



Millennium-scale stabilization of marine dissolved organic matter through thermogenesis

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The global pool of thermogenic dissolved organic matter (thDOM) in the ocean exceeds one petamole (10¹⁵ mole) carbon. Polycyclic aromatic compounds (PCAs) are unique molecular markers of thDOM and their concentration in the oceans exceeds that of any recognizable biochemical compound class, such as carbohydrates, proteins or lignin, making thDOM the most abundant class of organic compounds identified in the oceans.

The existence of dissolved PCAs in the deep sea is unambiguous proof that a fraction of marine DOM has undergone thermal alteration. Turnover rates of thDOM remain largely speculative and the ultimate source of thDOM is unknown. Aerosol deposition and rivers carry pyrogenic DOM to the ocean. Therefore, it seems reasonable to assume a combustion-derived origin of thDOM in the deep ocean. Geothermal heating of sediments and subsequent solubilization of thermogenic compounds and advective fluid transport could also explain the presence of thDOM in the deep ocean. In addition, seawater continuously penetrates the spreading oceanic ridge systems, is heated up and released in hydrothermal vents or diffusive systems. The relative importance of the above processes as sources of thDOM to the deep ocean remains unclear.

The spatial distribution of PCAs in the ocean provides indications on the source and turnover rates of thDOM. The Southern Ocean is particularly suited for studying these distribution patterns because several water masses of different origins and ventilation ages join there. Furthermore, the region off the Antarctic shelf is of global relevance because it is one of the major sites of deep water formation, where surface properties are transported into the deep basins of the three major world oceans. An extensive data set on PCAs was obtained for the Southern Ocean as part of the CLIVAR (Climate Variability and Predictability) Repeat Hydrography program. The objective of this study was to provide estimates on the global turnover of thDOM and to search for new indications of the source of this compound class in the deep ocean. For a validation of the findings on a global scale, the major deep water masses of the Atlantic and Pacific were included in this study.

We conclude that the global annual removal of deep-ocean thDOM is approx. 30 gigamoles (10⁹ mole) per year. Assuming a steady state this removal rate results in an average age of thDOM in the deep ocean of approx. 40,000 years, being the most refractory component of DOM identified on the molecular level to date. In the deep ocean, thDOM is a conservative property of seawater, and removal of thDOM was only observed at the sea surface. The observed surface depletion was carried into the deep sea by sinking of dense water masses in the Southern Ocean. These distribution patterns of thDOM indicate the existence of a major deep-sea source (e.g., hydrothermal fluids) of thDOM. Thermogenesis is the first mechanism identified so far responsible for millennium-scale stabilization of marine dissolved organic matter. This process therefore plays a major role in the global carbon cycle.