

Direct Determination of Dechlorination Rates Using Radiolabeled cis-DCE Enabling Optimized Risk and Plume Management

Rasmus Jakobsen (raj@geus.dk) and Christian Nyrop Albers (GEUS, Denmark)
Katerina Tsitonaki (Orbicon, Denmark)
Mette M. Broholm (DTU Environment, Denmark)
Liselotte Clausen (HOFOR, Denmark)
Nina Tuxen (Capitol Region of Denmark)

Background/Objectives. Contamination with chlorinated solvents often leads to a plume moving with the groundwater towards water supply wells. Is the plume a threat? An important factor in deciding this is to what extent the chlorinated compounds are degraded to harmless ethene and CO₂. Knowing the rate of degradation may enable a more economical plume treatment – or show that natural attenuation is adequate. Though all the degradation steps are interesting, plume studies have shown that the rate of cis-DCE degradation is most critical because degradation often stalls at cis-DCE. Therefore, we have focused the development of the method for the rate of transformation of cis-DCE. Using radiolabeled compounds enables improved and rapid determination of the extremely low rates of dechlorination at near natural conditions, compared to determinations derived from microcosm studies or observed changes in concentrations or stable isotope fractionation along a groundwater flowpath.

Approach/Activities. The method is based on how rates of methane production and oxidation in marine, lacustrine and groundwater sediments have been measured using ¹⁴C labeled bicarbonate and acetate. We obtained undisturbed cores of till and sand in plastic liners (to avoid H₂ production) using a Geoprobe®. The cores were segmented and the pieces capped and wrapped entirely in aluminum tape in the field to limit diffusion in and out of the core during incubation. C-14 labeled cis-DCE was injected into the core segments prior to incubation at in situ temperature, in an N₂ filled glass jar. Incubation was ended, processes stopped and products fixed in the sediment by freezing the entire glass jar. The frozen core is later brought into an extraction and separation system and heated to release cis-DCE and formed products. A prerequisite for the method is that the injected cis-DCE can be separated from its degradation products during the extraction. Haysep D held at -1°C was found to retain cis-DCE while letting VC and ethene pass. VC + ethene are oxidized to CO₂ with a catalyst at 600°C and trapped in Carbosorb so radioactivity can be determined by scintillation counting. The rate is found from the ratio of the radioactivity of the products over the injected ¹⁴C-cis-DCE, multiplied by the concentration of cis-DCE in the core segment, assuming that the injected ¹⁴C-cis-DCE reacts as the cis-DCE in the sediment.

Results/Lessons Learned. Tests of loss during incubation, and adsorption during extraction showed minor losses and extraction and oxidation efficiency were acceptable. Tests using pure gas standards have shown that the complete separation of cis-DCE from VC + ethene is possible, however, tests with ¹⁴C labeled cis-DCE injected in un-incubated sediment showed that with the current setup 0.05-0.15 % of the injected ¹⁴C appeared in the Carbosorb after the oven, potentially a problem if rates are very low. The first actual measurements, using 10 and 20 days of incubation, on samples from actual plumes have resulted in rates of the same order as rates obtained by analyzing stable isotope fractionation in the plume. With minor modifications, the methodology can give rates of vinyl chloride degradation. Because the sediment material is undisturbed and the target incubation time of ~10 days is short, the obtained rates should be close to the in situ rates enabling better safe decisions on optimized plume management.