MODELING ISOTOPE FRACTIONATION ASSOCIATED WITH AQUEOUS PHASE DIFFUSION

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During the last decade, many researchers have reported stable carbon/hydrogen isotope fractionation during the biodegradation of petroleum hydrocarbons and chlorinated solvents, both at the laboratory and field scale. Compound specific isotope analysis (CSIA) is now recognized as a novel and powerful tool for monitoring intrinsic biodegradation of organic contaminants in the subsurface. However, it is important to quantify the isotope effects related to other natural attenuation processes such as diffusion. In this way, one can determine whether or not isotopic changes in systems in which intrinsic biodegradation is occurring are significantly confounded by other less fractionating processes.

A numerical model was employed in this study to investigate the carbon isotope fractionation related to aqueous phase diffusion at a hypothetical field site under a range of hydrogeological conditions. In these simulations, the diffusion coefficients of methyl tert-butyl ether (MTBE) molecules containing only light 12C and MTBE molecules containing a heavy 13C at one position were related to their respective molecular weights. In the simulations of transport in an aquifer, the different diffusion coefficients of the light and heavy isotopes did not lead to significant isotope fractionation during MTBE transport when typical soil dispersivity values and groundwater flow rates were used. Any fractionation related to diffusion was completely masked by mechanical dispersion, because the mechanical dispersion coefficient was several orders of magnitude larger than the molecular diffusion coefficient.

When an aquifer is bounded by a low permeability clayey aquitard, MTBE may diffuse into the aquitard with transport within the aquitard dominated by diffusion. In this scenario, the model predicted significant isotope depletion in the aquitard at the leading edge of the diffusion front, although the difference of the diffusion coefficients of the two MTBE species was very small. Detection of these diffusion effects on i sotope depletion in the field would only be possible if localized water samples could be taken from within the clayey aquitard. Monitoring wells in most field investigations, with typical screen lengths, would sample preferentially from higher permeability zones where advection and dispersion would be dominant over diffusion. Therefore, it is likely that isotopic effects measured in most field investigations would not be related to diffusion processes.