

STABLE ISOTOPE FRACTIONATION RESULTING FROM BIOTIC AND ABIOTIC MTBE ATTENUATION PROCESSES

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Compound-specific isotope analysis (CSIA) is a technique gaining popularity in the studies of biodegradation of groundwater contaminants (such as BTEX, chlorinated ethenes and MTBE). The benefit of CSIA for environmental studies lies in providing a tool for monitoring *in-situ* biodegradation, eliminating the need to verify biodegradation potential of a site by microcosm experiments. This presentation will discuss the application of CSIA to MTBE attenuation studies. Results published to date¹⁻⁶ indicate that: (i) it is practical to distinguish between the effects of aerobic and anaerobic MTBE biodegradation by combined carbon + hydrogen CSIA (Figure 1); (ii) the magnitude of carbon isotopic fractionation in the anaerobic process is large and apparently consistent among different anaerobic microbial cultures (carbon isotope enrichment factors reported in literature for three different anaerobic cultures are between -9.2 ± 5.0 and -15.6 ± 4.1) and (iii) there is little evidence of mineralization of the tert-butyl group of MTBE (tert-butyl alcohol accumulates upon MTBE degradation).

This presentation will show new data from anaerobic, MTBE-degrading microcosms, aiming at accurate determination of carbon and hydrogen isotope effects. The values of carbon isotope enrichment factor were obtained from six different methanogenic and sulfate reducing cultures grown in agitated soil to assure uniform medium distribution and accurate calculation of enrichment factors. The resulting carbon isotope enrichment factors are similar to each other and higher than the previously reported ones, clustering between -17 and -20 . It is proposed that calculation of anaerobic biodegradation progress based on Rayleigh model should use the latter value (the maximum isotope effect necessary for conservative estimate of biodegradation). Hydrogen isotope data are consistent with the previously published results obtained from field samples^{3,6}. Hydrogen enrichment factor interpolated from the 2D-CSIA data is approximately -30 (i.e., the net hydrogen effect is similar to that of aerobic MTBE biodegradation).

Abiotic *in-situ* degradation of MTBE is possible either at sites treated by chemical oxidation remedies or due to spontaneous acid hydrolysis. Examples of isotope fractionation will be shown for laboratory experiments on Fenton reagent degradation and acid hydrolysis

of MTBE. In both cases, isotope effects are in agreement with the proposed reaction mechanisms. 2D-CSIA trends resulting from both reaction types are identical to those resulting from biological aerobic MTBE degradation.

Published data on isotope effects upon phase partitioning, volatilization etc. suggest that these processes result with minor isotope fractionation and should not interfere with the studies of biodegradation. It will be shown that under certain environmental conditions, measurable changes of carbon and hydrogen isotope ratios are likely due to MTBE volatilization from aqueous or hydrocarbon phase. While the magnitude of those changes is low in comparison with those due to anaerobic biodegradation, volatilization and aerobic biodegradation can be difficult to distinguish from each other.

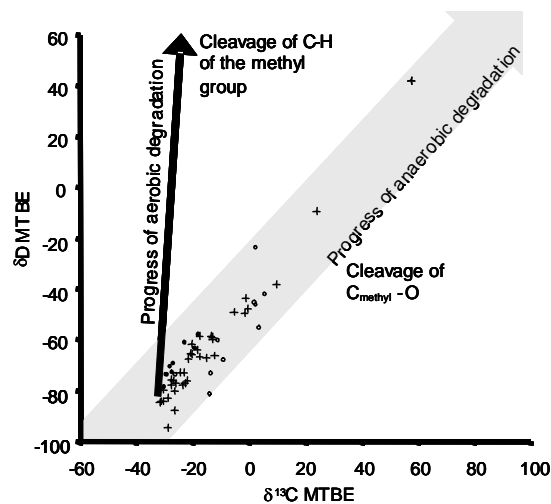


Figure 1. Bimodal distribution of 2-D CSIA data for aerobic and anaerobic degradation of MTBE.

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