In-field rapid precipitation of carbonate minerals for assessing hydrocarbon biodegradation rates through $^{14}CO_2$ apportionment

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Field Study –
Old Crow, Yukon

- Contaminant source – arctic diesel
- Contamination caused by historic fuel tank leaks, fuel line leaks and 50+ years of fuel handling resulting in accidental spills accumulating over time
- PHC impacts in soil and supra-permafrost water to ~ 2 mbgs
- Study conducted during site assessments before any active remedial techniques applied

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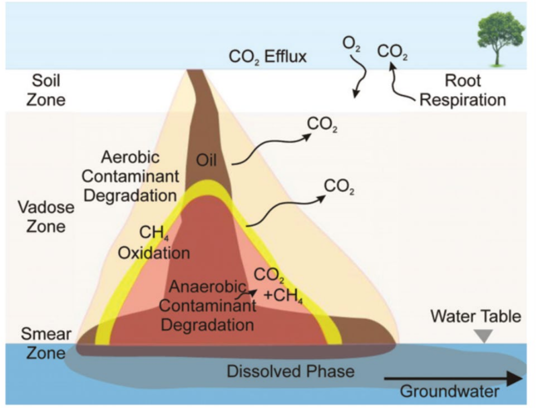
Soil Efflux CO_2 Measurements for Hydrocarbon Degradation

- Soil CO_2 flux commonly used to estimate biodegradation component of NSZD
- Differences in flux (J_{CSR}) from impacted areas (J_{TSR}) to background areas (J_{NSR}) used to apportion CO_2 derived from contaminant degradation

LI-8100A Automated Soil CO_2 Flux System and Long-Term Chamber

$$J_{CSR} = J_{TSR} - J_{NSR}$$

(units of μmol/m^{2}sec^{-1})



- **BUT,… This method does not accurately separate soil gas from contaminant degradation and natural soil respiration processes (Sihota & Mayer, 2013)**

Radiocarbon Principles

$$^{1}_{0}n + ^{14}_{7}N \rightarrow ^{14}_{6}C + ^{1}_{1}p \xrightarrow{O_2} ^{14}CO_2$$

Carbon Isotope	# Protons	# Neutrons	Atmospheric Abundance (%)
^{12}C	6	6	98.9
^{13}C	6	7	1.1
^{14}C	6	8	10^{-12}

- ^{14}C produced in atmosphere
- Equilibrated into carbon cycle through chemical and biological processes
- At metabolic death radiocarbon decay clock begins
- ^{14}C half life ~5730 years, maximum dating potential ~50,000 yr BP
- Hydrocarbon considered free of all ^{14}C

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$F^{14}C$ Corrections to soil efflux measurements

$$F_{NSR} = \frac{F^{14}C\ sample}{F^{14}C\ background}$$

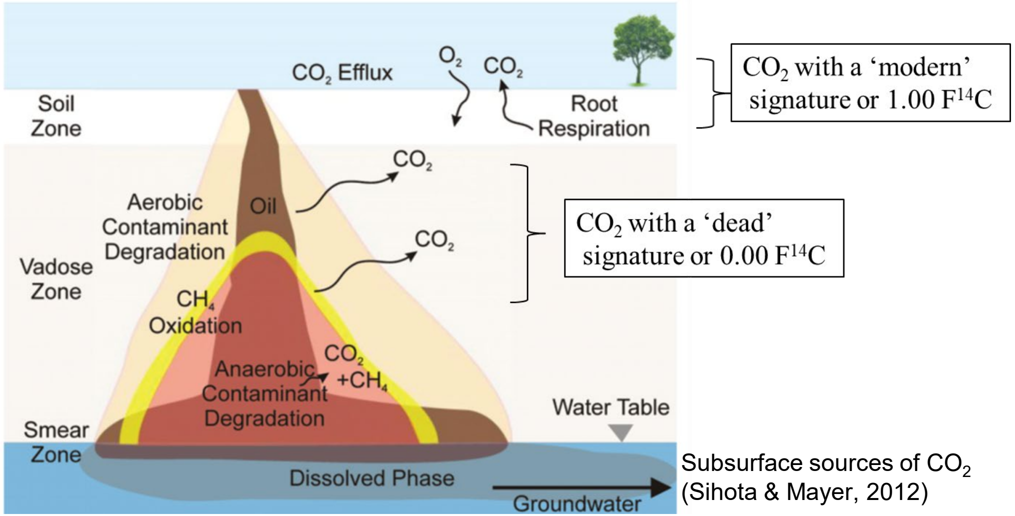
↓

$$F_{CSR} = 1 - F_{NSR}$$

↓

$$J_{CSR} = J_{TSR} * F_{CSR}$$

(units of $\mu mol/m^2 sec^{-1}$)



Subsurface sources of CO_2 (Sihota & Mayer, 2012)

F_{NSR} = Fraction derived from natural soil respiration
F_{CSR} = Fraction derived from contaminant respiration
J_{CSR} = Flux derived from contaminant soil respiration
J_{TSR} = Total flux from soil respiration
(flux measurement on plume)

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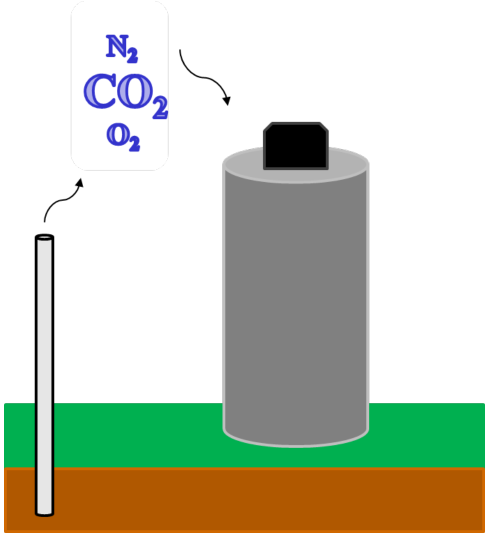
Traditional Soil CO_2 Sample Collection

- Samples collected as mixed soil gas in evacuated bottles (2x 250ml per sample)
- Mixed soil gas transported to lab for purification and graphitization for analysis by AMS
- Sample bottles prone to contamination through leaky seal or incomplete evacuation
- Large, fragile cumbersome sampling equipment



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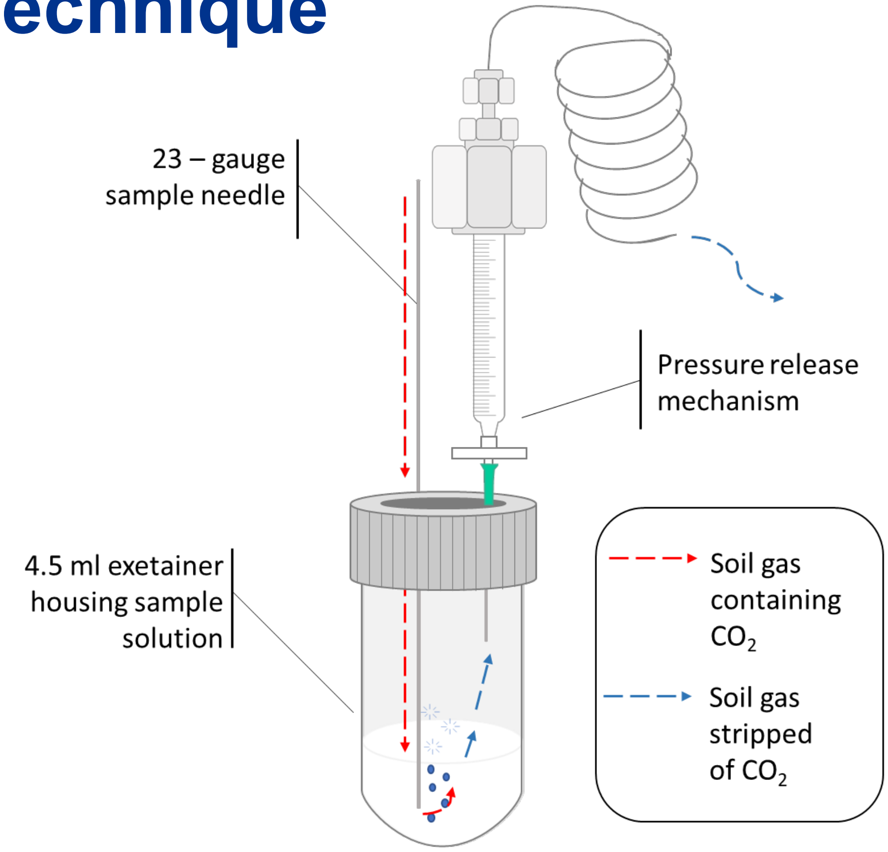
Novel $BaCO_3$ Sampling Technique

- Samples now collected as $BaCO_3$ precipitated in the field in 4.5ml exetainer
- Sample solution strips CO_2 from soil gases allowing other soil gas components to pass through
- Dramatically reduced sample equipment footprint
- Potential solution contamination can be observed before sampling begins



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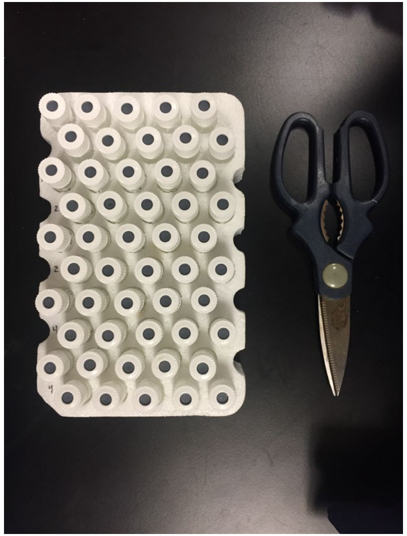
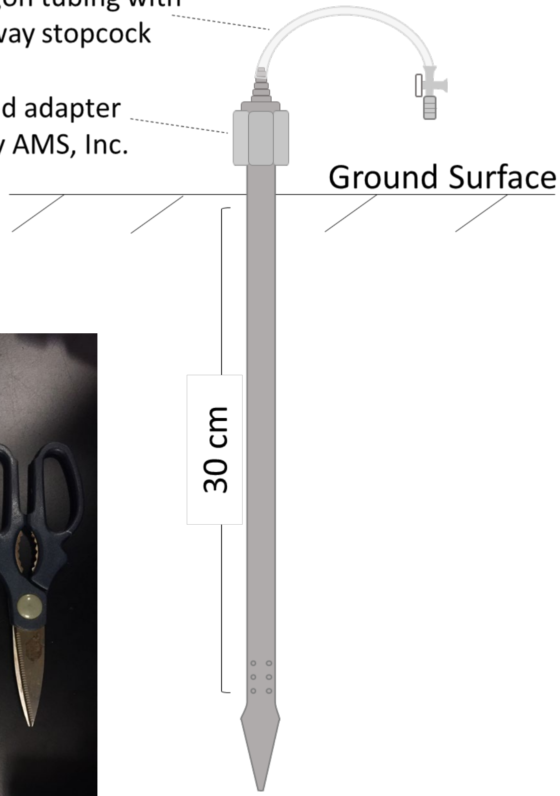
$BaCO_3$ Sampling Equipment





Simplified Laboratory Sample Pretreatment

- Excess solution removed and samples freeze-dried before being pressed into AMS ‘target’ with matrix material
- Sample is analyzed on Accelerator Mass Spectrometer (AMS)
- 2018 field campaign produced final radiocarbon data within one week

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$BaCO_3$ Data

2017 Sample Duplicates

Sample ID	Site condition	$F^{14}C$	+/-
RC41	Impacted	0.91	0.02
RC41 (DUP)	Impacted	0.89	0.02
RC13	Background	0.99	0.02
RC13 (DUP)	Background	0.99	0.02

2017 – 2018 Sample Duplicates

Sample ID	Site condition	Sampling Year	$F^{14}C$	+/-
RC57	Impacted	2017	0.84	0.02
RC18-57 (DUP)	Impacted	2018	0.84	0.02
RC46	Plume fringe	2017	0.89	0.02
RC18-46 (DUP)	Plume fringe	2018	0.90	0.02

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$BaCO_3$ vs Graphitized Sample Data – Old vs. New

Sample ID Graphite	$BaCO_3$	Site Conditions	Graphite $F^{14}C$	+/-	$BaCO_3$ $F^{14}C$	+/-
GRC18-3	RC12	Background	1.0203	0.00460	1.0390	0.02400
NSRC15-1	RC13	Background	0.9918	0.0027	0.9974	0.00780
--	RC19		--	--	0.9883	0.02366
GRC18-6	RC18-6	Impacted	0.4840	0.00220	0.4874	0.00595
GRC18-7	--		0.4878	0.00220	--	--
GRC18-4	RC49	Plume fringe	0.8656	0.00390	0.8353	0.00829
NSRC54-2	RC10	Impacted	0.9552	0.00360	0.9305	0.01124

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Field Blank Production

- $BaCO_3$ blanks can be made in the field using a source of ^{14}C free CO_2
- Blanks are precipitated in the same manner as representative samples
- Mixed gas field blank was produced from a bottle which was evacuated and transported to the site with all other mixed gas bottles before addition of standard gas in laboratory

Sample Type	Analysis	Blank Value ($F^{14}C$)
$BaCo_3$	Direct AMS	0.02
Mixed Soil Gas	Graphitization	0.02
Lab Standard	Graphitization	0.004

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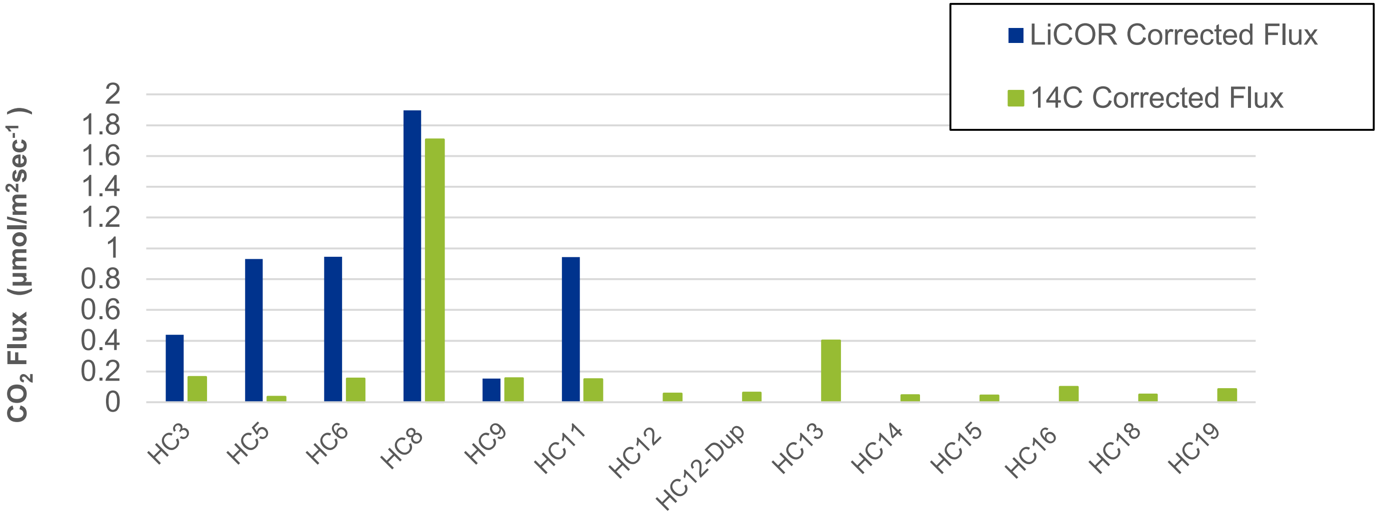
Radiocarbon paired efflux measurements



$$F_{NSR} = \frac{M^{14}C_{\,sample}}{M^{14}C_{background}} \rightarrow F_{CSR} = 1 - F_{NSR} \rightarrow J_{CSR} = J_{TSR} * F_{CSR}$$

(units of $\mu mol/m^2sec^{-1}$)

- Corrected to average background ^{14}C measurement of 0.95 $F^{14}C$ ($F^{14}C_{background}$)
- Interpretations can now be made where reduced flux was recorded

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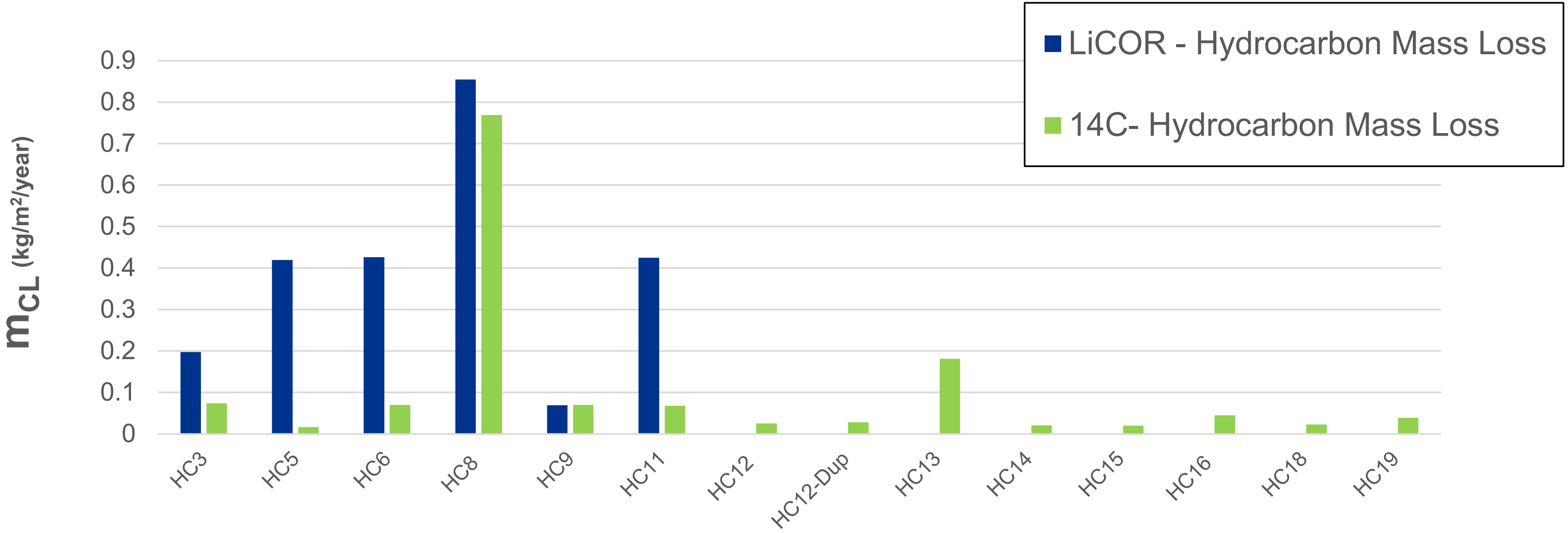
Refined Calculations of Hydrocarbon Mass Loss



$$\textbf{Contaminant Mass Loss } (m_{cl}) = J_{CSR} * \frac{1\mu molC_8H_{18}}{8\mu molC_8H_{18}} * \frac{1mol}{1*10^6\ mol} * \frac{114.23gC_8H_{18}}{1molC_8H_{18}} * \frac{1\ kg}{1000g} * \frac{3600sec}{1hr} * \frac{24hr}{1\ day} * \frac{365\ day}{1\ year}$$

(units of $\mu mol/m^2sec^{-1}$) **(units of kg/m^2year^{-1})**

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Concluding Remarks

- Radiocarbon as a tracer refines quantification of subsurface hydrocarbon mass loss (NSZD)

- New $BaCO_3$ precipitation method eases costs and logistics associated with applying radiocarbon to site studies

- $BaCO_3$ allows for reduced error and site specific background corrections

- Rapid turn around time of $BaCO_3$ samples allows for quick analysis

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