

Stable isotope fractionation of bioreactive compounds in a decay chain: analytical solutions and analysis of assessment methods

S. Jin, Department of Earth Sciences – Geochemistry, Utrecht University, Utrecht, The Netherlands

M. Thullner, Department of Environmental Microbiology, Helmholtz Centre for Environmental Research – UFZ, Leipzig, Germany

Key words: biodegradation, compound-specific stable isotope analysis, reactive transport simulation, analytical solutions

Introduction

Groundwater contamination caused by organic constituents, including pesticides, herbicides, solvents or mineral oil products is a major environmental problem in many industrial countries. In order to ensure safe water supply, in-situ biodegradation has frequently been considered as a site cleanup approach since it is efficient and cost-effective. Among the many strategies for monitoring and assessing biodegradation, compound-specific stable isotope analysis (CSIA) has become one of the most promising ones. For a quantitative analysis of stable isotope fractionation, the classical Rayleigh model, which relates concentration changes of the degraded compound to changes in its isotope signatures, has gained extensive usage. This model only accounts for single species undergoing a one-step reaction in a closed system. In a gradual biotransformation along a decay chain often encountered in the environment, intermediates are produced and consumed. An example of such a decay chain is the sequential reductive dechlorination reaction of trichlorobenzene (TCB) to dichlorobenzene (DCB) and then to monochlorobenzene (MCB). MCB might further be reductively dechlorinated to benzene, or it can also be completely mineralized under anaerobic conditions. In addition, the transport of these decay chain members in a system complicates the situation further as the different compounds might exhibit different mobilities. While the classical Rayleigh model cannot be used directly in this situation, new approaches are required to quantify the biodegradation of all members in a decay chain, and thus determine whether complete biodegradation of the original contaminant has occurred.

Many recent studies have focused on developing analytical approaches to calculate isotope signatures during biodegradation along decay chains. These approaches are however limited e.g., considering the same retardation (i.e., ignoring potential chromatographic effects) of all species or steady state conditions, or requiring rather complex and numerical inverse transforms to avoid the tedious process to deduce them analytically in the time domain. As a consequence of the limitations of these previous studies, there is still the necessity to obtain analytical solutions which are able to calculate isotope signatures of the intermediate species in a decay chain in reactive transport systems under transient conditions. Due to the difficulties assessing the fate of the individual species within a decay chain, an isotopic mass balance approach has been proposed to assess whether complete biodegradation has occurred or if any persistent (and potentially harmful) intermediates accumulate (e.g., [1]). However, this isotopic mass balance approach might be challenged under transient conditions and/or when each of the individual compounds has distinct physico-chemical properties. The later may lead to varying retardation factors of the involved compounds and a chromatographic effect with a preferential transport of the less retarded compounds will occur. Furthermore, to calculate the degree of total degradation of all compounds in a decay chain, Appeli et al. [2] presented an equation using a modified Rayleigh approach, which requires knowledge of an overall isotope fractionation factor for all compounds (α_{tot}). To calculate this overall isotope fractionation factor, Aeppli et al. estimated its maximum and minimum value for a decay chain. Since these methods have been applied without any verification, it would be of interest to examine them using analytical solutions or numerical models.

Used Approach and Results

This study introduces a newly developed analytical solution to calculate isotope signatures of intermediate species of a decay chain in a one-dimensional advective-dispersive transport system with first-order degradation under transient condition, which allows expressing isotope signatures as function of observables without the need of numerical solutions. The analytical solution is verified using numerical simulations considering the same processes. The presented analytical approach appropriately describes the transient behavior of an expanding plume without any knowledge of the “age” of the plume. The analytical results still depend on a priori unknown parameters. For application to real world data, knowledge of the parameter describing the conservative transport at a given site need to be obtained independently (e.g., by using tracer data). With this the only remaining unknown parameters are the first-order degradation rate parameters. By fitting the analytical solution to experimental data of concentrations and isotope signatures of species within a decay chain would allow estimating these rate parameters and thus determining the extent of degradation of the individual species. Numerical simulation were further used to investigate whether the isotopic mass balance approach is still valid in presence of chromatographic effects and at transient conditions, and to verify the previously presented methods for calculating the overall isotope fractionation factor α_{tot} for a decay chain. The obtained results show that the presence of chromatographic effects influences interpretation of $\delta^{13}C_{tot}$ values and the isotope mass balance approach for transient plumes. For the realistic case of the daughter products in a decay chain having a weaker sorption tendency than the respective mother species, the increase in $\delta^{13}C_{tot}$ due to a further degradation of the end member of the (balanced) decay chain is counter acted by the chromatographic effect. The isotope mass balance may thus suggest the absence of any end member degradation even if it takes place. However, at any circumstance an increase of $\delta^{13}C_{tot}$ values indicates the presence of such end-member degradation and the isotope mass balance approach provides a conservative estimate on the occurrence of this process. In the opposite case of daughter products having a stronger sorption/retardation than their respective mother species chromatographic effects and end member degradation would induce the same trend in the changes of $\delta^{13}C_{tot}$ values along a flow path. The isotope mass balance approach might thus lead to the false indication of end-member degradation. To our knowledge no real world examples exist for this problem and thus the application of the mass balance approach for the interpretation of field data is not limited. For the estimation of the overall isotope fractionation factor α_{tot} previously published approaches may fail for specific circumstances and we propose a more accurate modified estimation procedure.

References

- [1] N. Stelzer, G. Imfeld, M. Thullner, J. Poser, H.H. Richnow and I. Nijenhuis. Integrative approach to delineate natural attenuation of chlorinated benzenes in anoxic aquifers. *Environ Pollut.*, **157**, 1800-1806, (2009).
- [2] C. Aeppli, T.B. Hofstetter, H.I.F. Amaral, R. Kipfer, R.P. Schwarzenbach and M. Berg. Quantifying in situ transformation rates of chlorinated ethenes by combining compound-specific stable isotope analysis, groundwater dating, and carbon isotope mass balances. *Environ. Sci. Technol.*, **44**, 3705-3711, (2010).