



Application of CSIA and Groundwater Dating to Assess the Natural Attenuation of Chlorinated Ethenes in the Field: Potentials and Limitations.

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We have assessed the natural transformation of PCE and TCE in groundwater at the field scale by combining the use of groundwater dating techniques with compound-specific stable isotope analysis (CSIA). CSIA has been applied recently as an additional tool to mass balance calculations, to allocate contaminant sources and assess transformation. Our approach introduces the determination of groundwater age and combines it with CSIA in order to determine degradation rates at the field scale, and estimate the temporal and spatial evolution of the pollutant. Parallel to the application of this new approach in assessing the natural transformation of organic compounds in groundwater, we aim also to understand the potentials and limitations of our approach in different hydrological and contamination field settings.

We have targeted three field areas differing mainly in: the hydraulic regimes, scatter of contamination and redox conditions. The different scenarios have allowed us to point out in which field conditions are groundwater age determination and CSIA most relevant to be determined, and subsequently understand in which situations is it important to use those techniques combined (or isolated). Summarily:

Field 1 - Oxidic aquifer with short groundwater residence time showing no sign of natural attenuation. Due to the oxygenated conditions and very fast groundwater flow, it would be expected to have no on-going natural attenuation. In such cases CSIA seems not to be a relevant tool to be used.

Field 2 - Semi-anoxic aquifer with groundwater residence times of several years manifests some natural degradation to occur but not effective enough to eliminate the pollutant completely in the given groundwater residence time of 13 years. Groundwater dating is an essential parameter to be determined since despite relatively favorable redox conditions, it is shown that will take many years for natural attenuation to be complete.

Field 3 - Two structured aquifers separated by a wedge-shaped aquitard. In the upper anaerobic aquifer, high concentrations of chlorinated ethenes are found, from PCE to VC. The combination of low oxygen content and the long groundwater residence time, favor the natural dechlorination of the organic compounds. The aerobic lower aquifer has shorter groundwater residence times than the upper aquifer. In contrast to the upper aquifer, the lower aquifer contains only PCE which is isotopically different from the PCE of the upper aquifer, suggesting therefore a different source of that compound to these aquifers; in this case the combined use of groundwater dating and CSIA are essential to understand the complexity of the site and assess it in terms of natural attenuation.

We further suggest that the combined use of groundwater dating and CSIA techniques to assess the natural transformation of organic compounds in groundwater should become a rapid and cost-effective tool, to be applied before implementing remediation strategies, if any.