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Temporal dynamics of rare earth elements in the deep subsurface of the intertidal zone of a high energy beach

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Subterranean estuaries (STEs) are complex biogeochemical reactors, that generate important fluxes of nutrients, organic matter and trace elements to the costal ocean. At high-energy beach sites, the advective porewater flow and associated transport of organic and inorganic constituents reach deep into the subsurface and are subject to high temporal variations. Rare earth elements show differential behaviour across the element series and can therefore provide information on scavenging intensity, provenance, redox changes, and anthropogenic influence. In order to understand the biogeochemical dynamics in these understudied systems, we analysed rare earth elements (REEs) in the intertidal zone of the high-energy beach of Spiekeroog Island (Germany) as part of the research unit DynaDeep (Dynamic Deep Subsurface of High-Energy Beaches, [1]. Porewater samples were collected down to 24 m below ground surface (mbgs) every six weeks over the course of one year (Sept. 2022-Sept. 2023) and analysed for salinity, pH, temperature, dissolved organic carbon, oxygen, nutrients, dissolved trace metals, and concentrations of REE. The zonation of redox conditions remained essentially constant, with seasonal changes of nutrients and O_2 at 6 mbgs. At 12 mbgs, the presence of dissolved Mn indicates reduction of Mn oxides, with Fe oxide reduction starting at 18 mbgs [2]. The REE concentrations in the STE ranged from ~ 40 to 400 pmol/kg for Nd (18 and 12 mbgs, respectively), and from ~15 to 115 pmol/kg for Yb (18 and 12 mbgs, respectively). Although the high REE concentrations clearly point towards a prominent role of Fe/Mn oxide reduction on increasing porewater REE concentrations below 6 mbgs, temporal changes in REE concentrations were only affected by temporal changes in Mn reduction at 12 mbgs. At the other depths, correlation with Si suggests that mixing and porewater age play an important role in temporal REE variations.

[1] The DynaDeep observatory – a unique approach to study high-energy subterranean estuaries, Massmann et al. (2023), *Frontiers in Marine Science* 10, 1189281.

[2] Spatial and temporal dynamics of groundwater biogeochemistry in the deep subsurface of a high-energy beach, Reckhardt et al. (2024), *Marine Chemistry* 267, 104461.