

Dissolved organic matter characterization along an oxygen gradient in eutrophic coastal marine waters

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Ocean deoxygenation as a result of eutrophication and rising temperatures is an increasing global problem. Coastal waters are especially vulnerable to low oxygen, with large impacts on biogeochemical cycling. Dissolved organic matter (DOM) contributes to biogeochemical cycling in these systems in a variety of ways, for example by acting as a source of carbon and nutrients for microorganisms, or as a metal-binding ligand. These interactions depend on, amongst others, the composition of the DOM pool, which is to date not yet well characterized in coastal waters. Here, we assess changes in the composition of DOM along an oxygen and water depth gradient in the seasonally euxinic Scharendijke basin, located in the eutrophic coastal marine Lake Grevelingen, The Netherlands. Scharendijke basin is characterized by high input of organic material, and anoxic and sulfidic bottom waters during summer stratification. The stratification and absence of oxygen allows ammonium, methane and dissolved manganese to accumulate in the deeper waters of the basin. In this study, we used liquid chromatography to detect concentrations of (fractions of) DOM, such as biopolymers, humic substances, and low-molecular-weight compounds, and liquid chromatography-mass spectrometry for untargeted metabolomics. We find high concentrations of DOM in the lake water and show that, during summer stratification, DOM concentrations are typically highest in the oxic surface waters and remain relatively constant in the deeper, anoxic waters. Humic substances and neutral low-molecular-weight compounds are the most important fractions throughout the water column in terms of carbon concentrations. For humic substances, dissolved organic nitrogen (DON) concentrations and N/C ratios decrease with depth in surface waters, and are relatively constant at depth. DON concentrations and N/C ratios in biopolymers, however, show a minimum within the redoxcline. Proteins constitute an important component of biopolymers throughout the water column, with the protein fraction of biopolymers showing a minimum in the redoxcline, and a maximum in bottom waters. Metabolomics shows signals that correlate with the chemical characteristics of the stratified water column. This work provides insight in the dynamics of DOM along an existing oxygen gradient, which is relevant for the understanding of the effects of deoxygenation on coastal biogeochemistry.