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# Stable isotope fractionation resulting from biotic and abiotic MTBE attenuation processes

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This presentation will discuss the application of compound-specific isotope analysis (CSIA) to MTBE attenuation studies. Data in the literature indicate that: (i) the effects of aerobic and anaerobic MTBE biodegradation can be distinguished by combined carbon + hydrogen CSIA (2D-CSIA); (ii) the magnitude of carbon isotopic effects in the anaerobic process is large and consistent among different cultures (enrichment factors reported in literature for three different cultures are between -9.2 $\pm$ 5.0 and -15.6 $\pm$ 4.1) and (iii) there is little evidence of mineralization of the tert-butyl group of MTBE (i.e., tert-butyl alcohol accumulates). 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. The obtained 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 for conservative estimate of the extent of biodegradation. 2D-CSIA data are consistent with the previously published results obtained from field samples. Hydrogen enrichment factor interpolated from the 2D-CSIA is approximately –30 (i.e., similar to that of aerobic MTBE biodegradation). Abiotic in-situ degradation of MTBE can occur due to in-situ oxidation remedies or due to spontaneous acid hydrolysis. Examples of isotope effects will be shown for laboratory experiments on Fenton reagent degradation and acid hydrolysis. In both cases, isotope effects are in agreement with the proposed reaction mechanisms and their 2D-CSIA trends are similar to those resulting from aerobic biodegradation of MTBE. Published data on phase partitioning, volatilization etc. show only minor isotope effects and sug-

gest that they should not interfere with the studies of in-situ biodegradation. It will be shown that under certain environmental conditions, measurable changes of isotope ratios occur due to MTBE volatilization from aqueous or organic phase. While the extent 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.