Soil $^{14}CO_2$ source apportionment for biodegradation in contaminated soils in permafrost climates: A novel technique for rapid sample collection by barium carbonate precipitation

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Abstract

The rate of biodegradation of hydrocarbon contaminated soils can be studied using the radiocarbon (^{14}C) content of CO_2 efflux from the ground surface over an impacted area. ^{14}C is used as a tracer to distinguish modern ^{14}C CO_2 from natural respiration processes and ^{14}C depleted CO_2 derived from petroleum degradation. Studies have shown that this analysis provides reliable, quantifiable data and an effective means of correcting for background CO_2 which may present some natural depletion from older subsurface organics. The study area for this project is a remote community in Northern Yukon where organic rich sediments overlying continuous permafrost are contaminated by diesel oil. An objective of this study was to evaluate the use of ^{14}C to quantify background CO_2 in permafrost soils with abundant, older labile organics. A second objective was to test a new sampling technique to facilitate sample shipment from remote sites, which traps soil CO_2 in small sealed exetainers as a solid barium carbonate. Data obtained from established radiocarbon sampling procedures and this new novel approach were shown to be comparable and reproducible. This technique facilitated both sample collection and shipment as well as analysis by accelerator mass spectrometry (AMS), allowing for rapid, efficient sampling techniques to be deployed in remote areas. Results of this study show the carbonate method to be an economical and effective sampling method, and used at the Old Crow site, demonstrated that under current climate conditions, older organics in the subsurface do not confound the use of $^{14}CO_2$ for source zone biodegradation assessment at this hydrocarbon impacted permafrost site.

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This study would not have been possible without the welcome I received from the Vuntut Gwitchin First Nation – Mahsi' Choo. The entire community of Old Crow was welcoming to me and I am forever grateful to have had the opportunity to work and spend time with you in such a beautiful place.

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List of Acronyms

AMS	Accelerator Mass Spectrometer
AST	Above Ground Storage Tank
$BaCO_3$	Barium carbonate
$Ba(OH)_2$	Barium hydroxide
BGS	Below ground surface
CH_4	Methane
CO_2	Carbon dioxide
CO	Carbon monoxide
COC	Contaminant of concern
DIC	Dissolved Inorganic Carbon
EQ	Equation
$F^{14}C$	Fraction of radiocarbon
F_{CSR}	Fraction contaminant soil respiration
F_{NSR}	Fraction natural soil respiration
IRGA	Infrared gas analyzer
J_{CSR}	Flux attributable to Contaminant soil Respiration
J_{NSR}	Flux attributable to Natural soil Respiration
J_{TSR}	Flux attributable to Total soil Respiration
m.b.g.s	Metres below ground surface
MW	Monitoring well
NAD83	North American 1983 Datum
NBS	National Bureau of Standards
NSZD	Natural source zone depletion
OCHC	Old Crow Health Centre
OX-II	Oxalic acid standard
PHC	Petroleum hydrocarbon
PVC	Polyvinyl chloride
RPM	Revolutions per minute
SARU	Site Assessment and Remediation Unit
SC	Static chamber
SP	Soil probe
SPW	Supra-permafrost water
UTM	Universal Transverse Mercator
VPDB	Vienna Pee Dee Belemnite
YG	Yukon Government

Chapter 1 Introduction

1.1 Natural Source Zone Depletion at Contaminated Sites

Petroleum hydrocarbons (PHCs) are one of the most common contaminants of concern (COC) in contaminated sites throughout Canada (Canadian Council of Ministers of the Environment 2014). These sites pose a great fiscal and environmental liability for the Canadian government which currently lists 5,758 sites contaminated with PHCs as the primary COC in soil and groundwater alone (Table 1.1) (Government of Canada 2019). PHC contamination poses exposure risk to humans and wildlife through groundwater, soil and vapour inhalation pathways. Current Canadian remedial guidelines are dependant on the current and future use for an impacted site (Story and Yalkin 2014). Furthermore, site conditions can define which of the different active remedial methods including pump and treat, land farm treatment or in-situ remediation such as soil vapour extraction or chemical oxidation may be applied (Story and Yalkin 2014). Sites which may not be viable for active remediation techniques include those in remote or ecologically sensitive regions, or areas where these techniques could increase exposure risk to receptors (USEPA 2017). Some remedial campaigns have exploited Natural Source Zone Depletion (NSZD) in studies of subsurface contaminant fate. NSZD is the reduction of contaminants in the subsurface which naturally occurs as a result of volatilization, sorption, dissolution and biodegradation. When NSZD is proposed as the remedial action plan for a contaminated site, certain parameters must be met (USEPA 2017). Once the source of contamination has been contained and the contaminated area has been delineated, a project involving NSZD then requires accurate quantification of contaminant mass degradation rates. These rates are used to establish the timescale for remediation and demonstrate continual

improvement of site conditions. Biodegradation, the metabolic degradation of PHC compounds to benign end product such as carbon dioxide (CO_2) and methane (CH_4), is one of the drivers of NSZD and has been difficult to effectively quantify (Sihota et al. 2011).

Research conducted at the site of a pipeline rupture in Bemidji, Minnesota paired CO_2 efflux rates with the radiocarbon signature ($F^{14}C$) of the soil CO_2 to determine rates and quantities of subsurface hydrocarbon biodegradation. CO_2 efflux rate measurements were conducted using a LI-8100A dynamic closed chamber survey system and were representative of the rate of subsurface mass loss (Sihota et al. 2011). However, in natural ecosystems free of any PHC contamination, CO_2 efflux can still be observed as it produced by root respiration and degradation of naturally occurring soil organics (Sihota and Mayer 2012). The hypothesis behind this initial approach of soil CO_2 efflux for PHC mass loss was built on the assumption that a measured efflux (J_{TSR}) would be the product of efflux measured in unimpacted soil (J_{NSR}) and PHC impacted soil (J_{CSR}) and therefore corrections for efflux directly attributable to contaminant degradation could be made.

$$J_{CSR} = J_{TSR} - J_{NSR} \quad \text{[EQ 1.1]}$$

(Sihota et al. 2011)

The ^{14}C isotope of carbon lends itself well to PHC degradation CO_2 apportionment studies because of its relatively short half-life of 5730 ± 40 years (Goodwin 1962). Radiocarbon is produced as the result of cosmic ray neutron bombardment of nitrogen atoms in the upper atmosphere (Libby 1946). ^{14}C atoms are readily oxidized in the atmosphere to form carbon monoxide (CO) and CO_2, which is then taken up in the carbon cycle through chemical and

biological processes (Figure 1.1). Measurements of radiocarbon are presented as fraction of modern carbon ($F^{14}C$) and are normalized to a $\delta^{13}C$ value of -25‰ , corresponding to the Vienna Pee Dee Belemnite (VPDB) standard, which accounts for fractionation in both the environment and sample analysis (Reimer et al. 2004). The modern standard for radiocarbon measurements is the Natural Bureau of Standards (NBS) Oxalic Acid I using equation 1.2(Reimer et al. 2004, Stenström et al. 2011, Crann et al. 2017).

$$F^{14}C = \frac{(\frac{^{14}C}{^{13}C})_{S\,[-25\}}}{0.9558\,(\frac{^{14}C}{^{13}C})_{OxI[-19]}} \qquad \text{[EQ 1.2]}$$

(Reimer et al. 2004)

Living biomass is in equilibrium with atmospheric sources of ^{14}C though metabolic processes such as photosynthesis. Until metabolic death, biomass will have a modern $F^{14}C$. Hydrocarbons and other materials of geologic age have a 0.00 $F^{14}C$ as radiocarbon isotopes can only be measured accurately to maximum of 60,000 years before present (BP) (Crann et al. 2017). This difference in modern biomass and PHCs creates a two-end member system for source apportionment of CO_2 in soil gas (Sihota and Mayer 2012). Theoretically, any depletion from modern radiocarbon signature (F_{NSR}) can be attributed to a petrochemical source (F_{CSR}) (Figure 1.2). $F^{14}C$ as measured from soil gas CO_2 can be applied to flux calculations to correct CO_2 flux rate directly from hydrocarbon sources as shown through equations 1.3 – 1.5 (Sihota and Mayer 2012, Wozney 2016).

$$F_{NSR} = \frac{F^{14}C_{sample}}{F^{14}C_{background}} \quad \text{[EQ 1.3]}$$

$$F_{CSR} = 1 - F_{NSR} \quad \text{[EQ 1.4]}$$

$$J_{CSR} = F_{CSR} * J_{TSR} \quad \text{[EQ 1.5]}$$

(Wozney 2016)

Current techniques for soil CO_2 sampling and radiocarbon analysis involve the collection of mixed soil gas for eventual extraction and graphitization. Mixed soil gas samples are collected in glass bottles with a septum cap, that have been prepared in the laboratory by evacuating air contents using a vacuum pump. Subsequent leakage represents a possible pathway for CO_2 contamination to be introduced during storage or transport. Radiocarbon isotope abundance is on the order of 10^{-12} compared to ^{12}C (Clark 2015). Given the low concentrations of CO_2, 400 – 5000ppm, paired with the low abundance of ^{14}C, relatively large volumes of soil gas must be collected for analysis by AMS (Wozney 2016). Generally, two 250ml bottles have been used for the preparation of one radiocarbon sample to ensure enough CO_2 is present to meet sample mass requirements of 2mg C declared by the A.E. Lalonde AMS laboratory at University of Ottawa (Crann et al. 2017). The method of collecting mixed soil gas for AMS analysis by extraction and graphitization is costly, labor intensive and potentially problematic (Longworth et al. 2013), requiring shipment of dozens to hundreds of glass bottles.

Novel techniques for the sampling of CO_2 and other sources of ^{14}C have been presented in literature as a way to reduce cost and ease field deployment logistics (Longworth et al. 2013, McCoy et al. 2015). Sampling techniques have included the placement of passive samplers

which house some degree of sorbent or alkali media to trap soil CO_2 efflux from either the ground surface or within a monitoring well casing (Garnett et al. 2009, Boyd et al. 2015, McCoy et al. 2015). A common component of these sampling techniques is that once CO_2 has been collected, the resultant material is acidified, extracted and graphitized before AMS analysis – maintaining a high degree of sample preparation and potential contaminant exposure. Previously developed sampling techniques are summarized in Table 1.2.

Work by Longworth et al. (2013) and Bush et al. (2017) showed promise of direct target sputtering of solid calcium carbonate in AMS analysis. These methods utilize small quantities of marine paleontological materials such as corals and foraminifera. Preliminary results from this work showed promise for very small carbonate-based sampling by AMS technology. This research led to the development of an application for carbonate material generated by the extraction of dissolved inorganic carbon (DIC) from groundwater samples. Yang et al (2018) worked to refine the method of direct AMS analysis of carbonate materials using low solubility barium carbonate ($BaCO_3$) produced by introducing CO_2 generated from the acidification of water samples containing DIC. The carbonate material produced by this method is combined with tantalum powder (325 mesh) and pressed into an aluminum based AMS target. This method showed promising results for rapid field-analysis turnaround time, decreased costs and reasonably good agreement with established graphitized sample methodology (Yang et al. 2018). As radiocarbon isotope applications and research continue to evolve, they contribute greatly to the acceptance and the development of more stringent regulation surrounding NSZD as a remedial option.

The majority of radiocarbon application research is conducted in regions with temperate climates like the United States (Sihota and Mayer 2012, Wozney 2016, Garg et al. 2017). Though it is known that hydrocarbon spills are prevalent in an immense range of sizes and contexts in the world's Arctic communities, from large pipeline ruptures to small storage tank ruptures, there has been limited research conducted on in situ contaminated Arctic sites. Extreme conditions in Arctic regions paired with increasing hydrocarbon exploration and economic development pose risks for more accidental releases to occur (Naseri et al 2014). Remedial efforts in Arctic communities have included a wide array of techniques including physical, chemical, biological and thermal applications (Naseri et al 2014). Some situations have proven too costly or difficult for these methods to be effective based on harsh climates, remote locations, ecological sensitivities or a lack of necessary infrastructure. Just as in temperate regions, before a remediation technique can be proposed for a site, the efficiency of a proposed technique must be understood before it can be applied.

Soils within the tundra are known to be very carbon rich and host a wide variety of microorganisms adapted to cold temperatures (Flanagan and Bunnell 1980). Despite adaptation by these microorganisms to cold temperatures, there is a temperature threshold for microbial activities and respiration (Flanagan and Bunnell 1980, Clein and Schimel 1995, Hinkel et al. 2001). Ground temperatures measured 30cm below the ground surface in Barrow, Alaska fluctuate throughout the year between 2 and -22°C (Hinkel et al. 2001). Tundra soils rich with natural organic matter were shown to have measurable, though reduced, microbial activity down to -5°C (Clein and Schimel 1995). Furthermore, studies have shown that arctic conditions also do not fully inhibit PHC degradation in the subsurface (Flanagan and Bunnell 1980, Rike et

al. 2003). Therefore, there is potential for applied NSZD at Arctic sites contaminated with PHCs to be a successful remedial technique. The need to accurately apportion sources of CO_2 flux exists in arctic climates just as it does in temperate climates. Given the slow rate of microbial metabolic processes in arctic soils, natural organics may persist longer than in temperate regions creating the potential for older labile organics to produce a naturally depleted $F^{14}C$ signature.

1.2 Research Objectives

Research has shown that the $F^{14}C$ of CO_2 efflux over a PHC contaminant impacted site can be used to differentiate between contaminant-derived and natural soil respiration processes (Sihota and Mayer 2012, Wozney 2016). The research applying $F^{14}C$ corrections to soil CO_2 flux conducted in temperate climates has shown that the assumption of a two-end member system for the $F^{14}C$ signature of each respective source is applicable. However, in an Arctic region where subsurface organics undergo a slower rate of decay this assumption may become complicated. Therefore, a key objective of this research is to study the potential influence of older labile organics present throughout the site, in both contaminated and background areas, on the $F^{14}C$ signature of soil CO_2 efflux . Furthermore, studies of radiocarbon signatures have been conducted using an elaborate array of sampling equipment which is potentially prone to modern atmospheric contamination during preparation and transport. A second objective of this study is to develop and deploy a new novel sampling technique to precipitate soil CO_2 as a carbonate mineral for stable sample transport and direct AMS analysis. This new technique will provide an economical, easy and rapid technique for radiocarbon

sampling to be conducted at impacted sites regardless of limited infrastructure or remote locations.

In summary, the objectives of this study are:

- To study the potential of older, possibly labile, subsurface organics in Arctic regions and their contribution to soil efflux radiocarbon signatures
- To develop a novel technique for sampling CO_2 as barium carbonate to simplify sample collection and shipment and for direct AMS analysis

1.3 Research Approach

To investigate the radiocarbon signature associated with various source soil CO_2 flux a PHC impacted site in Old Crow, Yukon was selected (Figure 2.1). This site contains a point source arctic diesel spill contained approximately 2 meters below the ground surface atop a layer of continuous permafrost. Following methods outlined by Wozney (2016) soil CO_2 representative of soil efflux was collected using both 30cm soil probe and polyvinyl chloride 20 cm inner diameter static chambers. Two sample media types were collected, mixed soil gas for graphitization and a $BaCO_3$ precipitate. At various sampling locations, both media types were collected to serve as a dataset for comparative analysis of the techniques. Samples were collected in areas proximal to existing supra-permafrost water (SPW) monitoring wells (MWs) owned and monitored by Jacobs Engineering Limited (Jacobs). Historical SPW data was used to delineate where samples would be considered representative of background, off plume (close to impacts) or above plume (impacted) conditions. Sampling was also conducted with consideration to whether the point sampled was vegetated or not. During 2017 field work,

Jacobs Engineering Limited was on site installing new MWs, as well as sampling supra-permafrost water from existing wells. During drilling, below ground surface materials from a background non-vegetated site were collected from a split spoon sampler to study the $F^{14}C$ of the soil CO_2 efflux attributable to soil respiration. This soil material was collected, frozen and stored in a sterile Whirl-Pak and returned to the University of Ottawa for a benchtop microcosm experiment to yield CO_2 free of any potential affects of nearby hydrocarbon impacts.

Chapter 1 Tables

Table 1.1 *Canadian Petroleum Hydrocarbon Contaminated Sites (Government of Canada Contaminated Sites Inventory, 2019)*

Contaminated Media	Number of Sites
Surface Water	455
Groundwater	1.434
Sediment	699
Surface Soil	783
Soil	4,324
Air	44
Other medium	643

Table 1.2 *Sorbent trap methods for $^{14}CO_2$ sample collection*

Technique	**Study Authors**	**Deployment Location**	^{14}C Analysis Method
KOH static trap (no ^{14}C analysis)	(Kirita 1971)	Laboratory	N/A
NaOH solution (no ^{14}C analysis)	(Dorr and Munnich 1980)	Heidelberg, Germany	N/A
NaOH static trap (no ^{14}C analysis)	(Yim et al. 2002)	Yoshiwa, Japan	N/A
Zeolite molecular sieve	(Garnett et al. 2009)	Unknown	Graphitization
NaOH	(Boyd et al. 2015)	Coronado, USA	Graphitization
$Ca(OH)_2$	(McCoy et al. 2015)	Western USA	Graphitization

Figure 1.1 *Cosmogenic production of ^{14}C isotopes and subsequent oxidation to CO_2*

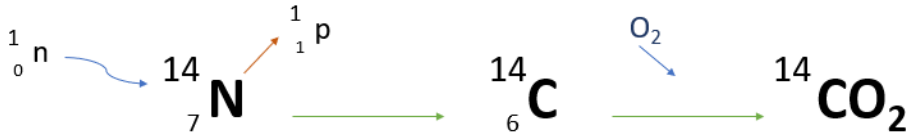
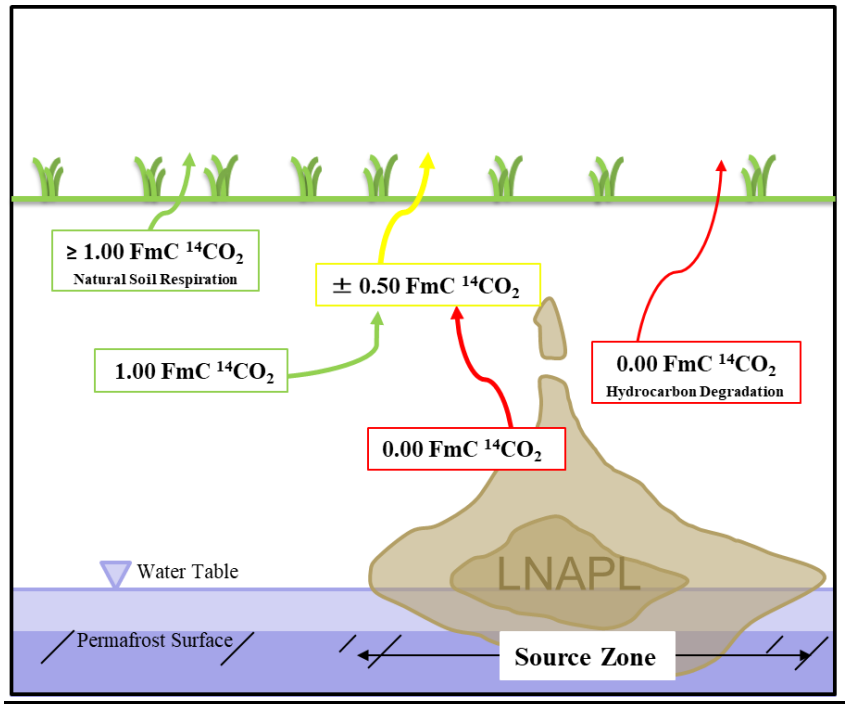


Figure 1.2 *Schematic of subsurface sources of soil CO_2 efflux in a permafrost site demonstrating the assumption of natural soil respiration products having a modern radiocarbon signature. (Modified from Sihota and Mayer 2012, Wozney 2016)*



Chapter 2 Methods of Sample Collection and Analysis

2.1 Introduction

The community of Old Crow (67.5696° N 139.8288° W) is situated in the continuous permafrost region within the Old Crow Flats of northern Yukon, Canada (Figure 2.1, Figure 2.2). According to weather station data, this region experiences the largest annual fluctuations in temperature in the Yukon (Yukon Ecoregions Working Group 2004). Permafrost soils exhibit an annual active layer – a shallow region prone to freeze and thaw cycling with seasonal temperature changes. The active layer thickness, and ground temperature therein, are reflective of surface air temperature in permafrost regions (Tarnocai 2008). Cold adapted soil microorganisms have shown increased metabolic activity through even minimal soil temperature increases allowing for maximum CO_2 production from degrading contaminants (Flanagan and Bunnell 1980).As such, sampling was conducted in early September after the sustained warmth of the summer months contributed to maximum active layer thickness and highest soil temperature.

2.1.1 Site Geology and Permafrost Hydrogeology

The Old Crow Flats region is characterized by thick Tertiary and Quaternary sediments deposited in a proglacial lake during the Wisconsinan glaciation (Yukon Ecoregions Working Group 2004, Zazula et al. 2004) and transected by the Porcupine River. While the Old Crow Flats region remained unglaciated even at the furthest eastern extent of the Laurentide ice sheet (Figure 2.3), local geology and geomorphology reflect the region's ice rich permafrost (Zazula et al. 2004). Current surficial geology in the Old Crow flats is characterized by oriented lakes and

meandering rivers with marshy oxbows (Yukon Ecoregions Working Group 2004). The glaciolacustrine deposits of the Old Crow Flats are overlain locally within the community of Old Crow by fluvial deposits from both the Old Crow and Porcupine rivers (CH2M 2016).

Permafrost throughout the community of Old Crow dictates local subsurface hydrological processes. Supra-permafrost water is found at approximately 2 metres depth and at the study site has shown no pronounced gradient or flow pattern. This is thought to be due to the relatively flat surface of permafrost acting as a small basin (CH2M 2016). This supra-permafrost water is recharged annually from the surface and from melting cycles in the active layer. Locally, the base of permafrost has been encountered at 63 metres below ground surface (Yukon Ecoregions Working Group 2004). Below the permafrost in the Old Crow community is a confined limestone and dolostone aquifer which serves as the source of drinking water (Figure 2.4). Wells for community water supply have been drilled to 70 and 120 metres below ground surface in the unfrozen talik along the channel of the Porcupine River.

The impacted site in Old Crow, Yukon is located near the community's Health Centre (OCHC). The site is 80m from the Porcupine River (Figure 2.5) and is underlain by fine-grained sand and silt deposits, supra-permafrost water and permafrost. The topography of the permafrost surface at OCHC has been shown in drilling campaigns to be elevated to the east of the property where a surface ditch divides the OCHC property and neighbouring private property. There is also a topographical high at the ground surface to the south of the OCHC where a natural berm has formed before dropping down to the banks of the Porcupine river, the permafrost mimics the surficial topography here (Figure 2.4). These two highs have created

an additional basin effect for supra-permafrost water and the contained PHC contaminants (CH2M 2016).

2.1.2 Site Petroleum Hydrocarbon Spill History

Prior to 2000, the original fuel (arctic diesel) storage infrastructure at the Old Crow Health Centre was comprised of four above ground storage tanks (AST) connected to a manually activated pump and smaller day storage tank. This day storage tank was in the crawlspace underneath the main building on the east side (Figure 2.6). Frequent complaints of hydrocarbon odors from inside the building led to a complete replacement of the heating equipment in the building, and removal of the day storage tank (Laberge Environmental Services 2011). Risk mitigation for potential PHC releases attributed to the day storage tank was limited to the installation of a ventilation system in the building. No ground material was removed from the former day storage tank area (Laberge Environmental Services 2011). A 2005 survey of the condition of the four ASTs revealed compromising damage to the berm located underneath the tanks, as well as standing water at the ground surface causing corrosion of the exterior of the single walled ASTs. In 2008 the four ASTs were replaced with the current 50,000L AST (Figure 2.6). During the removal of the four ASTs the subsurface berm was ripped and the old fuel lines were struck, causing a release of the stored arctic diesel. The site was backfilled with original material and capped with locally sourced gravel material; no ground material was removed from the site. Since the replacement of the four ASTs and the upgrade of the fueling system, the property and management have become responsibility of the Yukon Government (YG) and are overseen by the Site Assessment and Remediation Unit (SARU). Sources of contamination are considered under control and an extensive monitoring network

has been put in place to observe the presence and fate of contaminants contained in both the ground sediments and supra-permafrost water. Jacobs Engineering Ltd (formerly CH2M Hill) has served as prime contractor in seasonal site assessments and remedial action plan developments. Since 2014 monitoring wells, soil vapor ports, and thermistors have been installed on the site and are used to delineate the extent of known contamination exceeding fresh water aquatic life standards for soil and groundwater (CH2M 2018; Yukon Regulations Environment Act 2002). Current data shows one large interconnected plume exceeding CSR standards for LEPH contamination in groundwater and two disconnected plumes exceeding special waste CSR standards for LEPH in groundwater (Figure 2.7)(CH2M 2018). Information regarding current contamination at the site is summarized in annually conducted Phase 2 Environmental Site Assessment documents complied by Jacobs Engineering Ltd. Supra-permafrost water samples from 35 monitoring wells and soil analytical data from various years of site development were used in this study to delineate the existence of contamination in the subsurface (CH2M 2018).

2.2 Radiocarbon Field Sampling Methods

Samples of CO_2 representative of soil efflux were collected using both 30cm soil probe and polyvinyl chloride 20 cm inner diameter static chambers. Two samples media types were collected, mixed soil gas for graphitization and a $BaCO_3$ precipitate. Analytical supra-permafrost water (SPW) data was used to delineate where samples would be considered representative of background, off plume (close to impacts) or above plume (impacted). Sampling was also conducted with consideration to vegetation. Samples were collected as background, off plume

and above plume – and furthermore vegetated or non-vegetated. During 2017 field work, Jacobs Engineering Limited was on site installing new MWs, as well as sampling supra-permafrost water from existing wells. During drilling, below ground surface materials from a background non-vegetated site were collected from split spoon sampler to study the $F^{14}C$ of the soil CO_2 efflux attributable to soil respiration. This drill material was collected and stored frozen in a sterile Whirl-Pak and returned to the University of Ottawa for a benchtop microcosm experiment to yield CO_2 free of any potential affects of nearby hydrocarbon impacts.

2.2.1 Sample Collection Techniques

Radiocarbon samples were collected in order to apportion various sources of CO_2 to soil gas flux. Soil gas sampling in 2017 was conducted using two different tools:

I) static closed chamber (SC)

II) 30cm soil gas probe (SP)

Sampling in 2018 was conducted exclusively by soil probe.

During September 2017 field research, Jacobs Engineering Ltd. were on site conducting annual drilling and monitoring. Material from split spoon samplers was collected from an area of the site free of subsurface contamination. This material was sampled from within the active layer (0.76 – 1.83 m.b.g.s.) and within the permafrost (1.37 – 1.98 m.b.g.s.) for bench top microcosm studies of background sources of CO_2 representative of soil respiration.

I. Static Chamber (SC)

Static chambers were constructed in two ways. The first type of static chamber was made of 20 cm inner diameter cylindrical polyvinyl chloride (PVC) pipe. The chambers were 20

cm high and had a sealed PVC top (Figure 2.8 A). Sampling ports on the SCs were made with stainless steel Ultra-torr Swagelok vacuum fittings. The 1/8-inch NPT threaded base of the sampling port was further sealed with the use of Teflon tape. This allowed for a gas-tight sampling port with access by way of butyl septum. Static chambers were driven into the ground using a rubber mallet. While chambers were being driven into the ground the Swagelok adapter was removed to maintain equilibrium with atmospheric condition outside of the sampling chamber. After the chamber was driven to a minimum depth of 10cm and the Swagelok adapter was threaded back on with septum, sample chambers were left for 24 hours to allow for ground conditions to equilibrate and soil gas accumulation to occur by way of efflux.

The second type of SC construction was based on 20cm open ended cylindrical PVC pipe used in standard practice with long term LI-8200A surveys (LI-COR 2015). The cylindrical PVC pipe was installed earlier on the site according to standard LI-COR practice and had several days equilibration time(LI-COR 2015). Caps were made from sealed particle board cut to match the outer diameter (20.3cm) of the LI-COR PVC pipes. Sampling ports were drilled by drill press in the center of the caps and were fitted with the same stainless-steel Ultra-torr Swagelok vacuum fittings sealed with Teflon tape used in the first type of SC (Figure 2.8 B). These SCs had an additional epoxy fill around the inside of the sampling port to fill any voids left by displaced particle board during drilling. The base of the caps was modified with closed cell foam weather stripping adhered around the perimeter. The seam where the weather stripping completed the outer perimeter was cut at 45-degrees and caulked with silicon sealant. When placed atop the PVC collars the weight of the cap caused compression of the foam stripping and subsequent sealing on the PVC pipes, making closed chambers for soil gas accumulation. Chamber caps

were also taped around the side wall of the PVC collar to prevent shifting or displacement during sampling. After the cap was placed and sealed on the LI-8100A collar the sample chambers were left for 24 hours to allow for soil gas accumulation with composition representative of soil gas efflux. Samples were drawn from SCs via the butyl septum in the sampling port using a luer lock 60ml syringe and 23-gauge needle.

II. Soil Probe (SP)

Soil gas samples were also collected using a soil gas vapour probe manufactured by AMS, Inc. Samples were collected from 30 cm below ground surface (b.g.s.) (Figure 2.9). Soil probe installations were located within 50cm of complementary SC and/or monitoring well. The soil probe was driven straight into the ground using a rubber mallet rather than using the handle and a rotational drilling technique. This allowed for a reduction in the amount of annular space created during soil probe installation. Once the probe was driven down to 30cm b.g.s the top was fitted with a threaded 3/16" adapter manufactured by AMS, Inc. to allow the connection of 3/16" tygon tubing. The end of this tubing was fitted with a three-way gas tight stopcock. With the stopcock closed to atmosphere the soil probe was left to equilibrate for a minimum of 30 minutes before sampling. After equilibrium time the tygon tubing was then purged of 120ml of soil gas before any gas was collected for analysis.

2.2.2 Radiocarbon Soil Gas Sample Types

Two different methods of soil gas sample generation were used in this study. Samples were collected in 250 ml evacuated wheaton bottles for eventual CO_2 extraction, graphitization

and AMS analysis. A novel technique of field precipitation of barium carbonate ($BaCO_3$) was also used to trap soil CO_2 from the field site.

I. Mixed Soil Gas Collection for Graphitization

Glass wheaton bottles capped with grey butyl septum and crimp cap were evacuated down to approximately 60 millitorr pressure on a multi-purpose 10^{-5} kPa vacuum extraction line. Bottles under vacuum were transported to site where they were used to collect mixed soil gases. Samples were collected using either SP or SC and introduced to the wheaton bottles by a 60ml syringe with a 23G needle. Sample bottles were slightly over pressurized by the injection of 300ml of soil gas into the 250ml bottle.

II. Barium Carbonate Precipitation Method

Barium Hydroxide Solution Preparation

Barium hydroxide solution was prepared in laboratory at the University of Ottawa in an anaerobic nitrogen environment to prevent atmospheric CO_2 contamination. Under anaerobic conditions 0.5g of Barium Hydroxide ($Ba(OH)_2 \cdot 8H_2O_{(s)}$) crystals were weighed and placed in a 12 ml exetainer. 11ml of MilliQ water, ≤ 3ppb carbon (C), was added to the 12ml exetainer before closing with a butyl septum cap. The sealed exetainer was then removed from the anaerobic chamber and agitated with a vortex mixer for 60 seconds. The exetainer was placed in a centrifuge at 4000 RPM for 5 minutes to draw down any undissolved $Ba(OH)_{2(s)}$ crystals. The exetainer was placed back under anaerobic conditions before opening for the distribution of the solution to various 4.5ml field sampling exetainers. A pipette was used to draw 0.4ml aliquots of $Ba(OH)_2$ solution which was then transferred into a 4.5ml exetainer with butyl

septum cap. Sample containers were capped under anaerobic conditions as to contain a nitrogen filled headspace at standard pressure.

Field Barium Carbonate Precipitation Method

Samples were created in the field by introducing soil gas to the $Ba(OH)_2$ solution via 60ml syringe and 23-gauge, 8-inch needle. Sample soil gas was drawn from either SP or SC into the 60ml syringe. The 8-inch needle was used to pierce the septa and was inserted deep enough to allow the needle tip to be submerged in the $Ba(OH)_2$ solution. The syringe plunger was slowly pressed down to begin bubbling soil gas through the solution (Figure 2.10). After the introduction of approximately 5ml of sample soil gas, the exetainer became over pressured and a release mechanism was also inserted into the septum. The pressure release mechanism is made up of a 1 inch long, 23-gauge needle connected to a 0.45µm Whatman disk filter to trap any potential BaOH or $BaCO_3$ passing through the needle. The needle and filter were housed on the luer end of a modified 1ml syringe barrel with an outer diameter of 1/4-inch. Affixed to the other end of the 1ml syringe barrel was a 1/4-inch to 1/16-inch Swagelok reducer. The 1/16-inch end of the reducer was fitted with 1.2 m of coiled 1/16-inch outer diameter stainless steel tubing to prevent back flow and diffusion effects from atmospheric air (Figure 2.11). Upon introduction of sample soil gas to $Ba(OH)_2$ solution, $BaCO_3$ precipitate formation could be observed almost instantaneously. A total of 420ml of soil gas was bubbled through the $Ba(OH)_2$ solution for each sample collected. When there was approximately 5ml left of soil gas to push into the sample container, the pressure release mechanism was removed to further prevent

back flow of atmospheric air. All needles used in sample collection were discarded after each soil gas sampling event to prevent contamination between samples.

III. Barium Carbonate Field Blank Preparation Method

In order to determine possible introduction of atmospheric CO_2 during sampling method a field blank was prepared using similar techniques as field sampling. 10mg of laboratory standard 0.00 $F^{14}C$ sodium bicarbonate ($NaHCO_3$), used in the blank standard preparation at the Radiocarbon Laboratory at the A.E. Lalonde AMS Facility**,** was weighed and placed in a 40ml EPA amber vial. This vial was placed open and upright in a 60°C oven for 2 hours to desorb any laboratory atmospheric CO_2 from the $NaHCO_3$. The EPA vial septum cap was fitted with a secondary butyl rubber septum to prevent diffusion of CO_2 through the standard silicone septa. When the EPA vial was taken out of the oven it was promptly capped and evacuated down to approximately 60 millitorr pressure using a multi-purpose 10^{-5} kPa vacuum extraction line. In the field, both septa were pierced and 1ml phosphoric acid was injected to digest the $NaHCO_3$ releasing a source of ^{14}C-free CO_2 gas. The vial was set aside to allow complete digestion of the $NaHCO_3$. A 60ml syringe was used to draw the dead CO_2 gas from the vial for introduction to a $Ba(OH)_2$ sample vial. The same insertion and removal procedure of the pressure release mechanism used in field sampling was followed for the blank production.

2.3 Benchtop Microcosm Experiment on Drill Cuttings

Soil samples were collected from an unimpacted area of the field study site. These samples were collected to obtain $F^{14}C$ data representative of background soil respiration, free of any influence of nearby hydrocarbon impacts.

Drill stem material was collected at the drill site of 17MWNS50 (Figure 2.7) from split spoon sampler. Samples were collected from two different depth intervals, 0.76 – 1.83 m.b.g.s. and 1.37 – 1.98 m.b.g.s. (depth interval as interpreted by geotechnical lead on Jacobs Engineering Ltd. drilling team). The material sampled in the interval between 1.37 – 1.98 m.b.g.s. were below observed frozen ground, or permafrost. Samples were collected by hand with nitrile gloves, changed between samples, and stored in sterile Whirl-Pak bags in a cooler with abundant icepacks to maintain temperatures similar to ground conditions (< 4°C). Drilling material collected on site in Old Crow in September 2017 was stored at the University of Ottawa at -19°C until benchtop microcosm studies were conducted. Benchtop microcosm studies were conducted using 500ml iso jars with a threaded septum port cap. Iso jars were cleaned with deionized water and wiped with methanol before samples were introduced. Samples were stored sealed on laboratory bench top for 28 days before a 5ml aliquot of accumulated headspace gas in the iso jars was sampled for CO_2 content. Headspace CO_2 content was analyzed with an SRI 8610C gas chromatograph calibrated with a 10% CO_2 standard.

2.4 Radiocarbon Analysis

2.4.1 Preparation of Barium Carbonate Samples for Accelerator Mass Spectrometer Analysis

Before a sample returned to the laboratory can be prepared as a pressed AMS target, all barium hydroxide must be converted to barium carbonate. Upon opening an exetainer, any remaining $Ba(OH)_2$ will readily react with atmospheric CO_2, contaminating sample material. Based on equation 2.1 it can be assumed that a completely reacted sample vessel will contain precipitated barium carbonate and a solution with a near neutral pH:

$$Ba(OH)_2 \quad + \quad CO_2 \quad \rightarrow \quad BaCO_3 \quad + \quad H_2O \qquad \text{[EQ 2.1]}$$

The 4.5ml exetainers containing precipitated samples were centrifuged for 4 minutes at 2000 rpm to draw precipitate downward in the exetainer. Sample solution was drawn out of the exetainer using needle and syringe, and pH was tested. Solutions with a pH higher than 7 were filled with milli-Q water using needle and syringe and centrifuged again. This process was repeated until samples were neutralized. All excess solution was drawn off the precipitate using needle and syringe before samples were placed in a standard freezer for one hour. Once samples were frozen solid, they were freeze dried under vacuum for a minimum of 7 hours to remove all moisture from the $BaCO_3$ precipitate.

Freeze dried samples were weighed and sample yield masses were recorded. While samples were being weighed, a 325-mesh tantalum powder was baked at 200°C for 2 hours. Barium carbonate samples and tantalum were combined at weight ratio of 1:1.5 as per the method outlined in (Yang et al. 2018). Samples with small yields, <0.2mg $BaCO_3$, were combined with excess tantalum powder in order to yield the sample volume required for target pressing. A pressed target requires roughly 70 µL of the $BaCO_3$ - Ta mixture. Weighed materials were transferred to new 4.5ml exetainers and the two powders were homogenized by crushing and smearing against the exetainer bottom and walls with methanol cleaned glass stir rods. Homogenized material was scraped down from the inside edges of the exetainers using a small stainless-steel scoop and transferred from exetainers to press module funnels by 70µL microhematocrit capillary tubes. Samples were pressed into aluminum target bases using stainless steel press module equipment and copper pins. Hematocrit tubes were discarded, and

all press module equipment which came in contact with samples was cleaned by sonication in a methanol bath after each use (Crann et al. 2017). After pressing, targets are kept under vacuum conditions until they are loaded onto the 200-sample wheel for AMS analysis.

2.4.2 Carbon Dioxide extraction from Mixed Soil Gas Samples

For comparison with the barium carbonate method, a subset of CO_2 samples were duplicated and brought to the lab as gas samples for AMS analysis by the traditional graphitization method. The CO_2 content of mixed soil gas samples were purified and extracted at the Ján Veizer Stable Isotope Laboratory at the University of Ottawa. Sample extractions were conducted on the multi-purpose 10^{-5} kPa vacuum extraction line. Samples housed in 250ml wheaton bottles were introduced to a vacuum extraction line with helium carrier gas through nafion tubing toward a stainless-steel cryogenic u-trap (liquid nitrogen, -196°C). Helium flushing was conducted for ten minutes at a flow rate of 250ml per minute. The first u-trap contained a cluster of silver 'wool' to increase surface area for sample freezing. After the ten minutes elapsed the stainless-steel trap was isolated to the flushing line by pipe valve and excess helium was pumped away. The liquid nitrogen trap was moved along the multipurpose line to a glass u-trap, the secondary cryogenic trap. A liquid nitrogen and methanol slurry (approximately -80°C) was introduced to the first stainless steel trap which facilitated the release of frozen CO_2 while keeping water vapours frozen. After 2 minutes elapsed and CO_2 was completely frozen on the secondary cryogenic trap the sample was isolated on the liquid nitrogen trap. The process was repeated on a second glass u-trap to again isolate CO_2 and remove any remaining water vapour. After 2 minutes of freezing in the second glass u-trap the sample was isolated using pipe valve. The second glass u-trap includes a port which opens to a

calibrated volume pressure gauge. This pressure gauge was used to measure CO_2 sample yields in milligrams (mg) carbon for eventual graphitization. The samples were then moved along the multi-purpose line and trapped cryogenically in Pyrex break seals. The Pyrex break seals were baked at 200°C before housing samples to release any sorbed atmospheric CO_2. 5-10 grains of silver cobaltus were added to each break seal to remove any potential sulfur from the CO_2 sample during graphitization. Analysis blanks were prepared on the same multi-purpose line by introducing an aliquot of ^{14}C free laboratory standard gas through the helium carrier gas and on to the subsequent break seal.

For determination of inherent modern sample container contamination, either through bottle preparation or contamination during air transport, a travel blank bottle was prepared using the multi-purpose extraction line. This travel blank bottle was baked and capped in the same manner as all other graphitized sample bottles and transported to and from Old Crow with all sampling material. In the laboratory, the bottle was filled with ^{14}C free CO_2 laboratory standard gas. This laboratory prepared sample was then introduced to the multi-purpose line and subsequent break seal in the same manner as samples collected in the field.

2.4.3 Carbon Dioxide Extraction from Benchtop Microcosm Study

To test the potential contribution of CO_2 from respiration of older organics in the soil cores, microcosm experiments were undertaken to in-grow CO_2 in sealed exetainer jars. After 28 days of storage in sealed iso jars at ambient laboratory conditions (20°C) CO_2 had accumulated in the container headspace. CO_2 concentrations were determined by SRI 8610C gas chromatograph. The sample collected over a depth of 0.76 - 1.83 m.b.g.s. had a headspace

CO_2 concentration of 19%. The sample collected from the depth of 1.37 - 1.98 m.b.g.s. had a headspace CO_2 concentration of 5.9%. CO_2 concentrations were used to calculate the amount of gas to be extracted via iso jar butyl septum port for eventual 1mg carbon yield for CO_2 graphitization. The required aliquot of iso jar headspace gas was extracted using a gas tight syringe and needle and introduced to the multi-purpose 10^{-5} kPa vacuum extraction line at the Ján Veizer Stable Isotope Laboratory. Once the gas was introduced to the vacuum line extraction, purification and trapping in break seal was conducted in the same manner as mixed soil gas samples. An analysis blank was prepared on the same multi-purpose line by introducing an aliquot of ^{14}C free laboratory standard gas through the helium carrier gas and on to the subsequent break seal.

2.4.4 Preparation of Graphitized Samples for Accelerator Mass Spectrometer Analysis

The graphitization of all purified CO_2 samples, mixed soil gas and benchtop microcosm samples, was completed in the A.E. Lalonde AMS Laboratory – Radiocarbon Lab at the University of Ottawa. The graphitization procedure began with the conditioning of iron catalyst at 520°C for 20 minutes. The beginning of this conditioning involved an oxidation reaction to remove any sorbed CO_2 which would present as a modern contaminant to the samples.

$$2Fe + 2C + 3O_2 \rightarrow 2FeO + 2CO_2 \quad \text{[EQ 2.2]}$$

The second part of the iron conditioning used a reduction reaction to reduce the iron catalyst to elemental iron. This reaction proceeded for 30 minutes at 520°C.

$$FeO + H_2 \rightarrow Fe + H_2O \quad \text{[EQ 2.3]}$$

Once iron conditioning had completed, the CO_2 samples were released from Pyrex break seals. After the release of CO_2 from break seals, the samples were moved to a cryogenic trap to remove any water vapour. Any non-condensable gases present in the samples were pumped away while CO_2 remained frozen on cryogenic trap. CO_2 samples were then brought up to laboratory temperature to measure pCO_2. This pCO_2 was used to determine the quantity of H_2 gas needed to achieve a 2.5:1 ratio of H_2:CO_2. This new pressure was recorded and sample mixtures were heated to 650°C in the presence of the conditioned iron catalyst to facilitate the graphitization of the CO_2 gas sample according to the Bosch reaction (equation 2.4).

$$CO_{2\,(g)} + 2H_{2\,(g)} \rightarrow C_{\,(s)} + 2H_2O_{\,(g)} \qquad \text{[EQ 2.4]}$$

Once graphitization was complete, graphite samples were homogenized and hydraulically pressed into AMS aluminum target bases using stainless-steel press module equipment and copper pins. Press module equipment was cleaned by sonication in a methanol bath (Crann et al. 2017). After pressing targets were kept under vacuum conditions until they were loaded into the AMS for analysis.

2.5 Analysis by Accelerator Mass Spectrometer

2.5.1 Analysis of Barium Carbonate Samples

Barium carbonate samples were run on the gas source 3.0 MV tandem accelerator mass spectrometer at the A.E. Lalonde AMS Laboratory at the University of Ottawa. $BaCO_3$ targets are sputtered under optimized AMS tuning set to approximately 92Hz with upwards of 90% of the time dedicated to the counting of ^{14}C ions (Yang et al. 2018). Barium carbonate analyses are reported at $F^{14}C$ and are calculated following Reimer et al 2004 with normalization to

graphitized OX-II standards used in regular graphite based AMS analysis of ^{14}C. All $BaCO_3$ samples were corrected to a blank tantalum target run in each of the sample analysis events. Uncertainties presented for $BaCO_3$ samples represent AMS measurement errors. All $F^{14}C$ values are corrected for $^{13/12}C$ fractionation by online AMS measurement.

2.5.2 Analysis of Graphitized Samples

Graphitized samples were run on the gas source 3.0 MV tandem accelerator mass spectrometer at the A.E. Lalonde AMS Laboratory at the University of Ottawa. Radiocarbon analyses are reported at $F^{14}C$ and are calculated following Reimer et al 2004 with oxalic acid (1.34 $F^{14}C$, Ox-II) standards. All graphitized samples were corrected to a blank graphite target produced in the laboratory and run in each of the sample analysis events. Uncertainties presented for graphitized samples represent AMS measurement errors. All $F^{14}C$ values are corrected for $^{13/12}C$ fractionation by online AMS measurement.

Chapter 2 Figures

Figure 2.1 *Map of North America with inlay of Yukon Territory showing location of the community of Old Crow (Map Data from Government of Canada Open Data Portal, NAD83 Canada Atlas Lambert).*

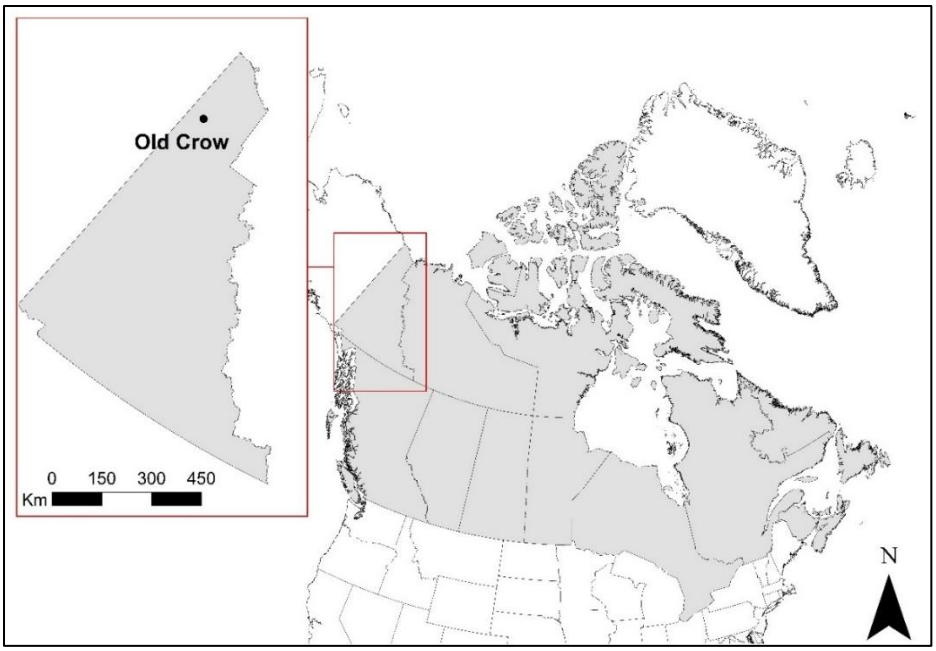


Figure 2.2 *Regional map showing the various permafrost regions of Yukon Territory, Canada and the extent of the continuous permafrost region (Data from Brown et al. 2002, NAD83 UTM7N)*

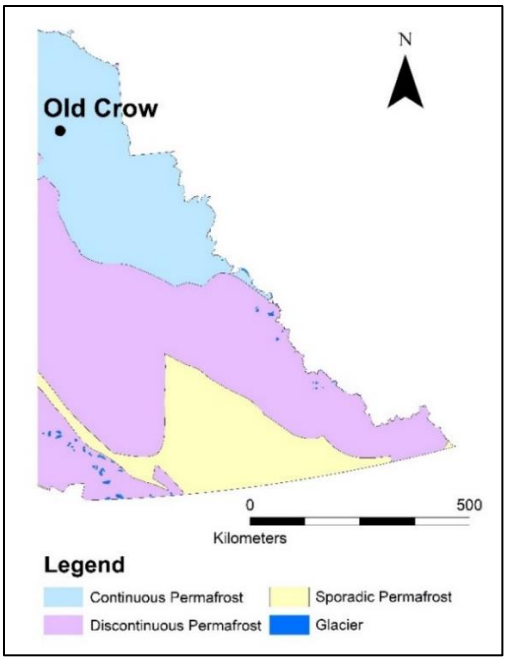


Figure 2.3 *Approximate maximum westward extent of Laurentide Ice Sheet in Northern Yukon and in relation to the community of Old Crow. (Modified from Zazula et al. 2004, NAD83 UTM7N)*

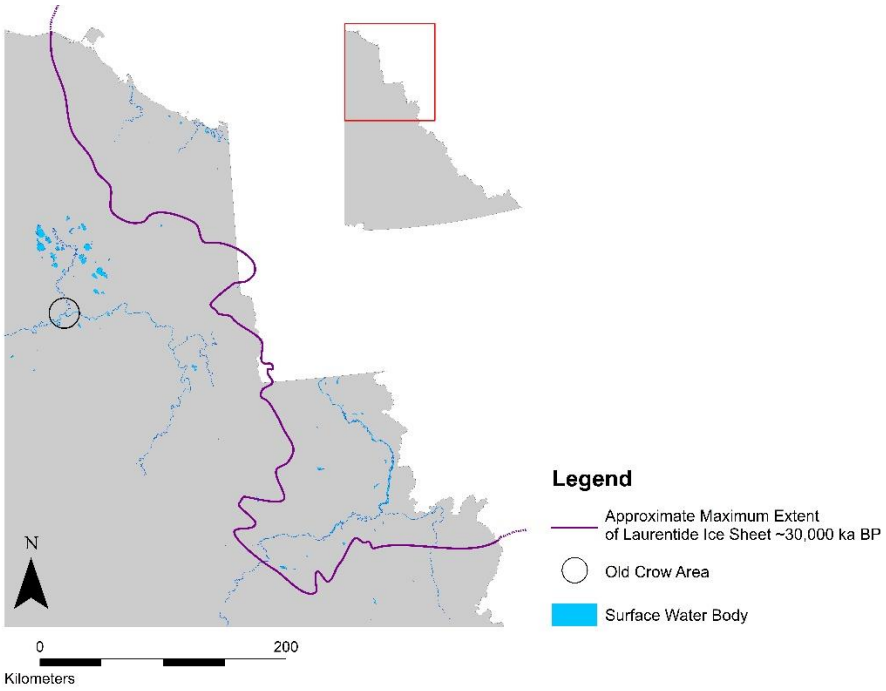


Figure 2.4 *Conceptual site model with stratigraphy, permafrost and hydrology. Southward zone of permafrost at the site mimics surficial topography creating a berm affect for the containment of supra-permafrost water and petroleum hydrocarbon contaminants (Image not to scale, adapted from CH2M 2016)*

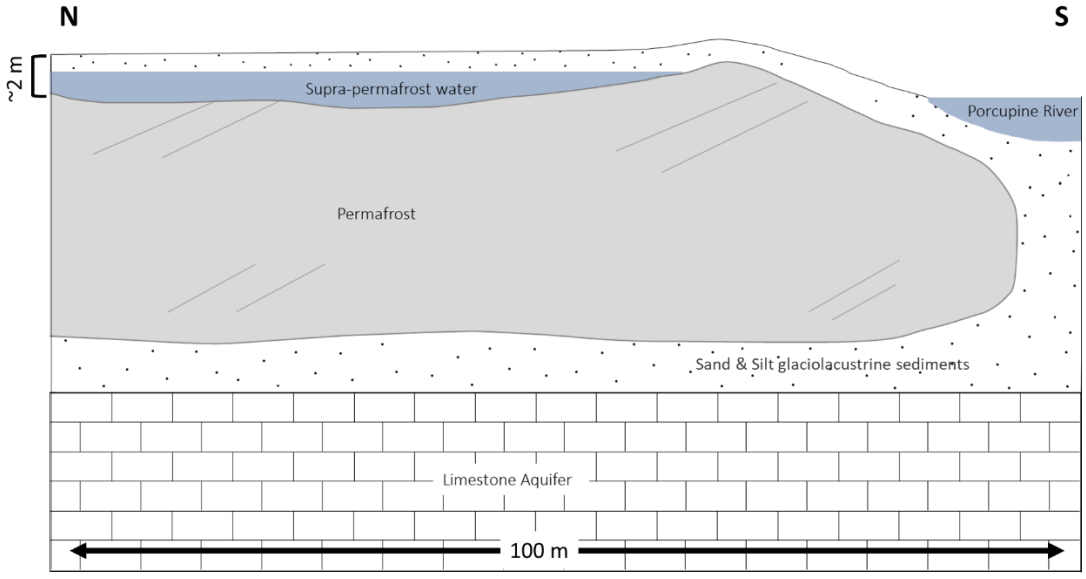


Figure 2.5 *Map of Old Crow Health Centre property and the proximity to the Porcupine River (Air photo from Yukon Government 2014, NAD83 UTM 7N)*

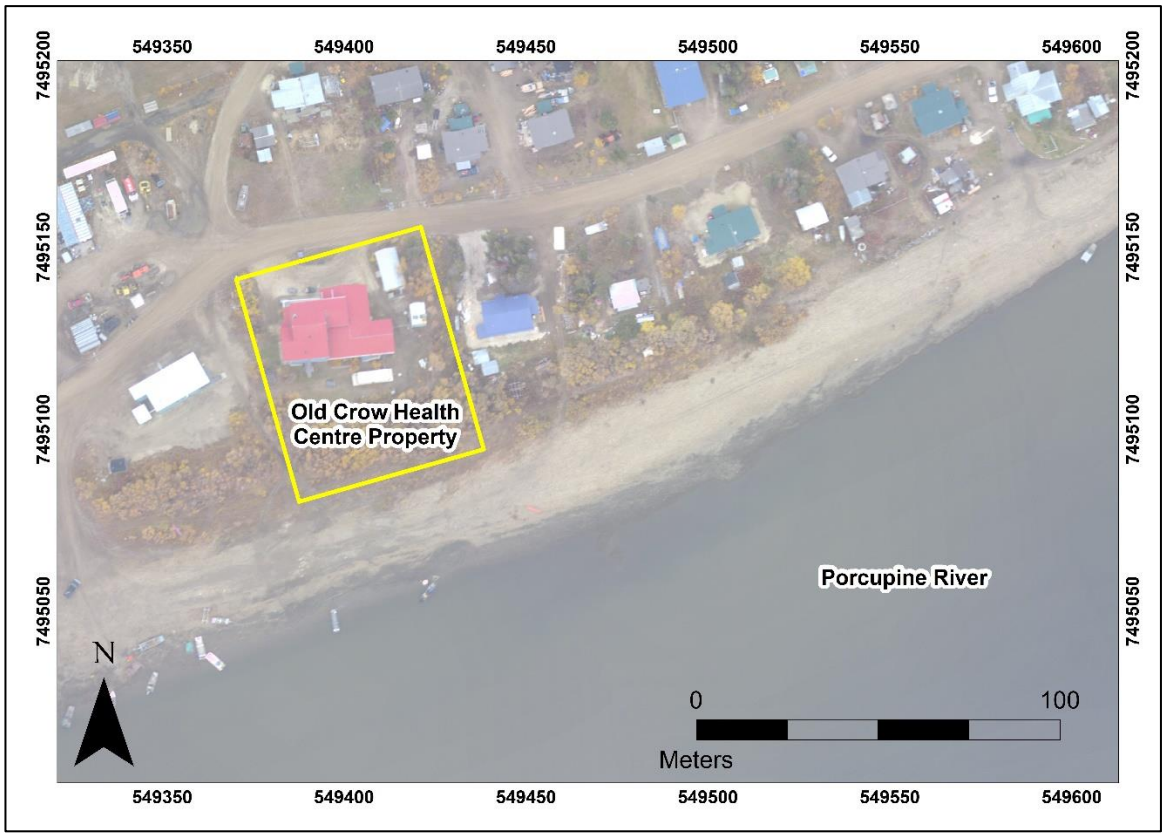


Figure 2.6 *Site Map of both present and former hydrocarbon storage infrastructure at Old Crow Health Centre, Yukon, Canada (Air photo from Yukon Government 2014, NAD83 UTM 7N)*

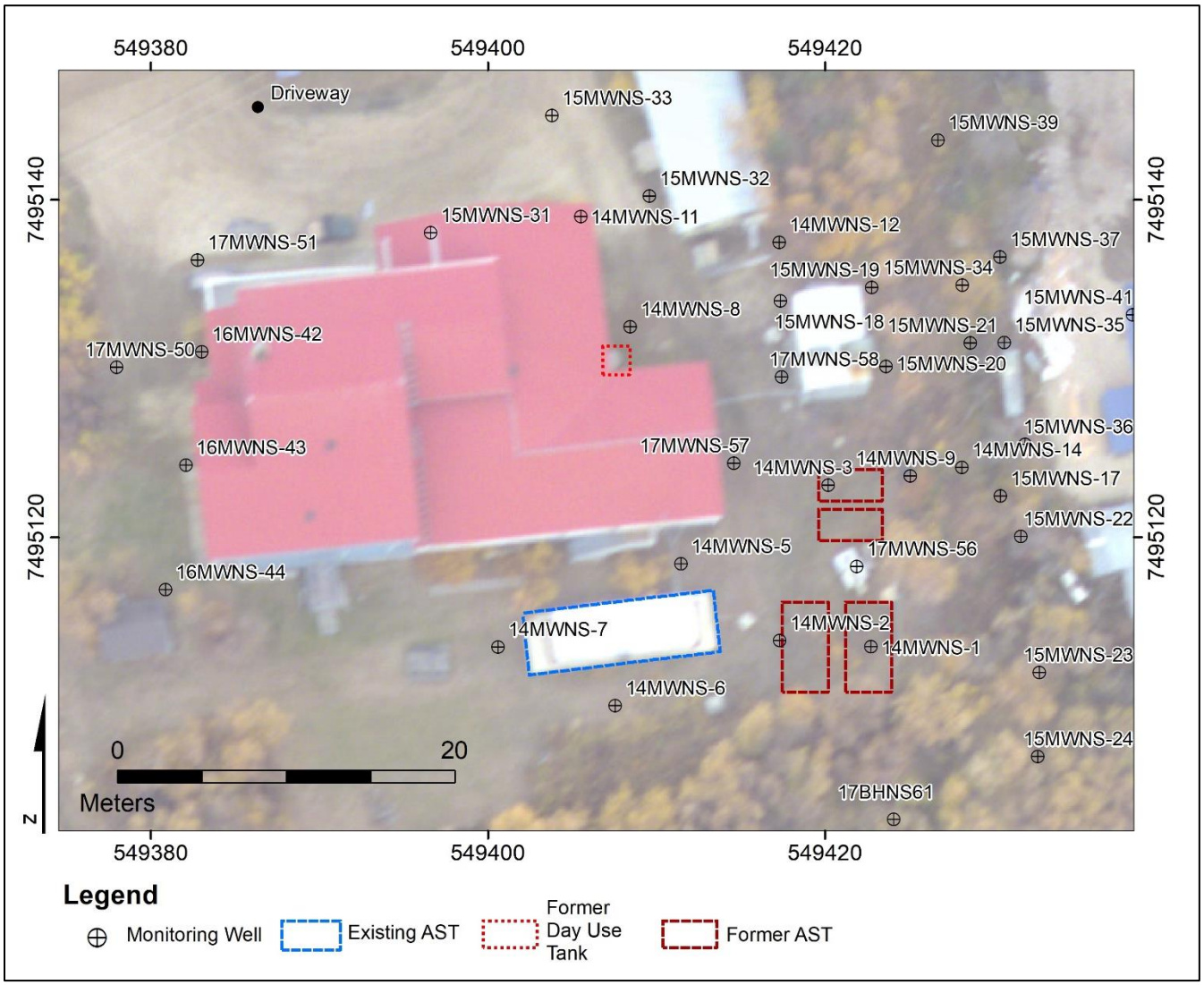


Figure 2.7 *Interpreted extent of LEPH contaminants in supra-permafrost water at Old Crow Health Centre, Yukon based on Yukon Government contaminated site regulations (Air Photo from Yukon Government 2014, NAD83 UTM 7N)*

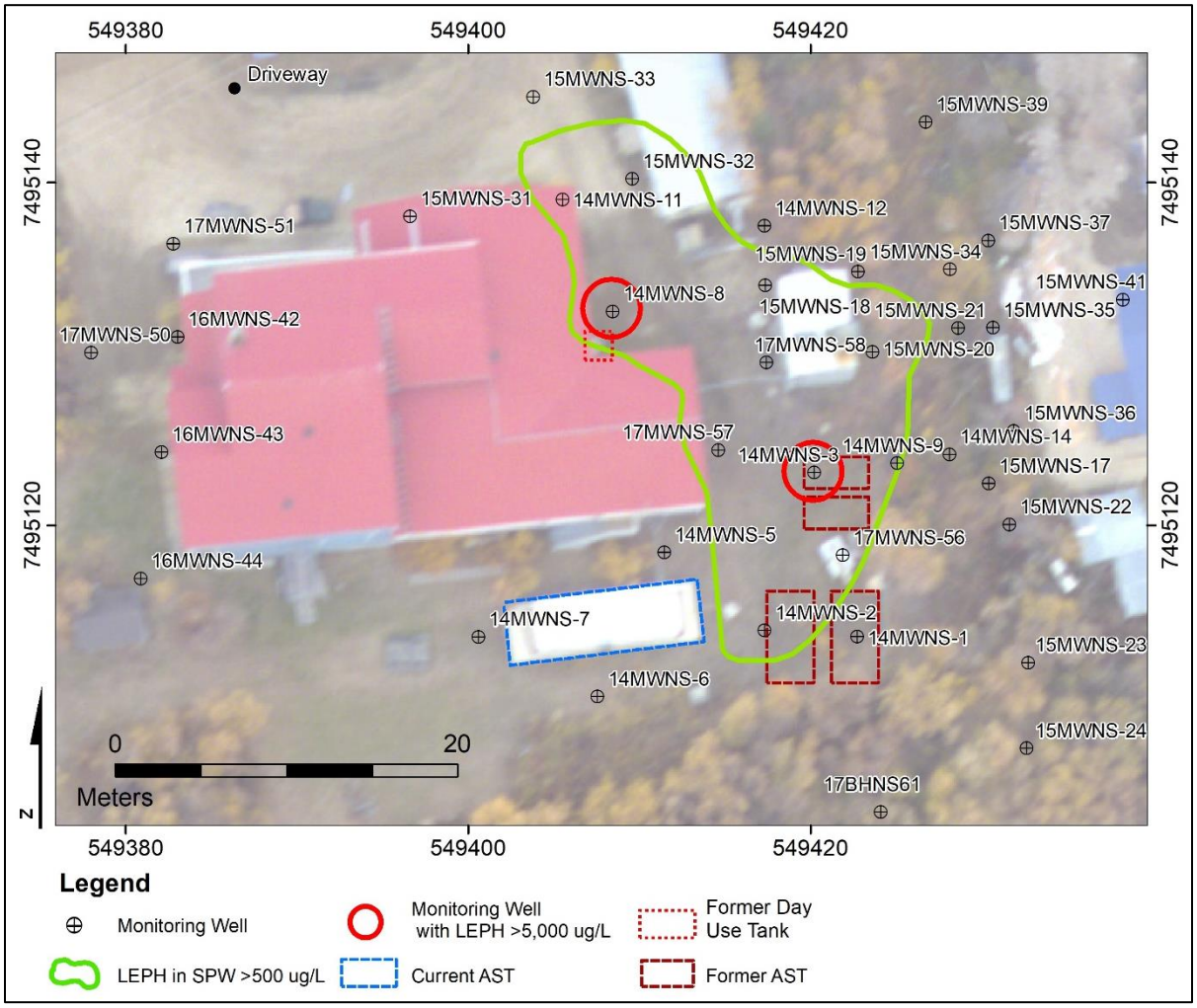
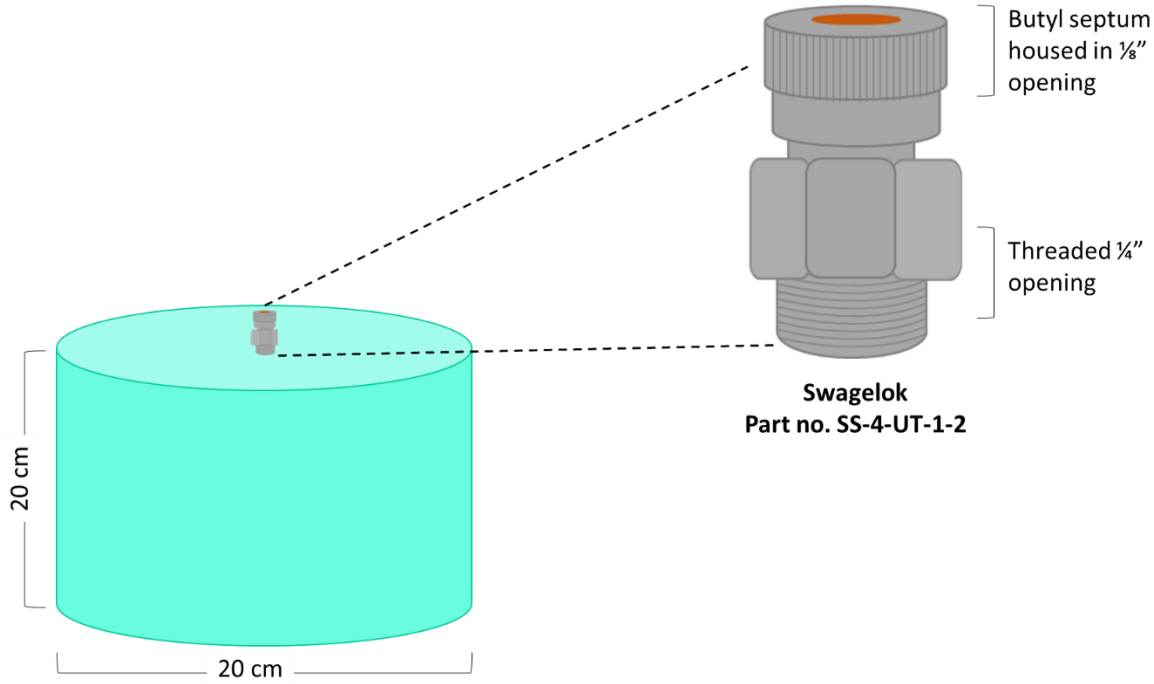


Figure 2.8 *Static chamber schematics for soil gas sample collection. A) standalone PVC chamber construction B) Adapted Li-COR collar construction*

A)



B)

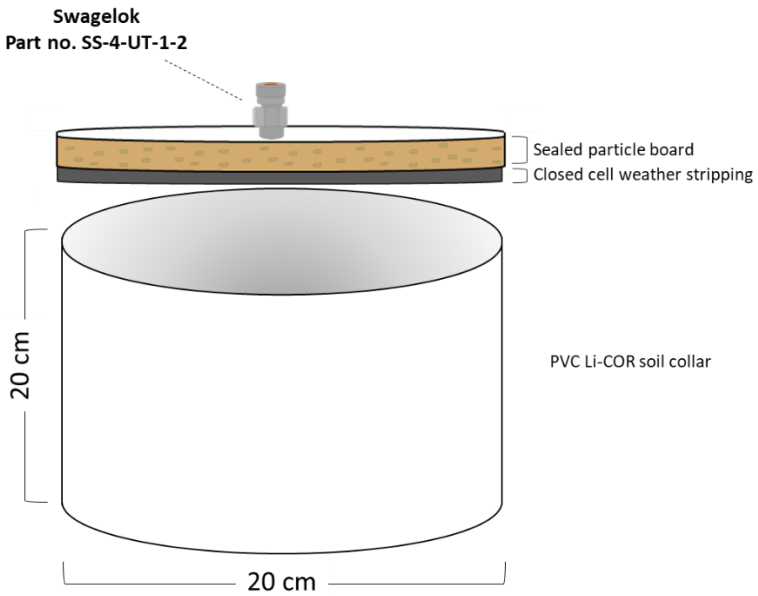


Figure 2.9 *Soil probe design for soil gas sampling (main soil probe made by AMS, Inc.)*

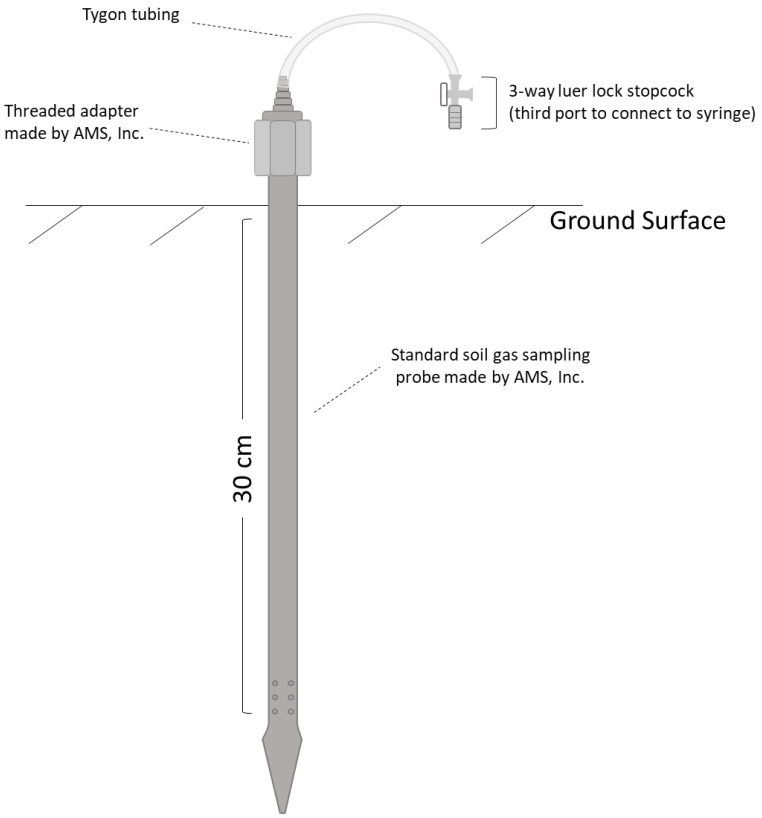


Figure 2.10 *Schematic of Barium Carbonate field precipitation method. Soil gas drawn from soil probe or static chamber is introduced to exetainer contents by 23G needle and after bubbling through hydroxide solution, exits the container through pressure release syringe mechanism.*

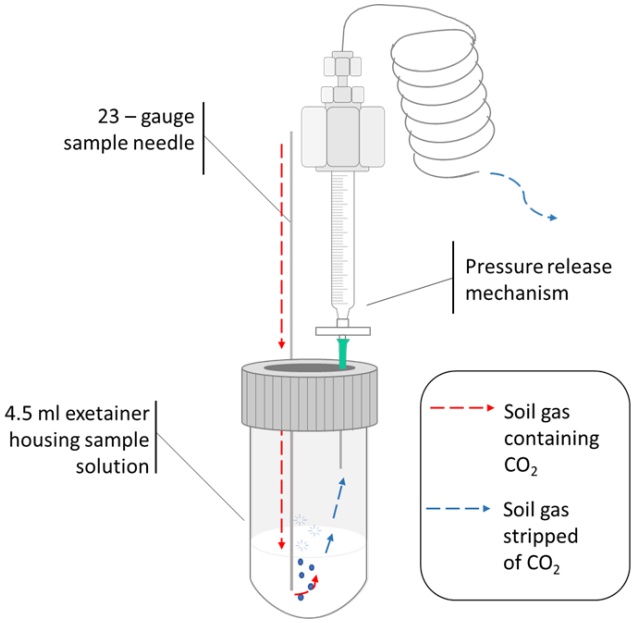
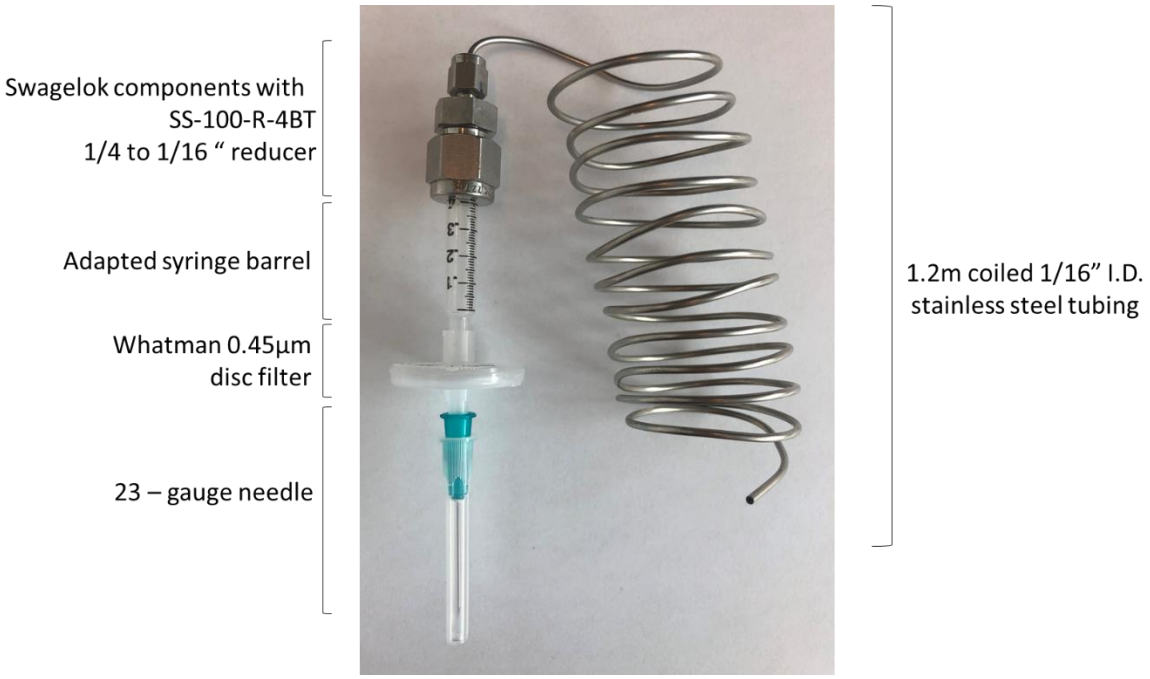


Figure 2.11 *Pressure release mechanism for $BaCO_3$ precipitation sampling method comprised of Swagelok gas fittings and standard laboratory syringe and needle components. Whatman disc filter used as stopper for potential BaOH solution or $BaCO_3$ sample transfer through 23-gauge needle.*



Chapter 3 Comparison of Barium Carbonate and Graphitized Samples

3.1 Introduction

Data from the analysis of samples collected at an arctic diesel contaminated site in Old Crow, Yukon, are reviewed and compared below. Samples were collected by two methods described in Chapter 2; including the $BaCO_3$ precipitation method for direct AMS analysis and the traditional mixed soil gas collection method for eventual graphitization.

Static chamber installation was problematic at the site in Old Crow. Difficulties arose in heterogeneities in the upper 10 cm of ground cover at the site. In some instances, chamber installation was interrupted once the chamber was partially installed by large conglomerate rocks or root networks from nearby vegetation. One sample chamber cracked along the side wall during installation on impact with a large buried rock. Static chambers which were installed successfully were in proximity to the contaminant plume where the ground was disturbed by drilling truck activities.

3.2 Results

3.2.1 $BaCO_3$ Collected by Soil Probe (SP)

$F^{14}C$ from the analysis of $BaCO_3$ samples collected from 30cm soil probes ranged from a maximum value of $F^{14}C$ 1.04 ± 0.024 to a minimum of 0.39 ± 0.009 (Table 3. 1). Maximum values were observed in areas considered background and vegetated (BV). BV values ranged from $F^{14}C$ 1.04 ± 0.024 to 0.97 ± 0.009. Background non-vegetated (BNV) values ranged from $F^{14}C$ 0.96 ± 0.009 to 0.83 ± 0.011. Values of $F^{14}C$ began to deplete with increasing proximity to subsurface contamination. Samples collected on the edge of the plume, considered off plume vegetated (OV) or off plume non-vegetated (ONV) showed the greatest range in $F^{14}C$ values. OV

values ranged from to $F^{14}C$ 0.99 ± 0.024 to 0.46 ± 0.008. ONV values ranged from $F^{14}C$ 0.89 ± 0.021 to 0.83 ± 0.08. On plume samples, both vegetated (PV) and non-vegetated (PNV) showed the greatest depletion. PV samples ranged from $F^{14}C$ 0.90 ± 0.009 to 0.88 ± 0.022. PNV samples ranged from $F^{14}C$ 0.94 ± 0.011 to 0.39 ± 0.009.

3.2.2 $BaCO_3$ Collected by Static Chamber (SC)

$F^{14}C$ from the analysis of $BaCO_3$ samples collected from static chamber ranged from a maximum value of $F^{14}C$ 1.00 ± 0.008 to a minimum of 0.70 ± 0.008 (Table 3. 2). Maximum values were observed in areas considered background and vegetated (BV). BV values ranged from $F^{14}C$ 1.00 ± 0.008 to 0.98 ± 0.009. No samples were collected for background non-vegetated (BNV) values as sample chambers could not be properly installed in the compacted ground. Values of $F^{14}C$ began to deplete with increasing proximity to subsurface contamination. Samples collected on the edge of the plume, considered off plume vegetated (OV) or off plume non-vegetated (ONV) showed the greatest range in $F^{14}C$ values. OV values ranged from $F^{14}C$ 0.84 ± 0.007 to 0.70 ± 0.014. Only one ONV sample was successful analyzed with a value of $F^{14}C$ 0.92 ± 0.008. On plume samples, both vegetated (PV) and non-vegetated (PNV) showed the greatest depletion. Only one PV sample was successfully analyzed with a value of $F^{14}C$ 0.99 ± 0.008. PNV samples ranged from $F^{14}C$ 0.96 ± 0.008 to 0.71 ± 0.013. Samples collected on plume by static chamber were collected in areas with a high degree of surface soil disturbance from drilling truck activity.

3.2.3 Field Blank Preparation by $BaCO_3$ Precipitation

Sampling in 2017 produced field blanks prepared by the method outlined in chapter 2 (section 2.2 – III) with $F^{14}C$ results of 0.015 ± 0.001 and 0.027 ± 0.001 in 2017. 2018 field sampling produced a field blank with $F^{14}C$ results of 0.050 ± 0.002. Sampling in 2018 was conducted by one field member and the extraction CO_2 from the 40ml EPA vial was difficult resulting in stress to the double septum where the needle pierced which may have allow the introduction of modern atmospheric CO_2. Sampling in 2017 was conducted with two field members and no complications arose in the extraction of field-produced ^{14}C free CO_2. Field process blank values are included in Table 3.1.

3.2.3 Graphitized Samples Collected by Soil Probe (SP)

$F^{14}C$ from the analysis of graphitized samples collected from 30cm soil probe ranged from a maximum value of $F^{14}C$ 1.02 ± 0.005 to a minimum of 0.48 ± 0.002 (Table 3. 3). Maximum values were observed in areas considered background and vegetated (BNV). BNV values ranged from $F^{14}C$ 1.02 ± 0.005 to 1.00 ± 0.005. Only one sample was collected for background non-vegetated (BNV) with a value of $F^{14}C$ 0.99 ± 0.003. Values of $F^{14}C$ began to deplete with increasing proximity to subsurface contamination. Samples collected on the edge of the plume, considered off plume vegetated (OV) or off plume non-vegetated (ONV) showed the greatest range in $F^{14}C$ values. Only one sample was collected for OV with a value of $F^{14}C$ 1.02 ± 0.005. Only one sample was collected for ONV with a value of $F^{14}C$ 0.87 ± 0.004. No on plume vegetated samples were successfully collected. On plume non-vegetated (PNV) samples were successfully collected with range in a value from $F^{14}C$ 0.96 ± 0.004 to 0.48 ± 0.002.

3.2.4 Graphitized Samples Collected by Static Chamber (SC)

$F^{14}C$ from the analysis of graphitized samples collected from static chamber ranged from a maximum value of $F^{14}C$ 1.00 ± 0.008 to a minimum of 0.84 ± 0.003 (Table 3.4). No samples were collected for background non-vegetated (BNV) or vegetated (BV) values as sample chambers could not be properly installed in the compacted ground. Samples collected on the edge of the plume, considered off plume vegetated (OV) or off plume non-vegetated (ONV) showed near modern $F^{14}C$ values. Only one OV sample was successfully collected with a value of $F^{14}C$ 1.00 ± 0.008. Only one ONV sample was successful analyzed with a value of $F^{14}C$ 0.95 ± 0.003. On plume samples, both vegetated (PV) and non-vegetated (PNV) showed the greatest depletion. Only one PV sample was successfully analyzed with a value of $F^{14}C$ 0.99 ± 0.003. PNV samples ranged from $F^{14}C$ 0.94 ± 0.003 to 0.84 ± 0.003.

3.3 Discussion

3.3.1 Analysis of Samples Collected from Soil Probe (SP)

I. $BaCO_3$ Samples Collected by Soil Probe (SP)

Samples collected as $BaCO_3$ precipitate from soil probes (SP) showed variance in $F^{14}C$ with proximity to known subsurface contamination. Background sampling produced a $F^{14}C$ of 1.04 ± 0.024. Other background samples which showed $F^{14}C$ depletion (R18-1, RC18-2, RC46) were collected in areas where no analytical data was available or showed the presence of subsurface contamination. Sampling directly above what was considered the area of highest concentration of LEPH contamination in supra-permafrost water, > 5,000 µg/L, resulted in maximum depleted $F^{14}C$ values of 0.39 ± 0.009 and 0.49 ± 0.006. Samples were collected along an approximate traverse ranged between these maximum and minimum values (Figure 3.1).

The results of $BaCO_3$ sampling by SP clearly support previous efforts to quantify contaminant respiration contributions to soil gas CO_2 efflux (Sihota et al. 2011, Wozney 2016).

Samples collected as duplicates in the same sampling year produced promising results of reproducibility (Table 3. 5). In September 2017, samples RC13 and RC19 (BV) were collected during the same SP installation approximately 30 minutes apart and had $F^{14}C$ values of 1.00 ± 0.008 and 0.99 ± 0.024, respectively. Also, in September 2017, samples RC41 and RC42 (PNV) were collected elsewhere on the site on the same SP installation and 30 minutes apart, and produced $F^{14}C$ values of 0.92 ± 0.002 and 0.90 ± 0.002, respectively. In September 2018, samples RC18-1 and RC18-2 (BNV) were collected for a location free of vegetation, northwest of the OCHC (sample location referred to as 'driveway' in Table 3. 5 and 3.1C). The ground cover here was highly compacted and installation of the soil probe was difficult. The resulting installation produced a small amount of annular space around the soil probe. This annular space had a noticeable affect on the resultant $F^{14}C$ data (Table 3.8 & Figure 3.3). Sample RC18-1 was collected first and produced a $F^{14}C$ value of 0.83 ± 0.011. The second sample drawn, 30 minutes later, was RC18-2 and produced a $F^{14}C$ value of 0.90 ± 0.009. A third sample, GRC18-2, was collected 30 minutes after RC18-2 for graphitized sample comparison and showed further enrichment in ^{14}C ($F^{14}C$ 0.99 ± 0.005). This trend of enrichment is likely attributable to atmospheric CO_2 incursion through the annular space.

Samples collected as duplicates in different years, September 2017 or 2018, also showed promising results of reproducibility (Table 3.6). Samples RC57 (2017) and RC18-17 (2018) were collected in the same location on the site but one year apart and produced $F^{14}C$ values of 0.84 ± 0.020 and 0.84 ± 0.008, respectively. Samples RC57 and RC18-17 were collected

from a sample location considered off plume – vegetated (OV). Samples RC46 (2017) and RC18-16 (2018) were collected in the same location on the site but one year apart and produced $F^{14}C$ values of 0.89 ± 0.021 and 0.90 ± 0.020, respectively. Samples RC46 and RC18-16 were collected from a sample location considered background – non-vegetated (BNV). The depletion in this area has been revealed to be attributed to the presence of LEPH slightly below the CSR exceedance of 500µg/L in supra-permafrost water (Yukon Regulations Environment Act 2002). At the time of sampling location selection, this well was identified as 'clean' and as such chosen to be representative of a background site. This quantity of contaminant is considered acceptable given the low site exposure pathway risk but has shown to have an influence on the $F^{14}C$ of sampled soil CO_2. Samples RC30 (2017) and RC18-9 (2018) were collected in the same location on the site but one year apart and produced $F^{14}C$ values of 0.89 ± 0.021 and 0.88 ± 0.010, respectively. Samples RC30 and RC18-9 were collected from a sample location considered on plume – non-vegetated (PNV).

Some of samples collected as duplicates in different years, September 2017 or 2018, showed less reproducibility, yet still produced good results. Samples RC3 (2017) and RC18-10 (2018) were collected in the same location on the site but one year apart and produced $F^{14}C$ values of 0.81 ± 0.008 and 0.90 ± 0.010, respectively. Samples RC3 and RC18-10 were collected from a sample location considered on plume –vegetated (PV). Samples RC11 (2017) and RC18-11 (2018) were collected in the same location on the site but one year apart and produced $F^{14}C$ values of 0.39 ± 0.009 and 0.53 ± 0.006, respectively. Samples RC11 and RC18-11 were collected from a sample location considered on plume – non-vegetated (PNV) and are at location of the highest level of supra-permafrost water contamination. In the 2017 sampling year drilling

activity was conducted on the site shortly before soil gas sampling had occurred. The ground cover around this sample location was very loose underfoot and had a fair amount of reworking due to drilling vehicle traffic around well 14MWNS8. Proximity to this monitoring well was the target for soil gas sampling at this site. In the 2018 sampling year there was no drilling activity and as such the sample site had a full year of ground settling. The ground cover at this sample location was noticeably more compact from the previous sampling year. There is potential that the reworking of the soil in 2017 allowed for a higher rate of diffusion from contaminant derived CO_2 upward to the soil probe sampling point.

Samples RC36 (2017) and RC18-5 (2018) show problematic results for reproducibility. Sample RC36, collected in 2017 produced a $F^{14}C$ value of 0.93 ± 0.022, whereas sample RC18-5, collected in 2018 produced a $F^{14}C$ value of 0.46 ± 0.008. These samples were collected in a vegetated area which appears to be the edge of the contaminant plume. There was no drilling activity proximal to this sampling point in 2017 which may have altered ground conditions. Given the dynamic nature of the active layer and the uneven surface of permafrost it is possible that from one year to the next small changes in the location of contaminant in supra-permafrost water may occur, especially on the edge of the plume.

II. Graphitized Samples Collected by Soil Probe (SP)

Samples collected as mixed soil gas for graphitization from soil probe (SP) technique showed variance in $F^{14}C$ with proximity to known subsurface contamination. Background sampling produced a $F^{14}C$ of 1.02 ± 0.005. Sampling directly above what was considered the area of highest concentration of contamination in supra-permafrost water, > 5,000 µg/L,

maximum $F^{14}C$ depleted values of 0.48 ± 0.002. Samples were collected along an approximate traverse ranged between these maximum and minimum values (Figure 3.2). The results of sampling mixed soil gas for graphitization sampling by SP clearly support previous efforts to quantify contaminant respiration contributions to soil gas CO_2 efflux (Sihota et al. 2011, Wozney 2016).

Samples collected as duplicates in the same sampling year produced promising results of reproducibility (Table 3. 7). In September 2018, samples GRC18-6 and GRC18-7 (PNV) were collected during the same SP installation approximately 30 minutes apart and had $F^{14}C$ values of 0.48 ± 0.002 and 0.49 ± 0.002, respectively. As mixed soil gas sampling by soil probe for radiocarbon analysis is a proven method (Wozney 2016), no studies of duplication between sampling years were taken for this method.

III. Comparison of $BaCO_3$ and Graphitized Samples collected by Soil Probe (SP)

Duplicate sample sets were collected by soil probe for comparative analysis of $BaCO_3$ and graphitization techniques. Sample sets are summarized in Table 3.8 and Figure 3.3. Duplication efforts between samples collected and $BaCO_3$ and mixed soil gas produced a high level of reproducibility for samples collected in areas considered background and in areas directly above know LEPH impacts in supra-permafrost water. In areas considered to be above the edge of the LEPH impacts there is a higher degree of variability between samples. The majority of pairs collected for method comparison showed good results for the $BaCO_3$ precipitation method. Problematic samples include a duplicate sample collected in highly compacted driveway soil conditions and continued the trend of modern $^{14}CO_2$ contamination

through poor soil probe installation. Other problematic samples include sets collected on the interpreted edge of the impacted supra-permafrost water (samples collected at 15MWNS12 and 15MWNS20). The effect of variance in $F^{14}C$ on plume edge was observed in samples from 2017 and 2018 at sample site 15MWNS20.

Analysis of Variance (ANOVA) on the $F^{14}C$ value for samples collected as $BaCO_3$ and mixed soil gas by SP technique showed no significant statistical differences for the two datasets ($F = 1.272$, $p= 0.276$). Despite the result of the ANOVA for these sampling methods, it is not possible to definitively state there are no statistical differences between these techniques given the small sample set included in this study ($BaCO_3$ n = 9, graphite n = 9). Statistical analysis is summarized in Table 3.11. Reduced accuracy should be considered for applications of the $BaCO_3$ sampling technique. Study areas w

3.3.2 Analysis of $BaCO_3$ Samples Collected from Static Chamber (SC)

I. $BaCO_3$ Samples Collected by Static Chamber (SC)

Samples collected as $BaCO_3$ precipitate from static chamber (SC) technique showed variance in $F^{14}C$ with proximity to known subsurface contamination. Background sampling produced a $F^{14}C$ of 1.00 ± 0.008. The maximum $F^{14}C$ depletion was observed as values of 0.70 ± 0.007. Samples were collected along an approximate traverse ranged between these maximum and minimum values (Figure 3.4). The results of $BaCO_3$ sampling by SC support previous efforts to quantify contaminant respiration contributions to soil gas CO_2 efflux (Sihota et al. 2011, Wozney 2016).

Samples collected as duplicates in the same sampling year produced problematic results of reproducibility (Table 3. 9). In September 2017, samples RC22 and RC24 (PV) were collected during the same SC installation approximately 30 minutes apart and had $F^{14}C$ values of 0.70 ± 0.013 and 0.90 ± 0.024, respectively. Once a SC is driven 10cm into the ground, chamber dimensions provide an interior volume of roughly 3 litres for accumulated soil gas to be sampled. For one sample collected by the $BaCO_3$ method, a minimum of 400 ml or roughly 14 percent of the gas headspace is drawn from the chamber. Given SC installation and equilibration over a span of 24 hours it can be assumed that standard air pressure would be observed within the SC. Once a sample has been drawn from the SC a vacuum would be imparted on the chamber. Duplication results appear to show that the incursion of modern atmospheric CO_2 occurs during this sampling technique (Figure 3.6). Given the problematic results for field sampling in 2017 by static chamber, the 2018 field sampling program saw deployment of only soil probe as a sampling tool.

II. Graphitized Samples Collected by Static Chamber (SC)

Samples collected as mixed soil gas static chamber (SC) technique showed only slight variance in $F^{14}C$ with proximity to known subsurface contamination (Figure 3.5). Samples collected in areas with known impacts ranged from a modern $F^{14}C$ value to a maximum depletion of 0.83 ± 0.0032. No duplicate samples for graphitization were collected from SC.

III. Comparison of $BaCO_3$ and Graphitized Samples collected by Static Chamber (SC)

Duplicate sample sets were collected by static chamber for comparative analysis of $BaCO_3$ and graphitization techniques. Sample sets are summarized in Table 3.10 and Figure 3.7.

In the case of sample set collected at 17MWNS57 the $BaCO_3$ sample was collected before the mixed soil gas sample with the result of ^{14}C enrichment in the graphitized sample. In the case of the sample collected at 15MWNS32, the enrichment is seen in the $BaCO_3$ sample which was collected after the mixed soil gas sample for graphitization. The sample set collected at 15MWNS21 showed a modern signature for both $BaCO_3$ and graphitized sample.

3.3.3 Comparative Analysis of Soil Probe and Static Chamber Sampling Tools

Results of this study show that both soil probe and static chamber sampling tools can be used to obtain $F^{14}C$ signatures for soil CO_2 efflux at PHC impacted sites. Statistical analysis of the sample sets presented in this study were inconclusive due to the small number of samples collected for each method. Analysis of Variance (ANOVA) on the $F^{14}C$ value for samples collected by soil probe and static chamber showed no significant statistical differences for the two datasets ($F = 0.683$, $p= 0.415$). Statistical analysis is summarized in Table 3.12. Despite the result of the ANOVA for these sampling methods, it is not possible to definitively state there are no statistical differences between these techniques given the small sample set included in this study (soil probe n = 18, static chamber n = 17). As such, a more qualitative assessment of the sampling techniques is applied in interpretation of the study outcome.

The study showed limitations with the static chamber technique of sample collection. Sample collection for duplication from SC showed a pattern of enrichment caused by the possible intrusion of modern atmospheric CO_2 when a slight vacuum was induced on the SC. SP sampling showed promising results for both sample duplication, even in triplicate results with comparative graphitized samples. A review with logistical consideration of the two methods

also shows limitations to the SC technique. The use of SC sampling tools at the field sampling site was problematic given heterogeneous materials at varying depths below the ground surface. SC installation in some cases was interrupted and restarted multiple times potentially causing ground disturbance and equipment damage. In cases of hard packed ground soil probe installation was difficult, but the creation of annular space was easy to observe and rectify.

Chapter 3 Tables

Table 3.1 *$F^{14}C$ results from samples collected as BaCO3 from 30 cm soil probe in Old Crow, Yukon*

Sample ID	***Site Location***	***Parameters***	***$F^{14}C$***	***±***
RC46	16MWNS43	BNV	0.8886	0.0214
RC18-1	Driveway	BNV	0.8318	0.0108
RC18-2	Driveway	BNV	0.9034	0.0085
RC12	17MWNS50	BV	1.0395	0.0249
RC13	16MWNS44	BV	0.9974	0.0078
RC19	16MWNS44	BV	0.9883	0.0237
RC60	17BHNS61	BV	0.9995	0.0239
RC37	14MWNS1	ONV	0.8917	0.0213
RC18-16	15MWNS43	ONV	0.8997	0.0209
RC18-18	14MWNS1	ONV	0.8807	0.0156
RC49	17MWNS58	PNV	0.9349	0.0224
RC57	14MWNS2	OV	0.8366	0.0200
RC7	15MWNS19	OV	0.9719	0.0072
RC36	14MWNS12	OV	0.9344	0.0224
RC18-5	15MWNW12	OV	0.4633	0.0083
RCW11	14MWNS14	OV	0.9170	0.0220
RC18-17	14MWNS2	OV	0.8440	0.0084
RC10	15MWNS32	PNV	0.9305	0.0112
RC11	14MWMS8	PNV	0.3906	0.0094
RC25	14MWNS9	PNV	0.8795	0.0211
RC30	17BHNS54	PNV	0.8917	0.0213
RC41	17MWNS57	PNV	0.9173	0.0220
RC42	17MWNS57	PNV	0.8995	0.0215
RC18-6	14NWNS3	PNV	0.4874	0.0060
RC18-11	14MWMS8	PNV	0.5334	0.0064
RC3	15MWNS20	PV	0.8190	0.0080
RC18-9	15MWNS20	PV	0.8753	0.0102
RC18-10	15MWNS20	PV	0.8991	0.0097
PB1 (2017)	Field Process Blank	--	0.0154	0.0009
PB2 (2017)	Field Process Blank	--	0.0272	0.0013
PB3 (2018)	Field Process Blank	--	0.0494	0.0019

Table 3.2 *$F^{14}C$ results from samples collected as BaCO3 from static chamber in Old Crow, Yukon*

Sample ID	Site Location	Parameters	$F^{14}C$	±
RC39	15MWNS39	BV	0.9980	0.0084
RC61	17BHNS61	BV	0.9971	0.0084
RC62	17BHNS61	BV	0.9795	0.0093
RC48	17MWNS57	ONV	0.9197	0.0080
RC51	14MWNS2	OV	0.7020	0.0075
RC20	15MWNS19	OV	0.7250	0.0141
RC58	14MWNS12	OV	0.8422	0.0072
RC28	15MWNS32	PNV	0.9559	0.0081
RC50	14MWNS9	PNV	0.9394	0.0147
RC22	15MWNS20	PV	0.7076	0.0130
RC24	15MWNS20	PV	0.8995	0.0245
RC38	15MWNS21	PV	0.9937	0.0080

Table 3.3 *$F^{14}C$ results from samples collected for graphitization from 30cm soil probe in Old Crow, Yukon*

Sample ID	Sample Location	Parameters	$F^{14}C$	±
GRC18-2	Driveway	BNV	0.9991	0.0045
GRC18-3	17MWNS50	BNV	1.0203	0.0046
NSRC15-1	16MWNS44	BV	0.9918	0.0027
GRC18-7	14MWNS3	DUP	0.4878	0.0022
GRC18-4	17MWNS58	ONV	0.8656	0.0039
GRC18-5	15MWNS18	OV	1.0187	0.0046
GRC18-6	14MWNS3	PNV	0.4840	0.0022
NSRC54-2	15MWNS32	PNV	0.9552	0.0036
NSRC-55-1	15MWNS20	PV	0.8610	0.0037

Table 3.4 *$F^{14}C$ results from samples collected for graphitization from static chamber in Old Crow, Yukon*

Sample ID	Sample Location	Parameters	$F^{14}C$	±
NSRC-18-2	17MWNS57	ONV	0.9519	0.0032
NSRC-63-2	15MWNS19	OV	0.9965	0.0079
NSRC-32-2	14MWNS8	PNV	0.8386	0.0032
NSRC14-1	15MWNS32	PNV	0.9443	0.0026
NSRC-56-1	15MWNS21	PV	0.9918	0.0025

Table 3.5 *2017 $F^{14}C$ Duplicate samples collected as BaCO3 from soil probe in Old Crow, Yukon*

Sample ID *A*	*B*	**Sample Location**	**Parameters**	Sample A **$F^{14}C$**	**±**	Sample B $F^{14}C$	**±**
RC13	RC19	16MWNS44	BV	0.9974	0.0078	0.9883	0.0237
RC41	RC42	17MWNS57	BNV	0.9173	0.0220	0.8995	0.0215
RC18-1	RC18-2	Driveway	BNV	0.8318	0.0108	0.9034	0.0085

Table 3.6 *$F^{14}C$ Duplicate samples collected as BaCO3 from soil probe over both sampling years in Old Crow, Yukon*

Sample ID *2017*	*2018*	**Sample Location**	**Parameters**	2017 **$F^{14}C$**	**±**	2018 $F^{14}C$	**±**
RC11	RC18-11	14MWNS8	PNV	0.3906	0.0094	0.5334	0.0063
RC57	RC18-17	14MWNS2	OV	0.8366	0.0200	0.8440	0.0019
RC46	RC18-16	16MWNS43	BNV	0.8886	0.0213	0.8997	0.0209
RC3	RC18-10	15MWNS20	PV	0.8190	0.0080	0.8991	0.0097
RC36	RC18-5	14MWNS12	OV	0.9344	0.0224	0.4633	0.0083
RC30	RC18-9	17BHNS54	PNV	0.8917	0.0213	0.8753	0.0102

Table 3.7 *2017 $F^{14}C$ duplicate graphitized samples from soil probe in Old Crow, Yukon*

Sample ID *A*	*B*	**Sample Location**	**Parameters**	Sample A **$F^{14}C$**	**±**	Sample B $F^{14}C$	**±**
GRC18-6	GRC18-7	14MWNS3	PNV	0.4840	0.0022	0.4878	0.0022

Table 3.8 *$F^{14}C$ Values of complementary BaCO3 and Graphitized samples collected by soil probe in Old Crow, Yukon*

Sample ID *Graphite*	*$BaCO_3$*	**Sample Location**	**Parameters**	Graphite **$F^{14}C$**	**±**	$BaCO_3$ $F^{14}C$	**±**
GRC18-2	RC18-1	Driveway	BNV	0.9991	0.0045	0.8318	0.0108
--	RC18-2			--	--	0.9034	0.0085
GRC18-3	RC12	17MWNS50	BNV	1.0203	0.0046	1.0390	0.0240
NSRC15-1	RC13	16MWNS44	BV	0.9918	0.0027	0.9974	0.0078
--	RC19			--	--	0.9883	0.0237
GRC18-6	RC18-6	14MWNS3	PNV	0.4840	0.0022	0.4874	0.0060
GRC18-7	--			0.4878	0.0022	--	--
GRC18-4	RC49	17MWNS58	ONV	0.8656	0.0039	0.8353	0.0083
GRC18-5	RC18-5	15MWNS12	OV	1.0187	0.0046	0.4633	0.0083
NSRC54-2	RC10	15MWNS32	PNV	0.9552	0.0036	0.9305	0.0112
NSRC55-1	RC3	15MWNS20	PV	0.8610	0.0037	0.8190	0.0080
GRC18-8	RC18-10	15MWNS20	PV	1.0064	0.0046	0.8991	0.0097

Table 3.9 *2017 $F^{14}C$ duplicate samples collected as BaCO3 from static chamber in Old Crow, Yukon*

Sample ID *A*	*B*	**Sample Location**	**Parameters**	Sample A **$F^{14}C$**	**±**	Sample B $F^{14}C$	**±**
RC22	RC24	15MWNS20	PV	0.7076	0.0130	0.8995	0.0245

Table 3.10 *$F^{14}C$ values of complementary BaCO3 and graphitized samples collected by static chamber in Old Crow, Yukon*

Sample ID *Graphite*	*$BaCO_3$*	**Sample Location**	**Parameters**	Graphite **$F^{14}C$**	**±**	$BaCO_3$ $F^{14}C$	**±**
NSRC18-2	RC48	17MWNS57	ONV	0.9519	0.0032	0.9196	0.0080
NSRC14-1	RC28	15MWNS32	PNV	0.9443	0.0026	0.9560	0.0081
NSRC56-1	RC38	15MWNS21	PV	0.9918	0.0025	0.9937	0.0080

Table 3.11 *$F^{14}C$ Analysis of Variance for samples collected by soil probe as $BaCO_3$ (n=9) and Graphite (n=9)*

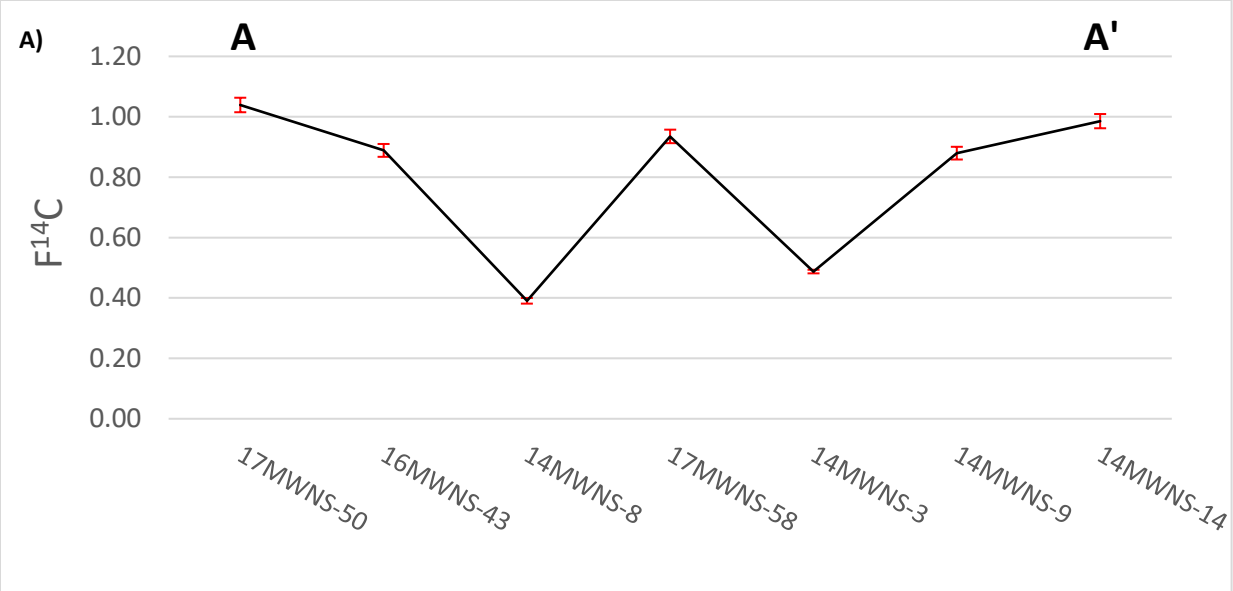
Source	DF	Sum of squares	Mean squares	F	Pr > F
Model	1	0.045	0.045	1.272	0.276
Error	16	0.568	0.036		
Corrected Total	17	0.613			

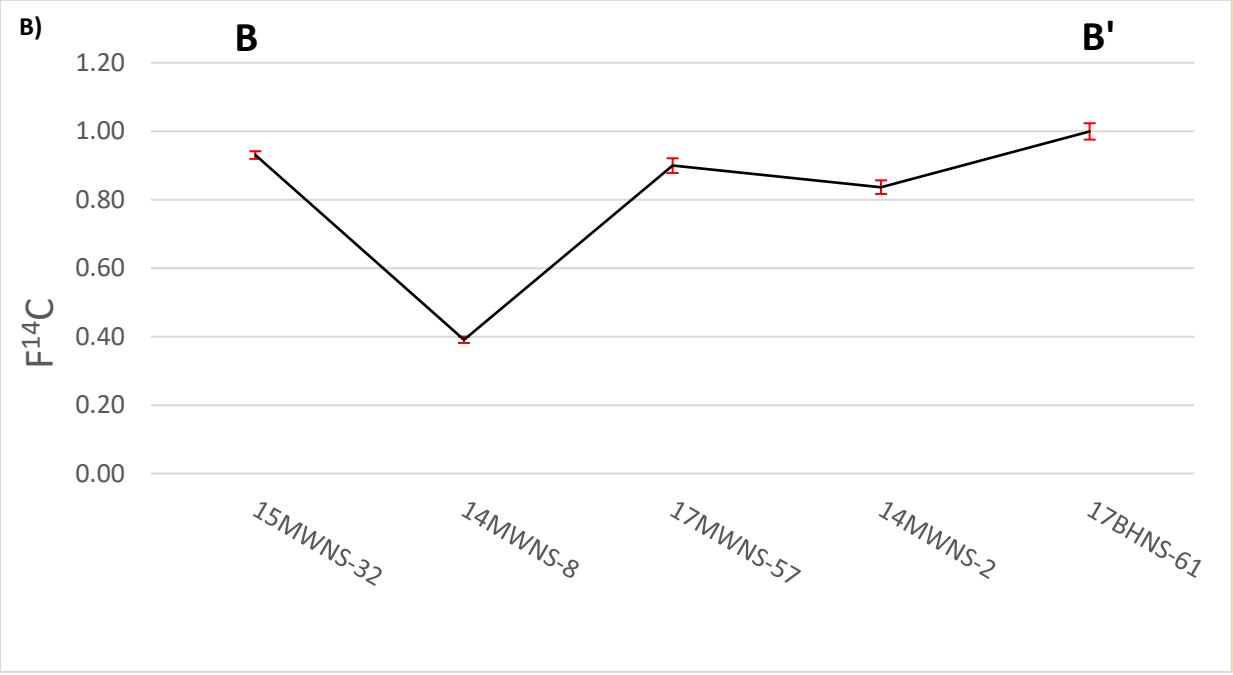
Table 3.12 *$F^{14}C$ Analysis of Variance for samples collected by soil probe (n=18) and static chamber (n=17)*

Source	DF	Sum of squares	Mean squares	F	Pr > F
Model	1	0.016	0.016	0.683	0.415
Error	33	0.788	0.024		
Corrected Total	34	0.805			

Chapter 3 Figures

Figure 3.1 *Cross sections of $F^{14}C$ obtained by $BaCO_3$ precipitation collected by soil probe A) A-A' cross section $F^{14}C$ data B) B-B' cross section $F^{14}C$ data C) Site map with corresponding cross sections*





C)

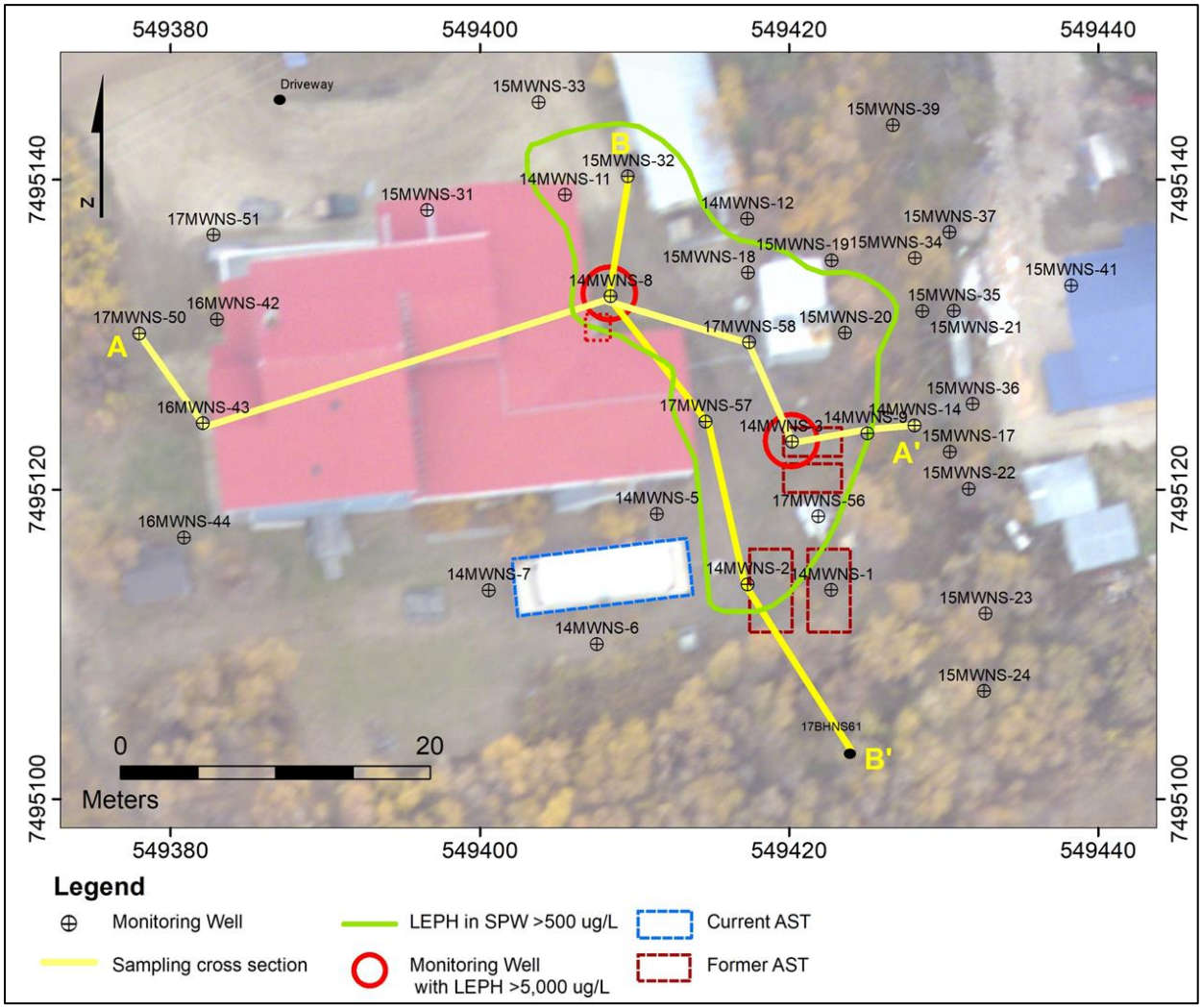
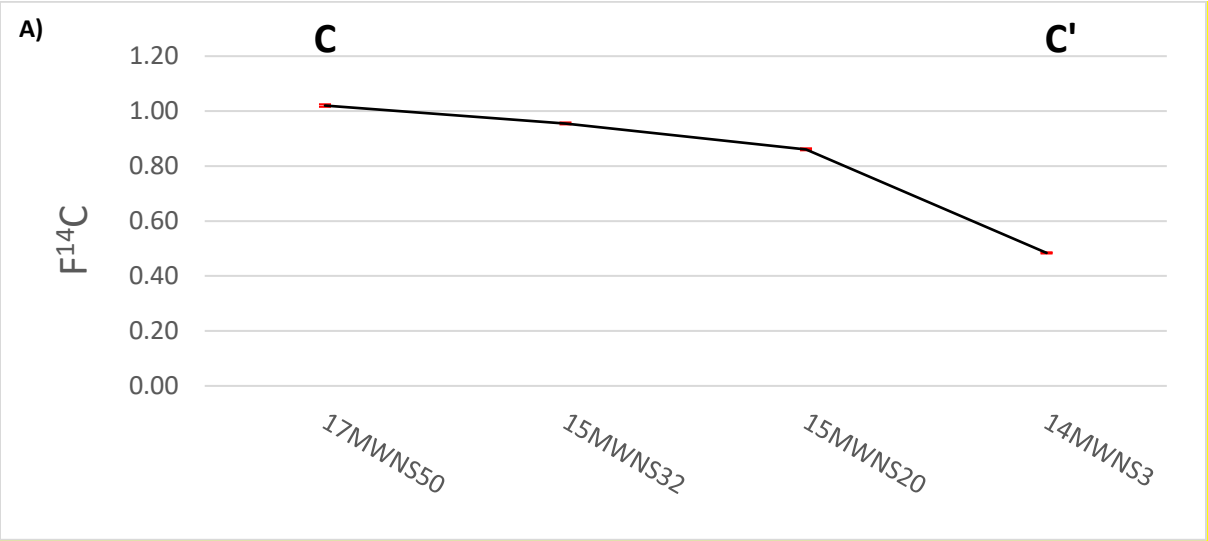

549380
549400
549420
549440
7495140
7495120
7495100
N
Driveway
15MWNS-33
15MWNS-39
B
15MWNS-32
14MWNS-11
15MWNS-31
14MWNS-12
15MWNS-37
17MWNS-51
15MWNS-19
15MWNS-34
15MWNS-18
15MWNS-41
14MWNS-8
16MWNS-42
15MWNS-35
17MWNS-50
15MWNS-20
17MWNS-58
15MWNS-21
A
15MWNS-36
16MWNS-43
17MWNS-57
14MWNS-14
14MWNS-9
14MWNS-3
15MWNS-17
A'
15MWNS-22
14MWNS-5
17MWNS-56
16MWNS-44
14MWNS-7
14MWNS-2
14MWNS-1
15MWNS-23
14MWNS-6
15MWNS-24
17BHNS61
B'
0
20
Meters
Legend
Monitoring Well
LEPH in SPW >500 ug/L
Current AST
Sampling cross section
Monitoring Well with LEPH >5,000 ug/L
Former AST

Figure 3.2 *Cross section of $F^{14}C$ obtained by graphitization collected by soil probe A) C-C' cross section $F^{14}C$ data B) Site map with corresponding cross sections*



B)

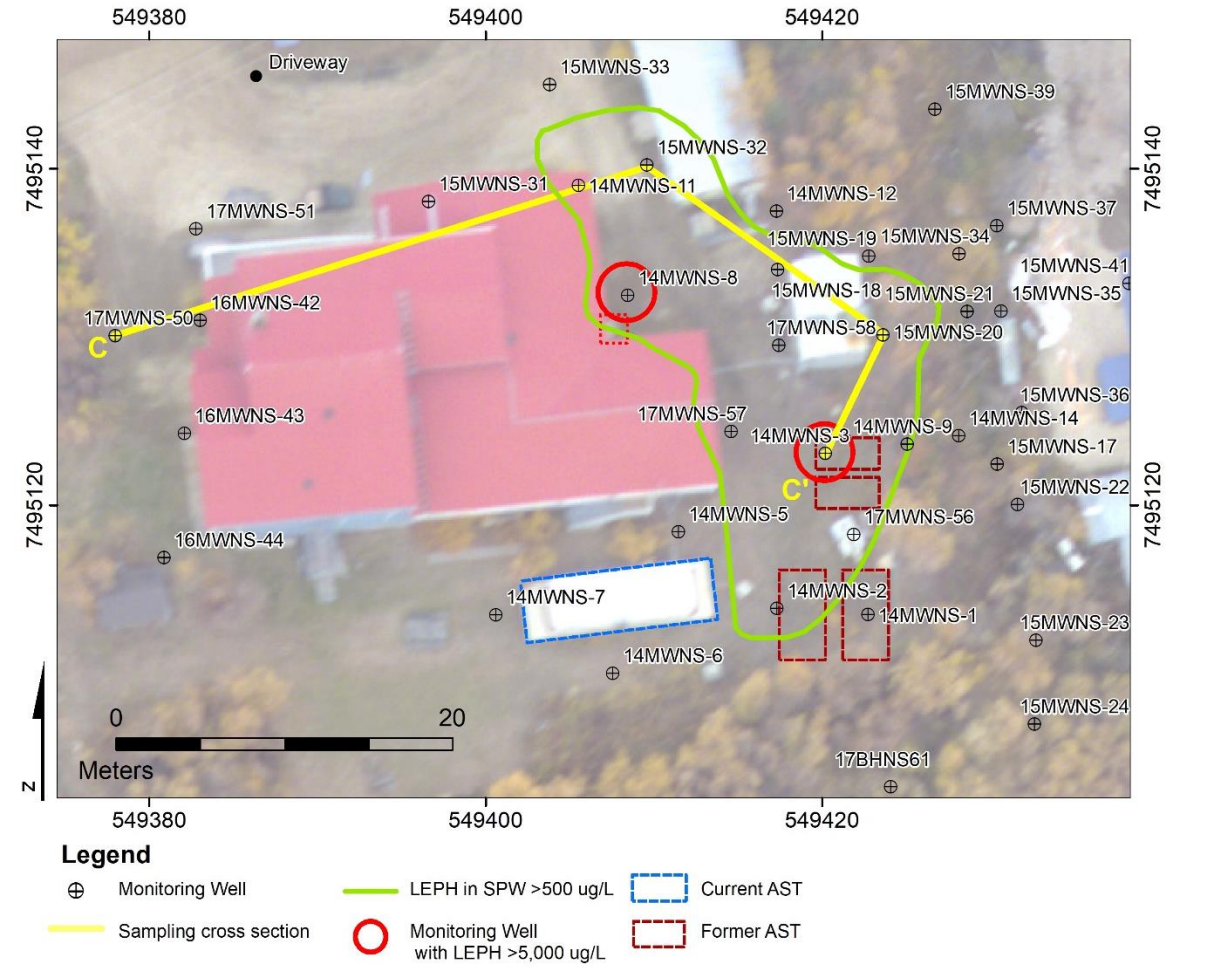


Figure 3.3 *Comparison of $F^{14}C$ values for $BaCO_3$ and graphitized samples collected by soil probe*

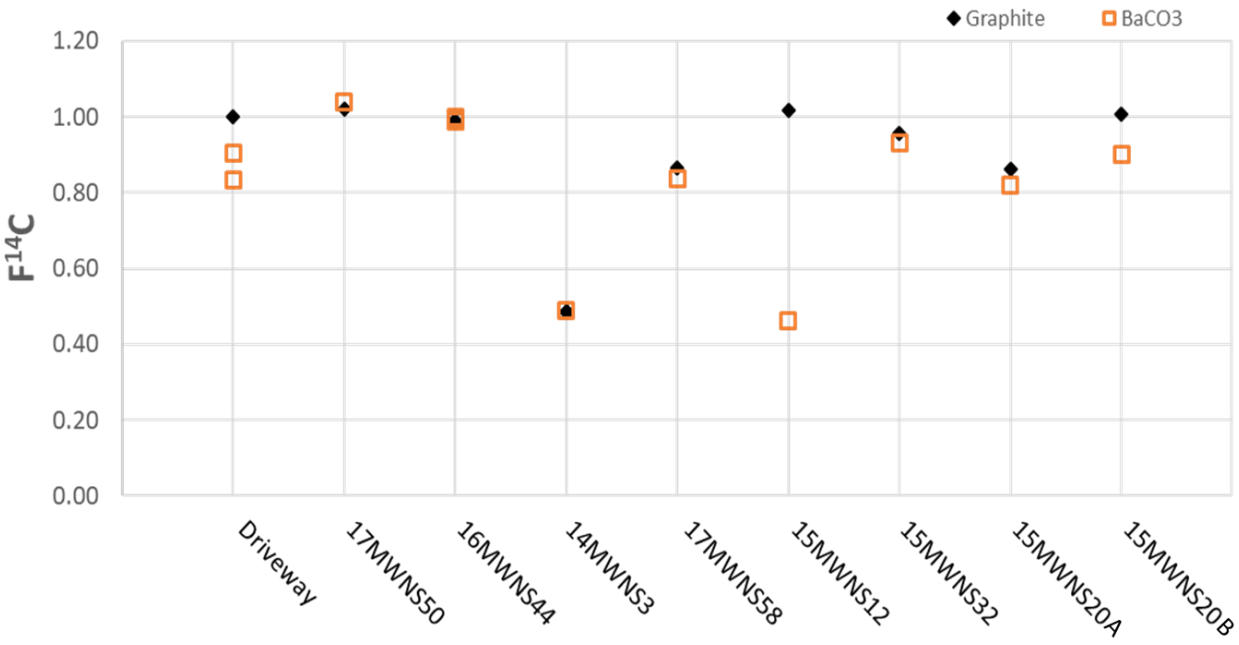
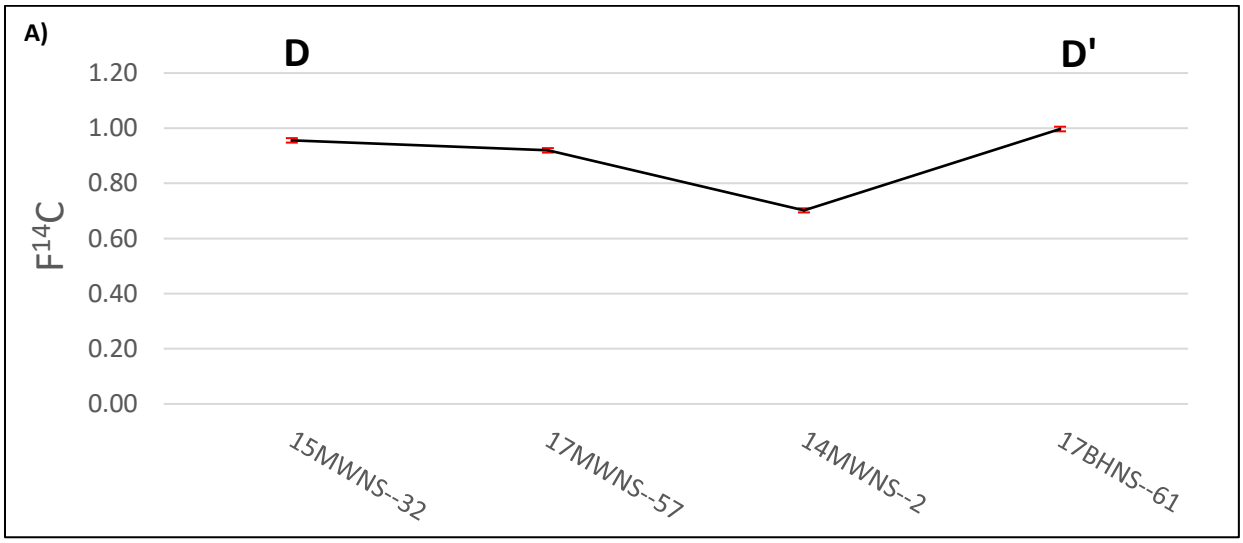


Figure 3.4 *Cross section of $F^{14}C$ obtained by $BaCO_3$ precipitation collected by static chamber A) D-D' cross section $F^{14}C$ data B) Site map with corresponding cross sections*



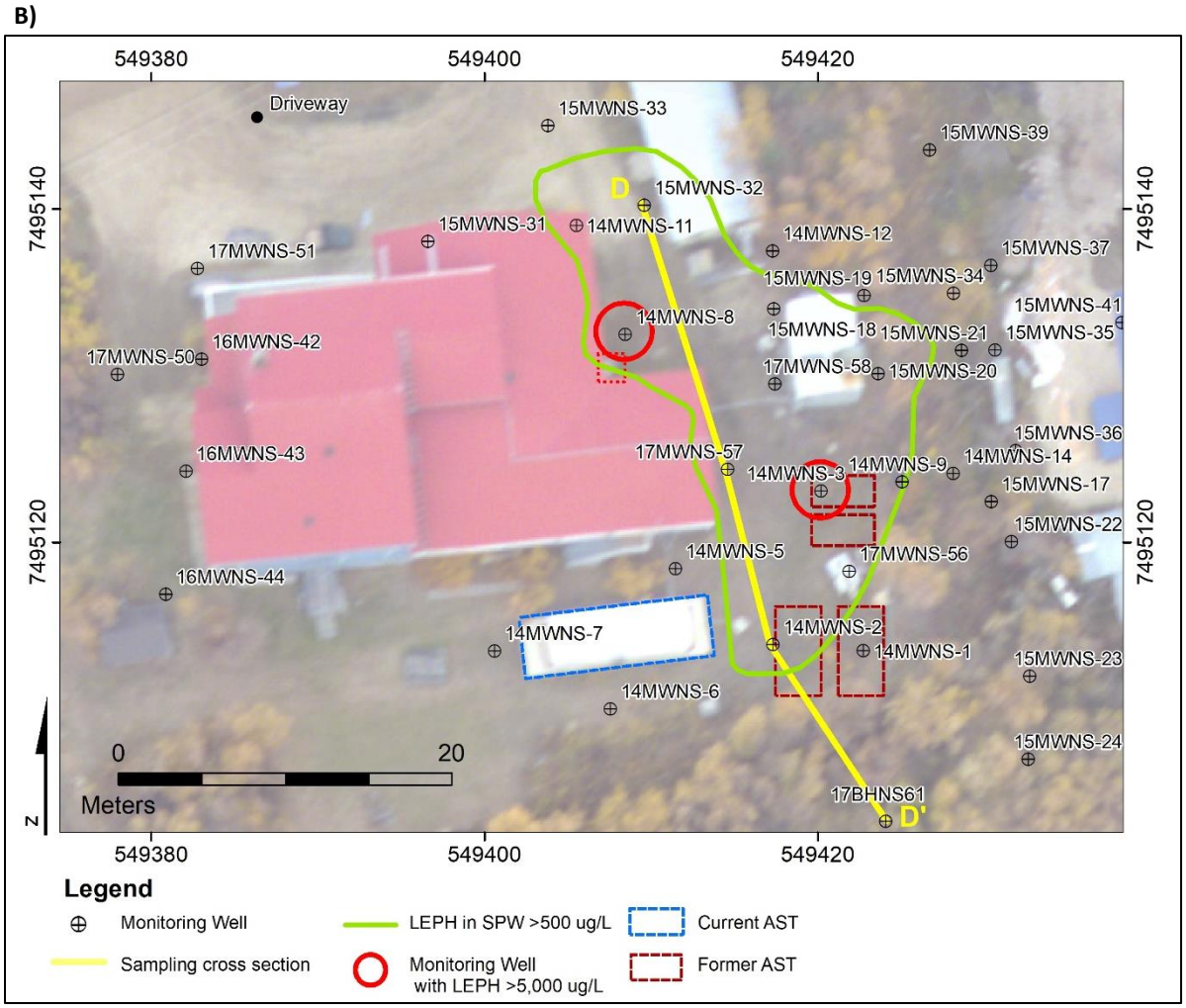
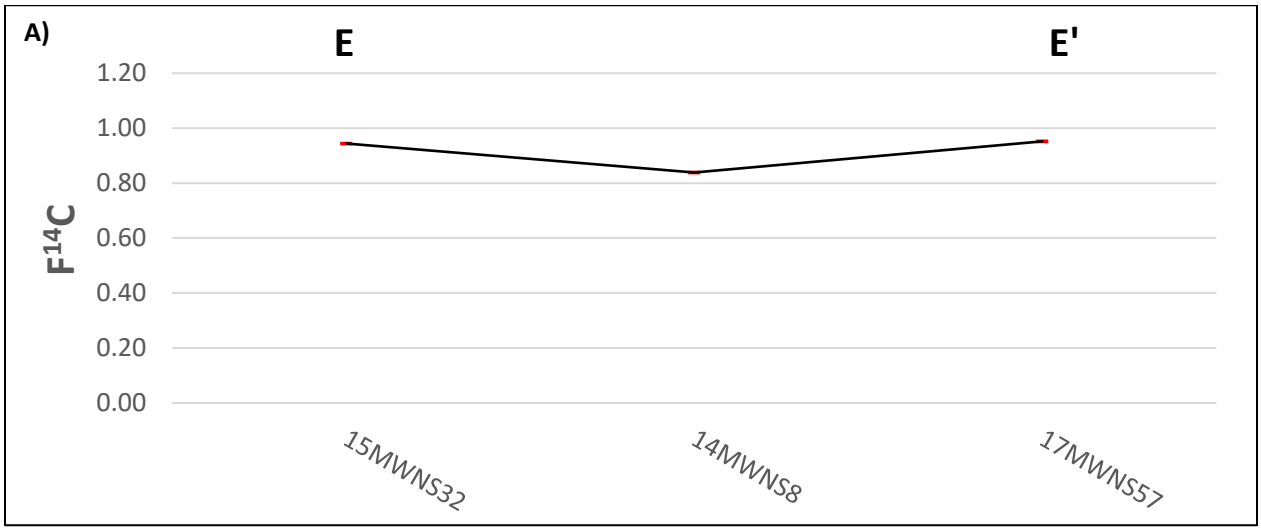


Figure 3.5 *Cross section of $F^{14}C$ obtained by graphitization collected by static chamber A) E-E' cross section $F^{14}C$ data B) Site map with corresponding cross sections*



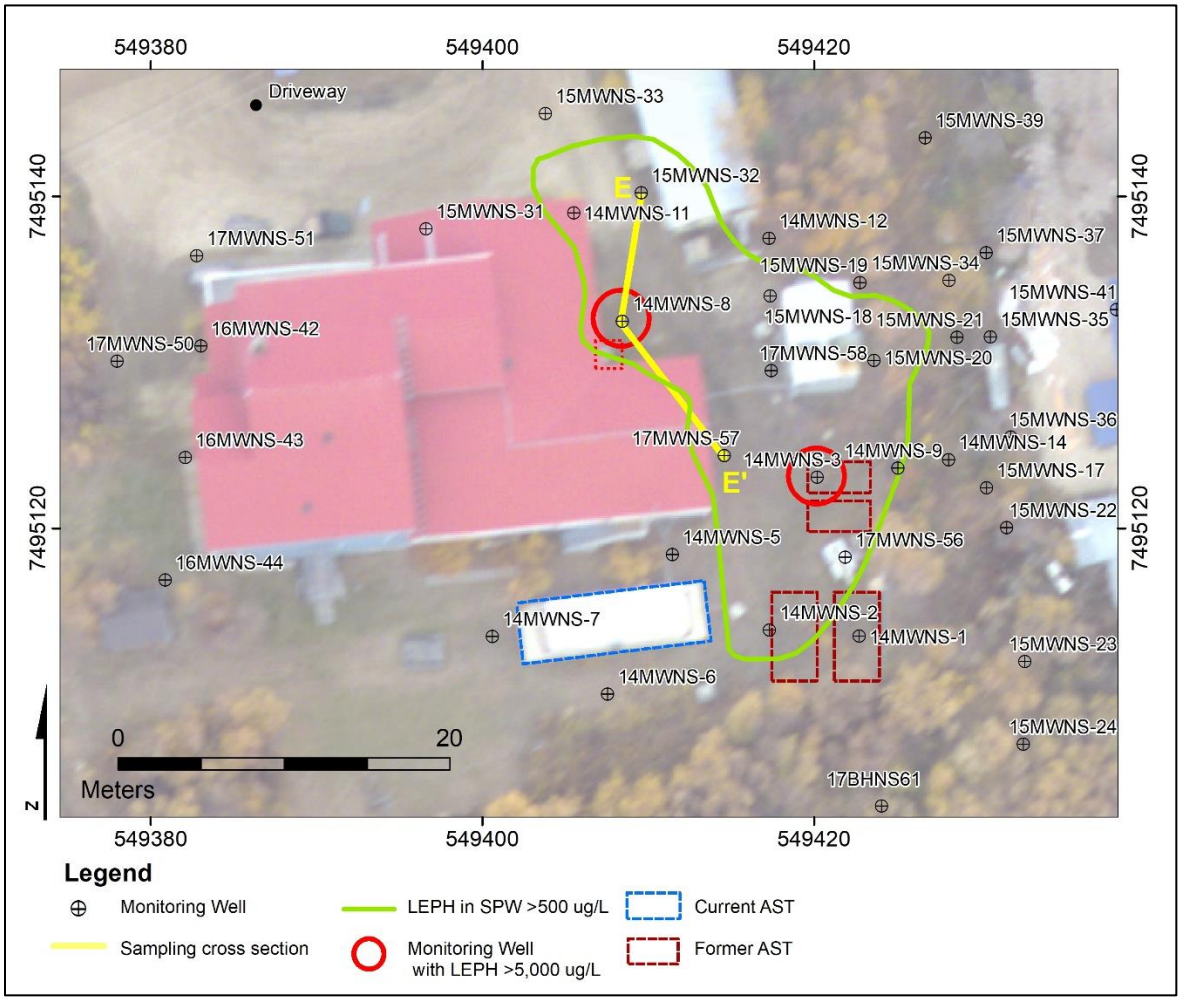


Figure 3.6 *Depiction of how sampling imparts vacuum conditions on static chamber sampling devices through multiple sample events*

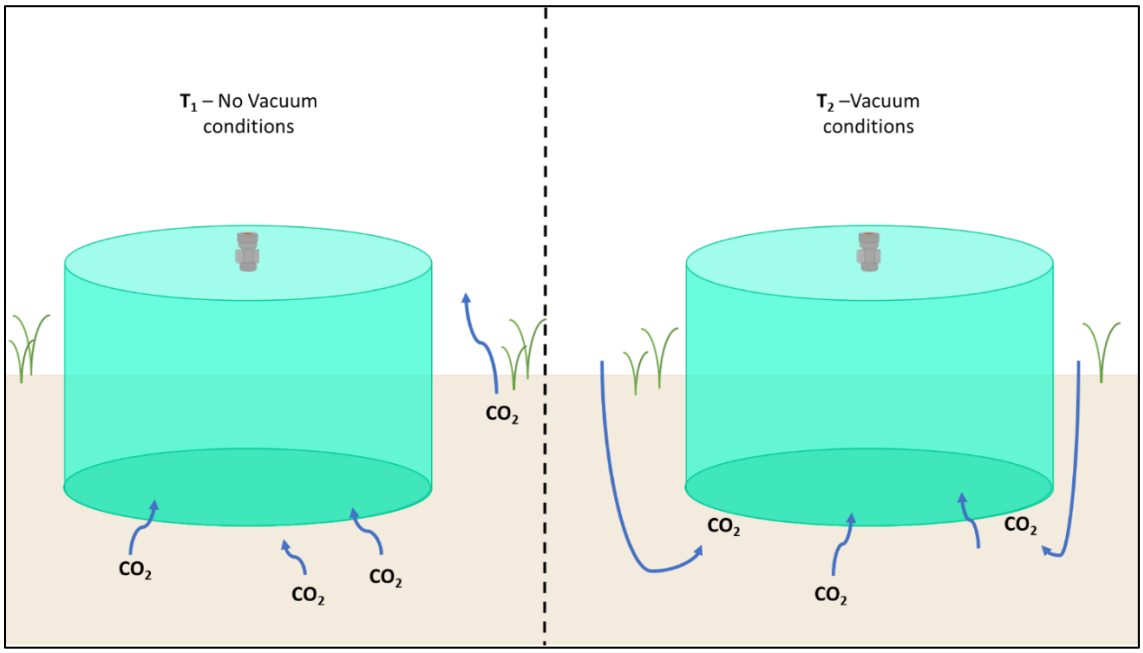
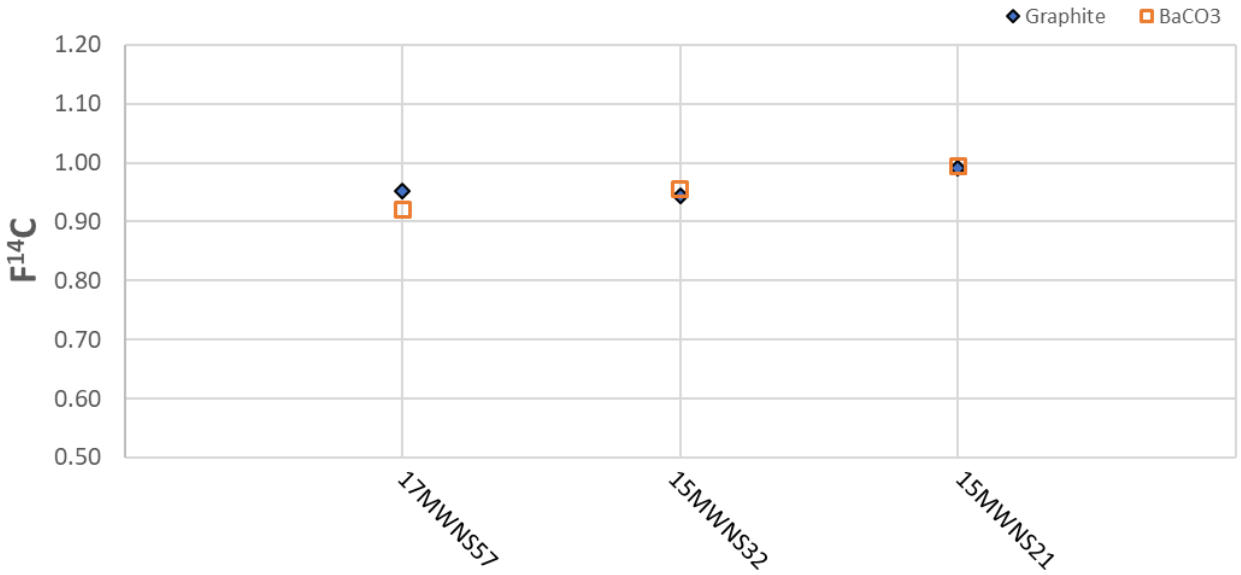


Figure 3.7 *Comparison of $F^{14}C$ values for $BaCO_3$ and graphitized samples collected by static +chamber (SC)*



Chapter 4 Determination of Background Organic Contributions to measured Soil CO_2 Radiocarbon Signature

4.1 Introduction

The proper apportionment of CO_2 in studies of PHC degradation is fundamental in accurate mass loss calculations. Corrections to measured soil efflux are made by understanding the true quantities of flux contributions from both modern soil respiration and PHC contaminant respiration sources. In temperate regions it has been shown that background measurements have produced $F^{14}C$ values as low as 0.926 (Sihota and Mayer 2012) and 0.978 (Wozney 2016). These values were obtained using below ground surface sampling techniques (0.5 m.b.g.s. in monitoring well and 0.3 m.b.g.s. soil probe, respectively) at the site of a pipeline rupture in Bemidji, MN. These studies show that in temperate regions there is a non-negligible component of CO_2 flux with a depleted signature. This depletion must be considered when correcting efflux representative of PHC mass loss.

Though rates are greatly reduced, research of soil microbial activity studies from Arctic regions have shown that organisms are capable of metabolizing organic matter in cold conditions (Clein and Schimel 1995). This knowledge, in addition to known abundance of organics in arctic soils, underlines the need for proper background corrections to be applied to soil efflux studies in Arctic regions (Flanagan and Bunnell 1980).

4.2 $F^{14}C$ Results of Background Site Sampling

4.2.1 Sample Collection Summary

Samples were collected from the western edge of the Old Crow Health Centre property near 17MWNS50 (Figure 2.6). The microcosm study presented here is the result of samples

collected in September 2017. Soil material was sampled during the drilling of 17MWNS50 and was collected out of a split spoon sampler (Figure 4.1a). The split spoon sampler was driven into the ground for sample collection before a drill stem auger was used to advance a borehole for the placement of monitoring well equipment (Figure 4.1b) A 30 cm soil probe was installed 6 days later proximal to the drill location and soil gas was collected as a $BaCO_3$ precipitate for AMS analysis.

Analytical data provided by Jacobs Engineering Ltd. pertaining to the 2017 sampling year showed that PHC compounds were either very close to or below the detectable limits of 20 µg/g indicating this location was a good fit for consideration of background parameters (Table 4.1). Presence of PHC compounds in analytical data were low, <100 µg/g, and in the $C_{19} – C_{32}$ range which likely corresponded to naturally-occurring carbon compounds, which can be misinterpreted as contaminant presence (Figure 4.3) (Wang et al. 2012).

4.2.2 $F^{14}C$ Results

Soil samples collected from the split spoon sampler were stored frozen until the commencement of benchtop microcosm studies. After 28 days of storage at ambient laboratory conditions, headspace gas was extracted and prepared as graphite for AMS analysis. Soil sampled at a depth of 0.76 – 1.83 m.b.g.s. had a $F^{14}C$ of 0.8730 ± 0.0022. Soil sampled at a depth of 1.37 – 1.98 m.b.g.s. had a $F^{14}C$ of 0.7322 ± 0.0019. Soil gas sampled at the background site with a 30 cm soil probe produced a $F^{14}C$ value of 1.040 ± 0.025. Results are complied in Table 4.2.

4.3 Discussion

The results of this benchtop microcosm study show that there is the potential for in situ soil microbial communities to metabolize naturally occurring sub-modern carbon sources at this site. However, this potential exists if the temperature at which microbial communities metabolize organic matter in sediment is increased. This was shown by depleted $F^{14}C$ values from soil gas generated in sealed iso jars at ambient laboratory conditions with a temperature of approximately 19°C. Soil gas collected at the site, with low temperature ground conditions (<4°C), and trapped as a $BaCO_3$ precipitate presented a modern signature for soil CO_2 efflux characteristic of background, nonimpacted ground conditions. This benchtop study shows that current climate site conditions minimize the metabolic decay of sub modern naturally occurring organics such that they do not contribute significantly to the efflux of CO2 from background soils which is dominated by the respiration of modern organics. Thus, the correction for background soil CO_2 efflux at this site can be made with a modern $F^{14}C$ signature.

Given the naturally depleted $F^{14}C$ signature in studies from temperate regions, and the modern signature attributed to soil gas efflux in a permafrost climate, it can be shown that site specific background corrections should continue to be considered in all soil $^{14}CO_2$ biodegradation efflux studies.

Chapter 4 Tables

Table 4.1 *Monitoring Well 17MWNS50 Soil Analytical Data as presented in Phase II Environmental Site Assessment by Jacobs Engineering Ltd. 2017*

Chemical	*Units*	**Yukon CSR Standards**	0.76 - 1.83 m.b.g.s.	1.37 - 1.98 m.b.g.s.
Benzene	µg/g	10	<0.02	<0.02
Toluene	µg/g	5	<0.05	<0.05
Ethylbenzene	µg/g	1	<0.05	<0.05
Xylene	µg/g	NS	<0.05	<0.05
Naphthalene	µg/g	5	<0.01	<0.01
Phenanthrene	µg/g	5	0.02	0.02
Pyrene	µg/g	10	<0.02	<0.02
EPH (C10 - C19)	µg/g	NS	26	<20
EPH (C19 - C32)	µg/g	NS	92	74
HEPH (C19 - C32)	µg/g	1000	92	74
LEPH (C10 - C19)	µg/g	1000	26	<20

Table 4.2 *$F^{14}C$ values for various background samples around monitoring well 17MWNS50*

Sample ID		Sample Depth	$F^{14}C$	±
RC12	Soil Probe	0.30 m	1.0395	0.0249
SGM-1	Microcosm	0.76 – 1.83 m	0.8730	0.0022
SGM-2	Microcosm	1.37 – 1.98 m	0.7322	0.0019

Figure 4.1 *Drilling equipment used in the installation of 17MWNS50. A) Split spoon sampler placed on table for observations and sample collection B) Drill stem auger used in monitoring well installation.*

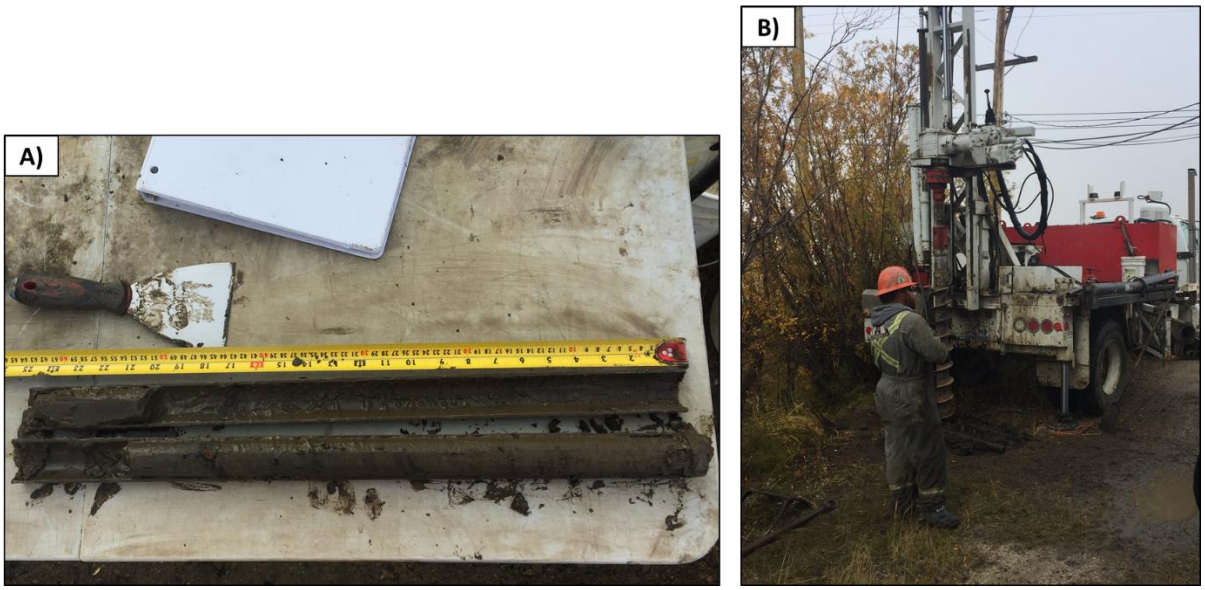
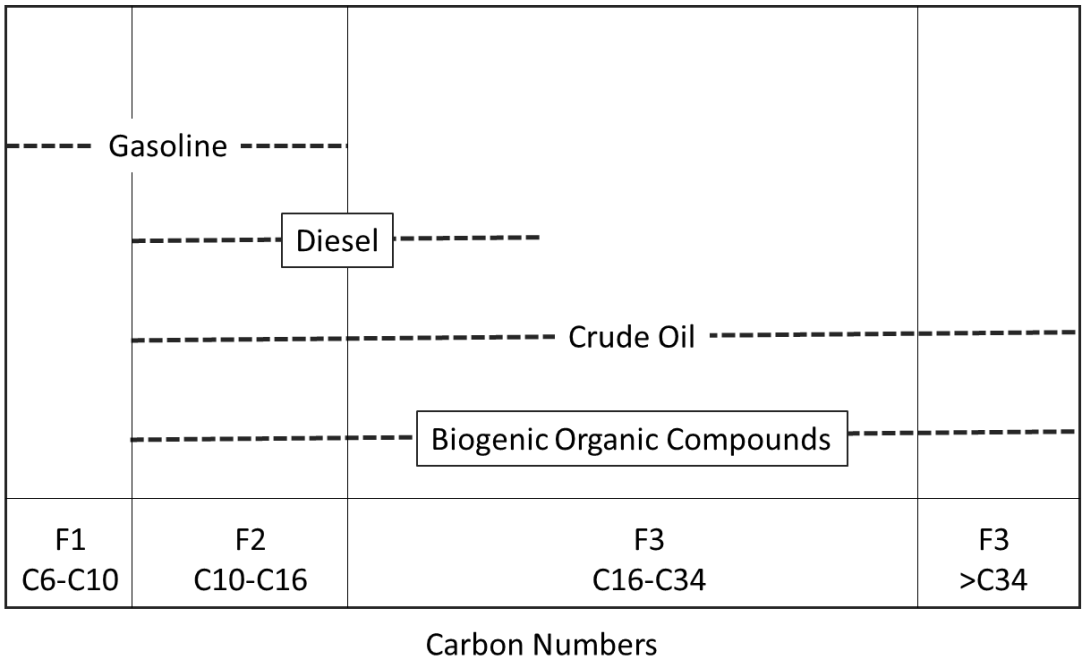


Figure 4.2 *Carbon number range overlap of natural biogenic organic compounds and PHC contaminants (Adapted from Kelly-Hooper 2015)*



Chapter 5 Summary and Conclusions

5.1 Summary

Radiocarbon isotopes are a useful tracer in the quantification of biological degradation rates of subsurface hydrocarbon contaminants. This isotopic tracer is particularly useful in applications which seek to quantify rates of mass loss in NSZD site monitoring and investigations. This study supports the findings of Sihota and Mayer (2012) and Wozney (2017). As this technique shifts into both regulatory and industrial realms, it is important to address issues of site-specific corrections, economics and logistics. The key products of this study are a novel technique in sample collection at a remote site and understanding that background corrections should continue to be applied based on site collected data.

5.1.1 Summary of $BaCO_3$ Collection Method

Samples collected from the study site as solid $BaCO_3$ precipitate showed highly comparable results with those obtained in the established mixed soil gas form. Samples showed variance in the associated $F^{14}C$ signature as collection moved from background areas in toward contaminated areas. This technique also allows quantifiable field-blanks to be obtained using standard radiocarbon laboratory materials. Sampling with the $BaCO_3$ precipitation technique minimizes sampling equipment and eliminates the need for shipment of glass gas-bottles, which simplifies and reduces expenses for the field work. Further, the BaCO3 greatly simplifies the AMS analysis of field samples, again reducing cost.

5.1.2 Summary of Soil Probe and Static Chamber Sampling Systems

While statistical analysis of variance between samples collected by either soil probe (SP) or static chamber (SC) showed no significant difference, logistical success in the study showed the soil probe was the superior sampling technique. Research by Wozney (2017) showed both the SC and SP methods were successful in pairing $F^{14}C$ and soil CO_2 efflux data in NSZD studies. However, this particular study found issues arising from the sampling tool. Issues stemmed from both chamber installation and data reproducibility. In areas with subsurface sediment heterogeneities, chambers could not be installed without significant ground disturbance to remove large stones. At a site where the subsurface conditions do not present these complications, the static chamber may still be a viable option. A secondary issue with the static chamber tool is the fact that more soil gas must be collected for one $Ba(CO)_3$ sample than one graphitized sample. When sampling duplicates in this study, accumulated air inside the static chamber would rapidly deplete imposing vacuum conditions within the chamber. These conditions led to the incursion of modern CO_2 from the surface into the chamber.

Soil probe sampling was conducted easily at the site and resulted in samples with reproducible values for $F^{14}C$. In situations where soil probe installation was problematic (creation of annular space) this issue was easily observed and the probe could be removed and replaced with minimal impacts to ground conditions.

5.1.3 Summary of Contributions of Background CO_2 Efflux to $F^{14}C$ Signatures

Sampling of soil efflux CO_2 from a background region of this study site showed a modern $F^{14}C$ signature. A concern in this study was given the cold climate and organic rich sediment, there may be a depleted $F^{14}C$ signature to soil CO_2 in this region not associated with hydrocarbon degradation. Further microcosm studies of material collected during site drilling showed that at laboratory temperature, respiration of older organics in the soil column does yield CO_2 with lower $F^{14}C$ which could potentially contribute to the background soil CO_2 efflux. However, the measured $F^{14}C$ of CO_2 efflux in background areas of this site provide no indication that such respiration of older organics contributes to background CO_2 under field conditions.

5.2 Conclusions

After comparison of $F^{14}C$ data obtained by samples collected as $BaCO_3$ or mixed soil gas for eventual graphitization, results show that the $BaCO_3$ technique is viable for use as a means to quantify subsurface hydrocarbon degradation with the use of radiocarbon as a tracer. $BaCO_3$ samples collected by soil probe for radiocarbon analysis of soil CO_2 were found to be representative of those collected by established SC methods and therefore could be used as a means to quantify subsurface hydrocarbon degradation in PHC impacted sites. This study showed that soil probe sample techniques allow for duplicate samples to be collected without imparting modern contamination.

Samples collected from the background areas of this study showed that in permafrost climates, under current environmental conditions, the assumption of soil CO_2 efflux from natural respiration processes has a modern $F^{14}C$ signature is valid. This study showed that the

$F^{14}C$ in CO2 efflux over the contaminant plume is variable, and underlines the importance of spatially-distributed sampling for background correction rather than a single correction for apportioning the efflux of CO2 for degradation of hydrocarbon in the subsurface. The study further showed that location and temporal corrections must continue to be made, considering the potential for the $F^{14}C$ of soil CO_2 to change to a depleted signature.

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