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Compound-specific chlorine and bromine-isotope analysis in organohalogens from the ambient environment

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The field of compound-specific halogen-isotope analysis (CSIA-dHal) is presently in rapid growth for applications in environmental organic chemistry, as a complement to mainly C and H isotopes. As demonstrated in this paper, CSIA-dHal provides an additional isotopic dimension for (i) quantification of biotransformation of regional pollutants, and (ii) source apportionment of compounds in the anthropogenic-natural spectrum. Monitoring of biotransformation of regional pollutants by CSIA-dHal can contribute substantially to the conventional methods of environmental chemistry, yet has been marginally explored. The strength of CSIA-d37Cl in degradation studies of regionally-dispersed anthropogenic organochlorines was tested for DDT, based on bioaccumulated samples from the blubber of Baltic Grey seal. The estimated remaining fraction of initially released DDT to the environment ($\sim$ 7%) is in agreement with similar estimates based on concentration data of DDT and metabolites.

CSIA-Hal may also prove useful to distinguish between chemically identical compounds from biotic (generally natural) and abiotic (generally anthropogenic) sources, respectively. Enzymatic halogenation is hypothesized to yield much depleted dHal

relative to the halogenation reactions used in the chemical industry, as evident from the kinetic isotope effects during enzymatic synthesis of chlorinated aromatics (d37Cl approx. -11‰, vs. -6 to +4 for non-enzymatic synthesis; Reddy et al., 2002). CSIA-?37Cl was performed on octachloro-dibenzo dioxin (OCDD) from ball clay in the Mississippi Embayment, U.S., which exhibit OCDD concentrations up to 1000 times higher than the average environmental background. A natural origin was already concluded in this case, but data from CSIA-d37Cl ($\sim$0 ‰) clearly indicated an abiotic origin. This supported the hypothesis of natural clay-surface mediated synthesis of OCDD in ball clay, as opposed to the alternative hypothesis of biotic enzyme-mediated synthesis.

Analysis for CSIA-d37Cl was performed by isolation of target compounds in preparative capillary gas chromatography, followed by sealed-tube combustion and thermal-ionization mass spectrometry (TIMS). This enabled analysis of the equivalent of 5 μg Cl. In order to persue investigations of biotransformation and source apportionment of organobromines, we currently develop CSIA-d81Br by means of gas chromatography hyphenated to inductively-coupled plasma multi-collector mass spectrometry (GC-ICP-MC-MS). Among the first applications will be analysis of compounds with similarity to metabolites of brominated flame retardants, in order to try and differentiate between an anthropogenic and a putative natural origin.

References:

C.M. Reddy et al. (2002) Journal of the American Chemical Society, 124, 14526-14527.