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Investigating abiotic and biotic degradation processes of chlorinated compounds using a new method for compound-specific stable chlorine isotope analysis

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During biodegradation and chemical transformation processes, a significant shift in stable isotope ratio can be frequently observed. Demonstrating the shift in stable isotope ratio within a contaminated plume can be strong evidence that degradation processes take place within the plume. Further, when the shift is quantified using e.g. stable isotope fractionation factors on a single or multiple elements, on-going degradation process in the plume can be specified (e.g. anaerobic or aerobic; abiotic or biotic) and the efficiency of the processes can be effectively evaluated.

Compound-specific stable isotope analysis (CSIA) is a technique to determine the shift in stable isotope ratios of environmental pollutants as well as to derive isotope fractionation factors. CSIA can be therefore one of the essential tools to investigate degradation mechanisms in contaminated groundwater and soil.

Currently, the majority of compound-specific stable isotopic studies on chlorinated compounds focus only on carbon isotopes because the application of the CSIA on chlorine, another relevant element, is still limited by the analytical techniques.

Unlike stable carbon isotope analysis, stable chlorine isotope analysis by traditional methods cannot be carried out without upstream, labor-intensive, offline pretreatments to convert chlorinated compounds into a molecule containing a single chlorine atom, such as methyl chloride (CH_3Cl) or cesium chloride (CsCl). By recently published online methods, compound-specific stable chlorine isotope analysis can be performed without upstream pretreatment. Yet, these methods require a dedicated mass spectrometer (e.g. GC/MC-ICPMS, CF-IRMS).

Supported by BMBF (German Federal Ministry of Education and Research) Funding Priority KORA, Institut WAR at Darmstadt University of Technology developed a new simple and rapid method to perform online chlorine CSIA by direct injection using a standard quadrupole GC/MS system. By this method, the CSIA for a typical groundwater sample that contains chlorinated ethenes and ethanes can be completed within 30 minutes.

The feasibility as well as accuracy of the method was demonstrated in a series of lab-experiments. Further, stable chlorine fractionation factors were derived through several batch tests, including (1) abiotic reductive dechlorination of TCE using zero-valent iron, (2) strict anaerobic dechlorination of PCE using *Sulfurospirillum multivorans* and (3) anaerobic dechlorination of TCE using a mixture of subspecies of *Dehalococcoides ethenogenes*. The results of these experiments indicate that compound-specific stable chlorine isotope analysis can be performed with sufficient precision by means of a conventional quadrupole GC/MS when significant fractionation takes place during biochemical degradation processes.