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Reactive iron and manganese in estuarine sediments of the Baltic Sea: Impacts of flocculation and redox shuttling

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Iron (Fe) and manganese (Mn) play important roles in sedimentary carbon cycling in both freshwater and marine systems. Dissimilatory reduction of Fe and Mn oxides is known to be a major pathway of suboxic organic matter remineralization in surface sediments, while recent studies have shown that Fe and Mn oxides may be involved in the anaerobic oxidation of methane deeper in the sediment column (e.g., Egger et al., 2015). Estuaries are transitional environments, characterized by gradients of salinity and redox conditions which impact on the mobility of Fe and Mn. In turn, the distribution of Fe and Mn in estuarine sediments, and the role of the two metals in carbon cycling, is expected to be spatially heterogeneous. However, few studies have attempted to describe the sedimentary distribution of Fe and Mn in the context of processes occurring in the estuarine water column. In particular, salinity-driven flocculation and redox shuttling are two key processes whose relative impacts on sedimentary Fe and Mn have not been clearly demonstrated.

In this study we investigated the coupled water column and sedimentary cycling of Fe and Mn along a 60km non-tidal estuarine transect in the Gulf of Finland, Baltic Sea. We show that riverine Fe entering the estuary as colloidal oxides associated with dissolved organic matter (DOM) is quickly flocculated and sedimented within 5 km of the river mouth, despite the shallow lateral salinity gradient. Sediments within this range are enriched in Fe (up to twice the regional average), principally in the form of crystalline Fe oxides as determined by sequential extractions. The high crystallinity implies relative maturity of the oxide mineralogy, likely due to sustained oxic conditions and long residence time in the river catchment. Despite the reducing conditions below the sediment-water interface, Fe is largely retained in the sediments close to the river mouth. In contrast, sedimentary Mn concentrations are highest in a deep silled basin more than 10km downstream. Throughout the estuary, Mn oxides are reductively dissolved shallower in the sediment column than Fe oxides, resulting in strong effluxes of dissolved Mn from the sediments. Subsequent oxidation of bottom water dissolved Mn to particulate oxides and lateral transport ("redox shuttling") account for the sedimentary Mn enrichments in the deep silled basin. Porewater data suggest that the heterogeneity of Fe and Mn availability in the estuarine sediments may influence the relative importance of the two metals for anaerobic oxidation of methane.

Egger, M. et al., Environmental Science and Technology 49(1), 277-283, 2015.