CH2MHILL

Assessment of Variability in Flux Chamber-based Soil CO_2 Efflux Measurements at Petroleum Remediation Sites

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Outline



- Why Perform Efflux Assessments?
- Technology
- Data Quality
- Uncertainties
  - Temporal and Barometric Variability
  - Site Geology and Ground Surface Cover
- Comparisons
  - Hydrocarbon Removal, Monitoring and Mass Budgeting
  - Efficiency and Cost
- Conclusions

Introduction



- Gas exchange takes place between soil and atmosphere
  - Downward movement of oxygen (O_2) and upward venting of CO_2
  - Affected by factors that change temperature/pressure and moisture
- CO_2 is derived from respiration processes occurring in both shallow aerobic, and deeper anaerobic, ecosystems

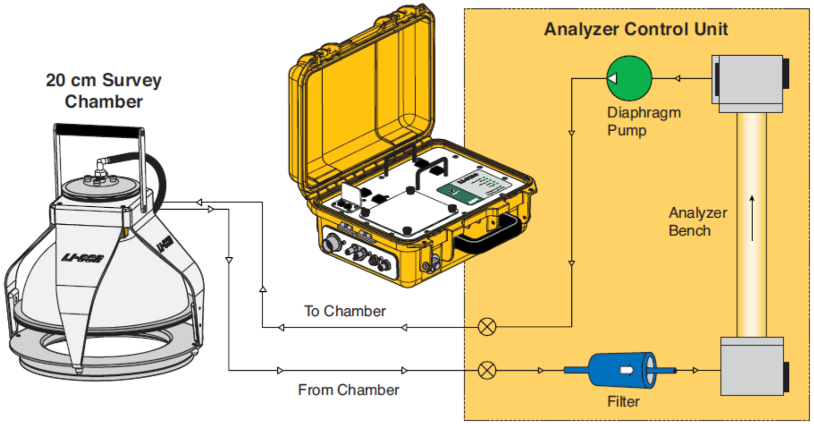



Why Perform Efflux Assessment

- Semi-quantitatively delineate source zones - free phase non-aqueous phase liquid (NAPL)
- Estimate site wide biodegradation
  - Better estimation of hydrocarbon removal rates
  - In lieu of groundwater natural attenuation indicator parameters (NAIPs) analysis
- Biodegradation vs mechanical extraction systems
- Monitored natural attenuation (MNA)
- Economical

Soil Flux System (LI-COR, Inc.)

- Equipment
  – Ground surface collar
  – Vented bellows-controlled flux chamber with rubber gasket
  – Application software, analyzer unit (infrared gas analyzer) and pump



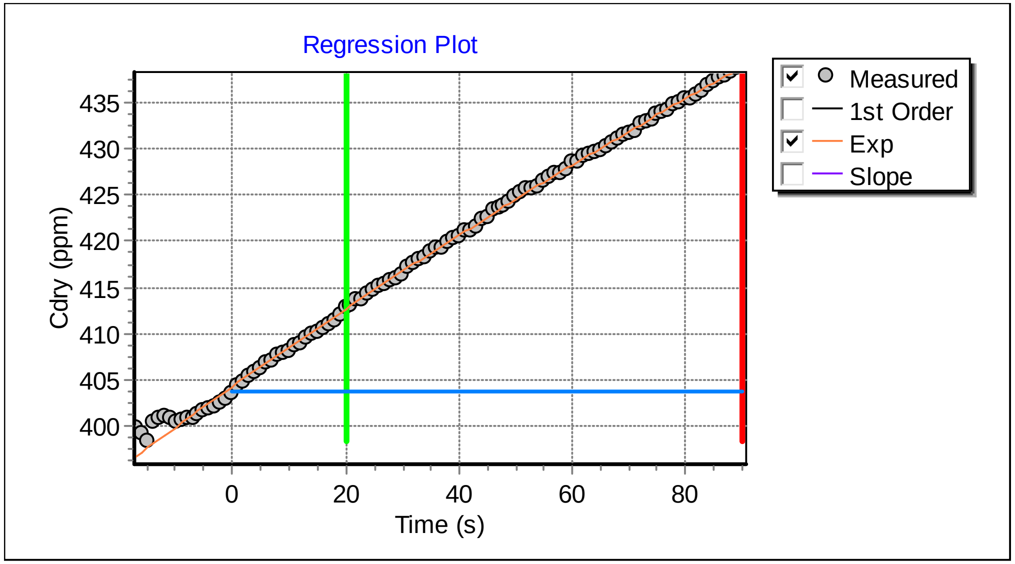
http://licor.com/env/products/soil_flux/

LI-COR Survey Procedures

- Theory
  - The rate of change of CO_2 concentration inside a vented flux chamber is equated to flux
  - Uses early time data before chamber accumulation effects occur

- Deadband = 20 seconds
- Observation Rate = 90 seconds
- Post-purge = 30 seconds

- Minimum Number of Measurements = 3 *



Fall 2013 and Summer 2014 Multisite CO_2 Survey

- 6 sites, 21 rounds of efflux monitoring, 163 locations, 1,529 measurements
- Site conditions from active gas plant to remote maintenance yard containing a variety of hydrocarbons

Site Name	Date(s) CO_2 Survey Performed	Type of Product	Release Age	Subsurface Soil Type	Estimated Size of LNAPL Footprint (ha)
Yukon	September, 2013 June, 2014	Arctic Diesel	Since 1960s	Fill, sand, and gravel	0.030
TransCanada[1]	September - October, 2013 July - August, 2014	Crude, Diesel, NGLs	Since 1966	Fill, silty sand	0.50
Ferrier 10-26	October, 2013	Crude	Since 1971	Clay underlain by sandstone bedrock	0.42
Ferrier 09-22	September, 2013	NGLs, LPG	Since 1968	Sand underlain by sandstone bedrock	0.98
Ferrier 01-20	September, 2013	Waste Oil	Since 1960s	Fill, silty sand, and gravel	1.3
Ferrier 07-20	October, 2013	Crude, NGLs	Since Aug 2006	Silt and clay underlain by sandstone bedrock	5.5

Background Correction

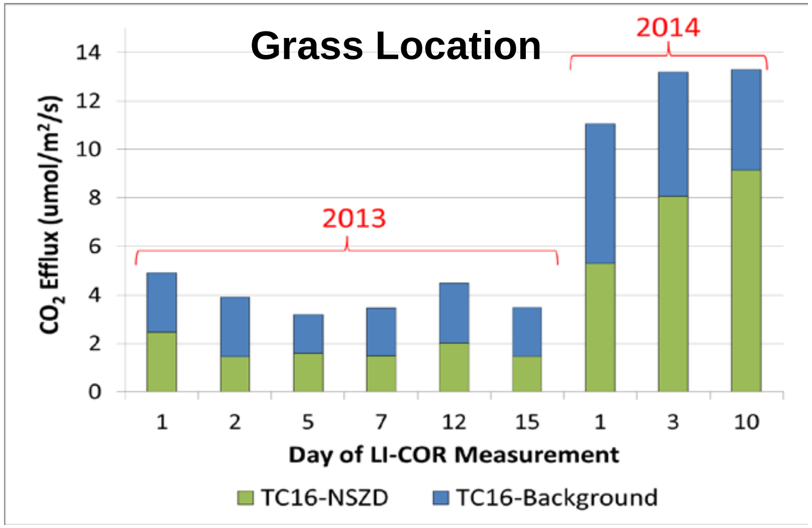


- Measurements averaged at each location for each monitoring round
  - 55 background locations
  - 108 locations over the LNAPL footprint
- NSZD-derived CO_2 efflux ($q_{CO_2\text{-NSZD}}$)

$$q_{CO_2\text{-NSZD}} = q_{CO_2\text{-Total}} - q_{CO_2\text{-Background}}$$

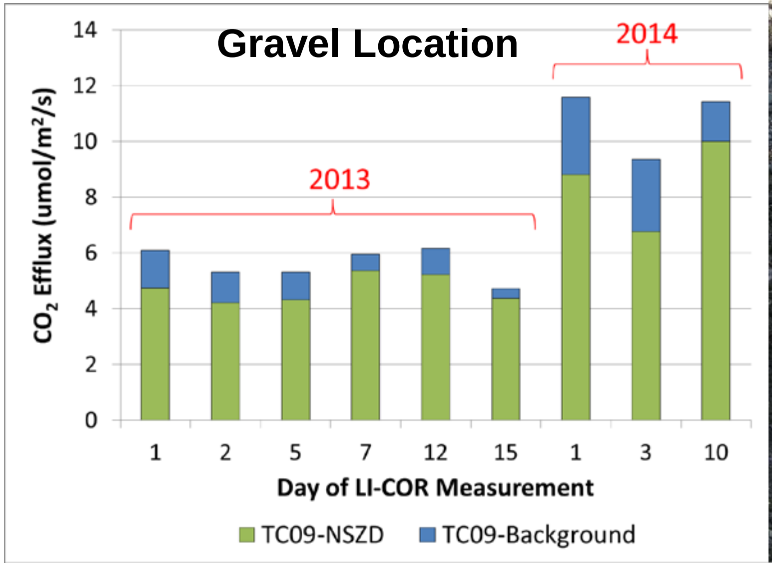
- Correction made for each monitoring round which spanned 3-5 hours time (15-30 collars)

Background CO_2 Contribution



- Background ranged from 0.6 to 5.3 μmol/m²/s (average 1.3 μmol/m²/s) – 2013

- Background ranged from 0.8 to 5.8 μmol/m²/s (average 3.2 μmol/m²/s) – 2014



Total CO_2 Efflux Measurement Precision

Site	Label	IV Date	Exp_Flux ($\mu mol/m^2/s$)	Exp_R2	Surface Cover	Pressure Average (kPa)	Temperature Average (°C)	CO_2 Efflux Average (µmol/m2/s)	Std Dev	% of Avg
Ferrier 09-22	01 - Day 1	9/29/2013 15:39	0.76	0.9903	Sand and gravel, dry	86.62	19.40	0.78	0.04	5%
		9/29/2013 15:41	0.75	0.9946						
		9/29/2013 15:44	0.82	0.9948						
Ferrier 07-20	01 - Day 1	10/6/2013 9:11	1.81	0.9989	Silt, some clay and sand, light brown, grass/alfalfa	88.59	5.52	1.80	0.03	1%
		10/6/2013 9:13	1.77	0.9986						
		10/6/2013 9:16	1.82	0.9982						
Yukon	01B - Day 1	9/14/2013 13:17	0.97	0.9929	Gravel covered, compacted	89.30	13.65	0.80	0.10	13%
		9/14/2013 13:19	0.70	0.9932						
		9/14/2013 13:22	0.79	0.992						
		9/14/2013 13:24	0.76	0.9946						
		9/14/2013 13:26	0.79	0.9945						
	01B - Day 3	9/16/2013 12:54	1.43	0.988		88.87	6.22	0.79	0.44	56%
		9/16/2013 12:56	0.53	0.9675						
		9/16/2013 12:58	0.51	0.9662						
		9/16/2013 13:01	0.67	0.9863						
	01B - Day 4	9/17/2013 13:46	0.97	0.9879		88.34	2.14	0.69	0.25	36%
		9/17/2013 13:49	0.51	0.9921						
		9/17/2013 13:51	0.59	0.9885						

- Across all sites, the std dev ranged from 3.1% to 30% of the average efflux (mean of 16%) in 2013; 9% to 13% of the average efflux (mean of 11%) in 2014
  - ~0.3 $\mu mol/m^2/s$ on overall average of 2.1 $\mu mol/m^2/s$ total CO_2 efflux - 2013
  - ~0.3 $\mu mol/m^2/s$ on overall average of 2.8 $\mu mol/m^2/s$ total CO_2 efflux - 2014

Range of Total Efflux

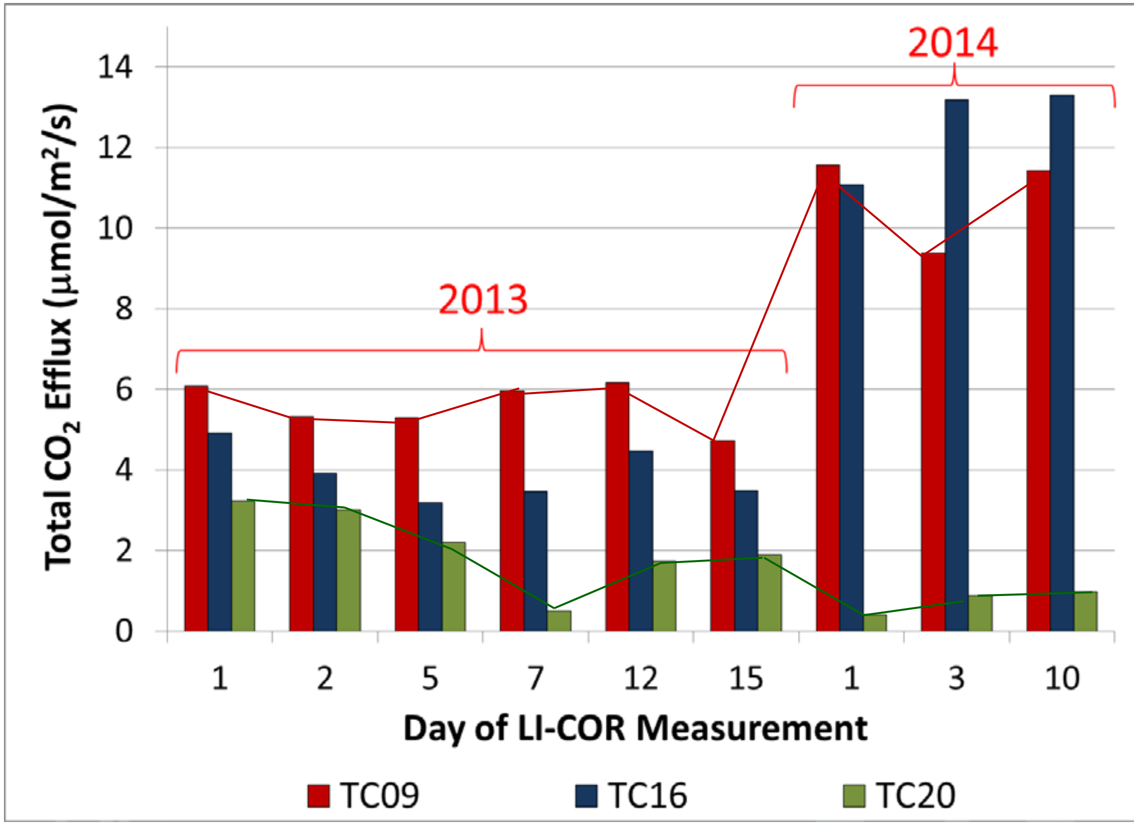


- Field replicate measurement results within ~0.25 $\mu mol/m^2/s$ in 2013; ~7.2 $\mu mol/m^2/s$ in 2014

- Corrected efflux ranged from 0 to 10.5 $\mu mol/m^2/s$ (average 1.27 $\mu mol/m^2/s$)

Total CO_2 Efflux
Multiday Measurements





Day 1 – Sun, 9-15°C, <5 km/h wind

Day 2 – Sun, 9-11°C, up to 30 km/h wind

Day 5 – Rain, 3-6°C

Day 7 – Light rain, 4-7°C, up to 15 km/h wind

Day 12 – Sun, 11-17°C, up to 45 km/h wind

Day 15 – Sun, 10-14°C, up to 20 km/h wind

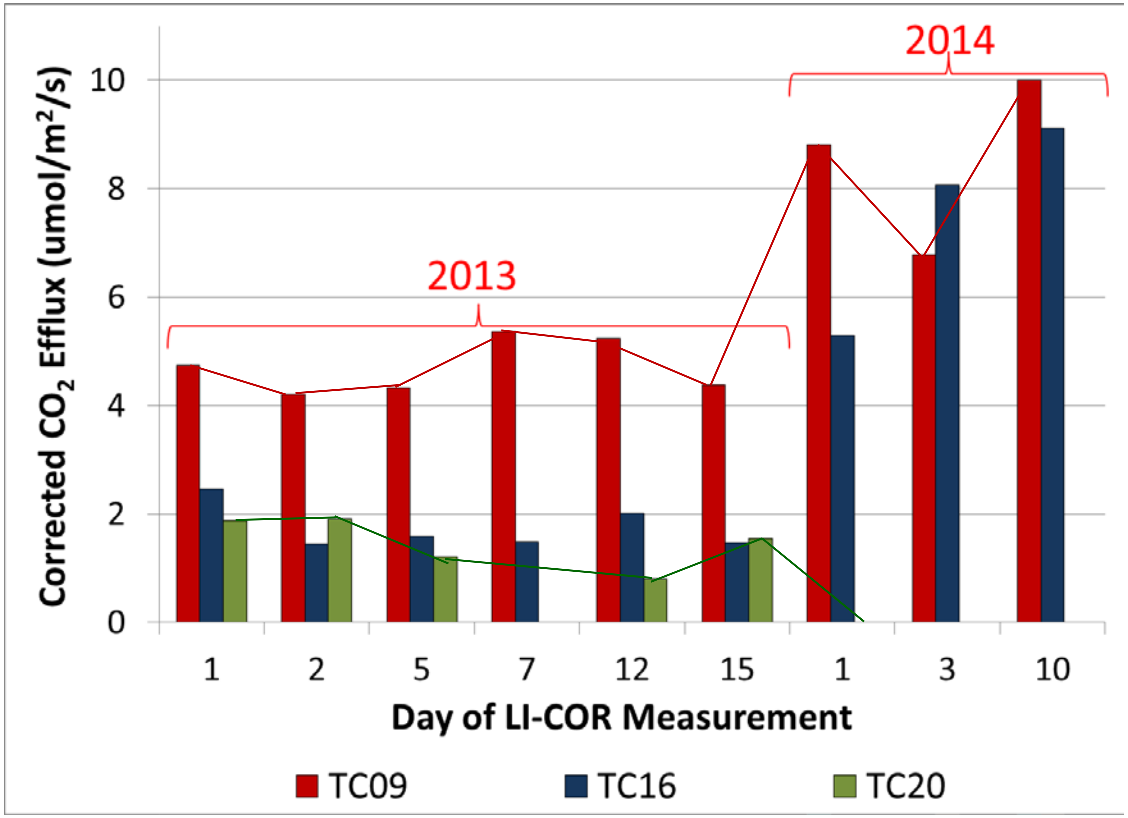
Day 1 – Rain overnight, sun, rain, and thunder, 16-24°C, up to 18 km/h wind

Day 3 – Fog, sun, 19-35°C, up to 15 km/h wind

Day 10 – Rain overnight, sun, 14-28°C, up to 12 km/h wind

- Average variation in total CO_2 efflux over two week period was 1.1 $\mu mol/m^2/s$ (2013) and 1.6 $\mu mol/m^2/s$ (2014) at all locations with multiple day measurements

Corrected CO_2 Efflux Multiday Measurements



Day 1 – Sun, 9-15°C, <5 km/h wind

Day 2 – Sun, 9-11°C, up to 30 km/h wind

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Day 3 – Fog, sun, 19-35°C, up to 15 km/h wind

Day 10 – Rain overnight, sun, 14-28°C, up to 12 km/h wind

- Similar average variation as total CO_2 efflux, 1.0 $\mu mol/m^2/s$ (2013), 1.2 $\mu mol/m^2/s$ (2014)
- Suggests combination of subsurface changes occurred to cause variability

Source Zone Depletion Rates

$$2C_8H_{10} + 17O_2 \text{ --> } 16CO_2 + 10H_2O$$

Site Name	Type of Ground Cover	Average Background CO_2 Efflux (μmol/m^2/s)	Avg. Corrected CO_2 Efflux (μmol/m^2/s)	Average LNAPL Degradation Rate (g/m^2/d)
Yukon	**Grass**	**3.0**	**3.5**	**4.3**
Ferrier 01-20	Grass	5.3	3.4	4.2
TransCanada	**Grass**	**5.0**	**1.9**	**2.3**
Ferrier 10-26	Grass	2.1	1.5	1.9
Ferrier 07-20	Grass	1.9	0.85	1.1
Yukon	Grass	1.2	0.79	0.96
TransCanada	Grass	2.2	0.45	0.55
Ferrier 09-22	Grass	2.3	0.20	0.24

Source Zone Depletion Rates

$$2C_8H_{10} + 17O_2 \dashrightarrow 16CO_2 + 10H_2O$$

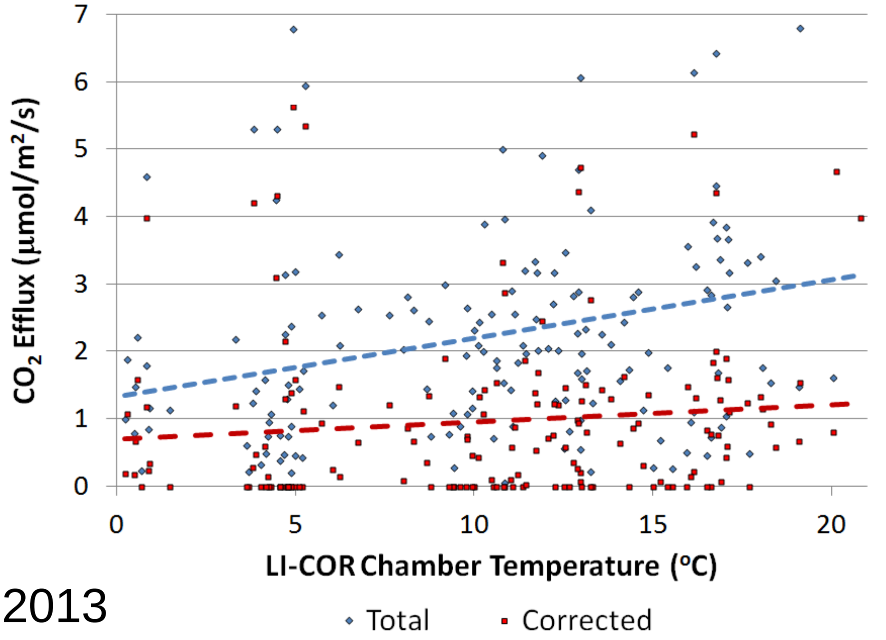
Site Name	Type of Ground Cover	Average Background CO_2 Efflux ($\mu mol/m^2/s$)	Avg. Corrected CO_2 Efflux ($\mu mol/m^2/s$)	Average LNAPL Degradation Rate ($g/m^2/d$)
TransCanada	**Gravel**	**2.3**	**2.0**	**2.5**
Yukon	Gravel	0.83	1.1	1.6
TransCanada	Gravel	0.95	1.2	1.6
Ferrier 01-20	Gravel	0.81	0.91	1.1
Yukon	**Gravel**	**1.1**	**0.68**	**0.83**
Ferrier 09-22	Gravel	0.62	0.36	0.44
Ferrier 10-26	Gravel	0.88	0.23	0.29
Ferrier 07-20	Gravel	-	-	-

Fall 2013 and Summer 2014 Multisite CO_2 Survey

- 6 sites, 21 rounds of efflux monitoring, 163 locations, 1,529 measurements
- Site conditions from active gas plant to remote maintenance yard containing a variety of hydrocarbons

Site Name	Date(s) CO_2 Survey Performed	Release Age	Estimated Size of LNAPL Footprint (ha)	Estimated Sitewide NSZF Rate (kg/yr)
Yukon	September, 2013	Since 1960s	0.030	120
	June, 2014			**146**
TransCanada[1]	September - October, 2013	Since 1966	0.50	1,900
	July - August, 2014			**6,842**
Ferrier 10-26	October, 2013	Since 1971	0.42	1,963
Ferrier 09-22	September, 2013	Since 1968	0.98	2,130
Ferrier 01-20	September, 2013	Since 1960s	1.3	8,307
Ferrier 07-20	October, 2013	Since Aug 2006	5.5	25,674

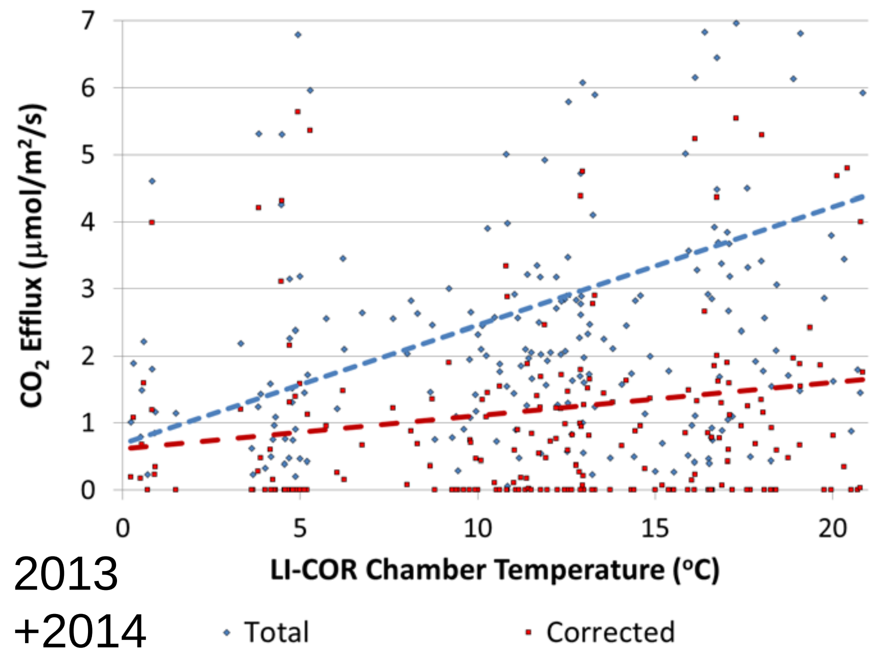
Ground Surface Temperature



2013

- Discernible effect on total CO_2 efflux

- Dampened effect of temperature to a level comparable to measurement variability (<0.6 µmol/m²/s)



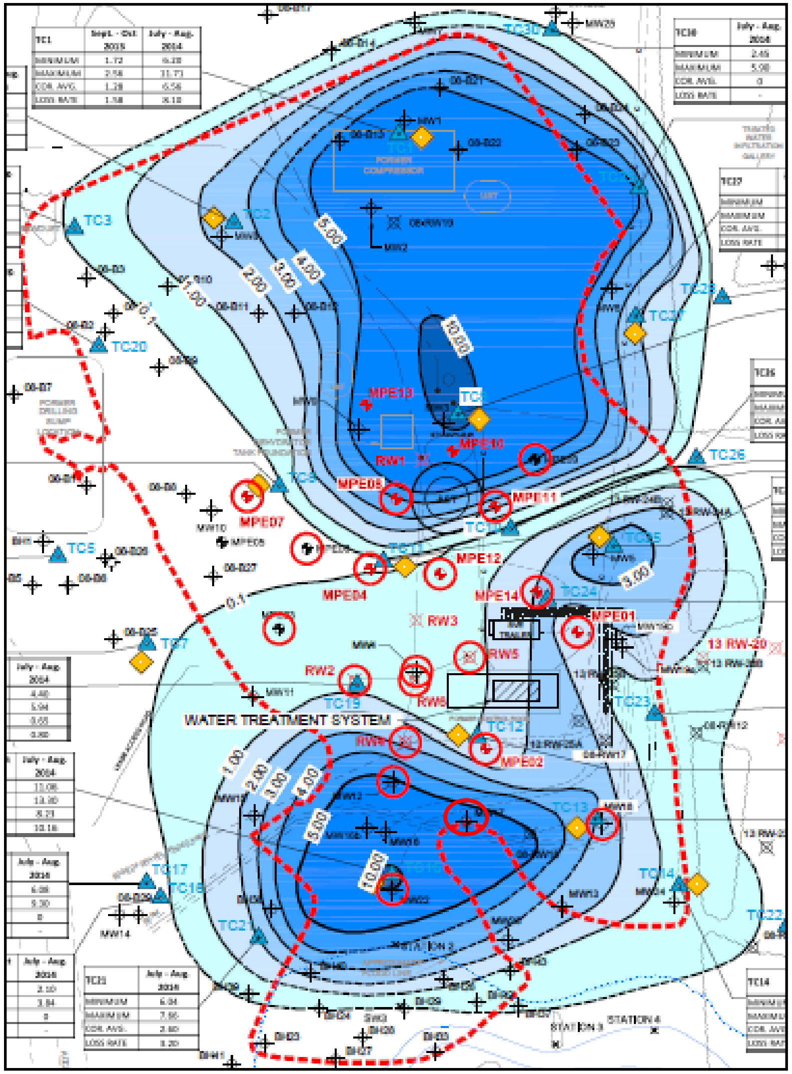
2013 +2014

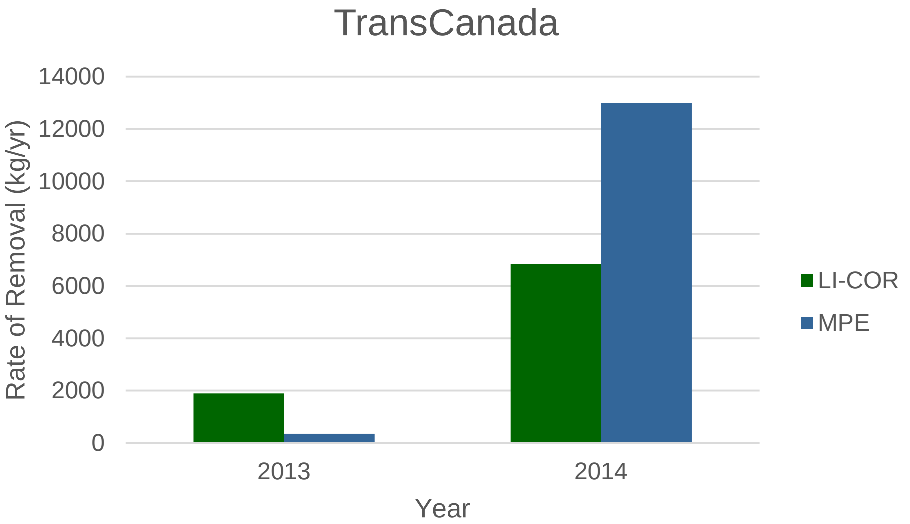


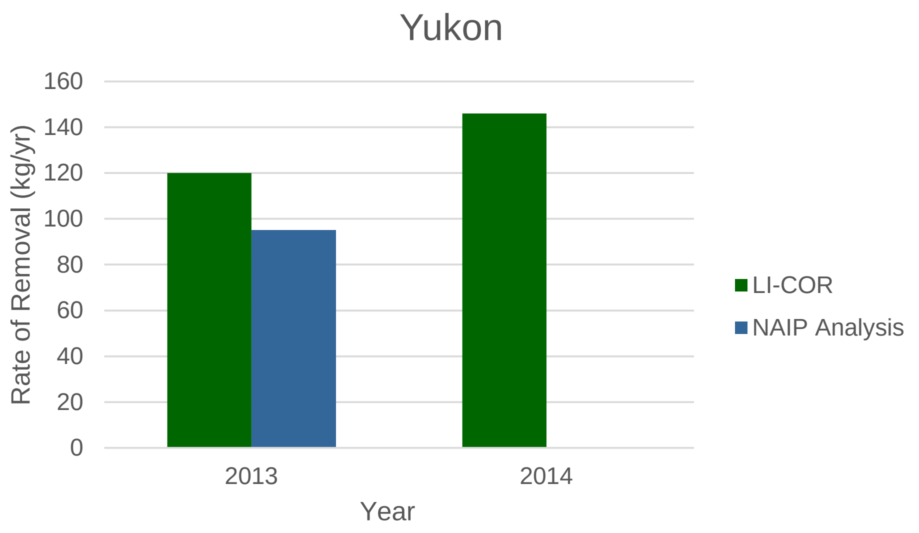
Pressure, Moisture, and Wind

- Indiscernible effect with pressure and moisture content
- Wind is a non-issue if instrument rubber gasket is in good shape and set correctly to isolate chamber from wind effects
  - Tortuous chamber vent prevents wind influencing measurements

LI-COR and Groundwater Monitoring







Efficiency and Cost

30 LI-COR locations v's 30 groundwater samples

	LI-COR	Current GW Sampling
Time	3-5 hrs/round	3 days/round
Cost	~$1800[a]	~$4500 - $4000[b]
Field Staff Required	1	2

[a] First month - ~$1800, subsequent months - ~$1000

[b] NAIPs only – nitrate/nitrite, sulphate/sulphite, alkalinity, ferrous iron, dissolved methane, dissolved oxygen and dissolved carbon dioxide.

Conclusions



- CO_2 Efflux Assessment
  - Semi-quantitatively delineate free phase NAPL
  - More realistic estimates of hydrocarbon removal rates through biodegradation
  - LI-COR precision observed: ~ +/- 0.3 $\mu mol/m^2/s$ (total efflux)
  - Time and cost efficient
  - Fewer field staff required
- Variability
  - Ecosystem-related (background) contributions to total CO_2 efflux are generally small ~1.3 – 3.2 $\mu mol/m^2/s$
  - Ambient air temperature showed most significant effects to total efflux

Managing Variability

- Standard installation protocol
  - 6 Standard weighted tamping device for re-compaction of soil to "natural" conditions
- Wait at least 4 hours after a precipitation event
- Maintain a 1.5-m distance from ground surface disturbances
- Regular practice of duplicate efflux systems approximately 1 m
- Create a detailed method for background corrections

Conclusions



- Further work
  - Next step assess effects of subsurface changes on efflux (i.e., seasonality) – Data analysis underway
  - Investigate effects of depth
  - Use at more sites across Canada
  - Recognize CO_2 efflux monitoring as a method for monitoring NA and NSZD

Thanks to Co-Authors

- Darcy Bye – TransCanada PipeLines Limited
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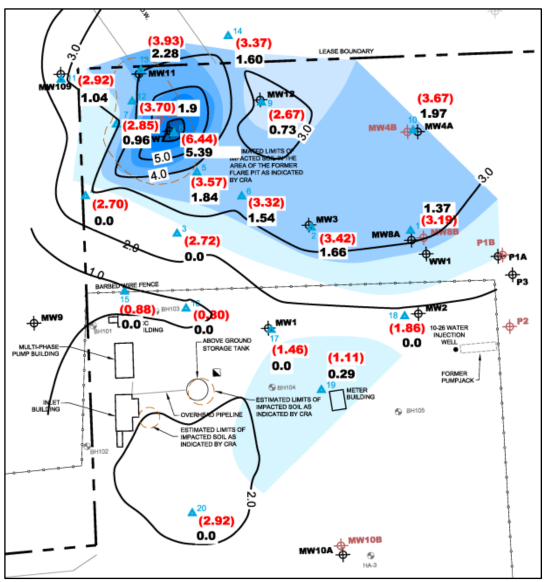
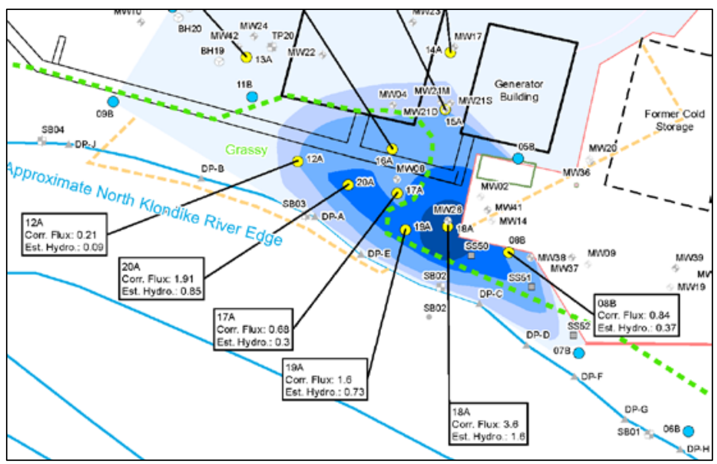
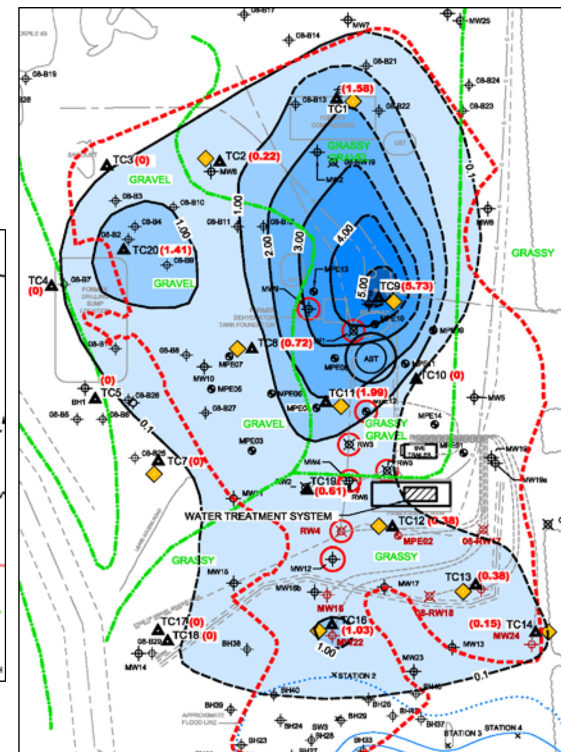
- Amy Jimmo – CH2M HILL, Edmonton
- Tom Palaia– CH2M HILL, Denver







Thank you for Your Time !