

The Combined Use of Environmental Tracers and Stable Isotopic Techniques to Assess the Degradation of Organic Compounds in Groundwater: a Case-Study.

Helena Amaral, Christoph Aeppli, Michael Berg & Rolf Kipfer

EAWAG – Swiss Federal Institute for Aquatic Sciences and Technology, Dübendorf, Switzerland.

Natural attenuation of organic compounds in aquatic systems has been a subject of research drawn by the necessity of remediation strategies. Contamination of aquifers by chlorinated compounds is one of the most common in industrialized countries. These substances are mainly used as solvents and enter groundwater by leaching, where they are present as a dense non-aqueous phase and tend to spread in complex spatial patterns. In aquifers, chlorinated substances are persistent and degrade very slowly under aerobic conditions.

For the assessment of natural degradation of organic compounds in contaminated aquifers at the field scale, it is proposed the application of both environmental tracers and stable isotopic methods. The phase of degradation of an organic compound can be evaluated by means of stable isotopic fractionation, and rates of degradation may be estimated by determining the groundwater residence time in an aquifer. The combination of both methods, represent a step forward in the understanding of the fate of these substances, under natural conditions, on the time and space scales. Therefore, our approach foresees a critical assessment of contaminated field sites, being a valuable additional tool to the traditional mass-balance studies.

The success of this application has advantages over the traditional mass-balance studies, which are commonly used to determine the transformation of contaminants at field sites. A decrease in the concentration does not necessarily indicate undergoing degradation since concentration values are highly dependent on dilution and sorption processes. In contrast, chemical-physical processes leading to natural attenuation can be reliably identified by stable isotope techniques.

The environmental tracers (tracers of natural origin) imprint the environmental conditions as natural processes take place. Noble gases are optimal tracers, as their equilibrium concentration in water is only dependant on the physical conditions prevailing (i.e. temperature, salinity and pressure), and are used to determine the groundwater flow and mixing processes. Transient tracers as the gases ^3H , SF_6 and CFCs have a time dependant input in the atmosphere, and are therefore mostly used for the determination of water residence time. The ^3H - ^3He dating method is based on the decay of the radioactive ^3H to the noble gas ^3He and the SF_6 and CFCs dating method on atmospheric input curves.

The progressive degradation of organic chlorinated compounds through dechlorination, leads to a carbon isotope fractionation, where the heavy isotope ^{13}C is commonly enriched in relation to the educt product, along the transformation chain. Similar isotopic shifts are observed if substances degrade subsequently along a contamination plume. Such isotopic fractionation inferred from the $\delta^{13}\text{C}$ of a single

compound can now be precisely determined on a routine basis, by the development of recent analytical protocols for Compound-specific Stable Isotope Analyses (CSIA).

We present data referring to a two-aquifer system, where the upper aquifer is highly contaminated in volatile organic compounds and the lower has very low concentrations of PCE only. The combined methods allowed the distinction of both aquifers, in terms of water residence time and flow directions, and the origin of the PCE present. The water in the upper aquifer has longer residence times than the lower one. The almost hydraulic stagnation of the upper aquifer has lead to reductive conditions, which permitted the natural degradation of the PCE. The PCE in the lower aquifer has a constant $\delta^{13}\text{C}$ along the flow path. The presence of aerobic conditions will probably not allow for the degradation of PCE.