

# Trace metal interactions at the particle/water interface: kinetic experiments in a mine polluted estuarine system

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This paper reports on a study of the processes occurring at the particle–water interfaces in a natural, metal polluted river-estuary system in Southwest Spain. The Rio Tinto and Odiel drain the Iberian Pyrite Belt, a region with important mining activities, which is still active nowadays. The rivers discharge into the Huelva estuary, where heavy industry adds to the pollution burden, before flowing into the coastal waters of the Gulf of Cadiz. As a result of the mining inputs, the freshwater end-members, of low water and sediment discharge, are characterised by a low pH (2 to 3) and a high dissolved metal contents (e.g.  $[\text{Fe}] = 0.1$  to 2 mM).

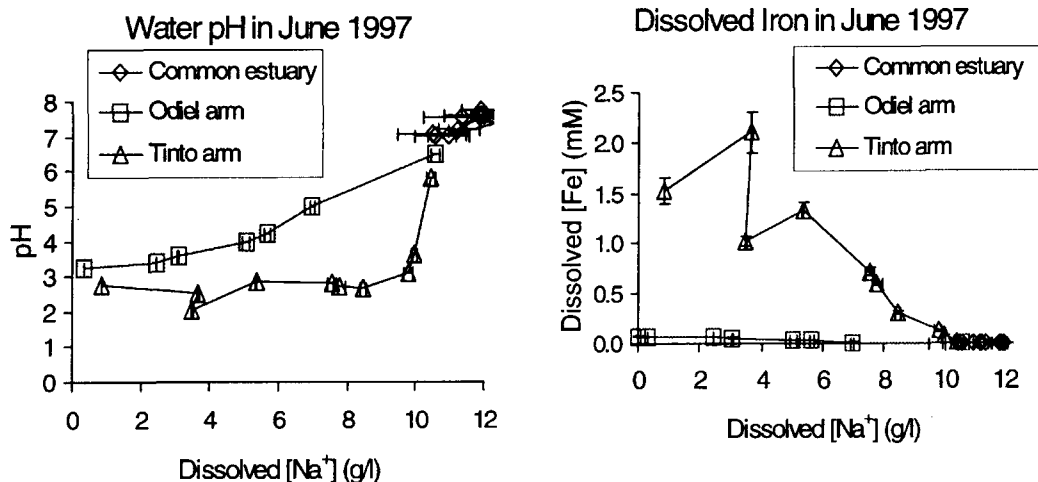
The estuarine mixing of the acidic river waters with the sea water is characterised by major changes in pH and salinity, inducing removal of dissolved metals from the water column.

In order to investigate the mechanism of removal of dissolved metals, kinetic studies were undertaken where natural estuarine particles collected in the Turbidity Maximum Zone (TMZ) of the estuary were

mixed with filtered river and sea water in order to study the adsorption and desorption processes affecting these particles.

In general, particles found in the TMZ of estuaries are characterised by a high surface area and can therefore strongly influence the trace metals in the dissolved phase through adsorption at its surface (Morris *et al.*, 1986; Glegg *et al.*, 1988; Millward *et al.*, 1992). However, our studied system is characterised by low pH and by its mining drainage origin. It could therefore be possible that for the Huelva system the particle surfaces found are positively charged, which would result in different processes governing the particle-water interactions than those observed under more 'natural' pH conditions (Newton and Liss, 1987).

For our study, kinetic experiments were undertaken for 24 hours, whereby a special emphasis was put on the first 2 hours. Both the dissolved and particulate phases (separated by vacuum filtration using a 0.45  $\mu\text{m}$  porosity filter) were subsequently



Figs. 1, 2. pH and dissolved Fe versus sodium in the Rio Tinto and Odiel and the Huelva estuary.

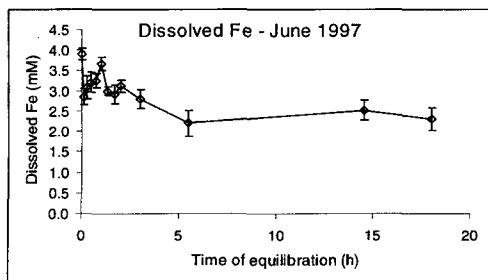


FIG. 3. Decrease in dissolved Fe concentration when filtered freshwater is let to equilibrate during 24 hours without addition of particles.

characterised. The use of adsorptive cathodic stripping voltammetry allowed us to speciate the dissolved phase into electrochemically-labile and organically complexed fractions for Cu, Zn, Cd, Pb, Ni and Co. In addition, a redox speciation of the dissolved Fe (as Fe(II) or Fe(III)) was performed. Special attention was also given to the physical and chemical characterisation of the particulate matter. The particulate phase was examined by scanning electron microscopy and the mineralogy of some key samples was determined by X-ray diffraction. The variation in the specific surface area of the particles was measured by the BET method. Aliquots of the sediments and particulate matter were also subjected to a sequential and total leaching procedure in order to assess the metal content of different solid fractions. Mixing experiments involving the unfil-

tered Rio Tinto and Odier freshwater end-members and the unfiltered coastal water were also performed in order to study the effect of increasing the major ion concentrations onto the removal of trace metals from the water column.

Preliminary results obtained in June 1997 showed that the mixing of filtered fresh water with TMZ particles did not produce a decrease in the dissolved trace metal concentrations and was explained by the positive charge of the particles. However, a spontaneous precipitation of dissolved Fe occurred in the filtered freshwater during equilibration without particles for a period of 24 hours.

The mixing of estuarine sea water with the TMZ particles showed evidence of desorption only for dissolved Cu, while a spontaneous precipitation of dissolved Fe, P, Ni, Pb and U occurred during a 24 hours equilibration with no addition of particles.

## References

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