In Situ Biodegradation Rates in Contaminated Sediments via a Novel High Resolution Isotopic Approach: A Field and Modelling Study

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Background/Objectives. A key challenge in developing conceptual and numerical fate and transport models for contaminated sites is to distinguish, quantify and apportion various mass removal processes controlling contaminant concentrations and distribution. Conventional approaches for calculating degradation rates, i.e., first-order rate calculations based on concentration data only, can overestimate degradation rates by attributing all concentration decreases to destructive biodegradation, and underestimate the proportion of non-destructive processes. This study presents a novel approach for the assessment of in situ biodegradation rate constants within a contaminated sediment site, by coupling concentration data with isotopic enrichment trends associated with biodegradation processes only. This approach facilitates the development of more accurate conceptual site models and helps to identify zones of maximum biodegradation rates.

Approach/Activities. Using semi-permeable membrane diffusion samplers (i.e., peepers), vertically distributed samples of sediment pore water were collected at a spacing of approximately 3 centimeters from sediment contaminated with monochlorobenzene (MCB) and benzene at a field site located in New Jersey, USA. Collected samples were used for compositional analysis of groundwater for nitrate, sulfate, total dissolved iron, chloride, and volatile organic compounds, as well as for carbon isotope analysis of MCB and benzene. Using representative elementary volume (REV) assumptions coupled with isotopic enrichment trends, the profiles of MCB and benzene were reproduced using the numerical modelling platforms MODFLOW (McDonald and Harbaugh, 1988), MT3DMS (Zheng and Wang, 1999), and RT3D (Clement, 1997). Rather than using a bulk first order degradation constant for the entire profile, simulated zones of biodegradation were ascribed based on CSIA enrichment profiles. The model results were compared to and found to be consistent with those of an independent analytical model proposed previously (Lampert and Reible, 2009; Passeport et al., 2016). Compared to the analytical model, the numerical model offered more versatility in term of number of zones with various fate and transport parameters.

Results/Lessons Learned. Biodegradation of both MCB and benzene across the sediment water interface (SWI) was indicated by the isotopic enrichment trends in ^{13}C for both MCB (up to 5.7 ‰) and benzene (up to 2.2 ‰). A critical zone of 10-15 cm with highest biodegradation potential was also identified in the sediments. Using both stable isotope-derived rate calculations and numerical modeling, we determined in situ biodegradation rates for both MCB and benzene in this critical biologically-active zone. We also showed that MCB degraded at a slower rate (0.1-1.4 yr^{-1} and 0.2-3.2 yr^{-1}, respectively) than benzene (3.3-84.0 yr^{-1}) within the most biologically active zone of the sediment. Compared to typical approaches, CSIA-derived rate calculations provided more conservative estimates of in situ biodegradation rate constants. This unique approach has the potential to identify critical biologically active sediment zones, determine realistic recovery times, and better understand sediment recovery processes. The

high resolution data can guide remediation experts in the selection and implementation of remediation actions such as monitored natural recovery and bioaugmentation.