Group 2

QUANTIFYING METHANE IN SOIL GAS EFFLUX DURING NSZD ASSESSMENTS

ARCADIS Design & Consultancy for natural and built assets

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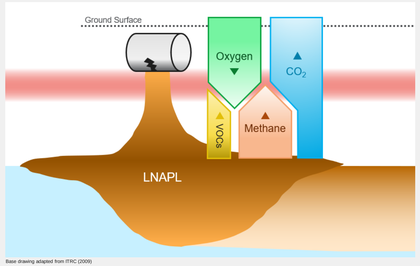
BACKGROUND

Natural source zone depletion (NSZD) assessments are usually composed of multiple complementary investigation methods to quantify different phases of degradation. Soil gas flux measurements are one of the most common components of NSZD assessments and can quantify NSZD rates based on vadose-zone indicators in a short time period and with minimal intrusive work.



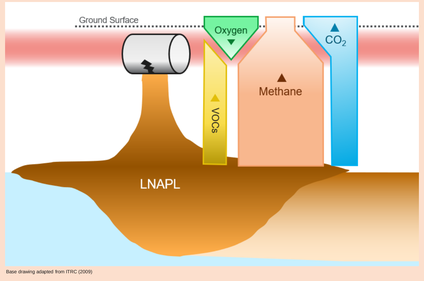
Base drawing adapted from ITRC (2009)

TYPICAL ASSUMPTIONS

Biodegradation of LNAPL in the saturated zone leads to production of methane (CH_4) and carbon dioxide (CO_2), which are vented to the vadose zone. As the soil gas continues to move vertically, it eventually reaches an oxic zone, wherein the CH_4 is bio-oxidized and converted to additional CO_2. Therefore, measuring CO_2 flux is sufficient to quantify the effects of NSZD.

ARE WE MISSING SOMETHING?

At some sites, unexpectedly low CO_2 efflux has been measured, leading to questions about whether significant unoxidized methane efflux was occurring. Measuring CO_2 flux and CH_4 flux together may result in a more accurate NSZD rate.



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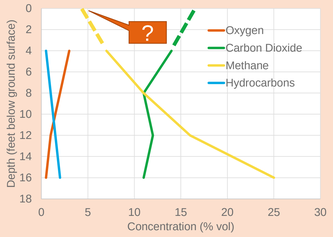
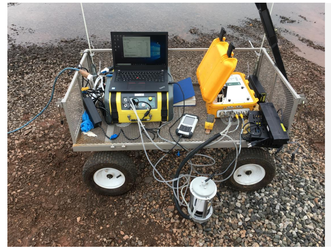


SITE SELECTION

Collecting CO_2 flux and CH_4 flux may be appropriate at many sites. 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 bio-oxidation zones near the ground surface are present (Garg et al. 2017). Methane efflux could be important, and of interest for the LNAPL conceptual site model, at sites with one or more of the following:

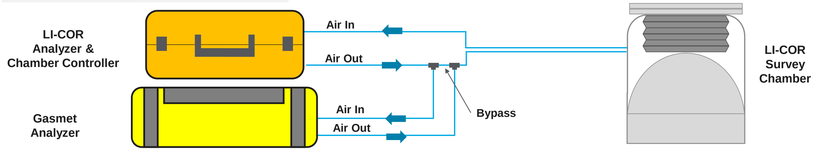
Very shallow LNAPL zones • Low permeability ground cover (such as pavement) • Unexpectedly low previous CO_2 flux measurements



FIELD METHODOLOGY

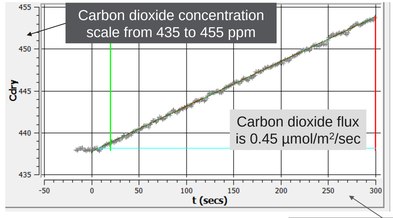
Simultaneous methane and carbon dioxide flux measurements can be made using two pieces of industry-standard equipment. Carbon dioxide flux is measured using a dynamic closed chamber and gas analyzer supplied by LI-COR while methane flux is measured by a separate methane gas analyzer (Gasmet DX4040 or similar).

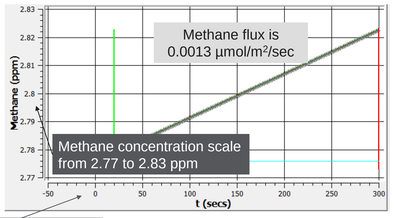
EXAMPLE EQUIPMENT SETUP



DATA ANALYSIS

The data can be analyzed by SoilFluxPro, the software produced by LI-COR. SoilFluxPro creates a chart of concentration over time and then calculates a flux from a line or curve fit on that chart. An estimated NSZD rate can then be calculated by stoichiometrically equating the soil gas efflux to a rate of hydrocarbon degradation. Example charts from SoilFluxPro are below.





Measurements taken over 5 minutes

Garg, S., C.J. Newell, P.R. Kulkarni, D.C. King, D.T. Adamson, M.I. Renno, and T. Sale. 2017. Overview of Natural Source Zone Depletion: Processes, Controlling Factors, and Composition Change. Groundwater Monitoring & Remediation 37(3): 62-81.

CASE STUDY

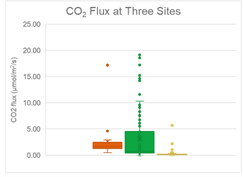
An initial NSZD assessment was conducted at a petroleum bulk terminal using CO_2 traps to measure degradation rates. The initial LNAPL degradation rates were low, on the order of 30 to 80 gal/acre/year. A second investigation was completed using a dynamic closed chamber and a gas analyzer for both carbon dioxide and methane to determine if methane flux would indicate higher rates of degradation. The second round of data confirmed that NSZD rates are low and that there is not a large amount of methane making it to the surface without being bio-oxidized. Wet ground conditions were present, which interferes with vertical soil gas flux and may be the cause of the low rates.

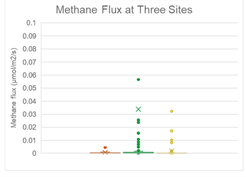
OTHER USES

The equipment used in these NSZD studies can be formatted to measure efflux of other gases. For example, in the case of a large release of a single-component NAPL (such as benzene), a direct measurement of the flux of that chemical to the atmosphere can be completed. This could help in the evaluation of loss rates, design of treatment systems, and assessment of potential exposures.

RESULTS

- Methane flux measurements were generally repeatable with the exception of a few outliers. The median percent difference between two measurements at one location was 1%. Approximately 60% of the methane flux measurements that were repeated were within 10% of the original measurement.
- The highest methane flux measured was 2.01 µmol/m²/sec. At that location the carbon dioxide flux was 6.72 µmol/m²/sec.
- On average, methane flux was about 5% of carbon dioxide flux. However, there was not a consistent ratio of methane flux to carbon dioxide flux. Methane flux as a percent of carbon dioxide flux ranged from 0% (no methane flux was measured) to 100% (carbon dioxide and methane flux were the same, and near zero).





Note – some zero or negative flux values were calculated due to measurement error/variability; those values not shown at left.

CONCLUSIONS

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. However, 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 sites will be screened for methane efflux where conditions indicate high levels may be present; that data will be used to continue to refine the understanding of whether methane efflux is a missing piece in some NSZD assessments. This will lead to an improved confidence in future data sets and support a more comprehensive understanding of NSZD.