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An innovative coupling between column leaching and oxygen-consumption tests to assess behavior of contaminated marine dredged sediments

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Abstract

Purpose: Contaminated dredged sediments are often considered hazardous wastes, so they have to be adequately managed to avoid leaching of pollutants. The mobility of inorganic contaminants is a major concern. Metal sulfides (mainly framboïdal pyrite, copper and zinc-sulfides) have been investigated in this study as an important reactive metal-bearing phase sensitive to atmospheric oxygen action.

Methods: An Oxygen Consumption-Test (OC-Test) has been adapted to assess the reactivity of dredged sediments when exposed to atmospheric oxygen. An experimental column set-up has been developed allowing the coupling between leaching and oxygen consumption test to investigate the reactivity of the sediment.

Results: This reactivity, which consisted of sulfides oxidation, was found to occur for saturation degree between 60 and 90% and until the 20th testing week, through significant sulfates releases. These latter were assumed to come from sulfides oxidation in the first step of the test, then probably from gypsum dissolution. Confrontation results of OC-Test and leachates quality shows that Cu was well correlated to sulfates releases, which in turn leads to Ca and Mg dissolution (buffer-effect). Cu, and mostly Zn, was associated to organic matter, phyllosilicates and other minerals through organo-clays complexes.

Conclusions: This research confirmed that OC-Test originally developed for mine tailings could be a useful tool in the dredged sediment field which can allow for intrinsic characterization of reactivity of a material suspected to readily reacting with oxygen and for better understanding of geochemical processes that affect pollutants behavior, conversion, and transfer in the environment.

Keywords: *dredged marine sediment, oxygen consumption test, sulfides, trace metals, leaching, oxidation, organic matter*

1. Introduction

Management of contaminated dredged sediment is a requirement of harbors administrators and authorities, which are in charge of the dredging operations. Up to 18.6 million ton of sediment (in dry matter) have been dredged in France (metropolitan and overseas) in 2010, 33.56 million tons in 2009, and 23.2 million tons in 2008 (Le Guyader 2011; Le Guyader 2013). Once extracted from their original environment, sediments are considered as waste materials that have to be adequately managed accordingly to existing regulations (European Council 2002; French Official Journal 2007). Marine sediments are composed mainly of minerals (quartz, various silicates, carbonates, iron and manganese oxy-hydroxides, and sulfides) as well as organic matter (OM). Contaminants are mainly sourced from urban contamination, industrial activities as well as nautical activities. Inorganic pollutants (Cu, Zn, Pb, Cr, Hg, As...) are particularly of concern due to their ubiquitous presence and their accumulation within sediments. Organometallics, mainly as tin compounds, and organic pollutants are also of significant concern. All those compounds are likely to be harmful towards the environment as well as human health even at low levels, and frequently encountered at various levels in marine sediments (Caplat et al. 2005; Casado-Martínez et al. 2009; Chatain et al. 2013a; Díez et al. 2002; Eek et al. 2008; Jones and Turki 1997; Lions et al. 2010; Mamindy-Pajany et al. 2012; Ribecco et al. 2011; Staniszewska et al. 2011). Sulfides minerals are likely to control the mobility of trace metals in anoxic layers as Cu or Zn (Morse and Luther Iii 1999; Salomons et al. 1987; Ye et al. 2011). Metal mobility depends on several processes, as discrete sulfide phases precipitation, complexation with bisulfides, polysulfides or OM, adsorption or coprecipitation within iron sulfides (Huerta-Díaz et al. 1998). Their immobilization into metallic sulfides in anoxic environment is not only controlled by thermodynamic parameters, but also depends on ligand exchange reaction kinetic and redox reaction pathways. For instance, Pb, Zn, and Cd form MeS (or MeS₂) phases, whereas Co or Ni are rather incorporated into pyrite (Morse and Luther Iii 1999). Furthermore, it was stated that pyrite (FeS₂) and iron monosulfide (FeS) play a central role in the iron and sulfur cycles in marine sediments (Schippers and Jørgensen 2002).

In fact, sulfides are known as reactive minerals very susceptible to the redox potential. Dredging and land-storing induces oxygen diffusion while water desaturation increases. Molecular oxygen is the main oxidant of reduced sulfur species in oxic environment, as shown in the equation (Eq.1) of pyrite oxidation by molecular oxygen and water (Lowson 1982).

Oxidation of sulfides can occur and lead to inorganic contaminants release, even at neutral pH (Salomons et al. 1987). In sulfide bearing sediments, the framboidal pyrite is considered as the most common form of pyrite in anoxic sediments as well as the most reactive (Pierret et al. 2000). Usually in marine sediments, pyrite concentrations are under 1 wt.% (Lowers et al. 2007; Schenau et al. 2002), and up to 20 wt.% in some rare cases (Pierret et al. 2000). Sulfides clearly play a central role towards trace metals mobility, and their reactivity is a key parameter towards assessment of the environmental impact of contaminated sediments. Most studies in the literature focused on sediment geochemical behavior through leaching tests, according to current regulations (Caplat et al. 2005; Chatain et al. 2013a; Chatain et al. 2013b; Guevara-Riba et al. 2004; Prokop et al. 2003;

Sundaray et al. 2011). Knowledge about parameters linked to this sulfide reactivity should be improved, given the challenges for better management of contaminated dredged sediments. Monitoring of parameters such as pH, oxido-reduction potential (ORP), or trace and major metal concentrations have been promoted during leaching test (Cappuyns and Swennen 2008). Moreover, it is worth mentioning that there are other approaches usually used in the characterization of sulfidic materials. For instance, some mining research scientists used during the last two decades an oxygen consumption-test (OC-Test) to assess the acid mine drainage (AMD) potential of sulfides-rich wastes (Demers et al. 2009; Elberling et al. 2003; Elberling and Nicholson 1996; Mbonimpa et al. 2003; Ouellet et al. 2006). In this study, the authors propose to adapt the OC-test to dredged sediment characterization in order to better understand the geochemical interactions between sulfides, OM and oxygen.

In this context, the main objective of the study is to assess the reactivity and geochemical behavior of dredged sediment by the use of an innovative experimental column set-up allowing the coupling between leaching test and OC-Test. The authors propose to link the oxygen consumption (OC) due to sulfides and OM oxidation to the quality of the leachates (trace metals, sulfates ...) released during a column leaching test on a contaminated harbor sediment.

2. Material and methods

2.1. Sampling, treatment, and preparation of sediment

The sediment used was dredged in a harbor located in the south of France. It was sampled with a mechanical shovel and sieved at 20mm. This marine sediment was stored for 5 years to undergo a natural weathering after a short aeration pretreatment. Prior to characterization, the sediment was homogenized by quartering and stored at 4°C in darkness.

2.2. Analytical methods

2.2.1. Sediment characterization

The sediment was characterized for particle size distribution (PSD), total sulfur and carbon, specific gravity (Gs), chemical composition, non-organic sulfur speciation and total organic carbon (TOC). PSD was determined by laser diffraction (Malvern Mastersizer 2000G) after sieving of the sediment at 1mm. During the PSD analysis, the ultrasounds were applied for 1 min to allow aggregates breakdown. Total sulfur and total carbon were determined by induction furnace analyser (ELTRA CS-2000). Gs of each sample was measured with an helium gas pycnometer (Micromeritics Accupyc 1330). Chemical composition was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Perkin Elmer Optima 3100 RL) after a HNO₃/Br₂/HF/HCl digestion. Determination of non-organic sulfur speciation was realized by HCl extraction according to a Sobek method (Sobek et al. 1978). Only HCl-extractable sulfur are determined, mostly sulfates and amorphous sulfides, giving by difference with total sulfur the amount of sulfur under crystallized sulfides forms and non-extractable

organic sulfur. Content in OM was determined by TOC through sample combustion within a furnace heated to 680°C. The released gas was then analyzed with non-dispersive infrared gas apparatus.

The mineralogy of samples was determined by X-ray diffraction (XRD) (Bruker AXS D8 advance) equipped with a copper anticathode, scanning over a diffraction angle (2θ) range from 5° to 70°. Scan settings were 0.02° 2θ step size and 4s counting time per step. The DiffracPlus EVA software (v.9.0 rel.2003) was used to identify mineral species and the TOPAS software (v 2.1) implementing Rietveld refinement was used to quantify the abundance of all identified mineral species (Young 1993). The absolute precision of this quantification method is of the order of ± 0.5 -1% (Bouzahzah et al. 2008; Raudsepp and Pani 2003). The samples mineralogy identification was completed by optical microscopy observations. Polished sections prepared with bulk samples (sediment impregnated within an epoxy resin) were observed by reflected light microscopy (Zeiss Axio Imager.M2m). The chemical composition of the individual minerals (stoichiometry) was determined using a scanning electron microscope (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 20keV, ~ 100 μ A and 15 mm working distance.

2.2.2. *Leachates analysis*

Leachates were immediately prepared after their recovery from column test for chemical analysis. All recovered leachates were limpid and were filtrated through Minisart 0.45 μ m syringe filters. To improve the interpretation of geochemical results and investigate the release patterns or involved reactions into the leaching of trace metals, parameters such as pH, ORP and conductivity, some anions (Cl^- and SO_4^{2-}), major elements (Ca, Mg, Mn, ...), and dissolved organic carbon (DOC) are monitored into leachates (Cappuyns and Swennen 2008). Leachates were analyzed for trace elements and major dissolved metals by ICP-AES after acidification with 2% HNO_3 . Sulfates and chlorides were analyzed using an ionic chromatography (Dionex DX320 HPIC®). DOC concentration was determined by a total organic carbon analyzer (Shimadzu TOC 5000A®). pH, ORP and conductivity measurements were done immediately after each column rinsing and leachates recovery. pH and conductivity were measured with an Epoxy pH Ag/AgCl electrode (Fisherbrand 90437BNC) and an epoxy conductivity electrode (Consort SK10T) on a pH/mV meter (Consort C3020), and ORP was measured using a Radiometer Analytical® combined platinum electrode [Pt/Ag/AgCl, +197mV vs. Normal Hydrogen Electrode (NHE)].

2.3. Leaching column and Oxygen Consumption-Test

Highly reactive minerals when exposed to oxidizing environment may lead to pollution by releasing acidity and metals. In this context, a column leaching test was used to assess the leachability of the studied sediment. The cell column is made with transparent Plexiglas® of approximately 10.1 cm diameter and 25.4 cm height (Fig. 1). Several openings are located around the chamber allowing probes and fluid inlet and outlet. The top of the device is a removable cap with a large opening for the oxygen sensor. A plastic plate pierced with low diameter holes (2mm) is set in the lower third of the chamber, to fill with the sample. Geotextile film is inserted between the sample and the plate. A drain is available in the bottom of the chamber for flushing the device. Sediment was

placed into the chamber in a manner to have same porosity ($n=0.6$) as its state when deposited in the field (Capilla et al. 2006). Testing consisted of 15 leaching cycles. The cell flushing was conducted each 14 days by addition 500mL of deionized water at the top of the column. Leaching behavior of the sediment was investigated in parallel with the OC-Test as shown in Fig. 1. An oxygen sensor (Teledyne Analytical Instruments R-17A) is inserted at the top of the sealed column. The sensor measurement principle is based on an electrochemical galvanic battery, using the half-cell Pb/PbOOH to reduce oxygen. Consumption of oxygen by the sensor itself is therefore considered as negligible. The induced current of the reaction is directly proportional to the partial pressure of oxygen in the gas phase; the sensor generates an output signal in form of voltage every 5 seconds. Accuracy of the sensor is 0.1% in oxygen concentration. A data-logger (OMEGA Engineering OM-CP-QUADVOLT-100MV) is connected to the sensor and converts the output signal which is recorded by software on a computer.

2.3.1. Oxygen flux assessment

Oxygen Consumption test is a method that allows linking the products of the oxidation reaction analyzed within the leachates (*i.e.*, sulfates and trace metals), with the main oxidant which is the oxygen (Lowson 1982). This approach was developed for mine tailings to assess their reactivity by measuring the consumption rate of air-oxygen (Elberling and Nicholson 1996; Elberling et al. 1994; Mbonimpa et al. 2012).

Essentially, the method consists in measuring the oxygen concentration decreases in an air filled chamber located above the column during a short time period. The decrease in O_2 concentration can be converted into an oxygen flux by using Fick's Laws. This method was initially designed for determining reaction rates of sulfide tailings. The consumption of oxygen in the chamber can be related to the reactivity of sulfides through oxidation with molecular oxygen. The relation between oxygen flux through the sediment and the decrease in oxygen concentration in the sealed chamber is based on fundamental gas diffusion laws (in this study, only Fickian gas transport mechanisms are considered). Solving Fick's second law expressed with a first-order kinetic reaction term for steady state flux and specified boundary conditions gives the following equation (Eq. 2) for the flux at the cover surface (Elberling et al. 1994):

$$F_L = C_0(K_r D_e)^{\frac{1}{2}} \quad (\text{Eq. 2})$$

where K_r [T^{-1}] is the first-order reaction rate coefficient for the system, D_e [LT^{-2}] is the effective diffusion coefficient and C_0 [ML^{-3} or $MolL^{-3}$] is the atmospheric concentration of oxygen. Solving the continuity equation (which reflects the oxygen being consumed in the head space) for the initial condition $C=C_0$ at $t=0$, the following solution is obtained (Eq. 3):

$$\ln(C/C_0) = -t(K_r D_e)^{\frac{1}{2}} \left(\frac{A}{V} \right) \quad (\text{Eq. 3})$$

where A [L^2] and V [L^3] are the area and the volume of the source reservoir, respectively. The slope of the plot of $\ln(C/C_0)$ versus time gives the value of $(K_r D_e)^{1/2}$ when A/V is known. This term is substituted into Eq. (2) to evaluate the flux of oxygen at the surface. The standard OC test requires only a small change in oxygen concentration (2 to 3% O_2) in the headspace over a 1- to 3-hour(s) period so that changes in oxygen

concentration within the pore spaces are insignificant during the testing period to comply with the interpretation assumption of steady state flux. Details of the interpretation method for the standard OC method are given in (Elberling et al. 1994) and (Mbonimpa et al. 2003).

2.3.2. Influence of saturation degree on sulfide reactivity

Sulfides minerals can be oxidized when exposed to water and O₂ action (Eq. 1). The degree of saturation (S_r) related to water content of samples has an important impact on sulfides reactivity (Bouzahzah et al. 2012; Mbonimpa et al. 2003). In fact, a low S_r (low water content) reduces the water availability reducing the oxidation reaction, while a high S_r reduces the oxygen availability due to the low solubility of O₂ in water (Ouanguwa et al. 2009).

A preliminary test was performed to study the sensitivity of the OC-Test to the S_r of sediments, and to provide the optimal duration of cycles (Fig. 2). The optimal S_r is comprised between 70 and 90%, with a maximum at 80%. Moreover, the S_r decrease from 90 to 70% took 2 weeks. According to those results, OC-Tests were carried out every 14 days, 12 days after the previous flush.

3. Results

3.1. Sediment characterization

The physical and chemical properties of the studied sediment are presented in Table 1. The measured G_s is 2.55 g/cm³, close to G_s of quartz and carbonate minerals which are usually the predominant constituents of sediments. PSD shows that the sediment can be classified as a fine silty sediment, with 50% of the particles under 20 μm (D₅₀ = 19.24 μm). Organic matter is an important constituent of the sediment. Indeed, TOC is about 6.3%, in the range of usual values for marine sediments (Tessier et al. 2011). The total sulfur content is about 2 wt.%, where 51% extractable with HCl would represent mostly sulfates minerals as gypsum (except barite), and potential reactive sulfides, the remaining 49% would represent mostly well-crystallized sulfides as pyrite, and the unassessed pool of organic sulfur.

Trace metals are investigated in the whole sediment (Table 2). Some trace metals, as Cu, Pb or Zn, are monitored in dredged sediments according to French regulation (French Official Journal 2007), relative to threshold levels to be taken into account for the analysis of a marine sediment sea rejection. Two threshold levels N1 and N2 are determined through this regulation. If the assessed sediment has one trace metal over the N2 level, it is treated as “contaminated sediment”, which means it cannot be rejected into the sea but needs to be managed and/or treated in a proper way. Iron (Fe) is related to some of the most important metal key phases in marine sediments, e.g. oxy-hydroxides and sulfides. The Fe is not concerned by regulation, and is usually found in the same extent that it is found in this marine sediment. Cu, Pb and Zn which are concerned by French regulation were measured in leachates. They are found in the sediment at very high levels, above ten times higher than N2 threshold level for copper, five times for the two others.

The sample mineralogy was determined by X-Ray diffraction (Table 3) and shows that 34.6 wt.% of minerals are silicates (19.3 wt.% of clays and 15.3 wt.% of quartz). The carbonate minerals represent 52.5 wt.% of the

sample, with 13.6 wt.% of dolomite and 38.9 wt.% of calcite. Pyrite is the only crystallized form of sulfide significantly found in the sediment, which accounts for 2 wt.% of the quantified minerals. In addition, 5 wt.% of gypsum is determined as well as about 1.1 wt.% of iron oxide (magnetite). Halite (0.8 wt.%) is also identified by XRD as some frequent minerals in marine sediment.

Optical and scanning electron microscopic (SEM-EDS) observations show well-preserved pyrite and some framboïdal ones in particular (Fig. 3a). A ferrous oxide layer is covering surface of massive pyrites, suspected to act as a protective layer (passivation) (Fig. 3b). Iron oxide layer seems to be Goethite, or Lepidocrocite, according to Fe/O ratio. Both massive and framboïdal pyrite are surrounded by clays and OM aggregate, containing calcite, quartz, and traces of copper and zinc. Sulfides might have been preserved from oxidation either by the protective passivation layer of iron oxy-hydroxides, and the organo-clays aggregate (Lions et al. 2010).

3.2. Column leaching test

3.2.1. Conductivity, pH and Eh parameters of leachates

The column leaching test was conducted over 30 weeks, with a flush every 2 weeks. Chemical parameters of recovered leachates are presented in Fig. 4. Initial conductivity was high at about 6.4 mS/cm, and decreased to 1.1 mS/cm after 16 weeks (Fig. 4a). In the early stage, the fast release of soluble products occurred, and then decreased strongly. The same behavior was observed for chlorides, which concentration decreased from 400 to 10 mg/kg (halite dissolution). During the column leaching test, leachates presented stable pH values around 7.5 (Fig. 4b). ORP oscillated around +500 mV/SHE for the 7 first cycles and then reached a second state around +370 mV/SHE until the end of the test.

3.2.2. Chemistry of leachates

Sulfates content in the leachates are presented in Fig. 5a. Sulfur total depletion during the 30 testing weeks was of 16%. Sulfates in leachates were highly concentrated especially at the beginning of the test (1200 mg/kg DM). Concentrations decreased to reach a plateau around 400 mg/kg DM between the 16th and 20th weeks. This leachable sulfur fraction would be linked either the oxidation of accessible framboïdal pyrites, or the dissolution of soluble sulfates mineral phases. Ca and Mg are significantly released during the first weeks of the leaching test (Fig. 5b). Their respective concentrations were 250 and 150 mg/kg DM at the beginning of the test, and decreased throughout weeks to reach a stable value around 130 and 25 mg/kg DM respectively. Accordingly to the sediment mineralogy, Mg and Ca are expressed mainly as dolomite and calcite. Ca is also associated to gypsum whose dissolution would cause the release of Ca into recovered leachates. Dolomite and calcite are responsible for buffering effect. As previously observed, it can be expected that leaching of those minerals reflects the acid (H⁺) neutralization following metallic sulfides oxidation. Carbone was also investigated on its dissolved forms into leachates. DOC has roughly the same behavior as chlorides which rapidly decreased after the first testing cycles at 49 mg/kg DM to 8 mg/kg DM at 5th cycle and then reached a plateau around 5 mg/kg DM.

Cu, Fe and Zn concentrations into leachates are presented in Fig. 6. Pb was under the detection limit of ICP-AES on all analyzed leachates and it is not discussed in this section. Pb's leachability is known to be very low in a range of pH between 6.5 and 12, and it is much more sensitive to acidic pH (Chatain et al. 2013b; Trefry and Metz 1984). Contrary to Pb, and as observed in literature (Dold and Fontboté 2002; Warwick et al. 1998), Zn was released during the whole experiment with concentrations between 0.1 and 0.4 mg/kg. Moreover, Cu decreased progressively from 0.2 to 0.01 mg/kg DM. Fe was released at very small concentrations indicating a probable precipitation of fresh Fe-oxi-hydroxides. Other trace metals (arsenic, chromium, manganese) were mostly under detection limit.

3.3. Oxygen consumption test

Contrary to mine tailings, $\ln(C/C_0)$ versus time plot provided a hyperbolic curve instead of a straight line, due to the weaker reactivity of sediments. A punctual reactivity is therefore taken into account to calculate the oxygen flux (F_L), represented by the slope of the curve ($\ln(C/C_0) = f(t)$) which is linear between 0 and 2 minutes. O_2 consumption was realized over the 30 weeks of the testing (Fig. 7). Important oxidation occurred at the beginning of the test (between the second and the eighth weeks) with more than $100 \text{ mol}(O_2).m^{-2}.s^{-1}$. This O_2 consumption then gradually decreased to reach zero consumption from the 20th week until the end of the test. The measured S_r during every O_2 consumption test varied roughly between 60 and 70% and no correlation was observed between the decrease of O_2 consumption and S_r .

4. Discussion

The objective of this study was to assess the reactivity and the geochemical behavior of the sediment by the use of an experimental column set-up, with the coupling between leaching test and OC-Test. Elucidation of this geochemical behavior depends on essential factors, environmental reagents, mineralogy of the sediment and products monitored into leachates, whose interactions are summarized in a schema (Fig.8). This set-up allows looking into main processes at work in the sediment coming from those interactions, which will be discussed afterward.

4.1. Oxygen consumption behavior

The fast decrease of oxygen consumption observed during the first cycles of testing let to make some interrogations. Firstly, OM is the major difference between mine tailings and marine sediments. Moreover oxidation of OM in aged marine sediment is considered to have minor or even no impact on OC, which is indicated by DOC and OC behaviors (Fig. 8). DOC has quickly reached a plateau after two cycles, whereas OC-Test has showed important variations until 5th cycle. And despite a possible residual oxidation of OM until the end of the test, no OC is monitored. Most of the reactive OM has been oxidized all along the years of storage. The remaining, regardless of its importance, is deeply linked to the sediment properties through aggregation and has a very slow microbial oxidation rate towards sulfides oxidation (Mtambanengwe et al. 2004; Puget et al. 2000). More generally, it was thought that differences in kinetic of the respective reactions, e.g. sulfides oxidation and organic matter mineralization, lead to observations at different timescale.

The Column leaching test was designed for 4 to 6 months in order to assess sulfides oxidation. The oxygen consumption progressively decreased after 10th week to reach zero at 20th week until the end of the test. In fact, this reduction in OC-Test may be attributed to a sulfide oxidation inhibition. Aggregation of sulfides with clays, OM and other minerals, as seen by SEM observations (Fig. 3a), can act as a protective layer towards oxygen. Moreover, passivation of sulfides' surface by precipitation of freshly produced Fe-oxy-hydroxides is considered to contribute to the decrease of OC during the testing (as seen in Fig. 3b). After the sample dismantling on column set-up, it was observed that the top layer of the sediment was hardened, reminiscent of the Hardpan phenomenon currently happening to sulfidic mine wastes (Blowes et al. 1991; Graupner et al. 2007). The induced decrease of oxygen consumption and diffusion into the sediment might be furthered by the diminution of the oxidant activity (ORP), as observed.

4.2. Oxidation/neutralization processes

Sulfates are oxidation products of sulfides, and though directly linked to oxygen consumption (Fig. 8). This reaction leads to acidity production (according to Eq. 1) which is mostly neutralized by carbonates (Eq. 4):

Thereby, oxidation is followed by concomitant production of neutralization products, such as Ca, Mg, and dissolved inorganic carbon (DIC) (Fig. 8). In mine tailings field, the geochemical behavior of a sample is graphically characterized by an oxidation-neutralization curve between neutralization cations (e.g. Ca, Mg, and Mn) and sulfates (Benzaazoua et al. 2004). This is particularly used to determine the long term acid-generating potential of hazardous tailings. In our case, by plotting Ca+Mg versus released sulfates, a proper alignment with good correlation is obtained (Fig. 9a). Mn is not considered because its concentrations into leachates are under the detection limit of ICP-AES. A good correlation between Ca+Mg versus sulfates illustrates the oxidation-neutralization effect that occurred in anoxic dredged sediment, as well as in mine tailings. Furthermore, sulfates leaching behavior is roughly similar with those of OC-Test, Eh, Ca, and Mg leachates analysis, with a high plateau from the beginning of the test until 10th week (600 to 1300mg/kg DM), and a lower one after (about 400mg/kg DM). This change in sulfates leaching behavior could be explained by two different origins of sulfates: oxidation of sulfides first according to sulfides' oxidation equation (Eq. 1) and OC-Test, and dissolution of sulfates mineral phases after.

Dissolution of sulfates compounds might release sulfates ions in leachates and participate to the observed correlation, when OC is over. Thus, according to XRD observations, the release of sulfates and calcium could be attributed to gypsum (Fig. 8). Indeed, Gypsum dissolution is known to be influenced by pH, temperature or competitive ions. Into distilled water, its maximum solubility is 2.85 g/L (16.6 mmol/L) between 30 and 40°C, reaching 3.8 g/L (22.1 mmol/L) into seawater. Gypsum solubility decreases in presence of common ions Ca^{2+} and SO_4^{2-} (Tanji 1969; Visconti et al. 2010).

Sulfates released in the first plateau exceed the theoretical concentrations of solubilized gypsum, even in the case of high ionic strength leaching solution without any competitive ions. In fact, after placing the sediment in the column for testing, reactive sulfides are oxidized and concomitant oxidation-neutralization products are released

into pore water. Dissolution of gypsum in those conditions might be not furthered, but if it occurred, dissolved concentrations released are much lower than those released by the sulfide oxidation. When oxidation decreased, oxidation-neutralization products have lessened. Dissolution of gypsum could have increased, or at least became more important than oxidation products, as other authors are observing same behavior for gypsum for column leaching test with distilled water (Lions et al. 2007). This hypothesis can be seen graphically by calculating molar ratios of calcium versus sulfates, and calcium versus magnesium (Fig.9b). Theoretically, oxidation-neutralization reactions produce a Ca versus sulfates ratio of 0.5, whereas in the case of a congruent dissolution of gypsum it must be 1. Moreover, according to a major competition between calcite and dolomite towards neutralization, Ca versus Mg ratio has to be close to 1 in the first case, and much higher for dissolution of gypsum.

By plotting those ratios versus time, Ca versus sulfates ratio is about 0.5 at the beginning, and close to 0.9 at the end of the testing. Ca versus Mg ratio is also close to 1 firstly and then reaches 7, which supports the fact that sulfates are mostly released from sulfides oxidation in the first part of the test. With the decrease of oxidation, gypsum (or other sulfates minerals) dissolution might become the major source of sulfates.

pH stabilization around 7.5 and the Ca and Mg content into leachates are the main direct observation of the buffer effect. Ca releases are increasingly found into leachates until the 10th week, issued from dissolution of carbonates minerals, calcite and dolomite, as neutralization response to acidity generated by sulfides oxidation. Ca concentrations then decreased to reach a plateau. Mg decreased gradually to reach a plateau after 14th week. It is in accordance with the lessening of oxygen consumption observed around the 10th week, linked to the decrease of the sulfides oxidation. Dissolved inorganic carbon into leachates is constantly found under 6 mg/kg DM throughout the testing. Carbonates precipitation must occur as pH remains neutral-basic into the sediment.

4.3. Trace metals behavior

According to the sediment's mineralogy, Fe appears mainly associated to clays minerals, (chamosite and illite), sulfides (mostly pyrite) and magnetite. Pyrite is the most probable leaching phase for Fe in the column-leaching test conditions, as physicochemical conditions do not particularly enhance reduction of iron oxides phases. Fe is very sensitive to redox potential and pH, and it precipitates under hydroxide form ($\text{Fe}(\text{OH})_3$) in neutral-oxidant environment, as this form predominates over pH 6 for Eh between 0 and 0.75V (Pourbaix et al. 1963).

Released concentrations of Cu in leachates are well correlated to oxygen consumption, and decrease constantly to reach a plateau when no oxidation is monitored. Cu is also found to be well correlated with released sulfates, especially in the first part of the test (Fig. 10a), and likewise DOC at the same time (Fig.10b). In fact, Cu is known to be linked to organic matter and sulfides (Caplat et al. 2005; Förstner et al. 1981). In the second part of the test, sulfates, Cu and DOC reached a plateau. Cu probably comes from the organo-clays aggregate observed in SEM picture (Fig. 3a and 3b), which is associated with minerals and organic matter, as well as trace metals as Cu and Zn.

Zn concentrations are more important into leachates than Cu during the whole test. It was reduced by half during the second part of the testing, after 14th week. Zn well correlates with sulfates and DOC (Fig. 10a and b). In case of sulfidic origins of Zn, Fe-oxi-hydroxides phases and phyllosilicates have been found to reduce Zn mobility after sulfides oxidation (Isaure et al. 2002; Isaure et al. 2005). Moreover, Zn^{2+} is a stable divalent cation which

has a strong affinity for OM (Sauvé et al. 2000), as well as carbonates (Chatain et al. 2013b). Those phases could explain Zn leaching, even at neutral pH. According to SEM pictures and diffuse leaching behavior, Zn is more probably associated to organo-clays aggregates.

5. Conclusion

Sulfides have been investigated in this sediment. Pyrite is found to be the major crystallized sulfides, still present despite aeration pretreatment. High reactivity of sulfides when exposed to atmospheric oxygen in sedimentary matrix was assessed with an experimental system. This reactivity was found to occur for saturation degree between 60 and 90%. A column leaching test coupled with an Oxygen Consumption-Test was carried out to better understand the behavior of dredged marine sediment when exposed to ambient air (Fig. 8). Oxygen consumption was found to occur firstly for some minutes when pilot is closed to run the test, and oxygen consumption was compared on the basis of the 2 first minutes.

This method showed a variation of oxidation activity which could correlate to the leaching behavior. We found that organic matter should have very little influence on oxygen consumption at such timescale, by monitoring DOC into leachates. Fe is suspected to mostly precipitate after oxidation of iron sulfides phases, whereas Cu readily leached from sulfides phases when oxidation occurred, and with dissolved organic matter then. Zn is associated to organo-clays complexes, which contained other reactive minerals as carbonates, and leached during the whole test. Sulfates are oxidation products of sulfides, and the acidity generated by the oxidation reaction is neutralized by carbonates minerals which released Ca and Mg ions as neutralization products into leachates. Sulfates released after the end of oxidation could be dissolution products of sulfates minerals phases, such as gypsum, favored by the decrease of competitive sulfates and calcium ions into pore water.

Despite the weathering of the material, and the oxidizing and natural leaching conditions to which it was subjected, this sediment was able to show a reactive leaching pattern such as oxidation-neutralization phenomenon. Storage and climatic conditions lead to modification of the physicochemical structure of the sediment, surface sealing at oxygen and water, inducing a decrease of Eh and leachability inside the batch. But, we notice that this apparent stabilization can be seen as a metastable state and modifications as sampling, dumping, staggering, may lead to more or less temporary reactive behavior, and subsequent leaching of hazardous substances, as it was stated before (Lions et al. 2007). This OC-Test originally developed for mine tailings was thus found to be a useful tool in the dredged sediment field, prior to assess the reactivity of a material suspected to readily react with oxygen.

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7. Conflicts of interest

The authors declare that there is no conflict of interests regarding the publication of this paper.

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Fig. 1 Schematic illustration of the experimental set-up for leaching and OC tests

Fig. 2 Dependence of OC to saturation degree with calculated oxygen flux from OC-Test in $\text{mol}(\text{O}_2).\text{m}^2.\text{s}^{-1}$

Fig. 3 SEM-EDS back-scattered electron images of sediment showing framboidal pyrite (Pf, a) surrounded by a complex aggregate containing quartz (Q, red color) and calcite (C, green color), and massive pyrite (P, b) with an Fe-oxi-hydroxides replacement (O)

Fig. 4 Evolution of leachates volume, conductivity (a), pH, and ORP (b) during the column leaching test; vertical dashed line in (b) indicates a change in geochemical behavior after 12th week

Fig. 5 Sulfates concentrations (mg/kg of dry matter (DM)), cumulative percentages of sulfates fraction of sulfur (in % from total sulfur) (a), Ca, and Mg concentrations (in mg/kg DM, b) in leaching solutions during the column leaching test; vertical dashed line indicates a change in geochemical behavior after 12th week

Fig. 6 Cu, Fe and Zn concentrations into leachates during the column leaching test; vertical dashed line indicates a change in geochemical behavior after 12th week

Fig. 7 Oxygen consumption into OC-Test with oxygen flux and corresponding saturation degree S_r ; vertical dashed line indicates a change in geochemical behavior after 12th week

Fig. 8 Reactional schema of involved components into marine sediments and methodological protocol analysis

Fig. 9 Cumulated Ca and Ca + Mg released molar concentrations versus cumulated sulfates released molar concentrations (a), evolution of Ca versus sulfates molar ratio, and Ca versus Mg molar ratio versus time (b) into leachates

Fig. 10 Correlation between cumulated Cu and Zn molar concentrations and cumulated sulfates molar concentrations (a), and cumulated DOC (b) in the leachates

Table 1 Physicochemical characteristics of the sediment

	Gs (g/cm ³)	Water content (wt.%)	Total carbon (wt.%)	TOC (wt.%)	Total sulfur (wt.%)	HCl-extractable sulfur (wt.%)	Other sulfur forms (wt.%)
Bulk Sediment	2.55	23.3	9.89	6.27	2.02	1.04	0.98

Table 2 Chemical composition of the sediment (ICP-AES) and comparison to the regulatory threshold levels N1 and N2 for trace metals (French regulation)

	Ca (wt.%)	Mg (wt.%)	Na (wt.%)	Fe (wt.%)	Cu (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
Bulk Sediment	19.7	2.07	0.3	3.38	930	1020	2250
N1 level	-	-	-	-	45	100	276
N2 level	-	-	-	-	90	200	552

Table 3 XRD mineralogical analysis of the sediment with concentrations calculated accordingly to Rietveld method (Young 1993)

Name	Formulas	Concentration
Quartz	SiO ₂	15.3
Muscovite	KAl ₂ (Si ₃ Al)O ₁₀ (OH,F) ₂	9.2
Chamosite	(Fe,Mg) ₅ Al(Si ₃ Al)O ₁₀ (OH,O)	4.5
Illite	(K,H ₃ O)(Al,Mg,Fe) ₂ (Si,Al) ₄ O ₁₀ [(OH) ₂ ,(H ₂ O)]	1.6
Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	4.0
Dolomite	CaMg(CO ₃) ₂	13.6
Calcite	CaCO ₃	38.9
Halite	NaCl	0.8
Pyrite	FeS ₂	2.0
Magnétite	Fe ₃ O ₄	1.1
Gypse	CaSO ₄ ·2H ₂ O	5.0