Quantifying Methane in Soil Gas Efflux during NSZD Assessments

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Background/Objectives. Soil gas flux measurements have become a common component of natural source zone depletion (NSZD) assessments. These assessments focus on measuring carbon dioxide (CO_2) soil gas efflux and stoichiometrically equating that to a rate of hydrocarbon biodegradation. This approach has appeared sufficient to quantify the rate of NSZD, because at most sites, the mixture of methane and CO_2 generated by dominant fermentation/methanogenic processes in the LNAPL smear zone is converted to nearly all CO_2 by bio-oxidation of methane in shallow soil. However, NSZD assessments at some sites have demonstrated unexpectedly low CO_2 efflux, leading to questions about whether significant unoxidized methane efflux may be occurring. If this is the case, it would lead to underestimates of NSZD rates. In other natural and anthropogenic systems where fermentation and methanogenesis are the dominant processes of biodegradation, such as peat bogs and landfills, methane efflux can be significant even when biooxidation zones near the ground surface are present (Garg et al., 2017) Similar situations may be relevant at petroleum hydrocarbon sites with very shallow LNAPL zones and/or low permeability ground cover (e.g., pavement) that create consistently anaerobic vadose zones limiting potential for methane bio-oxidation.

Approach/Activities. Using industry-standard CO_2 efflux measurement equipment (a dynamic closed chamber and gas analyzer supplied by LI-COR), in conjunction with a separate methane gas analyzer (the Gasmet DX4040), Arcadis has completed simultaneous CO_2 and methane flux measurements at several sites. Setup of the equipment required a clear understanding of each analyzer's components and functional specifications. Several of the sites included in the assessment are likely to have largely anaerobic vadose zones, due to shallow groundwater and/or impermeable surface cover, and two of the sites have previously exhibited atypically low CO_2 efflux values in NSZD assessments. The data from these measurements will support evaluation of the amount of unoxidized methane leaving the ground surface, and the extent to which this process is an "unseen" component of NSZD in customary assessment procedures.

Results/Lessons Learned. The methane efflux data described were relatively easy to collect and evaluate, suggesting that a methane measurement component should be added to soil gas flux NSZD scopes at sites where significant methane efflux is suspected. In the assessments completed to date, methane efflux was small compared to CO_2 efflux, suggesting that measuring methane efflux may not be a critical component to NSZD assessment at these sites. In these cases, CO_2-efflux-based NSZD rates may be low due to constraints by other factors, such as temperature or geochemical conditions. Additional results are forthcoming to confirm or refine this hypothesis, and data collection at other sites may indicate that methane efflux is a significant indicator of NSZD activity in different vadose zone conditions. The results will provide a valuable frame of reference for the previously unresolved question of whether methane efflux is a significant missing piece in some NSZD assessments, improving confidence in future data sets and supporting a more accurate and comprehensive understanding of NSZD processes in the future.