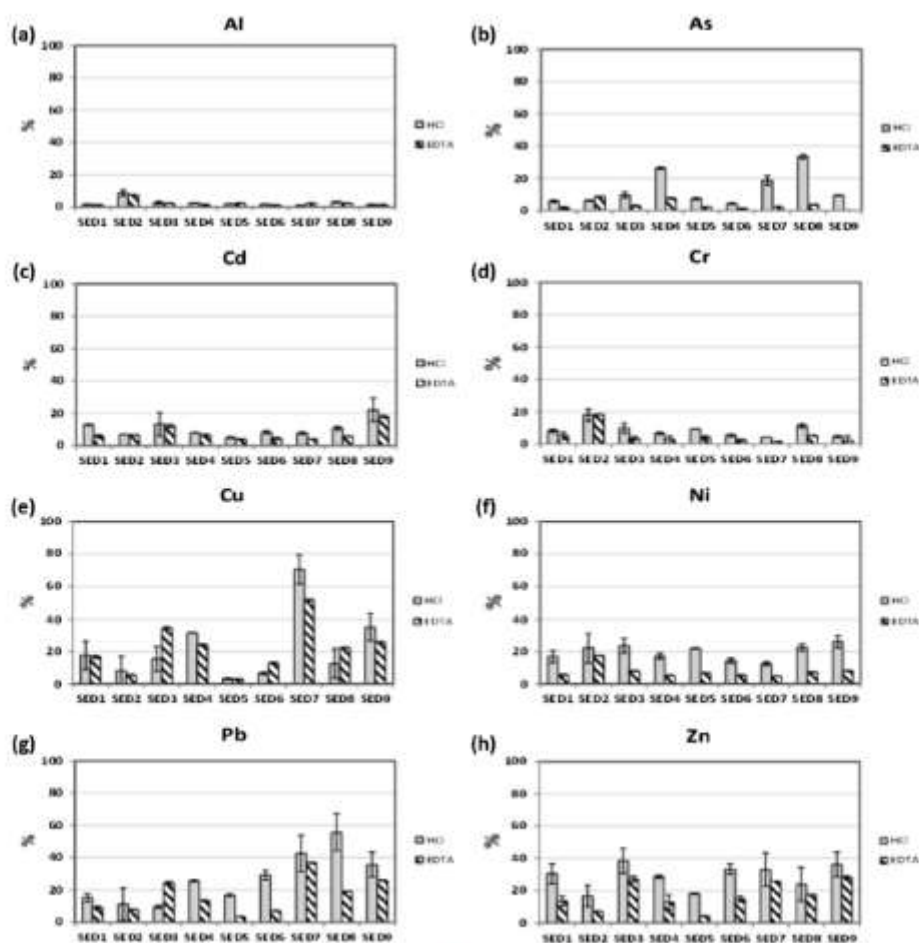


Fig. 3. Percentage of Al (a), As (b), Cd (c), Cr (d), Cu (e), Ni (f), Pb (g) and Zn (h) mobilized by HCl and EDTA for the nine samples (3 replicates were analyzed for each extraction).

Table 9

Percentage of Al, As, Cd, Cr, Cu, Ni, Pb and Zn mobilized by HCl and EDTA for the nine samples (3 replicates were analyzed for each extraction).

		Al	As	Cd	Cr	Cu	Ni	Pb	Zn
Sed1	HCl	1.4 ± 0.1	5.7 ± 0.6	12.9 ± 0.3	8.1 ± 0.8	17.7 ± 8.8	16.8 ± 3.7	15.0 ± 2.5	30.5 ± 6.0
	EDTA	1.2 ± 0.0	1.7 ± 0.8	5.7 ± 1.0	5.0 ± 2.1	16.8 ± 0.7	5.7 ± 0.3	9.0 ± 1.0	13.6 ± 3.1
Sed2	HCl	8.5 ± 1.8	6.1 ± 0.1	6.8 ± 0.1	17.9 ± 3.8	8.2 ± 8.8	22.2 ± 9.2	11.2 ± 10.1	16.9 ± 6.7
	EDTA	7.6 ± 0.0	8.8 ± 0.0	6.5 ± 0.0	18.1 ± 0.0	5.6 ± 0.2	17.5 ± 0.2	7.7 ± 0.0	7.3 ± 0.0
Sed3	HCl	2.5 ± 0.8	9.7 ± 2.0	13.2 ± 7.3	8.8 ± 3.0	15.4 ± 7.5	23.6 ± 4.4	9.5 ± 1.0	38.5 ± 7.9
	EDTA	2.1 ± 0.0	2.8 ± 0.3	12.0 ± 0.8	3.4 ± 1.2	34.8 ± 0.5	8.0 ± 0.3	24.3 ± 1.1	27.2 ± 1.9
Sed4	HCl	2.3 ± 0.2	26.3 ± 0.6	7.9 ± 0.1	6.6 ± 0.7	31.7 ± 0.2	17.1 ± 1.7	25.7 ± 0.6	28.7 ± 0.9
	EDTA	1.4 ± 0.1	7.6 ± 0.4	6.4 ± 0.6	2.5 ± 2.2	24.2 ± 0.7	5.4 ± 0.3	13.3 ± 0.4	12.8 ± 4.5
Sed5	HCl	1.7 ± 0.2	7.3 ± 0.7	4.9 ± 0.5	9.2 ± 0.1	3.0 ± 0.3	21.9 ± 0.2	16.8 ± 0.7	18.3 ± 0.1
	EDTA	2.2 ± 0.1	2.1 ± 0.0	3.9 ± 1.0	3.8 ± 1.0	2.8 ± 0.2	6.9 ± 0.2	3.5 ± 0.1	4.2 ± 0.2
Sed6	HCl	1.6 ± 0.2	4.2 ± 0.4	8.1 ± 0.8	5.4 ± 0.5	6.7 ± 0.7	14.4 ± 1.4	29.1 ± 2.9	33.3 ± 3.3
	EDTA	1.0 ± 0.2	1.2 ± 0.4	4.4 ± 0.7	2.1 ± 0.8	13.0 ± 0.5	5.4 ± 0.3	7.1 ± 0.0	14.9 ± 1.9
Sed7	HCl	0.9 ± 0.1	18.8 ± 2.9	7.7 ± 0.8	4.1 ± 0.0	70.4 ± 9.0	12.5 ± 1.3	42.5 ± 11.2	33.0 ± 10.3
	EDTA	2.1 ± 0.0	2.4 ± 0.1	4.1 ± 0.0	1.4 ± 0.0	51.4 ± 0.2	4.6 ± 0.2	36.8 ± 0.0	26.0 ± 0.0
Sed8	HCl	2.9 ± 0.3	33.4 ± 1.3	10.7 ± 1.1	11.2 ± 1.1	12.6 ± 9.3	22.6 ± 2.3	55.6 ± 11.6	24.0 ± 10.4
	EDTA	2.1 ± 0.0	3.7 ± 0.0	5.8 ± 0.0	5.1 ± 0.0	22.4 ± 0.2	7.3 ± 0.2	19.3 ± 0.0	17.7 ± 0.0
Sed9	HCl	1.3 ± 0.1	9.3 ± 0.1	22.1 ± 7.2	4.6 ± 0.5	35.2 ± 8.5	26.0 ± 3.6	35.6 ± 7.6	36.2 ± 7.6
	EDTA	1.2 ± 0.1	0.0 ± 0.2	17.8 ± 0.7	2.0 ± 3.0	25.7 ± 0.3	8.2 ± 0.3	25.9 ± 0.3	28.2 ± 0.9

(±Standard deviation).

### 3.5. Correlation between enrichment and mobility

Correlations analysis between element lability and enrichment factor are reported in Table 8. In the case of HCl extraction, the correlations presented indicate a positive correlation

between Cd, Cr, Ni, Pb and Zn mobilized with enrichment factor ( $r = 0.60-0.91$ ). For EDTA extraction, the correlations indicate a positive correlation between Cr, Pb and Zn lability and enrichment factor ( $r = 0.65-0.96$ ) showing a link between enrichment and mobility, as defined by the labile fraction. This indicates that the geochemical mobility of an element may depend on its level of enrichment.

Following the conclusion of these studies, a hypothesis can be advanced that the enrichments of Cr, Ni, Pb and Zn could be attributed to recent contamination (the recent connections can be weak and therefore easily reversible). According to Baize et al. (2009), Varrault (2012) and Leleyter et al. (2012) an anthropic enrichment can imply a high element mobility from sediments. Rao et al. (2010) show that the accidentally polluted soil (contaminated by mining activity) had the highest recoveries by HCl extraction; Rousseau et al. (2009) simulated enclosed harbors areas in order to study the impact of sacrificial anode dissolution. The experiment lasted 12 months proves an increase of zinc lability, due to contamination.

No relationship was found between the enrichment and mobility of As and Cu for both extractions ( $r = 0.16-0.10$ ). Indeed, samples with a high enrichment of Cd (14.9–68.9) present a weak mobility (5–22%) by HCl. Following the assumption made previously, anthropogenic inputs of As and Cu were likely caused by historic contamination. Indeed, these results could be explained by the fact that during the exposure period, the geochemical speciation of the elements had changed. Thus, a long period of exposure may alter the mobility of elements. Other possible explanations are that the significant enrichment is of natural origin and/or that HCl extraction could not be suitable for mobility assessment for these elements.

#### 4. Conclusion

The aim of this work was to determine the environmental risk assessment of harbor sediments. The harbor sediments sampled from English Channel and analyzed in this study were found to contain high concentrations of As, Cd, Pb and Zn which are indicated by the EF values to be due to anthropogenic input. The AEI values reveal that the sediments studied are likely to provoke adverse biological effect due to As, Cd, Cu and Zn. Linear regression showed that the EF and AEI are significantly linked, however a high EF is not systematically responsible for potential adverse effect (e.g. Pb).

The sediments studied are very different from one harbor to another which may explain the highly variable mobility of elements between sediments. As stated by Meybeck et al. (2007) each element has a specific contamination pattern, moreover, according to Sahuquillo et al. (2003) it is necessary to study the characteristics of each sample and apply different type of extractant in order to enhance the assessment of environmental risk. Correlations prove a strong link between mobility and potential enrichment for Cd, Cr, Ni, Pb and Zn. These results suggest a more recent contamination in Cd, Cr, Ni, Pb and Zn in port areas sampled.

Enrichment of an element in sediment can be one reason that the environmental risk of that sediment is increased; however a consideration of the relationship between mobility and enrichment as presented in this paper allows a more detailed understanding of the human impact and element mobility in dredged material.

## References

- Allen, J.R.L., Rae, J.E., 1986. Time sequence of metal pollution, Severn Estuary, southwestern UK. *Mar. Pollut. Bull.* 17, 427–431.
- Audry, S., 2003. Bilan géochimique du transport des éléments métalliques dans le système fluvial anthropisé Lot-Garonne-Gironde, Thèse de doctorat, Université de Bordeaux I, 415.
- Baize, S., Lemeille, F., Cushing, M., Schwenninger, J.L., Nicoud, G., 2009. Multidisciplinary approach to study the Vuache fault (France) – Part I: geological characterization of the fault, International Conference Provence 2009, Aix-en-Provence.
- Burton, E.D., Phillips, I.R., Hawker, D.W., 2005. Reactive sulfide relationships with trace metal extractability in sediments from southern Moreton Bay, Australia. *Mar. Pollut. Bull.* 50, 589–595.
- Chen, C.W., Kao, C.M., Chen, C.F., Dong, C.D., 2007. Distribution and accumulation of heavy metals in the sediments of Kaohsiung Harbor, Taiwan. *Chemosphere* 66, 1431–1440.
- Chiffolleau, J.F., Gonzales, J.L., Miramand, P., Thouvenin, B., 1999. Le cadmium: comportement d'un contaminant métallique en estuaire, 32.
- Christophoridis, C., Dedepsidis, D., Fytianos, K., 2009. Occurrence and distribution of selected heavy metals in the surface sediments of Thermaikos Gulf, N. Greece. Assessment using pollution indicators. *J. Hazard. Mater.* 168, 1082–1091.
- Covelli, S., Fantolan, G., 1997. Application of normalization procedure in determining regional geochemical baseline. *Environ. Geol.* 30, 34–45.
- Dickinson, W.W., Dunbar, G.B., McLeod, H., 1996. Heavy metal history from cores in wellington harbour, New Zealand. *Environ. Geol.* 27, 59–69.
- Di Palma, L., Mecozzi, R., 2007. Heavy metals mobilization from harbour sediments using EDTA and citric acid as chelating agents. *J. Hazard. Mater.* 147, 768–775.
- Di Palma, L., Ferrantelli, P., Medici, F., 2005. Heavy metals extraction from contaminated soil: recovery of the flushing solution. *J. Environ. Manage.* 77, 205–211.
- Di Palma, L., Ferrantelli, P., Pitzolu, I., Verdone, N., 2007. EDTA leaching of copper from contaminated soils: experimental study and transport model application for parameters estimation. *Environ. Technol.* 26, 189–198.
- Doherty, G.B., Brunskill, G.J., Ridd, M.J., 2000. Natural and enhanced concentrations of trace metals in sediments of cleveland bay, Great Barrier Reef Lagoon, Australia. *Mar. Pollut. Bull.* 41, 337–344.
- Dubrulle, C., Lesueur, P., Boust, D., Dugué, O., Poupinet, N., Lafite, R., 2007. Source discrimination of fine-grained deposits occurring on marine beaches: the Calvados beaches (eastern Bay of the Seine, France), *Estuarine. Coastal Shelf Sci.* 72, 138–154.

- Duinker, J.C., Van Eck, G.T.M., Nolting, R.F., 1974. On the behavior of copper, zinc, iron and manganese, and evidence for mobilization processes in the Dutch Wadden Sea. *Netherlands J. Sea Res.* 8, 214–239.
- Fangueiro, D., Bermond, A., Santos, E., Carapuça, H., Duarte, A., 2002. Heavy metal mobility assessment in sediments based on a kinetic approach of the EDTA extraction: search for optimal experimental conditions. *Anal. Chim. Acta* 459, 245–256.
- Guerra-Garcia, J.M., Garcia-Gomez, J.C., 2005. Assessing pollution levels in sediments of a harbour with two opposing entrances: environmental implications. *J. Environ. Manage.* 77, 1–11.
- Guevara-Riba, A., Sahuquillo, A., Rubio, R., Rauret, G., 2004. Assessment of metal mobility in dredged harbour sediments from Barcelona, Spain. *Sci. Total Environ.* 321, 241–255.
- Huerta-Diaz, M.A., Delgadillo-Hinojosa, F., Hernández-Ayón, M., Segovia-Zavala, J.A., García-Esquivel, Z., López-Zárate, H., Siqueiros-Valencia, A., Galindo-Bect, S., 2008. Diagnosis of trace metal contamination in sediments: the example of Ensenada and El Sauzal, two harbors in Baja California, Mexico. *Mar. Environ. Res.* 66, 345–358.
- Idris, M., 2008. Combining multivariate analysis and geochemical approaches for assessing heavy metal level in sediments from Sudanese harbors along the Red Sea coast. *Microchem. J.* 90, 159–163.
- Larner, B.L., Palmer, A.S., Seen, A.J., Townsend, A.T., 2008. A comparison of an optimized sequential extraction procedure and dilute acid leaching of elements in anoxic sediments, including the effects of oxidation on sediment metal partitioning. *Anal. Chim. Acta* 608, 147–157.
- Leleyter, L., Baraud, B., 2005. Évaluation de la mobilité des métaux dans les sédiments fluviaux du bassin de la Vire (Normandie, France) par extractions simples ou séquentielles. *Comptes Rendus Geoscience* 337, 571–579.
- Leleyter, L., Rousseau, C., Biree, L., Baraud, F., 2012. Comparison of EDTA, HCl and sequential extraction procedures, for selected metals (Cu, Mn, Pb, Zn), in soils, riverine and marine sediments. *J. Geochem. Explor.* 116–117, 51–59.
- Long, E.R., MacDonald, D.D., Smith, S.L., Calder, F.D., 1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. *Environm. Manage* 19, 81–97.
- Magesh, N.S., Chandrasekar, N., Vetha, Roy., D., 2011. Spatial analysis of trace element contamination in sediments of Tamiraparani estuary, southeast coast of India, *Estuarine. Coastal Shelf Sci.* 92, 618–628.
- Meybeck, M., Lestel, L., Bonté, P., Moilleron, R., Colin, J.-L., Rousselot, O., Hervé, D., De Pontevès, C., Grosbois, C., Thévenot, D.R., 2007. Historical perspective of heavy metals contamination (Cd, Cr, Cu, Hg, Pb, Zn) in the Seine River basin (France) following a DPSIR approach (1950–2005). *Sci. Total Environ.* 375, 204–231.

- Mulchi, C.L., Adamu, C.A., Bell, P.F., Chaney, R.L., 1992. Residual heavy metal levels in sludge amended coastal plain soils – II. Predicting metal levels in tobacco from soil test information. *Commun. Soil Sci. Plant Anal.* 23, 1053–1069.
- Muniz, P., Danulat, E., Yannicelli, B., Garcia-Alonso, J., Medina, G., Bicego, M.C., 2004. Assessment of contamination by heavy metals and petroleum hydrocarbons in sediments of Montevideo Harbour (Uruguay). *Environ. Int.* 29, 1019–1028.
- Muñoz-Barbosa, A., Gutiérrez-Galindo, E.A., Daesslé, L.W., Orozco-Borbón, M.V., Segovia-Zavala, J.A., 2012. Relationship between metal enrichments and a biological adverse effects index in sediments from Todos Santos Bay, northwest coast of Baja California, México. *Mar. Pollut. Bull.* 64, 405–409.
- Padox, J.M., Hennebert, P., Benard, A., Mancioppi, L., 2010. Qualité chimique des sédiments marins en France: Synthèse des bases de données disponibles, INERIS, rapport d'étude, 102.
- Pirrie, D., Camm, G.S., Sear, L.G., Hughes, S.H., 1997. Mineralogical and geochemical signature of mine waste contamination, Tresillian River, Fal Estuary, Cornwall, UK. *Environ. Geol.* 29, 58–65.
- Pirrie, D., Power, M.R., Wheeler, P.D., Cundy, A., Bridges, C., Davey, G., 2002. Geochemical signature of historical mining; Fowey Estuary, Cornwall, UK. *J. Geochem. Explor.* 76, 31–43.
- Pirrie, D., Power, M.R., Rollinson, G., Camm, G.S., Hughes, S.H., Butcher, A.E., Hughes, P., 2003. The spatial distribution and source of arsenic, copper, tin and zinc within the surface sediments of the Fal Estuary, Cornwall, UK. *Sedimentology* 50 (3), 579–595.
- Rao, C.R.M., Sahuquillo, A., Lopez-Sanchez, J.F., 2010. Comparison of single and sequential extraction procedures for the study of rare earth elements remobilisation in different types of soils. *Anal. Chim. Acta* 662, 128–136.
- Reddy, M.S., Basha, S., Sravan Kumar, V.G., Joshi, H.V., Ramachandraiah, G., 2004. Distribution, enrichment and accumulation of heavy metals in coastal sediments of Alang–Sosiya ship scrapping yard, India. *Mar. Pollut. Bull.* 48, 1055–1059.
- Rousseau, C., Baraud, F., Leleyter, L., Gil, O., 2009. Cathodic protection by zinc sacrificial anodes: impact on marine sediment metallic contamination. *J. Hazard. Mater.* 167, 953–958.
- Sahuquillo, A., Rigol, A., Rauret, G., 2003. Overview of the use of leaching/extraction tests for risk assessment of trace metals in contaminated soils and sediments, TrAC. *Anal. Chem.* 22, 152–159.
- Scouller, R.C., Snape, I., Stark, J., Gore, D.B., 2006. Evaluation of geochemical methods for discrimination of metal contamination in Antarctic marine sediments: a case study from Casey Station. *Chemosphere* 65, 294–309.
- Sorensen, P.G., Milne, J.R., 2009. Porirua Harbour targeted intertidal sediment quality assessment, Greater Wellington Regional Council, Publication. No.GW/ EMI-T, 136.

Sprovieri, M., Feo, M.L., Prevedello, L., Manta, D.S., Sammartino, S., Tamburrino, S., Marsella, E., 2007. Heavy metals, polycyclic aromatic hydrocarbons and polychlorinated biphenyls in surface sediments of the Naples harbour (southern Italy). *Chemosphere*. 67, 998–1009.

Szefer, P., Glasby, G.P., Pempkowiak, J., Kaliszan, R., 1995. Extraction studies of heavy-metal pollutants in surficial sediments from the southern Baltic Sea off Poland. *Chem. Geol.* 120, 111–126.

Turekian, K.K., Wedephol, K.H., 1961. Distribution of the elements in Some Major Units of the Earth's Crust. *Geol. Soc. Am. Bull.* 72, 175–192.

Varrault, G., 2012. Les contaminants dans les milieux récepteurs sous forte pression urbaine. Mémoire présenté pour l'obtention du Diplôme d'Habilitation à Diriger des Recherches, 89.

Wright, P., Mason, C.F., 1999. Spatial and seasonal variation in heavy metals in the sediments and biota of two adjacent estuaries, the Orwell and the Stour, in eastern England. *Sci. Total Environ.* 226, 139–156.