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POTENTIAL MOBILIZATION OF INORGANIC CONTAMINANTS IN A FRENCH HARBOR SEDIMENT

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RESUME

Dans la cadre d'un PRogramme de recherche sur les ECOtechnologies et le Développement Durable (PRECODD) financé par l'Agence Nationale de la Recherche (ANR) et intitulé "SEDiGEST" (GESTion durable des SEDiments de dragages des ports), les travaux présentés dans ce papier concernent plus particulièrement l'évaluation physico-chimique de la mobilisation potentielle des polluants inorganiques présents dans une matrice sédimentaire.

Dans cet objectif, une méthodologie, basée sur l'utilisation de tests de lixiviation et complétée par des analyses minéralogiques et texturales, a été développée et appliquée sur un sédiment fin sablo-argileux riche en matière organique (environ 12%) dragué dans un port français. L'analyse minérale multi-élémentaire a tout d'abord montré que ce sédiment présentait des teneurs importantes, principalement en calcium ($109\,000\text{ mg.kg}^{-1}$), fer ($32\,170\text{ mg.kg}^{-1}$), et soufre ($19\,660\text{ mg.kg}^{-1}$); ainsi qu'en zinc ($2\,120\text{ mg.kg}^{-1}$), cuivre ($1\,730\text{ mg.kg}^{-1}$), plomb (860 mg.kg^{-1}).

Les principaux résultats obtenus permettent ainsi de répondre qualitativement à la question du risque de mobilisation des polluants cibles minéraux (As, Cu, Pb et Zn) présents dans cette matrice. Ce risque de mobilisation lors d'un contact à l'eau est très faible (moins de 0,1 % du contenu total), du fait d'une part, du pH neutre à légèrement basique de la solution de sédiment dans ces conditions dites « naturelles », et du fait d'autre part de la stabilité de l'immobilisation de ces polluants sur les constituants des sédiments tels que la matière organique, les carbonates et/ou les sulfures. Un risque de mobilisation à plus ou moins long terme existe cependant dans des conditions de lixiviation particulières (pH < 6, présence d'un chélatant, etc.), pouvant notamment survenir dans le cadre d'un scénario de gestion de sédiments marins.

ABSTRACT

As part of a French national research program called “SEDiGEST” concerning the management and the environmental risk assessment of contaminated marine harbor sediments, the research presented in this paper focuses on the determination of the leachability of inorganic contaminants.

In this objective, a methodology was developed and applied to investigate the mobility of inorganic contaminants as a function of physicochemical conditions. This methodology is based on the use of leaching tests in conjunction with mineralogical and textural analysis. Muddy sediment with important Organic Matter (OM) content (*ca.* 12 wt %) has been selected and collected from a French harbor. This sediment contained also *ca.* 109 000 mg.kg⁻¹ calcium (Ca), *ca.* 32 170 mg.kg⁻¹ iron (Fe), *ca.* 19 660 mg.kg⁻¹ sulfur (S), *ca.* 2 120 mg.kg⁻¹ zinc (Zn), *ca.* 1 730 mg.kg⁻¹ copper (Cu), *ca.* 860 mg.kg⁻¹ lead (Pb) and *ca.* 150 mg.kg⁻¹ arsenic (As). In addition, this sediment had a natural pH and ORP (Oxidation Reduction Potential) of *ca.* 8.2 and *ca.* + 350 mV vs. Normal Hydrogen Electrode (NHE).

Main results shown in this study indicate that the release of target contaminants (As, Cu, Pb and Zn) during a contact with deionized water is very limited (*ca.* <-0.1 wt %) by the very low solubility of solids, like sulfides or carbonated phases, and by the stability of their bearing solid phases (*i.e.*, OM and/or sulfides) at natural slightly basic conditions. However, the natural pH of this matrix can vary with the loss of the buffering capacity and an increased mobilization is observed over the long term under specific leaching conditions (*i.e.*, pH < 6, or chelation effect, etc.) which can arise in a given scenario for the management of marine sediments.

1. INTRODUCTION

The French national research agency (ANR) initiated a three years program called “SEDiGEST”, concerning the management and the environmental risk assessment of contaminated marine harbor sediments. As part of this program, the research presented in this paper focuses on the determination of the leachability of inorganic contaminants. In this objective, a methodology was developed and applied to investigate the potential mobilization of inorganic contaminants [1-2]. This methodology, based on the use of leaching tests in conjunction with mineralogical and textural analysis, was firstly applied to an untreated French harbor sediment.

Therefore, the research presented here provides data concerning the solubility and mobility of inorganic contaminants (As, Cu, Pb and Zn) in this selected matrix as a function of the sediment composition and physicochemical conditions.

2. MATERIALS AND METHODS

2.1. Sediment sample collection and preparation

Raw sediment from a French harbor was used for the study. Prior to characterization and liquid-solid partitioning experiments, the matrix was sieved at 2 mm, homogenized, and stored at 4°C in the dark.

2.2. Physical and chemical characterization of the sediment

The structural characteristics were analyzed with a Grain size analyses by a laser diffractometer (a Malvern mastersizer 2000G[®]) with a range from 0.02 µm to 1000 µm. The non-aggregation of the sediment was previously checked. It was then

decided to fractionate the sediment into four particle size fractions (respectively, 630-1000 μm , 63-630 μm , 10-63 μm and $<10 \mu\text{m}$).

Total content of trace elements and major constituents was determined by acid digestion [3] and subsequent analyses using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES, Jobin-Yvon Ultima 2[®]) in the sediment and the fractionated fractions.

X-Ray Diffraction (XRD, Panalytical X'Pert Pro MPD diffractometer) was also used in conjunction with single [1-2; 4-5] and sequential chemical extraction techniques [6-7]. Single extraction techniques using deionized water and 0.05 M EDTA solution at pH 7 were performed to determine, respectively, the soluble and available fractions in the sediment [2; 4-5]. These single extractions were carried out in triplicate using an L/S ratio of 10 mL/g and a contact time of 48 hours, except for the EDTA extraction for which an L/S ratio of 100 mL/g was used. Additionally, a sequential chemical extraction procedure adapted from Tessier al. (1979) and Quevauviller et al. (1997) [6-7] was carried out in triplicate to determine the, operationally defined, distribution of four fractions: acid-extractable (0.11 M HOAc), reducible (0.5 M $\text{NH}_4\text{OH}\cdot\text{Cl}$ adjusted to pH 2), oxidizable (8.8 M H_2O_2 adjusted to pH 2 at 90°C followed by 1 M NH_4OAc adjusted to pH 2) and residual fractions (estimated from the total content obtained using acid digestion); for constituents of interest in the sediment.

Finally, liquid-solid partitioning of elements of interest was determined at varying pH. Thirteen subsamples of sediment were suspended in triplicate during 48 hours with solutions of varying equivalents of HNO_3 or NaOH at an L/S ratio of 10 mL/g to reach final pHs ranging between 1 and 13 (SR002.1 protocol, Solubility and Release as a function of pH [1]).

All leachates obtained were filtered through 0.45 μm pore size acetate-cellulose Whatman[®] membranes, and subsequently analyzed for concentrations of constituents of interest using ICP-AES. Sulfates and chlorides were analyzed using IC (ion chromatography, Dionex DX320 HPIC[®]). Total Organic Carbon (TOC) in solution was measured using TOC analyzer (Total Organic Carbon analyzer, Shimadzu TOC-5000A[®]).

3. RESULTS AND DISCUSSION

3.1 Sediment sample characterization

Results of the physical fractionation tend to show that this raw sediment was relatively fine and silty, with about 80% of particles with a diameter less than 60 μm .

Total content of trace elements indicated that this raw sediment contained mainly *ca.* 109 000 $\text{mg}\cdot\text{kg}^{-1}$ Ca, *ca.* 32 170 $\text{mg}\cdot\text{kg}^{-1}$ Fe, *ca.* 19 660 $\text{mg}\cdot\text{kg}^{-1}$ S, *ca.* 2 120 $\text{mg}\cdot\text{kg}^{-1}$ Zn, *ca.* 1 730 $\text{mg}\cdot\text{kg}^{-1}$ Cu, *ca.* 860 $\text{mg}\cdot\text{kg}^{-1}$ Pb and *ca.* 150 $\text{mg}\cdot\text{kg}^{-1}$ As. Moreover, it was characterized by a very high moisture content of *ca.* 61.5 %, and an important OM content (*ca.* 12 wt %). The fractionation revealed that the finer fractions ($< 63 \mu\text{m}$) were more concentrated with OM, major mineral elements like magnesium (Mg), aluminum (Al), Fe, potassium (K), S and Ca. Nevertheless, the heavy metal content was not significantly different in all the fractions even in the sandy ones.

Depending on particle size fractions, XRD analyses indicated the presence of quartz, feldspars, analcime, pyroxenes, gypsum, halite, chlorite, muscovite, calcite, dolomite, aragonite and pyrite.

3.2 Determination of the soluble and available fractions by single extractions

After 48 hours of contact with deionized water at a L/S ratio of 10 mL/g, the sediment solution presented a natural pH of 8.2 and an ORP of +350 mV (vs. NHE). Very low soluble (*ca.* < 0.1 wt %) fractions of inorganic contaminants were obtained at these natural conditions. In contrast, a significant available fraction of Pb and Zn was observed from the single extraction using EDTA (*ca.* 90 wt% and 80 wt%, respectively). An important available fraction of As, Cu and Fe was also measured from this extraction (*ca.* 40 wt %).

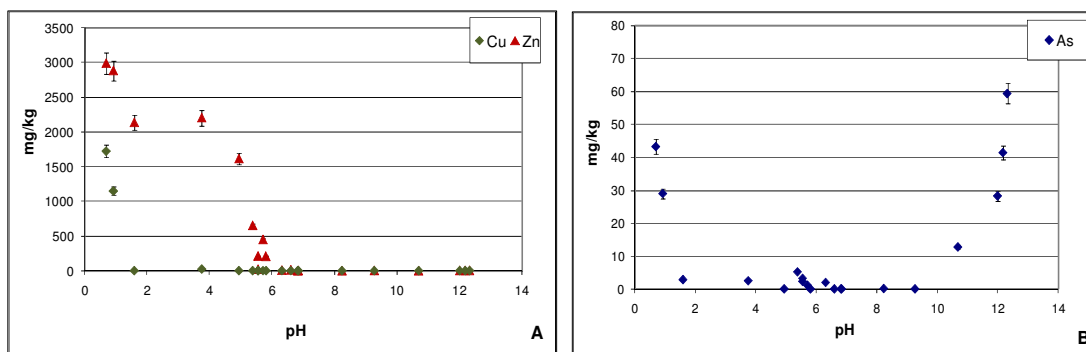
3.3 Fractionation by a sequential extraction procedure

Results from the sequential extraction procedure indicated that Cu and Zn were fairly mobile. About *ca.* 85% and 100% of the total content in Cu and Zn, respectively, were extracted within the first three extracts. These results indicated that most of the Cu and Zn was probably bound onto oxidizable fraction (*i.e.*, sulfides or organic matter) which is consistent with results from the XRD study, and with what is generally observed [8-11]. On the opposite, Pb, Fe and particularly As appeared essentially bound to the residual fraction (*i.e.*, silicates, or resistant OM and sulfides), suggesting a relatively low mobility of these elements.

3.4 Solubility and Release as a function of pH

Batch equilibrium leaching tests following the SR002.1 protocol [1] showed a very high buffering capacity of this sediment for pH values around 6. The important size of the buffering step is consistent with results from the XRD study (*i.e.*, carbonate minerals observed) and explained by the origin of the sediment (*i.e.*, marine environment with fragments of seashells).

Figure 1. Cu, Zn (A.) and As (B.) solubilization as a function of pH (contact time: 48 hours).



The liquid-solid partitioning of Cu, Zn and As at varying pH is shown in Figures 1A and 1B. Results of Zn and Cu solubilization as a function of pH (Figure 1A) indicated that the solubility of Zn and Cu remained very low for pH values above 6 and 2, respectively; and significantly increased for pH below these values. Results of As solubilization as a function of pH (Figure 1B) indicated that the solubility of As remained very low for pH values ranging from 2 to 11, and significantly increased for pH values below 2 and above 11.

4. CONCLUSION

Main results shown in this study indicate that the release of target contaminants (As, Cu, Pb and Zn) during a contact with deionized water is very limited by their

very low solubility in the sediment solution and by the stability of their bearing solid phases (sulfide phases and/or OM) at natural slightly basic conditions.

However, the natural pH of this matrix appears unstable and an increased mobilization is observed over the long term under specific leaching conditions (i.e., pH or ORP gradient, chelation effect, etc.) which can arise in a given scenario for the management of marine sediments.

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