



The source and distribution of thermogenic dissolved organic matter in the ocean

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Thermogenic organic matter (ThOM) is abundant in the environment. ThOM is produced at elevated temperature and pressure in deep sediments and earth's crust, and it is also a residue of fossil fuel and biomass burning ("black carbon"). Because of its refractory character, it accumulates in soils and sediments and, therefore, may sequester carbon from active cycles. It was hypothesized that a significant component of marine dissolved organic matter (DOM) might be thermogenic. Here we present a detailed data set on the distribution of thermogenic DOM in major water masses of the deep and surface ocean. In addition, several potential sources of thermogenic DOM to the ocean were investigated: active seeps of brine fluids in the deep Gulf of Mexico, rivers, estuaries and submarine groundwaters. Studies on deep-sea hydrothermal vents and aerosol deposition are ongoing.

All DOM samples were isolated from seawater via solid phase extraction (SPE-DOM). ThOM was quantified in the extracts as benzene-polycarboxylic acids (BPCAs) after nitric acid oxidation via high-performance liquid chromatography and diode array detection (HPLC-DAD). BPCAs are produced exclusively from fused ring systems and are therefore unambiguous molecular tracers for ThOM. In addition to BPCA determination, the molecular composition and structure of ThOM was characterized in detail via ultrahigh resolution mass spectrometry (FT-ICR-MS).

All marine and river DOM samples yielded significant amounts of BPCAs. The cold seep system in the deep Gulf of Mexico, but also black water rivers (like the Suwannee River) were particularly rich in ThOM. Up to 10% of total dissolved organic carbon was thermogenic in both systems. The most abundant BPCA was benzene-pentacarboxylic acid (B5CA). The molecular composition of BPCAs and the FT-ICR-MS data indicate a relatively small number (5-8) of fused aromatic rings per molecule. Overall, the molecular BPCA patterns were very similar independent of the source of ThOM. Petroleum-derived ThOM in the deep Gulf of Mexico had very similar structures than fused ring systems in asphaltenes, but also ThOM in the rivers and groundwaters was similar. First data on aerosols, on the other hand, show a clear difference between particulate and dissolved samples. ThOM from aerosols and most soils was characterized by an abundance of benzene-hexacarboxylic acid (B6CA), different from thermogenic DOM. Dissolution processes may cause partial breakdown of larger fused ring systems and thus cause similar structural units in all DOM samples.

In the deep ocean, the distribution of thermogenic DOM was relatively homogeneous throughout the water column. The concentration of carbon that resides in thermogenic polycyclic aromatic hydrocarbon varied between 610 and 800 nM (1.5-2% of total dissolved organic carbon). The total amount of thermogenic DOM in the deep ocean is approx. one Peta mole carbon globally. The relatively homogenous distribution of thermogenic DOM in the abyssal ocean indicates that thermogenic DOM behaves virtually inert in the abyssal environment.

One of the most striking features is that the oldest water masses, which are not enriched in industrial products (such as the Freon CFC-12) showed highest concentrations of thermogenic DOM. The younger water masses such as Antarctic bottom and intermediate waters are not particularly enriched in thermogenic DOM. This distribution suggests a preindustrial origin of ThOM in the deep ocean. Rivers and deep-sea seep systems were both identified as potential sources of ThOM to the deep ocean. Radiocarbon dating on BPCAs will provide further evidence for the origin of BC in the deep ocean.