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MULTIPLE LINES OF EVIDENCE FOR ESTIMATING NSZD RATES OVERLYING A SHALLOW LNAPL SOURCE ZONE

ANNE WOZNEY AND DR IAN HERS

13 October 2021

AGENDA

I. Using NSZD as a metric for LNAPL management decisions

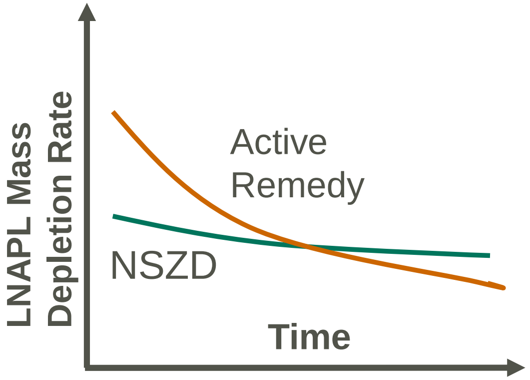
II. Methods for quantifying natural source zone depletion

III. Results and learning from a multi-year site investigation of vadose zone monitoring methods for estimating NSZD

Evaluation of LNAPL Management Strategies

EVALUATION OF ACTIVE AND PASSIVE MANAGEMENT

Compare Relative Performance of Technologies



- Active depletion rate < NSZD rate
- Important to conduct rebound tests

Hers et al 2009

Transition criteria:

1. Assessment of LNAPL source zone area stability (mobility)
2. Evaluation of Receptors and Environmental Impact Analysis
3. Decreased active remediation efficiency (recovery trends)
4. Comparison of active recovery rates to NSZD rates estimates
5. Long term monitoring costs and other impact metrics

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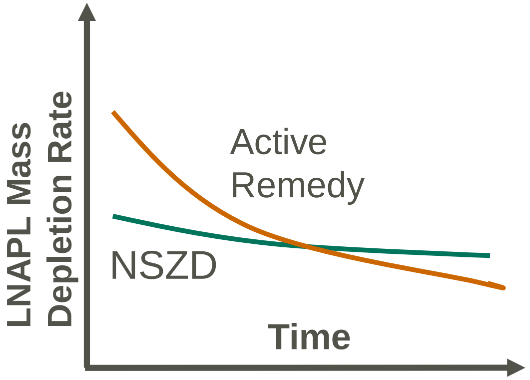

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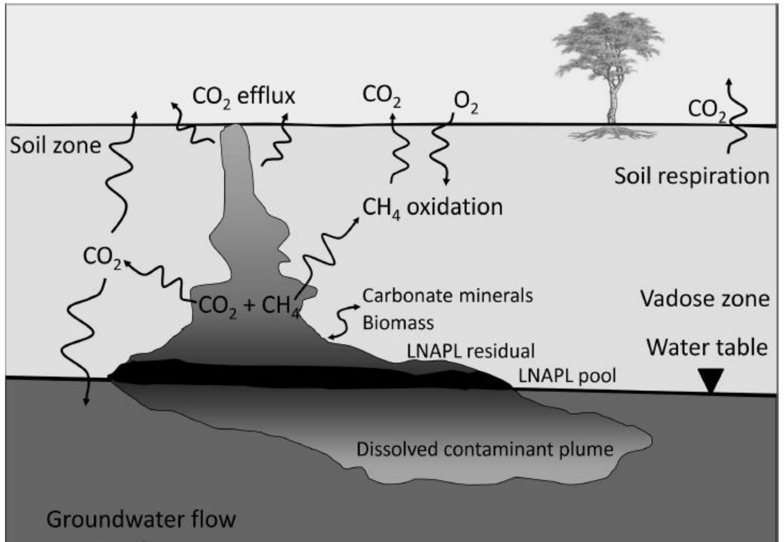
Objective:
1. How are NSZD rates measured?
2. Comparison of monitoring technologies being used to obtain rates
3. Assessment of annual variability
4. Development of standard procedure for NSZD evaluation

Vadose Zone monitoring methods

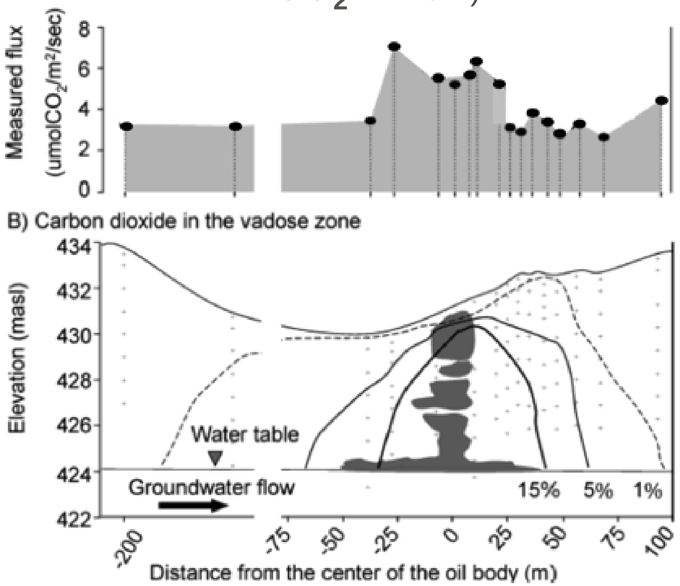
BIODEGRADATION OF HYDROCARBONS



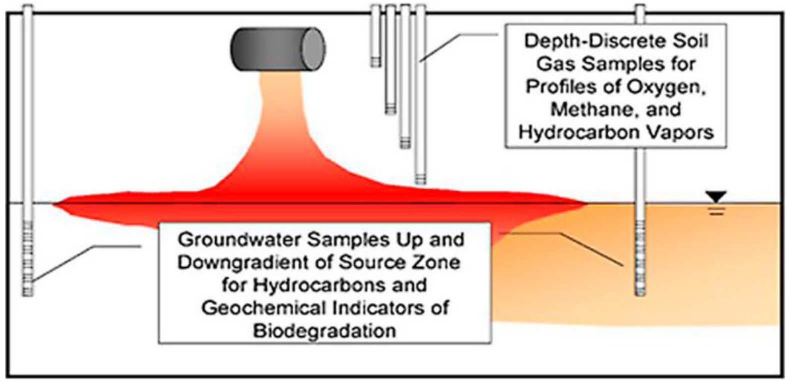
Sihota et al 2011

"PHC depletion studies focused solely on saturated zone processes estimate subsurface mass loss one to two orders of magnitude less than when unsaturated zone rates are quantified"(Garg et al. 2017).

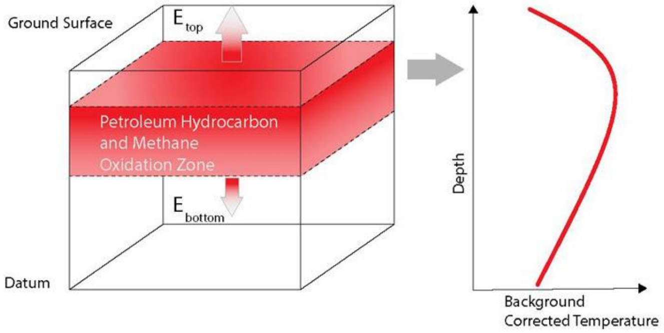
1. CO_2 Efflux)



2. Soil gas gradient



3. Thermal Gradient



ITRC, 2009

CO_2 Efflux Measurement Methods

LI-COR LI8100A

DISCRETE MEASUREMENT

- Dynamic flux chamber and infrared gas analyzer
- Soil collars (20 cm O.D.) installed 24 hr prior to measurement; collar installed 3-5 cm below ground surface
- Two-minute efflux (J_{TSR}) measurements (duplicate)
- Repeat measurements conducted at select locations to assess diurnal variability

E-FLUX

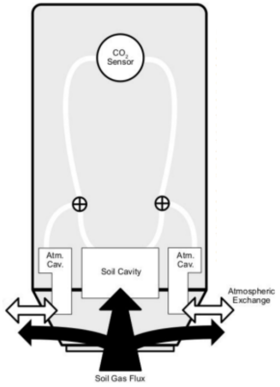
INTEGRATED MEASUREMENT

- E-FLUX Trap- sorbent Trap and infrared gas analyzer
- Time-integrated average flux measurements
- Soil traps (10 cm O.D.)
- Installed for 10 day period
- ^{14}C analysis to differentiate fossil fuel-generated CO_2 from modern CO_2 interference

EOSENSE(EOS_FD)

CONTINUOUS MEASUREMENT

- Forced Diffusion (FD) Chamber membrane-based chamber with non-dispersive infrared (NDIR) CO_2 gas sensor
- Installation of soil collars FD (7.6 cm O.D.) and FD-CH_4 (15.6 cm O.D)
- Measurements every 20 minutes for 9 month trial
- Intrinsically safe, solar powered



Radiocarbon correction (F_{CSR}) of CO_2 efflux (J_{TSR})

TO ESTIMATE FRACTION OF CONTAMINANT DERIVED EFFLUX (F_{CSR})

- Radiocarbon (^{14}C), which has half life of 5,730 years, is depleted in petroleum hydrocarbon (PHCs)
- Fraction of modern $F^{14}C$ ~ 1.02 to 1.05 in natural organic matter; $F^{14}C$ below detection in PHCs (Conrad et al 1999, Hua et al 2013)
- Fraction of Contaminant soil respiration (F_{CSR}) determined from $F^{14}C$-correction for of CO_2 efflux measurements (J_{TSR}) to determine contaminant flux (J_{CSR}) (Sihota and Mayer 2012, McCoy et al 2015)

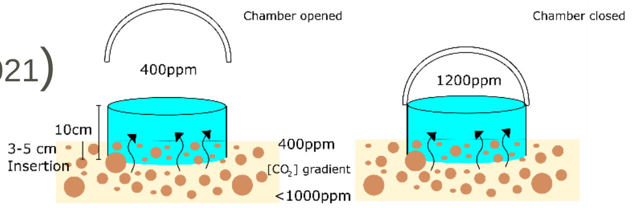
RADIOCARBON CORRECTION

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

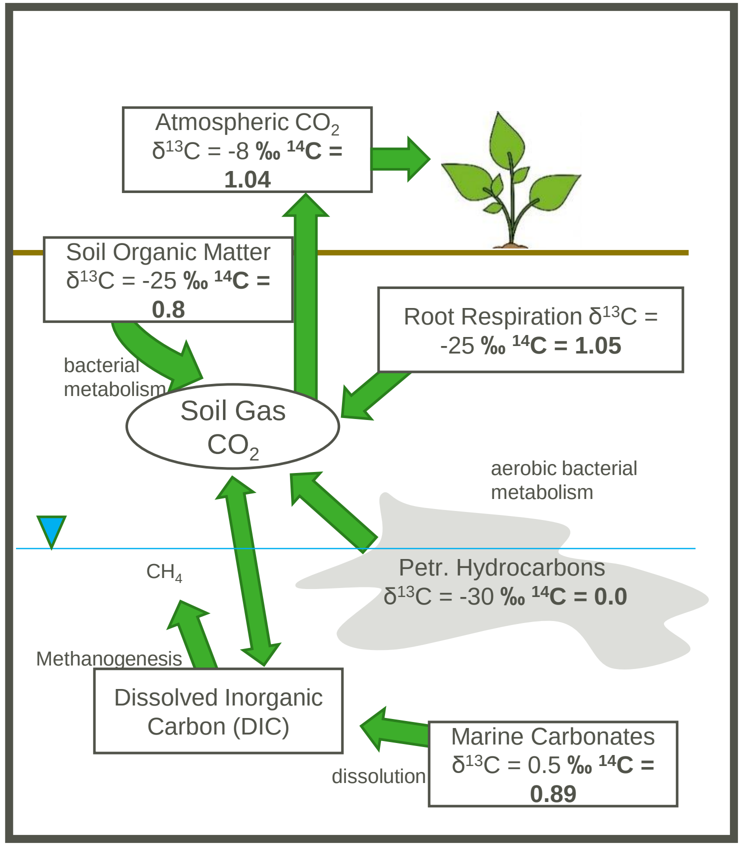
$F^{14}C$- correction

1) mass balance(LICOR/EOSENSE)(Wozney et al 2021)

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



2) or $F^{14}C$ sample obtained from lower sorbent (EFLUX) (McCoy et al 2015)



Modified from Conrad et al 1999

Soil gas gradient

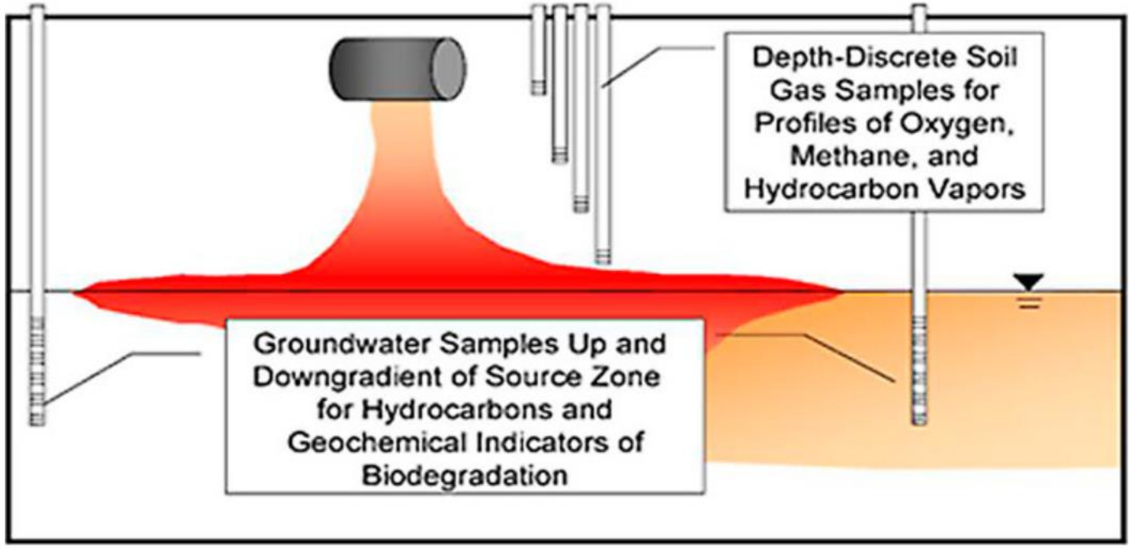
OXYGEN CONCENTRATION GRADIENT METHOD

$$J_{CGM} = D_{eff}\left(\frac{C_s - C_a}{\Delta z}\right)$$

Johnson et al 2006

$$D_{eff} = D_O \cdot \frac{\theta_a^{\frac{10}{3}}}{\phi^2} + \frac{D_w}{KH} \cdot \frac{\theta_w^{\frac{10}{3}}}{\phi^2}$$

Millington and Quirk 1961



ITRC, 2009

Converting gas flux to Natural Source Zone Depletion Rate

DECANE EQUIVALENT

$$J_{NSZD} = J_{CSR} \frac{M_w S \quad U}{\rho_o}$$

Aerobic Respiration

$C_{10}H_{22} + 15.5\ O_2 \rightarrow 10\ CO_2 + 11\ H_20$

ITRC 2009

J_{NSZD} – NSZD rate (US gal/acre/yr)

J_{CSR} – Contaminant flux rate (umol/m2/s)

M_w – molecular weight of hydrocarbon (e.g., 142 g/mol for decane equivalent),

S – stoichiometric ratio of mole of hydrocarbon degraded per mole either mole of oxygen consumed or carbon dioxide produced (e.g., 0.1 for CO_2 produced per decane equivalent)

ρ – the density of LNAPL (kg/L)

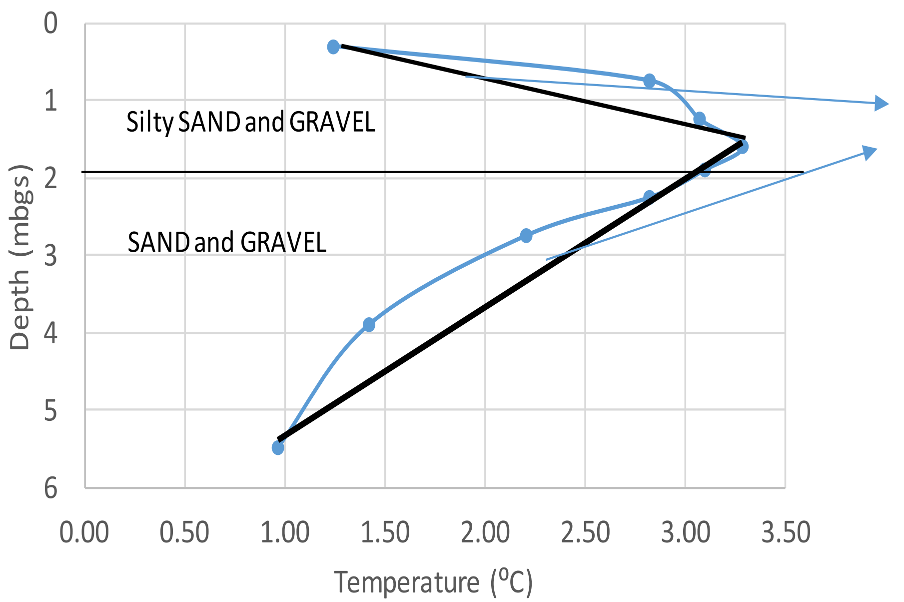
U – is the unit conversion factor $(3600 \times 24 \times 365\ s/year) \times (10^{-9}\ \mu g/kg) \times \frac{\left(4047 \frac{m^2}{acre}\right)}{\left(3.785 \frac{L}{gallon}\right)}$.

Temperature Monitoring Data

BACKGROUND CORRECTED THERMAL GRADIENT

Average Temperature above Contamination - Background

Field Data July: Avgerage Temperature - background



Sweeney and Ririe (2014)

$$Q_{NSZD} = Q_u + Q_l = -K_u \left|\frac{dT}{dz}\right|_u - K_l \left|\frac{dT}{dz}\right|_l$$

NSZD Rate = $Q_{NSZD}/\Delta H_{RXN}$ X UCF

- K Thermal conductivity of soil
- ΔH_{RXN} = 47680 J/g (Hers 2018 Battelle presentation) per Decane

$C_{10}H_{22} + 15.5\ O_2 \rightarrow 10\ CO_2 + 11\ H_20$

- UCF is the unit conversion factor equal to 3.893E+07 kg-s-L-m^2-US Gal/g-yr-kg-acre-L assuming a LNAPL density of 0.87 kg/L.

Multi Year Study - Site Overview

CONCEPTUAL SITE MODEL

Former refinery and distribution terminal

Petroleum hydrocarbon plume: weathered middle distillate with lesser amounts of lube oil

Shallow aquifer (2.7 - 4.7 m)

Apparent in-well LNAPL thickness 0.01 to 0.6 m

Soil stratigraphy:

- Silty Sand and Gravel (0 - 1.8 m) underlain by Sand and Gravel
- Shallow discontinuous Peat (0.1 - 1 m below ground surface (bgs))
- Deeper discontinuous Clay layer (2.4 - 3.7 m bgs)

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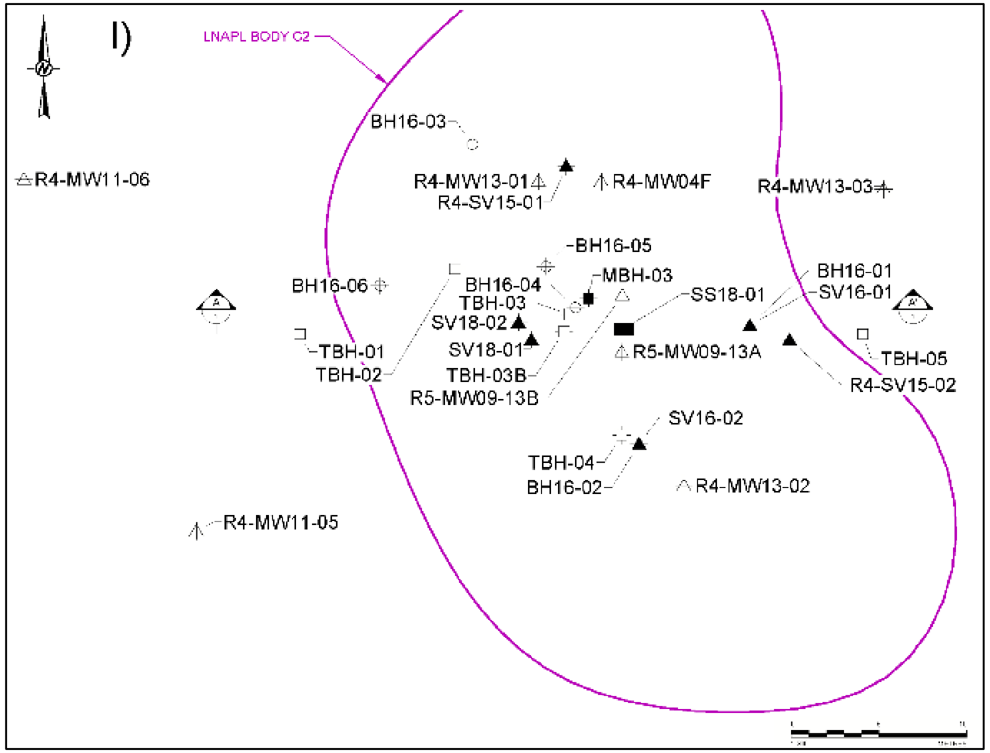
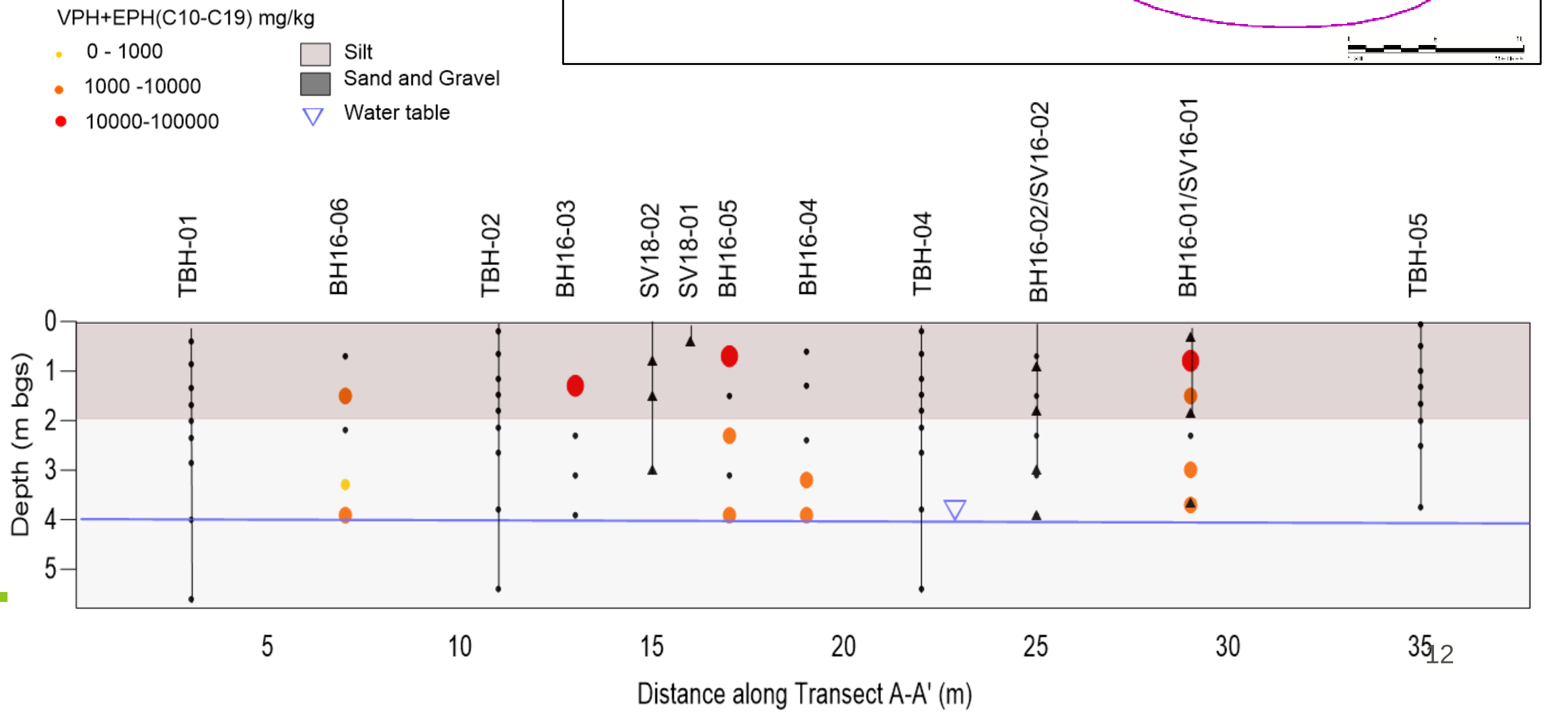
Multi-Year Study

BOREHOLE INVESTIGATION

- 2016 – Soil TPH concentration distribution:
  - (0.8 to 1.6 m bgs) - 3,990 to 102,800 mg/kg;
  - (2.3 to 2.4 m bgs) 3,000 to 3,900 mg/kg
  - Near water table (3.0 to 4.0 m bgs) 2,170 to 7,400 mg/kg

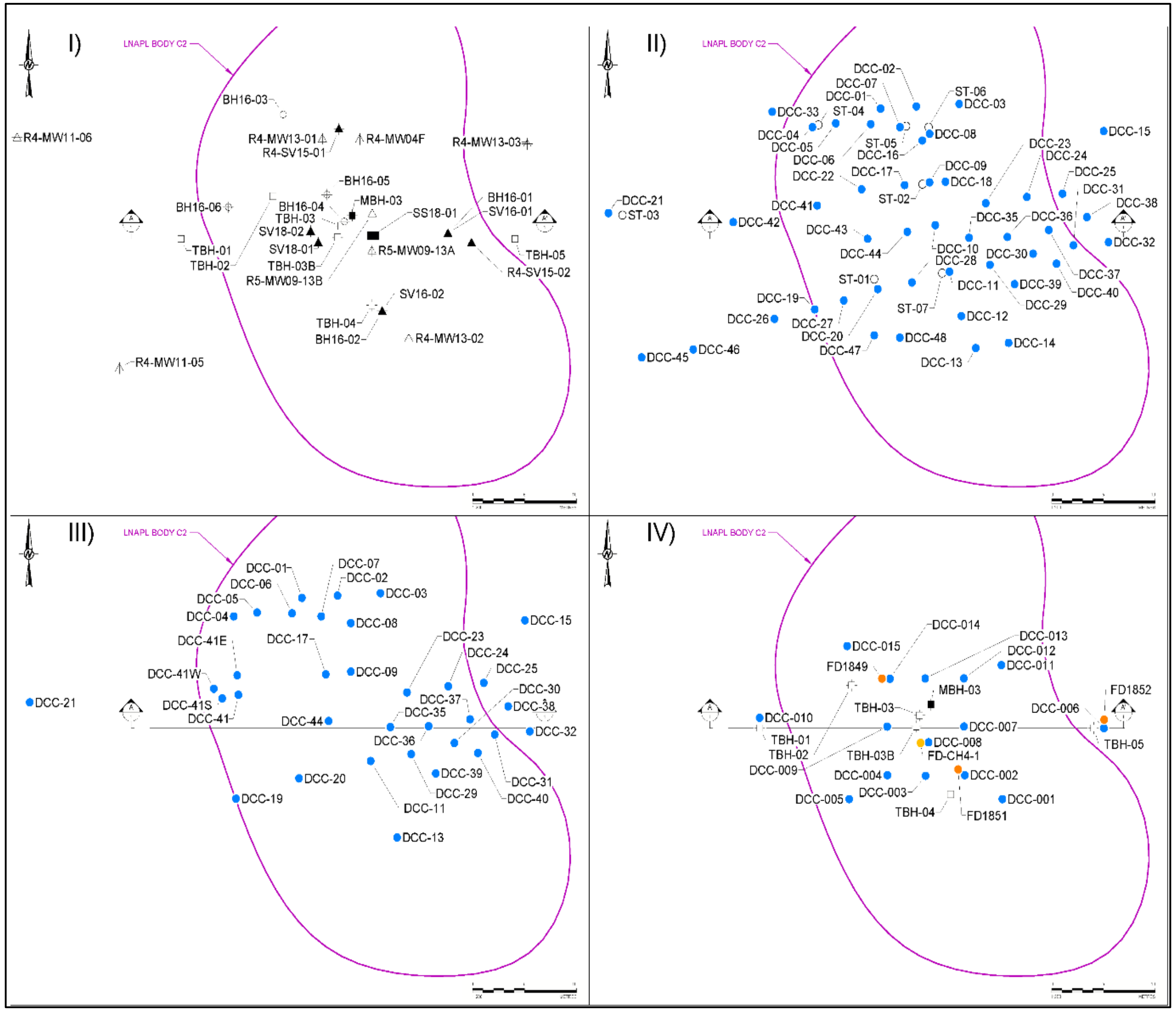




Multi-Year Study

2015- 2018

- Four Surveys overlying source zone area
  - 24 June – 1 July 2015 (46 locations, n = 220) – *LICOR* , E-FLUX
  - 12 − 24 October (24 location, n = 141) – *LICOR , soil gas gradient*
  - 25 − 26 July 2018 (15 locations, n = 77) *LICOR, EosFD, Thermal, soil gas gradient*
  - 3 − 5 October 2018 (15 locations, n = 56), *LICOR, EosFD, Thermal*



Multi-Year Study- Summer 2015

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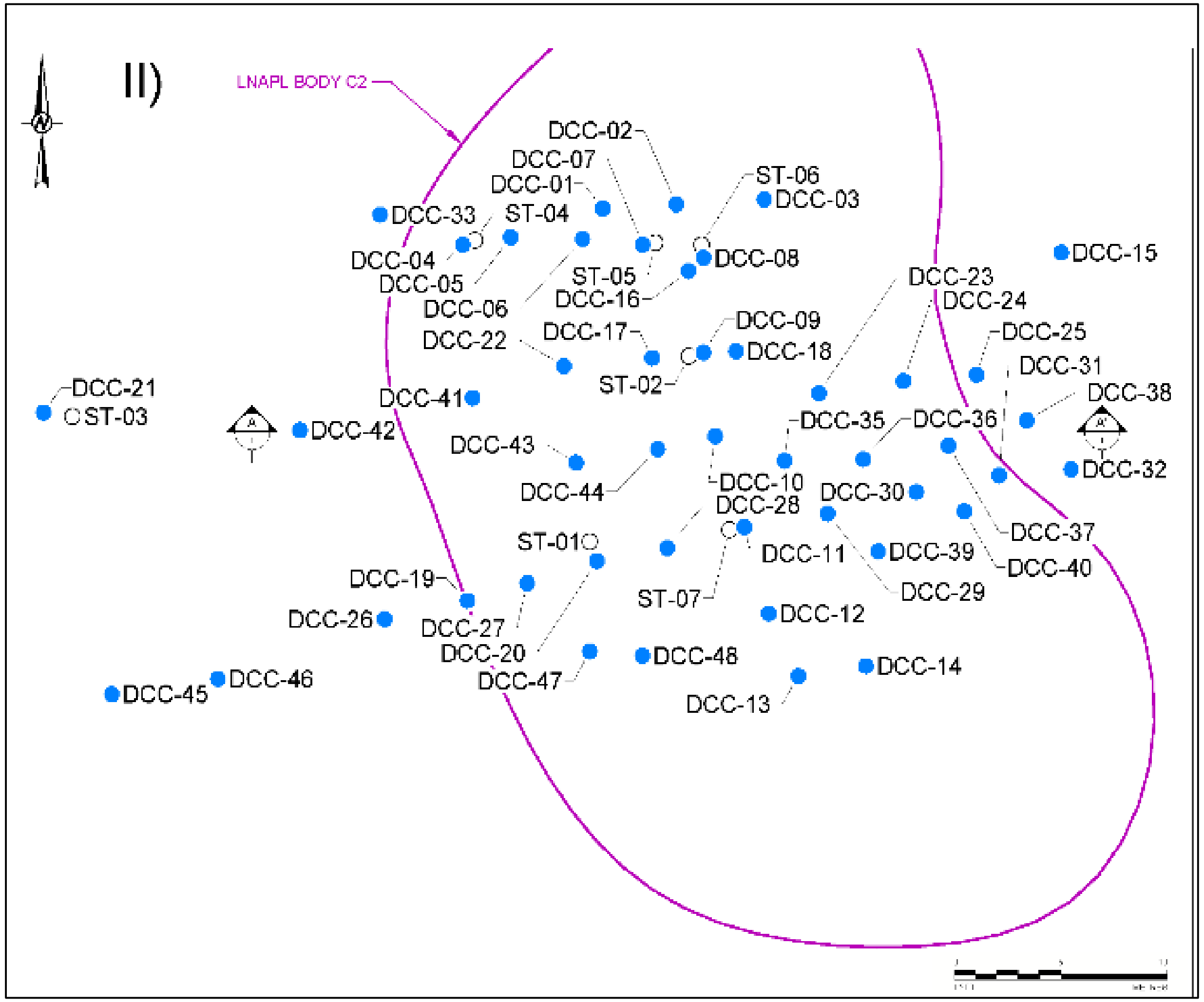

Multi-Year Study- Fall 2016

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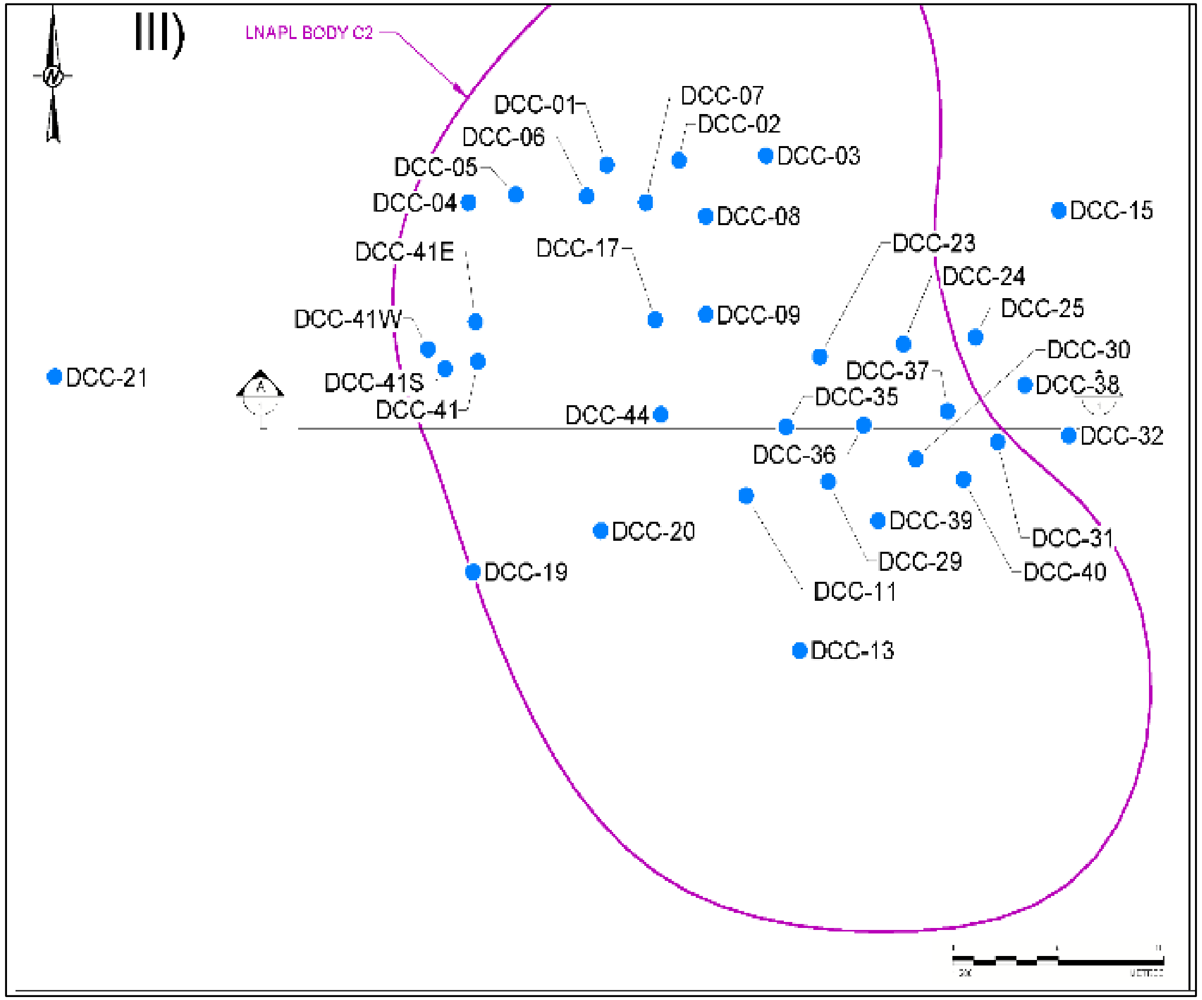

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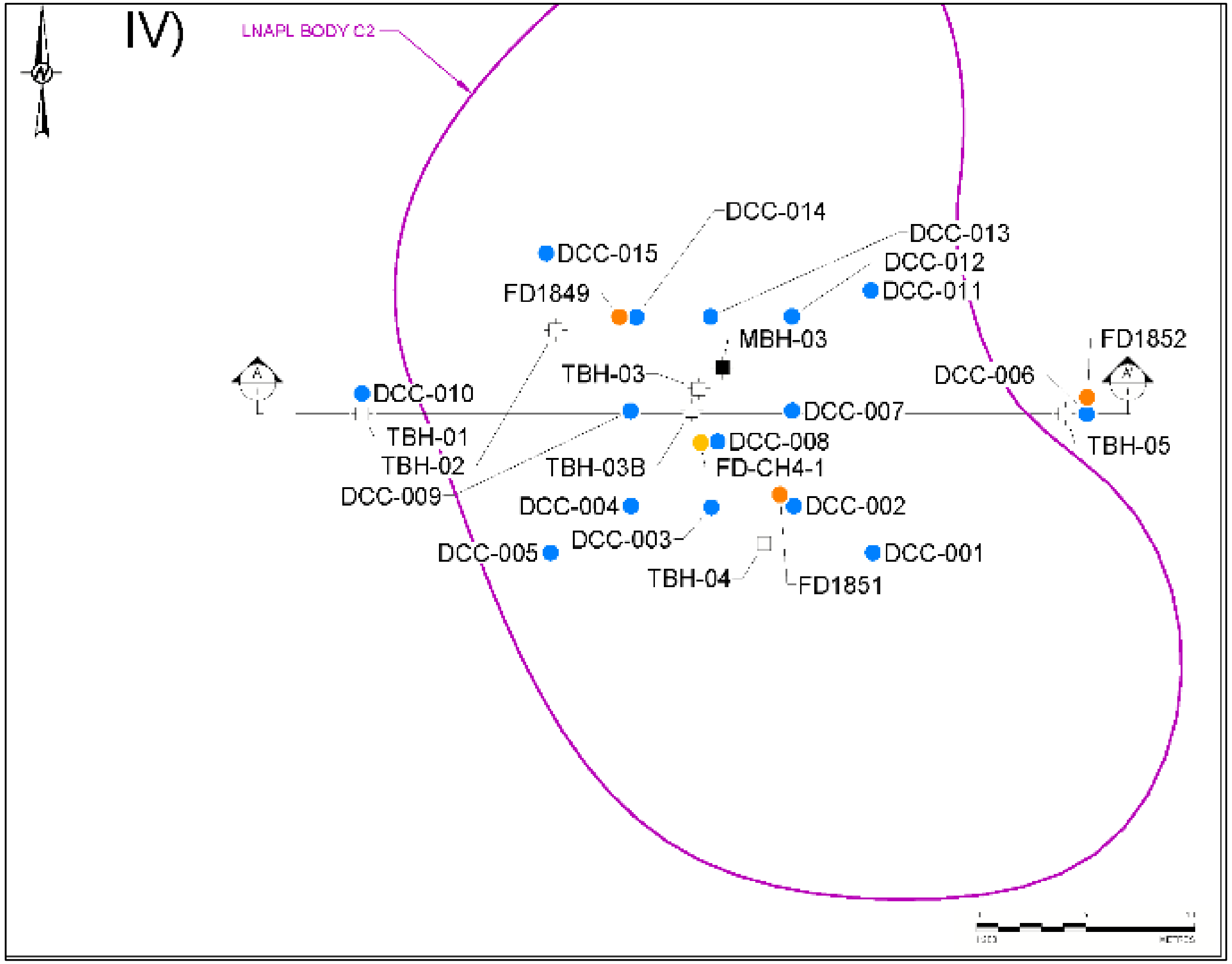

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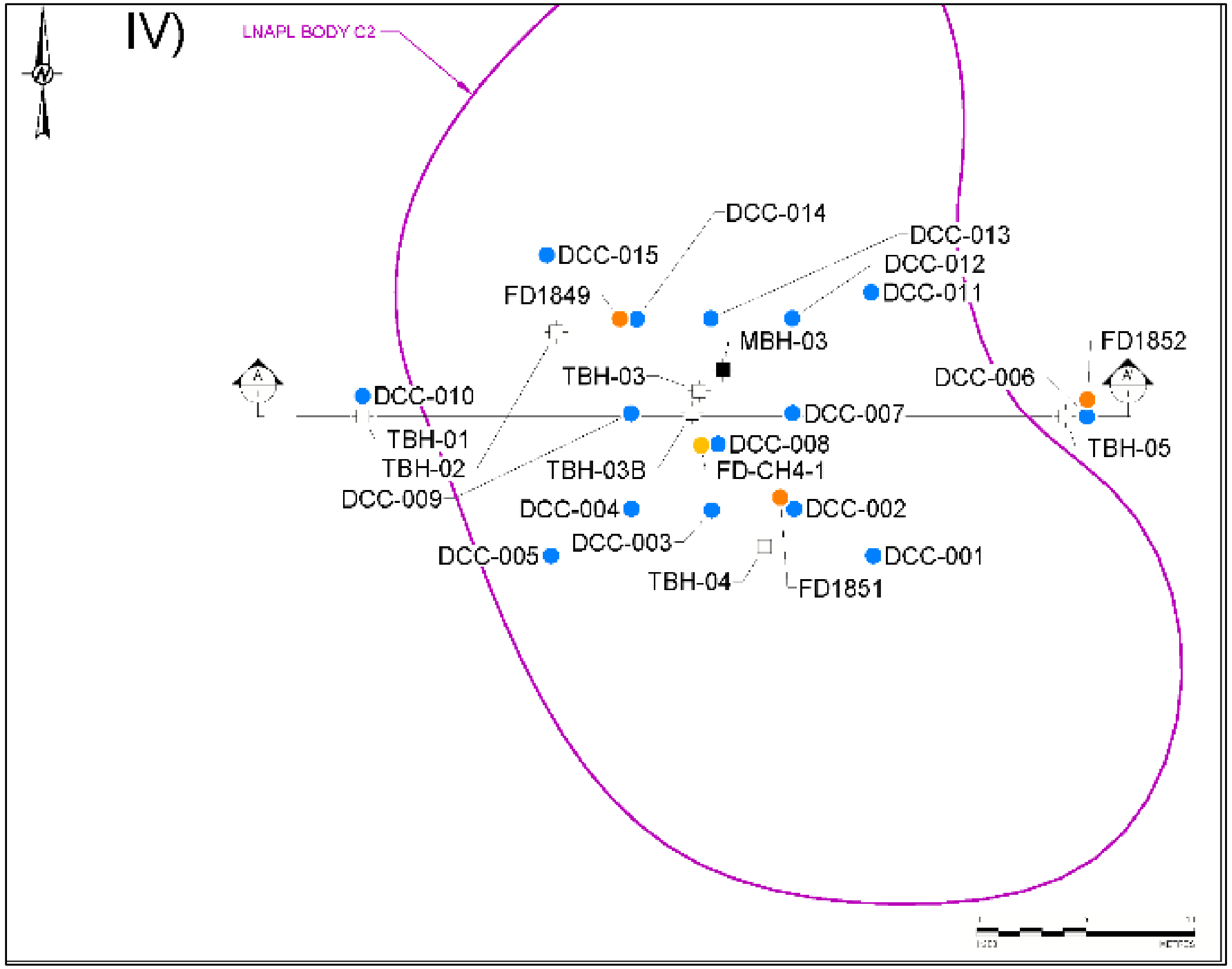
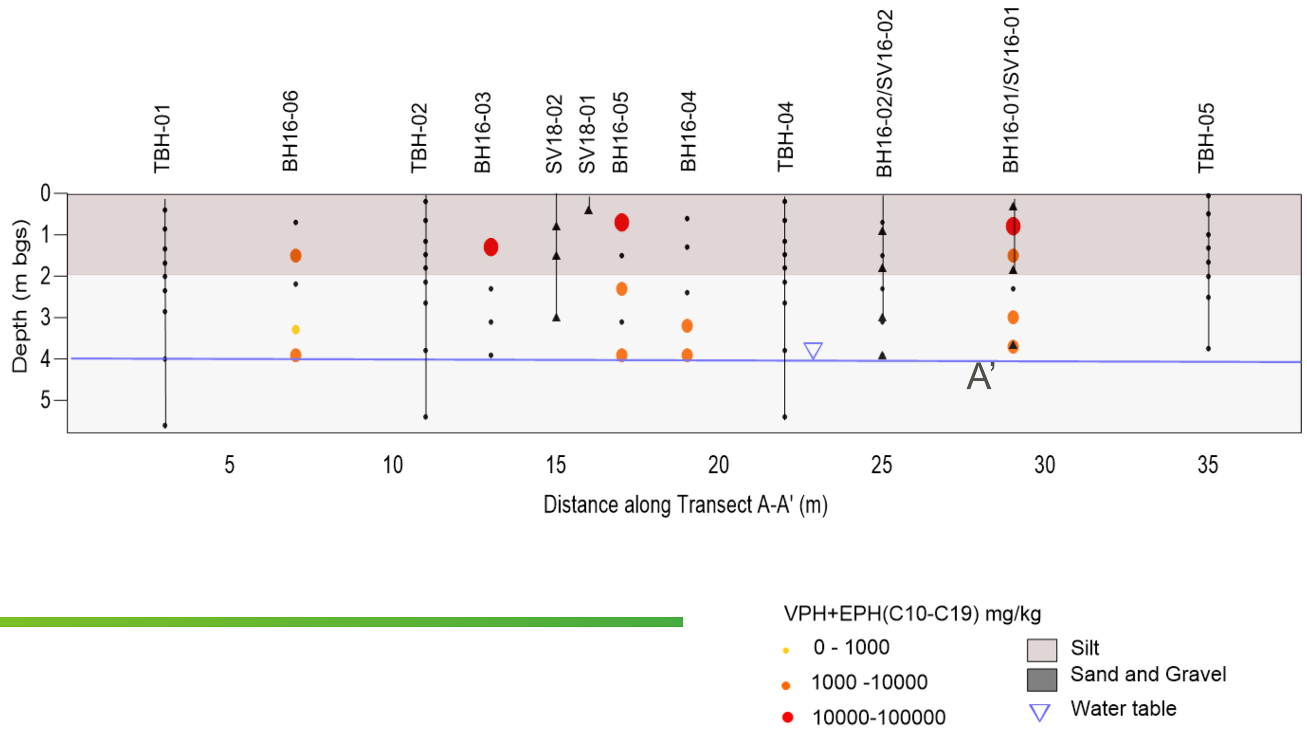


Multi –Year Study- Instrumentation

24 JULY 2018- 31 MARCH 2019

- Installation of 5 thermistor string (RST ThermArray digital sensors) w/ 9 ports installed (0.2– 5.6 m bgs) in June 2018
- Calibrated to −20 to 50 ˚C (resolution of 0.01 ˚C, accuracy of 0.07˚ C).
- Soil sampling of borehole for thermal properties (1.5 - 3.0 m bgs)
- Hourly measurements were conducted (Campbell Scientific) 23 July 2018 – 31 March 2019



Results – DISCRETE CO_2 Efflux Survey

LICOR- SEASONAL VARIABILITY

Season		Units	Summer	Fall	Summer	Fall
Measurement Date			24 Jun – 1 Jul 2015	12 – 24 Oct 2016	23 – 27 July 2018	3 – 5 Oct 2018
J_{TSR}	Mean (Min- Max)	µmol m^{-2} s^{-1}	3.8 (0.65−14.6)	1.4 (-0.7−24.9)	4.6 (1.2−7.8)	0.7 (0.2−1.9)
	Count	N	220	87	77	56
	Std Error	*± µmol m^{-2} s^{-1}*	*0.4*	*0.4*	*0.3*	*0.1*
f_{CSR}	Mean		0.36	0.25	0.49	0.27
	Count	N	3	6	3	3
NSZD Rate	Mean	US Gal/acre/yr	**760**	**25 − 190**	**1,250**	**100**
Rainfall 30-days Prior		(mm)	41-61*	131[2]	24.2[1]	236.5[1]
Temperature	Mean	Ambient Air (°C)	19.11	10.72	20.31	11.71
	Mean	Soil 0.05 m bgs[3] (°C)	-	-	25.64	10.80

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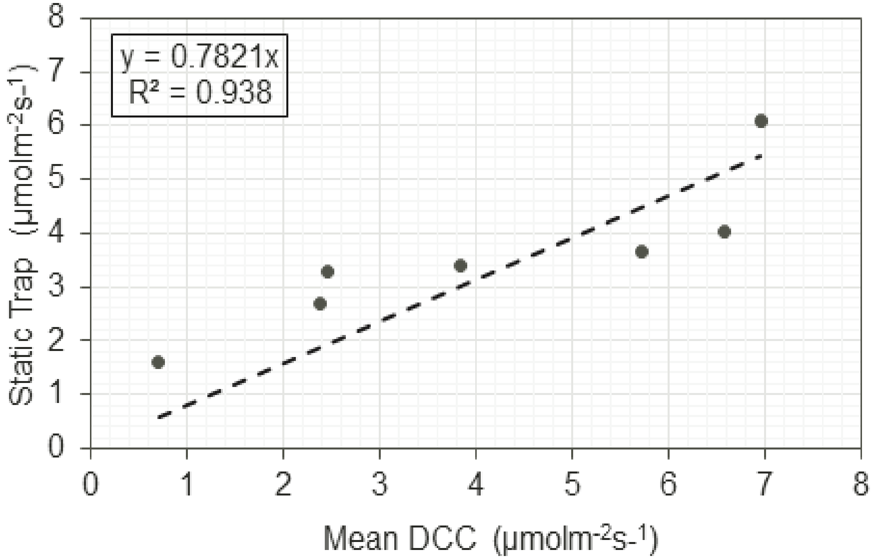
Method Comparison EFLUX vs LICOR

CO-LOCATED MEASUREMENTS DURING SUMMER 2015

Location	J_{TSR}	f_{CSR}	Standard Error	J_{CSR}	NSZD Rate
	μmol·m^{-2}s^{-1}	(as 1- F^{14}C)	± F^{14}C	μmol·m^{-2} s^{-1}	US gal/acre/yr
ST-01 *	1.62		0.0029	0.4	183
ST-02	3.67	0.26	0.0029	1.8	824
ST-03*	2.69	0.49	0.0032	0.6	275
ST-04	3.41	0.22	0.0035	1.1	504
ST-05	6.07	0.33	0.0035	3.9	1785
ST-06	4.02	0.64	0.0022	1.8	824
ST-07	3.28	0.45	0.0016	1.5	687
Mean	3.86	0.40	0.0028	1.8	817

*Background locations

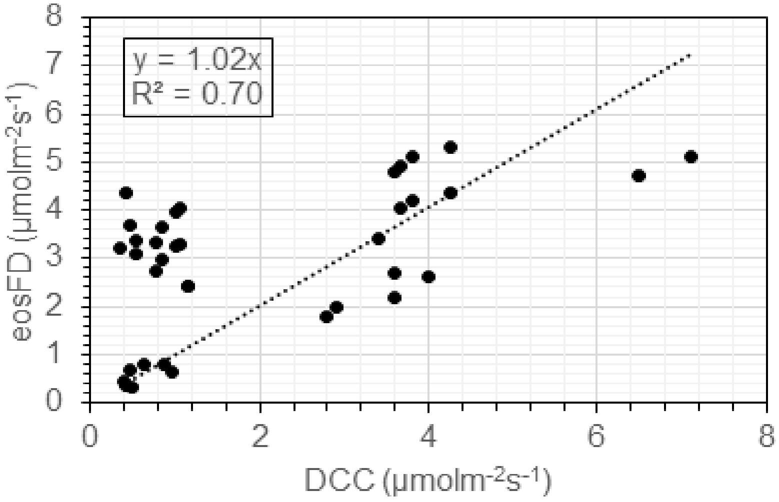


Method Comparison EOS-FD VS LICOR

CO-LOCATED MEASUREMENTS JULY 2018 – MARCH 2019

Month	Year	J_{TSR}	f_{CSR}		NSZD Rate
		Mean (Min – Max)	Mean (from DCC)[3]	Std Error	Mean
		μmol m^{-2} s^{-1}		±	US Gal/acre/yr
Jul[3]	2018	4.0 (2.5 −5.2)	0.49	0.81	1147
Aug[3]	2018	4.6 (2.0−7.0)	0.49	1.45	1319
Sep[4]	2018	2.5 (1.0−4.7)	0.27	1.11	427
Oct[4]	2018	1.6 (0.4 −2.4)	0.27	0.62	274
Nov[4]	2018	0.6 (0.3−1.0)	0.27	0.23	103
Dec[4]	2018	1.2 (1.1−1.4)	0.27	0.1	205
Jan[4]	2019	0.3 (0.3−0.4)	0.27	0.04	51
Feb[4]	2019	0.6 (0.2−1.0)	0.27	0.23	103
Mar[4]	2019	0.4 (0.1−0.6)	0.27	0.18	68

- Higher effluxes in summer resulted in better correlation (R^2 = 0.84)
- Low effluxes in Fall (<1 μmol m^{-2} s^{-1}) result in higher variability

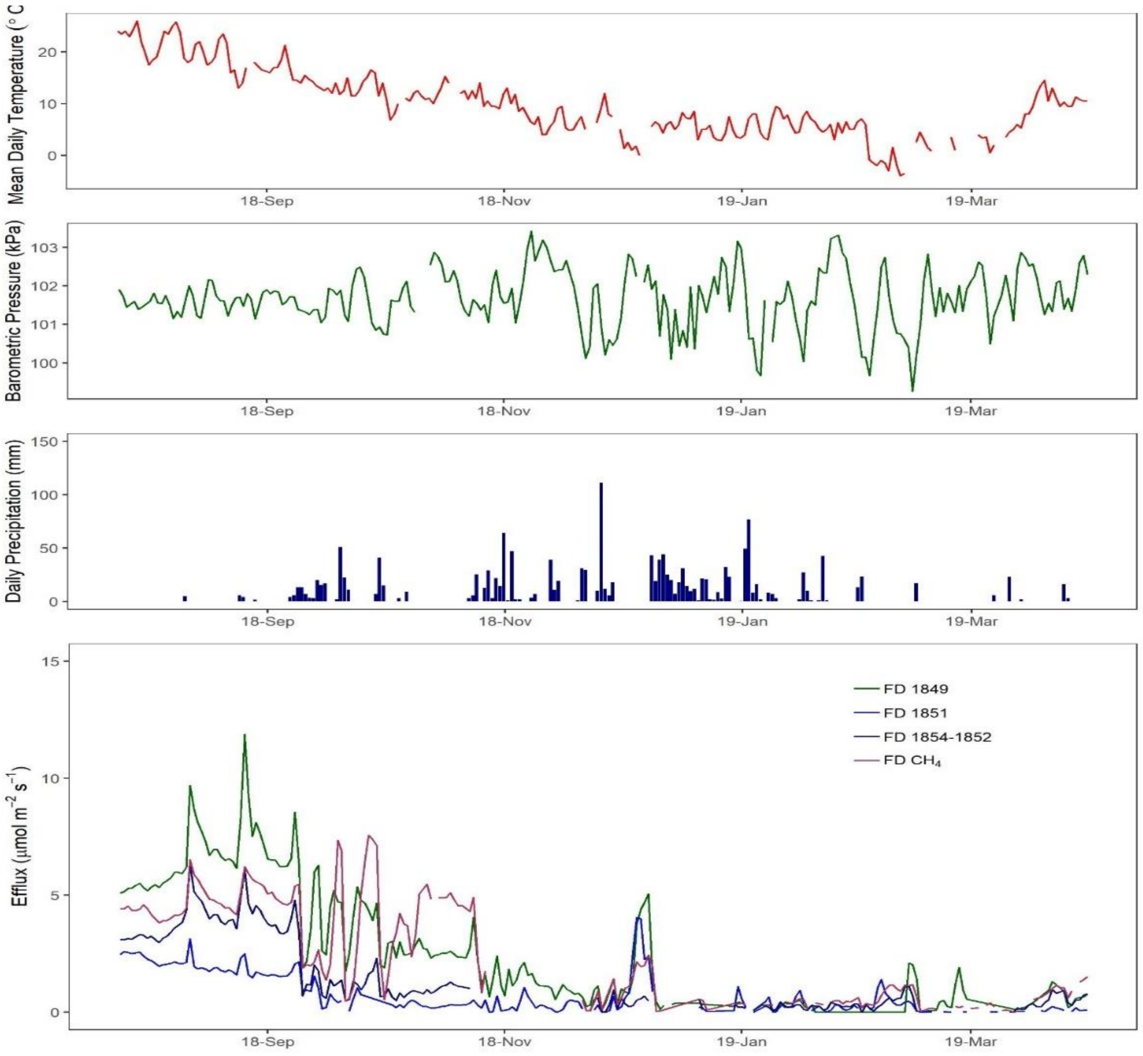


Wozney et al *In submission*

Results- Continuous CO_2 Efflux

EOSENSE- SEASONAL VARIABILITY

Month	NSZD Rate	Precipitation	Temperature	
	Mean	Cumulative Monthly	Mean	
	US Gal/acre/yr	mm	Ambient Air[1] (°C)	Soil[2] 0.05 m bgs (°C)
Jul 2018	1147	17	20.3	25.6
Aug 2018	1319	24	19.3	21.7
Sep 2018	427	14	14.6	15.8
Oct 2018	274	237	11.7	10.8
Nov 2018	103	414	7.7	7.6
Dec 2018	205	396	4.7	4.1
Jan 2019	51	268	5.9	3.8
Feb 2019	103	40	0.8	0.9
Mar 2019	68	50	8.1	4.2



Wozney et al *In submission*

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Soil gas gradient

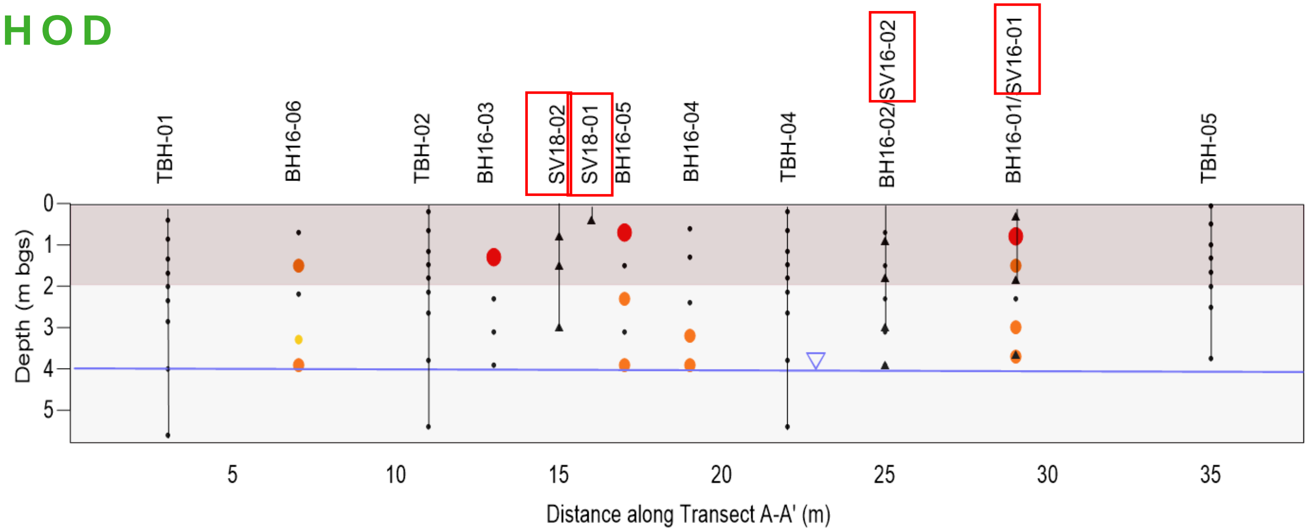
OXYGEN CONCENTRATION GRADIENT METHOD

$$J_{CGM} = D_{eff}\left(\frac{C_s - C_a}{\Delta z}\right)$$

Johnson et al 2006

$$D_{eff} = D_O \cdot \frac{\theta_a^{\frac{10}{3}}}{\phi^2} + \frac{D_w}{KH} \cdot \frac{\theta_w^{\frac{10}{3}}}{\phi^2}$$

Millington and Quirk 1961



Sampling Event		Soil Gas Monitoring Well	Δz[1]	ΔO_2 (%)	Porosity		Effective Diffusion Coefficient	f_{CSR} (O_2)[3]	NSZD Estimate[6] from O_2 Gradient	Sensitivity Analysis
			(m)	(%v/v)	Water-filled	Total	cm²/s		US gal/acre/yr	
Mid-range Estimates	16-Oct	BH16-01	0.5	1.7	0.38	0.5	1.4 E-02	0.34	120	8– 620
	18-Jul	SV18-01/02	1.5	3.3	0.175	0.47	6.0E-04	0.63	1,600	700– 3200

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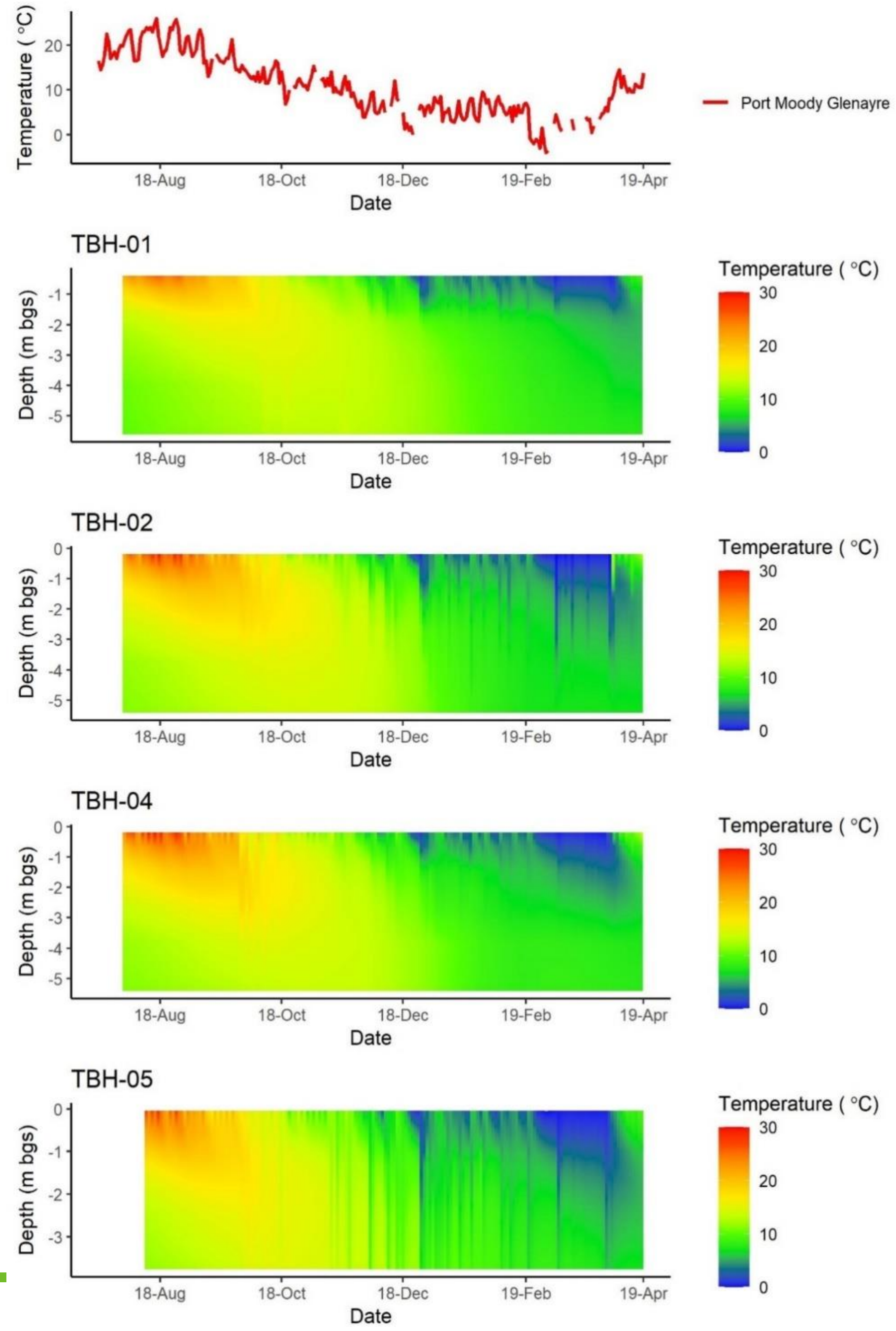
Thermal Monitoring

HOURLY DATASET

- 2 viable source zone data sets and 2 *background* data sets
- Soil physical properties
    - Moisture 4.7- 22% (1.7 to 4.5 mbgs)
- Soil thermal properties

Depth Range (m bgs)	Thermal Conductivity (K/mk)
0 – 1	0.95
1 – 2	1.05
2 – 3	1.35
3 – 3.5	1.6
3.5 – 4	1.9
> 4	2.5



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Thermal Monitoring

BACKGROUND CORRECTION

$$Q_{NSZD} = Q_u + Q_l = -K_u \left|\frac{dT}{dz}\right|_u - K_l \left|\frac{dT}{dz}\right|_l$$

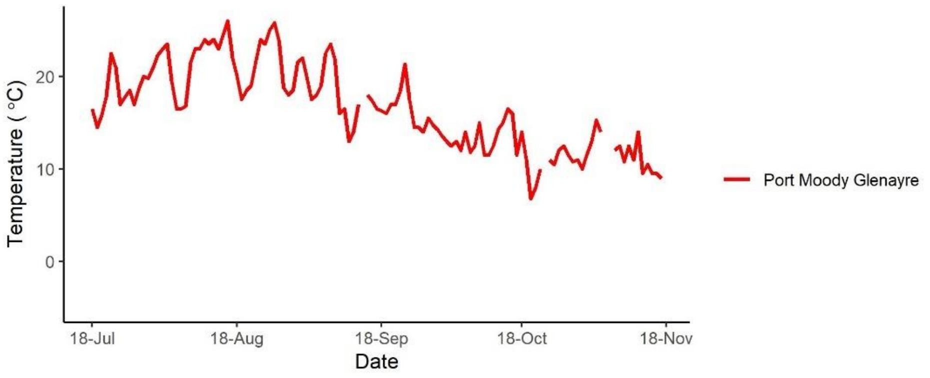
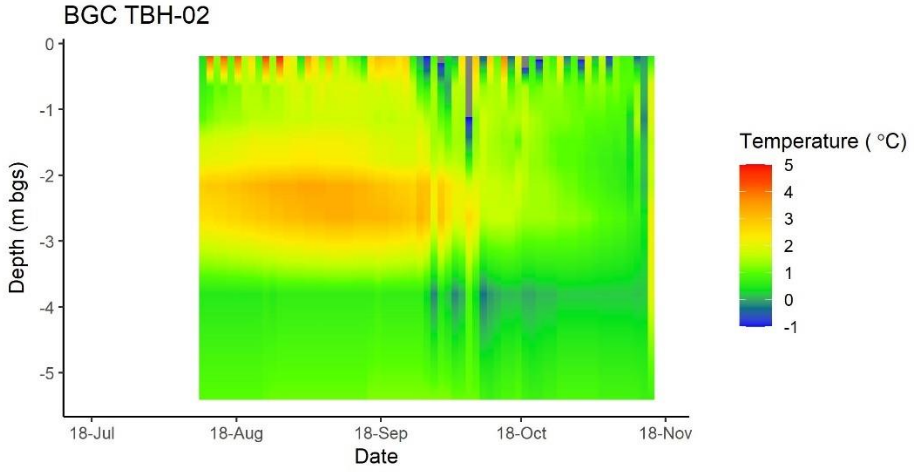
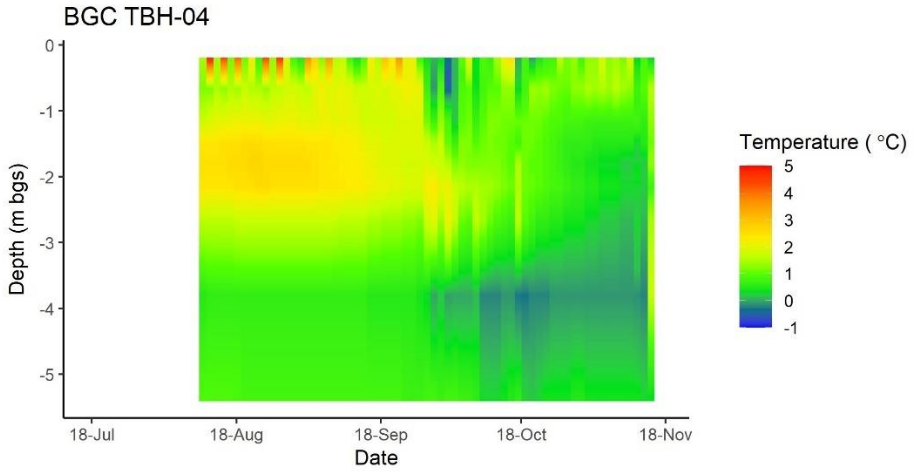


Table 8. Mean monthly source zone NSZD estimated from background corrected mean monthly temperature gradients at TBH-02 and TBH-04.

Month	Mean Monthly Heat Flux Total (Q_T)	Mean R_{NSZD}	Mean Source Zone Estimated NSZD Rate
	$J{\cdot}m^{-2}{\cdot}s^{-1}$	$g{\cdot}m^{-2}{\cdot}s^{-1}$	US gal/acre/yr
Jul-18	5.47	1.15E-04	2029
Aug-18	4.43	9.30E-05	1698
Sep-18	2.78	5.83E-05	1640
Oct-18	1.11	2.32E-05	408



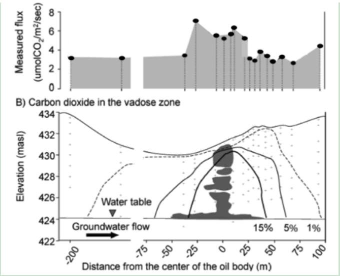
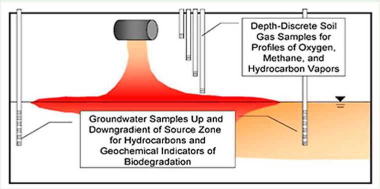
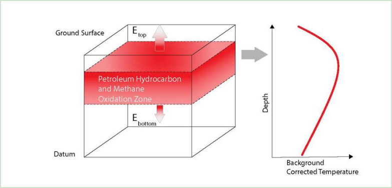


Other thermal correction including modelling :

- TempW (Hers et al *In progress*)
- Single Stick Correction (Askarani et al 2020)

Wozney et al *In submission*

Comparison of Vadose zone methods

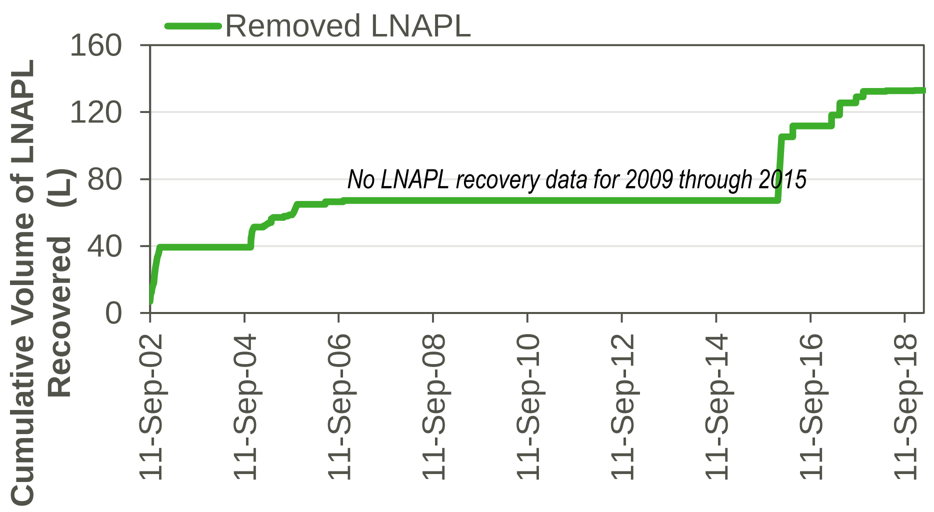
Method		Advantages	Disadvantages	Sources of Uncertainty
CO_2 efflux	 Sihota et al 2011	Non-intrusive Lower to moderate cost Techniques available to obtain continuous data	Limited application at sites with hard surfaces and carbonate soils, which may be a sink or source of CO_2	Correction for background natural soil respiration (NSR) either using radiocarbon data or site background locations Diurnal and seasonal variability when predicting annual estimates
Soil gas gradient (O_2)	 ITRC 2009	Soil gas data often can be readily obtained Lower to moderate cost	Discrete measurement Requires estimate of effective diffusion coefficient	Effective diffusion coefficient Correction for background NSR
Temperature	 ITRC 2009	Continuous data Long-term estimates Larger-scale "bulk" measurement	More complex analysis required Sites with thermal sinks or sources Moderate to higher cost	Determining background temperature or surface flux/temperature model to correct data Thermal conductivity

Summary of NSZD Estimates

2015- 2018

Method	Sampling Period	Year	Mean or Best NSZD Estimate (US gal/acre/yr)
DCC[a] (Discrete)	June – July	2015	760
	Oct	2016	25 – 190
	June	2018	1,300
	October	2018	100
FD (Continuous)	Summer	2018	1,200
	Fall	2018	340
	July – March	2018 – 2019	80 – 1,300
E-Flux Static Trap (Integrated)	June – July	2016	820
Concentration Gradient Method (CGM) (Discrete)	October	2016	120
	July	2018	1,600
Temperature Gradient (Continuous)	July	2018	2,000
	October	2018	410

Cumulative Volume of LNAPL Recovered
LNAPL Body



35 US gallons manually recovered
Sept 2002 – 2018

THANK-YOU

GOLDER
MEMBER OF WSP

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eosense environmental gas monitoring

HERS Environmental Consulting, Inc.

ExxonMobil

UBC

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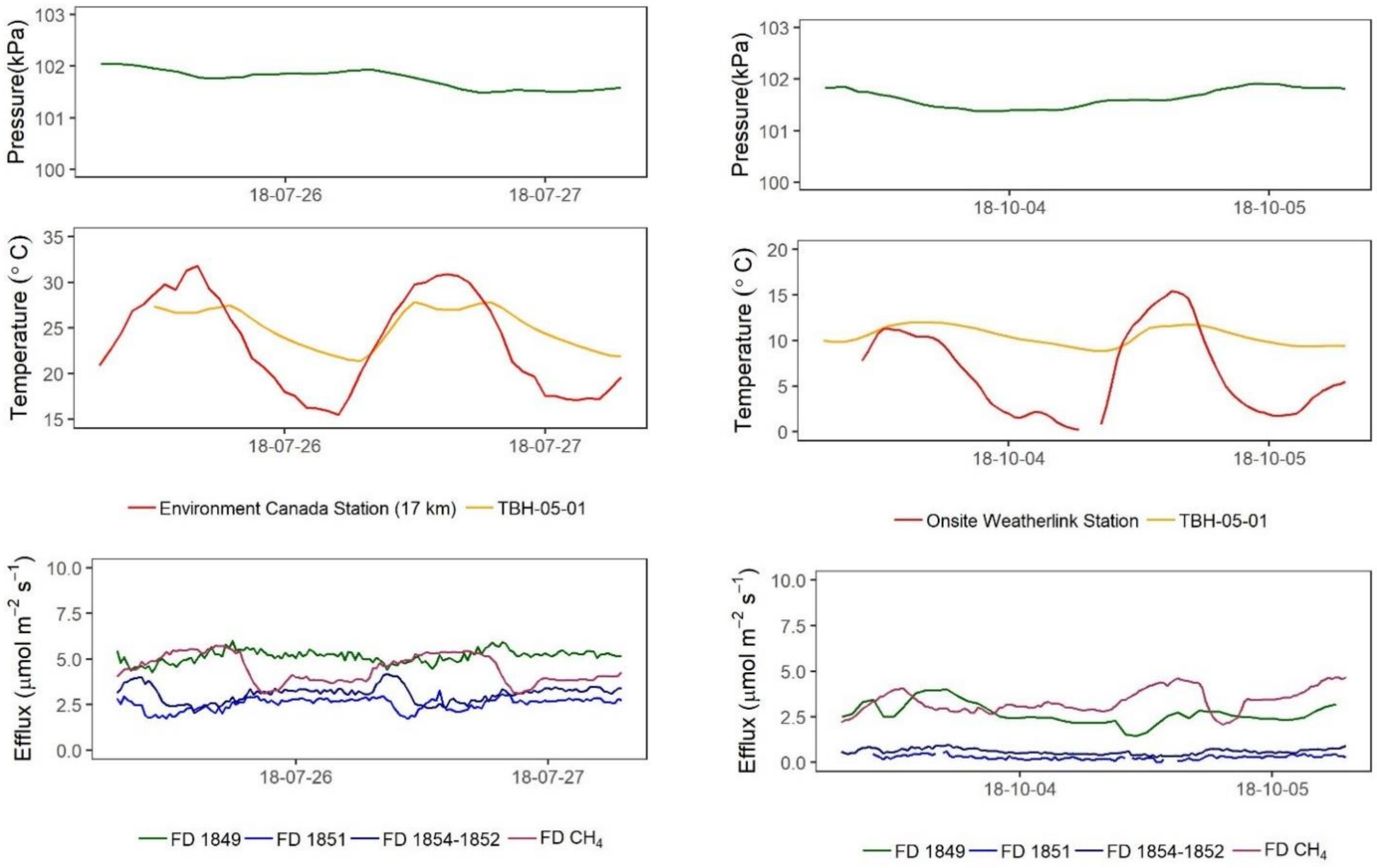
Results- Continuous CO_2 Efflux

EOSENSE- DIURNAL VARIABILITY



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