Low Rate Biodegradation Demonstration for Natural Attenuation of Benzene in Cold Saline Groundwater

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Background/Objectives. Deep groundwater beneath Onondaga Lake in Syracuse, New York has been impacted by the regional halite brine from salt beds and also leachate from Solvay Process waste historically placed in lakeshore settling basins. Benzene is one of the primary contaminants of concern, and the potential for upward discharge to the lake through confining sediments is the primary pathway of concern. Engineered hydraulic controls are in place to address shallow and intermediate groundwater along the shoreline.

Geochemical data suggested the potential for anaerobic biodegradation, but it was difficult to see temporal trends in the benzene data. It was clear that benzene was not biodegrading at rates found at many sites; however, even low rates of biodegradation would be protective of the lake given the slow groundwater flow. Modeling suggested a very long (over a thousand years) travel time for deep groundwater up though the sediments under the lake, and conventional lines of evidence for natural attenuation were of limited value. Therefore, a study was performed using less conventional methods to evaluate if benzene is biodegrading at low but significant rates given the low groundwater travel time from the deep groundwater to Onondaga Lake.

Approach/Activities. To evaluate the potential for low rates of biodegradation, a deep groundwater investigation was performed at the lakeshore sites involving the collection of conventional contaminant data, geochemical and natural attenuation parameters, and compound specific isotope analysis (CSIA) data. Carbon ($\delta^{13}C$) and hydrogen ($\delta^{2}H$) isotopes were analyzed from 21 deep groundwater wells. Isotope analysis was also performed where toluene and chlorobenzene were present at sufficiently high concentrations. The evaluation integrated and refined the conceptual site model (CSM) for the lakeshore sites and Onondaga Lake, geochemical data, organic data, and CSIA data. Half-lives calculated using the CSIA were utilized in the groundwater flow path analysis and compared with modeled vertical travel times from the deep groundwater zone below Onondaga Lake.

Results/Lessons Learned. The isotope data were analyzed consistent with EPA recommendations (EPA 600/R-08/148). The data indicated that natural attenuation of benzene is occurring in the deep groundwater along the lakeshore, albeit at biodegradation rates much lower than observed at many sites. A clear pattern of biodegradation was evident; the lighter carbon and hydrogen isotopes of benzene become depleted in the downgradient direction. The difference between high and low $\delta^{13}C$ and $\delta^{2}H$ was sufficient to provide unequivocal evidence of degradation. The benzene degradation half-life was estimated to be approximately 24 to 48 years. Although this half-life is relatively high in comparison to other sites, it is a small fraction of the groundwater travel time in the deep groundwater and upward to the Onondaga Lake. Although less data were available due to lower concentrations, the CSIA results for toluene and chlorobenzene showed a similar pattern.