Heavy Metals in Sediments from the Algerian Coasts of the Mediterranean Sea

By

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**Abstract**

The aim of this work is to assess the level of twelve metals including Al, Cd, Cr, Cu, Fe, K, Li, Na, Ni, Pb, Sr, and Zn in surface coastal sediments and to study the anthropogenic factors affecting their concentrations. Sediment samples (n =18) were collected from the Algerian Mediterranean coasts and analyzed for the twelve metals using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). Sediment samples were size-fractionated into three sizes: 1080-500 (coarse), 500-250 (medium), and < 250 μm (fine). Two third of the samples follow the following order of fractions percents medium > fine > coarse. Bulk sediments were subjected to both sequential extraction and total digestion to evaluate the reliability of the sequential extraction procedure (SEP), while the fractions have been only sequentially extracted for metals speciation. The metals were sequentially extracted into five phases namely exchangeable (P1), carbonates (P2), Fe-Mn oxides (P3), organic (P4) and residual (P5). Metal recoveries in sequential extractions were ± 20 % of the independently measured total metal concentrations; the high recovery rates indicate the good reliability of the SEP used in this study. The order of metal levels in the fractions was medium > fine > coarse for all the metals. Positive correlations were found for Ni, Li, Cr, Na, Pb, Cd, and Fe concentrations, with the medium fraction. Whereas only Cd and Zn had positive correlations with the fine fraction while no correlations at all were found with the coarse fraction. The average total extractable metal concentrations for Al, Cd, Cr, Cu, Fe, K, Li, Na, Ni, Pb, Sr, and Zn were 22959.7, 1.1, 8.8, 4.7, 1291.3, 515.0, 12.2, 2250.9, 13.9, 5.7, 178.4, and
20.4 \mu{g/g} respectively. The distributions of the studied metals vary in all locations except for K. The northeastern shelf had the lowest metal levels while the highest were in northwestern part mainly due to the significant tourism activities in the northwestern part. Comparison of our results to Earth's crust values and to previous studies points out that our samples were unpolluted.

Enrichment factors as the criteria for examining the impact of the anthropogenic sources of heavy metals were calculated, and it was observed that our samples were not contaminated with Cr, Cu, Fe, K, and Na, moderately contaminated with Li, Ni, Pb, Cd, and Sr and contaminated with Cd. This may be due to human activities and large urbanization. The P5 phase had the highest percents of Al, Cr, Cu, Fe, K, Li, Ni, and Zn. Cd and Pb were predominant in the P4 phase, while Na and Sr were predominant in the P2 phase. Al, Cu, Fe, Li, and Zn were distributed in the order P5 > P3 > P4 > P2 > P1. The following order of bioavailability was found with the heavy metals Pb > Cr > Cd > Ni > Zn > Cu > Fe. In term of affinity, Cr had the highest affinity in the exchangeable phase, Pb in the P2 phase, Fe in the P4 and Cd in both the P3 and P4 phases.

In addition to the ICP-OES, the samples were analyzed using a Scanning Electron Microscope technique equipped with Energy Dispersive X-ray microanalyzer (SEM-EDAX) in order to calculate the relative metal percents of Cd, Cr, Cu, Fe, K, Na, Ni, Sr, and Zn. The results obtained by SEM are comparable to those obtained by ICP-OES which was validated by the positive correlations obtained between the two techniques. Moreover, sample correlations for both SEM and ICP results confirm that no pollution can be considered in the studied areas.

*Keywords*: Mediterranean Sea; Algeria; Sediments; Metals; Speciation; Bioavailability; Sequential Extractions; ICP-OES; SEM-EDAX.