

# Determination of the Compound-Specific Isotope Signature of Chemical Pollutants

## New Perspectives in Contaminant Hydrology

Analytical methods have evolved to a point where it becomes possible to determine the isotopic composition of individual chemical compounds at low detection limits. These advances have opened new possibilities for the assessment of contaminated ground water. EAWAG intends to optimize established analytical methods for their application in contaminant hydrology.

Groundwater contamination by organic compounds is a common problem in industrialized countries. Chemicals that are used in large quantities, such as fuels or metal degreasing and dry cleaning agents, can reach the ground water directly from point sources (accidental spills, leaking underground storage tanks) or via diffuse pathways (atmospheric deposition, runoff from roads), and thereby compromise its use as a drinking water reservoir.

### Problems in the Clean Up of Contaminated Ground water

*In situ* methods are becoming increasingly more important in the clean up of contaminated ground water. These include all methods where the contaminant is degraded directly in the subsurface, either by natural or by stimulated processes. The financial

benefits of *in situ* over *ex situ* methods are tremendous. *Ex situ* remediation is typically very labor and resource intensive and requires excavation and removal of contaminated material. In the case of readily degradable contaminants, *in situ* remediation may simply be a matter of following the concentration of the contaminant over time in order to determine whether or not and how fast degradation is occurring. It is often difficult, however, to conclusively show that degradation is taking place. Traditional approaches are based on mass balances for the contaminants in the ground water. In the case of slow degradation rates, this can lead to unreliable results, since balances have to be established for extended periods of time and because the spatial distribution of the contaminant plume often is poorly documented. Even in areas with well-

defined hydrogeological conditions and a dense network of monitoring wells, it is rarely possible to determine unequivocally degradation or transformation rates in ground water. Whenever contaminant loss is observed, it is usually not possible to discern whether the disappearance was due to dilution, evaporation, sorption, microbial degradation or abiotic reactions. To make matters worse, transformation processes may not necessarily form exclusively harmless products, but can lead to products that are more difficult to degrade or more toxic than the original compound (Fig. 1). Before we can use the so-called "monitored natural attenuation" approach in complex contamination situations, we need a better understanding of the system.

### Assessment of Contaminant Behavior by Single Compound Isotope Measurements

The determination of stable isotope ratios for individual contaminants is an elegant method for gaining additional information about the efficiency of *in situ* degradation processes. Most elements occur in more than one stable isotopic form. The carbon atom, for example, can have a mass of 12 or 13 atomic units. Any organic molecule will contain both isotopes in a defined ratio ( $^{13}\text{C}/^{12}\text{C}$ ). Today, we are able to measure stable isotope ratios of the elements H, C, N, O, S and Cl for individual compounds present in environmentally relevant concentrations. The various transport and transformation processes in the ground water change the isotopic signature of the elements in the contaminants in different ways. The stability of a chemical bond depends on the isotopic composition. Bonds be-



Zurich city police

Following derailment of a train near Zurich-Affoltern in March of 1994, an estimated 70 tons of gasoline were spilled.

tween lighter isotopes (e.g.,  $^{12}\text{C}$ - $^2\text{H}$ ) are more readily broken than bonds between heavier isotopes (e.g.,  $^{13}\text{C}$ - $^2\text{H}$ ; see Fig. 2). Since chemical reactions occur at varying rates, depending on which isotopes are involved in the bonds being broken, the isotopic ratios in the reaction products are shifted relative to the ratios in the starting compounds. The isotopic signature of a particular compound as a function of location and time can, therefore, be used as a tracer for the type and rate of transformation processes occurring in the ground water (Fig. 3) [1–3]. Additionally, contaminants of different origin can have different isotopic signatures [4]. In such a case, isotopic ratios can be used to identify the source of the contamination or the polluters.

### Isotope Ratios of Individual Compounds as a Research Project at EAWAG

Determination of isotopic signatures of groundwater contaminants is a new approach in contaminant hydrology, where the contaminants themselves are the tracers. In the department “Water Resources and Drinking Water”, isotope analysis of individual compounds is currently being developed as a method specifically for the use in contaminant hydrology. The primary tool consists of a so-called GC-IRMS (gas chromatograph-isotope ratio mass spectrometer) that was recently purchased in cooperation with ETH-Zurich.

In a project that was initiated in 2000, EAWAG is studying the isotope effects of different degradation processes, both in the laboratory and in field experiments. Compounds being investigated include the solvents trichloroethylene, perchloroethylene, and the gasoline additive methyl tertiary butyl ether (MTBE). With the information gained from the project, we hope to identify degradation processes, quantify transformation rates, and identify the source(s) of contaminants in “real world” situations. In order to describe the behavior of persistent contaminants in the soil or in the ground

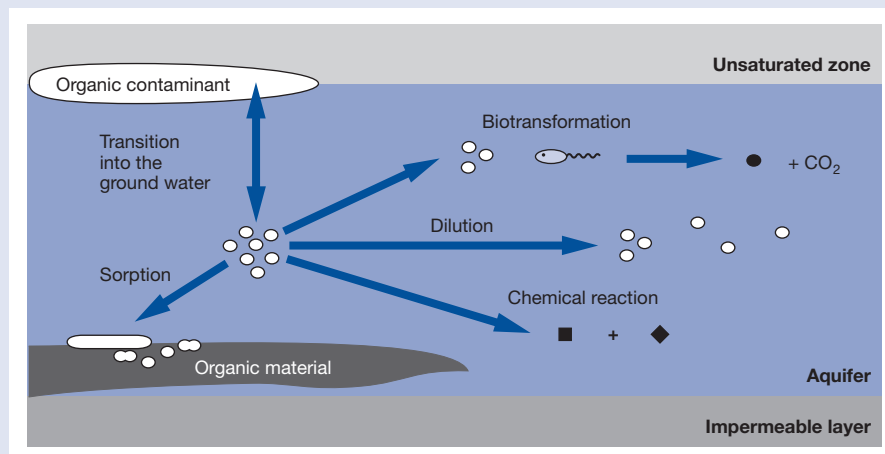


Fig. 1: Transport and transformation processes of organic contaminants in the ground.

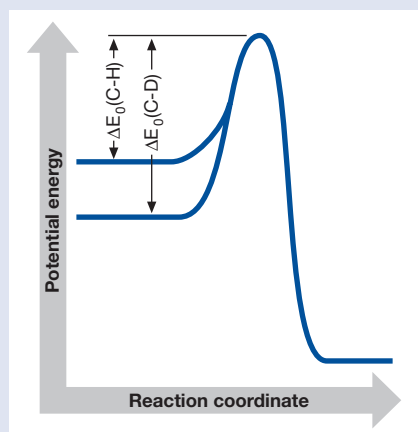


Fig. 2: Effect of isotopic composition on bond energies and reaction rates.

The potential energy of a carbon-deuterium bond (C-D) is lower than that of a carbon-hydrogen bond (C-H). For this reason, the C-H bond is broken seven times faster than the C-D bond at room temperature. During the degradation of a compound, molecules containing lighter isotopes react faster. Reaction products become enriched in lighter isotopes, while the starting material becomes enriched in heavier isotopes (see example in Fig. 3).

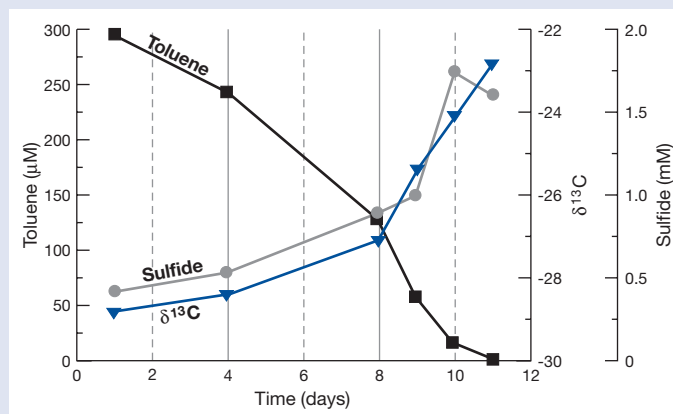


Fig. 3: Degradation of toluene under anaerobic, sulfate-reducing conditions [3]. The disappearance of toluene corresponds to the formation of sulfide and yields a closed electron balance. Anaerobic degradation of toluene leads to isotope fractionation. The  $\delta^{13}\text{C}$  value of toluene increases, i.e., the remaining toluene becomes enriched in the heavier carbon isotope.

water quantitatively, single compound isotope ratio methodology is combined with methods for groundwater dating and groundwater modeling.



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- [1] Bloom Y., Aravena R., Hunkeler D., Edwards E., Frapce S.K. (2000): Carbon isotope fractionation during microbial dechlorination of trichloroethene, cis-1,2-dichloroethene, and vinyl chloride: implications for assessment of natural attenuation. *Environmental Science and Technology* 34, 2768–2772.
- [2] Dayan H., Teophilo A., Abrajano J., Sturchio N.C., Winsor L. (1999): Carbon isotopic fractionation during reductive dehalogenation of chlorinated ethenes by metallic iron. *Organic Geochemistry* 30, 755–763.
- [3] Meckenstock R.U., Morasch B., Warthmann R., Schink B., Annweiler E., Michaelis W., Richnow H.H. (1999):  $^{13}\text{C}/^{12}\text{C}$  isotope fractionation of aromatic hydrocarbons during microbial degradation. *Environmental Microbiology* 1, 409–414.
- [4] BenetEAU K.M., Aravena R., Frapce S.K. (1999): Isotopic characterization of chlorinated solvents – laboratory and field results. *Organic Geochemistry* 30, 739–753.