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Sinks and sources of dissolved organic matter in permeable sediments of the coastal North Sea

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Pore water dynamics in permeable coastal sediments are driven by tides which enhance seawater circulation and advective pore water flow within the sand bodies. The regular tidal fluctuations of dissolved organic matter (DOM) and nutrient concentrations in the water column during tidal cycles illustrate that submarine groundwater discharge is a large source of nutrients to the coastal North Sea. However, little is known about the processing of DOM within the permeable sediments before discharge into the water column. Intertidal zones of the coastal North Sea have been chosen as study sites to investigate the turnover of organic matter from different sources under redox and salinity gradients in permeable sediments. To link the thousands of molecules of the DOM pool to biogeochemical processes we applied a non-targeted multi-tracer approach using ultrahigh-resolution Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR-MS). Pore waters were sampled seasonally down to several meters depth at transects covering the intertidal zones of an anoxic sand flat with seawater circulation and a mainly oxic beach where meteoric water mixes with seawater. The results show that in the tidal flat, sedimentary organic matter was mobilized and transformed into DOM by high microbial activity. A high proportion of organic sulfur compounds in the older sulfidic pore waters of the anoxic tidal flat indicate early diagenetic sulfurization. We therefore hypothesize that stabilization of DOM under sulfidic conditions may form a sizeable fraction of recalcitrant DOM in sediments, e.g. by polymerization due to sulfur crosslinks between unsaturated DOM molecules. Within the oxic beach, the molecular composition of DOM depended mainly on the extent of fresh and sea water input. Despite highly characteristic molecular patterns of DOM from the two study sites, oxic and anoxic pore waters shared around 70% of DOM compounds with coastal North Seawater. This molecular overlap indicates that a significant proportion of less-reactive DOM may be persistent enough to be exported to the coastal ocean.