

Mobility of Contaminated Heavy Metals and Metalloids in Sediments Caused by Recent Industrial Activities

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Abstract. Sequential leaches (sequential extractions) experiment of 62 elements were carried out for assessing the mobility of contaminated heavy metals and metalloids contaminated in natural sediments; river sediments of Oued El Harrach (Algeria) and lagoon sediments of Bizerte (Tunisia), North African Mediterranean coast. Applied extractants for the sequential leaches are: (A) distilled water for extracting water soluble components, (B) 1M sodium-acetate for extracting exchangeable cations by clay minerals and co-precipitations of carbonates, (C) 0.1M sodium-pyrophosphate for extracting the elements bound with organic matter, (D) 0.1M hydroxylamine for extracting the elements bound with amorphous Mn hydroxides, and (E) 0.25M hydroxylamine for extracting the elements bound with amorphous Fe hydroxides and more crystallized Mn hydroxides. According to the results of sequential leaches experiment, contaminated heavy metals, metalloids, and other potentially toxic element (PTEs) in the sediments are mostly presented as exchangeable cations by clay minerals, co-precipitations of carbonate compounds, binding complexes with organic matter, and/or amorphous manganese hydroxides. Mobility of contaminated heavy metal and metalloids is relatively larger in Algerian river sediment than in Tunisian lagoon sediments. However the mobility of the PTEs in the sediments can be easily changed if the depositional environment is altered by civil construction works.

Key words: Industrial pollution, Heavy metals, Sediment contamination, Leaching, North Africa

Introduction

River, lake, and lagoon bottom sediments located near industrial and urban zones often act as a sink for potentially toxic elements (PTEs; Alloway, 1995) including heavy metals and metalloids, where their concentrations show very high in comparison with the natural background levels. It is well known that the environmental behavior of PTEs, such as their reactivity, mobility, and availability in ecosystems, and biological/ecological impacts, strongly depends on their particular chemical form. PTEs are contaminated in the sediments as either water soluble species, as structural elements in solids, as adsorbed onto the surface of mineral particles, and/or as bound with organic matters. The PTEs contamination is often the result of industrial/commercial activities or disposal practices. For examples, disposal of batteries results in soil/sediment and water contamination by Pb, Cd, and Hg; exhaust from automobiles that burn gasoline pollutes air by Pb particulate and eventually accumulated in sediments; use of pesticides and

agro-chemicals results in soil contamination by Pb, Hg, and As; and mining activities discharges various kinds of heavy metals.

Actually, trace elements have concentrated numerous times in geologic history, which are described by geologists as ore-bodies. All ore-forming processes have in common the mobilization of the metal elements within a large reservoir by some agent such as hydrothermal liquid and the re-deposition in relatively small, high-grade ore-bodies. Weathering and erosion of such bodies at some later stage cause some dispersion of metal elements again. Rivers transport large amounts of dissolved substances to the sea.

Man-made sediment contaminations, environmental pollution, should be similarly considered by the aspect of the equilibrium of material balance in natural sediment. Natural sediments are heterogeneous media that contain a host of different materials; inorganic solid particles and organic materials. Some of contaminated elements are, thus, bonding with such materials, and some elements are easily soluble with water. The former case shows natural

sink for 'environmental protection' which immobilize toxic contaminants in the sediment, or allows them to enter the biosphere only at a lower concentration level and a lower rate that no harmful effects result. While the latter case permits the contaminated PTEs to mobilize and to merge into a food chain of biosphere through hydrosphere, which provokes environmental pollution problems for ecosystem and human beings. The former to latter case is sometimes easily transformed by the change of environment surrounding the sediments. Thus, the analysis of chemical speciation and mobility of PTEs is crucial factor for making environmental risk assessment.

In this paper, the author report the results of sequential leaches analysis of river and lagoon sediments in Algeria and Tunisia those have been significantly contaminated by heavy metals due to industrial activities.

Material and Method

Sampling

The studied site was located in the North African Mediterranean coast, Oued El Harrach river in Algiers, Algeria and Bizerte lagoon in Tunisia. Both sites were located near industrial/urban zones. Seven river sediment samples were collected from Oued El Harrach in April, 2004; OEH-01, 02, 03, 04, 05, 06, & 07, and four lagoon sediment samples were collected from the bottom sediments of Bizerte lagoon in March, 2002; LB-4L, 11L, 12L, & 29L, for the sequential leaches analysis. Detailed information about sampling was reported in Yoshida et al. (2005) for Algerian sites and Ghrabi et al. (2002) for Tunisian sites.

Analytical Procedure

Sediment samples were dried at room temperature, disintegrated by a porcelain mortar, then sieved through a 250 mesh screen. A 1.0 g sample split of the finer fraction was used for the analysis. Total 62 elements were measured, Ag, Al, As, Ba, Bi, Ca, Co, Cu, Fe, K, La, Mg, Mn, Mo, Na, Ni, Pb, Sb, Sr, Th, Ti, U, V, W, Zn, Se, Te, Au, Hg, Be, Cd, Ce, Cs, Dy, Er, Eu, Ga, Gd, Ge, Hf, Ho, In, Li, Lu, Nb, Nd, P, Pr, Pt, Pd, Rb, Re, Sc, Sm, Sn, Ta, Tb, Tl, Tm, Y, Yb, and Zr. The analysis of trace element was made using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) Parkin Elmer model Plasma Vision 2000 and Mass Spectrometry (ICP-MS) Parkin Elmer model Elan 6000. It is useful to apply sequential leaches or sequential extractions for characterizing the trace element in soil and the state of soil contamination. On the basis of the method developed by Tessier et al. (1979), in present study we used five extractants, A, B, C, D, and E, as follows:

- A. Distilled water (H₂O):
- B. 1M sodium-acetate (CH₃COONa)
- C. 0.1M sodium pyrophosphate (Na₄P₂O₇)

- D. 0.1M hydroxylamine (NH₂OH)
- E. 0.25M hydroxylamine (NH₂OH)

The analytical procedure applied is as follows:

(A) At the first step, 1.0 g sample was prepared from given dried sediment. Then the sample was mixed with 20mL distilled neutral water and extracted one hour (Leaching Process A). The mixture was centrifuged and the solution was analyzed. In this process mainly water-soluble component can be extracted.

(B) The residue of above-mentioned 'Leaching Process A' was retained for next leach, Leaching Process B, where the sample was mixed with 20mL of 1M sodium-acetate (CH₃COONa) solution and the leaching was made for one hour. The mixture was centrifuged and the solution was analyzed. In this process adsorbed and/or exchangeable cations by clay minerals and elements co-precipitated with carbonates are mainly extracted.

(C) The residue of above-mentioned 'Leaching Process B' was retained for next leach, Leaching Process C, where the sample was mixed with 20mL of 0.1M sodium pyrophosphate (Na₄P₂O₇) solution and the leaching was made for one hour. The mixture was centrifuged and the solution was analyzed. In this process elements adsorbed by organic matter (humic and fulvic compounds) can be extracted.

(D) The residue of above-mentioned 'Leaching Process C' was retained for next leach, Leaching Process D, where the sample was mixed with 20mL of 0.1M hydroxylamine (NH₂OH) solution and the leaching was made for one hour. The mixture was centrifuged and the solution was analyzed. This extractant is a reducing reagent, which extracts easily amorphous form of Mn oxides and hydroxides and the metals associated with them (Ure and Davidson, 1995; Pérez-Sirvent et al., 1999).

(E) The residue of above-mentioned 'Leaching Process D' was retained for next leach, Leaching Process E, where the sample was mixed with 20mL of 0.25M hydroxylamine (NH₂OH) solution and the leaching was made for one hour. The mixture was filtered and the solution was analyzed. In this higher concentration (0.25M hydroxylamine) treatment elements adsorbed by more crystalline Mn oxides/hydroxides and amorphous Fe hydroxides can be extracted.

According to the interference of leaching agents, Na, Cl, Br, S, and P could be analyzed in limited sequences only.

Results and Discussion

In order to determine the contribution of each leaching effect among the overall leaches, leaching ratios for each sample was calculated for each element as following equation:

$$L_X = [\text{Concentration in Leaching X}] / [\text{Sum of concentrations from the Leachings A to E}]$$

where X = A, B, C, D, or E.

Table 1. Summary of Sequential Leaches Experiment of Oued El Harrach (Algeria) river sediment samples. Marked elements are contaminated PTEs caused by industrial/urban activities.

Sequential Leaches Steps	Elements significantly leached out from the sediments	Elements relatively leached out from the sediments
<i>A (water soluble)</i>	Li, Se	K, Mo
<i>B (exchangeable cations)</i>	Ca, La, Mn, Pb, Th, <u>Hg</u> , Ce, Dy, Er, Eu, Gd, Ho, Nd, Pr, Sm, Tb, Y, Yb	<u>Ba</u> , Co, Sr, U
<i>C (organic bounded)</i>	Ag, <u>Al</u> , <u>Cu</u> , <u>Fe</u> , K, Mo, <u>Sb</u> , Th, V, <u>Hg</u> , Be, Cs, Rb, Zr	<u>As</u> , U
<i>D (amorphous Mn hydroxides)</i>	<u>As</u> , <u>Ba</u> , <u>Pb</u> , <u>Zn</u> , Cd	Ca, <u>Co</u> , <u>Fe</u> , La, <u>Mn</u> , <u>Ni</u> , Sr, U, V, Be, Ce, Dy, Er, Eu, Gd, Ho, Nd, Pr, Sm, Tb, Y
<i>E (amorphous Fe hydroxides and crystalline Mn hydroxides)</i>	Se	Au

Table 2. Summary of Sequential Leaches Experiment of Bizerte lagoon (Tunisia) sediment samples. Marked elements are contaminated PTEs caused by industrial/urban activities.

Sequential Leaches Steps	Elements significantly leached out from the sediments	Elements leached out from the sediments
<i>A (water soluble)</i>	Li, <u>Se</u>	<u>Mo</u>
<i>B (exchangeable cations)</i>	Sr, Mg, K, La, <u>Ba</u> , Mn, U, Cd, Ce, <u>Zn</u> , Rb, Y	Ni, <u>Co</u> , <u>Hg</u> , Tl, <u>Pb</u>
<i>C (organic bounded)</i>	Th, Sn, Be, Fe, Cu, <u>Al</u>	Sb, <u>As</u> , <u>V</u>
<i>D (amorphous Mn)</i>	Ag, <u>V</u> , <u>Hg</u>	Mn, <u>Co</u> , Ni, Cd, <u>Pb</u> , and Tl
<i>E (amorphous Fe hydroxides and crystalline Mn hydroxides)</i>	Be, Fe, Cu, Al, <u>Sb</u> , <u>As</u> , <u>V</u>	Cd, <u>Hg</u> , Se, Tl

If L_x is generally larger than 0.5, it is named as the “significantly leached out from the sediment”, and if averaged L_x is generally less than 0.5 but larger than 0.2, named as the “relatively leached out from the sediment”. According to previous researches on sediment contamination in these two sites, the Algerian river sediments in Oued El Harrach were contaminated by heavy metals and metalloids such as Hg, Cu, Pb, Zn, Ni, Co, Mn, Fe, As, Cd, Sb, Cr, Ba, Al, and Se possibly caused by industrial/urban activities (Yoshida et al., 2005), the Tunisian lagoon sediments in Bizerte were contaminated by heavy metals and metalloids such as Ba, Pb, Zn, As, Se, Al, Cr, Co, Mn, V, Mo, and Hg possibly caused by industrial/urban activities (Yoshida et al., 2002). Comparable contamination in Algerian sea sediment was reported by Alomary and Belhadj (2007). Based on the results of sequential leaches analysis, the mobility of contaminated heavy metals and metalloids in each site is examined as shown in Tables 1 and 2.

Conclusions

(1) For the river sediments collected from Oued El Harrach, Algeria, seven samples were analyzed and the general tendency of the pattern of sequential leaches is quite similar. Natural clay minerals and carbonates (lime) play important role for immobilization of contaminated

heavy metals and metalloids, such as Hg and Ba. Organic matters also play very important role for immobilization, in particular for major contaminated heavy metals and metalloids, Cu, Sb, Hg, and As. Adsorptions by amorphous manganese hydroxides is effective for immobilizing As, Ba, Pb, Zn, Co, and Ni.

(2) For lagoon sediments collected from Bizerte lagoon, Tunisia, four samples were analyzed and the general tendency of the pattern of sequential leaches is similar. The lagoon is occupied by sea water, so that salinity probably affects the mobilization of PTEs, where Se and Mo can be mobilized under fresh water condition. Natural clay, carbonates (lime) play very important roles for immobilization of Ba, Zn, Co, Hg, and Pb. On the other hand, organic matters immobilize Al, As, and V. Amorphous manganese hydroxides are effective to immobilize V, Hg, Co, and Pb. Immobilization by amorphous iron hydroxides and crystalline manganese hydroxides is also observed for Sb, As, V, and Hg.

(3) In general, mobility of contaminated heavy metal and metalloids is relatively larger in Algerian river sediment than in Tunisian lagoon sediments.

(4) Mobility of heavy metals, metalloids, and other PTEs bound with sediments can be easily changed if the river/lagoon bottom environment is altered by civil construction works, for example from anoxic to oxic conditions by dredging. One of the most toxic heavy

metal Hg in both sites can be certainly mobilized under a change of conditions. Thus, chemical speciation of PTEs in the sediments of Oued El Harrach is recommended to study prior to implement a counter-measure for de-pollution of river.

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