## Effects of Soil Heterogeneity on the Thermal Gradient Method for NSZD Rate Measurement

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**Background/Objectives.** Well-accepted methods for measuring natural source zone depletion (NSZD) rates are based on production rates of CO<sub>2</sub>, which is the main reaction product of contaminant biodegradation. These soil CO<sub>2</sub> production rates are quantified using CO<sub>2</sub> fluxes as measured at the ground surface. NSZD reactions are exothermic, meaning a heat balance might also be used to determine NSZD rates based on heat fluxes. The quantification of heat fluxes based on measured temperature changes in the soil column is known as the thermal gradient method.

The quality of heat flux-derived NSZD rates is assessed with respect to measured rates calculated from mass balance (e.g., CO<sub>2</sub>) methods. While field pilot studies have shown agreement between these two methods, additional sources of error inherent to the thermal gradient method should be explored. To this end, we have developed a mathematical model that can be used to determine the theoretical effects of soil heterogeneity on thermal gradient-based NSZD rates.

**Approach/Activities.** This 1-dimensional transient model uses site-specific data to predict depth-dependent soil temperatures and contaminant degradation rates by solving the carbon and heat balances associated with NSZD reactions. The model calculates contaminant biodegradation rates based on temperature-adjusted, Monod kinetics-based biodegradation rates, which depend on local contaminant concentration and temperature. Model-predicted, depth-integrated NSZD rates can be calibrated to field-measured, CO<sub>2</sub> flux-based NSZD rates to account for different site-specific factors (e.g., contaminant type or microbial community).

Comparison of NSZD rate estimates generated using CO<sub>2</sub>-based and thermal gradient-based methods enables us to test which parameters most impact the latter, and to what degree. We have previously shown that the thermal gradient method works best when an annual average heat flux is used, as opposed to a short-term or monthly average flux; additionally, previous work shows that using a background-location correction on soil temperatures is unnecessary. Here, we test the sensitivity of the thermal gradient method to a) diverse soil properties and differences in ambient/groundwater temperatures; b) temporal and spatial soil anisotropy derived from layers of different soil textures within the same soil column; and c) the effects of this anisotropy on thermal gradient-based estimates over several temperature measurement timescales.

**Results/Lessons Learned.** As previously shown, our model is consistent with field experiments showing that soil temperature increases can be caused by NSZD reactions, as well as with the known seasonal dependence of NSZD rates. However, short-term and monthly average heat fluxes used in combination with the background correction yield NSZD rates that are very sensitive to even small differences in soil properties. On the other hand, using annual average fluxes with the background correction provides satisfactory results when soil properties differ between the background and contaminated locations. These results will be updated to include effects of soil stratigraphy on rate estimates, including the degree of soil anisotropy that generates acceptable error rates when using the background correction.