

# Characterization by the Use of $^{37}\text{Cl}$ , $^{13}\text{C}$ and $^2\text{H}$ : Compound-Specific Isotope Analysis (CSIA), Biological Molecular Techniques (BMTs) and Numerical Modeling of a Site Contaminated by Monochlorobenzene

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**Background/Objectives.** Often chlorinated solvent-contaminated sites entail high management costs and often create significant impacts to the environment. For this reason, innovative tools such as compound-specific isotope analysis (CSIA), molecular biological techniques (MBTs) and fate and transport models can provide unequivocal information for site characterization and assessment of natural attenuation processes, particularly biodegradation. This contribution explores the potential for the multi-element CSIA approach, MBTs and transport models to study a heavy monochlorobenzene (MCB) and benzene contamination at a mega-site where potential multiple sources are present.

**Approach/Activities.** As a first step, microcosm experiments were developed to estimate enrichment factors for  $^{13}\text{C}$  and  $^{37}\text{Cl}$ , and to investigate specific biomarkers under different conditions (soil slurry, natural and stimulated, a- and anaerobic). Field investigations were performed including  $\delta^{37}\text{Cl}$ ,  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$  for MCB and benzene and illumina sequencing and qPCR coupled to reactive transport modeling efforts.

**Results/Lessons Learned.** A significant difference in the  $\delta^{13}\text{C}/\delta^2\text{H}$ ,  $\delta^{13}\text{C}/\delta^{37}\text{Cl}$ ,  $\delta^{37}\text{Cl}/\delta^2\text{H}$  and  $\delta^{13}\text{C}/\delta^{37}\text{Cl}/\delta^2\text{H}$  for MCB and  $\delta^{13}\text{C}/\delta^2\text{H}$  for benzene - in the high concentration spots - allowed distinguishing two distinct sources and plumes (merged at some areas). In addition, by the use of MNWs a detailed vertical distribution of the contaminants through the aquifer was also assessed.

Concerning natural attenuation processes, MBT results indicated the presence of mainly aerobic potential degraders within the indigenous community at the site and ruled out a significant presence of dehalococoides or dehalobacters. Microcosms experiments and soil slurry with in situ cultures showed a unique  $\delta^{13}\text{C}/\delta^{37}\text{Cl}$  trend with almost no enrichment for  $^{13}\text{C}$  but a  $^{37}\text{Cl}$   $\epsilon$  of  $-0.7$  ‰.

The dual  $\delta^{13}\text{C}/\delta^{37}\text{Cl}$  data also indicate aerobic biodegradation processes as the main natural attenuation mechanism. Finally, regarding benzene, the  $\delta^{13}\text{C}/\delta^2\text{H}$  data showed that benzene present at the site is probably not linked to MCB dehalogenation processes but is rather a primary contaminant; these data also showed benzene is being attenuated by biodegradation. Since not varying as a consequence of biodegradation processes,  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$  for MCB were used in combination with the transport models to estimate the contribution to the contamination from the two distinct sources. After estimating the mixing ratios among the plumes,  $\delta^{37}\text{Cl}$  was successfully used as a tracer to assess the natural attenuation processes at the site.

This contribution demonstrated the potential of combining tri-element CSIA in combination with other tools. Moreover, by applying tri  $\delta^{13}\text{C}$ ,  $\delta^{37}\text{Cl}$ , and  $\delta^2\text{H}$  CSIA analyses important insights regarding MCB natural attenuation were obtained.