Comparison of Thermal Methods for Quantifying NSZD Rates Overlying a Shallow Petroleum Hydrocarbon Source Zone

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Background/Objectives. Monitoring of subsurface temperature variation caused by biodegradation is an emerging method for resolving natural source zone depletion (NSZD) rates at petroleum hydrocarbon (PHC) contaminated sites. Estimated NSZD rates can be used to determine whether continuation or cessation of active remediation systems is warranted or to support passive remediation as a standalone strategy. While early work focused on use of soil gas gradients and CO₂ efflux, temperature has more recently been used as a measurement proxy for NSZD rates. The temperature method has potential advantages in providing bulk estimates of NSZD rates and estimation of seasonal NSZD rates through innovative methods for temperature sensing and data processing. Gaps in application of this method include limited documentation of methods transforming temperature data to NSZD rates and comparison of NSZD rates obtained from thermal and other methods. To address this gap, a multi-year study at a field research site was conducted involving different NSZD measurement methods with this study focusing on the temperature method.

Approach/Activities. Hourly temperature data from multi-depth temperature sensors obtained over eight months (July to March) were available from an extensively monitored research site with shallow liquid-phase PHCs and warm, dry summers and wet, cool winters. Temperature data are transformed to NSZD rates using 1) an analytical solution based on background correction of temperature data, 2) a commercially available numerical model (Temp/W) using subsurface and surface heating-cooling boundaries, and 3) an algorithm using subsurface temperature data to resolve both subsurface heating and surface heating-cooling boundaries according to the *Single Stick* method developed by Askarani et al. (2018). The numerical model and *Single Stick* method do not require a background temperature correction, which can introduce inaccuracies in the analysis for the background method because of variable surface energy balance and soil properties between site and background areas. Comparison of NSZD rates from thermal methods are used to evaluate the merits of each method

Results/Lessons Learned. Monitoring of subsurface temperature gradients created by biodegradation of shallow PHCs is shown to be an effective method for measuring NSZD rates. Notably numerical simulations were sensitive to seasonal temperature changes and soil thermal properties. Soil thermal properties estimated from laboratory tests and Fourier analysis indicated variable but increasing diffusivity with depth. Because of very wet late fall/winter conditions, inferred to limit oxygen fluxes and aerobic biodegradation, the analysis focused on results from July-October. For July-August and September-October periods, estimated NSZD rates were 1020-1860; 2100-3600; and 980-1700 USgal/acre/yr for the background corrected analytical, numerical and *Single Stick* models, respectively. The thermal NSZD rates from background-corrected analytical and *Single Stick* models were within a factor of 1.5 as compared to rates based on CO₂ efflux. The results from Temp/W model rates were approximately 2X higher than the background-corrected analytical solution and *Single Stick* rates. A promising aspect of estimating NSZD rates using temperature data is the ability to

efficiently obtain continuous NSZD rate data compared to often temporally sparse rates obtained for other measurement methods.