Identifying fluorophores in Arctic shelf seas by PARAFAC analysis of excitation-emission fluorescence spectra of seawater

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Dissolved organic matter (DOM) plays an important role in the environment by supporting growth of marine biota and participating in flocculation of colloid clay particles in estuarine zones; it is also an indicator of organic loadings in streams and terrestrial processing of organic matter.

Studying carbon transport requires the ability to distinguish its different sources. In seawater, carbon sources include autochthonous (of biological or aquatic bacterial origin) and allochthonous (terrestrial runoff) ones. DOM in seawater mostly consists of humic substances which have heterogeneous molecular structure. Detailed characterization of DOM is possible by means of high resolution mass-spectroscopy, which requires large sample volumes (5-10 l) to concentrate and is only possible under laboratory conditions. Different optical methods are also used to study DOM, especially spectrofluorometry. It is impossible to discern separate emission lines corresponding to individual compounds in DOM fluorescence spectra, so instead, a small number of fluorophores with defined optical characteristics is described and correlated to allochthonous protein-like compounds or terrigenous humic substances. Two-dimensional spectrofluorometry, with both excitation and emission wavelengths as independent variables, producing an excitation-emission matrix (EEM), is one of the most informative optical methods for DOM research.

Tensor rank decomposition methods (e.g. PARAFAC) are successfully employed to find the independent components (considered to be correlated to fluorophores) comprising each individual EEM in the dataset. There is still only fragmentary information on PARAFAC components of EEMs of Arctic seawater. In this work, 80 samples of DOM from shelf seas were collected during the cruises to the Kara Laptev, White and East Siberian seas in autumn (2015-2017) and spring (2016). A few samples were taken from freshwater ponds of Novaya Zemlya archipelago. EEMs were recorded in wide ranges of excitation (230–550 nm) and emission (240–650 nm) wavelengths. Spectra were normalized to the area of Raman water peak at 350 nm excitation wavelength. Due to hardware limitations, the data contained unfiltered scattering peaks. A PARAFAC model built from raw spectra did not provide an accurate description of fluorescence and the resulting components only correlated with scattering bands, therefore different techniques were tried to minimize the interference. Zeroing out the wavelength regions where scattering information was present caused step-like artefacts in obtained components, but most of fluorescence information was recovered. Replacing the zeroed out parts of the spectra with smoothly interpolated surfaces resulted in more interpretable components. Subtracting normalized spectrum of clean water did not get rid of scattering signal; resulting components

contained both unneeded scattering information and artefacts caused by attempts to remove them. Decompositions into 5 and 6 factors were obtained, which allowed evaluating the relative distribution of marine and terrigenous DOM in surface waters of the studied areas.

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