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Biogeochemical Chlorination of Marine Organic Matter

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Chlorine has the highest electron affinity of any element. In nature, Cl exists mainly as the chloride anion, which was long considered to be unreactive under environmental conditions. In terrestrial soils, that assumption has proved unfounded, largely due to the revelation of various chlorinating enzymes in soil fungi and other microbes. In seawater, however, there has been comparatively little evidence to change the enduring perception of the unreactivity of chloride. Halogenating enzymes in marine organisms are primarily bromoperoxidases that take advantage of abundant bromide with lower electron affinity. Known modes of natural marine chlorination produce volatile species such as methyl chloride, which is emitted by marine algae and likely forms through the action of methyl transferases.

Using synchrotron-based X-ray absorption spectroscopy at the “tender” energy of the Cl K-absorption edge (˜2,820 eV), we measured high concentrations of organochlorine in naturally degraded particulate organic matter from oceanic sediment traps. In addition, we used X-ray spectromicroscopy to reveal heterogeneously distributed aliphatic and aromatic fractions of organochlorine within the sediment trap material. The major precursor of sedimentary material is phytoplankton biomass, the detritus of which undergoes oxidative breakdown as part of the marine carbon cycle. We hypothesized that unsaturated lipid and protein moieties in phytoplankton detritus would be susceptible to chlorination through oxidative degradation. Using a series of model experiments and a novel X-ray spectroscopic technique, we have shown that algal particulates are readily chlorinated through various abiotic pathways, including photochemical and Fenton-like reactions. These processes produce organochlorine in particulate algal detritus at levels exceeding 0.1% by mass. We have also measured non-volatile natural organochlorine in several species of marine phytoplankton for the first time.

This discovery of abiotic pathways for large-scale chlorination of marine organic matter provided the first suggestion of a marine chlorine cycle involving chemical transformations of chloride. Chlorinated organic matter may represent a particularly stable component of marine organic carbon, with possible implications for preservation in sediments.

Primary author: LERI, Alessandra (Marymount Manhattan College)

Presenter: LERI, Alessandra (Marymount Manhattan College)

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