

Dissolved trace metal behaviour in a highly contaminated estuarine system in the south-west of Spain

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Two rivers, the Rio Tinto and Rio Odiel, drain parts of the Iberian Pyrite Belt, south-west Spain, which has been an area of intense metalliferous mining since Phoenician times. The rivers are rich in dissolved metals and low in pH as a result of natural sources and mining activities, and they join in a common estuary at the industrial centre of Huelva. The present study investigates the Tinto/Odiel system as a possible important contributor to the enrichment of the Gulf of Cadiz with dissolved trace metals. Riverine, estuarine and coastal water samples were taken during three surveys between November 1996 and April 1998. Dissolved metal concentrations in the rivers varied between surveys, and were extremely high (e.g. Rio Tinto fresh water in Nov, 1996/June, 1997: pH 2.43/2.55, 10.9/1.7 mM Fe, 172/112 μM Mn, 669/441 μM Zn, 448/255 μM Cu and 1.4/1.3 μM Cd). Dissolved metal concentrations decreased in the estuary by 2–4 orders of magnitude, as a result of dilution with seawater and geochemical processes. Strong correlation between the behaviour of dissolved Fe, Mn, Zn, Cu and Cd in the estuary suggests that the system may be controlled by the removal of iron from solution, which is pH-dependent. The dissolved speciation of Cu was

investigated, using modelling and voltammetric methods. Equilibrium speciation modelling (Mineql+) showed that the Rio Tinto end-member was dominated by sulphate (27 mM SO_4^{2-}), with a calculated 64% of the total dissolved Cu concentration present as $\text{CuSO}_4(\text{aq})$ (35.9% Cu^{2+}). Electrochemically labile Cu was measured in estuarine waters, using ligand competition with cathodic stripping voltammetry. In the mid estuary (pH 6.3, $S = 14$), the difference between total and labile dissolved Cu concentrations was small (> 93% labile). The strong labile character may have important implications for the toxicity of Cu, as the labile form of Cu is thought to be the most bioavailable. Towards the mouth of the estuary, the non-labile fraction of Cu increased to 64 % (pH 8.2, $S = 34.5$). This trend continued in coastal surface waters, where non-labile Cu formed more than 80% of the total (data from Nov, 1996). The decrease in labile Cu with increasing salinity can probably be attributed to the complexation of dissolved Cu by natural organic ligands, for which phytoplankton activity in coastal water may have been a possible source.