SPATIAL AND TEMPORAL VARIATION IN NSZD RATES AT A FORMER OIL REFINERY

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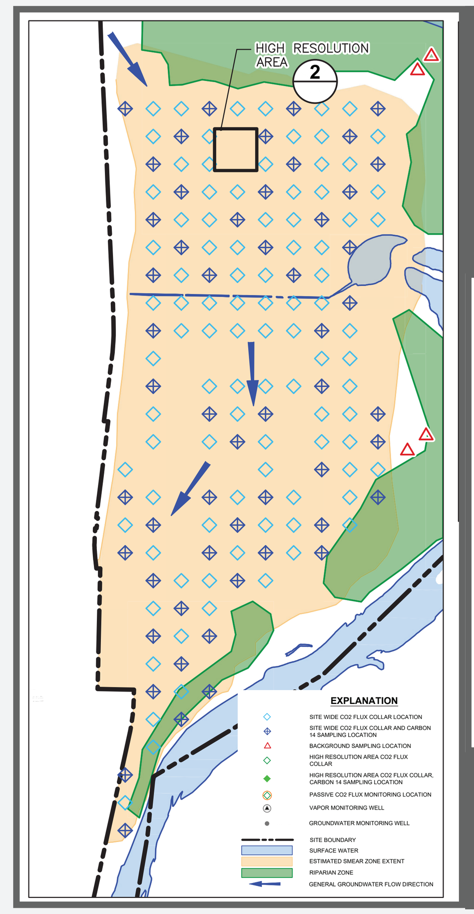
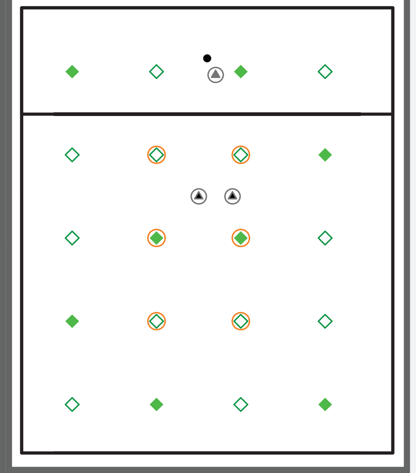
INTRODUCTION

Understanding the implications of vadose zone processes across spatial and temporal scales is challenging. At petroleum release sites, biodegradation of hydrocarbon compounds contributes to biogeochemical cycling through natural source zone depletion (NSZD). Considerable gaps remain in characterization at large sites. An evaluation of NSZD rates at a >200 acre (80 hectare) decommissioned oil refinery was conducted using a dynamic closed chamber (DCC). We characterized spatial variability and compared radiocarbon (^{14}C) and background corrected NSZD rate estimates. At a high resolution 1.25 acre (0.5 hectare) area, temporal variability in NSZD rate estimates was characterized and a method comparison was conducted for DCC and the concentration gradient method (CGM).

STUDY LAYOUT



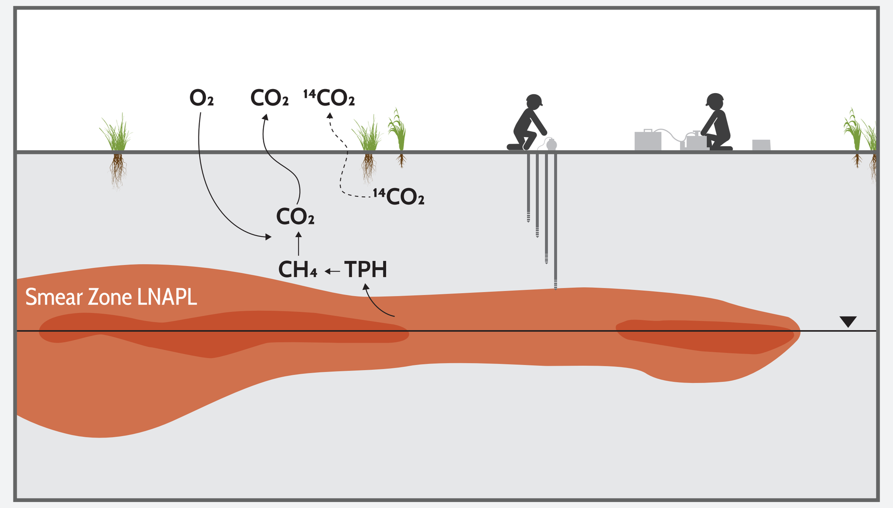
Site Map (left) - A sitewide CO_2 efflux study was conducted in fall 2013 using the DCC method. A LI-COR LI-8100A equipped with an IRGA (LI-COR Biosciences, Lincoln, NE) was deployed over a gridded area.



High Resolution Area (above) selected because it is well characterized through long period of environmental monitoring

The study was conducted at a decommissioned oil refinery adjacent to a river in the Midwest of the United States. Refinery operations terminated in the mid-1980s, and the distribution of LNAPL stabilized in the subsurface. Vertical smearing of the LNAPL occurred over time. The thickness of the smear zone generally increases from inches at the plume periphery, to as much as 20 feet (6 meters) in the central portion of the site.

CONCEPTUAL MODEL




Stationary Long-Term DCC


Nested Vapor Well Sampling for CGM analysis

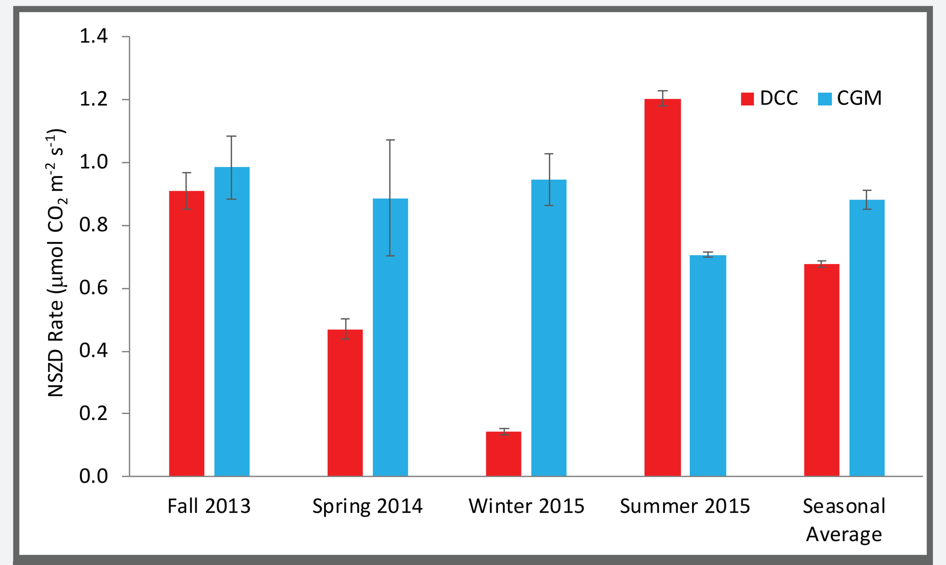
Quantifying NSZD processes involves estimating hydrocarbon losses within soil vapor as evidence that the LNAPL source itself is attenuating. Two methods have been explored in this study:

1. The dynamic closed chamber method (Sihota et al., 2011) measures real-time carbon dioxide (CO_2) efflux from ground surface over a two-minute time period with an infra-red gas analyzer (IRGA) connected to a chamber continually equilibrated to atmospheric pressure. For this method, the CO_2 efflux contaminant soil respiration (CSR) must be distinguished from natural soil respiration (NSR) either through ^{14}C analysis or by background correction.
2. The concentration gradient method (Johnson et al., 2006) uses measured profiles of oxygen, methane, and hydrocarbons above a smear zone to calculate soil vapor transport by diffusion. The method requires installation of nested soil vapor wells for collection of subsurface samples.

METHOD COMPARISON

DCC shows greater variability between sample events, while CGM estimates are relatively stable. The stability of CGM estimates may be related to:

- Selected subsurface gradient interval—the shallowest sampling interval was selected to best match available guidance (e.g., Johnson et al. 2006). This vertical interval was relatively unchanged over time, while deeper intervals were more variable. Use of different vertical intervals resulted in dissimilar estimates. This suggests sensitivity of the method to the calculation approach.
- The inputted vapor diffusion coefficient (VDC) to the CGM estimate was measured on only one event. Effort to measure the VDC for each soil gas sampling event could improve the NSZD rate estimates by this method.



Mean NSZD rates over four seasons for DCC and CGM. Error bars are +/- one standard error of the mean across the sample area for a given event. For the CGM, the mean and standard error are based on spatial weighting to account for position within the sampling area.

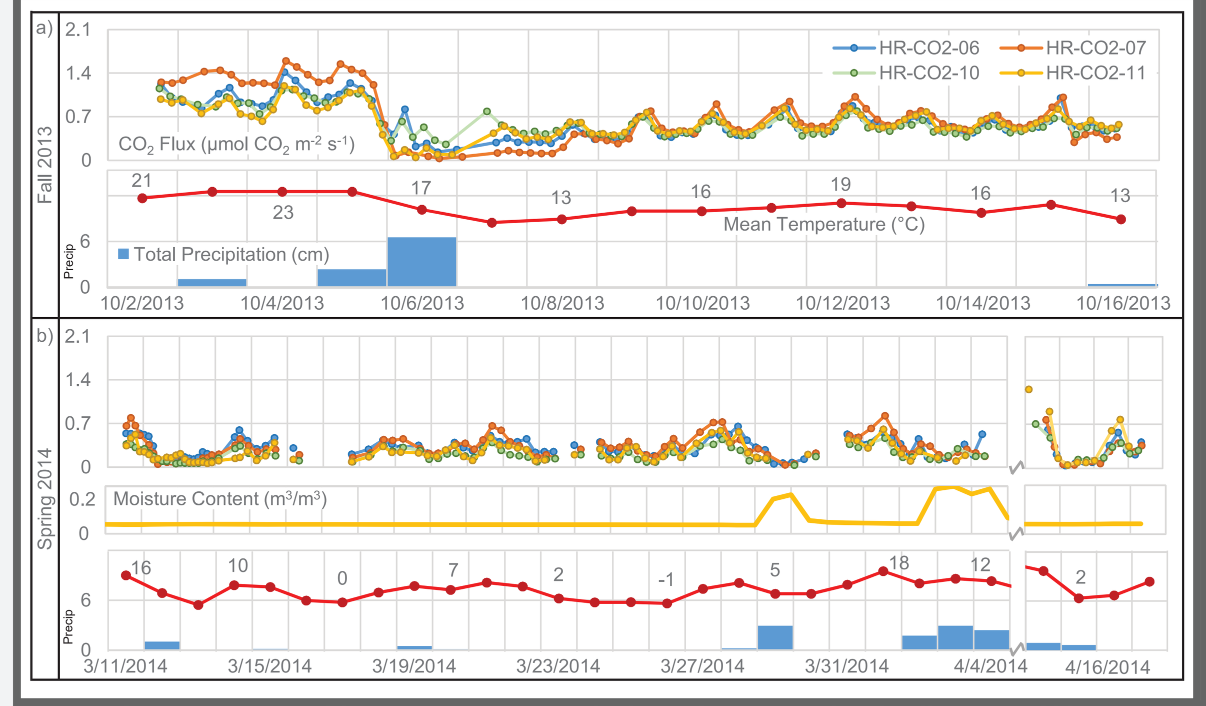
SITE WIDE SPATIAL DISTRIBUTION

Spatial distribution of sitewide fall 2013 fluxes. Top panels are mapped fluxes and bottom panels are area-weighted average fluxes with error bars representing one standard error. a) Total fluxes for full data set (n = 149), b) Total fluxes for ^{14}C data set (n = 53), c) NSZD rate for full data set using background correction, d) NSZD rate for ^{14}C data set using background correction, and e) NSZD rate for ^{14}C data set using ^{14}C correction.

The following conclusions can be made from the spatial distribution of NSZD rates at the sitewide scale:

- Higher rates were generally observed in the northern and central portions of the site where historical process units, storage tanks, and piping were located.
- Decreasing the sample size while using the background correction does not result in a change in the NSZD rate.
- Using the background correction resulted in an overestimate of NSZD rate estimates versus ^{14}C correction by an approximate factor of three. This may be related to variability in background values, which could mean imprecision when applying the average background value sitewide.
- ^{14}C correction on a smaller data set may have an advantage versus a larger background correction dataset.

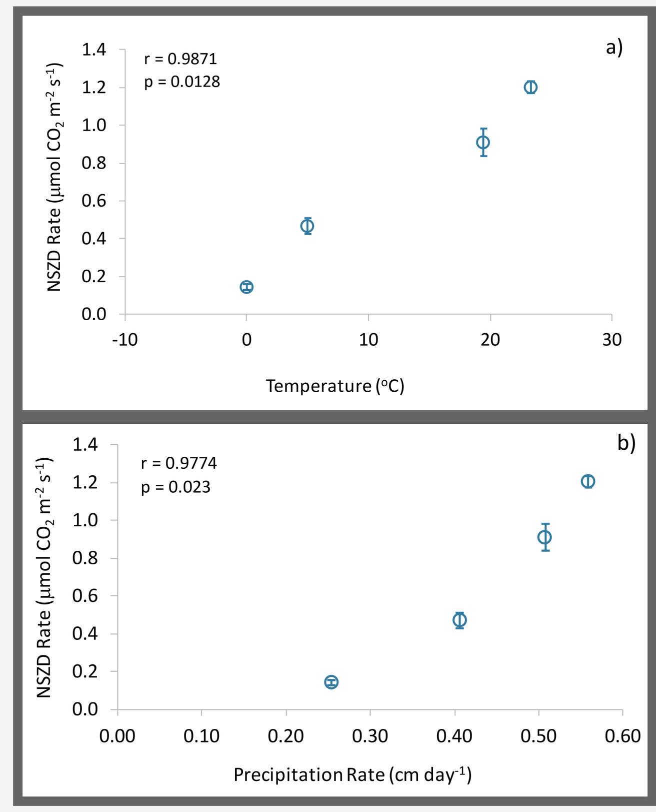
TEMPORAL VARIATION OF NSZD



Day-to-day environmental factors comparison in high resolution area for a) Fall 2013 and b) Spring 2014. Reported CO_2 efflux rates are 4-hour averages of long-term DCC chamber measurements.

In Fall 2013, rainfall accumulated at start of study, followed by a 90% reduction in CO_2 efflux rates. Subsequent to this reduction, CO_2 effluxes only slowly increased as mean air temperature remained lower.

In Spring 2014, a decrease in CO_2 efflux was observed during the rain event (associated with a sharp increase in soil moisture content); CO_2 efflux rebounded quickly as mean air temperature increased.



Season-to-season environmental factors comparison to NSZD rate: a) average temperature one month prior to measurements through the final survey measurement date, b) average daily precipitation one month prior to measurements through the final survey measurement date

- A strong correlation was found to exist between mean seasonal temperature and CO_2 efflux, with higher temperatures resulting in higher efflux rates on both the day-to-day and seasonal timescales, likely due to an increase in microbial activity at higher temperatures. Temperature also appeared to influence the CO_2 efflux rebound timeframe following precipitation events.
- Seasons with a greater rate of precipitation were more likely to have higher CO_2 efflux due to increase microbial activity, but a distinct drop in CO_2 efflux was observed during and following precipitation events due to dampening effluxes immediately following rain events . Thus, precipitation appears to have varying effects depending on the time scale.
- There was no recognized correlation between CO_2 effluxes and groundwater elevations or barometric pressure (data not displayed).

CONCLUSIONS

Overall the findings provide information on spatial and temporal variability in NSZD rates that will assist in setting expectations for other large sites. The following conclusions can be made:

- The spatial distribution of NSZD rates on the sitewide scale was consistent with historical activities.
- The estimated sitewide average NSZD rate using the location specific ^{14}C correction was significantly different from the average by the background correction method. This suggests that ^{14}C correction may be useful at sites with high variability in background CO_2 effluxes.
- In the high resolution area, NSZD rates estimated by DCC varied temporally, across seasonal and daily time scales.
- Temperature appeared to play a role (positive correlation), and precipitation was also important, particularly in dampening effluxes immediately following rain events.
- The estimates by DCC and CGM broadly agreed, although CGM showed relatively low variability between events. This appears related to calculation factors rather than actual field conditions.

REFERENCES

Johnson, P., Lundegard, P., Liu, Z., 2006. Source zone natural attenuation at petroleum hydrocarbon spill sites-I: Site-specific assessment approach. Groundw. Monit. Remediat. 26, 82–92.

Sihota, N.J., Singurindy, O., Mayer, K.U., 2011. CO2 -Efflux Measurements for Evaluating Source Zone Natural Attenuation Rates in a Petroleum Hydrocarbon Contaminated Aquifer. Environ. Sci. Technol. 45, 482–488. doi:10.1021/es1032585