

Lifting the iron curtain: Release of dissolved organic matter (DOM) in an iron(II) reduction zone of the subterranean estuary

HANNELORE WASKA^{1*}, JANIS AHRENS², DANIELA MAIER³, KAI SCHWALFENBERG³, HEIKE SIMON¹, OLIVER ZIELINSKI³, THORSTEN DITTMAR¹

¹ICBM-MPI Bridging Group for Marine Geochemistry, University of Oldenburg. *Email: hannelore.waska@uni-oldenburg.de

²Microbiogeochemistry Group, ICBM, University of Oldenburg

³Marine Sensor Systems Group, ICBM, University of Oldenburg

Subterranean estuaries (STEs) are underground mixing zones of meteoric, fresh groundwater, and tidally- and wave driven recirculated seawater in the coastal aquifer. Along the advective flowpath in the STE, the succession of respiration regimes on one hand and the intrusion of oxygen-rich seawater on the other can result in a complex redox zonation where constituents are either precipitated/scavenged or (re-) released. For example, the “iron curtain”, a zone of iron(III) (oxi)hydroxide precipitation in the STE, scavenges dissolved inorganics such as phosphorous and barium, as well as oxygen-rich, phenolic fractions of dissolved organic matter (DOM) which are characteristic of a terrestrial origin. Here, we report the release of DOM in an iron(II) reduction zone of an STE. This STE is within a wave-exposed beach of a barrier Island, Spiekeroog, located in the German North Sea. Fresh groundwater is seeping into the STE from a precipitation-fed freshwater lens. The STE has a strong marine component, caused by a mesotidal (~2.4 m) regime and turbulent wave-induced mixing. At the low tide waterline, high concentrations of dissolved iron(II) can be found in the porewater. Bulk concentrations of dissolved organic carbon (DOC) and fluorescent dissolved organic matter (FDOM, (Ex/Em 350nm/430nm) showed a positive relationship with iron(II) concentrations, but were weakly correlated to each other, indicating a delineation of sources for FDOM in the unconfined aquifer. FDOM was also negatively correlated with conductivity, pointing to a terrestrial origin of the measured fluorescent fraction. The analysis of solid-phase-extracted DOM via ultra-high resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) further elucidated the evolution of the DOM molecular fingerprint at different stages of iron(II) release.