

## **Experimental investigation of concentration and stable isotopes signals during organic contaminants back diffusion**

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Back diffusion of organic contaminants is often the cause of groundwater plumes' persistence and can significantly hinder cleanup interventions [1, 2]. In this study we perform a high-resolution investigation of back diffusion in a well-controlled flow-through laboratory setup. We considered cis-dichloroethene (cis-DCE) as model contaminant and we investigated its back diffusion from an impermeable source into a permeable saturated layer, in which advection-dominated flow conditions were established. We used concentration and stable chlorine isotope measurements to investigate the plumes originated by cis-DCE back diffusion in a series of flow-through experiments, performed in porous media with different hydraulic conductivity and at different seepage velocities (i.e. 0.4, 0.8 and 1.2 m/day). A two-centimeter thick agarose gel layer was placed at the bottom of the setup to simulate the source of cis-DCE back diffusion from an impervious layer. Intensive sampling (>1000 measurements) was carried out, including the withdrawal of aqueous samples at closely spaced (1 cm) outlet ports, as well as the high-resolution sampling of the source zone (agarose gel) at the end of each experiment. The transient behavior of the plumes originated by back diffusion was investigated by sampling the outlet ports at regular intervals in the experiments, each run for a total time corresponding to 15 pore volumes. The high-resolution sampling allowed us to resolve the spatial and temporal evolution of concentration and stable isotope gradients in the flow-through setup. In particular, steep concentration and stable isotope gradients were observed at the outlet. Lateral isotope gradients corresponding to chlorine isotope fractionation up to 20‰ were induced by cis-DCE back diffusion and subsequent advection-dominated transport in all flow-through experiments. A numerical modeling approach, tracking individually all chlorine isotopologues, based on the accurate parameterization of local dispersion, as well as on the values of aqueous diffusion coefficients and diffusion-induced isotope fractionation from a previous study [3], provided a good agreement with the experimental data.

### References

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- [3] Jin, B., Rolle, M., Li, T., Haderlein, S.B., 2014. Diffusive fractionation of BTEX and chlorinated ethenes in aqueous solution: quantification of spatial isotope gradients. *Environ. Sci. Technol.* 48, 6141–6150.