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Site-Specific Stable Carbon Isotope Study of the Oxidation of Methyl tert-Butyl Ether by Potassium Permanganate using an Advanced On-line Position Specific Stable Isotope Analysis System.

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Microbial attacks on contaminants in the subsurface always involve the breaking or the forming of a chemical bond. Isotopic fractionation might occur during the reaction. Studies of the environmental fate of contaminants have demonstrated that while non-degradative processes, such as volatilisation and sorption, have less significant effects on stable isotopic signatures, some microbial degradation may generate substantial carbon or hydrogen isotopic fractionation. Therefore, the study of the evolution of the isotopic signatures of contaminants through time and space using compound specific isotope analysis (CSIA) has been extensively used in the last decade as a tool for calculating the extent of biodegradation and its overall contribution to the natural attenuation of contaminants in the subsurface. Combined carbon and hydrogen CSIA data have also been used for elucidation of biodegradation pathways; the unique combination of the carbon and hydrogen Rayleigh enrichment factors of biodegradation reactions may enable distinction between mechanisms.

Carbon isotopic fractionation occurring during microbial degradation, however, is the most important at the site of attack whilst the stable isotope ratios of the other carbon atoms in the molecules remain mainly unchanged. While the intra-molecular isotopic variations are hidden in CSIA, position specific or site specific isotope analysis (PSIA) can unveil which moieties are affected by the degradation. PSIA of contaminants therefore has the potential to 1) identify the sites of microbial attack and therefore help in the elucidation of biodegradation pathways, 2) monitor the biodegradation by determining the local kinetic isotope effect and 3) link a contaminant to its source using the stable carbon isotopic signature of the non reacting moieties.

We developed a new tool for on-line continuous flow PSIA. In this on-line position carbon stable isotope analysis (carbon PSIA) system, the analyte of interest is first pyrolysed before that the carbon isotopic signature of its pyrolysis fragments is determined.

In this study, we present the site specific isotope analysis of the oxidation by potassium permanganate of the gasoline oxygenate methyl tert-butyl ether (MTBE). The oxidation was chosen because it is thought to involve the same reaction pathway as some aerobic microbial attacks on MTBE and that its isotopic effects have been well characterised in the literature.

Optimal pyrolysis of MTBE through the on-line PSIA system produces two pyrolysates, isobutylene and methanol, which are representative of the two functional groups of the ether: the methoxy group and the 2-methyl propane group. Absolute δ13C values for these two groups could be determined through the system with 95% confidence intervals of 0.4‰ and 0.5‰ respectively. After 676 minutes of reaction with potassium permanganate, the carbon isotopic signature of the 2-methylpropyl group remained unchanged while the δ13C value of the methoxy group became enriched by 22.8‰ identifying the carbon atom of the methoxy group as the site of attack of the reaction and the 2-methylpropyl group as a non reactive group.

The enrichment factors for the whole MTBE molecule were also established using classic CSIA for hydrogen (εH=-38‰\$±3‰ (95% CI)) and carbon (εC=-4.9‰\$±0.1‰ (95% CI)). The combination of a low carbon enrichment factor with a more significant hydrogen enrichment factor found was in agreement with results previously published for this reaction and also pointed towards the oxidation of the methyl group as the first step of the reaction.

These results obtained with a well-characterised reaction permitted to validate the on-line PSIA system as a tool for identification of the first site of attack in chemical or biochemical reactions involving MTBE.