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Quantitative Assessment of Natural Source Zone Depletion Rates at a Former Refinery Site

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Background/Objectives. The management approach for petroleum hydrocarbon sites increasingly includes an evaluation of natural source zone depletion (NSZD). Emerging research indicates NSZD is often a significant process for longer-term LNAPL mass reduction and compositional change, and a potential benefit may be sustainability of NSZD compared to other remedial measures. However, better and more quantitative assessments of NSZD rates are required to support remedial decision making and to identify appropriate strategies. The objective of this study is to demonstrate the application of recent advances in measurement techniques of CO_2 efflux, radiocarbon (^{14}C) analysis and predictive modeling tools to quantify the NSZD rates at a former refinery site.

Approach/Activities. The study approach builds on a previous NSZD assessment at the site where two methods of CO_2 efflux measurements were compared for dry and warm summer conditions: 1) dynamic closed chamber (DCC) method for short-term measurements and high spatial coverage; and 2) the static trap method for longer-term average measurements. Additional measurements of CO_2 efflux using the DCC method were conducted in the moist to wet fall season (October and November 2016) to complement the summer data, as well as two new techniques for the ^{14}C correction of the CO_2 efflux. In addition, the CH_4 efflux was measured to estimate its potential influence on NSZD rates. High resolution monitoring of soil moisture, temperature and soil gases was conducted to support conceptual site model development and data interpretation. The field program was complemented by the data driven application of the Vadose Zone Biodegradation Loss (VZBL) model and estimates of NSZD rates in the saturated zone.

Results/Lessons Learned. Seasonal conditions, predominantly soil moisture and to a lesser extent temperature, had a significant influence on the CO_2 efflux and estimates of hydrocarbon NSZD rates. There was a very large seasonal variability in CO_2 efflux measurements, which were on average 1,100 US Gal/acre/year during the dry and warm season, 246 US gal/acre/year during the moist and cool season, and 5.5 US Gal/acre/year during the wet and cool season (note the low values were measured after a period of prolonged higher than normal rainfall). The rates are considered to span the likely seasonal range of NSZD rates at the site, however, the lowest value represents a rate for an extreme short-term condition. The site-wide estimate of mass loss from the VZBL model was higher than estimates from contaminant CO_2 efflux measurements, but within the same order of magnitude. Groundwater geochemistry data were used to estimate NSZD rates through saturated zone biodegradation and dissolution processes (about 100 US gal/acre/year), which exceeded the low range of the unsaturated zone biodegradation rates measured during wet weather. The results of the various ^{14}C correction techniques indicated that the mass balance method based on combined measurements of $F^{14}C$ and CO_2 concentrations during LI-COR measurements or in static chambers were most promising.