

## **Application of novel model approaches to enhance the strength of stable isotope analysis in quantifying pollutant degradation in groundwater**

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**Abstract** Compound-specific isotope analysis (CSIA) has been applied to detect the degradation of low-molecular-weight priority organic pollutants in groundwater such as chlorinated aliphatic hydrocarbons (CAHs), mono-aromatic hydrocarbons (BTEX), methyl tert-butyl ether (MTBE), and perchlorate. The CSIA method is based on the fact that the heavy isotopes (e.g.  $^{13}\text{C}$ ) of an element in a molecule become relatively slower degraded than the more abundant light isotopes (e.g.  $^{12}\text{C}$ ) resulting in an increase in isotope ratio (e.g.  $\delta^{13}\text{C}$ ) of the residual molecule. The ratio of the degradation rate constants of the two isotopes, the kinetic isotopic fractionation factor, is usually constant, and relates the increase in isotope ratio with the extent of transformation. Since other nondegradative processes such as sorption only involve negligible isotope fractionation, any observed increase in isotope ratio is thought to reflect the occurrence of mass destruction. Although the research field of CSIA is rapidly progressing, the development of models that enable accurate quantification of (bio)degradation based on CSIA data has remained behind. The Rayleigh equation (R-eq) developed by Lord Rayleigh in 1896 is commonly applied but it suffers from some major limitations including not describing the sequential degradation of intermediate degradation products. The R-eq is in fact an analytical approximation obtained from combining and integrating the individual transformation rates of the two isotopes of an element in a substrate. An alternative approach that overcomes the limitations of the R-eq and opens huge possibilities is the incorporation of isotope fractionation processes in reactive transport models (RTMs). Recently, I developed both reactive transport models that incorporate isotope fractionation, as well as extended analytical Rayleigh-type equations in order to improve both the accuracy as well as the potential of CSIA to quantify pollutant degradation processes in groundwater. I will illustrate the strength of these novel modeling approaches to cases including (i) the degradation of a MTBE pollution plume as occurring via both aerobic and anaerobic degradation by means of an improved solution to two-dimensional isotope analysis (e.g.  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$  combined), and (ii) the potential competition among biological reductive dechlorination, abiotic reduction, and biological (anaerobic) oxidation of chlorinated aliphatic compounds like trichloroethene (TCE) as investigated at six field sites in the Netherlands, where accumulation of intermediates such as cis-1,2-dichloroethene (cDCE) and vinyl chloride (VC) was observed.

**Key words** compound-specific isotope analysis; reactive transport modeling; chlorinated ethenes; MTBE