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# Environmental behavior of inorganic pollutants present in raw and desalinated French marine sediments

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## ABSTRACT

In the frame of long-term management of contaminated dredged sediments, this paper is centered on the determination of the mobility of inorganic contaminants. A methodology derived from waste characterization has been developed and applied to marine sediments from Lazaret bay (Toulon, southern France) to determine the potential mobilization of inorganic pollutants in specific conditions. It consists of mineral and textural analysis combined with leaching tests. This methodology was applied to untreated, 5.8 % organic matter, light sandy silt harbor sediment and to the same sediment after a desalinization treatment. In both untreated and desalinated sediments, the contaminant content was around 26.1, 0.18, 42.5, 34, 31, 35 and 99 mg kg<sup>-1</sup> for As, Cd, Cr, Cu, Ni, Pb and Zn, respectively. After 24 hours of time contact between deionized water and sediments, contaminant release of metals was very low (ca. <0.7 total mass %, for all studied elements) due to low solubility of the bearing solid phases (organic matter, carbonates and sulfides), while Mo and B were widely released. After 48 hours, Cd, As, Mo and B release was higher while more significant but no clear differences for other metal appeared.

Keywords: Dredged sediment; metal mobilization; Acid Neutralization Capacity.

## 1-Introduction

Seaworthiness of waterways and harbors was guaranteed by annual dredging of about 40 million tons of marine sediments in France. Dredged sediments were defined as complex matrices, of variable particular size classes, with different minerals, organic matter content as well as highly variable concentration of organic and inorganic contaminants (Cappuyns and Swennen, 2005). Based on the august 9<sup>th</sup> 2006 French decree and especially N1 and N2 thresholds, about 8 million of these sediments could be contaminated by inorganic and organic pollutants and could require a terrestrial management. According to French regulation, contaminated dredged sediments were considered as waste but sediments management stay problematic due to high content of water, salt, organic matter as well as large volume. Since a couple of years different studies and research programs have been developed to improve sediment treatment and reuse channels or/and to assess environmental impacts of the reuse and deposit (Lions, 2004; Lions et al., 2007; Piou et al., 2009). Today, it is necessary to have information on long term environmental behavior of sediment in reuse scenario. The study dealt with this topic and evaluated the mobilization of inorganic pollutants present in fresh raw marine sediment from Toulon Bay (South of France) and its desalinated analogue, in a target of reuse. The methodology applied was inspired by waste characterization (Kosson et al., 2002) and linked textural, mineral and organic matter characterization with different leaching tests in laboratory and outside

lysimeter. A model will then be created with experimental data to validate the different assumptions and to be applied for other types of sediments or reuse scenarios.

## **2-Materials and Methods:**

### ***2-1 Sampling and preparation.***

The studied marine sediment was chosen to present an intermediate contamination content between thresholds N1 and N2, according to French regulation (August 9, 2008 decree). Therefore, the dredging area was established from previously available data concerning the spatial distribution of inorganic contaminants in the sediments from Toulon Bay, France (Tessier et al., 2011). The sediments from the Lazaret Bay (43°05.3644 N, 05°54.6679 S) were selected to be studied and the first 20 centimeters of the sediments was sampled by divers at 7 meters-depth. About 900 kg of sediment were this way collected on April 2011. One part of the sediment was sieved at 2 mm, homogenized and stored at 4°C to the shelter of the light and under a 20 cm sea water layer or freeze-dried, in order to preserve its physico-chemical properties until analysis and experiments. Another part of the sediment was desalinated with tap water until an electrical conductivity (EC) was lower than 4.5 mS.cm<sup>-1</sup>. About 1600 L of tap water were used to desalinate 550 kg of raw sediment. Before reuse, some marine dredged sediments are sometime washed and the desalinated sample was done in take into account this pre-treatment.

### **2-2 Physical and chemical characterization**

Size particles distribution was determined using a laser diffraction particle-size analyzer (LS 200 Beckman Coulter) with a range from 0.03 µm to 2000 µm. Total concentrations of trace metals and major elements were measured by Inductively Coupled Mass spectrometry (Perkin Elmer Elan DRC II) and ICP-Atomic Emission Spectroscopy (Perkin Elmer-Optima 7200-DV) respectively, after optimized semi-total aqua regia digestion. 100 mg of sediment and 10 mL of aqua regia (HNO<sub>3</sub>: HCl 1 V:3 V, Fisher Scientific Trace Analysis grade, HNO<sub>3</sub> 70%-16 M, HCl 37%-12 M) were placed in 50 mL Teflon (PTFE) bombs and submitted to a controlled elevation of pressure and temperature in a microwave oven (Anton Paar Multiwave 3000). Sample extractions and analysis were realized in triplicate and the accuracy and precision of the analysis was checked using an international certified reference material (PACS, Table 1).

Particulate organic and inorganic carbon (POC and PIC, respectively) concentrations were determined using a TOC-V analyzer (Shimadzu) coupled with a SSM-5000A (Benner and Strom, 1993). Organic carbon was calculated by difference between total and inorganic carbon contents.

The mineralogy of the raw and desalinated sediment were identified by X-Ray Diffraction (Panalytical X'pert pro NPD)

Following the recommendations of Kosson et al. (2002), single and sequential selective extractions were realized in order to evaluate the behavior and speciation of each contaminant. Single extraction was performed using deionized water and acetic acid and aims at determining respectively soluble and available fractions of the sediment (Lebourg et al., 1996). Liquid on solid (L/S) ratios were 10 and 40 mL g<sup>-1</sup> for deionized water and acetic acid, respectively; and time contact was 24 and 48 hours for water and 16 hours for acetic acid. Sequential extractions were performed in triplicate using the BCR protocol (Tessier et al., 1979; Quevauviller et al., 1997). Four fractions were obtained: the first one was acid-extractable (0.11 M of acetic acid), the second one reducible (0.5M hydroxylamine hydrochloride), the third one oxidizable (8.8M H<sub>2</sub>O<sub>2</sub> adjusted to pH2 with HNO<sub>3</sub> concentrated at 85°C followed by ammonium acetate 1M adjusted to pH2) and the last one is residual fractions (calculated by difference with total contents obtained using aqua regia digestion) (J.Morillo et al., 2003).

Acid neutralization capacity tests (ANC) (Kosson et al., 2002, Chatain et al., 2004; Cappuyens et al., 2004; Dijkstra et al., 2004) were realized to evaluate the sediment buffering capacity and the liquid-solid partitioning of the different targeted elements. About 80.8 grams of wet sediments (which corresponded to 30 grams of dry matter) were leached with a 10 mL g<sup>-1</sup> L/S ratio during 48 hours in

HNO<sub>3</sub> and NaOH solutions in order to obtain final pH values ranging from 4 to 12 for raw sediment and from 1 to 12 for desalinated sediment.

All the obtained leachates were filtered using 0.45 µm pore size acetate-cellulose syringe membranes (Minisart, Sartorius-stedim biotech) and then analyzed using ICP-AES and ICP-MS. Anions and cations ( including, phosphates, sulphates and chlorides) were analyzed by ion chromatography (Dionex-120). Dissolved concentrations of TOC (Total Organic Carbon) were estimated by the difference between total carbon and inorganic carbon measured by the carbon analyzer (Shimadzu TOC-5000A).

Table 1 Results (mean ± standard deviation) obtained from certified reference materials analysis

	Certified value (mg/Kg)	Measured value (mg/Kg)
PACS 2		
Cu	310±12	316 ± 0,89
Pb	183±8	136 ± 0,82
Zn	364±23	368 ± 1,35
Ni	39,5±2,3	38,4 ± 0,11
Cd	2,11 ± 0,15	2,6 ± 0,03
Cr	90,7±4,6	73,9 ± 0,84
As	26,2±1,5	29,8 ± 0,17

### 3-Results and discussion

#### 3-1 Sample characterization

The raw sediment was characterized by high moisture content, around 61%. The physical fractionation results are given in Table 2. Both raw and desalinated sediments were mainly fine and silty with 65 and 51% of particles smaller than Ø 50 µm, respectively. According to the USDA triangular diagram of textural classes of soils, both materials are light sandy silt. Desalinated sediment had values lower for silt-sized particles (2-50 µm) and higher for coarse sand particles (200-2000 µm), indicating aggregation during desalination process. Organic matter (OM) content was relatively low (5.6 and 6.02 %) for raw and desalinated sediment, respectively). This concentration was closed to the values of Spanish harbor (Guevara-Riba et al., 2004; Casado-Martinèz et al., 2009).

Table 2 General properties of both sediment

type of sediment	Raw	desalinated
pH	7,8	7,5
Total Organic carbon (%)	3,3	3,6
Inorganic Carbon (%)	3,4	3,5
Particule size distribution	% of total mass	
2000 - 200 µm	8,7	22,9
200 - 50 µm	26,6	26,9
50 - 20 µm	19,6	15,5
20 - 2 µm	37,6	29,8
<2 µm	7,5	5,2
Total fraction	100	100

Total elements contents are given in Table 3. Ca was the most important major element and it would be present in calcite, aragonite and to a less extent in dolomite in both sediments, from the XRD results. The other major elements would be constituent of quartz, phyllosilicates (muscovite, kaolinite, clinocllore), plagioclase (albite), pyrite and halite for both sediments. Alunite, a sulfate mineral, was only present in the desalinated sediment. Total As and Hg contents were higher than thresholds proposed by the environmental French group GEODE within the framework of OSPAR convention, when Cu and Ni were nearby the N1 threshold.

Table 3 Total concentration of elements. Rw: untreated sediment; Ds: desalinated sediment; N1, N2: environmental thresholds \*values from Eurofins Cofrac Lab

	Rw	Ds	N1	N2		Rw	Ds
	mg kg <sup>-1</sup> (dry mass)					g kg <sup>-1</sup> (dry mass)	
As	25.3 ±2.1	30.2 ±2.3	25	50	Si	5.9 ±1.2	6.8 ±1.4
Cd	0.2 ±0.004	0.2 ±0.006	1.2	1.4	Al	25 ±2.2	30.4 ±2.9
Cr	42.5 ±8	60.6 ± 9.2	90	180	Mg	8.5 ±0.7	8.7 ±0.7
Cu	33.6 ±2.7	40.9 ±2.9	45	90	Ca	174.9 ±7.7	207.5 ±8.4
Ni	31.1 ±1.2	33.5 ±3.1	37	74	K	8.0 ±0.9	9.4 ±1.1
Pb	34.7 ±1.5	39.6 ±2.6	100	200	Na	16.0 ±0.8	1.6 ±0.4
Zn	98.6 ±18.9	107.4 ±22.6	276	552	Fe	25.0 ±1.7	17.2 ±1.4
Hg*	0.9	0.9	0.4	0.8	Cl	34.1	3.0
Mn	103.9 ±5.3	97.5 ± 7.6			S	11.8	9.7
Co	5.6 ±0.4	5.2 ±0.4					
B	211.6 ±21.2	175.9 ±27					

The desalination protocol has leached more than 90% of Na and Cl, 31% of Fe and about 18% of S. Fe and S leaching were probably associated to pyrite (FeS<sub>2</sub>) oxidation, and alunite (KAl<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>) formation. Pyrite often contains trace contaminants, like Ni, Cu, Zn, Pb, Hg (Lions, 2004; Lors et al., 2004 ; Caille et al., 2003). In this case, desalination and pyrite oxidation seem not to be responsible of inorganic contaminants release. For the contaminants, only B could be significantly released during the desalination.

### 3-2 Determination of water and acido-soluble extractible fractions

Long term behavior of chemical contaminants depends on its speciation within the matrix. Trace contaminants are retained by minerals, organic matter and as adsorbed species; the behavior of the bearing phases during leaching (dissolution, precipitation, mineralization...) explains the more or less mobility of the contaminants (Chaurand et al., 2007). Contaminant release was first studied using deionized water and acetic acid solution, then the bearing phases were evaluated using sequential selective extractions.

The physico-chemical parameters of solutions obtained after water extraction during 24 hours and a liquid/solid ratio of 10 L/kg (W24) were quite similar for both sediments. The pH was 7.8 and 7.5 for the raw and desalinated sediments, respectively; the redox potential was greater than 190 mV/ENH for both sediments. The electro-conductivity diminished from 10.9 mS.cm<sup>-1</sup> in raw sediment to 2 mS.cm<sup>-1</sup> in desalinated sediment, due to the washing process. No clear difference appeared after 48 hours of extraction (W48, L/S= 10) for physic-chemical properties, we observed only a slight decrease of redox potential on the both sediment (160 mV after 48 hours). Percentages of contaminant extracted are presented on figure 1. Cu and Al were neither released with water nor with acetic acid. Cr, Ni, Pb, Zn and Co were only extracted with acetic acid. Pb and Zn have suffered a release by acetic acid (AA

treatment) between 6.5 and 9.6 Tw% (percent of total weight) in both sediments. Ni was released by AA treatment with 16.9 and 17.3 Tw% in raw and desalinated sediment, respectively. A contact time of 48h was necessary to release Cd with water which was also extracted with acid acetic. Cd suffered a similar release by W48 and AA treatment (19.9 and 15 Tw% in raw sediment and 9.3 and 12.8 Tw% in desalinated sediment, respectively). As was leached with acid acetic for both sediments (9.2 and 4.4 Tw% in raw and desalinated sediment, respectively), but was weakly released (3.7 Tw%) with water (48 hours) only for the raw sediment. The B and Mo were strongly extracted for all treatment. B extraction with acetic acid was greater than water extraction, while Mo was more extracted with water; about 55% were extracted with water for the raw sediment. Generally, inorganic contaminant extraction was more strongly emphasized for raw sediment compared to desalinated sediment, a higher ionic strength might promote inorganic contaminant extraction. Similar results were found for cadmium which presents an affinity for chlorides (Lions, 2004). The results indicated that Cu wasn't bounded to bearing phases soluble in water or acetic acid. Ni, Pb, Zn and Co were associated with carbonates extracted in acetic acid such as calcite. As, Cd, B and Mo were both leached with water and the acetic acid treatment, and the release of pollutants was increased by a longer time contact.

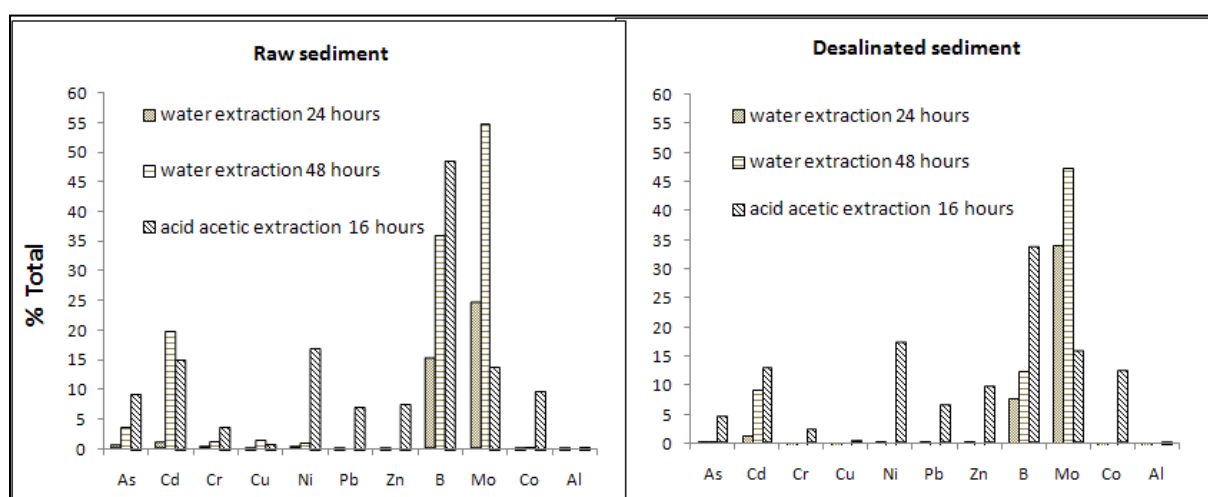


Figure 1. Comparison of metal concentrations extracted by deionized water and acetic acid

### 3-3 Operational speciation: fractionation by sequential selective extractions

Sequential selective extractions showed similar distribution of contaminants in the four fractions, for both raw and desalinated sediments. More than 20% of B and Mn were bound to the acid-extractable fraction, indicating high availability and easy release. More than 15% of Ni and Cd were also in this acid-extractable fraction. Cr and Cu were mainly bound to the oxidisable fraction, i.e. organic matter as already observed for Cu by Caplat et al. (2005) on harbor contaminated sediments. Cd was dominantly in the reducible fraction, i.e. bound to Fe- and Mn-oxides. Ni, Co, Zn, As, Mo and Pb were more distributed between fractions when Al and Fe were mainly in the residual fraction, indicating that they are included in the low soluble mineral phase (Caplat et al., 2005). These results showed the complexity of sedimentary matrix : inorganic minerals were associated with different phases of the sediments. Nevertheless, some elements like Cu, Cr, B and Mn showed affinity for, respectively, organic matter or acid-extractible fraction.

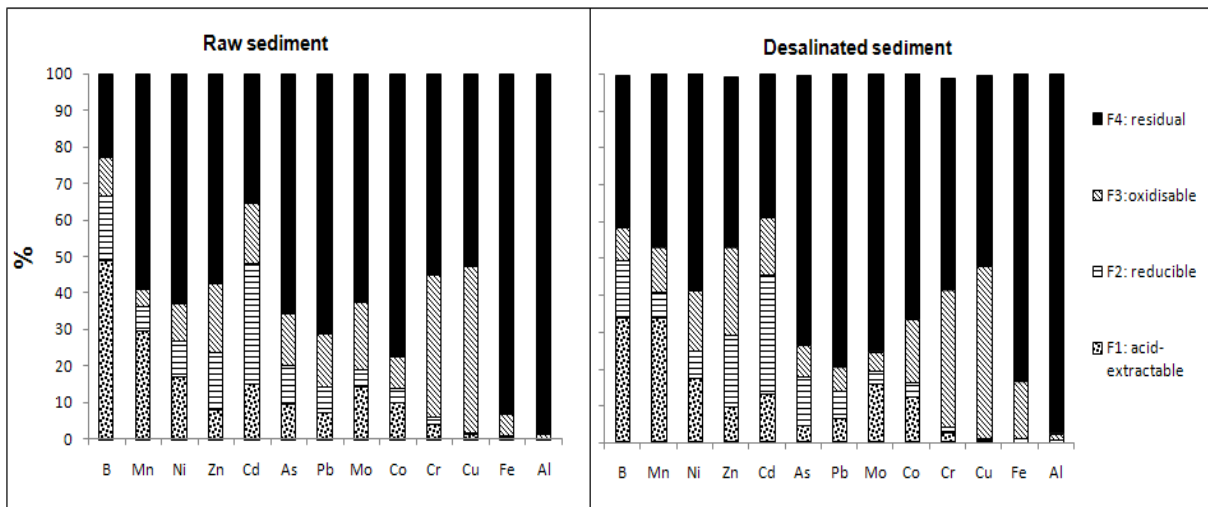


Figure 2. Element fractionation by sequential extraction (% of total weight).

### 3-4 Solubility and Release as function of pH: ANC test XP CEN/TS 14429 X 30-458

Evolution of the pH in the water solution containing increasing protons concentration, i.e. sediments acid neutralization capacity, is shown on figure 3. ANC titration (Fig. 3) showed that the desalinated sediment had a strong buffering capacity for pH values comprised between 5.5 and 6.8. Such buffering capacity is likely due to a high content of carbonate originating from seashells.

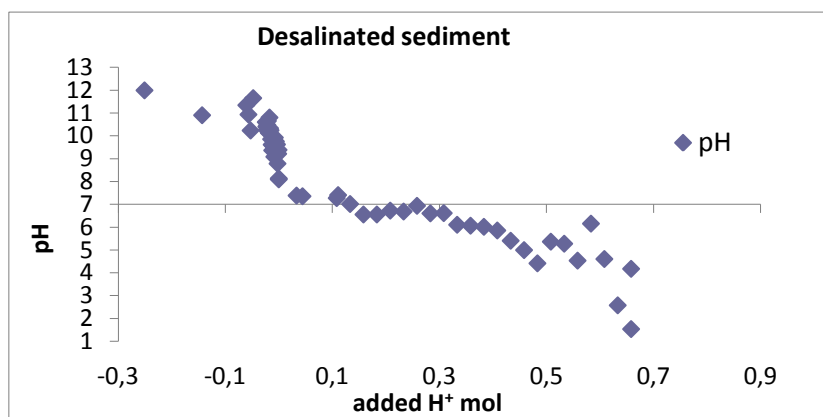


Figure 3. Evolution of the pH of water sediments versus added  $H^+$  mol

The liquid-solid partitioning of Cu, Pb, Zn and As at various pH are given in Figure 4 for desalinated sediment; the same trends were found for raw sediment. The solubility of these elements presented a typical "V shape", with lower solubility between pH 3.8 and 8.0 for Cu and As, as already observed by Chatain et al. (2005), and between pH 6.5 and 8 for Pb and Zn. Behavior of Zn was close to these of Pb, when behavior of Cu was close to these of As (correlation coefficient  $R^2=0.89$  for pH values above 2) . Zn and Pb were the more released at acid pH (from  $pH < 5.5$ ), although a significant release

occurred at  $\text{pH} > 8$ . High As and Cu release occurred at both acid ( $< 3.5$ ) and basic ( $> 8$ ) pH. Under acidic conditions, Pb release occurred at higher pH than observed by Cappuyns et al., 2004 from land-disposed dredged sediments.

Most of the variations of the considered metals with pH can be explained by the solubility in water of their cationic and hydroxylated species. However, the shape of the solubility curve at basic pH can be also determined by the release of organic matter – element complexes. This hypothesis is strengthened by high correlation coefficient between dissolved organic carbon (DOC) and Cu and As for pH higher than 5.5 ( $R^2 = 0.946$  and  $0.93$  for Cu and As, respectively), same trends were found for raw sediment.

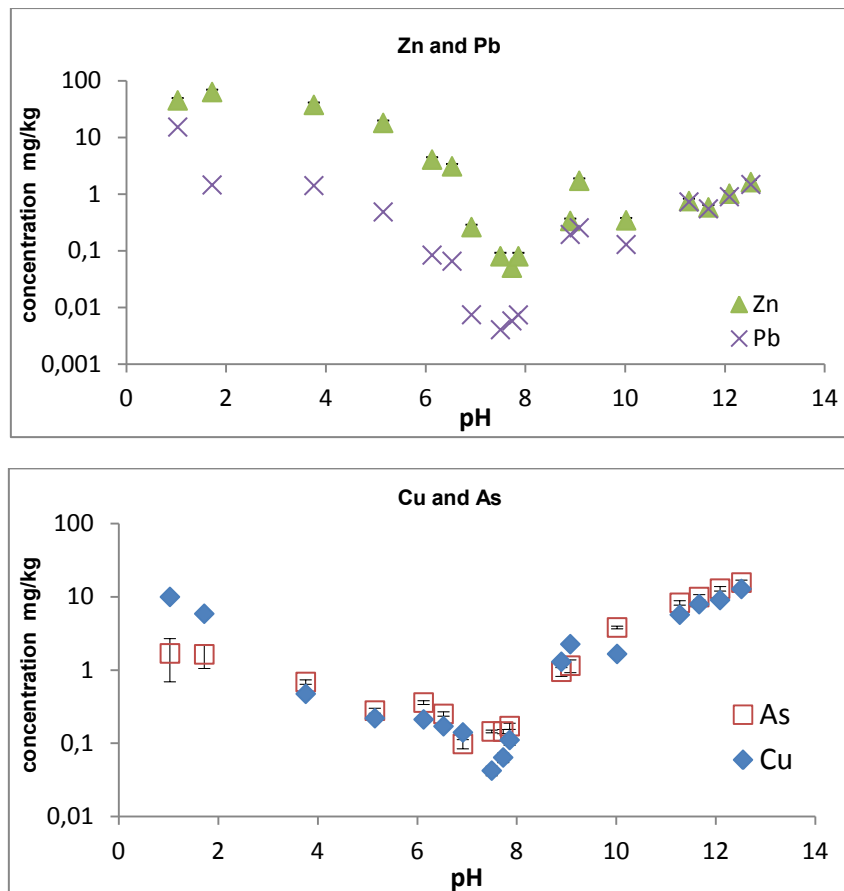


Figure 4: Zn, Pb, Cu and As solubilization in leachate as a function of pH (time contact 48 hours, L/S 10)

#### 4- Conclusion

A combination of methods used in the present study allowed a differentiated characterization of the behavior of potentially toxic elements present in the studied sediments. With regard to elements having concentrations over the environmental threshold in the raw sediment, results indicated that Cu appeared poorly mobile at pH between 5 and 7.5, and mainly retained by the oxidizable fraction of the sediment, i.e. organic matter. This leaching behavior could change with time due to an oxidation of the sediment natural organic matter, as a result of changing physico-chemical conditions during oxidation/reduction cycles (Calmano et al., 1993) or of bacterial action (Lors et al., 2004). Arsenic has a similar leaching behavior; it was strongly associated to organic matter. Arsenic could also be



mobilized after oxides dissolution. Ni is released with acetic acid attack, it was easily mobilisable. Mo was mainly dissolved in water, it was easily available. The sediment desalination released Na, Cl but also Fe and S, probably due to pyrite oxidation into alunite. Desalination also promotes particle aggregation and elements leaching, but the contaminants distribution into the different sediments fractions remains quite the same. Treatment of the outside lysimeter results and modeling are in process.

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