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Spatial and Temporal Variation in NSZD Rates at a Former Oil Refinery

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Background/Objectives. Petroleum release sites present a challenge for remediation such that active remediation is often used in tandem with natural source zone depletion (NSZD) to meet regulatory goals. While some work has been conducted at large sites to estimate NSZD rates using CO_2 traps and nested vapor wells (i.e., the concentration gradient method), there are considerable gaps in the understanding of how rates vary spatially and across seasons. The dynamic closed chamber (DCC) appears well suited to address such gaps. It allows for rapid measurements of CO_2 effluxes at ground surface, which means large sample sizes for good spatial coverage and multiple replicates in time. While the DCC has been deployed at small petroleum sites, data collection at large sites has not yet been reported.

Approach/Activities. A sitewide CO_2 efflux evaluation was conducted using DCC at 149 locations. Static chambers were used for gas collection at a subset of 55 locations for radiocarbon analysis. These results provide sufficient information to calculate NSZD rates across the site. In addition, replicate DCC measurements over four seasons were taken within a smaller “high resolution” area to evaluate temporal variation. The high resolution measurements were supplemented with concurrent nested vapor well samples, for comparison of measured NSZD rates under different seasonal conditions and using different monitoring techniques. Environmental parameters such as soil moisture content and atmospheric temperature were also tracked during these seasonal measurement events.

Results/Lessons Learned. The sitewide average CO_2 efflux for the fall season was approximately 7.8 mol CO_2 m^{-2} s^{-1} (SE = 0.5), converting to NSZD rate by background correction to 3.4 mol CO_2 m^{-2} s^{-1} (SE = 0.4). Radiocarbon analysis for the 55 sample subset estimated an NSZD rate of 1.2 mol CO_2 m^{-2} s^{-1} (SE = 0.3). While the radiocarbon analysis resulted in a significantly lower average NSZD rate estimate, it also identified locations with some NSZD component whereby background correction of the NSZD rate was estimated as zero. Within the high resolution area, seasonal NSZD rate estimates by DCC and radiocarbon analysis ranged from 0.1 to 1.2 mol CO_2 m^{-2} s^{-1}, with the lowest rate in the winter and the highest rate in the summer. Seasonal NSZD rate estimates by the concentration gradient method were higher (0.7 to 1.0 mol CO_2 m^{-2} s^{-1}) and showed less variability due to relatively stable subsurface gas profiles. The differences in NSZD rate estimates between methods are likely related to such factors as measurement time interval, input parameter sensitivity, and radiocarbon sampling method. The temporal NSZD rates is correlated with ambient temperature and precipitation rates, possibly indicating environmental factors that affect hydrocarbon loss rates across seasons. Overall, the results provide an estimate of sitewide spatial variability and smaller-scale temporal variability that can be used as a reference when developing characterization programs at other petroleum release sites.