Field applications of Compound Specific Isotope Analysis (CSIA) at sites contaminated with chlorinated solvents

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Background/Objectives. Groundwater contamination with chlorinated compounds continues to be a widespread threat towards groundwater resources. Therefore, monitoring of contaminated sites and having a precise understanding of the distribution and possible degradation is essential for protecting clean water resources, as also indicated by UN's goal no. 6. Many contaminated sites are complex with numerous source zones, complex geology and flow paths and varying geochemical conditions. In recent years compound specific isotope analysis (CSIA) has been applied to interpreting contaminant pathways and assessing natural degradation. CSIA offers the possibility to differentiate between source zones, and when applying dual-CSIA for both carbon and chlorine isotope ratios ($\delta^{13}C$ and $\delta^{37}Cl$) the ratio between them is affected differently dependent on the degradation pathway. Thereby CSIA offers the possibility of distinguishing between biotic and abiotic degradation which makes optimizing in situ remediation of chlorinated solvents possible and degradation rates can be determined. CSIA has been applied at a contaminated site in in Denmark where the area is densely populated and heavily trafficked which made placement of boreholes difficult. Furthermore, the geology is complex and several source zones of both tetrachloroethene (PCE) and trichloroethene (TCE) exist. The overall objective of this project is to differentiate between different source zones, determine transport pathways and assess/verify degradation in the contaminant plume as a second line-of-evidence. The results should lead to a better risk assessment and thereby a decision on whether remediation is necessary.

Approach/Activities. The project is focused on field application of CSIA at the above-mentioned contaminated site, as well as drawing on experience from other contaminant sites around Denmark where CSIA and specific degraders have been applied. In all cases, groundwater was sampled and analyzed for dual-CSIA ($\delta^{13}C$ and $\delta^{37}Cl$) as well as traditional groundwater analysis.

Results/Lessons Learned. The use of CSIA at the urban contaminated site proved a useful tool. It was possible to identify and separate PCE and TCE source zones with overlapping contaminant plumes and determine areas where incomplete degradation of PCE and TCE occurred. Furthermore, some groundwater samples showed clear signs of how transport and flow paths affected the contaminants in the plume. For example, an area where the CSIA-results of PCE, TCE and cis-dichloroethene (cDCE), were all within ± 2 ‰ from $\delta^{13}C$ in the source zone. Therefore, there was no direct indication of degradation taking place despite degradation products being present in the samples. The samples indicate that PCE and TCE are being degraded upstream to cDCE and that degradation products are transported at a faster speed. Thus, degraded PCE and TCE are not detected in the sample itself. Overall CSIA results aided in setting up a conceptual model and was a good support in verifying zones where degradation was taking place. This resulted in a more precise risk analysis.

Further lessons learned included that at simple contaminated sites where traditional monitoring methods indicate degradation the application of CSIA may be redundant. At complex sites interpretation of dual-CSIA may be challenging and ambiguous. However, at complex contaminant sites the field application of CSIA has always aided in a more reliable risk assessment and a second line of evidence. More CSIA groundwater samples were sampled in the spring of 2021 and the full interpretation of CSIA results will be ready in late 2021.