## Why Is the Plume Disappearing Faster than it Should? Mass Loss Investigations at the Orica Botany Site

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Background/Objectives. Approximately 12 years ago, a groundwater treatment plant (GTP) was installed to contain and remove high concentrations of chlorinated solvents at the Orica Botany site in New South Wales, Australia. This site had very high concentrations (nearing solubility levels) of multiple chlorinated hydrocarbons, in particular 1,2-dichloroethane (1,2-DCA), but also carbon tetrachloride (CTC), tetrachloroethene, trichloroethene, and other related degradation daughter products including chloroform and vinyl chloride. Multiple dense, nonaqueous phase liquid (DNAPL) source zones were identified to exist on site, creating four distinct plumes with differing chemical signatures. Plume response to operation of the GTP has been tracked over the operational period. After ten years of operation, it became apparent that some areas of the plumes were attenuating faster than mass removal from extraction alone could account for, while other areas had persisting mass. Calibration of a detailed numerical model to the observed concentration changes required incorporation of significant attenuation over much of the plume, faster than is typically observed under natural attenuation at most sites. This was unexpected, given the challenging geochemical conditions present (concentrations high enough to be inhibitory and very low pH). Understanding where contaminant mass is persisting or degrading faster without intervention will inform future remedial strategy decisions.

**Approach/Activities.** Mass loss investigations were initiated in 2015 through first mining the historical dataset to identify areas of stable, growing, or attenuating plumes, and plume attenuation/source decay models were fitted to concentrations and dissolved mass temporal changes. This information was used to identify areas of the plumes and sources where attenuation behavior differed, and source mass decay models were incorporated into the numerical models to better represent concentration changes within the sources over time as the DNAPL attenuates. While the data mining exercise was useful in identifying areas of high or low attenuation behavior and approximate attenuation rates, the mechanism(s) driving the unusually rapid attenuation could not be discerned without additional characterization. Treatability studies were undertaken along with expanded groundwater geochemical analyses (monitored natural attenuation parameters), soil coring and subsampling to quantify reactive iron species (that drive abiotic degradation mechanisms) and identify soil parameters driving sorption/desorption, detailed microbial community profiling using next generation sequencing and quantitative polymerase chain reaction analysis, and compound specific isotope analysis.

**Results/Lessons Learned.** Rapid degradation of CTC (18-day half-life) appears to be occurring within peat layers where reactive iron species are low, pH is low, and microbial diversity is also very low; as a result, sorption to the peat is not a significant attenuation mechanism for CTC. A first-order decay model was not appropriate for CTC decay, except within the DNAPL source areas. Sorption does appear to be significant for the other constituents. In the first two years of GTP operation, sorption of 1,2-DCA was the predominant sink for dissolved phase mass as the high concentration plume core was pulled into areas of lower concentrations. Desorption is now a significant factor in plume persistence. The 1,2-DCA plume and source decay exhibited first-order decay behavior and appeared to be approaching asymptotic levels after 10 years. Studies are ongoing to identify specific degradation mechanisms and identify areas where the rate of mass loss is fast or slow.