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Environmental Geochemistry of Organic - Inorganic Interactions from Alluvial to Estuarine Systems: A Case Study of the River Conwy, North Wales

James Brydie (jbrydie@fs1.ge.man.ac.uk) & **David Polya** (dpolya@fs1.ge.man.ac.uk)

Department of Earth Sciences, University of Manchster, Oxford Road, Manchester, M13 9PL., UK

The controls on the distribution of Pb between river and estuarine waters and oxic sediments in the River Conwy, North Wales, have been investigated through a combination of field studies, laboratory adsorption experiments and speciation modelling using PHREEQC. Predominant controls placed on metal concentrations were determined to be sediment composition, water composition and type of sedimentary organic matter. Metals mainly result from drainage of the historic Llanrwst Mining District (with attendant tailings dumps) in the upper catchment, and from domestic sewage and limited industrial effluent within the estuary. Field and laboratory techniques were used to determine the predominant controls, particularly with respect to sediment and water composition, on Pb and Zn distribution within oxic alluvial sediments. The <63µm sediment size fractions of nine sediments contained 50 - 90% of heavy metals present in the <2000µm size fraction of oxic alluvial sediments, even though this size fraction only constituted 9% (1 - 30%) of sediment mass. Regardless of alluvial sediment mineralogy (predominantly quartz in the Conwy system), sequential chemical extraction indicated that dissolved Pb and Zn were adsorbed onto operationally-defined sedimentary Fe-Mn (hydr)oxide and organic phases, which are the predominant sinks for heavy metals in the Conwy system. Zn was also associated with sedimentary carbonate phases. The similar grain-scale spatial association of Fe, Pb and Zn, determined using electron probe micro-analysis, clearly showed elevated grain boundary metal concentrations. The adsorption of Pb and Zn onto sediment Fe-Mn (hydr)oxides was found to be mass dependent with Pb and Zn in the sediment Fe-Mn (hyd)roxide phase strongly correlated with abundance of sedimentary Fe-Mn (hydr)oxide (Pb : r = 0.899, Zn : r = 0.799). The relative abundance of Pb and Zn associated with organic matter, compared to Pb and Zn associated with Fe-Mn (hydr)oxides, generally increased upstream. However, poor correlation of Pb and Zn associated with sedimentary organic matter and measured sediment total organic carbon (TOC), indicated that the type of sedimentary organic matter may be important with regard to Pb and Zn sorption capacity.

Batch Pb adsorption experiments in 0.01M and 0.1M $NaNO_3$, and 0.01M, 0.1M and 0.7M NaCl solutions onto the < 63 µm size fraction of whole and H_2O_2 - treated (to remove organic matter) sediments, revealed Pb to be adsorbed by an inner sphere mechanism (chemisorption). Reduced Pb adsorption in concentrated chloride solutions, by up to 55%, was attributed to the formation of poorly adsorbed aqueous Pb-chloride complexes. Adsorption of Pb onto treated sediments exhibited further reduction in Pb adsorption due to the missing organic component. Desorption experiments indicated that adsorbed Pb is unlikely to be desorbed into the water column over the time-scale of a tidal cycle, even with tide associated increases in ionic strength and chloride concentration, hence reducing its bio-availability to all but benthic organisms.

To determine the role of specific organic molecules in metal distribution, oxic alluvial sedimentary organic matter from three type localities along the river, representative of upper catchment, upper- and lower estuary, was characterised and quantified using titrimetric analysis of sediment TOC, thin-layer chromatography, gas chromatography and coupled gas chromatography - mass spectrometry. Carboxylic acids methyl-esters, alcohols, and homologous series of aliphatic hydrocarbons (and phthalates in the estuary) were the most abundant molecules present within each total organic extract (TOE). However, measured sediment TOC concentrations at these localities revealed the TOE to constitute only 8.16×10^{-3}, 1.61×10^{-2} and 3.13×10^{-2}% of TOC at each site, the remainder being humic substances and polymeric organic matter. Comparison of the amounts of TOE and TOC at each site suggests that the organic molecules identified within the TOE may have a limited effect on metal accumulation due to their low concentration in the sediment.