Reducing Sampling Bias Through Continuous Monitoring of CO_2 Efflux at NSZD Sites

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INTRODUCTION

Recent research has shown that soil carbon dioxide (CO_2) efflux can be used to quantify the rate of contaminant degradation - either natural or enhanced - occurring at petroleum hydrocarbon impacted sites. Point sampling programs with traditional flux chambers are currently the status quo for measuring CO_2 effluxes in the field, but this approach is problematic for gaining a thorough understanding of Natural Source Zone Depletion (NSZD) rates. In general, soil respiration rates can exhibit a large degree of daily and seasonal variation, potentially introducing biases to the measurements depending on the environmental conditions at the time of day or season during which sampling occurs. Point sampling programs fail to capture much of this natural variability in CO_2 effluxes, which can inadvertently introduce biases when quantifying contaminant degradation rates. Due to the spatial variability of CO_2 effluxes observed at NSZD sites, an incomplete understanding of temporal variability further complicates data interpretation, reducing confidence in derived NSZD rates. Using ecological models, we demonstrate the degree of natural variability in soil CO_2 effluxes and highlight the biases that may be introduced by point sampling to show that continuous monitoring helps eliminate these biases and allows for accurate quantification of contaminant degradation rates.

WHAT IS NSZD AND HOW DOES IT RELATE TO CO_2 FLUX?

NSZD is a mass balance approach used to assess contaminant loss resulting from the depletion of Light Non-Aqueous Phase Liquids (LNAPLs) via the naturally occurring processes of volatilization, dissolution, biodegradation and sorption. In recent years NSZD has gained significant attention as a remediation method because it provides a low cost, in-situ approach for managing LNAPL contamination in an environmentally and economically sustainable manner (Sihota, 2014). NSZD also provides an important benchmark for comparing the performance and assessing the effectiveness of active remediation methods (ITRC, 2009). The NSZD conceptual model described below follows Garg et al. (2017) and defines three distinct subsurface zones; the methane generation zone, the methane oxidation zone, and the aerobic transport zone (see Figure 1). The processes occuring in each zone are complex, but all play key roles in the overall process of NSZD and the subsequent generation of CO_2 in the subsurface - a brief overview of each zone is provided here, but for a comprehensive review see Garg et al. (2017).

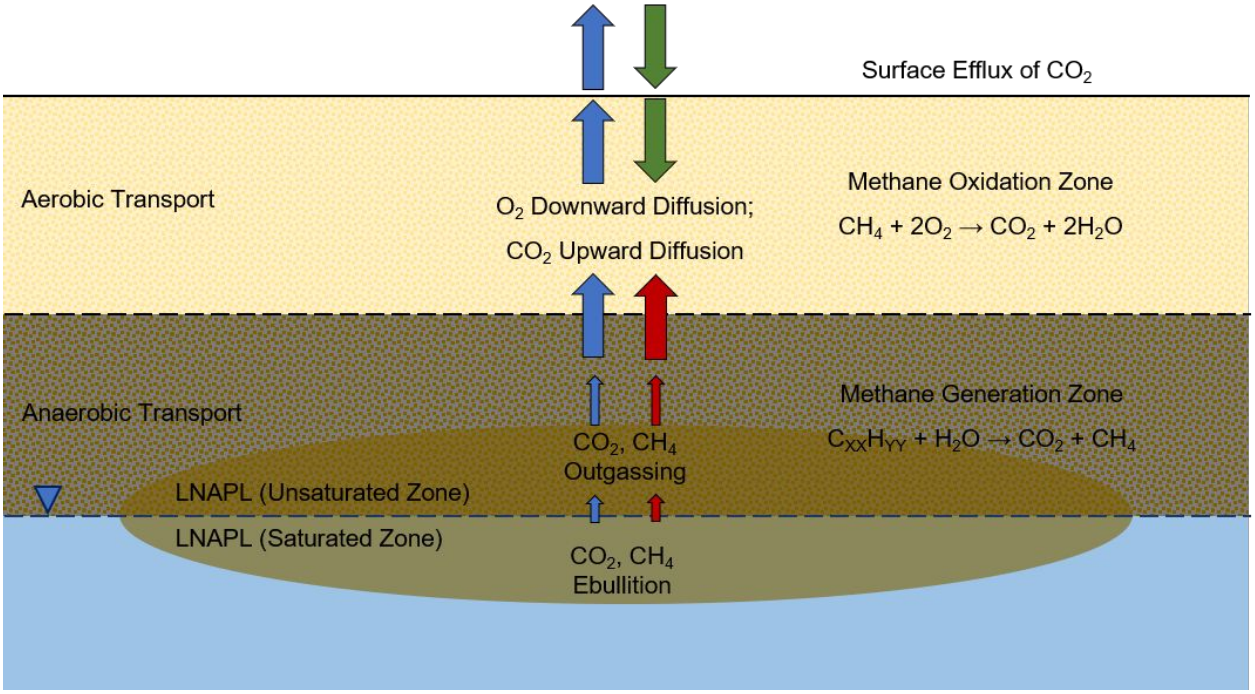

Figure 1. Schematic diagram illustrating the NSZD conceptual model and the relative positions of the methane generation zone, the methane oxidation zone and the aerobic transport zone, as well as the processes occurring within each zone.

The Methane Generation Zone

The methane generation zone is characterized by the production of methane (CH_4) through a process known as methanogenesis. Methanogenesis is a form of anaerobic respiration used by microbes called methanogens. As a result of their metabolic processes, methanogens break down organic compounds, including LNAPL constituents, and produce CH_4 and CO_2 as byproducts. Many factors influence the rate of methanogenesis in the methane generation zone. For example, higher temperatures tend to increase the rate of CH_4 production, whereas the presence of oxygen (O_2) slows methane generation because O_2 is highly toxic to methanogens. As shown in Figure 1, the gases produced by the anaerobic respiration of methanogens migrate upward through the anaerobic transport zone, where they enter the methane oxidation zone.

The Methane Oxidation Zone

Within the methane oxidation zone (Figure 1), CH_4 migrates upward through the vadose zone where it is oxidized to CO_2 by methanotrophs in the subsurface. In addition to the presence and abundance of methanotrophs, the efficiency of CH_4 oxidation in soil is primarily controlled by soil type, soil moisture and temperature because these parameters determine the degree of microbial activity in the soil (Garg et al., 2017). Increases in temperature tend to increase microbial activity. Soil moisture can both enhance and diminish microbial activity; too much water can inhibit the downward diffusion of O_2 and reduce CH_4 oxidation, whereas insufficient water limits microbial activity (Pumpanen et al., 2003).

The Aerobic Transport Zone

The aerobic transport zone extends from the ground surface down to the methane oxidation zone, as shown in Figure 1. The thickness of the aerobic transport zone is generally controlled by the downward diffusion of O_2 into the soil and the upward diffusion of CO_2 produced in the methane oxidation zone (Garg et al., 2017). The final product of the hydrocarbon degradation process is the production of CO_2. Eventually the CO_2 generated during the degradation of petroleum hydrocarbons is emitted to the atmosphere through the soil surface. Because CO_2 is a conservative gas in the degradation process, CO_2 efflux measured at the surface can be used to help quantify the rate of hydrocarbon degradation.

THE IMPORTANCE OF CONTINUOUS MONITORING

Soil CO_2 efflux occurs naturally in uncontaminated soil as a result of biological processes. Numerous ecological studies have shown that plant root respiration and oxidation of organic materials by microbes are responsible for CO_2 production in soils (Pumpanen et al., 2003, and references therein). Production of CO_2 varies vertically within the soil profile, as well as both temporally and spatially in response to variable local supply of organic material, soil temperature and soil moisture content (Davidson et al., 2006). However, the production of CO_2 in the subsurface is not necessarily indicative of effluxes measured at the surface, because surface effluxes are primarily controlled by diffusive properties of the soil. These natural soil gas effluxes show significant cyclical variations over daily, seasonal and interannual time scales. Weather events can exaggerate or interrupt cyclical behaviours, further complicating interpretation of CO_2 effluxes resulting from ecological and NSZD processes. Therefore, robust characterization of soil respiration is critical to accurately estimating contaminant degradation rates via CO_2 effluxes.

MODEL DESCRIPTION

A simple numerical model was used to illustrate the influence of daily and seasonal temperature variations on ecological effluxes and demonstrate the biases that can be introduced to efflux measurements by sparse point sampling programs. The model calculates efflux as a function of temperature ($R(T)$), using the following equation:

$$R(T) = BQ_{10}^{(T/10)}$$

Where T is temperature (°C), B is the basal respiration, and Q_{10} is the temperature coefficient. To isolate the influence of temperature, basal respiration was assumed to be constant and assigned a value of $B = 1$. Similarly, the Q_{10} temperature coefficient was assigned a value of $Q_{10} = 2$, which is in line with commonly used values from the literature (e.g. Raich et al. (1991), Raich and Schlesinger (1992), Potter et al. (1993)). Hourly temperature data provided by Environment Canada was used from the weather station located at the Edmonton International Airport.

MODEL RESULTS

The response of ecological soil gas effluxes to seasonal temperature variations are shown in Figure 2. Effluxes are positively correlated with temperature, as a result, effluxes in fall and winter are lower compared to those in spring and summer. Furthermore, daily temperature ranges tend to be smaller in fall and winter compared to spring and summer, causing daily ranges in efflux to also be smaller in fall and winter compared to spring and summer.

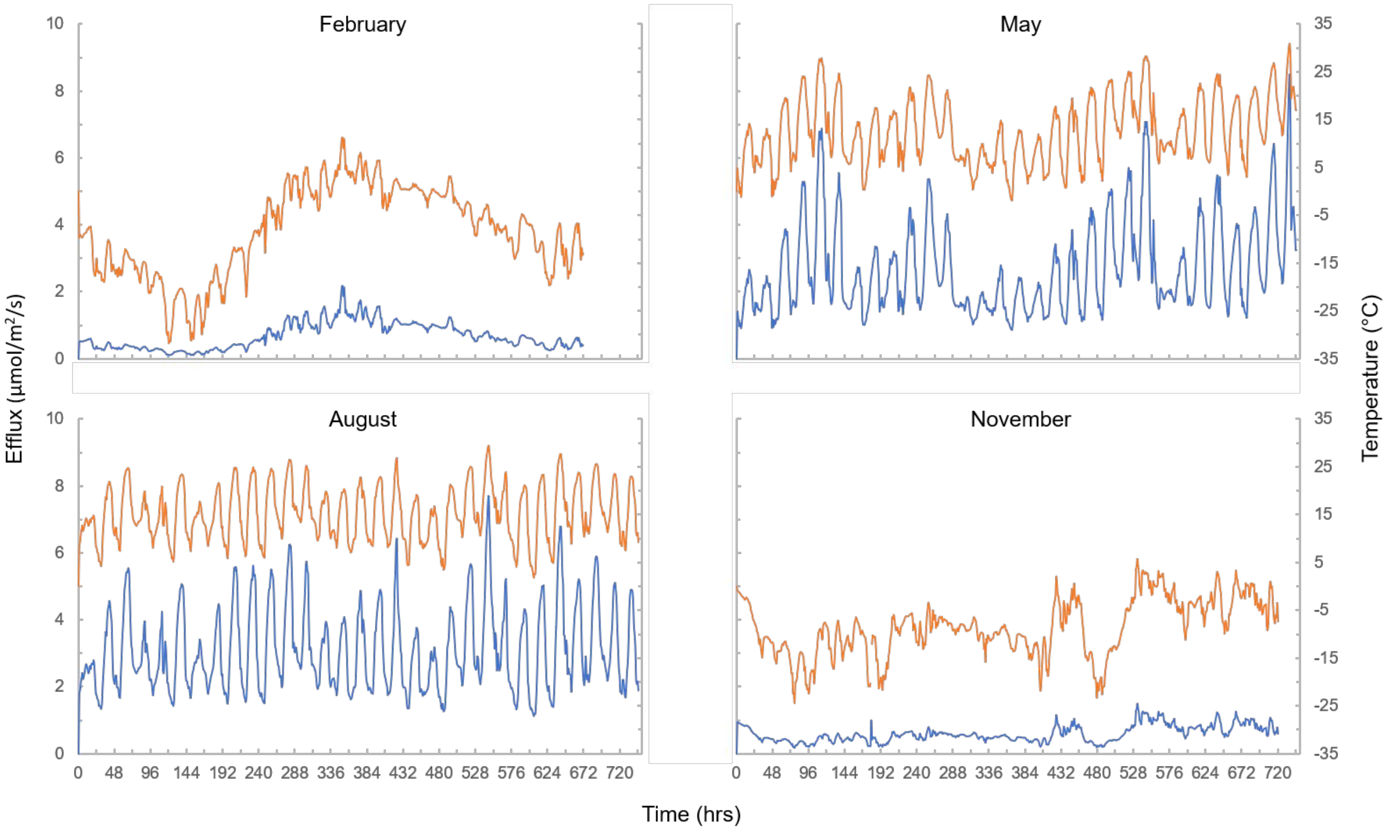

Figure 2. Model results comparing variations in soil gas efflux (blue line) in response to daily and seasonal temperature variations (orange line) in February, May, August and November.

In general, surveys of soil gas efflux tend to be conducted during the warmer months when constraints on logistics and site access tend to be minimal, and sampling programs may be further dictated by site access, weather conditions, staff availability, and other such factors. The highly variable soil gas effluxes shown in Figure 2 illustrate the biases that can be introduced when extrapolating measurements from the field over an entire year. If the temperature dependence of effluxes is not carefully considered when interpreting and extrapolating data collected during the warmer months, the ecological baseline may be overestimated, resulting in an underestimation of the portion of efflux attributed to NSZD. This is problematic, as it could make NSZD appear to be a less viable option for remediation, potentially wasting time and financial resources. For example, collecting measurements in the spring (May) will lead to an estimated ecological baseline that is 4.5 times larger than an estimate based on data collected in fall (November), and 1.56 times larger than the average annual baseline correction. Similarly, for measurements collected in August, the range of estimates for ecological baseline efflux rate is 1.13 to 7.67 µmol/m^2/s, which could lead to an estimate that is between -34% and +343% of the annual average emission rate. The impact of this sampling time bias is fullter illustrated below.

Point sampling programs may attempt to minimize biases in the data caused by cyclical daily variations in the ecological background efflux by collecting efflux measurements at approximately the same time everyday. Figure 3 shows an example of two such sampling programs and their respective inferred ecological baselines. In both programs, soil gas efflux measurements are collected once per day for seven days. However; in Program A the measurements are collected at 8 am, while in Program B measurements are collected at 2 pm. When compared with hourly baseline efflux (thin blue line, Figure 3), we see that neither Program A nor Program B will capture the true range of variation in the ecological baseline. Furthermore, neither sampling program accurately captures the true daily average of the baseline efflux (bold blue line, Figure 3). Program A results in a 15% underestimation of the daily average ecological baseline efflux, whereas Program B overestimates it by 153% (Table 1).

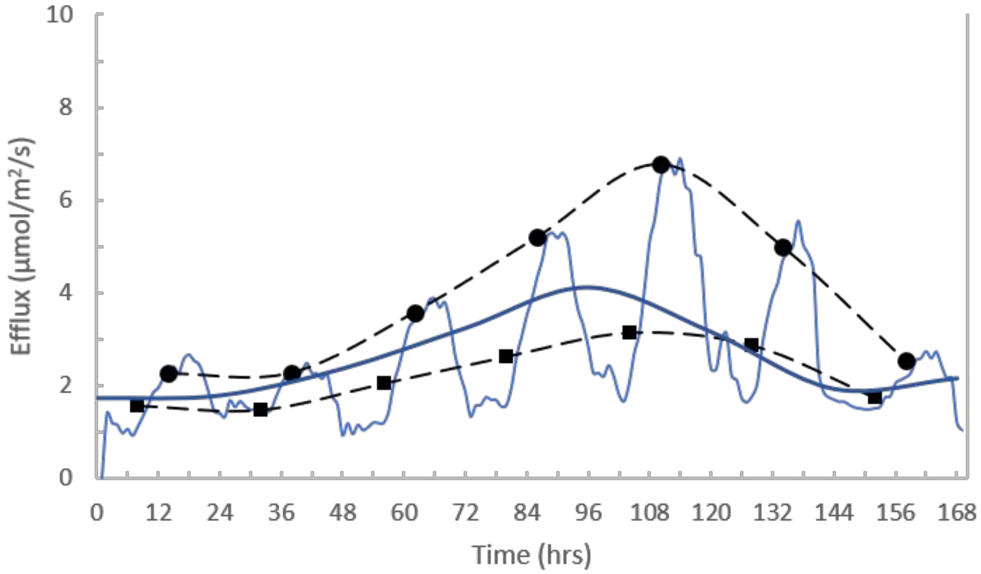

Figure 3. Inferred baseline soil efflux resulting from daily collection of samples at 8 am (Program A, dashed grey line with square markers) and 2 pm (Program B, dashed black line with circular markers) during a one week sampling program in May, compared to hourly efflux (light blue line) and the daily average efflux (bold blue line).

	Hourly Data	Program A	Program B
Efflux Range ($\mu mol/m^2/s$)	0.9 - 6.9	1.5 - 3.1	2.3 - 6.8
Average Efflux ($\mu mol/m^2/s$)	2.6	2.2	4.0
% Difference	N/A	-15%	+153%

Table 1. Differences between the average effluxes and efflux ranges derived from 1 week of continuous monitoring (hourly data) and 1 week of daily point sampling Program A and Program B.

CONCLUSIONS

Measuring surface efflux of CO_2 can be a powerful tool for delineating contaminant source zones and quantifying contaminant degradation rates. However; this study has shown that status quo point sampling programs can introduce measurement bias resulting in an incomplete understanding of natural background effluxes. This complicates interpretation of the data and can reduce confidence in derived contaminant degradation rates. Inadequate temporal resolution also impedes reliable interpolation of data across a site spatially, potentially leading site professionals to misinterpret spatial variability in CO_2 effluxes or NSZD rates at a site. Most importantly, as Figure 3 and Table 1 show, an incorrect or incomplete characterization of the ecological baseline at a site can result in under or over estimated rates of NSZD. Consequently, inaccurate estimation of NSZD rates could unnecessarily discourage selection of NSZD as a viable remediation method or result in extended remediation timelines at NSZD sites.

Continuous monitoring of CO_2 effluxes is superior to point sampling programs because it avoids these complications by providing a comprehensive dataset capable of robustly characterizing soil respiration. As a result, continuous monitoring gives site professionals confidence in estimated contaminant degradation rates at NSZD sites. Continuous monitoring also captures other non-cyclical trends in the data that are likely to be either only partially captured or entirely missed by sparse, point sampling programs. These non-cyclical trends may provide additional insight into NSZD processes at a site and prevent the misinterpretation of such events.

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