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## Molecular properties of dissolved organic matter (DOM) in the subterranean estuary of a high-energy beach: Finding proxies for reactive transport

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Advective flows of sea- and fresh groundwater through coastal aquifers form a unique ecohydrological interface, the subterranean estuary. Here, freshly produced marine organic matter and oxygen mix with groundwater, which is low in oxygen and contains aged organic carbon from terrestrial sources. Along the underground flow paths, dissolved organic matter (DOM) is degraded and inorganic electron acceptors are successively used up. Because of the different DOM sources and ages, exact degradation pathways are often difficult to delineate, especially in high-energy environments with dynamic changes in beach morphology, source composition, and hydraulic gradients. From a case study site on a barrier island in the German North Sea, we present detailed biogeochemical data from pore water samples collected in the shallow layer of the subterranean estuary. The samples were taken along the major flow paths of recirculating sea water and discharging fresh, meteoric groundwater, and analyzed for physico-chemistry, electron acceptors, and dissolved organic carbon (DOC). DOM was isolated and measured with soft-ionization ultra-high-resolution mass spectrometry, and chemical DOM characteristics were derived by assigning exact molecular formulae to the thousands of intact masses found in each sample. Using geographic and physico-(geo)chemical parameters (longitude, salinity, dissolved silicate, dissolved iron) as indicators of water origin and residence time, we evaluated the behavior of chemical DOM characteristics (H/C and O/C ratios, aromaticity) along the underground flow paths. Overall, DOC concentrations and an H/C-based molecular lability boundary index (MLB) decreased with decreasing oxygen concentrations and parallel increases of dissolved (reduced) iron and dissolved silicate concentrations, in line with the assumption that high H/C ratios are a trait of labile DOM which is continuously degraded. On the other hand, aromaticity indices and relative abundances of a “humic-like” fluorescent DOM fraction increased along the flow paths, likely through accumulation of compounds less susceptible to microbial attack. Our data indicates that even in a highly complex advective flow system like the subterranean estuary, molecular properties of DOM can be harnessed to identify key, perhaps

even site- and season-specific biogeochemical processes.