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Heavy Metal Mobility from Marine Sediments due to Erosion and Resuspension

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Abstract. This study examines the effects of specific natural attenuation processes such as erosion, resuspension and diffusion, on leaching of metals from natural marine sediments and spiked sediments, to the water column. The role of pH of the water column on the concentration of dissolved metals is investigated by submitting sediments to a modified elutriation test, using leachants with different pH. Sediment samples were collected from several stations in the inner port of Piraeus, Greece. The Gust Microcosm apparatus was used mainly for the experiments. Increasing shear stress caused resuspension of solids from sediment to the water column, and metal concentrations in the water column was found to closely follow the concentration of suspended solids. When natural sediments where subjected to the resuspension tests, no significant quantities of dissolved metals were released to the water column. Furthermore, metal mobility at different pH values was found to be very low as a result of the buffered final pH of the leachant, after the completion of every leaching procedure.

Keywords: sediments, metals, mobility, erosion, attenuation

1. Introduction

Many aquatic environments are contaminated with high concentrations of anthropogenically introduced metals, and marine sediments are the ultimate receptor of these contaminants. Metals adsorbed to the sediment can easily be remobilized and transferred back to aquatic environment and to aquatic organisms. Sediments can therefore act as a sink, but also as a source of pollution by metals.

Management of contaminated sediments in coastal areas is a critical issue (Pantazidou *et al*., 2009). Natural attenuation can be applied as a remediation technique to sites that have a low potential for contaminant migration. According to the USEPA (1999), ‘the natural attenuation processes include a variety of physical, chemical or biological processes that under favorable conditions, act to reduce the mass, toxicity, mobility, volume or concentration of contaminants’. Natural attenuation is subject to hydrological changes and can take a substantial period of time (Mulligan and Yong, 2004). The key parameter which controls the transport and the behavior of metal in the sediment is pH (Calmano *et al*., 1993). In this case, it is important to estimate the potential mobility and the transport of the metals which are influenced by environmental conditions such as pH, and the interactions between the metals and the sediment-water interface.

A significant number of extractions tests, elutriation tests and sequential extraction procedures have been designed with the aim to deduce information on the mobility and bioavailability of trace elements in soils and sediments (Calmano *et al*., 1993). These procedures try to simulate chemical reactions, i.e., adsorption/ desorption, reduction-oxidation, that can occur in sediments and can modify the concentration of metals in solution.

Another process that influences the mobility of metals and the resuspension of sediments is erosion. According to ISO/TS 14569 -2:2001 3.8, erosion ‘is the progressive loss of original material from a solid surface due to mechanical interaction between that surface and a fluid’. Erosion was studied using the Gust Microcosm apparatus which is calibrated to apply a uniform shear stress on the sediment.

This study extends previous work on characterization of dredged marine sediments (Katsiri *et al*., 2009) and focuses on the assessment of metal mobility and the effects on mobility caused by sediment resuspension in aerated water, (as might happen during dredging) and in acidified water.

2. Materials and Methods

2.1. Sample collection and Handling

The sediments samples were collected with a stainless grab sampler, from sampling stations 17 and 24, in the inner port of Piraeus, Greece (Figure 1). The sampling location was recorded by a global positioning system (GPS). All samples were kept in closed airtight containers under nitrogen atmosphere at 4 ^{o}C (Damikouka and Katsiri, 2009).

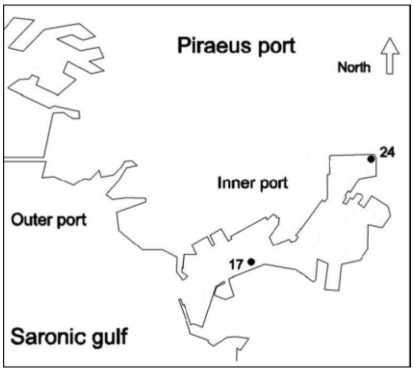

Figure 1. Location of the sampling sites in the inner port of Piraeus

2.2. Reagents and Chemicals

Ultrapure water (18.2 MΩ*cm^{-1}) was produced by the EasypureII, RF ultra pure water system (Barnstead). Nitric Acid (HNO_3) 65% was suprapur grade for trace analysis (Merck) and all other chemicals were of analytical reagent grade. All glassware was pre-cleaned and acid-washed with 10% HNO_3 before use. All working standard solutions of copper (Cu), lead (Pb), zinc (Zn), nickel (Ni) prepared daily by dilution of certified stock standard solutions (1000 mg/L, CertiPUR, Merck).

Quality control was achieved by analysis of a certified reference material (sediment) for extractable metals, BCR 701 (Certified Reference Material, European Commission, Brussels). A good agreement between measured and certified values was achieved and the extraction yields were 72% for Zn, 94% for Cu and 97% for Pb (Damikouka and Katsiri, 2011).

2.3. Apparatus/Instrumentation

The determination of metals -Cu, Zn, Pb, was performed by air/acetylene flame atomic absorption in a Perkin Elmer AAS. Hollow-cathode lamps of each metal were used as a radiation source. Quantification was achieved using matrix-matched standards. Relative standard deviations on triplicate analysis were below 5% for all elements. The concentrations of metals were reported on a dry mass basis, by drying a portion of sediment to constant weight at 105 ^{o}C for 24 h.

Another device used, was the Gust Microcosm apparatus (Gust, 1991). The device was calibrated to apply a uniform shear stress on the sediment/water interface by setting the appropriate velocity of the rotating disk (Figure 2), and was used for the study of erosion, diffusion and the effects of changes in pH values of the water column to the leaching of metals from the sediment.

Elutriation tests were conducted using a roller mixer Stuart SRT9.

2.4. Methods

The samples where subjected to the following experiments:

- A series of experiments involved the elutriation tests with ultrapure water in different initial pH values: 4, 5, 6, 6.5, 7 and 8. Sediment from sampling station 24 was subjected to elutriation for 24 h in a roller mixer using a water to solids ratio of 2 L/kg. The liquid phase was separated from the solid phase by centrifugation. The procedure and the calculations were based on the leaching test for the characterisation of waste EN 12457/1: 2002. Samples taken from the liquid phase were analyzed for the concentration of dissolved Cu, Pb, Zn, and for final pH values.

- Three series of experiments using the Gust Microcosm apparatus.

In the first series of experiments the applied shear stress was constant, and the sediments used were from sampling stations 17 and 24. The supernatant water column was oxygenated ultrapure water at different pH values, 2.5, 3.0, 3.5, 5.0, 5.7, 8.5. Each test was applied for 2 h, in order to establish steady state conditions. Samples taken from the supernatant column were analyzed for the concentration of suspended solids, the concentration of dissolved and total Cu, Pb, Zn, and for several physical parameters such as pH and conductivity.

During the second series of tests, the process of diffusion was examined. Increased shear stress velocities were applied in two cycles, to a sediment spiked with metals.

Figure 2. The Gust Microcosm apparatus

Between the two cycles the spiked sediment was left standing in the Microcosm apparatus for over 24 h. Applied velocity was varied from 0.4 to 1.6 cm/s. Each step was applied for 2 h. Samples taken from the supernatant column were analyzed for the concentration of dissolved Cu, Pb and Zn.

The procedure for the spiking of the sediment was: 2 kg of the sediment from the position 17 was mixed with 500 ml of solution of ultrapure water with concentration, 100 mg/L of Cu, 100 mg/L of Pb and 100 mg/L of Zn. A correction of pH with sodium hydroxide solution was necessary from 2.5 to 7.5. After the correction of pH, the solution and the sediment were mixed together, and were left to equilibrate for 2 months before use.

In the third series of experiments, the effect of the duration of stirring on the resuspension which probably results in the flocculation of the suspended solids, and the mobility of the metals is investigated. The supernatant column was oxygenated ultrapure water. Applied shear stress velocity was varied from 0.5 to 1.5 cm/s, in increments of 0.5 cm/s. Each step was applied for 2 h and 20 h. Samples taken from the supernatant column were analyzed for the concentration of suspended solids, the concentration of dissolved and of metals -Cu, Pb, Zn- in suspended solids.

- Analysis for the concentration of metals in suspended solids: According to 3030E method of Standard methods for the Examination of Water and Wastewater (APHA, 1992), 100 mL of sample was digested with 5 mL of concentrated nitric acid.

3. Results and Discussion

The depth of sampling sites, physicochemical characteristics and concentrations of total metals are presented at the table 1 (Damikouka and Katsiri, 2009).

Table 1. Physicochemical characteristics and total concentration of trace elements in sediment samples expressed in mg/kg dry matter

Parameter	Sample location	
	17	24
Depth (m)	11.6	7.8
pH	7.93	7.85
Volatile solids (%DM)	4.8	10.2
Dry matter (%DM)	60.9	58.2
% of coarse solids (>74 μm)*	19	62
% of fine grained solids (< 74 μm)*	81	38
Cu mg/kg	144.0	375.0
Pb mg/kg	139.0	478.0
Zn mg/kg	233.3	811.5
Ni mg/kg	113.4	178.8

*(Katsiri *et al*., 2009)

Particle size distribution analysis performed for selected samples and reported previously (Katsiri *et al*., 2009) showed that samples with high volatile solids content also had a high percentage of fine material (< 74 μm) as sample from sampling station 24. Sample from site 24 also had higher concentration of metals than the sample from site 17.

During the elutriation tests, with different initial pH values, from 4 to 8, for the elutriation water, pH did not have any effect on metal mobility as it is depicted for Cu and Zn at figure 3. After every experiment the pH of the liquid phase was increased and became neutral to alkaline (7.4- 8.0). In case of Zn a stable amount and higher than the other measured metals (Pb, Cu) is released to the liquid phase independently of the initial pH values, mainly attributed to the high concentration of Zn at the sediment, as depicted at the table 1. The percentages of the leached amount of metals to the total concentration of metals at the sediment, in case of initial pH 4, were 0.002% for Pb, 0.02% for Cu and 0.08 % for Zn.

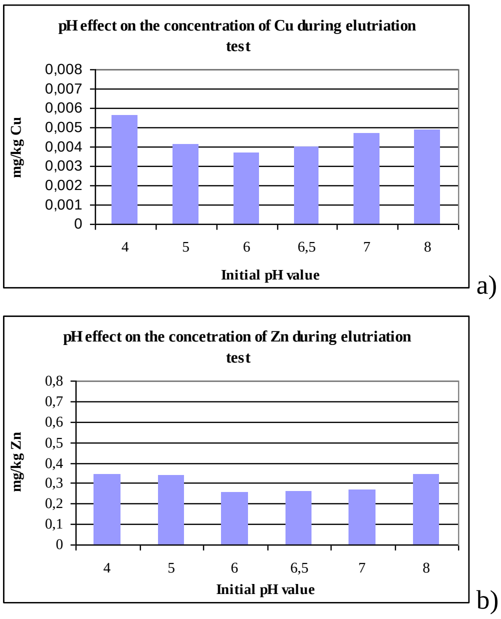

Figure 3. Concentration of dissolved metals in mg/kg during elutriation tests (a) Cu, (b) Zn, in relation to different initial pH values, from 4 to 8, of the water column

In the first series of experiments with the Microcosm apparatus, when the pH of the water column was varied from 2.5 to 8.5, the concentration of the metals – Cu, Pb, Zn, Ni- released to the water column was low. Only Cu showed a tendency to dissolve when pH was raised to 8.5. The concentration of dissolved Cu and Ni are depicted at the Figure 4. In all cases, the pH of the water column after mixing with the sediment was increased and became neutral or even alkaline. It seemed that the buffering capacity of the sediment was able to restore the pH to above neutral conditions within the 2 h duration of the experiment, thus preventing additional release of metals in the water column.

During the second series of experiments with the Microcosm apparatus, when increased shear stresses were applied in two cycles, to the spiked sediment, and the spiked sediment was left standing in the Microcosm apparatus for more than 24 h between the two cycles, significant leaching of dissolved metals to the water column was observed, -from 3 to 125 μg/L for Pb, from 6 to 81 μg/L for Cu and from ND to 0.26 mg/L for Zn.

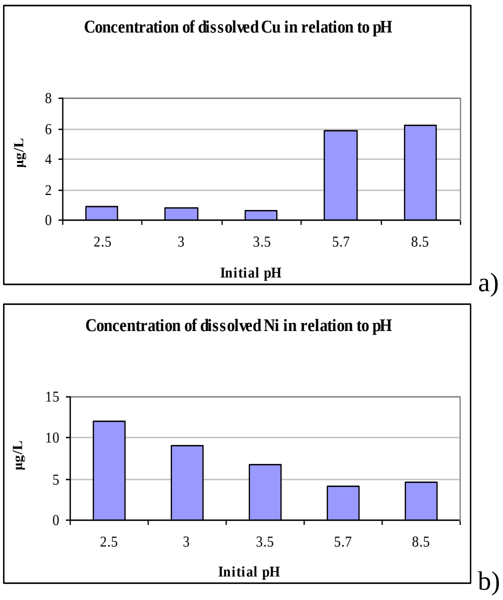

Figure 4. Concentration of dissolved metals (a) Cu, (b) Ni, in relation to pH during the experiments

This indicates that diffusion is probably the predominant leaching mechanism of soluble metals to the water column. The concentration of Cu leached into the water column from the sediment from sampling station 17, is depicted in Figure 5.

In the third series of experiments, the effect of the duration of stirring to the resuspension was investigated. Applied velocities were varied from 0.3, 0.6 and 1.0 cm/s. Each step was applied for 2 h and 20 h. Increasing shear stress caused resuspension of solids from sediment to water column, in concentrations ranging from 30 to 642 mg/L, depending on the sample when the duration of the experiment was 2 h.

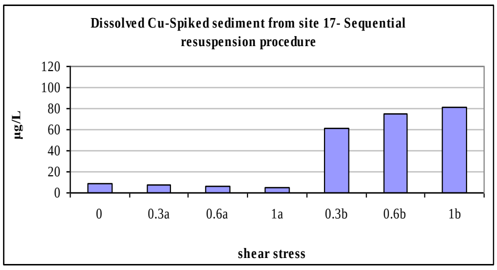

Figure 5. Concentration of dissolved Cu, when increased shear stresses were applied to the spiked sediment in sequential resuspension procedures

The concentration of metals in suspended solids in the water column followed closely suspended solids concentration and ranged from 13 to 229 μg/L for Pb and 10.5 to 860 μg/L for Cu. However, the concentration of metals in the dissolved phase was always very low, ranging from 0.9 to 3.8 μg/L for Pb and 3 to 9.5 μg/L for Cu, whereas Zn, Ni and Cd were almost always non detectable.

The increase in the duration of stirring from 2 h to 20 h caused a decrease in the concentration of suspended solids probably due to flocculation which resulted in the sedimentation of the suspended solids, and respectively, the decrease in the concentration of metals on suspended solids. The concentration of the dissolved Pb (Figure 6) and Cu, did not appeared to be increased due to the increase in duration and the applied shear stress.

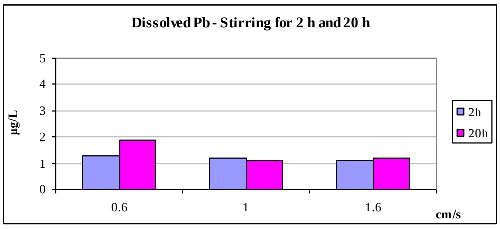

Figure 6. Concentration of dissolved Pb. Each step was applied for 2 h and 20 h.

4. Conclusions

The leaching of metals from contaminated sediments to the water column caused by erosion/resuspension or elutriation was very low. The amount of metal leached depends on the characteristics and the components of sediment which influence the final pH value, with carbonates, and in general, the buffer capacity of the sediments playing a significant role. When sediments were subjected either to resuspension in the Gust microcosm system or to elutriation for 24 h with acidified water, no significant quantities of metals were released, indicating that metal mobility is not affected by “mild” interventions in environmental conditions. The buffer capacity of sediments, which is mainly attributed to carbonates, but also to other mineral phases in sediments, such as organic matter, clay and aluminum hydroxides, eliminates the changes in pH of the water column, when the water column is acidified. In case of the sediment with high concentration at the mobile phase or at pore water, diffusion seems to be the predominant leaching mechanism of soluble metals to the water column and to a much lesser extent erosion as indicated in spiked sediment tests. Furthermore, given the fact that suspended sediment tends to settle very fast due to flocculation, it can be concluded that the effect of erosion to water column pollution by metals will be of a temporary nature and will not result in a permanent increase in the levels of dissolved metals.

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