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## Transfer of chemical elements from a contaminated estuarine sediment to river water. A leaching assay

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Wastes of a former Portuguese steel industry were deposited during 40 years on the left bank of the Coina River, which flows into the estuary of the Tagus River near Lisbon. The aim of this study was to evaluate the release of the chemical elements from the contaminated sediment to the river water. A leaching experiment (four replicates) was performed using 1.6 kg/replicate of sediment from a landfill located in the Coina River bank, forming a lagoon subject to tidal influence. River water coming from this lagoon was collected during low tide. This water (200 mL) was added to the moist sediment, contained in cylindrical reactors, and was collected after 24 h of percolation. The leaching experiments were conducted for 77 days being leachates collected at time zero, after 28, 49 and 77 days with the sediment always moist.

The sediment was characterized for: pH, electric conductivity (EC), total organic carbon (TOC), extractable phosphorus and potassium, mineral nitrogen, iron from iron oxides (crystalline and non-crystalline) and manganese oxides. Multi-elemental analysis was also made by ICP-INAA. Leachates and river water were analysed for pH, EC, hydrogencarbonate and sulfatetot by titrations, chloride by potentiometry, and multi-elemental composition by ICP-MS. The sediment presented pH=7.2, EC=18.5 dS/m, TOC=147.8 g/kg, high concentrations of extractable phosphorous (62.8 mg/kg) and potassium (1236.8 mg/kg), mineral nitrogen=11.3 mg/kg. The non-crystalline fraction of iron oxides corresponds to 99% (167.5 g Fe/kg) of the total iron oxides, and manganese from manganese oxides was low (52.7 mg/kg). Sediment is considered contaminated. It contained high concentrations (g/kg) of Zn (2.9), Pb (0.9), Cr (0.59), Cu (0.16), As (0.07), Cd (0.005), and Hg (0.001), which are above Canadian values for marine sediments quality guidelines for protection of aquatic life. River water had: pH=8.2, EC=28.6 dS/m, csulfate=1.23 g/L, and [Cl-]=251.6 mg/L. The concentrations of Cd (0.001 mg/L) and Hg (0.02 mg/L) were above Canadian water quality guidelines for protection of aquatic life.

Leachates had pH $\approx$ 7.9 and EC=38.7 dS/m (mean values), and high concentrations of hydrogencarbonate (723.7 mg/L), sulfatetot (1.8 g/L) and chloride (252.2 mg/L). Over the experiment, only pH (7.6-8.0) and EC (35.7-55.2 dS/m) values showed statistical differences, increasing over time. Regarding multi-elemental contamination, statistical differences were found between some elements concentrations (Co, Cu, Cr, Mn, Ni, Sb, U, V, W, Zn) in the leachates/kg of sediment collected after river water percolation in the four periods. However, only the concentrations of Ni (4.7-9.2  $\mu$ g/kg), Sb (0.08-0.14  $\mu$ g/kg), W (0.16-1.1  $\mu$ g/kg) and Zn (1.72-5.74  $\mu$ g/kg) have increased. The concentration of the elements in the leachates when compared to the same elements concentration in the sediments corresponds to a fraction lower than 1%. When comparing the concentrations of the elements in the leachates and in the river water used for sediments leaching, the values in leachates are in general lower, being the highest obtained for Ni, W and U, which correspond to 62, 61 and 50% of the river water values, respectively. Chemical elements transfer from sediments to river water can be considered very low.