☒ Talk ☐ Poster

How X-ray Absorption Spectroscopy Has Illuminated Widescale Halogenation of Natural Organic Matter

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The use of synchrotron-based X-ray spectroscopy and microspectroscopy has transformed our understanding of natural halogen biogeochemistry in terrestrial and marine ecosystems over the past 25 years. X-ray absorption near-edge structure (XANES) measurements differentiate between inorganic halides (e.g., Cl^-, Br^-) and organically bound halogens in complex natural organic matter (NOM) samples. Applications of this technique have revealed that NOM is ubiquitously halogenated in a variety of ecosystems, from forest soils to marine sediments to the Arctic tundra.[1] This talk will highlight the major synchrotron-based discoveries that have shaped our knowledge of how chlorine and bromine interact with organic carbon in terrestrial and marine environments. Chlorine bonds to electron-rich substrates in decaying plant litter, forming organochlorine as a likely by-product of oxidative breakdown processes on the forest floor.[2] The organochlorine in plant litter is heterogeneously distributed as aliphatic and aromatic fractions, as revealed by X-ray microspectroscopy.[3] Bromine, appearing at much lower concentrations, acts as a limiting reagent in the bromination of NOM in soils,[4] which occurs through abiotic as well as enzymatic mechanisms.[5] New XANES measurements of Patagonian peat cores show that all bromine is bonded to aromatic carbon; these results, combined with FTIR data, suggest that bromination shields aromatic carbon from degradation over millennial timescales in peat ecosystems.

In marine sediments, a long-observed correlation between organic carbon and bromine[6] has been definitively shown by XANES spectroscopy to be attributable to covalent C-Br bonds,[7] which originate from processes involving iron-catalyzed, photochemical, and enzymatic mechanisms.[8] Seawater chloride undergoes similar transformations, leading to high organochlorine concentrations in marine particulate organic matter.[9] Recent X-ray microspectroscopy results reveal distinct fractions of organically bound Cl and Br in particulate detritus from the oceanic water column, implying that bromination and chlorination occur as separate processes in the marine environment.

References

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