

# Development of Protocol for Carbon Dioxide Efflux Measurements Using Dynamic Closed Chamber for NSZD Estimates

Parisa Jourabchi, Anne Wozney and Ian Hers (Golder Associates, Ltd., Vancouver, BC, Canada), Harley Hopkins (ExxonMobil Environmental Services Company, Houston, TX, USA), Nayyara Mandjee, (Imperial Oil Resources Limited, Calgary, AB, Canada)

### **Objectives and Rational**



Natural source zone depletion (NSZD) is an emerging approach for the management of sites impacted with petroleum hydrocarbons (PHCs). CO<sub>2</sub> efflux at ground surface can be used to estimate NSZD rates. The CO<sub>2</sub> efflux can be measured using a Dynamic Closed Chamber (DCC) (Sihota et al., 2011). The method, however, requires differentiating contaminant soil respiration (CSR) from natural soil respiration (NSR) through radiocarbon (14C) analysis of collected air samples or background measurements (Sihota and Mayer, 2012).

The DCC method with <sup>14</sup>C correction was used and further developed at a former refinery in two field trials to evaluate seasonal differences and a site-wide assessment to quantify NSZD rates in six LNAPL areas.

Key Point: Development of protocol for a non-intrusive and efficient metho to quantify NSZD rates at petroleum hydrocarbon sites.

at a former refinery.

### PROTOCOL ROADMAP

- 1. Site Evaluation for Applicability of Method
- 2. CO<sub>2</sub> Efflux Survey
- 3. Air Samples for <sup>14</sup>C Analysis
- 4. Data Analysis for NSZD Assessment
- 5. Method Uncertainties and Limitations

## 1. Site Evaluation for Applicability of Method

- The conceptual site model (CSM) is important for determining sampling design and project
- Review available data for determining lateral and vertical extent of the LNAPL source zone, LNAPL type, depth to groundwater and groundwater flow direction
- Key site investigation data are 1) biodegradation reactions and 2) soil gas transport in vadose zone:
- 1) Data related to biodegradation reactions include:
- Dissolved-phase concentrations in groundwater samples collected from the impacted zone, upgradient and downgradient locations in terms of changes in redox conditions, concentrations of electron acceptors and metabolic by-products (e.g., CH<sub>4</sub>, ferrous iron).
- Soil gas concentrations in samples collected from soil gas probes or headspace of
- depleted O<sub>2</sub> concentrations relative to atmospheric;
- elevated CO<sub>2</sub> and CH<sub>4</sub> concentrations; and
- lower N<sub>2</sub> concentrations relative to atmospheric, which is associated with generation of biogenic gases leading to the displacement of  $N_2$ .
- 2) Data related to soil gas transport in the vadose zone include:
- LNAPL and water level monitoring data that includes seasonal monitoring and data on variability
- Soil type and moisture content from vadose zone samples
- Depth to impacted soil from laboratory analytical results of hydrocarbon concentrations in soil
- Field screening measurements of organic vapours to infer the vertical depth profile of LNAPL source zone
- Hydrogeological data on soil stratigraphy and groundwater flow direction

### **KEY SITE CONSIDERATIONS**

### **Ground surface conditions:**

- Ground surface cover: presence of infrastructure or pavement that result in a capping effect and reduce the diffusive flux of  $CO_2$ .
- Presence of vegetation: vegetation acts to increase the signal-to-noise ratio in CO<sub>2</sub> efflux measurements (i.e., fraction of contaminant relative to natural soil respiration). Avoid large trees and roots and conduct brush clearing of smaller vegetation, where feasible.
- Vadose zone soil conditions:
- Significant peat horizons: could lead to overestimation of NSZD rates due to high CO<sub>2</sub> efflux from
- Very course-grained material: Wind and barometric pressure changes can dilute shallow soil gas with atmospheric air (Görres et al., 2016). Such effects in part will depend on depth of vadose zone (i.e., there is greater potential for barometric pressure pumping for deep vadose zones).
- Submerged LNAPL source zone or in confining layer: although CO, produced from anaerobic biodegradation reactions occurring below the water table can migrate to the vadose zone, the resulting efflux could be lower than for source zones above the water table.
- Depth to source: there is greater uncertainty regarding application of CO<sub>2</sub> efflux method to source zones > approximately 10 m depth. For very shallow sources, measurement of CH<sub>4</sub> efflux may be

Presence of utilities or other preferential pathway for soil gas that can impact the CO<sub>2</sub> efflux at ground surface.

### EFFECTS OF WEATHER AND SEASONAL CONSIDERATIONS

- Highest CO<sub>2</sub> efflux measurements are expected during the summer (in northern
- hemisphere) during relatively dry and warm weather conditions
- Recommend conducting at least two field programs in contrasting seasonal conditions
- Avoid sampling during rainfall or during snowmelt
- Depending on the regional climate, can include measurements in relatively colder and sub-
- freezing temperatures. Cold climate studies on biodegradation of petroleum hydrocarbons in the subsurface indicate the significance of biodegradation even at low temperatures (e.g., Hers et al., 2014; McFarlin et al., 2014; and Prosser et al., 2016).
- To assess the influence of rainfall events on soil moisture conditions, similar considerations to soil vapour sampling are recommended
- Water retention curves for different soil types and use of models to predict the moisture profile for varying infiltration rates can be used to determine number of days following heavy rainfall for conducting measurements (California DTSC, 2015)
- California DTSC (2015) present soil drainage curves for a simulated instantaneous infiltration of 1 cm.
- Based on these analyses, suggested wait times after a moderate rainfall event are a minimum of one day for sandy soils and three to five days for silty soils.

## 2. CO, Efflux Survey



#### **BASIC STEPS**

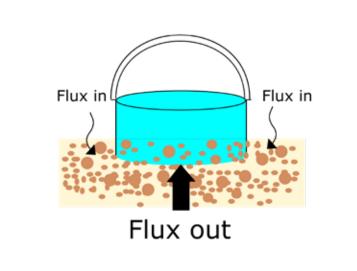
(one per location of measurement)

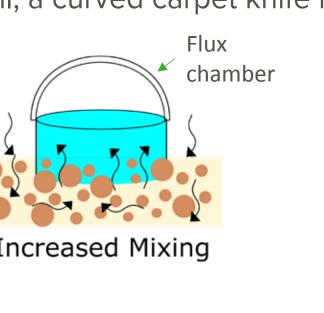
- 1. Insert soil collars ~24 hours prior to measurement at insertion depth of 5 to 8 cm
- 2. Measure and record offset (height of collar above ground surface)
- 3. Conduct CO<sub>2</sub> efflux measurements in duplicate

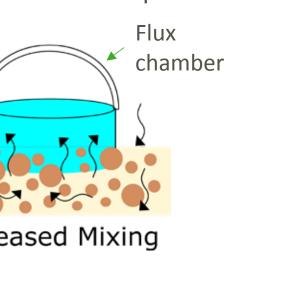
	Instrument Setting	Value
	Observation length	2 minutes
	Observation number	2
il	Deadband	30 seconds
	Pre-purge	1 minute

### **EFFECTS OF SOIL TYPE**

- Clear all roots and plant litter from collar area.
- At sites with coarse-grained (e.g., gravel, cobbles) or dense material where the collar cannot be directly pushed into the ground to the desired depth, remove the top layer of soil material prior to
- Ensure as good a seal as possible by lightly compacting disturbed and backfilled soil around the
- Remove larger soil particles (i.e., > approximately 3 cm diameter) from backfill.
- Place soil in lifts and nominally compacted.
- For dense cohesive soil, a curved carpet knife may be used to assist in collar insertion.







### MEASUREMENT LOCATIONS

Where the LNAPL plume has been delineated, soil collars can be placed along transects perpendicular and parallel to groundwater flow where often there is an added downgradient directional component to LNAPL migration. Additional collars can be deployed in a grid system for effective contouring of efflux measurements during post

Factors to consider in terms of access to testing locations are vegetation, infrastructure, pavement, steep terrain, boggy saturated conditions, as well as limitations in time and budget. It is practical to plan for conducting duplicate measurements at approximately 20 to 30 locations per day.

It is important to cover areas of varying soil type and vegetation, factors that in addition to LNAPL source zone distribution have the greatest effect on spatial variability in

### MEASUREMENT FREQUENCY AND QUALITY CONTROL

It is recommended to conduct the CO<sub>2</sub> efflux survey in contrasting seasonal conditions, but to avoid extreme weather events with respect to wind and precipitation, as well as freeze-thaw events that could result in saturated conditions in near surface soils (see Effects of Weather and Seasonal Considerations)



n duplicates to measure precision and co-located neasurements to evaluate small-scale variability. ocated measurements

## 3. Air Samples for Radiocarbon Analysis

Type B: Samples containing a mixture of ambient air and soil gas collected from the

### **KEY EQUIPMENT**



ultra-low vacuum pump





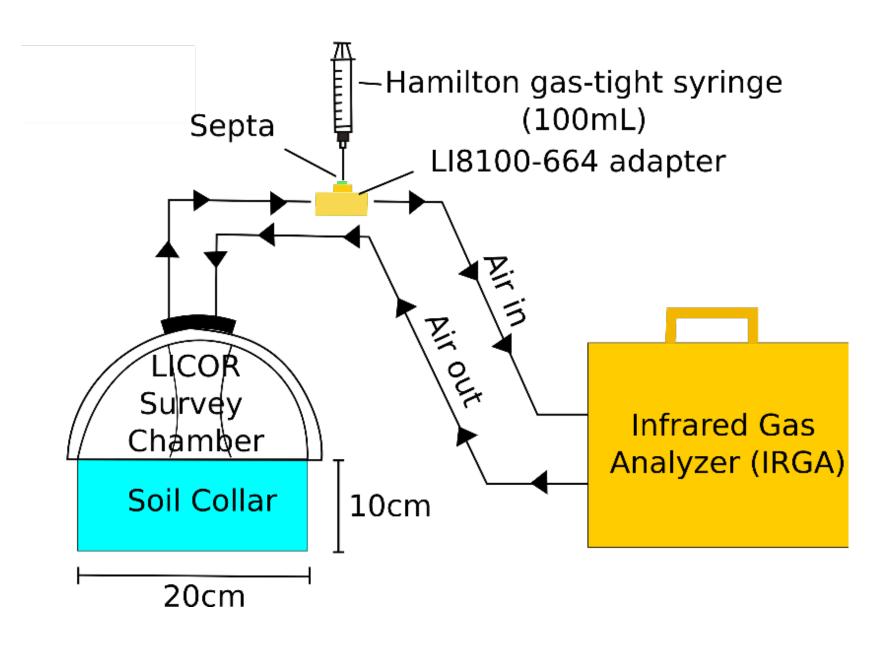
100 mL Luer lock gas-tight syringe (Hamilton 1000 series)

250 mL borosilicate Wheaton bottle which is pre-evacuated using a vacuum chamber and then over pressured to 300 mL during sampling

### COLLECTION OF CHAMBER (TYPE B) SAMPLE FOR <sup>14</sup>C ANALYSIS

Instrument Setting	Value	C
Observation length	20 to 60 minutes	
Observation number	1	
Deadband	30 seconds	C
Pre-purge	1 minute	

LI-8100A Input Parameters for Sample Collection

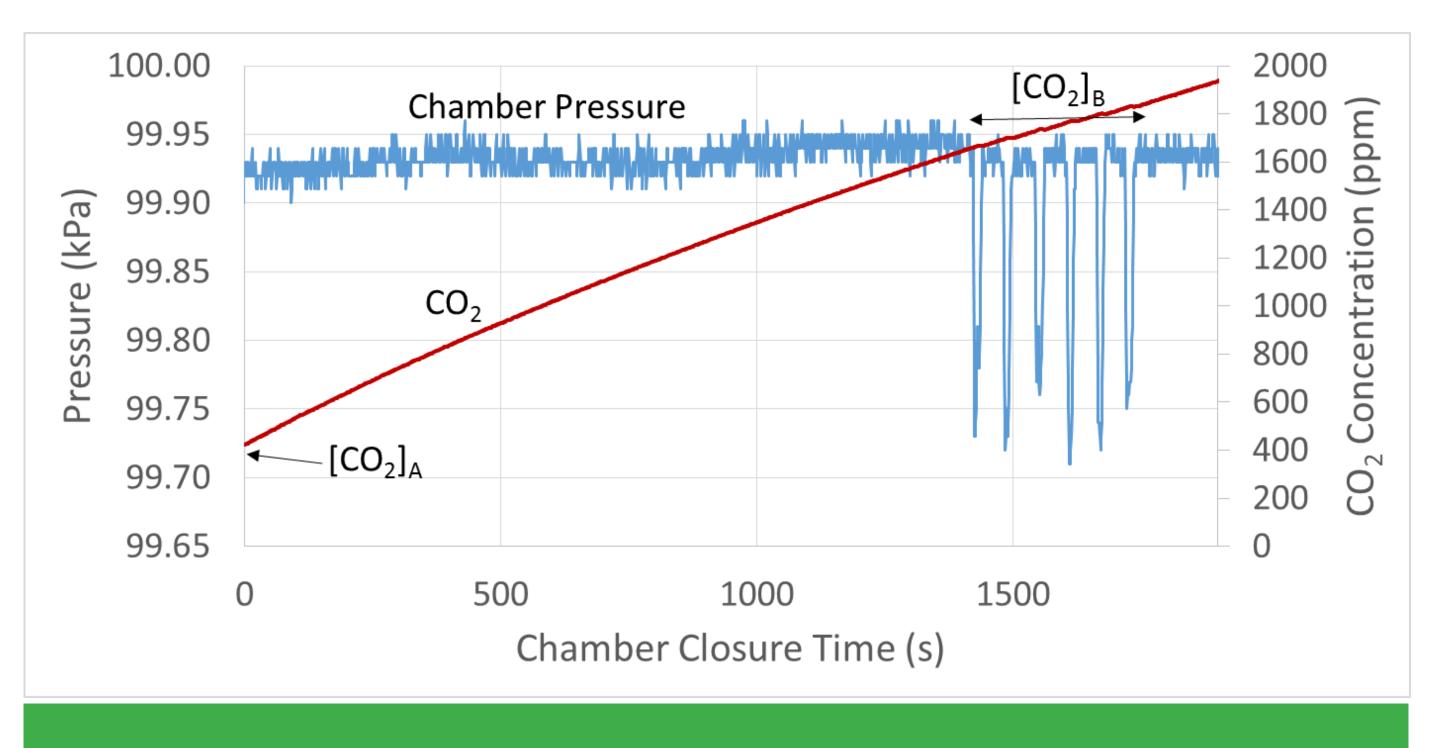


### NUMBER AND LOCATION OF SAMPLES

- Type A (Ambient air): Minimum of one sample per LNAPL area under assessment (paired samples at each location are not necessary because of typically low <sup>14</sup>C variability in ambient air). Additional samples are recommended for larger LNAPL impacted areas and/or if there are changes in topography with the LNAPL area (e.g., low lying areas).
- Type B (Chamber air): Depends on two main factors that affect natural soil respiration: soil organic carbon content and surface vegetation. Are recommended at least 10% of locations (subject to minimum of two radiocarbon samples) where CO<sub>2</sub> efflux measurements are collected. Additional samples may be required in areas that have relatively greater spatial variations in soil organic content and surface vegetation (based on professional judgement).
- Sample Volume: Radiocarbon analysis requires a minimum of 0.2-1.0 mg C depending on laboratory requirements, e.g., an ambient air sample containing approximately 400 ppm CO<sub>2</sub> requires a minimum of 4 x 250 mL pre-evacuated Wheaton bottles.

### CO, CONCENTRATIONS IN AIR SAMPLES FOR 14C ANALYSIS

- chamber sample collected for  $^{14}$ C analysis  $[CO_2]_B$
- LI-COR IRGA provides sufficiently accurate data for this purpose



## 4. Data Analysis for NSZD Assessment

### RADIOCARBON ESTIMATION OF CONTAMINANT SOIL RESPIRATION

$${\rm CO_2}$$
 Efflux = Contaminant Soil Respiration + Natural Soil Respiration 
$$J_{CO2} = J_{CSR} + J_{NSR}$$

Objective: to estimate  $J_{CSP}$  or the fraction of  $J_{CSP}$  to  $J_{NSP}$ 

$$F_{CSR} = \frac{J_{CSR}}{J_{CO2}}$$

Radiocarbon or <sup>14</sup>C analysis has been used to differentiate between CO<sub>2</sub> derived from fossil fuel and natural sources of atmospheric CO<sub>2</sub>.

Technique relies on <sup>14</sup>C analysis, a carbon isotope with a half-life of approximately 5,700 years generated by cosmic rays in the atmosphere.

Fraction of <sup>14</sup>C content of carbon (F<sup>14</sup>C) is measured by accelerator mass spectrometry.

(ey Point: Contemporary (modern) organic carbon is 14C-rich, while fossil fu arbon is <sup>14</sup>C-depleted

### MASS BALANCE EQUATION

$$F_{CSR} = \left(1 - \frac{{}^{14}F_B[CO_2]_B - {}^{14}F_A[CO_2]_A}{[CO_2]_B - [CO_2]_A}\right)$$

### RADIOCARBON CORRECTION

$$J_{CSR} = F_{CSR} J_{CO2}$$

### **NSZD RATE ESTIMATE**

$$J_{NSZD} = J_{CSR} \frac{M_w S_{HC:CO2} U}{O_0}$$

 $J_{NSZD}$  = Natural source zone depletion rate in gallons/acre/year

- $M_w$  = Molecular weight of hydrocarbon (e.g., 142 g/mol for decane)
- $S_{HC,CO2}$  = Stoichiometric ratio of mole of hydrocarbon degraded per mole of CO<sub>2</sub> produced (e.g., 0.1 for decane)
- $\rho_o$  = Density of LNAPL (kg/L)

5. Method Uncertainties & Limitations

- **BASED ON PRIMARY ASSUMPTIONS**
- 2. Petroleum hydrocarbons are the major source of radiocarbon depletion (no other
- major ancient carbon sources, i.e., old peat horizons, carbonate dissolution). Understanding the site geology and characterizing the background radiocarbon signature of CO2 is therefore important to understanding the potential effect of other
- Consideration could be given to collecting of vegetation samples (i.e., root mass) where there are ancient peat deposits to assess the site specific F14C signature.
- 3. Methane is oxidized to CO2 in the vadose zone.

sources of ancient carbon.

- If methane concentrations are elevated to percent levels in shallow soil gas (i.e., at or less than 1 m depth), there is greater potential for methane efflux and as such measurement of methane efflux is recommended.
- The methane efflux can be quantified using a Greenhouse Gas Analyser (GGA) interfaced with the LI-COR system to monitor CH4 concentrations within the LI-COR

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