Soil Gas Gradient Method for Estimating Natural Attenuation Rates of NAPL and Specific Chemicals of Concern

Iason Verginelli (University of Rome Tor Vergata, Rome, Italy)
Matthew Lahvis and George DeVaull (Shell, Houston, TX, USA)
Parisa Jourabchi (parisa@arisenv.ca) (ARIS Environmental Ltd., Vancouver, BC, Canada)

Background/Objectives. There has been rapid progress in the understanding of the processes responsible for the depletion of non-aqueous phase liquids (NAPL) and development of methods and guidance for the measurement of natural source zone depletion (NSZD) rates. The earliest efforts in quantifying the rates of natural attenuation were based on concentration gradients of chemicals in groundwater (e.g., Weidemeier et al., 1995), or in soil gas (e.g., Lahvis and Baehr, 1996). The methods have expanded to include other indicators of biodegradation of NAPL such as CO_2 efflux at the ground surface, or gradients in the vertical temperature profile of the soil. In their review of natural attenuation rates, Garg et al. (2017) highlighted the significant role of the vapor phase processes in the vadose zone as demonstrated by the application of the soil gas gradient method at a large former refinery site by Johnson et al. (2006) who reported bulk depletion rates through analysis of O_2 and CO_2 concentrations. Similarly, for a small fuel release site, Mackay et al. (2018) reported higher rates of natural attenuation in the vadose zone than those obtained from groundwater monitoring.

The available technologies and approaches in data interpretation generally fall into five categories of methods as defined in the new ASTM Standard Guide (ASTM E3361-22) for estimating the natural attenuation rate of NAPL: CO_2 efflux; temperature gradient; soil gas gradient; groundwater monitoring; and NAPL composition. Of these methods, the soil gas gradient method can be used to estimate the attenuation rate of specific chemicals of concern (COCs), however, its most common application has been for measurements of bulk depletion rate of the NAPL. This is due to easier field-based measurements of O_2 and CO_2, as well as simplified approach to data interpretation based on an analytical solution to the diffusion-reaction model in 1D (Verginelli and Baciocchi, 2021). We propose to expand this approach for the estimation of COC-specific natural attenuation rates with the advantage of using available database of soil gas concentrations.

Approach/Activities. The simplified analytical 1-D solution allows to estimate the COC-specific natural attenuation rates based on the maximum soil gas concentration, the effective diffusion coefficient and the diffusive reaction length calculated from the vertical soil gas concentration gradient profiles. The proposed approach is evaluated through comparison of rate estimates for benzene and TPH and compared to results obtained using BioVapor. A range of rate estimates are derived from the application of both methods to available database of soil gas concentrations, based on the maximum concentration of COC measured at depth and estimates of the reaction length. The results are interpreted based on factors affecting the effective diffusion coefficient such as soil type (and moisture content), as well as analysis of other fixed gases (e.g., O_2, CO_2 and CH_4) for validating the underlying assumptions in terms of oxygen availability and potential for advective soil gas flow. Applicability of the approach also includes assessment for potential confined NAPL conditions. The proposed approach includes a checklist of site conditions to practically assess the method's applicability to a specific site.

Results/Lessons Learned. The preliminary results indicate a reasonable correlation between the simplified approach and results obtained using BioVapor. Broader adoption of this approach for a screening assessment of COC-specific attenuation rates enables the application of monitored natural attenuation (MNA) beyond groundwater monitoring. The approach can be used as a screening tool based on soil gas measurements obtained from existing groundwater monitoring wells screened across the water table (e.g., Sweeney and Ririe, 2017). This simplified approach also provides a practical tool to evaluate the temporal variability in the natural attenuation rates, since they have been shown to vary both seasonally (Sihota et al., 2016) and over years and decades (Davis et al., 2022). This work highlights the advantages and limitations of the proposed simplified approach for estimating natural attenuation rates of NAPL and specific COCs using the soil gas gradient method.