Geophysical Research Abstracts,
Vol. 10, EGU2008-A-01668, 2008
SRef-ID: 1607-7962/gra/EGU2008-A-01668
EGU General Assembly 2008

An integrated geochemical and mineralogical assessment of contaminated aquatic urban sediment: improving risk assessment models

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Urban centres are often key sites for water-side regeneration, with reslting economic, social and ecological benefits. However, such centres have suffered a legacy of pollution which has degraded both water and sediments. It is, therefore, critical that we have an understanding of the interaction between sediment, water and contaminants in these systems if we are to undertake effective environmental risk assessment and remediation. The research presented here is focussed on highly contaminated dock sediments in Manchester in northwest England, and describes the detrital mineralogy, early diagenetic reactions and authigenic mineral precipitates.

The sediments contain a mix of natural and anthropogenic detrital grains. Detrital grains are dominated by quartz and clay grains, whilst anthropogenic grains are dominated by metal-rich glass grains, concentrated at a depth of 12 to 17 cm in the sediment as a result of historical inputs. Sediment porewaters contain significant concentrations of Fe, Mn, Zn and phosphate. Bacterial Fe(III) and Mn(IV) reduction are hypothesised to supply $Fe^{2+}$and Mn^{2+} to porewaters, with phosphate released from Fe oxide reduction or organic matter oxidation. Petrographic observations indicate that the metal-rich glass grains are undergoing chemical dissolution during early diagenesis, supplying Fe and Zn to porewaters, indicating that detrital grain dissolution is an important source of metals to the water column.

The most abundant authigenic mineral in the sediments is vivianite ($Fe_3(PO_4)_2.8H_2O$), containing a significant level of redlingite ($Mn_3^{2+}(PO_4)_2.8H_2O$), with minor framboidal pyrite (FeS_2). Electron microprobe analysis shows the vivianite to contains Zn, Cu and Pb, suggesting that vivianite acts as a long-term sink for these metals in this sediment. EXAFS modelling of the Zn K-edge data, together with linear combination XANES fitting of model compounds, indicates that Zn is incorporated into the vivianite as a Zn-phosphate structure. This implies that authigenic vivianite in this freshwater sediment may act as a long-term sink for metals, in a similar manner to sulfides in marine sediments.

This study highlights that the nature of detrital and diagenetic mineralogy, in addition to porewater and sediment chemistry, needs to be considered in assessing the environmental risk of contaminated sediments.