Effects of mineral amendments on trace elements leaching from pre-treated marine sediment after simulated rainfall events

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A B S T R A C T

Bauxite extraction by-products (red mud) were used to evaluate their potential ability to stabilize trace elements from dredged and aerated/humidified marine sediment. The investigated by-products were: bauxaline™ (BX) that is a press-filtered red mud; bauxsol™ (BS) that is a press-filtered red mud previously washed with excess of seawater, and gypsum neutralized bauxaline® (GBX). These materials were separately mixed to dredged composted sediment sample considering 5% and 20% sediment: stabilizer ratios. For pilot experiments, rainfall events were regularly simulated for 3 months. Concentrations of As, Mo, Cd, Cr, Zn, Cu, and Ni were analyzed in collected leachates as well as toxicity. Results showed that Cd, Mo, Zn, and Cu were efficiently stabilized in the solid matrix when 20% of BX, BS, and GBX was applied. Consequently, toxicity of leachates was lower than for the untreated sediment, meaning that contaminants mobility was reduced. A 5% GBX was also efficient for Mo, Zn and Cu stabilization. In all scenarios, As stabilization was not improved. Compared to all other monitored elements, Mo mobility seemed to depend upon temperature-humidity conditions during pilot experiments suggesting the need of further investigations.

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1. Introduction

In the mid-1960s, environmental concerns arose in most European countries and national governments started to be more active in their attempts to monitor and control environmental pollution. Major focus was devoted to develop and implement environmental quality guidelines in policies and regulations (Van Wezel, 1999). Special attention was dedicated to the disposal of sediment resulting from dredging activities of port channels and seaways in order to maintain maritime navigation. Yearly, in France approximately 50 × 10^6 m^3 of sediment are dredged out (Alzieu, 1999; Duclay et al., 2010). Recent studies have shown that the Mediterranean coastal sediment can be heavily contaminated due to industrial, port and anthropogenic activities (Andral et al., 2004; Tessier et al., 2011; Pougnet et al., 2014). Sediment pollution is associated with potential economic, social and environmental problems (Eggleton and Thomas, 2004; Förstner, 2006; Arizzi Novelli et al., 2006; Libralato et al., 2008; Lofrano et al., 2016a). The management of dredged sediment must comply with the World London Convention for the prevention of marine pollution as a result of waste dumping (Duncan, 1973), and the OSPAR convention for the protection of marine natural environments of the North-East Atlantic (OSPAR, 1992). Sediment monitoring can be carried out through physico-chemical analyses and toxicity testing that became a widespread regulatory requirement of potential environmental hazards helping in decision-making about contaminated sediment (Prato et al., 2015). In France, dredged materials are managed considering quality guidelines including two regulatory levels (N1 and N2) defined on the basis of contaminant concentrations (trace elements and PCBs) in sediment. When the concentration of pollutants is < N1, sediment is classified as lightly contaminated with no significant impacts on the environment. Sediment is considered as contaminated if pollutants are between N1 and N2 levels thus dredging impacts must be investigated specifically. Highly contaminated sediment are
ranked > N2. Toxicity testing is necessary in the case of contaminated and highly contaminated sediment to assess their potential environmental impact. To facilitate sediment risk assessment, several toxicity tests have been proposed such as bivalve embryo-toxicity and Microtox® assays (Alzieu and Quiniou, 2001; Libralato et al., 2008). When the pollutant concentrations found in sediment is >N2, direct landfill is prohibited, and contaminants must be immobilized before dumping on land (Alzieu, 2005). For this reason, stabilization/solidification techniques involving the use of mineral amendments were found to be cost effective and promising treatments. They amplify the rate of stabilization by enhancing adsorption, precipitation and complexation reactions onto soil or sediment components (Peng et al., 2009; Scanferla et al., 2009). The most studied mineral amendments are phosphate materials, aluminosilicates (clay and zeolites), alkaline materials and iron bearing compounds (zero valent iron, goethite, hematite, and ferrihydrite). Aluminosilicates and iron-based materials are able to immobilize the highest number of pollutants (Kumpiene et al., 2008; Komarek et al., 2013; Mamindy-Pajany et al., 2013).

In a previous work, sediment toxicity after stabilization with mineral amendments was evaluated using Microtox® solid phase test which was widely used to evaluate the toxicity of polluted sediments (Doherty, 2001; Oonorati and Mecozzi, 2004; Gonzalez-Merchan et al., 2014). Dredged sediment samples were first aerated/humidified for 4 months to biologically reduce the organic contamination (i.e. pre-treatment), and then stabilized with three commercial mineral additives: i) hematite; ii) zerovalent iron; and iii) zeolite. Results showed that all mineral additives acted as stabilizing agents decreasing the levels of dissolved metal concentrations and sediment toxicity, but their employ could be expensive due to the use of commercial products (Mamindy-Pajany et al., 2012). Amongst the non-commercial potential additives, red mud (RM) could represent an interesting solution. RM is a very alkaline (pH 10-13), reddish brown in color with a fine particle size distribution containing Al, Fe, Si, and Ti oxides and hydroxides (Nadaroglu et al., 2010).

ALTEO plant (Gardanne, Bouches-du-Rhône, France) that supplies specialty alumina since 1893 from bauxite, provided RM for this study. Press-filtered raw RM is commercially known as bauxsol® (BX) and its composition is given in Table 2. Despite its interesting mineral composition, BX use has been hindered because of its high alkalinity. To overcome this limitation, neutralization treatments have been investigated. One of these treatments consists in promoting the formation of hydroxalite, calcite and brucite from RM by precipitation of alkaline species from seawater (i.e. soluble Ca(OH)2 and Mg(OH)2). Using excess seawater resulted in neutralization of RM to approximately pH 8.5 (Burke et al., 2013; Kirwan et al., 2013). In this study, the resulting neutralized RM was bauxsolTM® (BS) (Table 2). Another possible treatment consists in pH neutralization by gypsum addition (CaSO4·2H2O) that is a soluble Ca2+ source expected to buffer BX alkalinity similarly to seawater effect (Kirwan et al., 2013). The resulting neutralized BX was called “gypsum neutralized BX” (GBX) (Table 2). For this study, BX and BS were provided by ALTEO plant (Gardanne, France), and GBX by INERIS Méditerranée (France).

2.3. Experimental setup

Experiments lasted 3 months and were conducted in Nice
According to the described protocol, during the first week and every 3 days during the second week. Each spraying procedure was equivalent to 12.5 mm of rainfall. Then, it was repeated once a week until the end of the experiment. Thus we could evaluate the benefit of mineral amendment, avoiding increased pollutant mobility provoked by artificial acid rainwater addition. Carbonate ions from the tap water used in ES1 and ES2 can contribute to limit the mobility of pollutants by complexation or co-precipitation processes. Leachates were collected in plastic containers placed under each box after 1 h of natural drainage through the materials. For all samples, after rainfall simulation, leachates were filtrated (through 0.45 μm regenerated cellulose membranes Minisart RC15, Sartorius), collected in 3 different plastic tubes and acidified with 10 μL of concentrated nitric acid. To evaluate the benefits of RM, we have chosen to focus on As, Cd, Cr, Cu, Ni, and Zn, which are among the elements pointed out by sediment quality guidelines, and also Mo since a previous work has shown that it was highly mobilized from sediment during leaching experiments (Mamindy-Pajany et al., 2013). Unlike cationic elements, the availability of Mo to higher plant species generally increases with increasing soil pH and can be toxic (McBride et al., 2000; Jiang et al., 2015). Therefore, European Council included this element in the list of regulatory level for inert waste. Analysis of As, Cd, Cr, Cu, Ni, and Zn was performed with ICP-OES (Perkin Elmer, Optima 7300DV) previously calibrated with mono-elementary certified standard solutions (SCP Sciences). The variability of leachates collection was considered to be equal to the standard deviation obtained through analysis of the set of 3 tubes collected after each leaching procedure. Electrical conductivity (EC) and pH were monitored in leachates obtained after each rainfall event simulation. Climatic conditions (precipitation and temperature) during ES1 and ES2 are given in Table 3.

### 2.4. Leachate toxicity

Microtox® test was carried out with the Gram-negative marine bioluminescent bacteria *Vibrio fischeri* using the Microtox® Model500 Test System (ISO, 2007). This method allowed measurement of light outputs at a wavelength of 490 nm with readings after 30 min time exposure at 15 ± 1 °C to samples serial dilutions in triplicate. The light loss as a consequence of bacteria exposure to the reference toxicant were carried out to comply with quality assurance and quality control procedures. Light emission was recorded and the output data analyzed using MicrotoxOmm® software Version 1.18 (Libralato et al., 2010a). Toxicity with *V. fischeri* was measured for leachates obtained after the first day (day 1) and last day (day 89) of experiment. In addition, the toxicity of BX, BS and

<table>
<thead>
<tr>
<th>Material</th>
<th>Acronym</th>
<th>pH</th>
<th>Composition</th>
<th>Trace elements (mg/kg)</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bauxaline</td>
<td>BX</td>
<td>10.6</td>
<td>Al2O3 (14%)</td>
<td>As &lt; DL</td>
<td>Press-filtered RM; highly alkaline (pH 10–13)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Fe2O3 (50%)</td>
<td>Cd: 0.69</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ti2O3 (11.5%)</td>
<td>Cu: 20.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>SiO2 (6%)</td>
<td>Mo &lt; DL</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>CaO (5.5%)</td>
<td>Ni: 7.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Na2O (3.5%)</td>
<td>Zn: 13.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cr: 1864</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>V: 942</td>
<td></td>
</tr>
<tr>
<td>Bauxsol</td>
<td>BS</td>
<td>9.4</td>
<td>Al2O3 (14%)</td>
<td>As &lt; DL</td>
<td>RM with excess seawater to lower alkalinity</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Fe2O3 (50%)</td>
<td>Cd: 0.58</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ti2O3 (11.5%)</td>
<td>Cu: 14.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>SiO2 (6%)</td>
<td>Mo &lt; DL</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>CaO (5.5%)</td>
<td>Ni: 7.15</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Na2O (3.5%)</td>
<td>Zn: 7.03</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cr: 1579</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>V: 1051</td>
<td></td>
</tr>
<tr>
<td>Neutralized bauxaline</td>
<td>GBX</td>
<td>9.02</td>
<td>Al2O3 (16%)</td>
<td>As &lt; DL</td>
<td>BX neutralized by addition of gypsum</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Fe2O3 (50%)</td>
<td>Cd: 9.00</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Ti2O3 (11%)</td>
<td>Cu: 6.20</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>SiO2 (6%)</td>
<td>Mo &lt; DL</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>CaO (5.5%)</td>
<td>Ni: 6.20</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>Na2O (3%)</td>
<td>Zn: 3.70</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cr: 1978</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>V: 1646</td>
<td></td>
</tr>
</tbody>
</table>
GBX as a whole was evaluated. Toxicity was expressed both as percentage of effect (PE) and median effective concentration (EC50) if calculable. Microtox EC50 values were obtained after linear regression between sample concentration and the fraction of light loss to light remaining (G) in a logarithmic scale with 95% confidence limit values. After the verification of homoscedasticity (F test, p < 0.05) and normality (Shapiro-Wilk test, p < 0.05) of data, the significance of differences among average values of different experimental treatments and controls was assessed by the analysis of variance (ANOVA, p < 0.05). When ANOVA revealed significant differences among treatments, post-hoc tests were carried out with Tukey’s test (p < 0.05). Leachates were verified for pH compliance with standard protocol requirement (ISO, 2007) within the range 6.0–8.5 and adjusted with drops of HCl 1 M if necessary.

Physico-chemical and toxicity data were elaborated looking for the relationships between variables and the variation present in the dataset matrix via biplotting both the ordination component scores and the relationships between variables and the variation present in the dataset matrix via biplotting both the ordination component scores.

### Table 3

Average temperatures (min. and max.), cumulated precipitations, and differences from normal temperatures and precipitations recorded in Nice (France) during ES1 and ES2 (source [http://www.infoclimat.fr](http://www.infoclimat.fr)).

<table>
<thead>
<tr>
<th>Month</th>
<th>T_{av,min} (°C)</th>
<th>Diff. from norm. (°C)</th>
<th>T_{av,max} (°C)</th>
<th>Diff. from norm. (°C)</th>
<th>Cumul. ppav (mm)</th>
<th>Diff. from norm. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ES1 (2013)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>March</td>
<td>7.8</td>
<td>+0.6</td>
<td>13.3</td>
<td>−1.2</td>
<td>243</td>
<td>+245</td>
</tr>
<tr>
<td>April</td>
<td>11.2</td>
<td>+1.5</td>
<td>17.3</td>
<td>+0.6</td>
<td>82.2</td>
<td>+32</td>
</tr>
<tr>
<td>May</td>
<td>13.1</td>
<td>+0.1</td>
<td>19.1</td>
<td>−0.7</td>
<td>115.8</td>
<td>+138</td>
</tr>
<tr>
<td>June</td>
<td>17</td>
<td>+0.5</td>
<td>22.8</td>
<td>−0.5</td>
<td>25.7</td>
<td>−28</td>
</tr>
<tr>
<td>ES2 (2014)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>April</td>
<td>12.4</td>
<td>+2.6</td>
<td>18.2</td>
<td>+1.5</td>
<td>8</td>
<td>−87</td>
</tr>
<tr>
<td>May</td>
<td>14.1</td>
<td>+1</td>
<td>20.6</td>
<td>+0.8</td>
<td>18.8</td>
<td>−61</td>
</tr>
<tr>
<td>June</td>
<td>18.9</td>
<td>+2.4</td>
<td>25.4</td>
<td>+2.1</td>
<td>10.3</td>
<td>−71</td>
</tr>
<tr>
<td>July</td>
<td>20</td>
<td>+0.7</td>
<td>26</td>
<td>−0.4</td>
<td>28.4</td>
<td>+82</td>
</tr>
</tbody>
</table>

3. Results and discussion

3.1. Trends of pH and EC

Trends of pH and EC during 3 months observation were presented in Fig. 1 and in Fig. 2 for 5% and 20% of amendment, respectively. Evolution of pH is comparable to control sediment (CS) when 5% BX and 5% BS were added (Fig. 1). pH values slightly increased during the experiment, starting at pH = 8 and ending up at pH > 8.10. When 5% GBX was added, pH was systematically higher than for CS, 5% BX and 5% BS due to the partial dissolution of gypsum. Addition of 20% of BX and BS (i.e. alkaline materials) (Fig. 2) induced a global increase of the pH value compared to Fig. 1. This global increase in pH was amplified when GBX was added to sediment. Hence, the addition of mineral amendment has minor impact on pH as long as it is introduced at low rate. Amendment with gypsum provoked an increase in pH values whatever the amendment rate due to partial dissolution of gypsum. Sediment from this study has a natural buffer capacity due to its carbonate content. Since pH has a crucial impact on pollutant mobility, this parameter has to be considered in data interpretations.

Regarding EC, it decreased (from approx. 50 mS/cm to 15 mS/cm) irrespectively of the amendment rate during the first 10 d, then kept a constant value (approx 15 mS/cm) from day 10–40. From day 1–40, the decrease and stabilization of EC is coherent with addition of tap water with low EC, resulting in the decrease of natural sediment salinity. Zhang et al. (2014) reported that high salinity can inhibit the growth and activity of sulfate reducing bacteria by increasing cell osmotic pressure and repressing metabolic enzymes, and thus affected the reduction of SO4²⁻ and the decomposition of organic matter in sediment, resulting in increasing metals bioavailability. The decrease in salinity provoked by tap water addition to dredged sediment could decrease metals bioavailability; nevertheless the aerobic experimental conditions encountered during ES1 and ES2 are not favorable to reduction reactions (Zhang et al., 2014). After 40 d, EC varied significantly up to the end of experiments probably due to the partial dissolution of mineral phases of sediment or amendment. ES2 was conducted during a
period that was hotter and dryer than ES1 (Table 3). Cumulative precipitations were abnormally lower than the normal precipitations observed from April to June and average temperatures were above the temperatures usually recorded during the same period. The unusually hot and dry climatic conditions during ES2 may probably have an impact on the experimental setup, explaining the high variation of EC from day 40 observed for 20% amendment (Fig. 2) and 5% GBX (Fig. 1) in addition with mineral dissolution. Inversely, ES1 was carried out in temperature conditions under normality compared to the temperature usually recorded, but humidity was higher compared to the normal conditions (up to +245%).

3.2. Trends of elements concentrations

The concentration of As, Cd, Cr, Cu, Ni, Mo, and Zn measured in leachates collected after day 1 and day 89 during ES1 and ES2 are displayed in Fig. 3 and Fig. 4, respectively. Arsenic behavior during ES2 and ES1 did not significantly differ from CS meaning that bauxite residues are not convenient to stabilize As since adsorption conditions are not favored (As adsorption occurs at acidic pH values). After dredging, aerobic conditions could have induced partial or total oxidation of iron oxides and organic matter from the sediment matrix leading to an increased mobility of As (Dang et al., 2014). The addition of gypsum did not improve As stabilization since the increase in competing anions due to gypsum dissolution could limit As adsorption on bauxite additive surface. As mobility has already been reported both at basic and acidic pH and this very specific behavior was attributed to the acid-base properties (amphoteric nature) of aqueous As (Saussaye et al., 2016; Tabelin et al., 2014).

When 5% amendment was applied, the amount of Cr in all leachates was <15 μg/kg. On the other hand when 20% amendment was considered, Cr in the leachates reached up to 30 μg/kg. Concentration of Cr found in BX, BS and GBX (Table 2) confirmed that Cr is supplied to sediment by the amendment. Nevertheless it can be noticed that the leached amount of Cr when 20% GBX was used is lower than when 20% BX and 20% BS amendments were considered. Despite its direct presence in amendments, Cr is rapidly leached during the first days of experiment and a significant decrease in its concentration was observed after day 89. Saussaye et al. (2016) noticed that in alkaline pH conditions, Cr mobility was limited in a larger extent. When 20% GBX was added, the pH of the media was slightly higher than for the other amendments. The limited mobility of Cr observed in these conditions could be directly linked to the pH conditions due to precipitation of Cr (hydr)oxide in circumneutral pH (Burke et al., 2012), by formation of inner sphere surface complex (CrSO4) following gypsum dissolution or by formation of organic-Cr(III) surface complex (Aström and Corin, 2000).

Stabilization of Mo in sediment was significantly more effective when high amounts of amendment were used. When 20% BS and 20% BX were added to sediment, the amount of leached Mo was significantly reduced compared to CS, 5% BS and 5% BX. GBX seemed to effectively stabilize Mo even at low amendment rates (5%). But a similar trend was observed in CS without any additive in ES2, but not in ES1. This event could be related to ES2 climatic conditions (up to +2.6 °C and –87% precipitations compared to the normal conditions). Indeed, Fox and Doner (2002) evidenced that Mo turns into water-soluble forms after air-drying.

In both ES1 and ES2, Cd was easily leached from sediment after day 1. Previous works showed that Cd was linked to the redox sensitive fraction of sediments (Baraund and Leleyter, 2012; Hamdoun et al., 2015). Regular aeration by manual homogenization of sediment during experiments (ES1 and ES2) favored oxidation reactions and, probably, an increased mobility of Cd. The addition of BX, BS, and GBX to sediment decreased the amount of leached Cd starting from day 1. The amount of leached Cd was lower during ES2 compared to ES1 suggesting that high amendment rates are more performing. No significant changes in leached Cd were observed when GBX was used compared to BX and BS, meaning that Cd preferentially adsorbs at the surface of bauxite residues.

In CS and in 5% GBX, the concentrations of Zn (303 μg/kg and 231 μg/kg) and Cu (244 μg/kg and 152 μg/kg) in leachates were high after day 1 (Fig. 4). After day 89, Zn and Cu amounts in leachates were significantly lower than after day 1 (inferior to 20 μg/kg and inferior to 70 μg/kg, respectively) meaning that a rate of amendment equal to 5% can be efficient for their stabilization in sediment. According to literature data, Zn and Cu are mainly present in the acid-soluble, redox sensitive fraction, and the organic/sulphide fraction of sediments, respectively (Hamdoun et al., 2015; Emili et al., 2016). As noticed for Cd, manual aeration of sediment during ES1 and ES2 could enhance mobilization of Cu and Zn due to oxidation of mineral phases. Addition of BX, BS and GBX at high and low rates significantly decreased the leached amounts of Zn and Cu after day 1. This means that Zn and Cu are highly reactive towards bauxite residues, and adsorption process is favored in the
experimental conditions even at low amendment rate.

Ni concentrations in leachates of CS, 5% BX and 5% BS were < 3 μg/kg after day 1. After day 89, leached Ni was slightly higher (<4 μg/kg) than day 1. Ni has a very limited mobility as shown by the concentrations measured in leachates from ES1 and ES2. Ni is generally linked to the alumino-silicate fraction of sediments (Algan et al., 2004), which is not soluble or oxidizable at the pH conditions encountered during ES1 and ES2. Addition of 20% amendment increased Ni stabilization compared with 5% amendment since Ni concentration was below the detection limit of ICP-OES. For this reason, no results about Ni are provided for ES2.

Leaching rates during the whole experiment were calculated considering the cumulated leached concentration of each element and accounting for the total concentration of each element measured in the whole sediment sample as previously described (Taneez et al., 2015; Taneez et al., 2016) (Table 4). In the case of As and Mo, leaching rates were similar to the ones obtained in CS, meaning that stabilization was not improved by the addition of 5% amendment. When 20% amendment was used, leaching rates remained <1% for all elements except for Mo compared to their

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**Fig. 3.** As, Cd, Cr, Cu, Mo, Ni, Zn concentrations (μg/kg) in ES1 leachates after day 1 (1) and day 89 (89); data with different letters (a, b, c, d, e, and f) are significantly different (Tukey’s test); CS – control sediment; BX – bauxaline®; BS – bauxsol™.
total concentration in sediment matrix, meaning that less than 1% of total contaminants are available, while 99% are stored in the sediment (Salomons, 1998).

It can be concluded that addition of 5% BX or 5% BS did not significantly improve stabilization of trace elements and, sometimes, sediment heterogeneity can mask the performance assessment of mineral amendments at low rate. Nevertheless, for Mo, Zn and Cu, satisfactory stabilization results were obtained as soon as 5% GBX was applied. Amendment with 20% of additive is more performing to stabilize trace elements in aerated/humidified sediment especially for Cd, Cu, Mo and Zn. ES2 was conducted during a hot and dry period (May–July 2014), whereas ES1 was carried out from March to June 2013, which was an unusually humid and cold period. Climatic conditions during ES2 could explain the increased mobility of Mo during the dryer period as previously reported (Fox and Doner, 2002). This variation in climatic conditions makes difficult the direct comparison between ES1 and ES2. The governing factors for the metal retention and leaching are chemical conditions such as surface site saturation, redox conditions, biological processes, pH, competing ions, and associated kinetics. Kumar et al. (2013) observed that metal mobility and bioavailability increased as a function of time during sediment leaching. This suggested a

Table 4
Total leaching rates (%) obtained after ES1 and ES2.

<table>
<thead>
<tr>
<th>Elements Leaching rate (%)</th>
<th>Control sediment ES1</th>
<th>Control sediment ES2</th>
<th>S+5% BX</th>
<th>S+5% BS</th>
<th>S+5% GBX</th>
<th>S+20% BX</th>
<th>S+20% BS</th>
<th>S+20% GBX</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>0.20</td>
<td>&lt;0.10</td>
<td>0.21</td>
<td>0.19</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
</tr>
<tr>
<td>Cd</td>
<td>0.60</td>
<td>0.63</td>
<td>0.33</td>
<td>0.34</td>
<td>0.47</td>
<td>0.21</td>
<td>0.23</td>
<td>0.28</td>
</tr>
<tr>
<td>Cu</td>
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<tr>
<td>Zn</td>
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<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
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<tr>
<td>Cr</td>
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<td>&lt;0.10</td>
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kinetically controlled transfer of trace elements towards exchangeable fraction. Sediment dredging and aerobic disposal activities are expected to drastically disrupt the initial equilibrium since trace elements partitioning in anoxic sediments is dominated by the formation of sulfide phases. Oxidative conditions encountered during disposal of dredged sediments determined the release of trace elements, increased acidity, and iron and sulfate release (Chatain et al., 2013). To prevent mobilization of contaminants from dredged sediments during land management, treatments such as cement addition (Chatain et al., 2013) and mineral amendment have been investigated (Mamindy-Pajany et al., 2013). When cement addition was considered, a very limited release of Pb, Cu, and Zn was observed. Cement stabilization induced high buffering capacity controlled by the dissolution of cementitious phases for pH values between 10 and 12 promoting metal fixation. However, under specific leaching conditions, a risk of contaminant mobilization exists, specifically for anionic pollutants (Chatain et al., 2013). When commercial mineral amendments were used, hematite was found to be the most effective for trace elements stabilization compared to goethite and Fe(0), except for As which was continuously leached whatever the amendment (Mamindy-Pajany et al., 2013). The use of industrial by-products such as bauxite residues offers satisfactory results for the stabilization of cationic pollutants and Mo, when high amendment rates are applied. Nevertheless, some limitations can be pointed out about their use. Indeed, the regulatory levels N1 and N2 that were defined for dredged sediment do not include elements such as V, which is present in high concentrations in bauxite residues (Table 2).
Vanadium is a key contaminant of concern identified in RM (Burke et al., 2012). At basic pH, vanadate dominates the aqueous speciation and, when pH is lowered, vanadate adsorption is expected to increase onto the mineral phases (either the neoformed ones or the RM intrinsic ones). Nevertheless, effective adsorption of vanadate has not been observed at circumneutral pH, especially when surface loadings are elevated, making neutralization inefficient in removing aqueous V (Burke et al., 2012). Hence, at neutral pH, V represents a potential secondary pollution risk since neutralized RM could be a source of soluble V. On this basis, it is not sufficient to limit studies to the elements that have been focused in compliance with regulatory standards. Specific regulations relative to the use of industrial by-products for chemical stabilization purposes should be elaborated looking at the End-of-Waste Directive (Council Regulation (EU) n. 333/2011).

3.3. Toxicity with Vibrio fischeri

Toxicity effects of leachates after ES1 and ES2 were summarized in Fig. 5 including the toxicity of BX, BS and GBX. Results from negative and positive controls were in line with the standard protocol. BX and BS toxicity was not significantly different (Fig. 5A) and equal to 12% ± 2% and 11% ± 3%, respectively. Data indicated slight acute toxicity effects (Libralato et al., 2010b), but proxy to 10% effect compared to the toxicity of leachates after day 89 was 61% ± 3%, 39% ± 11%, 37% ± 3%, and 43% ± 5% for CS, 20% BX, 20% BS, 20% GBX, and 5% GBX, respectively (Fig. 5C). Toxicity of leachates after day 1 showed to be not significantly different between treatments. The toxicity of leachates after day 89 was 52% ± 1%, 46% ± 2%, 30% ± 6%, 24% ± 3%, and 40% ± 1% for CS, 20% BX, 20% BS, 20% GBX, and 5% GBX, respectively. Toxicity showed to significantly decrease (65%) only after the addition of 20% GBX reaching effects not significantly different from GBX (20% ± 3%). All other treatments did not significantly remove toxicity.

In general, sediment leached after ES2 showed lower amounts of As, Cd, Cu, and approximately the same amounts of Mo of ES1 leachates. Conversely, the amount of Cr and Zn leached during ES2 was slightly greater compared to ES1. About toxicity, ES2 leachates were less toxic than ES1 correlating with the general lower amount of leached elements. The higher amount of Cr leached during ES2 when 20% BS, 20% BX and 20% GBX were administered, had no impact on leachate toxicity.

Results from principal component analysis (Fig. 6) showed that the first two principal components accounted for 47.52% and 20.38% of the variation, respectively. The biplot regarding component loadings suggested that F1 scores are influenced by As (11%), Ni (11%), V_fischeri toxicity (13%), Cd (24%), Cu (24%), and Zn (13%), while F2 by Cr (37%) and Mo (34%). Looking at the ordination plot of component scores in the F1 and F2 biplot, samples could be clustered in four main groups (clockwise in Fig. 6): i) samples relatively significantly influenced by the considered variables (G1); ii) samples influenced by F2 variables (G2); iii) samples averaged influenced by F1 and F2 variables (G3); and iv) samples influenced by F1 variables (G4). Leachates clustered in G4 appeared the most toxic and contaminated, and conversely for G1 specimen. According to Pearson’s correlation coefficients, toxicity was correlated to Cu (0.573), Cd (0.624) and Ni (0.755). Cu was also correlated to As (0.533), Cd (0.723), Ni (0.641), and Zn (0.879). Cr and Mo were significantly correlated each other (0.538).
4. Conclusion

Stabilization of trace metals was investigated using bauxite extraction by-products (red mud) as mineral amendment (bauxaline®, bauxsol® and gypsum neutralized bauxaline®) to pre-treated dredged marine sediment. As, Cd, Cu, Ni, and Zn were selected for this research study since their monitoring is compulsory according to sediment quality guidelines; Mo was included too since its presence was recorded in sediment. Application of bauxaline®, bauxsol® and gypsum neutralized bauxaline® at any rate (5% or 20%) was found to be not efficient for As stabilization. Application of 5% bauxaline® or bauxsol® was not adequate to significantly reduce Cd, Mo, Ni, Zn and Cu in leachates, while application of 5% gypsum neutralized bauxaline® slightly improved stabilization of Zn, Cu and Mo. In the present study scenarios, the higher amendment rate (20%) (bauxaline®, bauxsol® and gypsum neutralized bauxaline®) was more efficient in trace metal stabilization compared to 5%, except for As. During the first days of experiments, Cr was leached when bauxite residues were added to sediment. Leachates collected from the sample containing experiments, Cr was leached when bauxite residues were added to bauxaline. Considering toxicity and chemical results, gypsum neutralized bauxaline® should be preferred for stabilization purposes. From EC and metal leaching measurements, on land storage of dredged marine sediments investigated should not exceed 40 days especially when sediment is exposed to regular and intense rainfall. Indeed, mineral dissolution as a consequence of regular and intense rainfalls, pH variation, and aerobic conditions should increase trace elements mobility. For stabilization purposes, the use of industrial by-products mixed with contaminated sediment should be submitted to specific regulations since pollutants such as Cr and V (among others) stemming from the mineral amendment can be importantly leached. In the present study, despite that experiments were conducted outside and under cover, very dry and hot periods influenced metal mobility (especially Mo), but this point deserves deeper investigations. Hence, climatic conditions should not be neglected, specifically when sediments have to be managed on land. Additional pilot experiments such as the one described in this study should be carried out considering other treatments of bauxite extraction by-products such as acid, thermal or combined chemical/thermal treatments to get an exhaustive comparative study.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2016.09.072.

References


