

Bioavailability and toxicity of metals in an estuary contaminated by acid mine drainage

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Motivated by the need for a better understanding of the human impact on ecosystems (Water Framework Directive), we combined a bioassay (*Crassostrea gigas* larva) with high temporal resolution *in situ* metal speciation measurements to assess the temporal variability, biological availability and toxicity of dissolved metals in an estuary affected by historic (tin streaming) and contemporary (acid mine drainage) metal sources. Voltammetric *in situ* Profilers were deployed in the estuary for a tidal cycle to determine Cd and Cu species ('dynamic') in a size range (<4 nm) highly relevant for uptake by organisms [1]. Oyster larvae were exposed to discrete samples taken at regular intervals during the survey.

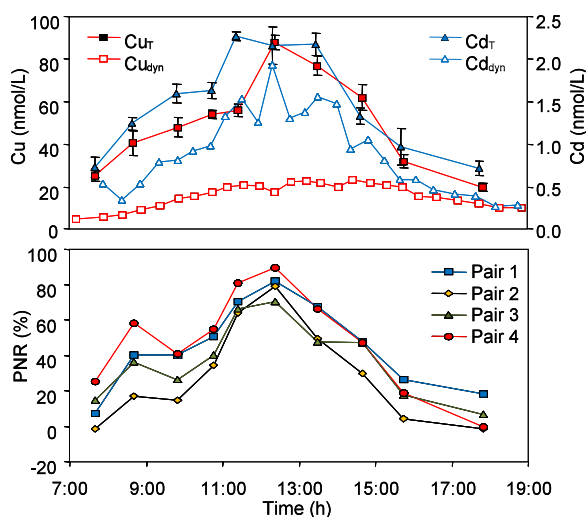


Figure 1: Dynamic (Cu_{dyn} , Cd_{dyn}) and total (Cu_T , Cd_T) metal concentrations and percent net response (PNR) of oyster larva.

Oyster larva responded to the highest dynamic Cu and Cd concentrations with maximum abnormal development (71-90% (Fig.1). Synergistic toxicity and model calculations suggest that bioavailable metal concentrations in this estuary are likely to severely compromise the ecosystem structure [2].

[1] Buffle, Tercier-Waeber (2005) TRAC **24**, 172-191. [2] Rivera-Duarte *et al.* (2005) ES&T **39**, 1542-1546.

Biotite dissolution: The effect of organic ligands and pH

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Traditionally mineral weathering studies are based on abiotic and, more recently, dissolution in the presence of living organisms. However, for biotite, a key nutrient bearing mineral (i.e., K), the piece of the puzzle linking abiotic [1] and biotic [2] dissolution rates - the effect of organic ligands - is still missing. Here we fill this gap via biotite dissolution experiments conducted with various organic ligands typical in soils or groundwaters to better quantify the full range of processes affecting rock weathering and soil formation.

Batch (pH = 2, 4, 6, 12 hrs) and flow-through (pH = 3.3 and 6, 96 hrs) experiments were carried out at 25°C with biotite with and without oxalic and citric acids and desferrioxamine-b (DFO-B) or a mixture of these. Aqueous Si, Al, Mg, K and Fe concentrations, analysed by UV-VIS, AAS, or ICP-MS, BET surface area and EMPA compositional analyses, were used to derive rate constants.

Our results show that the presence of organic ligands can enhance the dissolution rate of biotite by up to 2 orders of magnitude (Fig. 1). The degree of enhancement of the ligand promoted dissolution, compared to the abiotic dissolution, increases with increasing pH due primarily to the speciation and extent of surface complexation of the organic ligands.

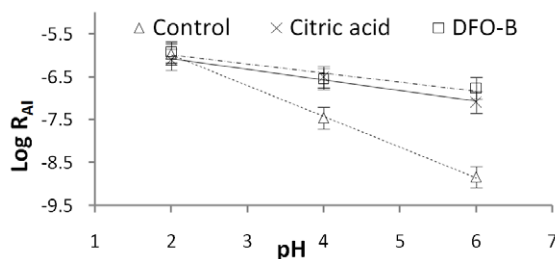


Figure 1. $\log R_{AI}$ ($\text{mol}_{(\text{biotite})} \text{m}^{-2} \text{h}^{-1}$) vs pH from the batch dissolution experiments (control = no organics). Rates were calculated from elemental release data (here Al) and normalised to the EMPA derived biotite stoichiometry.

[1] Malmström and Banwart (1997) GCA **61**, 2779-2799 [2] Bonneville *et al.* (2009) Geology **37**, 615-618