# ACCUMULATION OF METALS IN HARBOR SEDIMENTS : A COMPREHENSIVE ASSESSMENT OF THE ENVIRONMENTAL RISK THANKS TO THE COMBINED ESTIMATIONS OF ANTHOPOGENIC ENRICHMENT, BIOAVAILABILITY AND POTENTIAL ADVERSE BIOLOGICAL EFFECTS

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**ABSTRACT**

Marine and estuarine harbor sediments are subject to anthropogenic input, including elevated concentrations of potentially toxic metals and their accumulation is based on various factors including mineralogical texture, natural background levels of metals, recent and historical anthropogenic inputs, dredging activities and port development. Metal toxicity and bioavailability depend on numerous parameters such as metal speciation; pH, redox potential, temperature,…. The determination of the total concentration of heavy metals in sediments is not sufficient to predict the potential adverse effect of those metals. Thus, to achieve a comprehensive assessment of the environmental risk presented by a sediment, three aspects have to be considered : the anthropogenic enrichment of the metallic elements in the sediment, the measures of the bioavailability and the potential adverse biological effects.

This study reports the results obtained from 13 dredged habour sediments, focusing here on the Zn element. The total concentrations are determined after microwave assisted mineralization. A sequential extraction (1) is conducted to get information on the geochemical distribution of Zn and its mobility, then potential bioavailability. Indices of contamination are then used to evaluate the sediments with respect an Enrichment Factor (EF calculated according to (2)) and the estimation of the Zn adverse biological effects (AEI, as recommended by (3)). Correlation between enrichment, mobility and biological effects are investigated. In all the samples an important enrichment is shown at levels known to induce adverse biological effects according to the calculated AEI values. Some strong correlations between EF and mobility are also noticed.

*Keywords: dredged sediment, zinc, sequential extraction, EF, AEI.*

## INTRODUCTION

Significant dredging activity is constantly required to enlarge, deepen and maintain harbor access and activities. However, the management of the dredged sediments is an issue, particularly when contaminant concentrations prevent immersion at sea or land disposal.

The accumulation of pollutants such as heavy metals in sediments depends on various parameters such as natural background levels, mineralogical characteristics of the sediments, anthropogenic inputs.

The total concentrations of metals are useful to calculate various contamination indexes, but are not sufficient to predict the real potential adverse effect on the environment: the metals toxicity depends on other parameters such as mobility and bioavailability. Indeed, adsorbed metals are potentially available from the sediments as they may be dissolved due to changes in salinity, pH, redox conditions, organic chelators occurrence... [1].

This potential mobilization (or lability) can be estimated by chemical extractions. Sequential extraction procedures (several steps) are used to differentiate mobile from residual fractions, and to characterize the different labile fractions [1-4], which is sometimes designed as mineralogical speciation or geochemical fractionation /partitioning / distribution.

The sequential procedure uses various chemicals reagents to carry out successive leachings of the specific geochemical fractions and several different protocols are proposed in the literature [1, 4, 5, 6] Despite the possible lack of selectivity and re-adsorption phenomena [7-8], sequential extractions are still widely used to predict the mobility and potential bioavailability of metals.

Few studies report on the anthropogenic enrichment of elements in the sediment in combination with measures of the bioavailability and potential adverse biological effects of those elements.

This paper focuses on the zinc element and reports the results obtained from 13 harbors sediments sampled on both the UK and French side of the English Channel. We investigate the possible relationships between the zinc total content, its fractionation and calculated indexes of contamination such as Enrichment Factor (EF) and adverse biological effects (AEI).

## MATERIALS AND METHODS

### Sediments samples

The 13 studied sediments (designed hereafter from A to M) were sampled in 13 harbors on each side of the English Channel (Fig.1), using either a diver, a grab or a suction dredger, depending on the available techniques [9]. After homogenization, the sediment samples were air-dried for 4 days, sieved at 500µm using a nylon sieve, then ground manually (agate mortar and pestle), and finally stored at 4°C before further analysis.

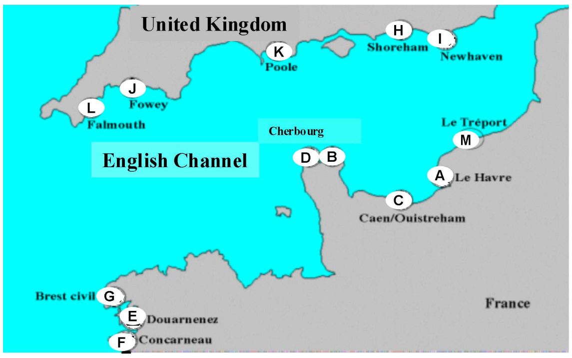


Fig. 1 Location of the 13 sampling points;

### Zinc total levels and geochemical partitioning

*Total concentration*

To get the total content of zinc, 0.2g of dried sediment was digested with 10 mL of aqua regia ($HCl/HNO_3$, 3:1) in a Berghof speedwave MWS-2 microwave oven. The analytical quality of the data was controlled using certified reference material HR-1 (Canada Center for Inland Waters National Laboratory for Environmental). Each digestion was performed in triplicate.

*Sequential extraction*

The procedure used [1, 10] is detailed in Table 1.

Table 1 sequential extraction procedure according [1].

| | reagent | C (M) | pH | $t_{min}$ |
|---|---|---|---|---|
| F1 | Water | | 5.7 | 30 |
| F2 | $Mg(NO_3)_2$ | 1 M | 5.0 | 120 |
| F3 | NaOAc/HOAc | 1 M | 4.5 | 300 |
| F4 a | $NH_2OH$ HCl | 0.1 M | 3.5 | 30 |
| F4 b | $(NH_4)_2C_2O_4$ + $H_2C_2O_4$ | 0.2 M<br>0.2 M | 3.0 | 240 |
| F4 c | $(NH_4)_2C_2O_4$ + $H_2C_2O_4$ + $C_6H_8O_6$ | 0.2 M<br>0.2 M<br>0.1M | 2.3 | 30 |
| F5 | $H_2O_2$ + $HNO_3$ then $NH_4OAc$ | 35%/<br>0.02 M<br>3.2 M | 2.0 | 300 |

C (M) : reagent concentration in mol.L$^{-1}$; $t_{min}$ = agitation time in minute; M = mol.L$^{-1}$.

This procedure reveals the geochemical partitioning of the elements between 5 operationally defined fractions: F1:water soluble, F2: exchangeable, F3: acid-soluble, F4: reducible and F5: oxidisable. The sum of these five fractions (ΣF) represents the total labile fraction. The remaining part is designed as the residual fraction.

Three replicate of each step (L/S : 1/10) are performed. After filtration of the solid/liquid mixture at 0.45 µm, the leachates are stored at 4°C prior to chemical analysis. The detailed procedure is reported elsewhere [1, 11].

*Chemical analysis*

All the leachate solutions and acid digests were analysed using ICP-AES (inductively coupled plasma-atomic emission Spectrometry, Varian, Vista MPX). The detailed quality criteria controlled are reported elsewhere [10, 11].

### Indices of contamination

*Enrichment Factor (EF)*

To detect possible anthropogenic contamination the calculation of an enrichment factor (EF) is used by several authors [12-15].

The EF formula proposed by [16] involves an internal reference element (a normalizer): aluminium was chosen for this purpose in the present study (detailed description of Al analysis and results are given elsewhere [9]). Geochemical background data are also needed to calculate EF: the average shale values reported by [17] are retained in our case, as proposed by many authors [13, 18, 19]. Then, EF is calculated as follow:

$$EF = ([Zn]/[Al])_{sediment}/([Zn]/[Al])_{reference} \quad (1)$$

with $[X]_{sediment}$ = concentration (mg.kg$^{-1}$) of X in the sediment sample and $([Zn]/[Al])_{reference}$ = (95/80) according to [19].

Then, as many authors [14, 20, 21], we considered:
- metal deficiency to low enrichment for EF < 2;
- moderate to significant enrichment for 2 ≤ EF < 20;
- very high enrichment for 20 ≤ EF < 40;
- extremely high enrichment for EF ≥ 40.

Moreover, EF above 4 would indicate that the metal is mostly provided by anthropogenic influence [14, 20, 21].

*Adverse Effect Index (AEI)*

EF cannot be used to evaluate the probability of toxic effects on biota. In the absence of toxicity studies, [22] suggest that element concentrations can be compared with Threshold Effect Level (TEL) sediment quality guidelines (SQG) developed by [23] in order to assess an Adverse Effect Index (AEI). AEI is calculated as follow:

$$AEI = [Zn]/TEL \qquad (2)$$

with TEL = 124 mg.kg$^{-1}$ for Zn [23].

If AEI < 1, the metal concentration is not sufficient enough to induce negative biological effect (or moderate impact are suspected), whereas important adverse effects on biota are probable when AEI ≥1 [22].

## RESULTS

### Zn total Concentration, EF and AEI values

Table 2 reports the total concentrations of zinc determined in the 13 sediments.

Table 2 Total concentration of Zn (mg.kg$^{-1}$), Enrichment Factor (EF) and Adverse Effect Index (AEI).

| Sediment | [Zn] | EF | AEI |
|---|---|---|---|
| A | 235 ± 15 | 6.2 | 1.9 |
| B | 120 ± 3 | 4.6 | 1.0 |
| C | 286 ± 21 | 9.4 | 2.3 |
| D | 213 ± 11 | 4.5 | 1.7 |
| E | 1226 ± 50 | 59.6 | 9.9 |
| F | 290 ± 19 | 7.8 | 2.3 |
| G | 120 ± 3 | 5.3 | 1.0 |
| H | 53 ± 1 | 3.4 | 0.4 |
| I | 233 ± 19 | 12.3 | 1.9 |
| J | 123 ± 1 | 3.0 | 1.0 |
| K | 233 ± 18 | 18.6 | 1.9 |
| L | 393 ± 8 | 10.1 | 3.2 |
| M | 289 ± 29 | 7.8 | 2.3 |

These results were then used to calculate EF and AEI (see Table 2) according to Eq. (1) and Eq. (2) respectively.

The sediment H, with the lowest total content and low EF values (respectively 53 mg.kg$^{-1}$ and 3.4), is also the only sediment with a value of AEI < 1 (AEI = 0.4). All the other calculated AEI equal or exceed 1, indicating possible biological adverse effects due to zinc in the sediments.

The correlation between EF and AEI values is displayed on Fig. 2.

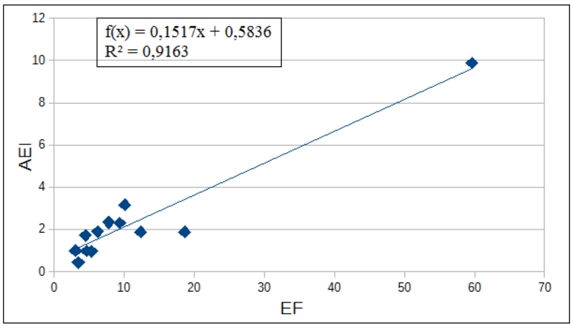


Fig. 2 AEI versus EF for Zn considering the 13 sediments.

The linear regression then obtained, with $R^2$ = 0.92, confirmed the link between enrichment and possible negative effect on biota. The linear regression equation (see Fig. 2) can be used to estimate the threshold value of enrichment (EF value) over which the sediment could be considered as toxic (as soon as AEI ≥ 1). In our case, AEI =1 for EF = 2.8, which suggests that any enrichment above 2.8 could correspond to toxicity incidence of the sediment. This value is similar to the one estimated by [22] and suggests that for zinc, even quite low enrichment could induce negative biological effect. In our case, it confirms that all the dredged sediments should not be disposed at sea before further analysis.

### Zn geochemical distribution

Figure 3 displays the zinc fractionation, according the sequential procedure applied, for each studied sediment: the % of the total Zn mobilized in each fraction is reported.

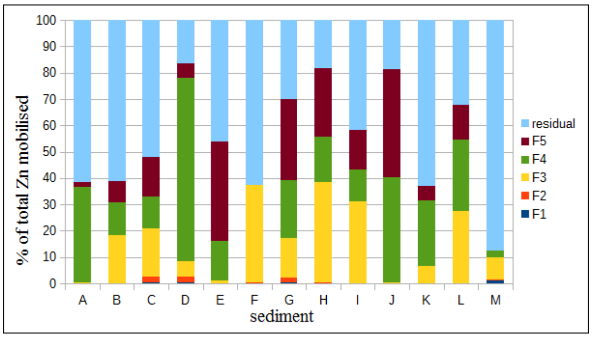


Fig. 3 Zinc fractionation in the 13 sediments according the applied sequential extraction.

Except for the sediment M (∑F = 12.5%), the total labile fraction of Zn exceeds 30% for all the sediments, and even 50% for most of them. This is in agreement with several studies that consider that Zn is one of the most mobile metals, as mainly associated with the non-residual fraction [29-33] . As generally reported in the literature [33- 36] Zn is found mainly associated to the acido-soluble, reducible and oxidable fractions, with a distribution that can vary from one sample to another. For example, no zinc is associated to the acido-soluble fraction in the sediments A, E and J. On the other hand, no mobile Zn is associated to the oxidable fraction in sediments F and M.

The lack of Zn in the water soluble and exchangeable fractions (often considered as the most environmentally available fractions [14]) is probably resulting from the natural *in-situ* leaching of these marine sediments by the sea water.

### Relationship between EF, AEI and Zn mobility

We then investigate the possible relationship between the Zn distributions and the Zn enrichments or possible adverse effects.

Table 3 Pearson correlation coefficients (r) between mobile Zn ($mg.kg^{-1}$) and EF or AEI for the geochemical operationally defined fractions.

| mobile fraction : | EF | AEI |
|---|---|---|
| F1 | -0.14 | -0.04 |
| F2 | -0.20 | -0.11 |
| F3 | -0.09 | 0.02 |
| F4 | 0.64 | 0.70 |
| F5 | 0.95 | 0.94 |
| ΣF | 0.91 | 0.96 |

*NB : "strong correlation": 0.8 < r ≤1.0; "affinity" 0.6 <r ≤ 0.8*

Correlation analysis between mobile zinc (quantities of zinc, in $mk.kg^{-1}$, mobilized in each fraction) and EF, then AIE, for the 13 sediments, were realized. The correlation coefficients are reported in table 3.

The r values are similar for EF and AEI, obviously as a consequence of the relationship between these two parameters, as previously noticed (Fig. 1).

The results show a strong link between the total labile fraction contents (ΣF) and the enrichment or possible adverse effect (r = 0.91 and 0.96 respectively for EF and AEI).

This suggests that the more enriched the sediment is, the more the quantity of labile (then available) Zn is. Therefore, the increase of negative biological effect could be logically expected with the rise of the amount of available zinc.

The geochemical fractions involved are the reducible (r = 0.64 and 0.70 respectively for EF and AEI) but mainly the oxidable fractions r = 0.95 and 0.94 respectively for EF and AEI).

No correlation exists with the water-soluble nor the exchangeable fractions (r from -0.2 to -0.04), which is obviously due to the lack of Zn in these fractions, for all the studied sediments.

However, despite significant quantities of Zn in the acido-soluble fraction, often considered as a pool of easily available elements, there is no significant link between the quantities mobilized in this fraction and possible negative effects on organisms (r = 0.02 for AEI).

## CONCLUSIONS

The aim of this work was to assess the environmental risk for 13 dredged marine sediments sampled in 13 harbors from the English Channel, focusing on the potential impact of zinc. The determination of the total content of Zn, then the calculated enrichment factor (EF) derived from these values, indicate moderate to extremely high enrichment for these sediments that can be attributed to anthropogenic inputs. This is in agreement with the zinc contamination reported by other authors, associated either to harbor activities, mining activities or river contamination in estuaries zones for several of the studied locations (see details in [9]). These enrichments are linked to possible adverse effect on biota, that were estimated by the calculation of the AEI values for each sediment.

The zinc mobility was estimated thanks to a sequential extraction procedure and correlation with EF or AEI were searched. As usual reported the mobile (then available) zinc is mainly associated to the reducible, oxidable fraction and/or acido-soluble fractions. The link between probable negative biological effects and the total labile fraction is observed. Moreover, despite the oxidable fraction (mainly constituted by organic matter and sulfides) is generally considered as the most stable, a strong link between this fraction and adverse biological effect is noticed for zinc in our case.

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