Making radiocarbon more accessible for the study of biodegradation

A new and affordable rapid sampling technique

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Presentation Overview

- Field Study – Old Crow, YT
- Radiocarbon Principles
- Radiocarbon Applications
- $BaCO_3$ Method Development
- Data/Results
- Q&A

Field Study – Old Crow, YT

- Historic spill of arctic diesel due to fuel handling practices and accidental release during AST upgrade

- PHC impacts in soil to estimated 2mbgs and within suprapermafrost water

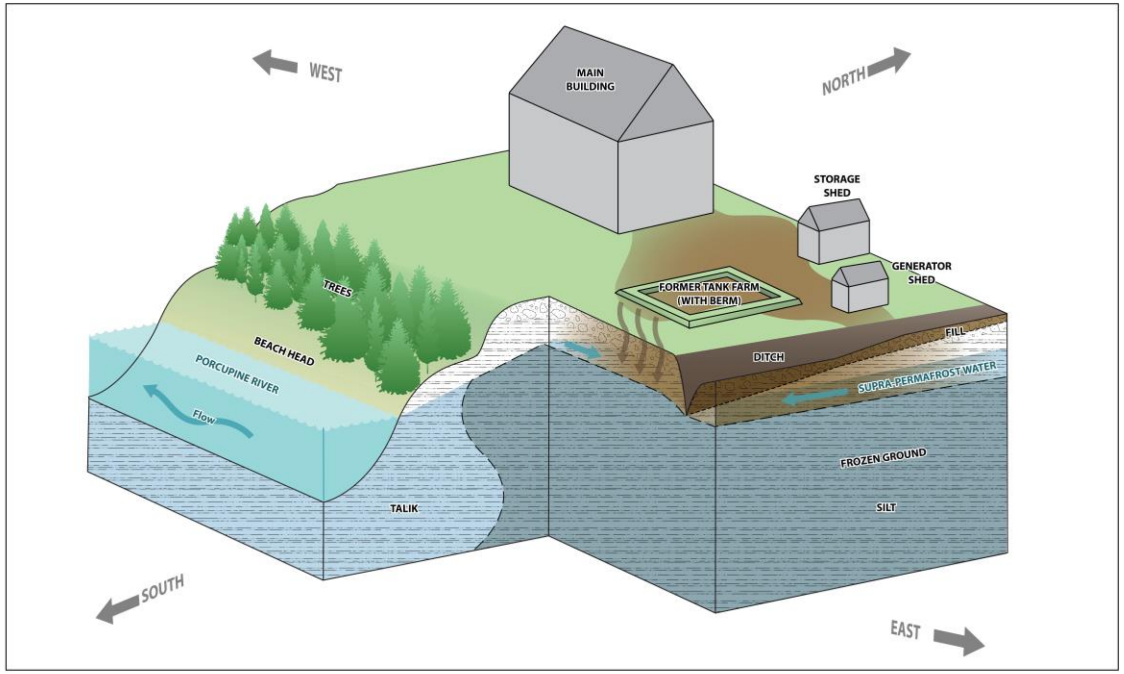
- Shallow (~2mbgs) permafrost, proximity to Porcupine River and remote location poses challenges for remedial efforts

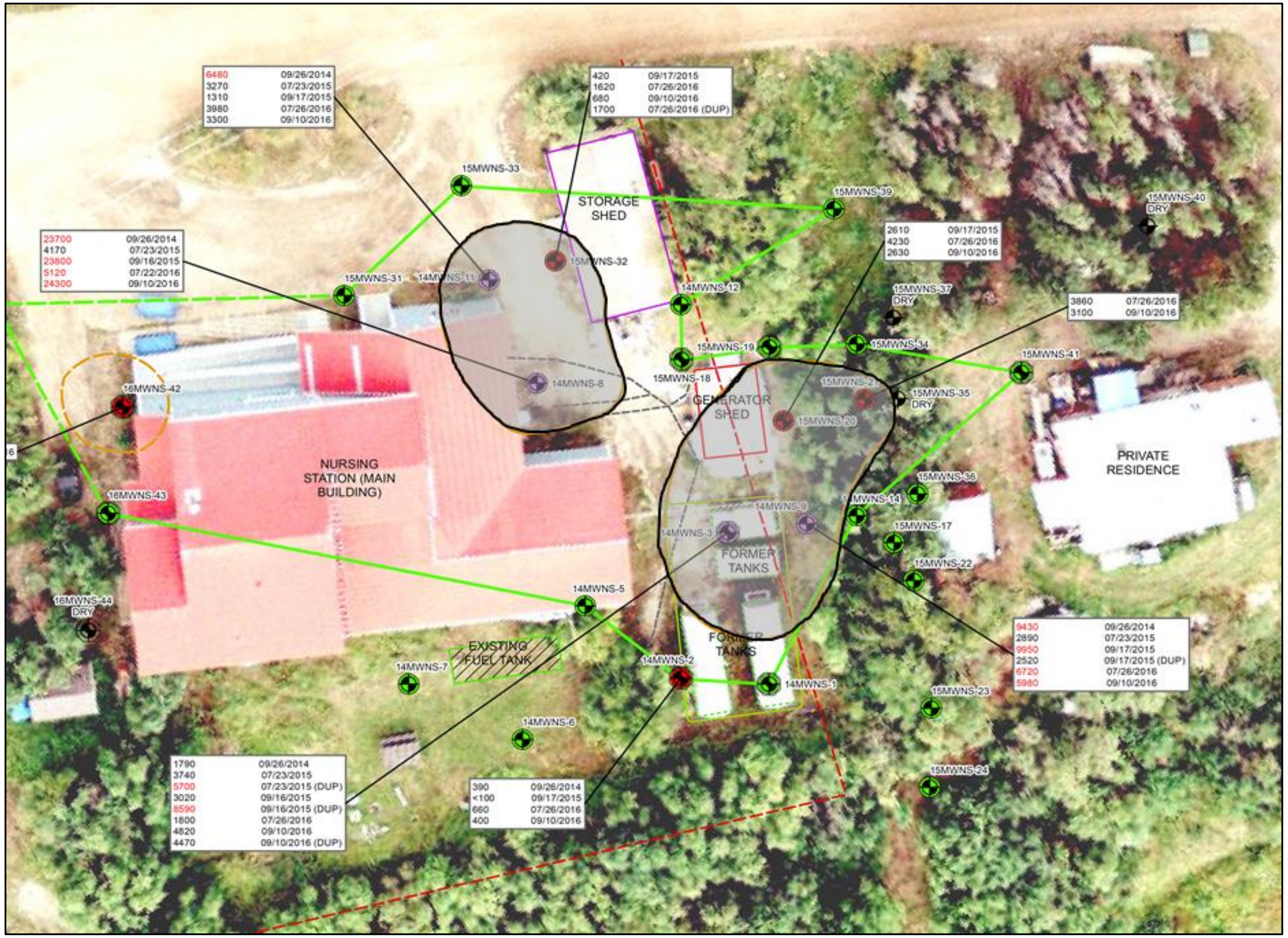
(CH2M, 2016 & CH2M, 2015)

Making a case for Natural Source Zone Depletion (NSZD)

(CH2M, 2016 & CH2M, 2015)

- Shallow Permafrost
- Proximity to Porcupine River
- Remote location





Soil Gas flux measurements

Soil CO_2 flux commonly used to estimate Natural Source Zone Depletion (NSZD)

Traditional methods involve measurements both on and off plume

Differences in flux are used to correct for background and apportion CO_2 derived from contaminant degradation

This method does not quantitatively separate soil gas from contaminant degradation and natural soil respiration processes (Sihota & Mayer, 2013)

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

https://www.licor.com/corp/history.html

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

(units of µmol/m²sec⁻¹)

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

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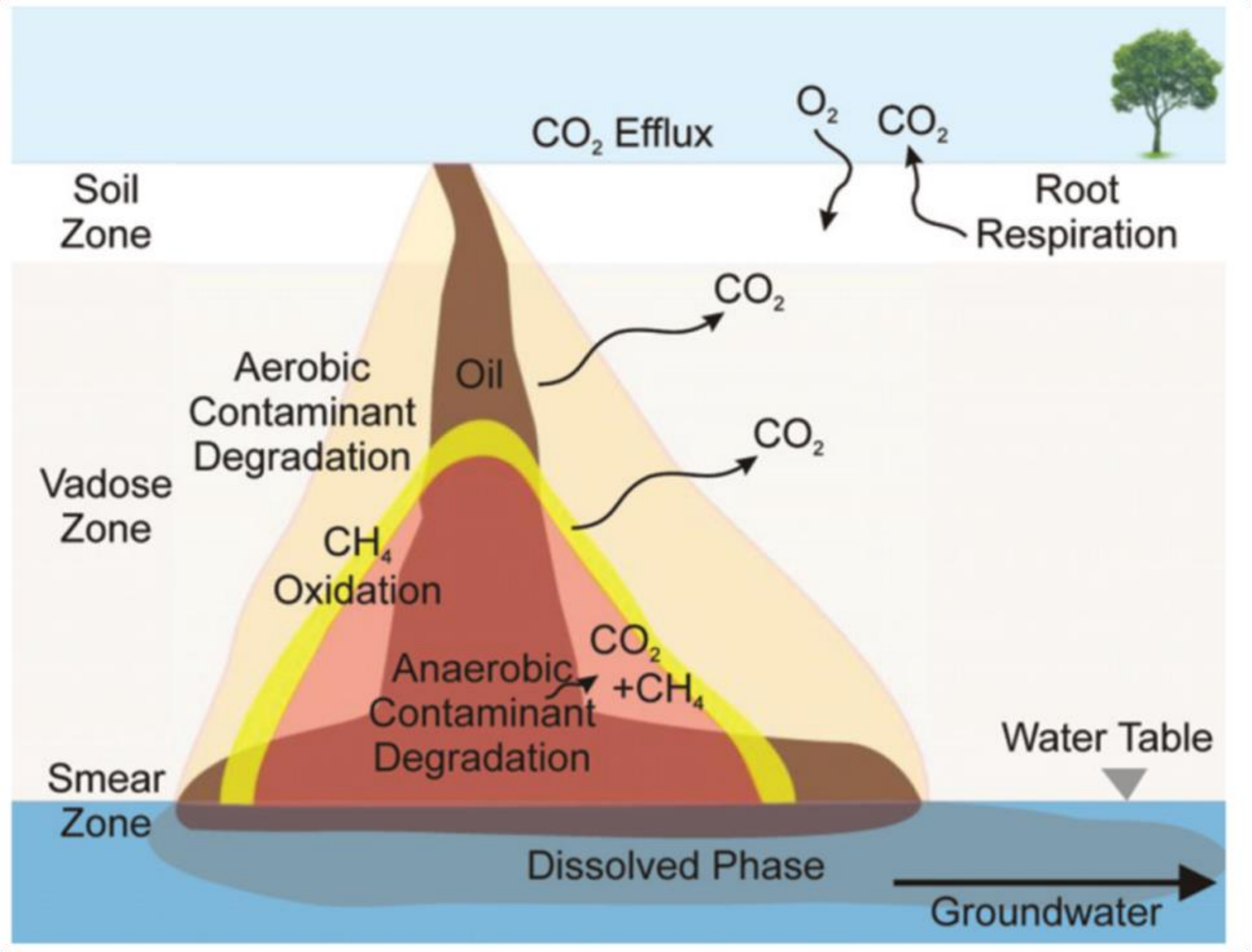


Subsurface sources of CO_2
(Sihota & Mayer, 2012)

Radiocarbon Principles

Natural Abundances of Carbon Isotopes

98.9%	^{12}C
1.1%	^{13}C
10^{-12}	**^{14}C**

Half life of ~5730 years

Maximum dating age of ~50,000 BP

Applications in archaeology, palaeontology, geochemistry, hydrogeology…

Measured by Accelerator Mass Spectrometry (AMS) as an abundance ratio

STABLE ISOTOPES

RADIOACTIVE ISOTOPE

^{12}C
6 proton
6 neutron

^{13}C
6 proton
7 neutron

^{14}C
6 proton
8 neutron

Radiocarbon Production

Cosmogenic production

- cosmic rays interact with atmospheric nitrogen

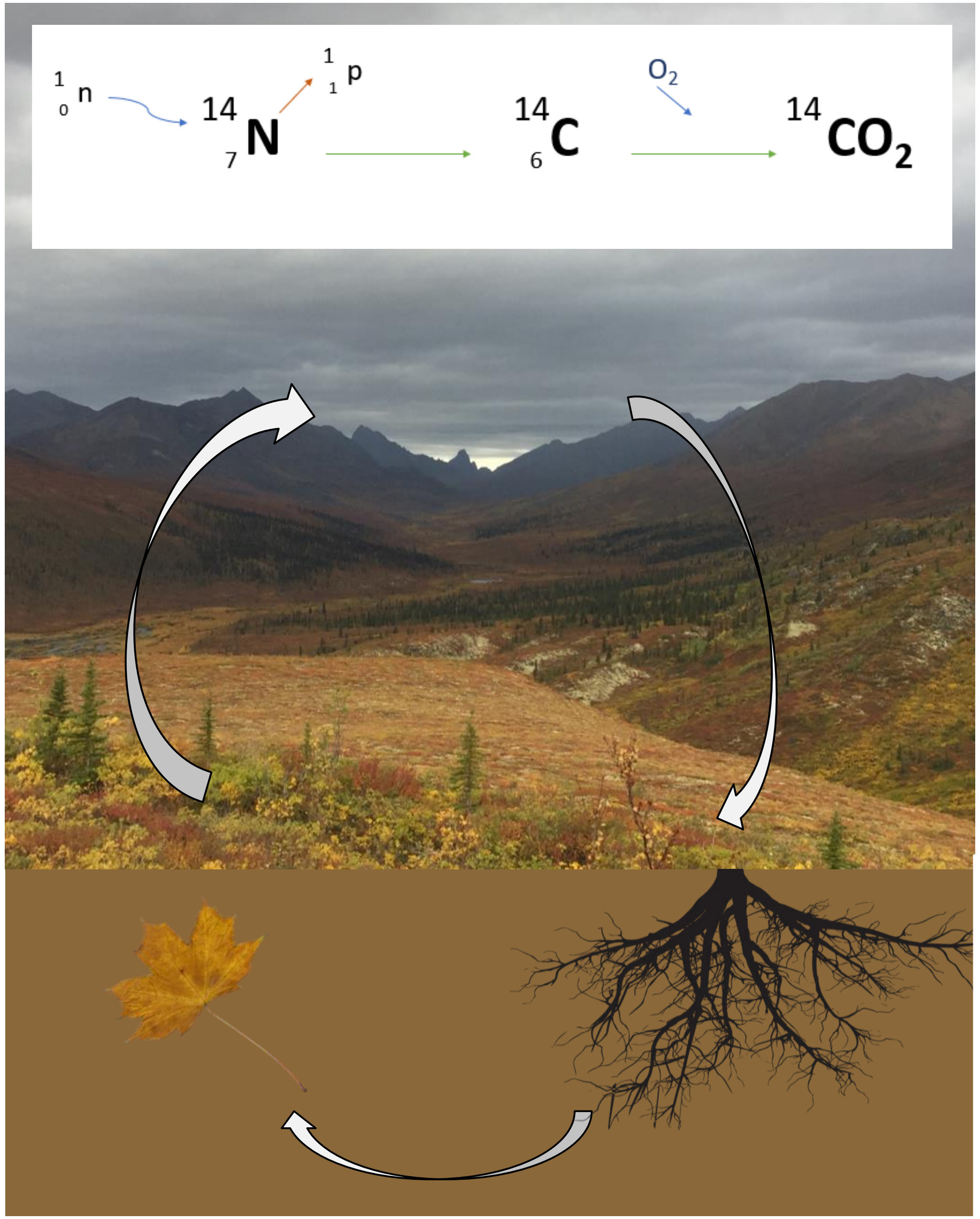
^{14}C quickly oxidizes to form ^{14}CO and $^{14}CO_2$ compounds

Enters carbon cycle through chemical and biological processes

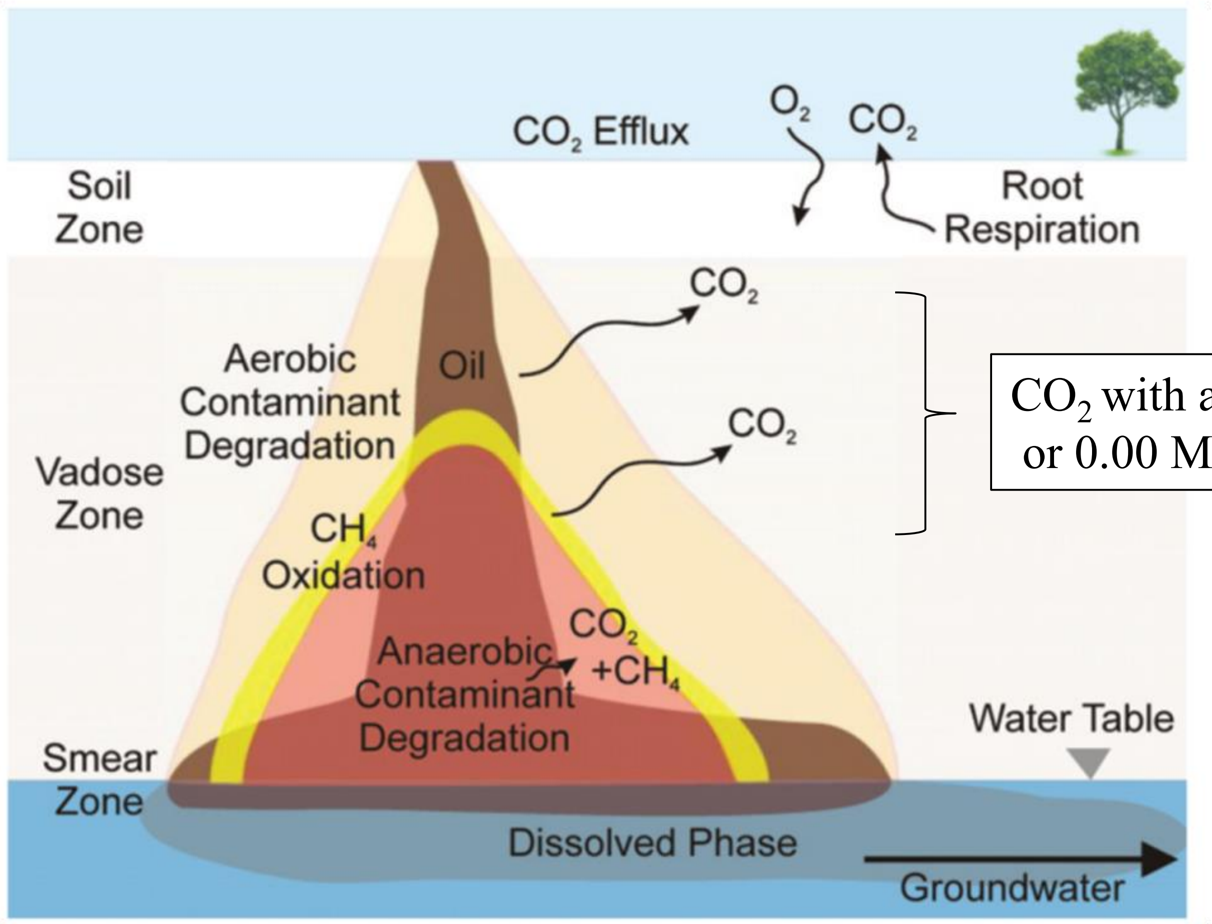
All living things are in equilibrium with atmospheric $^{14}CO_2$

Once metabolic processes end, radioactive decay clock begins

Hydrocarbons are considered radiocarbon free due to geologic age



A measured value of say, **0.80 $M^{14}C$,** shows **80% of CO_2** contributions **from modern processes** and **20% of CO_2** derived **from hydrocarbon degradation.**



CO_2 with a 'modern' signature or 1.00 $M^{14}C$

CO_2 with a 'dead' signature or 0.00 $M^{14}C$

Subsurface sources of CO_2 (Sihota & Mayer, 2012)

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Radiocarbon Applications

^{14}C is useful to distinguish CO_2 derived from contaminant sources (Conrad et al. 1997)

Soil CO_2 sampled from on and off plume is analyzed for radiocarbon content

Various radiocarbon signatures are paired with flux measurements to correct for natural soil respiration contributions to flux

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

$$\Downarrow$$

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

$$\Downarrow$$

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

(units of µmol/m²sec⁻¹)

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)

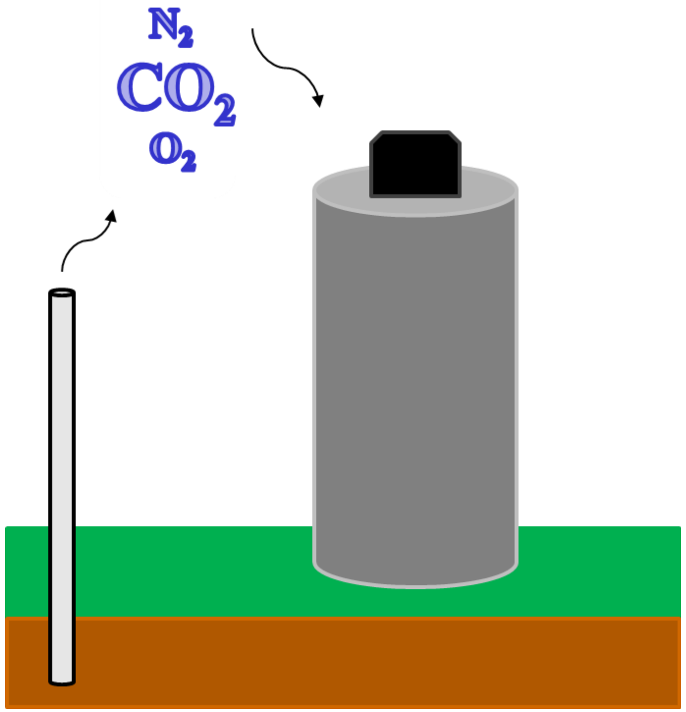
Current Radiocarbon Sampling Methods

Current sampling methods include:

- Collection of mixed soil gas in pre-evacuated 250ml bottles
- Sorbent soil gas traps

These sampling methods involve large costs, extensive sample pre-treatment, and are logistically challenging for remote locations

Mixed Soil Gas Sampling Protocol

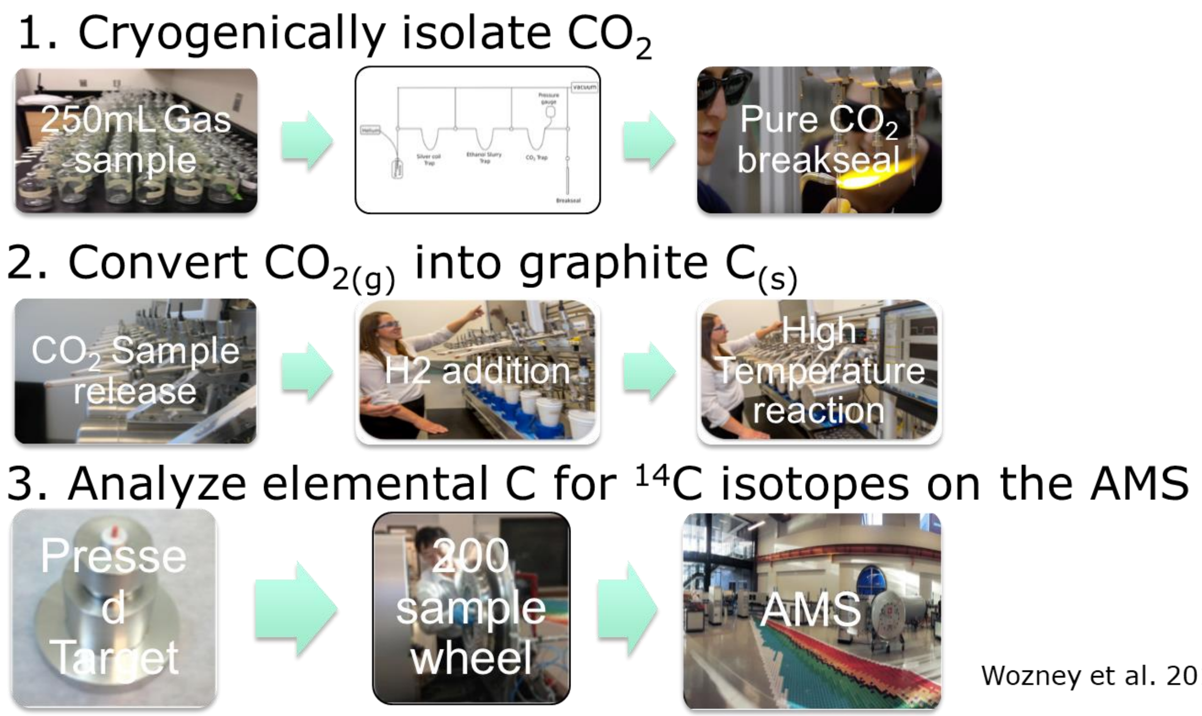


- 250ml glass sample bottles are cleaned before capping and evacuating contents

  (< 60 mtorr)

- Mixed soil gas is collected in the field and contained in evacuated bottles via syringe and butyl septa before samples transported for analysis

Mixed Soil Gas Lab Pre-treatment



Wozney et al. 2017

- Samples are returned to laboratory and CO_2 is isolated and graphitized before being pressed into AMS 'target'
- Sample is analyzed on Accelerator Mass Spectrometer (AMS)

Method Development

Radiocarbon research has begun exploring the use of solid carbonate samples for direct analysis in AMS

Longworth et al., 2013
Bush et al., 2013

University of Ottawa explored various compound and matrix combinations to generate best results and a sustainable Accelerator Mass Spectrometer (AMS) current

Yang et al. 2018 (Article in press)

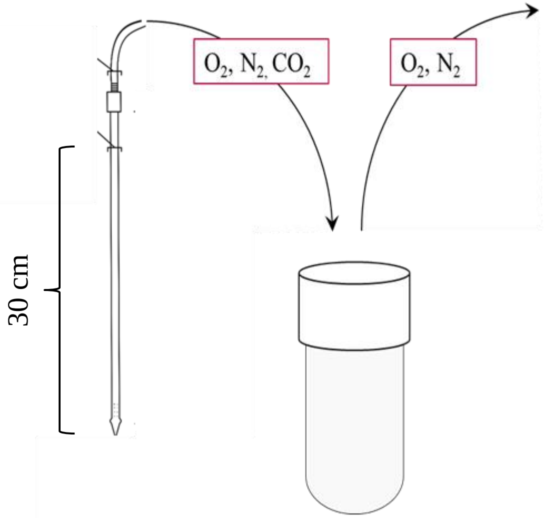
Exploration of applications for Barium carbonate in environmental sampling begin

Main drivers – develop novel technique, decrease cost, ease logistics

Barium Carbonate Sampling Protocol

I)

II)



III)

- Vials are prepared with hydroxide solution
- Soil gas is injected to sample vials in field
- CO_2 is stripped from air and $BaCO_3$ is left behind

Barium Carbonate Lab Pre-treatment

- Excess solution removed and samples freeze-dried before being pressed into AMS 'target' with matrix material
- Sample is analyzed on Accelerator Mass Spectrometer (AMS)

✓ Decrease cost ✓Ease logistics

- 2017 sampling containers
- Bottles in photo represent 10 samples (10 of many, many more…)

- 2018 sampling containers
- Photo of 50 samples

✓ Develop Novel Technique

Sample Type	Background ($M^{14}C$)	Blank ($M^{14}C$)	Sample [4] ($M^{14}C$)
Mixed Soil Gas	Ox II (1.05)	0.02 [3]	0.95
Sorbent Trap	1.05 [1]	0.70	0.93
$BaCO_3$	0.95 [2]	0.02	0.92

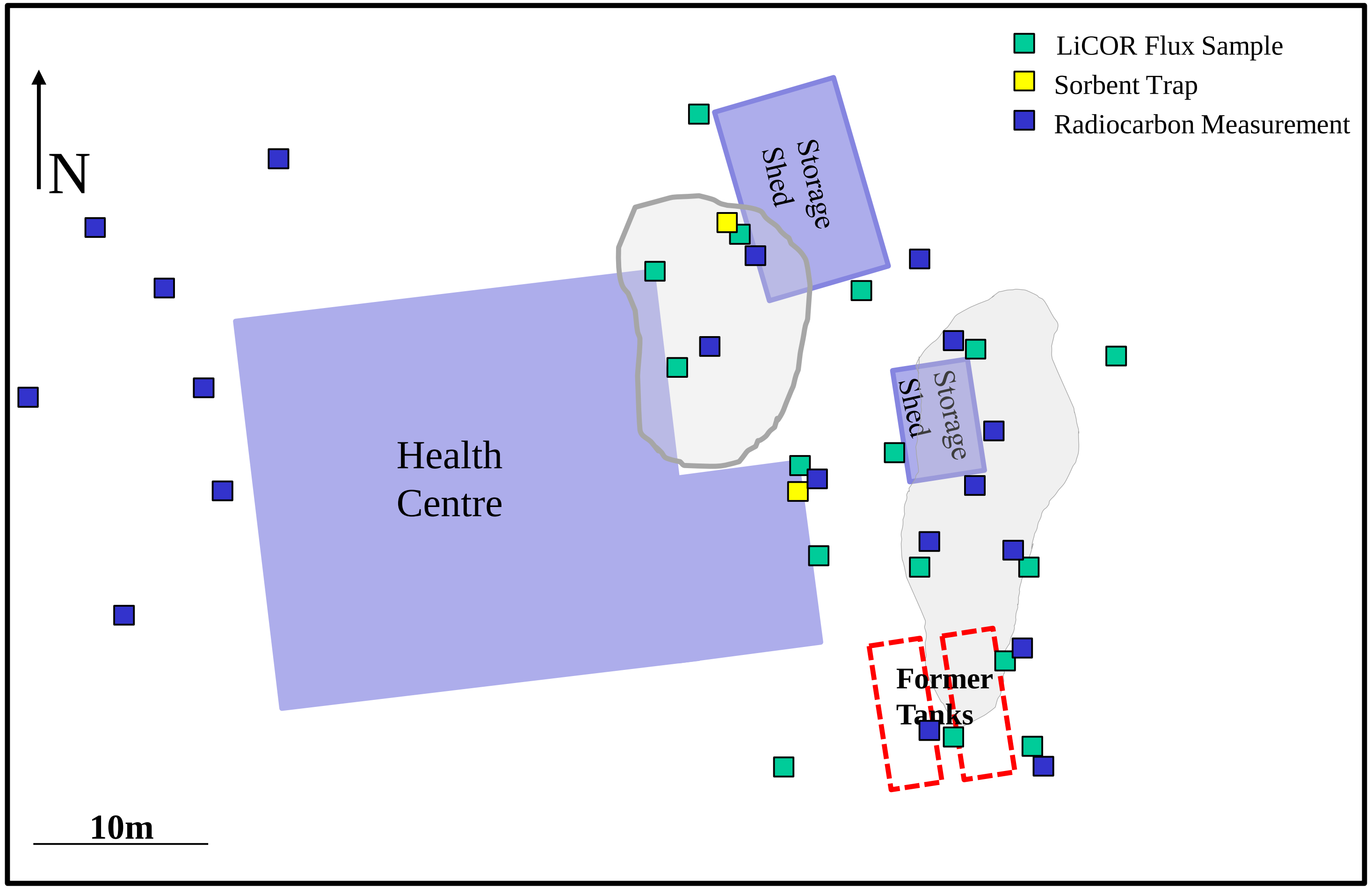
[1] value from Hua et al. 2013, atmospheric ^{14}C after bomb spike
[2] background value measured from site specific to this study
[3] mixed soil gas blank high in this dataset, normal values ~0.004 M14C
[4] samples taken on interpreted fringe of plume in non-vegetated area

Duplications

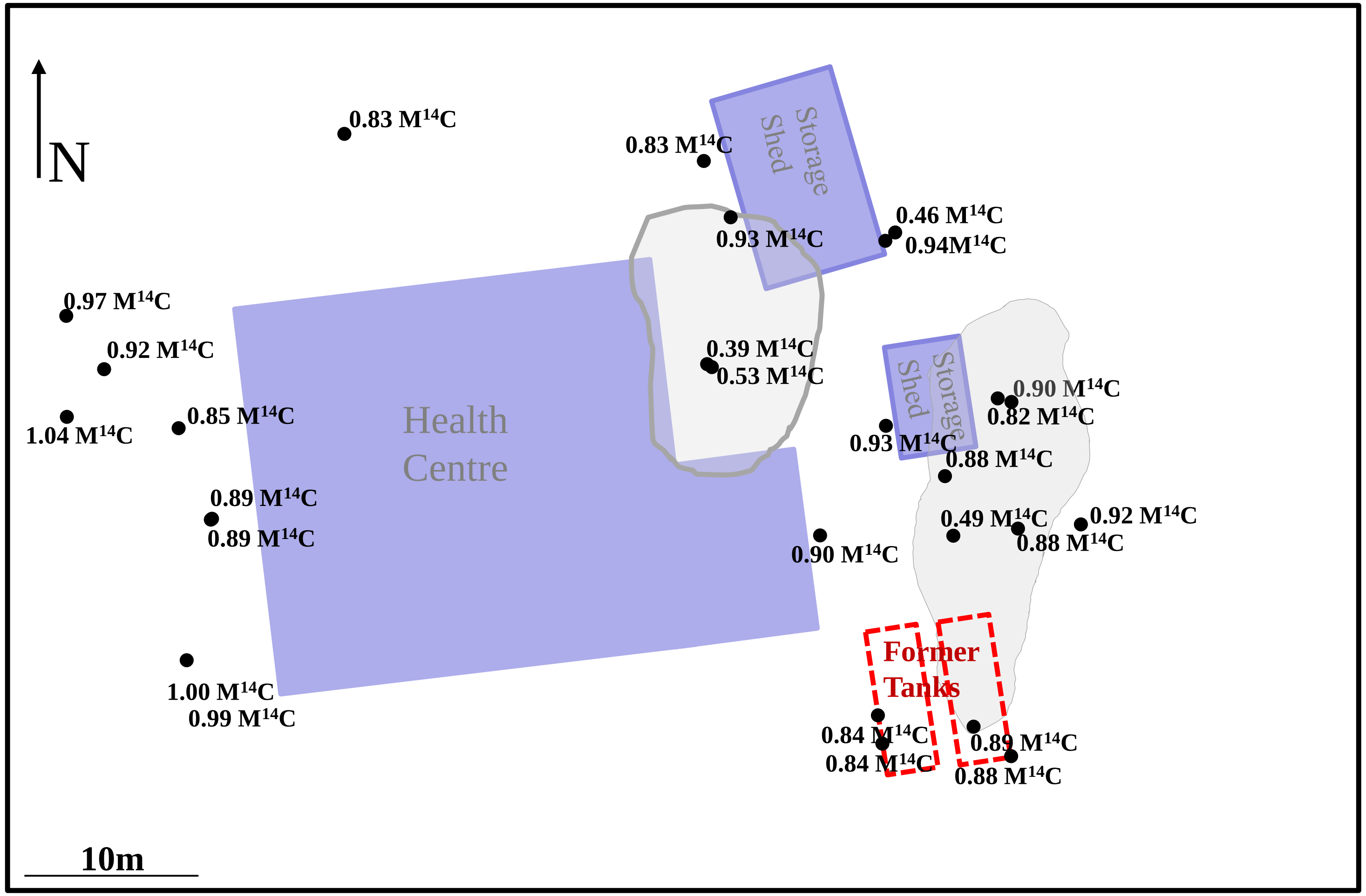
Sample ID	Site Parameter	Sampling Year	$M^{14}C$	+/-
RC41	Non vegetated - plume	2017	0.91	0.02
RC41 (rep)	Non vegetated - plume	2017	0.89	0.02
RC13	Vegetated – off plume	2017	0.99	0.02
RC13 (rep)	Vegetated – off plume	2017	0.99	0.02

Sample ID	Site Parameter	Sampling Year	$M^{14}C$	+/-
RC57	Vegetated – plume	2017	0.84	0.02
RC57 (rep)	Vegetated - plume	2018	0.84	0.02
RC46	Non-vegetated – off plume	2017	0.89	0.02
RC46 (rep)	Non-vegetated – off plume	2018	0.90	0.02

Old Crow Site Sampling

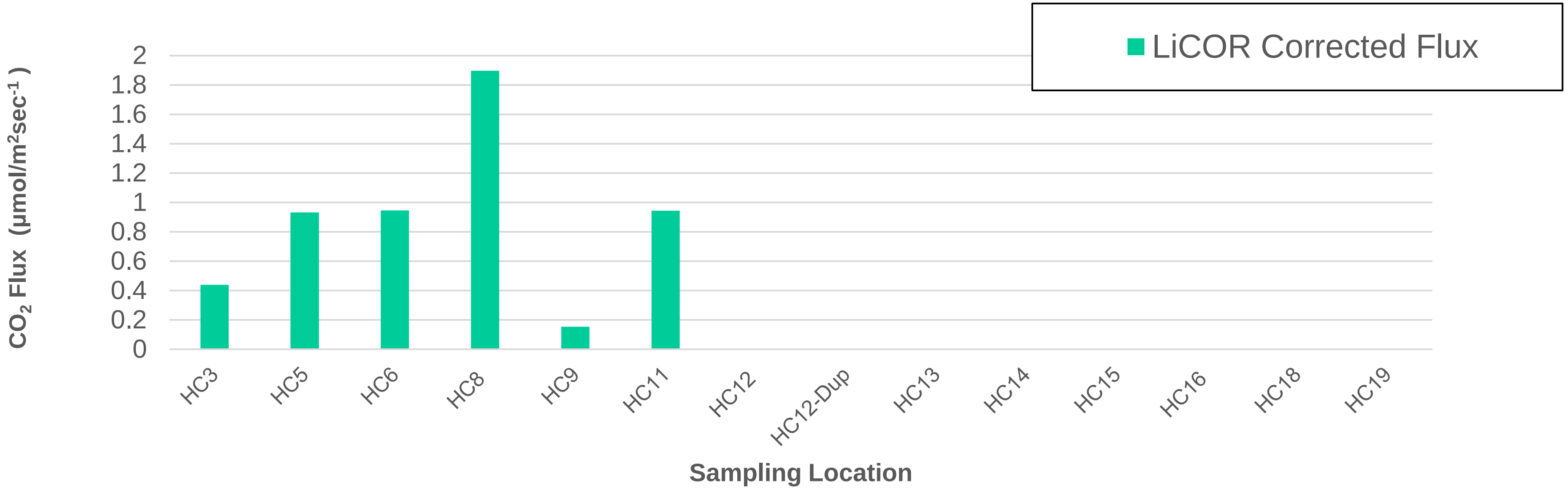


- Extensive Flux sampling program by Jacobs (CH2M) using LiCOR in 2017
- 2 sorbent trap ^{14}C samples collected in 2017
- Site wide application of $BaCO_3$ sample collection in 2017 and 2018



- Variance in $M^{14}C$ values can be observed in interpreted areas of known contamination
- Background values range from 1.04 $M^{14}C$ (vegetation) to 0.83 $M^{14}C$
- Central plume $M^{14}C$ shows greatest depletion

Flux Measurements



$$J_{CSR} = J_{TSR} - J_{NSR}$$ (units of $\mu mol/m^2sec^{-1}$)

- Corrected to average background flux measurement of 1.15 $\mu mol/m^2sec^{-1}$ (J_{NSR})
- No interpretation can be made in areas where flux measured is lower than background (where $J_{TSR} < J_{NSR}$)

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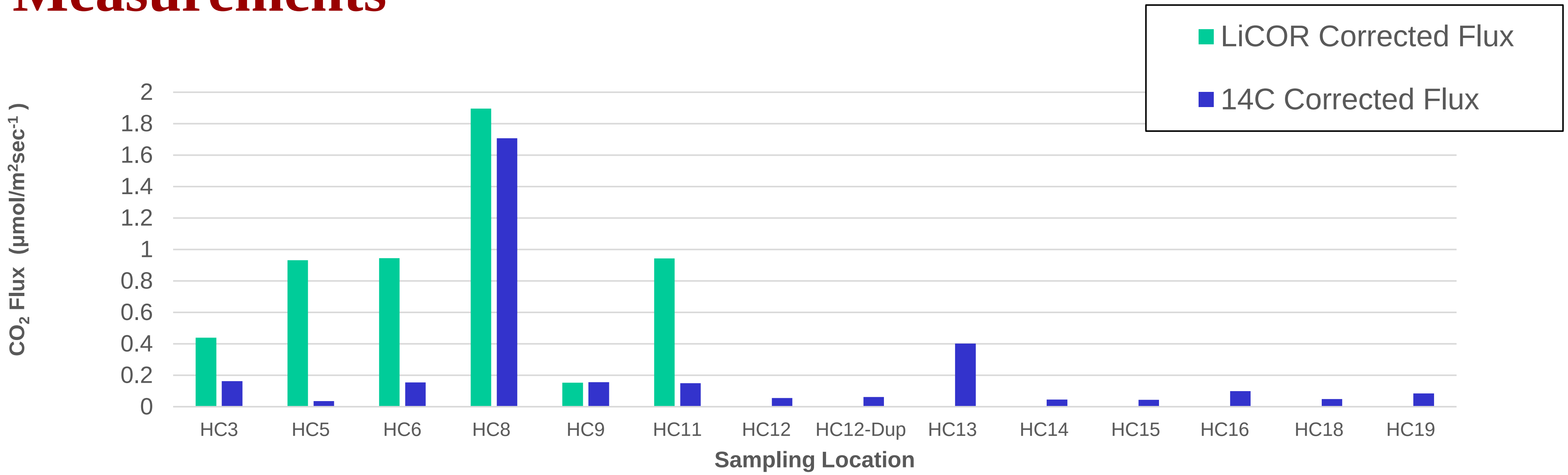
Flux Measurements



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

(units of μmol/m^{2}sec^{-1})

- Corrected to average background ^{14}C measurement of 0.95 M14C (M14C$_{\text{background}}$)
- Interpretations can now be made where reduced flux was recorded

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Calculation of Mass Loss

(flux corrected to $M^{14}C$)

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

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

Used to calculate the site mass loss in units of $kg/m^2/year$.

- Corrected flux measurements can be used to determine subsurface mass loss rates

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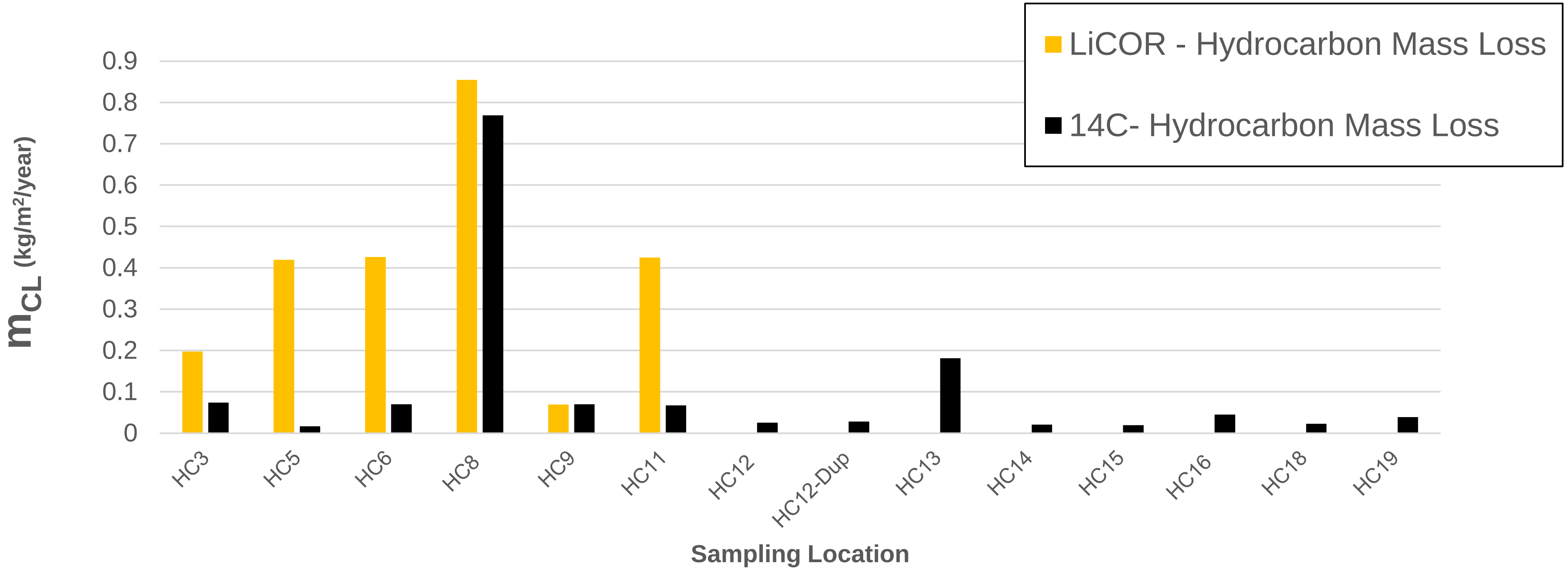
Hydrocarbon Mass Loss

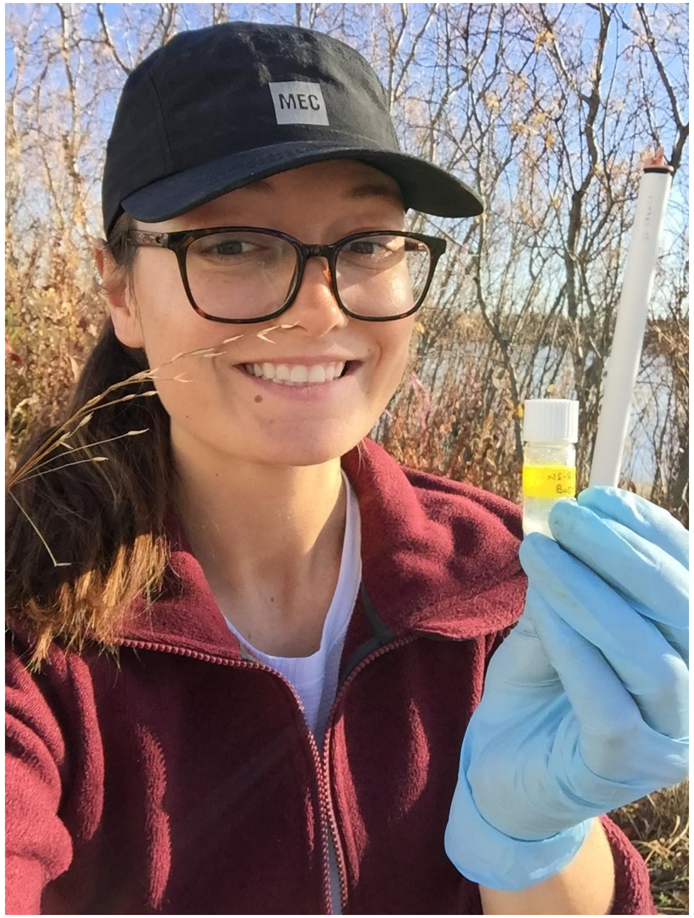


$$\text{Contaminant Mass Loss } (m_{cl}) = J_{CSR} * \frac{1\mu molC_8H_{18}}{8\mu molC_8H_{18}} * \frac{1mol}{1*10^6\ mol} * \frac{114.23gC_8H_{18}}{1molC_8H_{18}} * \frac{1\ kg}{1000g} * \frac{3600sec}{1hr} * \frac{24hr}{1\ day} * \frac{365\ day}{1\ year}$$

(units of $kg/m^2/year$)

Conclusions

- 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 (2018 samples presented here collected in mid-September)



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A.E. Lalonde AMS Laboratory – Ottawa, ON

^{14}C Corrections

** F on this slide denotes FRACTION, not FLUX

Mass Balance Correction

$$F_{CSR} = \frac{(1-F^{14}C_{final})[CO_2]_{final} - (1-F^{14}C_{initial})[CO_2]_{initial}}{[CO_2]_{final} - [CO_2]_{initial}}$$

Simplification (1 sample)

$$F_{NSR} = \frac{F^{14}C_{\,sample}}{F^{14}C_{Background}}$$

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

Atmospheric ^{14}C

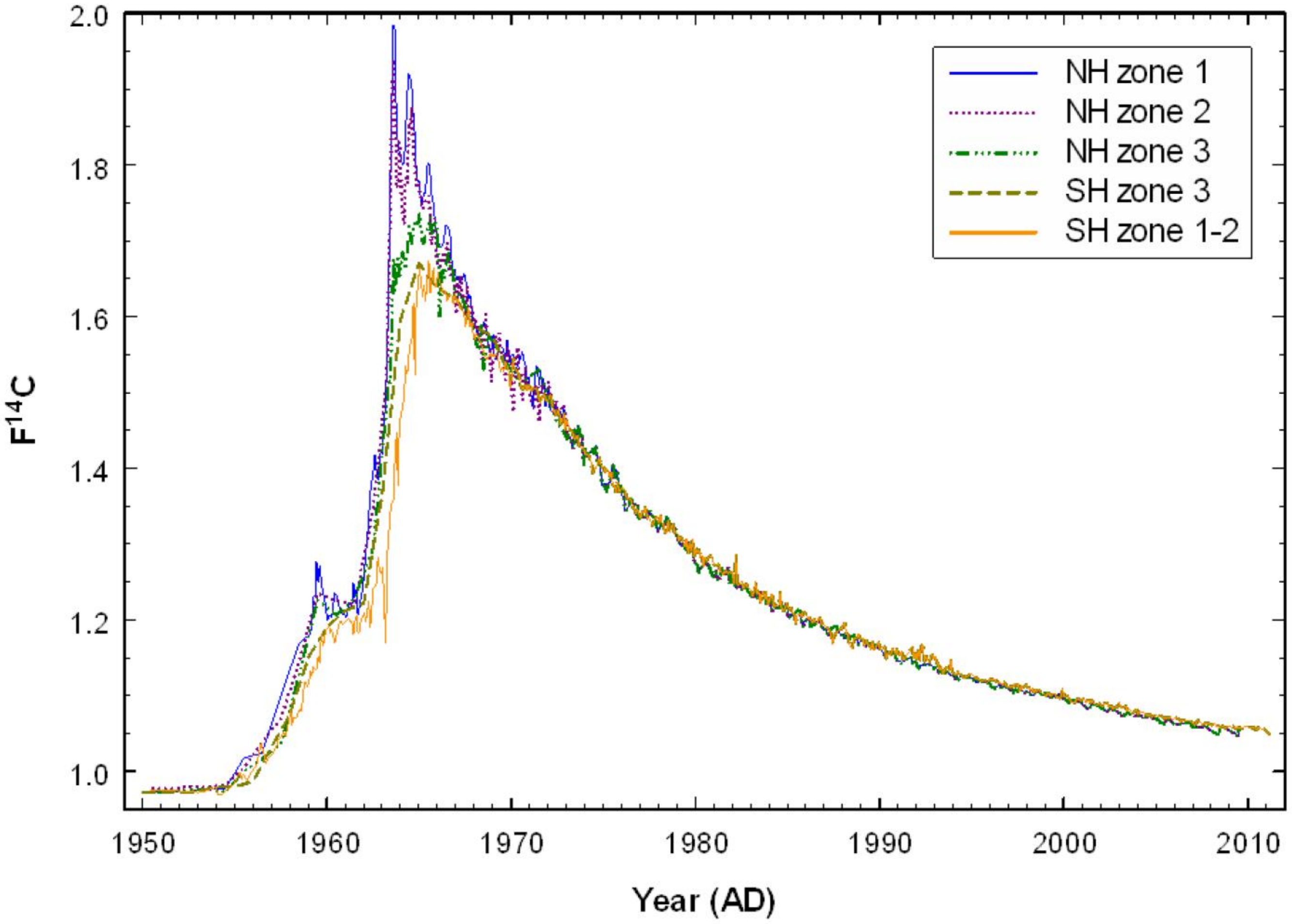

Figure 5 Compiled (extended) monthly atmospheric ^{14}C curves for 5 different zones (NH zone 1, NH zone 2, NH zone 3, SH zone 3, and SH zone 1-2). The compiled data sets are reported in Tables S3a–e (online Supplementary Material).

Hua et al. 2013

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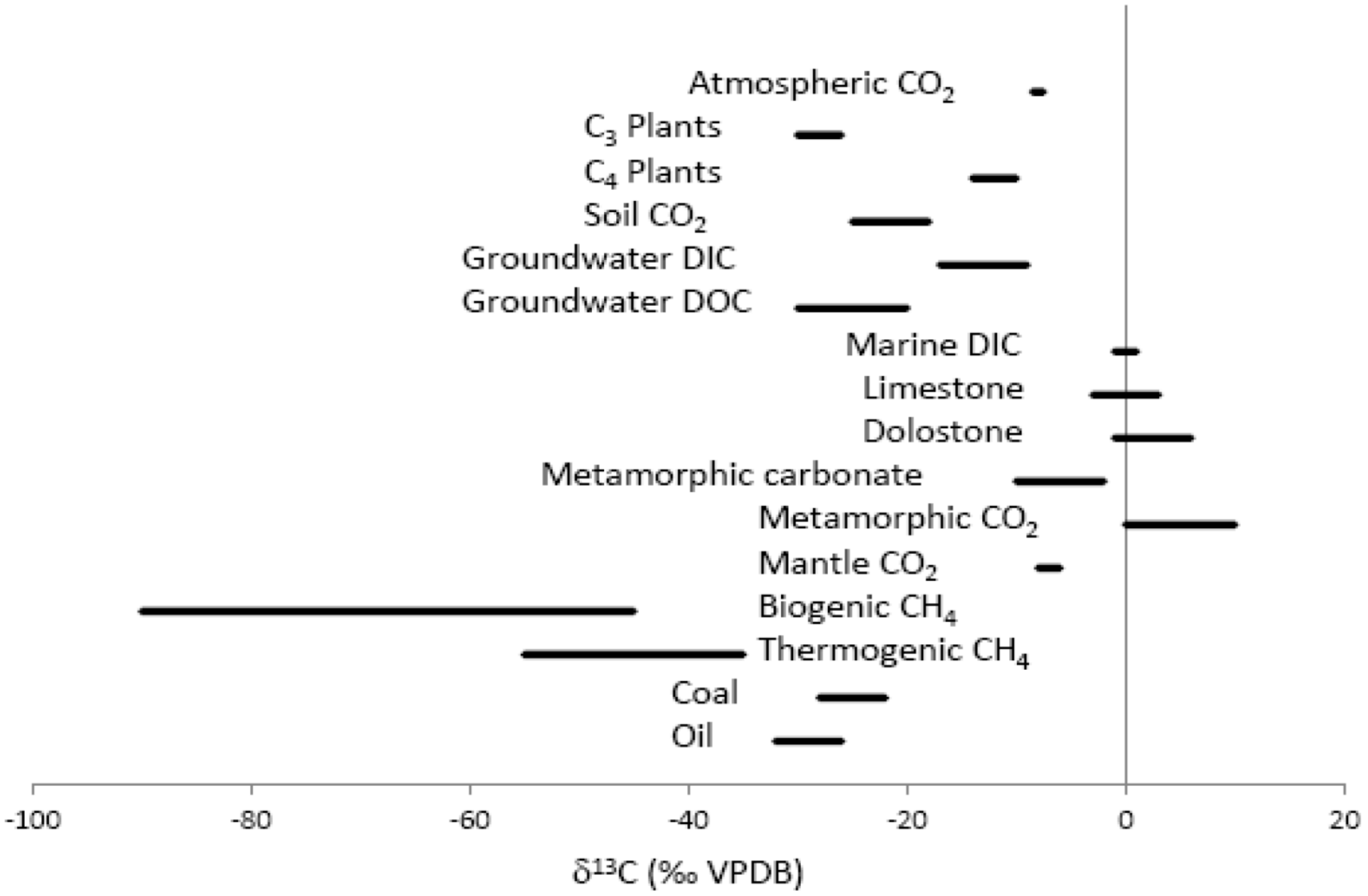
$^{12}C/^{13}C$ Ratio



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