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Tracking degradation as part of metolachlor plume evolution in a fractured bedrock aquifer using Compound-Specific Isotope Analysis

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Demonstrating degradation of a contaminant within a groundwater plume can be challenging, as decreasing concentrations do not necessarily reflect mass reduction. Compound-Specific Isotope Analysis (CSIA) addresses this limitation by exploiting isotope fractionation during contaminant transformation: molecules containing light isotopes degrade at different rates than those containing heavy isotopes, resulting in measurable isotope fractionation and providing direct evidence of compound transformation. This presentation illustrates the case of a metolachlor (herbicide) plume discovered in the early 1990s from inadvertent releases into a fractured dolostone aquifer in Ontario, Canada. Sequestration of metolachlor within the rock matrix has led to present-day conditions in which back-diffusion from the matrix into groundwater flowing through the fracture network sustains a persistent low-concentration plume [1]. The objectives of this study were to: 1) provide evidence of metolachlor degradation at the site; 2) determine metolachlor degradation rates; and 3) tentatively identify the degradation processes involved. Two sampling campaigns were conducted in 2017 and 2024, during which several monitoring wells and multilevel system ports were sampled near the source area and along the plume centerline. Groundwater was analyzed for general hydrochemistry and multi-element CSIA (carbon and chlorine isotopes) was performed for metolachlor. The results indicate that metolachlor is degraded both in the source area and along the plume, irrespective of concentration trends. This degradation appears to be predominantly controlled by a single pathway, most likely anaerobic biodegradation, although process identification requires further investigation through process-specific studies. Chlorine isotope data spanned a wider range of values than carbon isotope during a given campaign ($\Delta\delta^{37}Cl$ = 9.4 ‰ versus $\Delta\delta^{13}C$ = 2.5 ‰ in 2017), highlighting the greater sensitivity of chlorine isotopes as evidence of degradation and supporting their more systematic inclusion in future studies. Half-life estimates based on CSIA range between 3 and 7 years and will be useful for informing reactive transport modelling for predicting future plume conditions in a water supply aquifer.

[1]Parker, et al., Metolachlor dense non-aqueous phase liquid source conditions and plume attenuation in a dolostone water supply aquifer, in Groundwater in Fractured Bedrock Environments: Managing Catchment and Subsurface Resources. 2019, Geological Society of London. https://doi.org/10.1144/sp479.9