

Characterization of how contaminants arise in a dredged marine sediment and analysis of the effect of natural weathering

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Abstract

Millions of tons of contaminated sediments are dredged each year from the main harbors in France. When removed from water, these sediments are very reactive, therefore their geochemical behavior must be understood in order to avoid dispersion of contaminated lixiviates in the surrounding soils. In this objective, it is necessary to evaluate the principal physicochemical parameters, and also achieve advanced mineralogical characterization. These studied sediments are highly contaminated by metals, notably copper (1445 and 835 mg/kg, in the unweathered and naturally-weathered sediments, respectively), lead (760 and 1260 mg/kg, respectively), zinc (2085 and 2550 mg/kg, respectively), as well as by organic contaminants (PAH, PCB) and organometallics (organotins). A high concentration of sulfide minerals was also observed both in the unweathered sediment preserved under water (3.4 wt.% of pyrite especially), and in the naturally weathered sediment (2 wt.% pyrite), and in particular framboidal pyrite was observed in the two materials.

The presence of reactive mineral species in the naturally-weathered sediment can be explained by the deposit of a protective layer, composed of sulfide and their oxidation products (sulfate and iron oxides), thus preventing oxygen from diffusing through to the sulfide minerals. Additionally, the presence of aluminosilicates aggregates coating the sulfide minerals could also explain their presence in the naturally-weathered sediment. As organic matter is one of the principal constituents of the sediments (5.8 and 6.3 wt.% total organic carbon in the unweathered and weathered sediment, respectively), the aggregates are probably partially constituted of refractory humic material. It therefore appears that the natural weathering has led to a significant decrease in PAHs and organotins, but not in PCBs. The evolution of the granulometric structure and the distribution of the metallic contaminants could therefore lead us to consider a treatment by size separation, and a possible valorization of the dredged sediments in civil engineering.

Keywords: Biogeochemical reactivity; Contaminated marine sediment; Sulfides; Leaching; Oxidation; Organic matter

1.1 Introduction

Careful management of the dredged sediment is necessary for the good operation of ports and navigable waterways. In 2010, about 18.6 million tons of sediment (dry weight) were dredged in mainland France and France's overseas territories, 33.56 million tons in 2009, and 23.2 million tons in 2008 (Le Guyader, 2011; Le Guyader, 2013). According to European legislation, once the sediments are extracted from their natural environment, they are considered as waste and thus must be consequently managed according to the legislation in force (*Commission Decision of 3 May 2000 Replacing Decision 94/3/EC Establishing a List of Wastes, 2002*; JORF 2007).

These marine sediments are mainly composed of mineral species (quartz, silicates, carbonates, iron and manganese oxyhydroxides and sulfides, etc.) and organic matter. As they accumulate by the deposit of solid and colloidal matter, marine sediments are also the final "reservoir" for numerous contaminants coming from industrial and port activities, urban effluent, nautical activities or deposited in the form of aerosols. In this way, they integrate and amplify the contaminant concentrations (DelValls et al., 1998). Inorganic pollutants such as copper, zinc, lead, chromium, mercury, and arsenic, are a particular issue due to their ubiquity and persistence in the environment (Frémion et al., 2017; Jones and Turki, 1997; Caplat et al., 2005; Eek et al., 2008; Lions et al., 2010; Chatain et al., 2013a). A large number of organic pollutants also accumulate in the marine sediments such as PCBs, PAHs, residues of medicines

and endocrine disruptors, as well as organometallic compounds e.g. organotin compounds principally coming from antifouling paints used to prevent aquatic organisms from attaching to boats. These compounds, frequently encountered at various concentrations in the dredged marine sediments, are considered dangerous for the environment as well as for human health (Diez et al., 2002; Mamindy-Pajany et al., 2012; Casado-Martínez et al., 2009; Ribocco et al., 2011; Staniszewska et al., 2011).

To set up a long-lasting management plan for the dredged sediment, it is necessary to have more precise knowledge and more than just the degree of contamination. Therefore, it is essential to determine how the contaminants are distributed in the sedimentary matrix. Furthermore, these sediments are renowned for being particularly reactive materials following their abrupt change in surroundings after dredging; for example, when the saturation in water greatly diminishes, the redox potential increases significantly due to an increased availability of molecular oxygen. Wind and rain also induce cycles of lixiviation and drying favoring the formation of secondary mineral phases likely to control the mobility of dissolved metallic elements (Tack et al., 2006). Following these changes, these metals can be released into the lixiviation water and thus contaminate the soil if the effluent is not controlled (Caille et al., 2003; Chatain et al., 2013b; Stephens et al., 2001). Actually, the paper aim in characterizing the contaminant mineralogical speciation and their geochemical evolution during weathering under natural conditions. From this in-depth characterization, adapted management solutions could be proposed and evaluated.

2.2 Material and methods

2.1.2.1 Sampling, storage and treatment

The two sediments in this study come from the same sampling point, from a port in the south of France, submitted to an extensive anthropic activity during many centuries and contaminated by industrial activity. They were collected by dredging the 50–80 first centimeters of the harbor seabed with a mechanical shovel. The unweathered sediment was immediately put in 50 L opaque containers under a 10 cm layer of sea water to preserve the anoxic conditions and stored in a dark cold room at 4°C. Underwater storage enables the physicochemical parameters of the environment before dredging to be conserved as much as possible. Indeed, this conditioning is to avoid any reactivity of the sediment that comes from an anoxic environment. Sulfides content and organic matter are very instable and may oxidize quickly if exposed to air (Couvidat et al., 2016b). The preservation method was inspired from what recommended during sulfides mine waste handling (Benzaazoua et al., 1999).

A part of this sediment was sieved (20 mm) and underwent bioremediation pretreatment lasting 5 months during which it was regularly watered and aerated by turning-off with a mechanical shovel, then stored for a further 5 years outdoors without any special protection. These samples are called *the naturally-weathered sediment*. Storage of the sample in the open air under weather condition without being covered, enables natural alteration to be simulated for long-term storage conditions. For the naturally-weathered sediments, the samples to be analyzed were taken from different parts of the stored sediment and then mixed to produce a more homogeneous sample, stored also in the dark at 4°C.

3.3 Characterization of dredged sediments

3.1.3.1 Physicochemical parameters

Physicochemical parameters measurements were performed on both sediments. The natural pH, ORP (oxidation-reduction potential, which was afterward utilized to determine the Eh by using the standard reference electrode potential, SHE of 204 mV), and conductivity were measured on a sediment slurry with a water-sediment ratio of 1:2; after a contact time of 48 hours using an Accumet® combined glass electrode. The redox potential of the sediment (ORP) was measured using a portable multi-meter (VWR SympHony SB90M5) supplied with a pH Ag/AgCl electrode (Fischer AccupHast 13-620-114), and an Eh Ag/AgCl electrode (Cole Palmer EW-05990-55), while conductivity was determined according to Standard Method 4110 (APHA, 2005). Water content was estimated by using the gravimetric method NF EN 12880 (X 33-005). Organic matter content was determined as TOC concentration through dry combustion in a furnace following the standard NF ISO 10694. Three current organotin compounds (monobutyltin, dibutyltin, and tributyltin) were analyzed into both sediments by low-resolution MS. Sixteen PAHs were also measured (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, dibenzo[*a,h*]anthracene, benzo[*g,h,i*]perylene, indeno[1,2,3-*c,d*]pyrene) with GC/MS quantitative analysis following hexane/acetone extraction, according to the XP X 33-012 method. PCBs content was calculated according a similar method as for the HAPs, represented by the sum of 7 regulated PCB species (PCB 28, 52, 101, 118, 138, 153, and 180).

Sulfides within sediments are often not solely crystallized and other forms of reduced sulfur exist, which considerably induce microbiological activity and metals mobility (Chatain et al., 2013b; Couvidat et al., 2016b). The acid volatile sulfides (AVS) method consists of the generation of H₂S from acid-sensitive sulfides by the addition of HCl while stirring for 60 min, with a solution-sediment ratio of 1:10 (5 g of sample in 500 mL of 1 N HCl), and to absorb the producing gas into 10 mL of a Sulfide Anti-Oxidant Buffer (SAOB) solution, to be towards analyzed for soluble sulfides (Brouwer and Murphy, 1994; Leonard et al., 1996; Rickard and Morse, 2005). The SAOB solution was analyzed for dissolved sulfides by spectrophotometry (HACH DR-890 Colorimeter) using the methylene blue method (equivalent procedure to USEPA 376.2 or Standard Method 4500-S₂-D for wastewater).

Analysis of major and trace inorganic compounds was carried out on 6 granulometric fractions (< 25 μm , 25–80 μm , 80–200 μm , 200–1000 μm , 1–2 mm, > 2 mm). Particle-size distribution (PSD) was conducted by wet sieving according to an adaptation of the XP P 94–041 standard. After mineralization by alkali fusion with LiBO_2 , and acid solubilization in $\text{HNO}_3\text{-H}_2\text{O}_2$, total Inorganic species analysis was realized by ICP-MS (Inductively Coupled Plasma – Mass Spectroscopy) accordingly to the internal procedure of the SARM laboratory (Carignan et al., 2001).

Specific gravity was determined with a helium gas pycnometer (Micromeritics Accupyc 1330). Total sulfur was determined by induction furnace analyzer (Eltra CS-2000). A modified Sobek method (Sobek et al., 1978) was carried out on both sediments for the sulfur characterization, while organic sulfur forms were considered as negligible. Then, just the HCl 40% extraction was used, to obtain the HCl-extractable sulfur forms, mostly amorphous sulfides and sulfates, as well as other sulfur forms, mostly sulfides, by difference with total sulfur. The acid-generating Potential (AP) was calculated by the Paktunc method using the sulfides content determined by the X-ray diffraction (Paktunc, 1999a; Paktunc, 1999b), and the neutralization potential (NP) was determined by the Sobek et al. (1978) method modified by Lawrence and Wang (1997) (Lawrence and Wang, 1997; Sobek et al., 1978).

3.2.3.2 Mineralogical analysis

The mineralogy of both sediments was carefully analysed using Optical Microscopy (OM), X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM).

The XRD analysis was carried out using a Bruker apparatus (AXS D8 advance) equipped with a Cu anticathode, by scanning over a diffraction angle (2θ) range from 5° to 70° . Scan settings were 0.02° 2θ step size and 4 s counting time per step. The DiffracPlus EVA software (v.3.2) was used for mineral species identification, while the TOPAS software (v 4.1), with the implementation of the Rietveld refinement, was used to quantify the abundance of all identified mineral species (Young, 1993). The precision of the Rietveld quantification is in the order of ± 0.5 to 1% (Bouzahzah et al., 2008; Raudsepp and Pani, 2003). The mineralogical identification was also achieved by microscopy observations on polished section prepared with bulk sediment samples impregnated in an Epoxy resin. The optical microscopy observations was performed by a reflected light microscope (Zeiss Axio Imager.M2m) and allowed to define selected area for further scanning electron microscope (SEM) examination. Thus, the chemical composition of the individual minerals (stoichiometry) was determined using an SEM (Hitachi S-3500N) equipped with an Energy Dispersive Spectrometer (EDS, Silicon Drift Detector X-Max 20 mm^2 , Oxford) operated under the INCA software (450 Energy). The operating conditions were 20 keV, $\sim 100 \mu\text{A}$ and 15 mm working distance.

3.3.3.3 Kinetic test: weathering cells

The weathering cells test, mostly used in mining environment to sulfide-rich materials, enables to accelerate the weathering processes within materials in order to assess their reactivity (Bouzahzah et al., 2014; Cruz et al., 2001; Villeneuve et al., 2009).

About 70 g of both sediments were placed on a 0.45 μm paper filter positioned in a Büchner-type funnel, and twice a week leached by 50 mL of deionized water (pH is between 6.5 and 8.5). Each leaching was separated by consecutively two and three days of drying. The Eh, pH and conductivity of the leachates were instantaneously determined, before the analysis of inorganic compounds of interest by ICP-AES. These physicochemical parameters were realized over 18 cycles, until reaching a geochemical equilibrium of the leachates.

4.4 Results

4.1.4.1 Physicochemical characterization

The values for the principal physicochemical parameters measured for the unweathered and naturally-weathered sediments are given in Table 1. As the samples come from the same sampling point they have some common characteristics for certain parameters, notably the density of 2.5 g/cm^3 which is close to that of quartz (2.65 g/cm^3) or carbonates ($2.6\text{--}2.8 \text{ g/cm}^3$) and a natural pH of 7.3 for both sediments. However, the bioremediation treatment and the method of conservation for the weathered sediment, lead to significant physicochemical differences. First, the electrical conductivity of the water extracted from the pores is 25 mS/cm for the unweathered sediment and decreases to 5 mS/cm for the weathered sediment, probably due to the natural lixiviation under open-air storage. Aeration leads to a much more oxidized state in the weathered sediment which thus induces a higher redox potential (ORP) (572 mV/SHE for the weathered sample compared to 331 for the unweathered sediment), and a change in speciation of the elements, notably those of sulfur. There is little variation in the total sulfur content, around $2 \text{ wt}\%$. The fraction which cannot be extracted in HCl and is mainly composed of crystallized sulfides, decreases between the unweathered and weathered samples from 1.6 to $1.0 \text{ wt}\%$. However, the fraction that can be extracted in HCl which includes the amorphous sulfides and almost all of the sulfate minerals, increases from 0.3 to $1.0 \text{ wt}\%$. In a similar way, the acid-generating potential (AP), associated to sulfide minerals, is higher in the unweathered sediment ($50 \text{ kg CaCO}_3/\text{t}$) than for the weathered one ($32 \text{ kg CaCO}_3/\text{t}$). However, the neutralization potential (NP) is about 7 to 10 times greater than the AP in both samples. The quantity of sulfides making up the AVS class, mainly the amorphous sulfides, polysulfides and clusters, decreases from $4.3 \times 10^{-3} \text{ g(S)/kg}$ in the unweathered sample, to $9.4 \times 10^{-5} \text{ g(S)/kg}$ in the weathered samples. Both sediments are rich in organic matter, with almost $6 \text{ wt}\%$ of TOC. However, a significant decrease in the loss on ignition is observed (12.5 and $7.9 \text{ wt}\%$, for the unweathered and weathered samples, respectively), as well as the quantity of PAH (62 and 22 mg/kg on average, for the unweathered and

weathered samples, respectively) and organotin compounds (65.5 compared to 5.9 mg/kg, for the unweathered and weathered samples, respectively). Chemical analysis of the two sediments also highlights their significant contamination by trace metals, particularly by copper (1445 and 835 mg/kg), lead (760 and 1260 mg/kg) and zinc (2085 and 2550 mg/kg), for the unweathered and weathered samples, respectively. The concentrations of these three metals is above the N2 thresholds set by the French regulation in the decree of 09 August 2006 for the disposal of waste in the sea, which are 90, 200 and 552 mg/kg MS for Cu, Pb and Zn, respectively. These decree sets two threshold N1 and N2 for concerning trace metals in dredged sediments; when metals concentrations are below N1 threshold, the potential impact is considered as negligible and the sediment can be rejected to the sea, whereas one trace metal exceeds N2 threshold, the sediment is treated as “highly contaminated”, cannot be rejected in the sea, and need to undergo proper management. The chemical form, and in particular the mineral phases containing these metals, will be discussed with the mineralogical results.

Table 1 Physicochemical characteristics of the sediments.

alt-text: Table 1

Parameter	Unit	Unweathered	Weathered
pH		7.4	7.3
ORP	mV/SHE	331	572
Conductivity	mS/cm	25	5
Water content	wt. %	47	23
Loss on ignition	wt. %	12.5	7.9
TOC	wt. %	5.8	6.3
∑ PAHs	mg/kg	62.18 x 62.4	21.93 x 22.35
∑ PCBs	mg/kg	0.96 x 0.97	1.07 x 1.21
∑ Organotins	mg/kg	65.5	5.9
Sulfur	wt. %	1.89	2.02
HCl-extractable Sulfur	wt. %	0.29	1.04
Other sulfur forms	wt. %	1.61	0.98
AVS	g(S)/kg	4.3 x 10^{-3}	9.4 x 10^{-5}
NP	kg(CaCO ₃)/t	384	536
AP	kg(CaCO ₃)/t	50	31
Iron	wt. %	3.7	3.4
Copper	mg/kg	1445	835
Lead	mg/kg	760	1260
Zinc	mg/kg	2085	2550

Both sediments have a fine granulometry, with about 45 to 50% v/v of the particles having a diameter less than $\leq 20 \mu\text{m}$ (Fig. 1). In fact, the D_{50} of the unweathered sediment is $22 \mu\text{m}$, and that of the weathered samples $19 \mu\text{m}$. The fraction where the diameter of particles is greater than $\geq 100 \mu\text{m}$ decreases in the weathered samples whereas the finest fractions increase. This results in a substantial decrease in the D_{90} from 153 to $80 \mu\text{m}$ between the unweathered and weathered sediment.

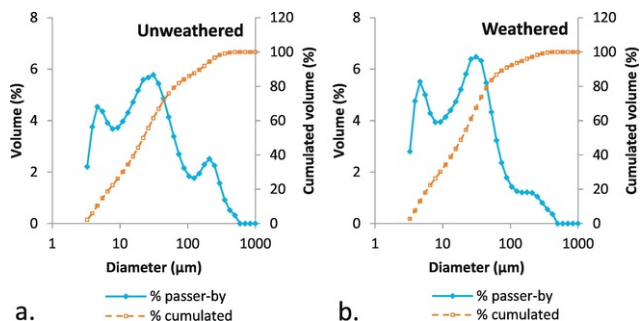


Fig. 1 Particles size distribution by laser diffraction of unweathered (a) and weathered (b) sediments (% in volume).

alt-text: Fig. 1

In addition to the PSD studied by laser diffraction, based on a model working with the volume of particles, the size distribution of particles in both sediments was analyzed with a mechanical sieving. This analysis results in the particle mass distribution, in order to determine the distribution of trace metals in the different fractions of unweathered (Fig. 2a) and weathered (Fig. 2b) sediments.

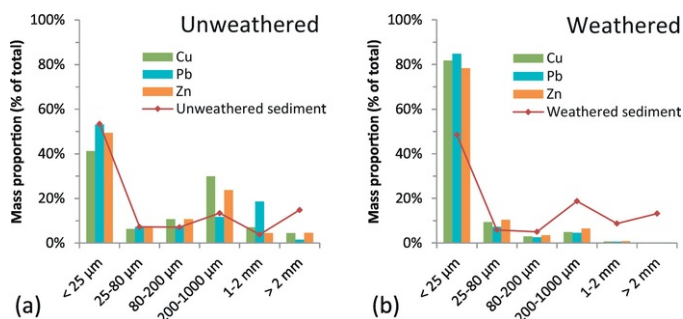


Fig. 2 Analysis of the repartition of the sediment particles, copper, lead and zinc in 6 granulometric fractions of unweathered (a) and weathered (b) sediments (uncertainties are < 5% for Cu and Pb, and < 10% for Zn and for the > 2mm fraction for Cu).

alt-text: Fig. 2

Sieving revealed that both sediments are mainly composed of fine particles where the < 25 μm fraction represents 53% and 48% by mass of the unweathered and naturally-weathered sediments, respectively. The fine fraction of the sediment is known for concentrating the metallic pollutants due to the large specific surface area intrinsic to the substances it is composed of, such as clays (Eggleton and Thomas, 2004, Isaure et al., 2002, Maity et al., 2017). As stated above, the three metals targeted in this study are Cu, Pb and Zn due to their high concentration. Figure 2a and 2b show the distribution of these elements between the different granulometric fractions. The finest fraction (less than < 25 μm) of both sediments is the highest concentrated for those three elements. The > 2 mm fraction contains about 5% of the total quantity of these elements in the unweathered sediment, but this percentage does not go above 0.3% in the weathered sediment. Furthermore, these three metals are observed as more concentrated in the < 25 μm fraction in the weathered sediment, whereas they are distributed more homogeneously between the different granulometric fractions for the unweathered sediment. However, in order to estimate the distribution of these metals in the different fractions, it is necessary to take into account their mass proportion. Thus, in the < 25 μm fraction of the unweathered sediment, Cu is present at 41%, Pb at 53% and Zn at 49%. This distribution increases to 82%, 85% and 78% in the weathered sediment for the same three metals, respectively. This suggests a possible treatment by size separation to separate the contaminated fine fraction from the cleaner coarse fraction of sediments. In a second time, the coarser fraction could be used as a secondary unweathered material in an integrated valorization pathway.

4.2.4.2 Mineralogical characterization

The mineralogical data obtained by XRD is presented in Table 2. The two samples contain 45 and 35 wt% silicates minerals (quartz, muscovite, chamosite, illite and kaolinite) respectively in the unweathered and naturally-weathered sediments. Carbonate minerals (calcite and dolomite) also represent a main content of both sediments with respectively 38 and 52 wt%. Pyrite (FeS₂) is the main sulfide minerals with 3.4 and 2 wt% in the unweathered and weathered samples, respectively. The quantity of pyrite decreased in the naturally-weathered sediments probably because of their oxidation after exposure to the atmosphere and natural weather changes. Chalcopyrite (CuFeS₂) occurs in trace level in the unweathered sediment (0.3 wt%) whereas we observed halite (NaCl) in quantities of 3.7 wt% which decreased to 0.8 wt% in the naturally-weathered sediments. This decrease is connected to the significant

decrease in the conductivity of the sediments linked to the natural lixiviation (washing) by rainwater of the sediments during storage (Table 1). Finally, we observed the appearance of gypsum and magnetite in the naturally-weathered sediments in quantities of 5 and 1 wt%, respectively.

Table 2 XRD mineralogical analyses of unweathered and weathered sediments.

alt-text: Table 2

Mineral		Chemical formula	Composition (wt.%)	
			Unweath.	Weath.
Silicates	Quartz	SiO ₂	15.65	15.3
	Muscovite	KAl ₂ (Si ₃ Al)O ₁₀ (OH,F) ₂	< LDM	9.24
	Chamosite	(Fe,Mg) ₅ Al(Si ₃ Al)O ₁₀ (OH,O)	6.5	4.47
	Illite	(K,H ₃ O)(Al,Mg,Fe) ₂ (Si,Al) ₄ O ₁₀ [(OH) ₂ ,(H ₂ O)]	13.2	1.55
	Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	9.8	4
Carbonates	Dolomite	CaMg(CO ₃) ₂	6.8	13.6
	Calcite	CaCO ₃	31.05	38.9
Sulfides	Pyrite	FeS ₂	3.45	1,98
	Chalcopyrite	CuFeS ₂	0.33	< LDM
Other minerals	Halite	NaCl	3.75	0.76
	Gypsum	CaSO ₄ ·2H ₂ O	< LDM	5
	Magnetite	Fe ₃ O ₄	0.2	1.1

The mineralogical characterization was completed by optical and scanning electron microscopy (SEM) observations. These confirmed the presence of quartz, calcite and framboidal pyrite in both sediments (Fig. 3). The framboidal pyrite is composed of micro-cubes of pyrite where the average size is about 1 μm (Fig. 3b and d). This form of pyrite is considered as the most common in anoxic media, as well as the most reactive one (Pierret et al., 2000). In the weathered sediment, an aluminosilicate-bonded agglomerate was observed containing aluminosilicates, copper and zinc components with pyrite, quartz and calcite (Fig. 3b and c). These agglomerates could explain the preservation of pyrite oxidation in oxic conditions. In fact, framboidal pyrite in agglomerates is always present and does not show any sign of oxidation (Fig. 4). However, free pyrite shows signs of transformation into iron oxide as shown in Figure 4a and b. In the unweathered sediment, pyrrhotite (Fe_{1-x}S) was observed and shows signs of transformation into hematite (Fe₂O₃) and magnetite (Fe₃O₄) (Fig. 4c and d).

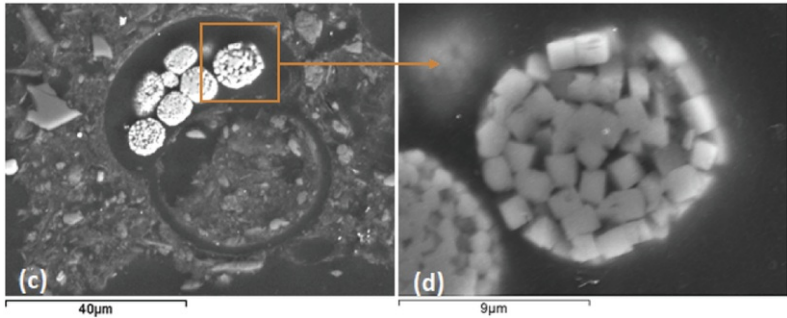
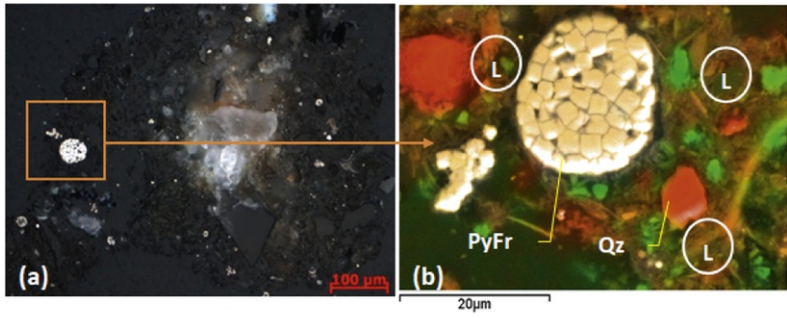


Fig. 3 Optical and scanning electron microscope images: a,b) weathered sediment: framboidal pyrite (PyFr) included into an aluminosilicate-bonded agglomerate rich of copper and zinc (L) and containing quartz (Qz) and calcite (Cal); c,d) unweathered sediment: framboidal pyrites.

alt-text: Fig. 3

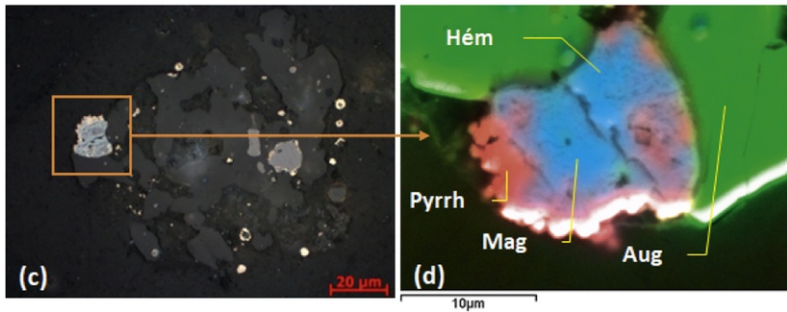
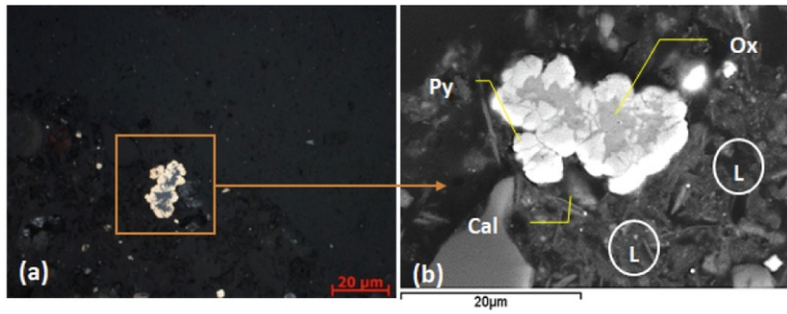


Fig. 4 Optical and scanning electron microscope images: a,b) weathered sediment: pyrite (Py) turning into iron oxide (Ox) included into an aluminosilicate agglomerate rich of copper and zinc (L) and containing calcite (Cal); c, d) unweathered sediment: pyrrhotite (Pyrrh) associated

to an augite (Aug) showing signs of transformation into magnetite (Mag) and hematite (Hém).

alt-text: Fig. 4

Chemical analysis has shown that the granulometric distribution of Pb, Zn and Cu in the two sediments is very different. It is probable that the speciation of these elements has changed with the natural weathering and bioremediation treatment. The SEM observations and element microanalyses were able to determine their distribution and identify the phases containing these metals (element speciation). The copper is in the form of chalcopyrite and covellite (Fig. 5a and b), copper (Fig. 5c) or mixed-metal sulfide complexes such as CuFe_4S_5 (Fig. 5d). Cu and Zn can also be found in dispersed and concentrated forms in the aluminosilicate agglomerates (Figs. 3b and 4a). Zn and Pb are not found in any crystallized mineral form. Figure 6 illustrates the X-ray mapping of Zn showing its association to sulfur distribution, but not occurring as sulfide minerals.

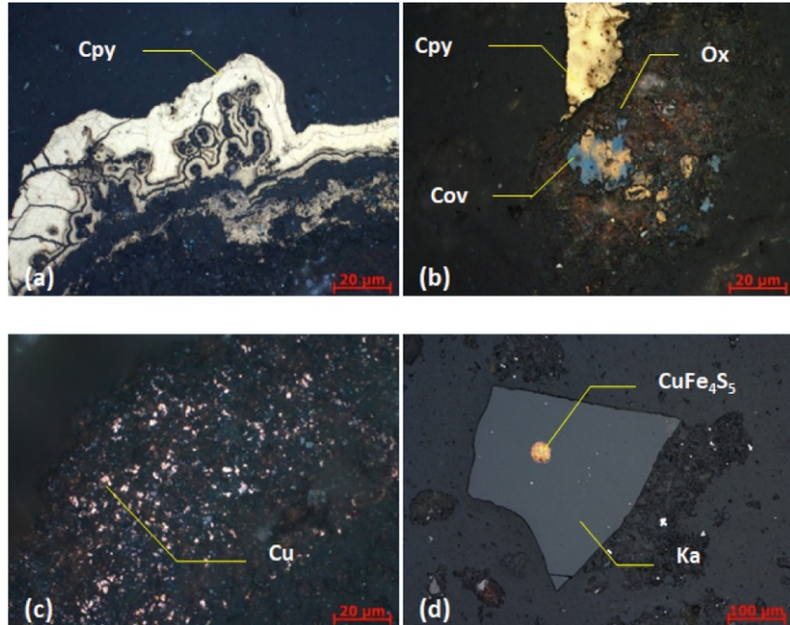


Fig. 5 Optical microscope images of unweathered sediment: a, b) chalcopyrite (Cpy) and covellite (Cov); c) native copper (Cu); d) iron and copper mixed sulfide CuFe_4S_5 included into Katophorite (Ka).

alt-text: Fig. 5

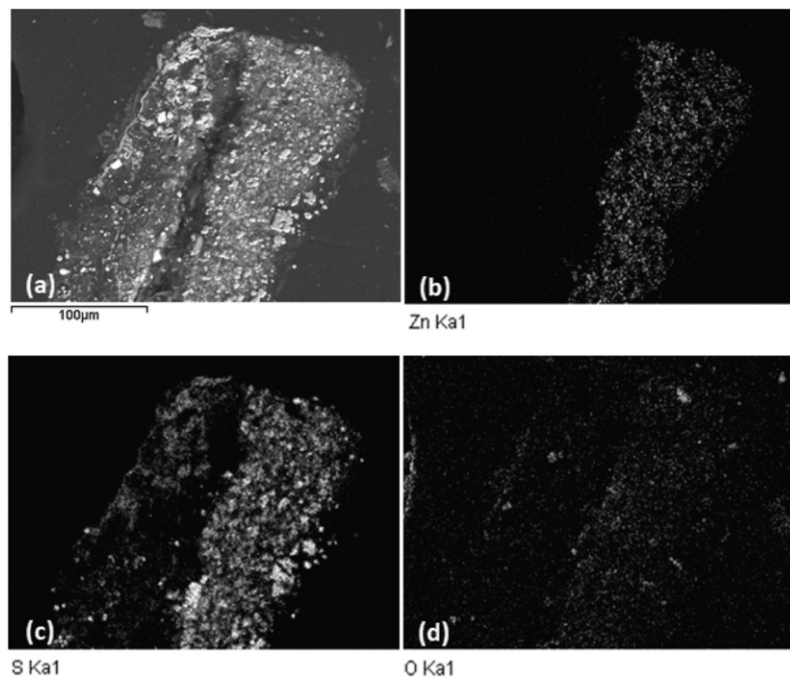


Fig. 6 a) Scanning electron microscope image of a grain in unweathered sediment; b, c, d) X-mapping images showing zinc, sulfur and oxygen distribution in the grain of unweathered sediment.

alt-text: Fig. 6

4.3.4.3 Leaching tests in weathering cells

The mineralogical study of the two sediments has shown that they contain sulfide minerals. The latter are particularly sensitive to oxidation by oxygen and water, as organic matter which is known for controlling the mobility of certain metal ions such as copper and lead (Chatain et al., 2013b; Couvidat et al., 2015; Morabito et al., 2017). The use of a leaching test in weathering cells has enabled to assess the reactivity of the sediments according to the protocol described previously.

The pH of the leachates varies very little, and globally oscillates around the « natural » pH of sediments, i.e. 7.5 to 7.7. This pH is related to the presence of carbonated minerals (calcite and dolomite, Table 2) which buffer the pH. The conductivity which is initially very high in the unweathered sediment (54 mS/cm) decreases very rapidly to finally reach a pseudo-stationary state after 5 leaching cycles. The initial conductivity of the weathered sediment is much less (9 mS/cm) but also decreases rapidly to reach values approaching those of the unweathered sediment. The redox potential oscillates throughout the test from 500 to 600 mv/SHE, explained by the oxidizing conditions in the two sediments.

The release of Cu, Pb and Zn is low, even with the highly oxidizing redox potential in the two sediments (Fig. 7). In fact, the accumulated quantity of copper in the leachates does not go over 2.5 mg/kg for the weathered sediment, and 0.7 mg/kg for the unweathered sediment, whereas the accumulated quantities in lead and zinc do not exceed 0.5 mg/kg for the two sediments (Fig. 7a, 7b and 7c). The copper and lead were mainly released during the first 5 cycles. However, the Zn behaves differently for the two samples, in that the quantity released during the last 4 cycles is greater than that in the previous ones. Figure 7d shows a linear relation between the charges accumulated in calcium and magnesium on the one hand, and sulfates on the other, which is linked to the oxidation-neutralization phenomenon which occurs in materials rich in sulfides and carbonates (Benzaazoua et al., 2004). The oxidation-neutralization curve is almost linear for the weathered sediment, thus showing a strong correlation between the release of sulfur and calcium and magnesium ions. However, for the unweathered sediment, the curve shows an inflection during the first 4 cycles before becoming linear, which might mean that release of S, Ca and Mg into the lixivates is probably partially disconnected.

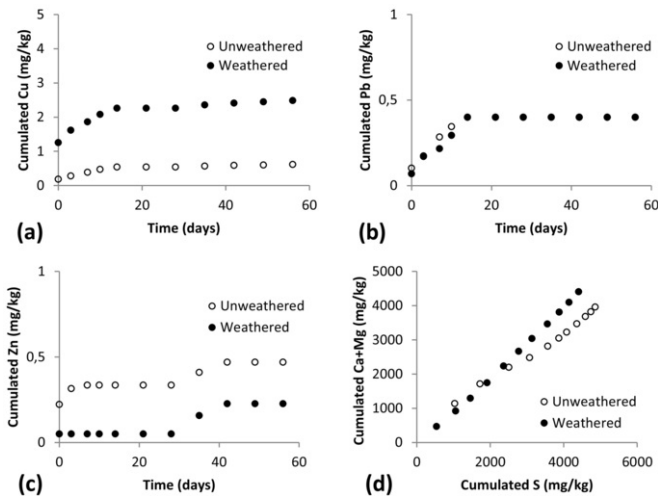


Fig. 7 Temporal evolution of copper (a), lead (b), zinc (c), and evolution of calcium and magnesium as a function of sulfur (d) in weathering cells leachates of unweathered and naturally-weathered sediments (quantification uncertainties are < 10% for Cu and < 25% for Pb and Zn).

alt-text: Fig. 7

5.5 Discussion

Although the two sediments studied come from the same sampling campaign, the conditions in which they were kept have significantly influenced their physicochemical characteristics. First of all, the impact of storage in the open air after bioremediation treatment influences their redox state which increases as the saturation in water decreases. In fact, oxygen diffuses into the sediment to reach the phases sensitive to oxidation, such as the sulfides and organic matter. In the presence of molecular oxygen, which is the main oxidant of reduced sulfur species in oxic environments, water is necessary as shown by the oxidation equation for pyrite (Eq. [1]) (Lowson, 1982):



The atmospheric oxygen combined to the meteoritic water enables oxidation at the same time as the leaching of most of the mobile elements such as chlorides and oxidation products such as sulfates.

The aging phenomenon, by weathering in open air, had the effect of modifying the distribution of the metallic elements in the different granulometric fractions of the sediments. In fact, we observed that the fractions **less than** $\leq 80 \mu m$ were enriched in Cu, Pb and Zn when going from the unweathered to the naturally-weathered sediments (Fig. 2). These elements are concentrated in the $\leq 80 \mu m$ fraction in the naturally-weathered sediments, whereas in the unweathered sediments, distribution is more likely to follow the mass distribution of the fractions. The redistribution of the metals, in particular in the sulfide phases towards the more accessible reactive phases (labile or acid-soluble), was also observed after aeration and drying of the sediment (Claff et al., 2010; Calmano et al., 1993).

The aging phenomenon also had the effect of varying the weight of the different unweathered and weathered sediment fractions, notably for the $< 25 \mu m$ fraction which decreased in favor of the $200-1000 \mu m$ and $1-2 mm$ fractions, with an increase of 5.3 and 4.9%, respectively. Particle agglomeration is probably the cause of this granulometric modification. In the naturally-weathered sediments, the SEM observations revealed the presence of aggregates composed of alumino-silicates (Fig. 3b and 4b), maybe clay-humus complexes considering the high content in organic matter (Table 1). These are considered as being relatively stable, and come from a modification of the structure of the organic matter (Puget et al., 2000; Capel et al., 2006; Sutton and Sposito, 2005). With weathering, the organic matter partially degrades, and recombines to produce acid humic complexes. In the weathered sediment, we also observe a significant degradation, or volatilization, in particular of the PAHs and the organo-tins, compared to the unweathered sediment, but not for the PCBs which are very persistent molecules (Table 1). Bioremediation and weathering act relatively efficiently on the degradation of the hydrocarbon-type organic or organo-metallic molecules (Juhász and Naidu, 2000; Straube et al., 2003; Beolchini et al., 2014; Mulligan et al., 2001; Rulkens, 2005; Cruz et al., 2017).

The speciation of sulfur also evolves but differently for the two sediments. We observed a decrease in the crystallized or amorphous sulfides after weathering and an increase in oxidized sulfur, mainly in the form of sulfates. This evolution can be noticed with the decrease of pyrite and chalcopyrite concentrations from unweathered to weathered sediments and the appearance of gypsum in unweathered sediments (Table 2), with the decrease in the quantity of AVS from unweathered to weathered, or also with the increase of soluble sulfur in HCl acid from unweathered to weathered (Table 1). XRD also revealed the appearance of secondary minerals in the naturally-weathered

sediments which are the products of sulfide oxidation, in particular gypsum and iron oxides. Those oxidation products derived mainly from the oxidation taking place within the sediments, because of the 5-years open air storage. In fact, sulfides are sensitive to oxidation in presence of water and oxygen (Jerz and Rimstidt, 2004). However, despite the aging conditions of the naturally-weathered sediments, sulfides are still present including the particularly reactive framboidal form of pyrite. It is more likely than minerals from inner layers of the sediment may have been protected from oxidation, either by surface precipitation of oxidation products and subsequent surface coating (Fig. 4b), or by aggregation into aluminosilicates binders as observed by SEM (Fig. 3b). Less surprisingly, sulfides can be observed in the unweathered sediments, their persistence being explained by the underwater conservation limiting the diffusion of oxygen in the sedimentary layers.

For the marine sediments, the release of metals is very sensitive to pH variation (Chatain et al., 2013b; Calmano et al., 1993; Frémion et al., 2017). The leaching test in weathering cells showed that the pH of the leachates of the two sediments is neutral. It is buffered by the large quantity of carbonates, as foreseen by the very large NP value calculated for both sediments, much greater than the calculated AP (Table 1). These characteristics therefore prevent any acidity being generated in the sediment following oxidation of the sulfides. We also observed that in the same pH and ORP environmental conditions as those of the weathering cells, Cu and Zn are re-adsorbed rapidly after release by the organic matter, the organo-clay complexes or the Fe/Mn oxides (Caille et al., 2003; Stephens et al., 2001; Lions et al., 2007; Tack, 2016). In particular, Zn is known to be adsorbed in a reversible way between the iron oxihydroxides and the organic matter after oxidation of the metal sulfides (Piou et al., 2009). Therefore, even though the sediments are strongly buffered, it is necessary to prevent all risk of leaching of the pollutants they contain by other mechanisms such as ORP modification, or by percolation of a chelating agent (Bäckström et al., 2004; Mayer et al., 2008). A treatment could be envisaged, even valorization, for example in a road building material, or in civil engineering by treatment with hydraulic binders (Paria and Yuet, 2006; Pinto et al., 2011; Wang et al., 2012; Couvidat et al., 2016a; Bao et al., 2016; Saussaye et al., 2016).

6.6 Conclusion

The characterization of dredged sediment is essentially done in order to choose and ensure the right management strategy. Both sediments studied possess a mineralogical composition typical of marine sediments. They are essentially constituted of quartz, aluminosilicates, evaporites (halite) and carbonates (37 and 52 wt.% in the unweathered and naturally-weathered sediments, respectively). The two sediments contain framboidal pyrite which shows significant signs of oxidation. In the weathered sediment, the pyrite seems to be preserved in the agglomerates composed of aluminosilicate minerals. The unweathered sediments contain organic matter, PAHs, organotin compounds and PCBs. The weathering of the unweathered sediment in the open air and bioremediation led to an evolution in the organic matter (degradation), a decrease in the PAHs and organotins, whereas the PCBs are preserved as they are more persistent.

The quantity of metals appears high, in particular for copper which reaches 1445 and 835 mg/kg, lead at 760 and 1260 mg/kg, and zinc at 2085 and 2550 mg/kg in the unweathered and naturally-weathered sediments, respectively. Only copper sulfides are detected as chalcopyrite and covellite, and zinc is found associated with sulfur but not in the form of sphalerite or sulfates. Cu is also present in its native form. However, lead is not found in any mineral form. Zn and Cu are also associated in aggregates composed of aluminosilicate minerals and refractory organic matter. The latter prevent pyrites from being oxidized, in particular in the weathered sediment.

The leaching test in weathering cells revealed the low potential for release of Cu, Pb and Zn. The presence of carbonates in large quantities in the two sediments enabled leachates to have a neutral pH during the whole lixiviation test, as indicated by the elevated NP. As the AP is lower than the NP, we can suppose that this sediment will not release acidic leachates. Even if this is the case, in order to prevent the dispersion of the contaminants by other possible mechanisms, a treatment and/or valorization could be envisaged, in civil engineering or the road-building domain, for example (Couvidat et al., 2016a; Saussaye et al., 2016; Bao et al., 2016).

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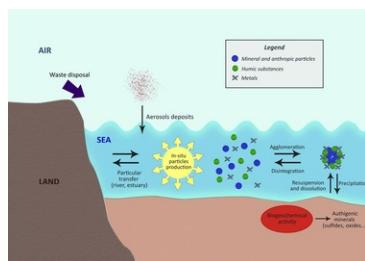
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Graphical abstract



alt-text: Image 1

Highlights

- In-depth study of contaminated sediments is advised for accurate management.
- Reactive mineral species in particular framboidal pyrite were observed in materials.
- The natural weathering has led to a significant decrease in PAHs and organotins.
- The leaching test revealed the low potential for release of Cu, Pb and Zn.
- Size separation and/or a valorization in civil engineering could be envisaged.

Queries and Answers

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