Spatial variability in pore water biogeochemistry and trace element cycling of a subterranean estuary

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Studies investigating biogeochemical processes in subterranean estuaries (STE) are mostly based on coast-perpendicular transects, reflecting only snapshots of the system with regard to its high spatial variability. However, spatial and temporal heterogeneity in pore water biogeochemistry might lead to uncertainties when concentrations are used to extrapolate submarine groundwater discharge to larger areas. This study assesses the spatial biogeochemical variability of an STE and shows how to use small scale inhomogeneities to deduce biogeochemical processes such as release or fixation mechanisms of trace elements. Study site is the intertidal zone of a mesotidal STE of the southern North Sea barrier island Spiekeroog, located in northern Germany. Pore waters were sampled at 50 cm and 100 cm below the sediment surface on a high resolution grid (200 m x 200 m, 230 samples) and analysed for salinity and Fe. A high spatial variability in salinity and Fe-concentrations was observed. Fe concentrations were generally increasing approaching low water line. There co-occuring local minima of Fe and salinity were found. A process generating such Fe minima can be Fe fixation by Fe-sulfide precipitation due to mixing with Fe depleted, sulfidic fresh groundwater in the freshwater discharge tube. Additionally two coast-perpendicular pore water profile transects, with only 4 m distance in-between, were analysed for nutrients and redox-sensitive trace elements. Site comparisons show that seawater infiltration leads to oxygenated conditions with release of certain trace elements such as Tl, which exceeds seawater concentrations up to 200%. At sites with elevated fresh, but oxygen-poor, groundwater proportions the removal of U, Re, Tl or even Mo from solution was observed as expected under suboxic to anoxic conditions. The transect comparison reveals that the pore water biogeochemistry shows a strong response to changes in redox conditions with respect to changing proportions of seawater and fresh groundwater.