Natural Source Zone Depletion Studies at the Botany Groundwater Cleanup Program

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Background/Objectives. At light non-aqueous phase liquid (LNAPL) sites such as refineries and terminals, there has been a strong movement to capitalize on recent scientific research that shows that the natural source zone depletion (NSZD) of the LNAPL body is much faster than originally envisioned and establishes new technologies for measuring NSZD. These NSZD studies have been performed at numerous sites in the United States, Australia, and other locations and have shown that the NSZD rate at these hydrocarbon sites is typically 1,000s to 10,000s of liters per hectare per year or several metric tons of contaminant degraded per hectare year (e.g., Garg et al., 2017). One relatively recent NSZD measurement technology is carbon dioxide traps where a receptacle with CO_2 adsorbent captures carbon dioxide leaving the subsurface. The amount of carbon dioxide in the trap can then be measured and converted to a degradation rate (E-Flux, 2015; McCoy et al., 2014). Currently, it is the most common method to obtain NSZD rates at hydrocarbon sites. The most recent version of these traps employ a ^{14}C correction to separate modern carbon from the ancient petroleum based contaminants in the subsurface.

While NSZD measurement using CO_2 traps has almost exclusively been applied to hydrocarbon sites, there is good basis that NSZD rates can be applied at Dense Non-Aqueous Phase Liquids (DNAPL) sites such as the Botany Groundwater Cleanup site as well (Boyd et al., 2014). However, there are three complicating factors for measuring the NSZD rate at the Botany site:

1. At hydrocarbon sites, the petroleum hydrocarbons degrade largely to methane that is then converted to carbon dioxide in the unsaturated zone. At this site, the chlorinated ethenes and ethanes will be degrading to ethene and ethane.
2. The presence of carbon dioxide from significant peat layers at the Botany site may complicate the analysis of the data from the CO_2 traps. The peat is approximately 10,000 years old and complicates the application of the ^{14}C correction.
3. Any non-chlorinated compounds released with the DNAPL compounds can also provide an NSZD signal, complicating the calculation of the NSZD rate for the chlorinated compounds.

Approach/Activities. As part of the NSZD pilot program, five E-Flux CO_2 traps were installed over the C1 source zone at the Botany site. Two locations were over background locations, and three were situated over the DNAPL source or high dissolved concentration plume at the site. Results of total carbon efflux rates with the ^{14}C correction were analyzed using three different approaches to estimate NSZD rates.

Results/Lessons Learned. Preliminary results show NSZD rates in the Botany C1 source zone of several metric tons per hectare per year. More work is being performed to determine if non-chlorinated compounds are contributing to this rate; if the presence of impervious cover is affecting the results; and if the carbon dioxide efflux rate from the peat is being evaluated accurately. Once these issues have been resolved, the potential range of NSZD rates for the C1 source zone will be reported. These values will be compared to the dissolved plume biodegradation rates of the dissolved plume being calculated as part of the Botany Groundwater Cleanup Project and used to better define the overall mass balance in the conceptual site

model.