



# Effects of mineral amendments on trace elements leaching from pre-treated marine sediment after simulated rainfall events<sup>☆</sup>



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## ABSTRACT

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<sup>®</sup> (BX) that is a press-filtered red mud; bauxsol<sup>™</sup> (BS) that is a press-filtered red mud previously washed with excess of seawater, and gypsum neutralized bauxaline<sup>®</sup> (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  $50 \times 10^6$  m<sup>3</sup> 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

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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 embryotoxicity and Microtox<sup>®</sup> 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, alumino-silicates (clay and zeolites), alkaline materials and iron bearing compounds (zero valent iron, goethite, hematite, and ferrihydrite). Alumino-silicates 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<sup>®</sup> solid phase test which was widely used to evaluate the toxicity of polluted sediments (Doherty, 2001; Onorati 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 by-product obtained after bauxite ore extraction (according to Bayer process) for aluminum (Al) production. It is produced in huge amounts since 1 ton of extracted Al generates in 0.5–1 ton of RM (Genç et al., 2003). It is characterized by the presence of Fe- and Al-oxy-hydroxides making this by-product an interesting material to be reused for metals or organics removal, for hydrogenation, or as an additive for cement and brick industries (Singh et al., 1993; Llano et al., 1994; Alvarez et al., 1995; Peng et al., 2005). Considering the amount of the produced RM and its adsorption properties, research activities on its potential reuse as a cost effective and safe material for environmental purposes are of great interest for Al producers. Actually, less than 3% of bauxite residues produced annually is used in a productive way (Evans, 2016).

On the basis of Mamindy-Pajany et al. (2012), the aim of this research study was to investigate the use of RM as a low cost mineral amendment in *ex situ off site* stabilization of trace inorganics in pre-treated dredged sediment samples. Pilot scale experiments were carried out for 3 months considering various RM formulations (i) bauxaline<sup>®</sup> (BX); ii) bauxsol<sup>™</sup> (BS); iii) bauxaline<sup>®</sup> neutralized by the addition of gypsum (GBX). BX, BS and GBX were mixed with dredged sediment including two “additive: sediment” ratios: i) 5% and ii) 20%. Treated sediments were regularly exposed to simulated rainfall events and leachates were collected and measured in order to evaluate its feasibility to stabilize sediment inorganic pollutants to be landfilled.

## 2. Material and methods

### 2.1. Sample collection

Sediment samples resulting from dredging activity in the Toulon French Navy harbor (Mediterranean Sea) were considered. After

dredging, sediment was kept on land and regularly aerated/humidified for 4 months by port authority. This procedure consisted in i) sediment mixing once a week promoting microbial consortia growth and, thus, biological degradation of contaminants as well as lowering salt and organic matter content, and ii) sediment humidification with tap water. Two sub-samples of this sediment were collected to carry out laboratory scale experimental activity. Sediment was already fully characterized (Mamindy-Pajany, 2010). Data from X-ray diffraction (XRD) of dredged sediment indicated the presence of calcite, feldspar, quartz and illite minerals. Mineralogical analysis of the fraction <2 µm showed that sediment clay fraction contained illite (73%), kaolinite (19%) and smectite (8%) (Mamindy Pajany et al., 2010). According to Table 1, sediment is highly contaminated by inorganics and can be classified as >N2 level for inorganic pollutants requiring *ex situ off site* management (Taneez et al., 2015, 2016).

### 2.2. Industrial by-products used as mineral amendment

We used an industrial by-product from bauxite extraction as mineral amendment to stabilize trace elements in marine dredged sediment. Bauxite by-product, commonly known as RM, is generated during alumina production from bauxite ore. RM is highly 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 bauxaline<sup>®</sup> (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 hydrotalcite, calcite and brucite from RM by precipitation of alkaline species from seawater (i.e. soluble Ca<sup>2+</sup> and Mg<sup>2+</sup>). 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 bauxsol<sup>™</sup> (BS) (Table 2). Another possible treatment consists in pH neutralization by gypsum addition (CaSO<sub>4</sub>·2H<sub>2</sub>O) that is a soluble Ca<sup>2+</sup> 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

**Table 1**

Total content of elements in sediment sub-samples (ND: not defined) (dark grey cells: concentration > N2). Data for 1<sup>st</sup> sediment sub-sample are from (Taneez et al., 2015); and for 2<sup>nd</sup> sediment sub-sample from (Taneez et al., 2016). Regulatory levels are from (Alzieu and Quiniou, 2001) and (Alzieu, 2005).

Elements	1 <sup>st</sup> sediment sub-sample (mg/kg)	2 <sup>nd</sup> sediment sub-sample (mg/kg)	French regulatory levels (mg/kg)	
			N1	N2
As	150	201	25	50
Cd	4.7	4.8	1.2	2.4
Cu	1721	1881	45	90
Mo	9.1	7.4	ND	ND
Ni	27	21	37	74
Zn	1869	3069	276	552
Cr	59	43	90	180

**Table 2**  
Composition of bauxaline<sup>®</sup>, bauxsol<sup>™</sup> and neutralized bauxaline<sup>®</sup>; RM = red mud.

Material	Acronym	pH	Composition	Trace elements (mg/kg)	Properties
Bauxaline <sup>®</sup>	BX	10.6	Al <sub>2</sub> O <sub>3</sub> (14%) Fe <sub>2</sub> O <sub>3</sub> (50%) TiO <sub>2</sub> (11.5%) SiO <sub>2</sub> (6%) CaO (5.5%) Na <sub>2</sub> O (3.5%)	As < DL Cd: 0.69 Cu: 20.2 Mo < DL Ni: 7.00 Zn: 13.0 Cr: 1864 V: 942	Press-filtered RM; highly alkaline (pH 10–13)
Bauxsol	BS	9.4	Al <sub>2</sub> O <sub>3</sub> (14%) Fe <sub>2</sub> O <sub>3</sub> (50%) TiO <sub>2</sub> (11.5%) SiO <sub>2</sub> (6%) CaO (5.5%) Na <sub>2</sub> O (3.5%)	As < DL Cd: 0.58 Cu: 14.4 Mo < DL Ni: 7.15 Zn: 7.03 Cr: 1579 V: 1051	RM with excess seawater to lower alkalinity
Neutralizedbauxaline <sup>®</sup>	GBX	9.02	Al <sub>2</sub> O <sub>3</sub> (16%) Fe <sub>2</sub> O <sub>3</sub> 56(%) CaO 7 (%) TiO <sub>2</sub> 12 (%) SiO <sub>2</sub> 6 (%) Na <sub>2</sub> O (3%)	As < DL Cd < DL Cu: 9.00 Mo < DL Ni: 6.20 Zn: 3.70 Cr: 1978 V: 1646	BX neutralized by addition of gypsum

(French Riviera, France) in a covered area. For each experiment one replicate was performed due to the limited amount of dredged sediment available for this study. The first run (ES1 -first sediment sub-sample) was carried out from March 2013 to June 2013, and the second one from April 2014 to July 2014 (ES2-second sediment sub-sample). Experiments were carried out in wooden boxes (40 × 40 × 20 cm). The inner surface was covered with low porosity geotextile to limit the loss of fine particles and the bottom presented a plastic square mesh (0.5 cm × 0.5 cm) allowing leaching water passing through. For ES1, 3 boxes were used, while 5 boxes were necessary for ES2. An amount of 6 kg of sediment was placed into each box. During ES1, 5% of BX and BS were added to sediment and manually homogenized. During ES2, 5% of GBX and 20% of BX, BS and GBX were added to sediment and manually homogenized. Both ES1 and ES2 included control sediment made of untreated sediment (Table 1). After treatment administration to sediment samples, rainfall events were simulated pouring 2 L of tap water (72.05 mg/L of Ca<sup>2+</sup>; 9.79 mg/L of Mg<sup>2+</sup>; 3.35 mg/L of NO<sub>3</sub><sup>-</sup>; 10.65 mg/L of Na<sup>+</sup>; 1.35 mg/L of K<sup>+</sup>; 10.5 mg/L of Cl<sup>-</sup>; 116.05 mg/L of SO<sub>4</sub><sup>2-</sup>; 175 µg/L of F<sup>-</sup>) according to the following steps: 1) 1 L of tap water was sprayed homogeneously on sediment surface; 2) sediment was aerated manually using a garden shovel; and 3) 1 L of water was sprayed. This procedure was repeated every two days during the first week and every 3 days during the second week. Then, it was repeated once a week until the end of the experiment. Each spraying procedure was equivalent to 12.5 mm of rainfall. According to the described protocol, during the first month, it corresponded to 87.5 mm of rainfall, then 50 mm of rainfall for the second and the third month. During three months of experiment an average rainfall of 62.5 mm was then applied. Considering that average rainfall 61.66 mm/month is observed in Nice (French Riviera, France) this experimental protocol is coherent with the average rainfall in the area. Rainfall events were simulated during ES1 and ES2 by successive leaching/aeration of sediment using tap water. We used tap water to keep the same water that port authority considered during previous aeration/humidification procedures. 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, Mo, 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<sup>®</sup> test was carried out with the Gram-negative marine bioluminescent bacteria *Vibrio fischeri* using the Microtox<sup>®</sup> 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 samples was the endpoint. A negative control (dilution water) and reference toxicant were carried out to comply with quality assurance and quality control procedures. Light emission was recorded and the output data analyzed using MicrotoxOmni<sup>®</sup> 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 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>).

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

GBX as a whole was evaluated. Toxicity was expressed both as percentage of effect (PE) and median effective concentration (EC50) if calculable. Microtox<sup>®</sup> 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 between 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.

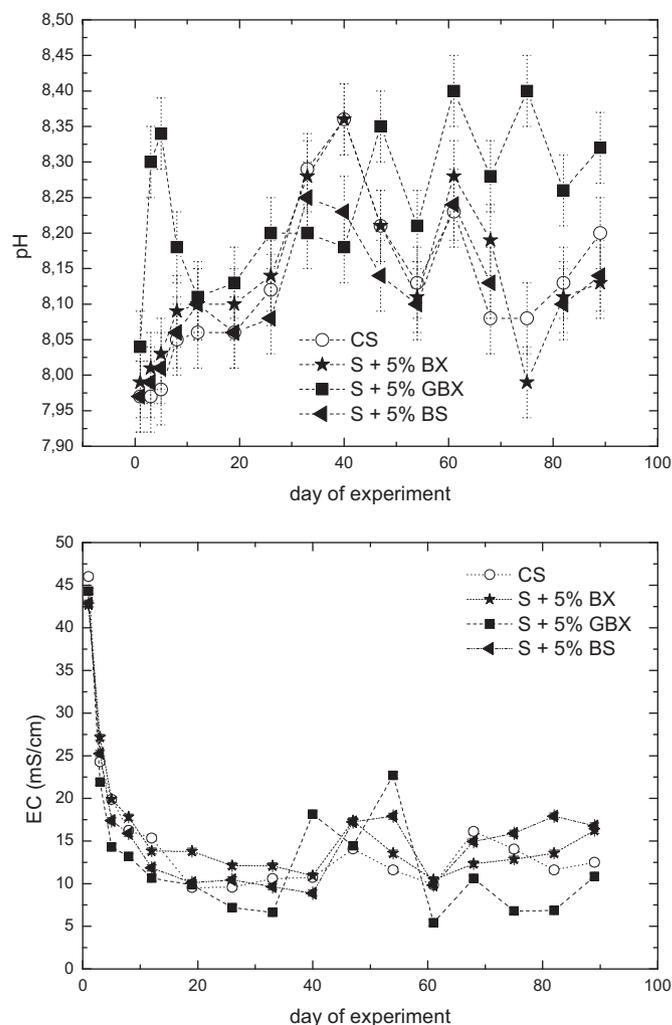
Physico-chemical and toxicity data were elaborated looking for the relationships between variables and the variation present in the dataset matrix via biplotting both the ordination component scores and the variable loading coefficients through Principal Component Analysis (PCA) based on the Pearson's correlation matrix; no data transformation was necessary. Statistical analyses were carried out using Microsoft<sup>®</sup> Excel 2013/XLSTAT<sup>®</sup>-Pro (Version 7.2, 2003, Addinsoft, Inc., Brooklyn, NY, USA).

### 3. Results and discussion

#### 3.1. Trends of pH and EC

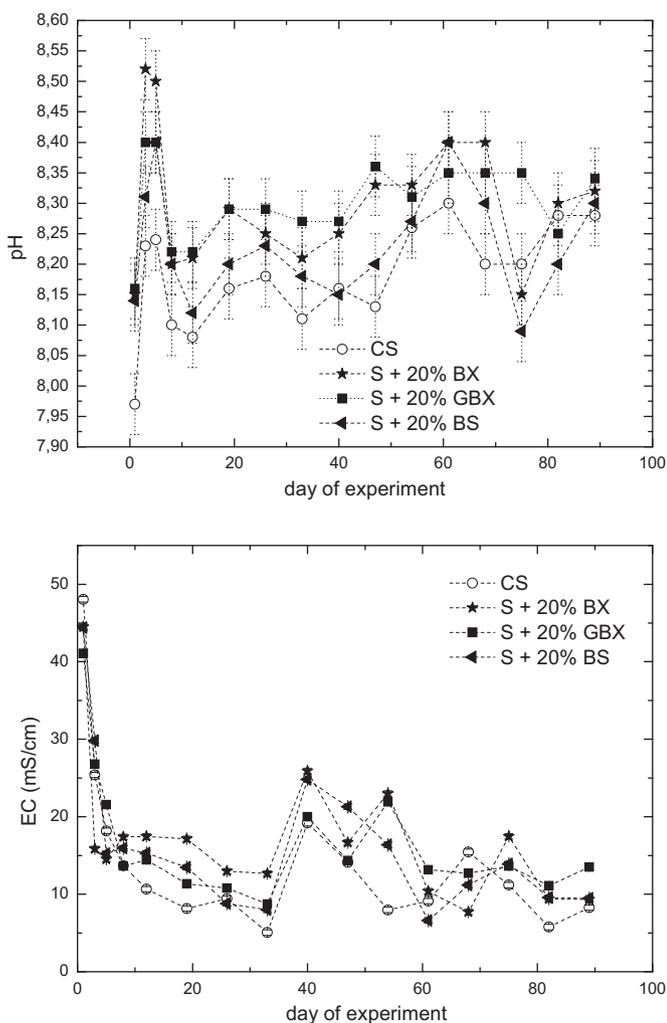
Trends of pH and EC during 3 months observation were presented in Fig. 1 and in Fig. 2 for 5% and 20% of amendment, respectively. Evolution of pH is comparable to control sediment (CS) when 5% BX and 5% BS were added (Fig. 1). pH values slightly increased during the experiment, starting at pH = 8 and 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



**Fig. 1.** Trends of pH and electrical conductivity (EC) for 5% amendment; CS = control sediment; BX = bauxaline<sup>®</sup>; BS = bauxosol<sup>™</sup>; GBX = bauxaline<sup>®</sup> with gypsum (standard deviation for EC:  $\pm 0.35$  mS/cm; standard deviation for pH:  $\pm 0.05$ ).

increasing cell osmotic pressure and repressing metabolic enzymes, and thus affected the reduction of  $\text{SO}_4^{2-}$  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



**Fig. 2.** Trends of pH and electrical conductivity (EC) for 20% amendment; CS = control sediment; BX = bauxaline<sup>®</sup>; BS = bauxsol<sup>™</sup>; GBX = bauxaline<sup>®</sup> with gypsum (standard deviation for EC:  $\pm 0.35$  mS/cm; standard deviation for pH:  $\pm 0.05$ ).

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

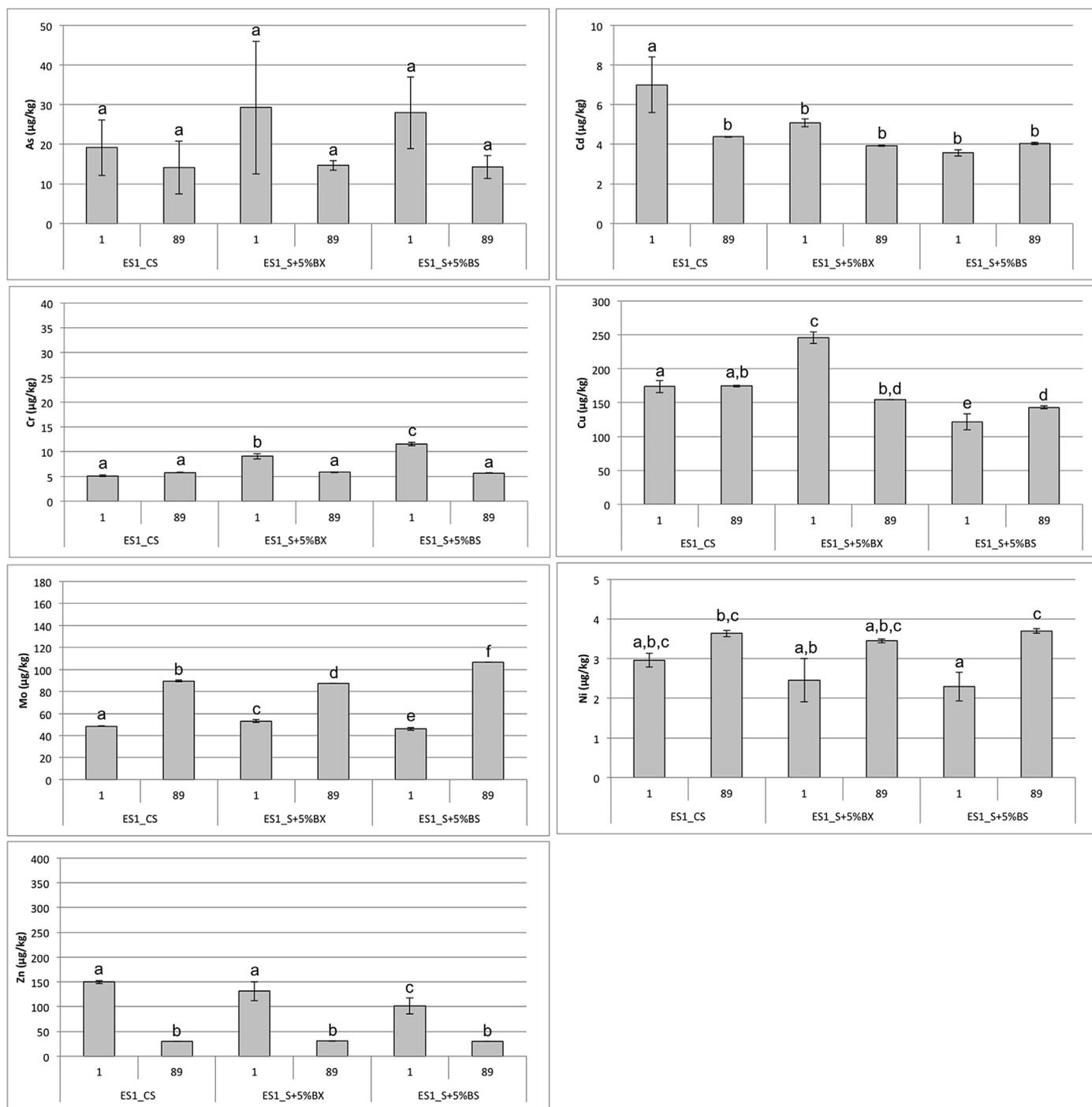
sediment matrix leading to an increased mobility of As (Dang et al., 2014). The addition of gypsum did not improve As stabilization since the increase in competing anions due to gypsum dissolution could limit As adsorption on bauxite additive surface. As mobility has already been reported both at basic and acidic pH and this very specific behavior was attributed to the acid-base properties (amphoteric nature) of aqueous As (Saussaye et al., 2016; Tabein et al., 2014).

When 5% amendment was applied, the amount of Cr in all leachates was  $<15$   $\mu\text{g}/\text{kg}$ . On the other hand when 20% amendment was considered, Cr in the leachates reached up to 30  $\mu\text{g}/\text{kg}$ . 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 hydroxide in circumneutral pH (Burke et al., 2012), by formation of inner sphere surface complex ( $\text{CrSO}_4^+$ ) 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  $+2.6$   $^\circ\text{C}$  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 (Baraud 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  $\mu\text{g}/\text{kg}$  and 231  $\mu\text{g}/\text{kg}$ ) and Cu (244  $\mu\text{g}/\text{kg}$  and 152  $\mu\text{g}/\text{kg}$ ) 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  $\mu\text{g}/\text{kg}$  and inferior to 70  $\mu\text{g}/\text{kg}$ , 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



**Fig. 3.** As, Cd, Cr, Cu, Mo, Ni, Zn concentrations ( $\mu\text{g/kg}$ ) 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<sup>®</sup>; BS = bauxsol<sup>™</sup>.

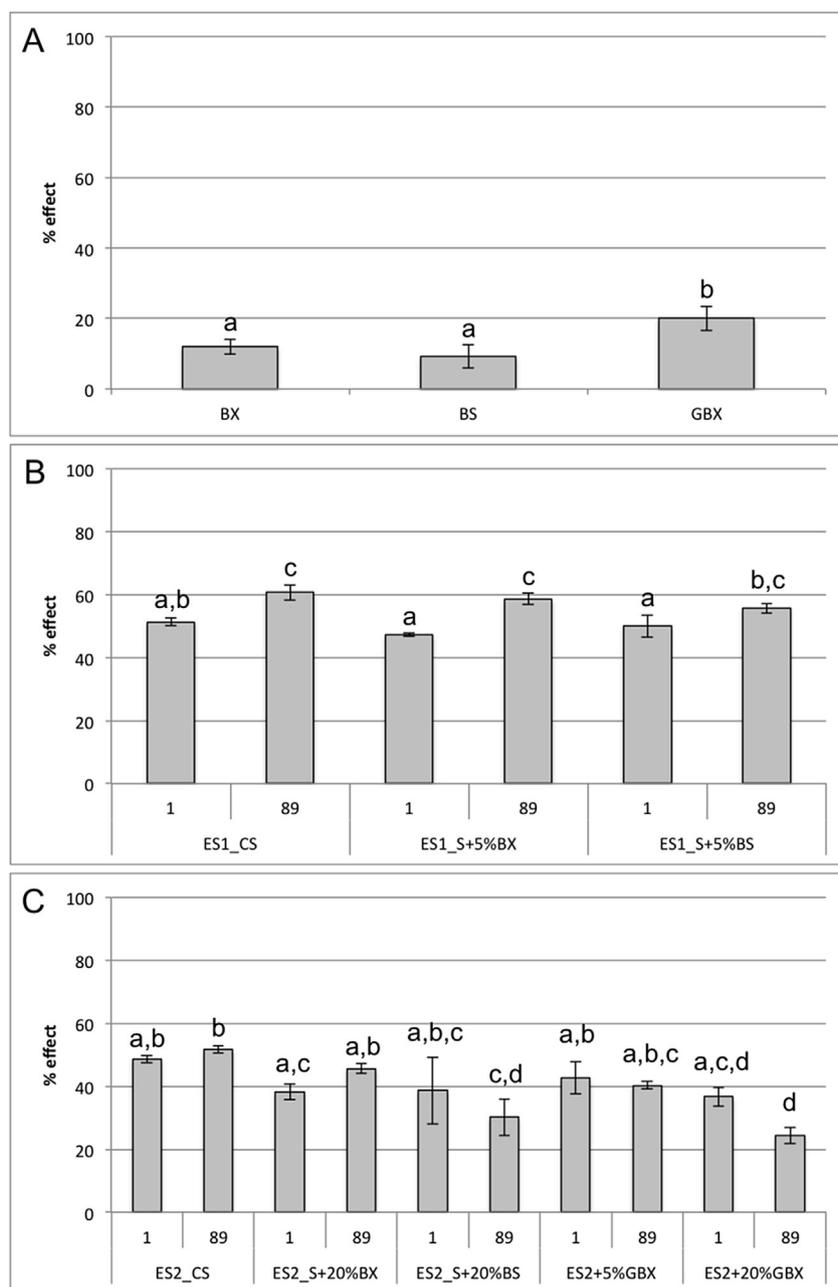
experimental conditions even at low amendment rate.

Ni concentrations in leachates of CS, 5% BX and 5% BS were  $< 3 \mu\text{g/kg}$  after day 1. After day 89, leached Ni was slightly higher ( $< 4 \mu\text{g/kg}$ ) 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 (Tanez et al., 2015; Tanez 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





**Fig. 5.** Toxicity trend with *V. fischeri* as percentage of effect (%) after 30 min contact time considering A) the amending agents (BX, BS and GBX); B) ES1 leachates after day 1 and day 89; and C) ES2 leachates after day 1 and day 89; ES1 = experiment 1; ES2 = experiment 2; CS = control sediment; BX = bauxaline<sup>®</sup>; BS = bauxsol<sup>™</sup>; data with different letters (a, b, c, and d) are significantly different (Tukey's test).

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  $12\% \pm 2\%$  and  $11\% \pm 3\%$ , respectively. Data indicated slight acute toxicity effects (Libralato et al., 2010b), but proxy to 10% effect that is generally considered a non-toxicity threshold in most toxicity tests (Lofrano et al., 2016b). GBX presented slight acute toxicity effects ( $20\% \pm 3\%$ ) probably related to the dissolution of gypsum contained in GBX.

EC50 values were not calculable either for ES1 or for ES2 for all leachates. Thus only the percentage of effect is available.

During ES1, the toxicity of leachates after day 1 was  $51\% \pm 1\%$ ,  $47\% \pm 1\%$ , and  $50\% \pm 3\%$  for CS, 5% BX and 5% BS, respectively. The toxicity of leachates after day 89 was  $61\% \pm 3\%$ ,  $59\% \pm 2\%$ , and  $56\% \pm 2\%$  for CS, BX and BS, respectively. According to Fig. 5B, the toxicity significantly increased after the treatment period (day 1–89) both in CS and treatments (BX and BS) suggesting that 5% BX and 5% BS did not provide a significant contribution to treated

sediment stabilization and thus toxicity reduction/removal, confirming physico-chemical data.

During ES2, the toxicity of leachates after day 1 was  $49\% \pm 1\%$ ,  $38\% \pm 3\%$ ,  $39\% \pm 11\%$ ,  $37\% \pm 3\%$ , and  $43\% \pm 5\%$  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  $52\% \pm 1\%$ ,  $46\% \pm 2\%$ ,  $30\% \pm 6\%$ ,  $24\% \pm 3\%$ , and  $40\% \pm 1\%$  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 ( $20\% \pm 3\%$ ). 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 components 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 slightly influenced by the considered variables (G1); ii) samples influenced by F2 variables (G2); iii) samples averagely 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).

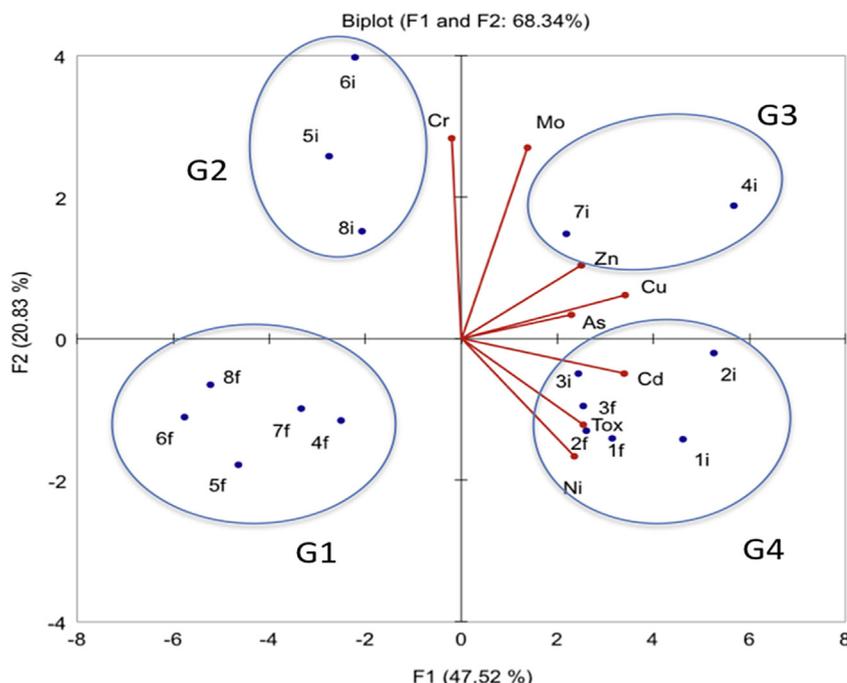


Fig. 6. Principal component analysis (PCA) of chemical and toxicity data obtained for ES1 and ES2; Tox = *V. fischeri* 30 min toxicity; for label conversion please see S2.

#### 4. Conclusion

Stabilization of trace metals was investigated using bauxite extraction by-products (red mud) as mineral amendment (bauxaline<sup>®</sup>, bauxsol<sup>™</sup> and gypsum neutralized bauxaline<sup>®</sup>) 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<sup>®</sup>, bauxsol<sup>™</sup> and gypsum neutralized bauxaline<sup>®</sup> at any rate (5% or 20%) was found to be not efficient for As stabilization. Application of 5% bauxaline<sup>®</sup> or bauxsol<sup>™</sup> was not adequate to significantly reduce Cd, Mo, Ni, Zn and Cu in leachates, while application of 5% gypsum neutralized bauxaline<sup>®</sup> slightly improved stabilization of Zn, Cu and Mo. In the present study scenarios, the higher amendment rate (20%) (bauxaline<sup>®</sup>, bauxsol<sup>™</sup>, and gypsum neutralized bauxaline<sup>®</sup>) 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 amendment of gypsum neutralized bauxaline<sup>®</sup> (20%) were less toxic compared to the control, and approximately as toxic as the control when 5% of amendment was used. A decrease in toxicity was also observed at the end of the experiment when 20% of amendment rate was applied compared to the first day of experiment. Considering toxicity and chemical results, gypsum neutralized bauxaline<sup>®</sup> should be preferred for stabilization purposes. From EC and metal leaching measurements, on land storage of dredged marine sediment 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>.

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