



The response of dissolved and particulate metals to early diagenesis processes in the freshwater reaches of a macrotidal estuary

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Vertical profiles including the water column, the fluid mud and the consolidated sediment were sampled in the freshwater reaches of the Gironde Estuary during a complete neap tide-spring tide cycle. The vertical distribution of dissolved major redox parameters, dissolved metals (Mn, Fe, Cd, Cu, V, Co, Ni, Mo and U), reactive particulate metals from single selective leaching was determined. The results indicate that the soft mud and the consolidated sediment are affected by the typical redox sequence of organic matter (OM) mineralization. The trace metals show differential release behavior during diagenesis: (1) Cd, Cu and V are released in porewater from OM in the soft mud layer, (2) Co and Ni from Mn oxi-hydroxides during reductive dissolution, and (3) U and Mo from both OM and Mn oxi-hydroxides. Iron is suggested to play a minor role in trace metal release, as low amounts of reactive Fe oxides (lower than 5% of the total Fe content) prevent significant reductive dissolution of Fe oxi-hydroxides. The observed concentration-depth profiles are transient, likely due to soft mud sliding that has induced new redox fronts. Manganese and trace metals previously associated with Mn oxi-hydroxides are revealed to be sensitive indicators of transient diagenetic conditions while trace metals associated with OM do not have record the transient pattern. At depth, Mn is trapped as carbonate, and trace metals are removed from porewater, following the order that defines their respective affinity for sulfides: $Cd > Cu > V > U > Mo > Ni > Co$. However, a non negligible part of the trace metals is trapped in the sediment under exchangeable form, and therefore is susceptible to be mobilized during remobilization of estuarine sediment by strong river flood and/or dredging.