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Basis for ^{14}C Analysis

Differentiating Petroleum Hydrocarbon and Modern Carbon using CO$_2$ Flux Traps

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1.0 Introduction

E-Flux provides services to measure CO_2 fluxes at ground level, to estimate the rates of natural degradation of light non-aqueous liquids (LNAPL). This technology was developed at CSU and now licensed exclusively to E-Flux. Additional details on this technology are available in the literature (McCoy et al, 2015)

Unimpacted soils have natural CO_2 flux generation rates, due to microbial root zone activity and/or the degradation of natural organic matter (NOM). As a result of this, the total CO_2 flux measured at an impacted location is the sum of both natural soil respiration processes and due to LNAPL degradation.

The CO_2 flux due to natural soil respiration can be estimated by measuring CO_2 fluxes at unimpacted locations, and subtracting such rates from the total CO2 fluxes at LNAPL impacted locations in order to estimate CO2 flux due to LNAP degradation (Sihota et al, 2011. This is known as the "background correction" and assumes that the rates of natural soil respiration are similar for both impacted and unimpacted locations.

However, at many industrial facilities it is difficult to find unimpacted locations, and/or the unimpacted locations have very different vegetation to that at the impacted locations. This document provides the basis to use carbon isotope analysis as an alternative to determine the contributions from both natural soil respiration processes and due to LNAPL degradation.

2.0 Carbon Isotope Analysis Methodology

Upon sampling and analysis of the samples by the methods described before (McCoy et al, 2015), the analysis for carbon isotopes is conducted on the archived homogenized solid samples (containing carbonates, after the neutralization reaction between CO_2 and the solid sorbent SodaSorb).

Unstable isotopic analysis has been previously used to differentiate anthropogenic (due to fossil fuel-burning) and natural sources of atmospheric CO, CO_2 and methane (for example, Klouda and Connolly, 1995; Levin et al, 1995; Avery et al, 2006). The technique relies on the analysis of ^{14}C, an unstable carbon isotope (with a half-life of approximately 5600 years) generated by cosmic rays in the atmosphere. Thus, contemporary (modern) organic carbon is ^{14}C-rich, while fossil fuel carbon is ^{14}C-depleted. Furthermore, contemporary samples and atmospheric samples have the same characteristic amount of [14]C. The detection limit of ^{14}C by accelerator mass spectrometry enables dating of samples younger than 60,000 years, while older samples (such as fossil fuels) have non-detectable ^{14}C activity (Stuiver and Polach, 1977).

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For a sample that contains carbon from both modern and fossil fuel carbon sources, measurement of the ^{14}C enables quantitation of both source contributions. The fossil fuel fraction of the sample, ff_{sample}, and the remaining non-fossil fuel or contemporary ($1-ff_{sample}$), are related by the two-component mass balance:

$$Fm_{sample} = ff_{sample}\left(Fm_{ff}\right)+\left(1-ff_{sample}\right)\left(Fm_{atm}\right)$$

In this formula, Fm_{sample} is the measured modern fraction of the sample, Fm_{ff} is the fraction of modern carbon in fossil fuel ($Fm_{ff} = 0$), and Fm_{atm} is the fraction of modern carbon in contemporary living material ($Fm_{atm} = 1.05$) (Hua et al., 2013). By convention, the carbon isotope analysis and reporting is based on a 1950 NBS oxalic acid standard, synthesized when the ^{14}C atmospheric levels were lower than current ones due to nuclear tests. Due to reporting conventions, Fm_{sample} is reported as if the analysis was done in 1950. Thus, Fm_{atm} is counter-intuitively larger than 1.

3.0 Expected Results and Recommendations

Our previous results suggest that the ^{14}C-based technique offers a built-in correction for fossil fuel as an alternative to the background correction typically done at these sites. Earlier data on a limited amount of samples suggested that results using the ^{14}C-correction were equivalent to the background correction (McCoy et al, 2015; Sihota et al, 2011). However, a recent compilation at 4 sites comparing results from the background correction to the ^{14}C-correction suggests that modern carbon fluxes are highly variable within a site (Zimbron, 2015). This finding suggests that the background correction assumption that a constant carbon flux that is characteristic of an entire site might introduce large errors in the correction for petroleum-biodegradation derived CO2 fluxes. Contrary to the background correction, the ^{14}C-based correction is collocated with the measurement, and thus spatially unbiased by uncertainties at background locations (i.e., due to different vegetation and lithology, unknown impacts, different gas transport regimes, high sensitivity to soil moisture, etc).

The fossil-fuel carbon content on the unexposed sorbent SodaSorb is non-zero (as high as approximately 30%). This might be the result of either a background fossil fuel signature of the sorbent SodaSorb (due to process or mineral sources), or due to material handling (exposure to fossil fuel fumes). However, the total mass is very small and the error contribution to the fossil-fuel fluxes at impacted locations is negligible.

The ^{14}C analysis is done on archived CO_2 sorbed samples, after homogenization. Thus, the procedures for the CO_2 trap sampling, deployment and analysis (described in the original proposal) do not require any modifications or deviations from the original plan.

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4.0 References

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