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Technical Note

Ex situ remediation of contaminated sediments using mineral additives: Assessment of pollutant bioavailability with the Microtox solid phase test

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ABSTRACT

The aim of this work is to assess the potential ecotoxicological effects of contaminated sediments treated with mineral additives. The Microtox solid phase test was used to evaluate the effect of mineral additives on the toxicity of sediment suspensions. Four Mediterranean port sediments were studied after dredging and bioremediation: Sample A from navy harbor, sample B from commercial port and samples C and D from pleasure ports. Sediment samples were stabilized with three mineral additives: hematite, zero-valent iron and zeolite. Results show that all studied mineral additives can act as stabilizer agent in highly contaminated sediments (A and C) by decreasing dissolved metal concentrations and sediment toxicity level. On the contrary, for the less contaminated samples (B and D) hematite and zeolite can provoke toxic effect towards *Vibrio fischeri* since additive particles can favor bacteria retention and decrease bioluminescence emission.

1. Introduction

A number of studies carried out in recent years have shown the presence of a wide range of contaminants in port sediments and especially in the Mediterranean region. Metals (As, Cd, Cu, Hg, Ni, Pb, and Zn) (Caplat et al., 2005; Casado-Martínez et al., 2006; Kostakis et al., 2006; Martín-Díaz et al., 2008; Schintu et al., 2009), organic compounds (Gómez-Gutiérrez et al., 2007; Martínez-Lladó et al., 2007; Mille et al., 2007; Casado-Martínez et al., 2009) and organotins (Díez et al., 2002, 2006; Cassi et al., 2008) can accumulate in port sediments. In the Mediterranean basin this is mainly due to the particular hydrodynamic characteristics (semi-enclosed sea with limited water exchanges) that favor the accumulation of contaminants in sediments. For maintenance purposes, dredging operations are carried out by port authorities and an average of about 50 million m^3 of sediment are dredged each year in the main commercial and maritime ports (Alzieu, 1999). In many sediment risk assessment studies (Perrodin et al., 2006; Apitz et al., 2007; Macken et al., 2008; Caeiro et al., 2009; Choueri et al., 2010), toxicity tests are associated with chemical data in the framework of tiered decision since bioassays provide ecologically relevant information and are rapid and cost-effective screening tools.

Most of contaminated dredged materials are discharged into terrestrial sites; the part of reused sediment is relatively low since decontamination treatments are not often economically feasible considering the contamination level and the large quantity to be treated. After dredging, sediments are considered as wastes and must be treated prior to beneficial reuse or disposal in storage centers (European Council, 2002). A large volume of contaminated sediments has elevated concentrations of anionic and cationic elements making the solution to the problem more complex. In this case, the most suitable technique for the management of contaminated waste is to immobilize contaminants in the solid phase by chemical stabilization. The aim of this treatment is to reduce the bioavailability of pollutants using mineral additives (Kumpiene et al., 2006; Maurice et al., 2007). Iron based additives such as hematite and zero-valent iron (ZVI) have been well studied in soil remediation, especially for metal-contaminated soils. The surface of hydroxide particles can be positively or negatively charged depending on pH making the Fe hydroxides amphoteric (Kumpiene et al., 2008). Iron based additives (hematite and ZVI) have already shown their efficiency for remediation of soils contaminated with cationic and anionic inorganic pollutants, such as wood impregnation chemical chromated copper arsenate contaminated soil (Hartley et al., 2004; Kumpiene et al., 2006, 2009). Otherwise, zeolites (aluminosilicate mineral with tetrahedral pore structure), due to their large surface area and strong capability of ion ex-

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change and adsorption, are one of the low-cost and available materials which have been used to reduce the leaching of Cd, Cu, Ni and Zn in contaminated soils (Querol et al., 2006; Mahabadi et al., 2007; Lee et al., 2009).

In previous work, we have shown that mineral additives can decrease the toxicity of sediment elutriates towards oyster larvae (Mamindy-Pajany et al., 2010). However, the toxicity of suspended particles was not taken into account in embryo-toxicity test on oyster larvae since toxic effects were measured on aqueous extracts. The aim of the present paper is to assess ecotoxicological effects of mineral additives on sediment suspensions. The Microtox solid phase test (MSPT) was used since it allows an evaluation of the toxicity of re-suspended sediment. In this test the bioluminescent bacteria (*Vibrio fischeri*) can have contact with toxicants both in the particulate and dissolved phases. Moreover, the MSPT is a widely accepted toxicity test in environmental monitoring for its ecological relevance and sensitivity (Libralato et al., 2008; Ghirardini et al., 2009).

2. Materials and methods

2.1. Sediment sampling and characterization

Four sediment samples (A, B, C and D) were provided by French port authorities after dredging and bioremediation treatment (Grosdemange et al., 2008). Two sediments were dredged from Côte d'Azur area (navy harbor, sample A and commercial port, sample B), while two others (samples C and D) from Mediterranean pleasure ports. Physico-chemical data: fine particle (<63 μm) content, organic carbon and water content, As, Cd, Cu, Ni, Pb, Zn, tributyltin (TBT), dibutyltin (DBT), monobutyltin (MBT), PAH ($\sum$ Fluoranthene, Benzo(b)fluororanthene, Benzo(k)fluoranthene, Benzo(a)pyrene, Benzo(ghi)perylene, Indeno(1,2,3-cd)pyrene) and PCB (congeners 28, 52, 101, 118, 138, 153, 180) concentrations in the whole sediment (sieved at 2 mm) are reported in previous paper for sediments A, B, C and D (Mamindy-Pajany et al., 2011). Fine fraction, playing an important role on pollutant bioavailability in MSPT, increases in the following order: A (22%) < D (28%) $\leqslant$ C (28%) < B (65%).

2.2. Suspension preparation and physico-chemical analyses

Untreated (control samples) and treated sediments (sediment samples mixed with 5% of mineral additive), previously prepared in Mamindy-Pajany et al. (2010), were used to perform the MSPT. Three different minerals were studied: Hematite (Alfa Aesar), ZVI (Sigma Aldrich) and natural zeolite (NZ) containing 84% of clinoptilolite (Zeochem). The sizes of mineral particles are: 0.2–4 μm for hematite, 1.65–120 μm for ZVI and 0.45–45 μm for NZ. In the MSPT, 10 g of solid phase (control samples, treated samples, hematite, ZVI and NZ) are re-suspended in 100 mL of diluent solution with magnetic stirring at 1000 rpm for 10 min. Sediment suspensions were used to perform the toxicity tests and physico-chemical analyses. Values of pH was monitored by a WTW pH meter, with a combined pH electrode, calibrated using buffer solutions at pH 7.01 and 4.00 at 25 °C. Samples were also acidified, filtered through 0.45 μm with an acetate cellulose filter and analyzed for inorganic pollutants (As, Cd, Cu, Pb, Mo, Ni, Se and Zn) using ICP-MS (ELAN DRC II).

2.3. MSPT

The MSPT was performed using the standard protocol of Azur Environmental (1998) and light emission was measured after 15 min for each sample. Detailed experimental procedure was reported in Mamindy-Pajany et al. (2011). Effective concentration required to induce toxic effect on 50% of the population (EC50) was determined. Toxic Unit at 50% (TU50) of the population exhibiting a response was determined as 100/EC50 to provide values directly correlated to the toxicity magnitude. When samples were colored at the concentration close to the EC50 value, absorbance correction was realized using the color correction procedure and Microtox Omni Software (Azur Environmental, 1998).

2.4. Data analysis

Statistical analyses concerning TU50s were carried out using the software XLSTAT. Data were tested for homogeneity of variance and normal distribution. One way ANOVAs were used in the analysis of toxicity data to test for differences in toxicity level according to the treatment with additives. Post-hoc comparisons between control and treated samples were made using the Fisher's test to determine which values significantly differed. Principal component analysis (PCA) was considered to summarize the relationships between chemical data and toxicity response for untreated sediment (A, B, C and D) and account for the variation present in the dataset matrix via biplotting both the ordination component scores and the variable loading coefficients.

3. Results

3.1. Chemical composition of the liquid phase in MSPT

Metal concentrations were determined on sediment suspensions (untreated and treated samples) filtered through 0.45 μm (Table 1). Results show that metals such as Cd, Cu, Pb and Zn are higher in sample A than in other samples (B, C and D). Oxyanionic pollutants, Mo and Se are found in lower concentrations in A compared with other samples. Cd, Cu and Zn are in higher concentration in C than in other samples except in A whereas there is no significant difference between contaminants level in samples B and D. In all elutriate samples (control and treated samples), pH values are nearly the same (7.7 ± 0.2).

For sample A, hematite decreases As, Cd, Cu, Mo, Pb, Se and Zn concentrations compared with the control. Metal stabilization is particularly efficient for Cu, Mo, Pb and Zn in diminishing their levels (25%, 63%, 65% and 37%, respectively). ZVI decreases Mo levels (29%) in elutriates and to a lesser extent Cu concentration (4%). NZ decreases Cd, Cu, Mo, Pb and Zn levels (16%, 12%, 34%, 60% and 28%, respectively). For sample B, hematite and ZVI decrease significantly Mo (46% and 28%, respectively) and to a lesser extent Cu and Se (18% and 15% for both additives, respectively). NZ has no effect on metal removal in sample B. In sample C, hematite decreases significantly Mo concentration (69%) and, to a lesser extent, As, Cd, Cu, Zn levels (ca 40%). Ni level diminishes (19%) compared with the control. ZVI and NZ decrease in the same way Mo and Cu levels in suspensions (32% and 22%, respectively). ZVI has a slight effect on Zn concentration (decreased by 5%). In sample D, hematite and ZVI decrease only Cu and Mo levels whereas NZ increases metal concentrations. Hematite decreases Cu and Mo levels (16% and 56%, respectively). Treatment with ZVI provokes a slight effect on Cu and Mo levels (decreased by 10%).

3.2. Toxicity results

Toxicity data are shown in Table 2. One-way ANOVA performed on TU50 is significant. Significance of post hoc comparisons are also shown in Table 2. Toxicity of untreated sediments decreases in the following order: C > A $\geqslant$ B > D. Toxicity levels are not significantly different for samples A and B. Toxicity data obtained for additive