



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

Julien Couvidat, Vincent Chatain, Hassan Bouzahzah, Mostafa Benzaazoua

► To cite this version:

Julien Couvidat, Vincent Chatain, Hassan Bouzahzah, Mostafa Benzaazoua. Characterization of how contaminants arise in a dredged marine sediment and analysis of the effect of natural weathering. Science of the Total Environment, 2018, 624, pp.323-332. 10.1016/j.scitotenv.2017.12.130 . hal-01956525

HAL Id: hal-01956525

<https://hal.science/hal-01956525>

Submitted on 15 Dec 2018

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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

Julien Couvidat^{1a}
Vincent Chatain^{1a, *}
Vincent.Chatain@insa-lyon.fr

Hassan Bouzahzah^{3c}
Mostafa Benzaazoua^{1a, 2b}

^{1a}Université de Lyon, INSA Lyon, Laboratoire Déchets Eaux Environnement Pollutions (DEEP) - EA 7429, 7 rue de la Physique, 69621 Villeurbanne Cedex, France
^{2b}UQAT-Polytechnique, ^{1c}Institut de Recherche en Mines et Environnement (IRME), 445 Boul. de ^{1d}Université, Rouyn-Noranda J9X 5E4, Canada
^{3c}Université de Liège (ULG), Laboratoire de Génie Minéral, Matériaux et Environnement (GeMMe), Allée de la découverte, 13/A. Bât. B52/3 Sart-Tilman, 4000 Liège, Belgium.

*Corresponding author.

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 framboïdal 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 LiBO₂, and acid solubilization in HNO₃-H₂O₂, 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 analysedanalyzed 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 mm², Oxford) operated under the INCA software (450 Energy). The operating conditions were 20 keV, ~ 100 µA 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/cm³ which is close to that of quartz (2.65 g/cm³) or carbonates (2.6–2.8 g/cm³) 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 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 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 wt%. In a similar way, the acid-generating potential (AP), associated to sulfide minerals, is higher in the unweathered sediment (50 kg CaCO₃/t) than for the weathered one (32 kg CaCO₃/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 × 10⁻³ g(S)/kg in the unweathered sample, to 9.4 × 10⁻⁵ g(S)/kg in the weathered samples. Both sediments are rich in organic matter, with almost 6 wt% of TOC. However, a significant decrease in the loss on ignition is observed (12.5 and 7.9 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 × 10 ⁻³	9.4 × 10 ⁻⁵
NP	kg(CaCO3)/t	384	536
AP	kg(CaCO3)/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 ≤ 20 μm (Fig. 1). In fact, the D₅₀ of the unweathered sediment is 22 μm, and that of the weathered samples 19 μm. The fraction where the diameter of particles is greater than ≥ 100 μm decreases in the weathered samples whereas the finest fractions increase. This results in a substantial decrease in the D₉₀ from 153 to 80 μm between the unweathered and weathered sediment.

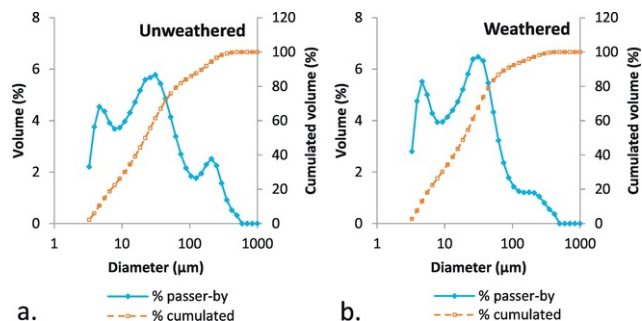


Fig. 1 Particles size distribution by laser diffraction of unweathered (a) and weathered (b) sediments (% in volume).

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.

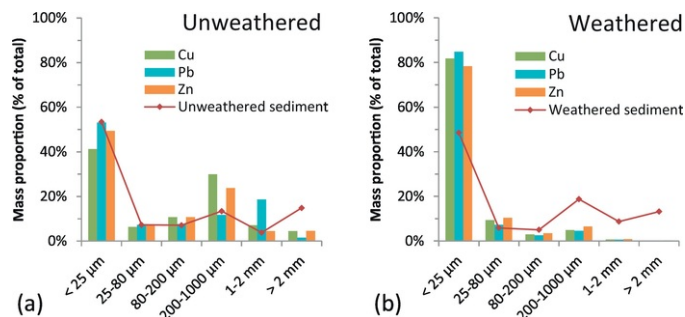


Fig. 2 Analysis of the repartition of the sediment particles, copper, lead and zinc in 6 granulometric fractions of unweathered (a) and weathered (b) sediments (uncertainties are < 5% for Cu and Pb, and < 10% for Zn and for the > 2mm fraction for Cu).

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.

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).

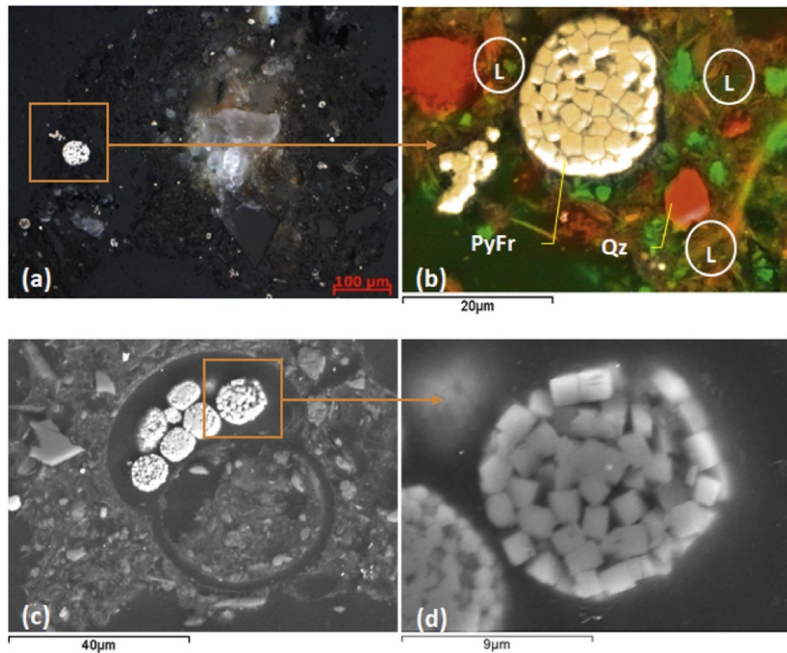


Fig. 3 Optical and scanning electron microscope images: a,b) weathered sediment: framboidal pyrite (PyFr) included into an aluminosilicate-bonded agglomerate rich of copper and zinc (L) and containing quartz (Qz) and calcite (Cal); c,d) unweathered sediment: framboidal pyrites.

alt-text: Fig. 3

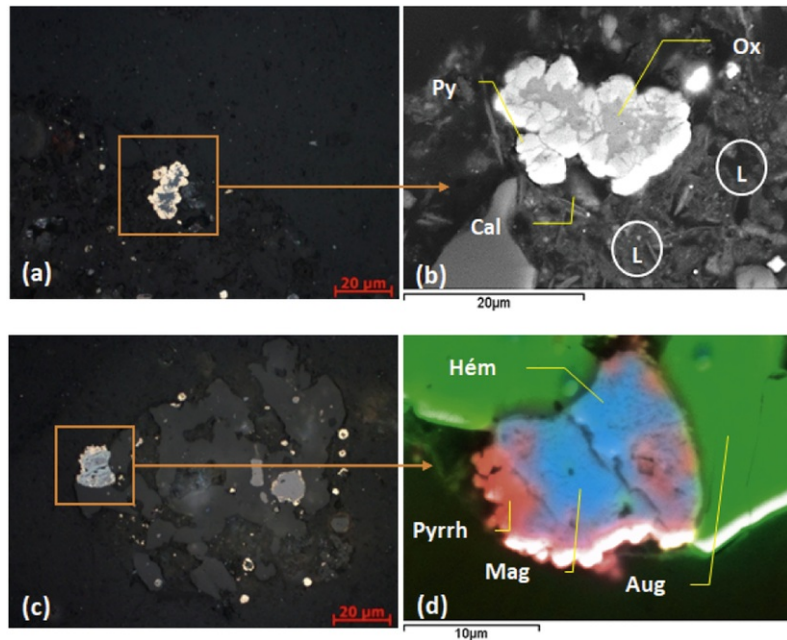


Fig. 4 Optical and scanning electron microscope images: a,b) weathered sediment: pyrite (Py) turning into iron oxide (Ox) included into an aluminosilicate agglomerate rich of copper and zinc (L) and containing calcite (Cal); c, d) unweathered sediment: pyrrhotite (Pyrrh) associated with magnetite (Mag)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

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.

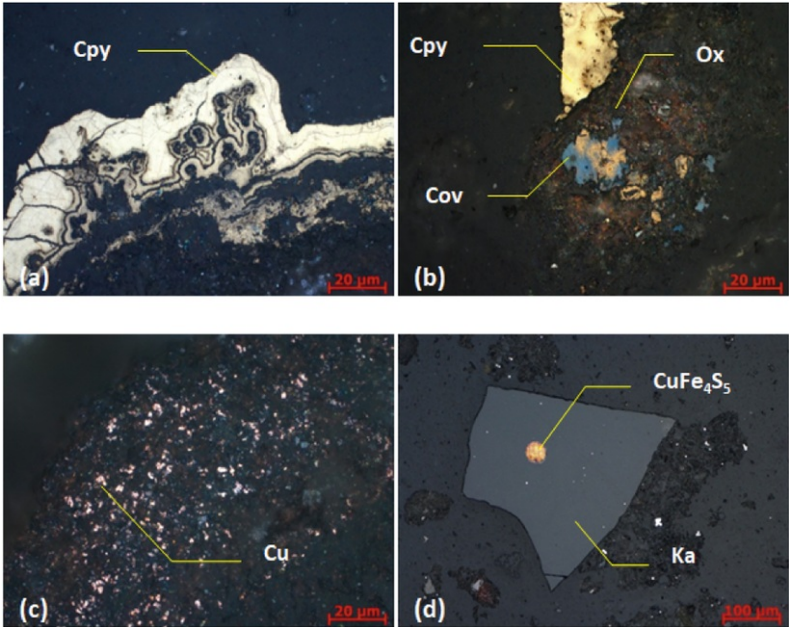


Fig. 5 Optical microscope images of unweathered sediment: a, b) chalcopyrite (Cpy) and covellite (Cov); c) native copper (Cu); d) iron and copper mixed sulfide CuFe_4S_5 included into Katophorite (Ka).

alt-text: Fig. 5

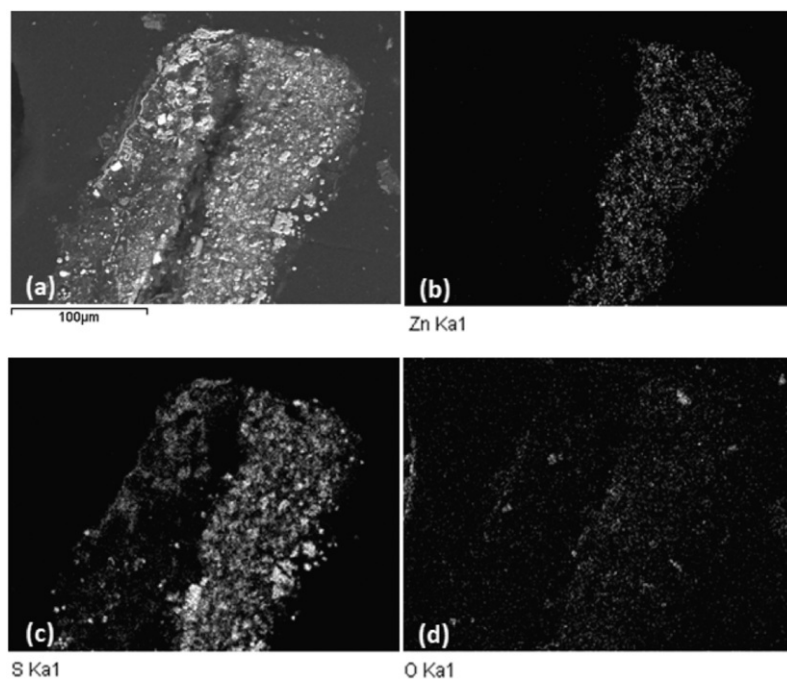


Fig. 6 a) Scanning electron microscope image of a grain in unweathered sediment; b, c, d) X-mapping images showing zinc, sulfur and oxygen distribution in the grain of unweathered sediment.

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.

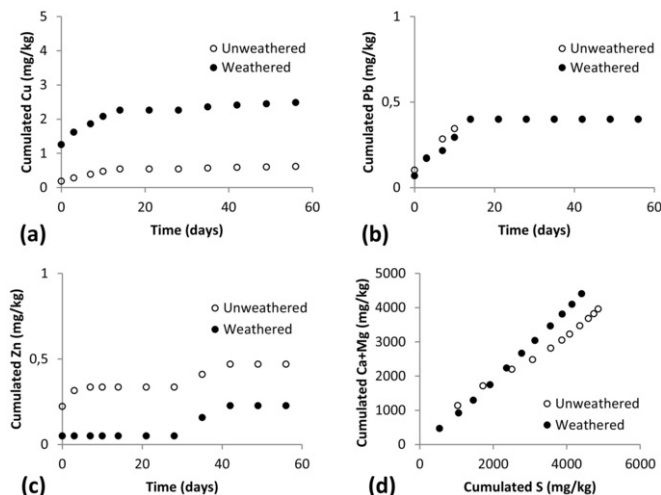


Fig. 7 Temporal evolution of copper (a), lead (b), zinc (c), and evolution of calcium and magnesium as a function of sulfur (d) in weathering cells leachates of unweathered and naturally-weathered sediments (quantification uncertainties are < 10% for Cu and < 25% for Pb and Zn).

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 **<** $80 \mu m$ 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's 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 oxyhydroxides 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).

Acknowledgments

The authors are grateful to the EEDEMS platform (French research network on waste and polluted materials management) for experimental support. The authors also acknowledge the Research and Service Unit in Mineral Technology (URSTM), University of Quebec in Abitibi-Temiscamingue (UQAT) for their experimental support.

References

- APHA, Standard ~~m~~Methods for the ~~e~~Examination of ~~w~~Water and ~~w~~Wastewater, 21st edn, 2005, (Washington, DC, USA).
- Bäckström M., Karlsson S., Bäckman L., Folkesson L. and Lind B., Mobilisation of heavy metals by deicing salts in a roadside environment, ~~Water-Research~~*Water Res.* **38** (3), 2004, 720-732.
- Bao J., Wang L. and Xiao M., Changes in speciation and leaching behaviors of heavy metals in dredged sediment solidified/stabilized with various materials, ~~Environmental Science and Pollution Research~~*Environ. Sci. Pollut. Res.* **23** (9), 2016, 8294-8301.
- Benzaazoua M., Ouellet J., Servant S., Newman P. and Verburg R., Cementitious backfill with high sulfur content ~~P~~physical, chemical, and mineralogical characterization, ~~Cement and Concrete Research~~*Cem. Concr. Res.* **29** (5), 1999, 719-725.

- Benzaazoua M., Bussière B., Dagenais [A. M. A. M.](#) and Archambault M., Kinetic tests comparison and interpretation for prediction of the Joutel tailings acid generation potential, [Environmental Geology Environ. Geol.](#) **46** (8), 2004, 1086-1101.
- Beolchini F., Rocchetti L. and Dell'Anno A., Degradation kinetics of butyltin compounds during the bioremediation of contaminated harbour sediments, [Chemistry and Ecology Chem. Ecol.](#) **30** (5), 2014, 393-402.
- Bouzahzah H., Califice A., Benzaazoua M., Mermillod-Blondin R. and Pirard E., Modal analysis of mineral blends using optical image analysis versus X ray diffraction, In: *Proceedings of International Congress for Applied Mineralogy ICAM08, Brisbane, Australia: AusIMM*, 2008.
- Bouzahzah H., Benzaazoua M., Bussiere B. and Plante B., Prediction of acid mine drainage: importance of mineralogy and the test protocols for static and kinetic tests, [Mine Water and the Environment Mine Water Environ.](#) **33** (1), 2014, 54-65.
- Brouwer H. and Murphy [F. P. T. P.](#), Diffusion method for the determination of acid-volatile sulfides (AVS) in sediment, [Environmental Toxicology and Chemistry Environ. Toxicol. Chem.](#) **13** (8), 1994, 1273-1275.
- Caille N., Tiffreau C., Leyval C. and Morel [J. L. L.](#), Solubility of metals in an anoxic sediment during prolonged aeration, [Science of The Total Environment Sci. Total Environ.](#) **301** (1-3), 2003, 239-250.
- Calmano W., Hong J. and Förstner U., Binding and [m](#)Mobilization of [h](#)Heavy [m](#)Metals in [e](#)Contaminated [s](#)Sediments [a](#)Affected by pH and [r](#)Redox [p](#)Potential, 1993, Technische Universität Hamburg-Harburg.
- Capel [E. L. E. L.](#), de la Rosa Arranz [J. M. I. M.](#), González-Vila [F. J. F. J.](#), González-Perez [J. A. J. A.](#) and Manning [D. A. C. D. A. C.](#), Elucidation of different forms of organic carbon in marine sediments from the Atlantic coast of Spain using thermal analysis coupled to isotope ratio and quadrupole mass spectrometry, [Organic Geochemistry Org. Geochem.](#) **37** (12), 2006, 1983-1994.
- Caplat C., Texier H., Barillier D. and Lelievre C., Heavy metals mobility in harbour contaminated sediments: [T](#)he case of Port-en-Bessin, [Marine Pollution Bulletin Mar. Pollut. Bull.](#) **50** (5), 2005, 504-511.
- Carignan J., Hild P., Mevelle G., Morel J. and Yeghicheyan D., Routine [A](#)analyses of [T](#)race [E](#)lements in [G](#)eological [S](#)amples using [F](#)low [I](#)njection and [L](#)ow [P](#)ressure [O](#)n-[L](#)ine [L](#)iquid [C](#)hromatography [C](#)oupled to ICP-MS: [A](#)a [S](#)study of [G](#)eochemical [R](#)eference [M](#)aterials BR, DR-N, UB-N, AN-G and GH, [Geostandards Newsletter Geostand. Newslett.](#) **25** (2-3), 2001, 187-198.
- Casado-Martínez [M. C. M. C.](#), Forja [J. M. I. M.](#) and DelValls [F. A. T. A.](#), A multivariate assessment of sediment contamination in dredged materials from Spanish ports, [Journal of Hazardous Materials J. Hazard. Mater.](#) **163** (2-3), 2009, 1353-1359.
- Chatain V., Benzaazoua M., Loustau Cazalet M., Bouzahzah H., Delolme C., Gautier M., Blanc D. and Brauer C., Mineralogical study and leaching behavior of a stabilized harbor sediment with hydraulic binder, [Environmental Science and Pollution Research Environ. Sci. Pollut. Res.](#) 2013a, 1-9.
- Chatain V., Blanc D., Borschneck D. and Delolme C., Determining the experimental leachability of copper, lead, and zinc in a harbor sediment and modeling, [Environmental Science and Pollution Research Environ. Sci. Pollut. Res.](#) 2013b, 1-9.
- Claff [S. R. S. R.](#), Burton [E. D. E. D.](#), Sullivan [L. A. L. A.](#) and Bush [R. T. R. T.](#), Effect of sample pretreatment on the fractionation of Fe, Cr, Ni, Cu, Mn, and Zn in acid sulfate soil materials, *Geoderma* **159** (1-2), 2010, 156-164.
- Commission Decision of 3 May 2000 Replacing Decision 94/3/EC Establishing a List of Wastes, Consolidated Version of 01 January, **2000D0532**, 2002.
- Couvidat J., Benzaazoua M., Chatain V., Zhang F. and Bouzahzah H., An innovative coupling between column leaching and oxygen consumption tests to assess behavior of contaminated marine dredged sediments, [Environmental Science and Pollution Research Environ. Sci. Pollut. Res.](#) 2015, 1-13.
- Couvidat J., Benzaazoua M., Chatain V., Bouamrane A. and Bouzahzah H., Feasibility of the reuse of total and processed contaminated marine sediments as fine aggregates in cemented mortars, [Construction and Building Materials Constr. Build. Mater.](#) **112**, 2016a, 892-902.
- Couvidat J., Neculita [G. M. C. M.](#), Benzaazoua M., Genty T. and Chatain V., Evaluation of biogeochemical reactivity of fresh and weathered contaminated dredged sediments, [Journal of Soils and Sediments J. Soils Sediments](#) **17** (2), 2016b, 543-556.
- Cruz R., Méndez [B. A. B. A.](#), Monroy M. and González I., Cyclic voltammetry applied to evaluate reactivity in sulfide mining residues, [Applied Geochemistry Appl. Geochem.](#) **16** (14), 2001, 1631-1640.
- Cruz A., Cavaleiro [A. J. A. J.](#), Paulo [A. M. S. A. M. S.](#), Louvado A., Alves [M. M. M. M.](#), Almeida A. and Cunha Â., Microbial remediation of organometals and oil hydrocarbons in the marine environment, In: Naik M.M. and Dubey S.K.,

(Eds.), *Marine Pollution and Microbial Remediation*, 2017, Singapore; Springer Singapore, 41–66.

DelValls [T.-Á.T.Á.](#), Forja [J.-M.J.M.](#), González-Mazo E., Gómez-Parra A. and Blasco J., Determining contamination sources in marine sediments using multivariate analysis, [TrAC Trends in Analytical Chemistry](#)[TrAC Trends Anal. Chem.](#) **17** (4), 1998, 181–192.

Díez S., Ábalos M. and Bayona [J.-M.J.M.](#), Organotin contamination in sediments from the [W](#)estern Mediterranean enclosures following 10 years of TBT regulation, [Water Research](#)[Water Res.](#) **36** (4), 2002, 905–918.

Eek E., Cornelissen G., Kibsgaard A. and Breedveld [G.-D.G.D.](#), Diffusion of PAH and PCB from contaminated sediments with and without mineral capping; measurement and modelling, *Chemosphere* **71** (9), 2008, 1629–1638.

Eggleton J. and Thomas [K.-V.K.V.](#), A review of factors affecting the release and bioavailability of contaminants during sediment disturbance events, [Environment International](#)[Environ. Int.](#) **30** (7), 2004, 973–980.

Frémion F., Mourier B., Courtin-Nomade A., Lenain J.-F., Annouri A., Fondanèche P., Hak T. and Bordas F., Key parameters influencing metallic element mobility associated with sediments in a daily-managed reservoir, *Sci. Tot. Environ.* **605-606** (Supplement C), 2017, 666–676.

Isaure M.-P., Laboudigue A., Manceau A., Sarret G., Tiffreau C., Trocellier P., Lamble G., Hazemann J.-L. and Chateigner D., Quantitative Zn speciation in a contaminated dredged sediment by μ -PIXE, μ -SXRF, EXAFS spectroscopy and principal component analysis, [Geochimica et Cosmochimica Acta](#)[Geochim. Cosmochim. Acta](#) **66** (9), 2002, 1549–1567.

Jerz [J.-K.J.K.](#) and Rimstidt [J.-D.J.D.](#), Pyrite oxidation in moist air, [Geochimica et Cosmochimica Acta](#)[Geochim. Cosmochim. Acta](#) **68** (4), 2004, 701–714.

Jones B. and Turki A., Distribution and speciation of heavy metals in surficial sediments from the Tees Estuary, north-east England, [Marine Pollution Bulletin](#)[Mar. Pollut. Bull.](#) **34** (10), 1997, 768–779.

JORF 2007, 17002, n°240 du 16 octobre. (texte n°1).

Juhász [A.-L.A.L.](#) and Naidu R., Bioremediation of high molecular weight polycyclic aromatic hydrocarbons: a review of the microbial degradation of benzo[a]pyrene, *Int. Biodeter. Biodegr.* **45** (1–2), 2000, 57–88.

Lawrence [R.-W.R.W.](#) and Wang Y., Determination of neutralization potential in the prediction of acid rock drainage, In: *4th Int. Conf. on Acid Rock Drainage, Vancouver, BC, Canada: Nat. Resour. Canada, Ottawa, ON*, 1997, 451–463.

Le Guyader C., Enquête “Dragage 2009” - Synthèse des données [Report], Margny Lès Compiègne: CETMEFEQ-CETMEF-12-05-FR, 2011.

Le Guyader C., Enquête “Dragage 2010” - Synthèse des données [Report], Margny Lès Compiègne: CETMEFEQ-CETMEF-13-06-FR, 2013.

Leonard [E.-N.E.N.](#), Cotter [A.-M.A.M.](#) and Ankley [G.-T.G.T.](#), Modified diffusion method for analysis of acid volatile sulfides and simultaneously extracted metals in freshwater sediment, [Environmental Toxicology and Chemistry](#)[Environ. Toxicol. Chem.](#) **15** (9), 1996, 1479–1481.

Lions J., van der Lee J., Guérin V., Bataillard P. and Laboudigue A., Zinc and cadmium mobility in a 5-year-old dredged sediment deposit: [E](#)xperiments and modelling, [Journal of Soils and Sediments](#)[J. Soils Sediments](#) **7** (4), 2007, 207–215.

Lions J., Guérin V., Bataillard P., van der Lee J. and Laboudigue A., Metal availability in a highly contaminated, dredged-sediment disposal site: [F](#)ield measurements and geochemical modeling, [Environmental Pollution](#)[Environ. Pollut.](#) **158** (9), 2010, 2857–2864.

Lowson [R.-T.R.T.](#), Aqueous oxidation of pyrite by molecular oxygen, [Chemical Reviews](#)[Chem. Rev.](#) **82** (5), 1982, 461–497.

Maity S., Sahu [S.-K.S.K.](#) and Pandit [G.-G.G.G.](#), Trace metals distribution and their dependence on some physico-chemical parameters in creek sediment, [Toxicological & Environmental Chemistry](#)[Toxicol. Environ. Chem.](#) **99** (2), 2017, 209–222.

Mamindy-Pajany Y., Geret F., Roméo M., Hurel C. and Marmier N., Ex situ remediation of contaminated sediments using mineral additives: [A](#)assessment of pollutant bioavailability with the microtox solid phase test, *Chemosphere* **86** (11), 2012, 1112–1116.

Mayer T., Rochfort Q., Borgmann U. and Snodgrass W., Geochemistry and toxicity of sediment porewater in a salt-impacted urban stormwater detention pond, [Environmental Pollution](#)[Environ. Pollut.](#) **156** (1), 2008, 143–151.

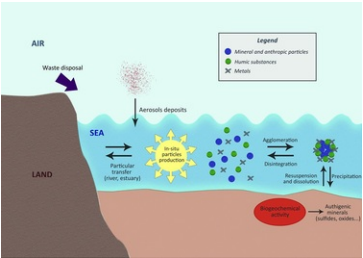
- Morabito E., Radaelli M., Corami F., Turetta C., Toscano G. and Capodaglio G., Temporal evolution of cadmium, copper and lead concentration in the Venice Lagoon water in relation with the speciation and dissolved/particulate partition, *Mar. Pollut. Bull.* 2017.
- Mulligan ~~C.N.C.N.~~, Yong ~~R.N.R.N.~~ and Gibbs ~~B.F.B.F.~~, An evaluation of technologies for the heavy metal remediation of dredged sediments, *Journal of Hazardous Materials*~~J. Hazard. Mater.~~ **85** (1-2), 2001, 145-163.
- Paktunc ~~A.D.A.D.~~, Characterization of mine wastes for prediction of acid mine drainage, In: *Environmental Impacts of Mining Activities*, 1999a, Springer, 19-40.
- Paktunc ~~A.D.A.D.~~, Mineralogical constraints on the determination of neutralization potential and prediction of acid mine drainage, *Environmental Geology*~~Environ. Geol.~~ **39** (2), 1999b, 103-112.
- Paria S. and Yuet ~~P.K.P.K.~~, Solidification-stabilization of organic and inorganic contaminants using portland cement: a literature review, *Environmental Reviews*~~Environ. Rev.~~ **14** (4), 2006, 217-255.
- Pierret M.-C., Blanc G. and Clauer N., Sur l'origine de la pyrite framboïdale dans les sédiments de la fosse Suakin (mer Rouge), ~~Comptes Rendus de l'Académie des Sciences - Series IIA - Earth and Planetary Science~~*C. R. Acad. Sci. Ser. II Earth Planet. Sci.* **330** (1), 2000, 31-38.
- Pinto ~~P.X.P.X.~~, Al-Abed ~~S.R.S.R.~~, Barth E., Loftspring C., Voit J., Clark P. and Ioannides ~~A.M.A.M.~~, Environmental impact of the use of contaminated sediments as partial replacement of the aggregate used in road construction, *Journal of Hazardous Materials*~~J. Hazard. Mater.~~ **189** (1-2), 2011, 546-555.
- Piou S., Bataillard P., Laboudigue A., Féraud J.-F. and Masfaraud J.-F., Changes in the geochemistry and ecotoxicity of a Zn and Cd contaminated dredged sediment over time after land disposal, *Environmental Research*~~Environ. Res.~~ **109** (6), 2009, 712-720.
- Puget P., Chenu C. and Balesdent J., Dynamics of soil organic matter associated with particle-size fractions of water-stable aggregates, *European Journal of Soil Science*~~Eur. J. Soil Sci.~~ **51** (4), 2000, 595-605.
- Raudsepp M. and Pani E., Application of Rietveld Analysis to Environmental Mineralogy, Environmental Aspects of Mine Wastes, **3**, 2003, Mineralogical Association of Canada Short Course, 165-180.
- Ribecco C., Baker ~~M.E.M.E.~~, Šášík R., Zuo Y., Hardiman G. and Carnevali O., Biological effects of marine contaminated sediments on *Sparus aurata* juveniles, *Aquatic Toxicology*~~Aquat. Toxicol.~~ **104** (3-4), 2011, 308-316.
- Rickard D. and Morse ~~J.W.J.W.~~, Acid volatile sulfide (AVS), *Marine Chemistry*~~Mar. Chem.~~ **97** (3-4), 2005, 141-197.
- Rulkens W., Introduction to the ~~T~~reatment of ~~P~~olluted ~~S~~ediments, *Reviews in Environmental Science and Biotechnology*~~Rev. Environ. Sci. Biotechnol.~~ **4** (3), 2005, 213-221.
- Saussaye L., Hamdoun H., Leleyter L., van Veen E., Coggan J., Rollinson G., Maherzi W., Boutouil M. and Baraud F., Trace element mobility in a polluted marine sediment after stabilisation with hydraulic binders, *Marine Pollution Bulletin*~~Mar. Pollut. Bull.~~ **110** (1), 2016, 401-408.
- Sobek ~~A.A.A.A.~~, Schuller ~~W.A.W.A.~~, Freeman ~~J.R.J.R.~~ and Smith ~~R.M.R.M.~~, Field and ~~L~~aboratory ~~m~~ethods ~~e~~applicable to ~~e~~overburden and ~~m~~inesoils, 1978, US Environmental Protection Agency.
- Staniszewska M., Burska D., Sapota G., Bogdaniuk M., Borowiec K., Nosarzewska I. and Bolalek J., The relationship between the concentrations and distribution of organic pollutants and black carbon content in benthic sediments in the Gulf of Gdańsk, Baltic Sea, *Marine Pollution Bulletin*~~Mar. Pollut. Bull.~~ **62** (7), 2011, 1464-1475.
- Stephens ~~S.R.S.R.~~, Alloway ~~B.J.B.J.~~, Parker A., Carter ~~J.E.J.E.~~ and Hodson ~~M.E.M.E.~~, Changes in the leachability of metals from dredged canal sediments during drying and oxidation, *Environmental Pollution*~~Environ. Pollut.~~ **114** (3), 2001, 407-413.
- Straube ~~W.L.W.L.~~, Nestler ~~G.C.C.C.~~, Hansen ~~L.D.L.D.~~, Ringleberg D., Pritchard ~~P.H.P.H.~~ and Jones-Meehan J., Remediation of polyaromatic ~~H~~ydrocarbons (PAHs) through landfarming with ~~B~~ioaugmentation, *Acta Biotechnologica*~~Acta Biotechnol.~~ **23** (2-3), 2003, 179-196.
- Sutton R. and Sposito G., Molecular ~~S~~tructure in ~~S~~oil ~~H~~umic ~~S~~ubstances: ~~T~~he ~~N~~ew ~~V~~iew, *Environ. Sci. Technol.* **39** (23), 2005, 9009-9015.
- Tack ~~F.M.G.F.M.G.~~, Metal bioavailability in land-disposed dredged sediments, In: Rinklebe J., Knox A.S. and Paller M., (Eds.), *Trace ~~e~~lements in ~~w~~aterlogged ~~s~~oils and ~~s~~ediments Advances in Trace Elements in the Environment* 2016, CRC Press; Boca Raton, FL, USA, 253-266.
- Tack ~~F.M.G.F.M.G.~~, Van Ranst E., Lievens C. and Vandenberghe ~~R.E.R.E.~~, Soil solution Cd, Cu and Zn concentrations as affected by short-time drying or wetting: ~~T~~he role of hydrous oxides of Fe and Mn, *Geoderma* **137** (1-2),

Villeneuve M., Bussière B., Benzaazoua M. and Aubertin M., Assessment of interpretation methods for kinetic tests performed on tailings having a low acid generating potential, In: *Proceedings, Securing the Future and 8th ICARD, Skelleftea, Sweden, 2009*.

Wang ~~D. X. D. X.~~, Abriak ~~N. E. N. E.~~, Zentar R. and Xu W., Solidification/stabilization of dredged marine sediments for road construction, ~~*Environmental technology*~~ *Environ. Technol.* **33** (1), 2012, 95–101.

Young ~~R. A. R. A.~~, The Rietveld Method, 1993, Oxford University Press; NYC, NY, USA.

Graphical abstract



alt-text: Image 1

Highlights

- In-depth study of contaminated sediments is advised for accurate management.
- Reactive mineral species in particular framboïdal 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

Query:

Your article is registered as belonging to the Special Issue/Collection entitled “AquaConsoil 2017”. If this is NOT correct and your article is a regular item or belongs to a different Special Issue please contact p.das@elsevier.com immediately prior to returning your corrections.

Answer: Yes

Query:

Please confirm that given names and surnames have been identified correctly and are presented in the desired order, and please carefully verify the spelling of all authors’ names.

Answer: Yes

Query:

The author names have been tagged as given names and surnames (surnames are highlighted in teal color). Please confirm if they have been identified correctly.

Answer: Yes

Query:

Please check and confirm if the authors' affiliations are presented correctly and amend as necessary.

Answer: I confirm that it is correct.

Query:

One parenthesis has been deleted to balance the delimiters. Please check and confirm if this was done correctly.

Answer: Yes

Query:

The data "IRME" has been deleted to avoid redundancy. Please check if the deletion is appropriate and amend as necessary.

Answer: I confirm that it is correct.

Query:

Please check the hierarchy of the section headings and confirm if correct.

Answer: Yes

Query:

The citation "European Council, 2002" has been linked to reference "Commission decision of 3 may 2000 replacing Decision 94/3/EC establishing a list of wastes, consolidated version of 01 january 2002 (2000D0532)". Please check if appropriate and amend as necessary.

Answer: I confirm that it is correct.

Query:

The citation "French Official Journal, 2007" has been linked to reference "JORF n°240 du 16 octobre 2007 p.17002 texte n°1". Please check if appropriate and amend as necessary.

Answer: I confirm that it is correct.

Query:

The citation "Sobek (1978)" has been changed to "Sobek et al. (1978)" to match the author name/date in the reference list. Please check if the change is fine and amend if necessary.

Answer: I confirm that it is correct.

Query:

Please check if the insertion of "2008" in this reference item is correct and amend as necessary.

Answer: I confirm that it is correct.

Query:

Please check if the insertion of "1997" in this reference item is correct and amend as necessary.

Answer: I confirm that it is correct.

Query:

Please provide the volume number and page range for the bibliography in Morabito et al., 2017.

Answer: In press, <https://doi.org/10.1016/j.marpolbul.2017.10.043>