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July 5, 2017

Mr. Randy Whitcher
New York State Department of Environmental Conservation
Division of Environmental Remediation
Remedial Bureau D
625 Broadway, 12th Floor
Albany, New York 12233-7020

Re: Vadose Zone Natural Source Zone Depletion Pilot Study Results
ExxonMobil Greenpoint Petroleum Remediation Project
Greenpoint, Brooklyn, New York

Dear Mr. Whitcher:

On behalf of ExxonMobil Oil Corporation (ExxonMobil), Roux Associates, Inc. (Roux Associates) has prepared this letter report to summarize the results of the Vadose Zone Natural Source Zone Depletion Pilot Study (NSZD Pilot Study) activities conducted in 2016 at the ExxonMobil Greenpoint Petroleum Remediation Project (EMGPRP) located in Greenpoint, Brooklyn, New York. The NSZD Pilot Study field activities were conducted from December 16, 2015 to October 17, 2016, in accordance with the Vadose Zone Natural Source Zone Depletion Pilot Study Work Plan dated December 3, 2015.

NSZD is a reduction in Light Non-Aqueous Phase Liquid (LNAPL) mass that occurs *in situ* through any one, or a combination of, naturally occurring processes, including dissolution, volatilization, and biodegradation (ITRC 2009). When LNAPL degrades in the vadose zone, microbes anaerobically convert petroleum compounds to methane, and then methane further breaks down to carbon dioxide (Suthersan et al. 2015). As such, carbon dioxide can be measured and used in an effort to quantify LNAPL degradation. The objective of the NSZD Pilot Study was to demonstrate that NSZD is occurring across the EMGPRP site (Site).

NSZD Pilot Study Methodology

NSZD Pilot Study activities were performed in four discrete seasonal events (December 2015, April 2016, July 2016, and October 2016) in an effort to capture seasonal differences. Two different methods were used to measure carbon dioxide (CO_2) flux (i.e., mass of CO_2 over time, per unit area), and therefore approximate LNAPL degradation. These methods are the measurement of CO_2 flux utilizing a CO_2 trap and a LI-COR® Soil CO_2 Flux System. Both were utilized at multiple, unpaved locations across the Site in an effort to have the data be representative of a variety of subsurface conditions and LNAPL plume characteristics. Additionally, atmospheric pressure, temperature, and rain data were collected from a nearby weather station to evaluate any potential correlations with measured CO_2 flux. The NSZD

Pilot Study methodology for each CO_2 flux measurement method was based on the methods implemented in "Measurement of Natural Losses of LNAPL Using CO2 Traps" by McCoy et al. and is described below.

Carbon Dioxide Traps

The CO_2 traps provided by E-Flux, LLC, in Fort Collins, Colorado, were installed in pairs at four locations across the Site. These locations were unpaved, open areas. Sample locations from areas 1 through 4 are shown on Figure 1. At one location, labeled "4" on Figure 1, an additional trap was placed in a cutout of a paved area just large enough for trap installation. This was done in an effort to understand the effect, if any, of paved surface on soil gas efflux. All of the CO_2 traps were placed on rubber receivers and topped with rain covers. An example of the CO_2 traps setup is shown on Figure 2. The traps contain two layers of sorbent soda lime material which reacts with CO_2 to form calcium carbonate ($CaCO_3$). The top layer prevents interference from atmospheric CO_2. The calcium carbonate resulting from the CO_2 and soda lime reaction in the bottom layer is analyzed to calculate CO_2 flux from the subsurface.

The traps were deployed for two weeks each event and then returned to E-Flux, LLC. Background conditions were estimated by conducting a carbon isotope analysis which allowed for the subtraction of modern carbon from the total carbon dioxide volume sorbed. Modern carbon is distinctly different from the carbon contained in petroleum due to the detectable presence of ^{14}C (i.e., carbon with a mass number of 14). Additional details regarding the carbon isotope analysis are provided in Attachment 1. The remaining amount of carbon dioxide sorbed was converted to LNAPL degradation expressed in gallons per acre per year. An average was taken of the two measurements at each location for each event, and these averages are provided in Table 1 below. An explanation of the E-Flux calculation is provided in Attachment 1.

LI-COR® Soil CO_2 Flux System

The LI-COR® Soil CO_2 Flux System (LI-COR System) was utilized to take real-time CO_2 flux measurements. This system uses a chamber placed on top of a PVC collar inserted into the soil. The control unit connected to the chamber analyzes the real-time CO_2 flux inside this chamber. In addition to CO_2 flux readings, the system measures soil temperature and soil moisture using probes attached to the control unit. These soil temperature and moisture readings were relatively shallow, as the probes were only capable of extending up to six inches into the soil. An example of the LI-COR System setup is shown on Figure 2.

The LI-COR System measurements were collected adjacent to the CO_2 traps, and also at an additional four locations, in an effort to provide more data on the spatial variations of CO_2 flux across the Site. Sample locations are shown on Figure 1. LI-COR and CO_2 trap measurements were recorded at areas 1 through 4 while only LI-COR measurements were recorded at areas A through D. During each seasonal event, the LI-COR System was utilized five to seven of the days within the 2-week CO_2 trap deployment. On these days, two measurements were recorded back-to-back, each for two minutes. An average of all the measurements was recorded and the E-Flux calculation shown in Attachment 1 was applied to the LI-COR System results to convert from CO_2 flux to LNAPL degradation expressed in

gallons per acre per year. The carbon isotope analysis results of the nearest CO_2 trap were utilized for each LI-COR measurement location.

Results

A summary of the results for both the CO_2 traps and LI-COR System as well as a comparison of the methods is presented below.

Carbon Dioxide Traps

LNAPL degradation rates measured with the CO_2 traps across the Site and throughout the NSZD Pilot Study range from 19 to 637 gallons per acre per year. A summary of the results is provided in Table 1 below.

Table 1. LNAPL Degradation Rates for CO_2 Traps in Gallons per Acre per Year

Location	December 2015	April 2016	July 2016	October 2016
1	21	102	452	220
2	19	128	637	212
3	106	567	342	314
4	146	116	269	98
4 – Chimney	4,888	1,789	2,313	994

The additional, pavement-surrounded CO_2 trap installed each event at Location 4 displayed results significantly higher than the pairs of traps installed in open, unpaved areas. LNAPL degradation rates measured for this additional trap ranged from 994 to 4,888 gallons per acre per year. The higher CO_2 flux detected at this additional trap is likely a result of the surrounding paved surface which restricts that path of CO_2 traveling from the subsurface to the atmosphere. This influence of the paved surface is often referred to as a "chimney effect", since the area covered in the trap acts a conduit for CO_2 and other soil gases to escape to the atmosphere. With only one point of exit from the subsurface, more CO_2 would flow through the area of the cutout than if the surrounding surface was not paved.

LI-COR System

LNAPL degradation rates measured with the LI-COR System across the Site and throughout the NSZD Pilot Study range from 14 to 1,860 gallons per acre per year. A summary of the LI-COR System results is provided below in Table 2.

Table 2. LNAPL Degradation Rates for LI-COR System in Gallons per Acre per Year

Location	December 2015	April 2016	July 2016	October 2016
1	14	134	446	133
2	38	182	998	256
3	223	540	804	514
4	436	231	459	144
A	389	363	1860	776
B	153	397	552	355

Location	December 2015	April 2016	July 2016	October 2016
C	22	495	77	50
D	173	321	482	234

Comparison of CO_2 Traps and LI-COR System

In general, the CO_2 traps method and the LI-COR System had results of the same magnitude when comparing the same location within each round. A summary of the results for locations with both methods applied is provided in Table 3 below.

Table 3. LNAPL Degradation Rates for Both NSZD Pilot Study Methods in Gallons per Acre per Year

	December 2015		April 2016		July 2016		October 2016	
Location	**Traps**	**LI-COR**	**Traps**	**LI-COR**	**Traps**	**LI-COR**	**Traps**	**LI-COR**
1	21	14	102	134	452	446	220	133
2	19	38	128	182	637	998	212	256
3	106	223	567	540	342	804	314	514
4	146	436	116	231	269	459	98	144

Calculated LNAPL degradation rates for both methods were highest in the warmest round (i.e., July) suggesting a positive correlation between LNAPL degradation rates and ambient temperature. This can be seen in the graphical representation of all of the NSZD Pilot Study results provided on Figure 3.

The LI-COR System results were generally higher than CO_2 traps method, although they were of the same order of magnitude. A graphical comparison of the values can be seen on Figure 4. The R^2 value of 0.72, as shown on Figure 4, represents a significant correlation between the degradation rates measured by the LI-COR System vs. the CO_2 traps.

Conclusions

As discussed above, the NSZD Pilot Study was conducted in an effort to demonstrate that NSZD is occurring across the Site. The following conclusions were reached based upon an evaluation of the data generated during the NSZD Pilot Study:

- The CO_2 traps and LI-COR System methods resulted in similar values when collected at the same location and in the same round. This validates the magnitude of the CO_2 flux rates measured by both methods.

- NSZD is not only occurring across the Site, but also occurring at a magnitude that will be an important contribution to LNAPL degradation/removal as other remedial technologies reach their limits of efficient operation.

- Roux Associates anticipates continuing to monitor NSZD as part of regular monitoring activities, likely at a reduced schedule compared to the NSZD Pilot Study.

Please let us know if you have any questions or comments.

Sincerely,

ROUX ASSOCIATES, INC.

Ian Holst
Project Engineer

Andrew Baris
Principal Hydrogeologist/
Vice President

Attachments

cc: Andrew G. Frank, Esq., Assistant Attorney General
Benjamin A. Conlon, Esq., NYSDEC (Electronic File Only)
John Parker, Riverkeeper (Electronic File only)
Todd Ommen, Esq., Pace University School of Law (Electronic File Only)
Frank Messina, Exxon Mobil

References

ITRC, 2009. Evaluating Natural Source Zone Depletion at Sites with LNAPL. Interstate Technology & Regulatory Council, LNAPLs Team.

McCoy, K., J. Zimbron, T. Sale, and M. Lyverse. 2015. Measurement of Natural Losses of LNAPL Using CO_2 traps. Ground Water. Vol. 53, No.4, pp. 658-667.

Suthersan, Suthan, Koons, Brad, and Schnobrich, Matthew. 2015. Contemporary Management of Sites with Petroleum LNAPL Presence. Groundwater Monitoring & Remediation 35, no.1, pp. 23-29.

FIGURES

1. CO2 Flux Measurement Locations
2. CO2 Trap and LI-COR System Setup
3. Summary of NSZD Pilot Study Results
4. Comparison of LI-COR and CO2 Trap Results



LEGEND

1 LOCATION AND DESIGNATION OF CO2 TRAP AND LI-COR SURVEY MEASUREMENT

A LOCATION AND DESIGNATION OF ADDITIONAL LI-COR SURVEY MEASUREMENT

FREE PRODUCT EXTENT (SEPTEMBER 2015)

EMGPRP BOUNDARY

N

500 0 500 1,000 Feet

Title:

CO2 FLUX MEASUREMENT LOCATIONS

EXXONMOBIL
GREENPOINT PETROLEUM REMEDIATION PROJECT
GREENPOINT, BROOKLYN, NEW YORK

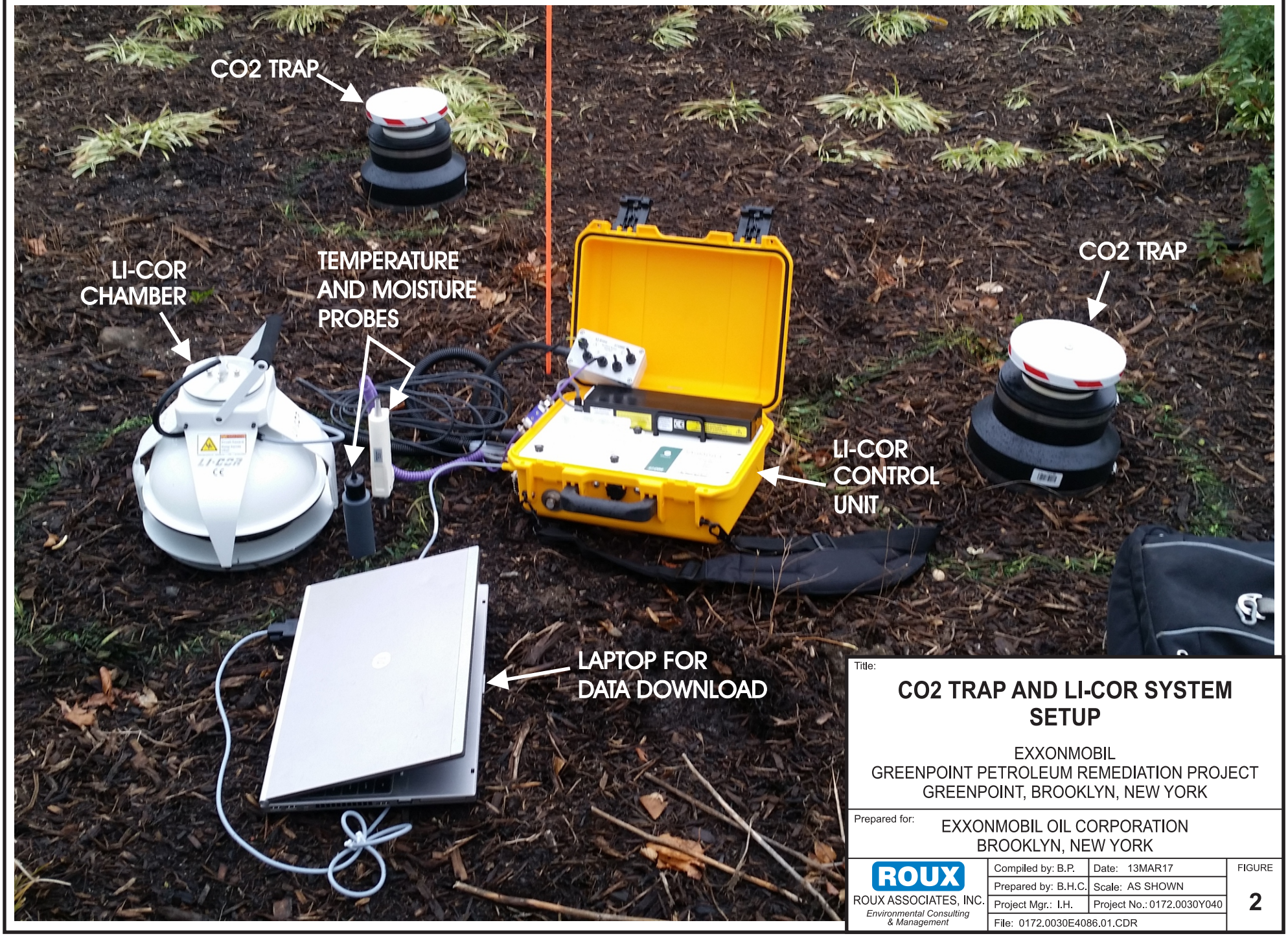
Prepared for: EXXONMOBIL OIL CORPORATION
BROOKLYN, NEW YORK

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Environmental Consulting & Management

Compiled by: B.P.	Date: 10MAR17	FIGURE
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Title:

CO2 TRAP AND LI-COR SYSTEM SETUP

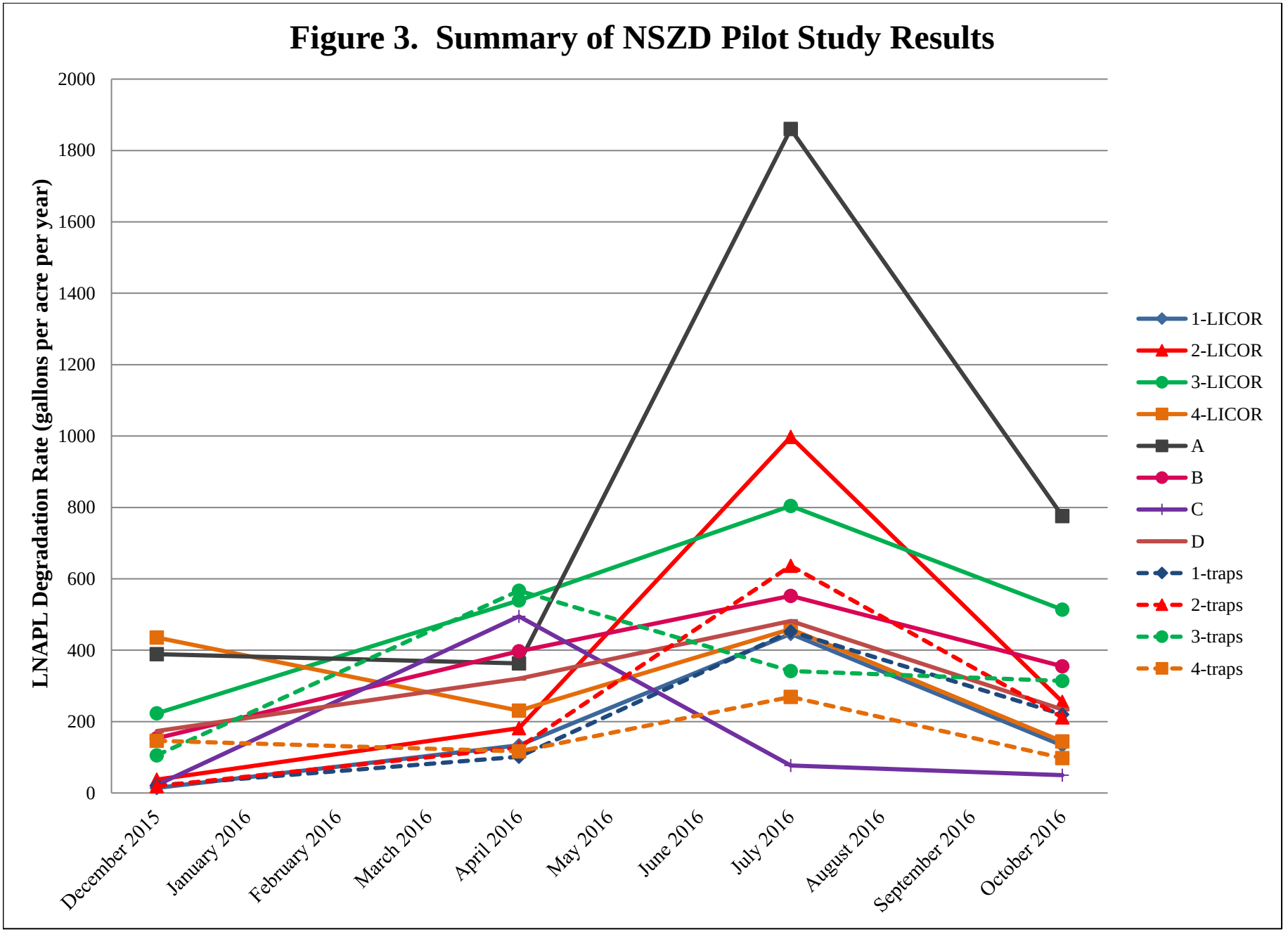
EXXONMOBIL
GREENPOINT PETROLEUM REMEDIATION PROJECT
GREENPOINT, BROOKLYN, NEW YORK

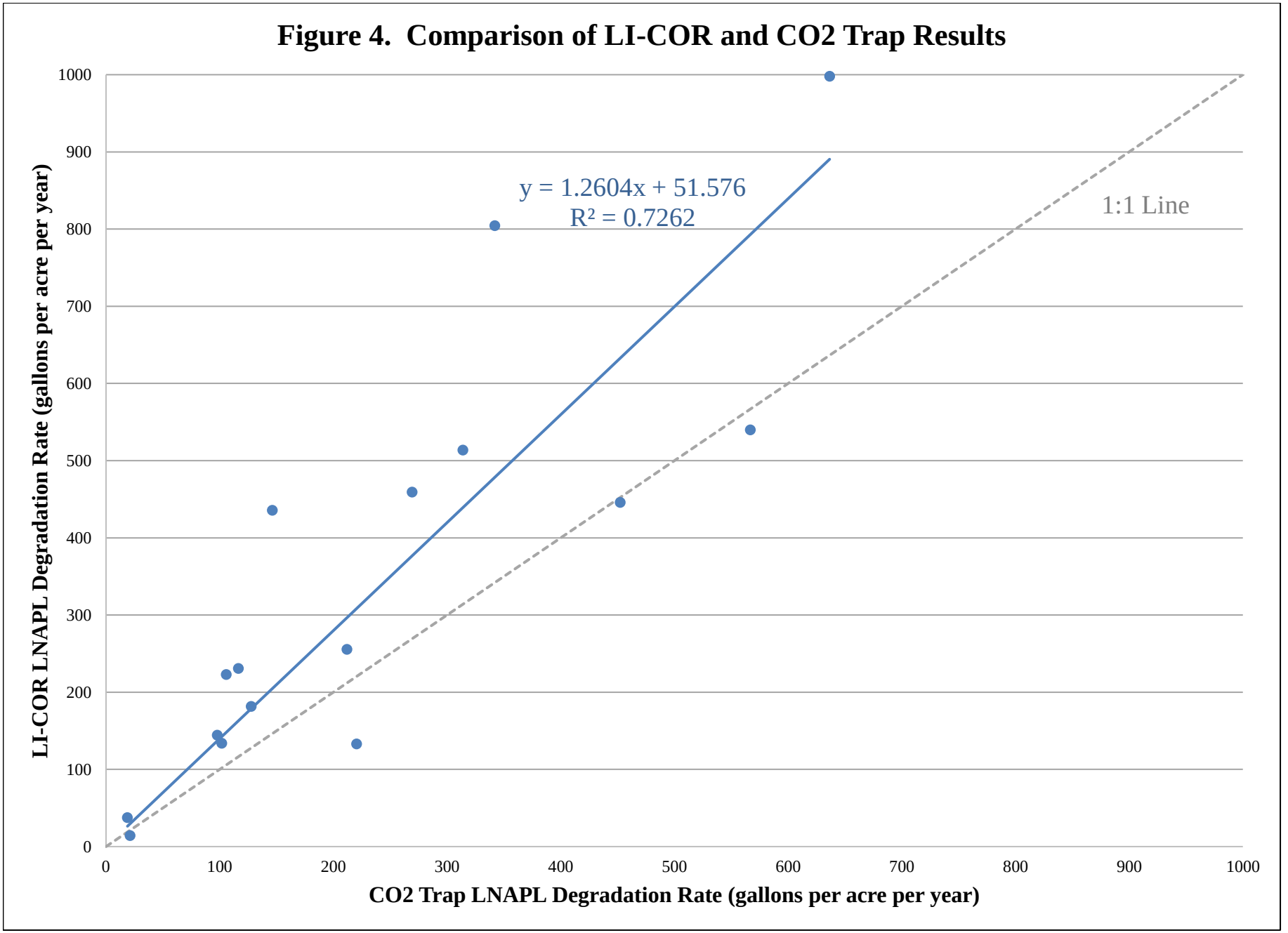
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BROOKLYN, NEW YORK

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Prepared by: B.H.C.	Scale: AS SHOWN	2
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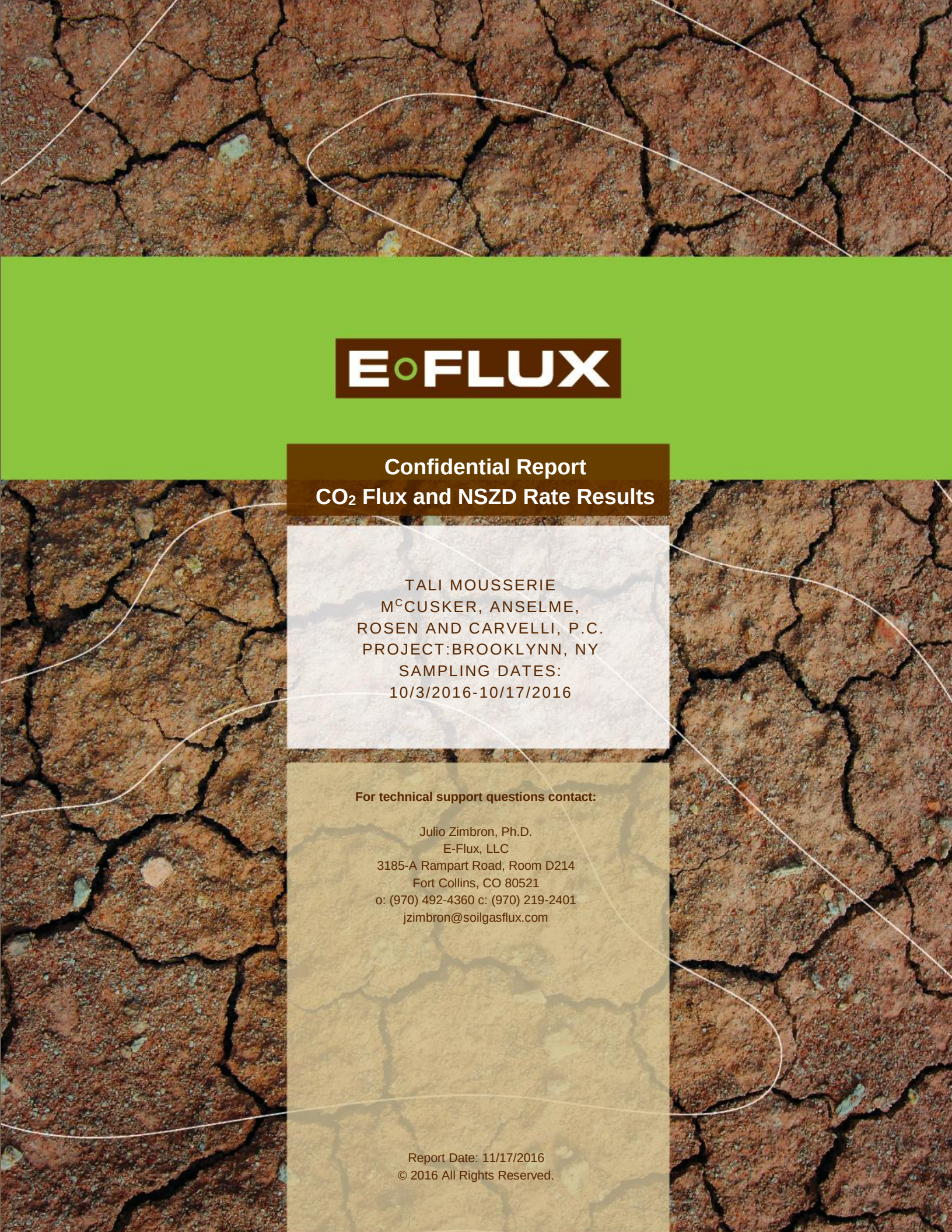
Figure 3. Summary of NSZD Pilot Study Results




Figure 4. Comparison of LI-COR and CO2 Trap Results
LI-COR LNAPL Degradation Rate (gallons per acre per year)
CO2 Trap LNAPL Degradation Rate (gallons per acre per year)
y = 1.2604x + 51.576
R² = 0.7262
1:1 Line
0
100
200
300
400
500
600
700
800
900
1000

ATTACHMENT 1

E-FLUX October 2016 Results Report



Confidential Report
CO_2 Flux and NSZD Rate Results

TALI MOUSSERIE
M^{C}CUSKER, ANSELME,
ROSEN AND CARVELLI, P.C.
PROJECT:BROOKLYNN, NY
SAMPLING DATES:
10/3/2016-10/17/2016

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Report Date: 11/17/2016

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The purpose of this document is to provide sample calculations of the results reported here and to explain the basis for differentiating petroleum hydrocarbon-derived CO_2 (i.e., fossil fuel CO_2) from modern CO_2 interferences. The following topics are addressed:

- The Value of ^{14}C Analysis
- Site Specific Study Results and Applicable Notes
- Calculation Explanations
- References

The Value of the ^{14}C Analysis

How to differentiate petroleum hydrocarbon-derived CO2 from modern CO_2 interferences using CO2 flux traps.

Unimpacted soils have natural CO_2 flux generation rates, due to microbial root zone activity and/or the degradation of natural organic matter (NOM). Thus, the total CO_2 flux measured at an impacted location is the sum of both natural soil respiration processes and those related to LNAPL degradation (Sihota et al, 2011).

The CO_2 flux due to natural soil respiration can be estimated by measuring CO_2 fluxes at unimpacted locations, and subtracting such rates from the total CO_2 fluxes at LNAPL impacted locations in order to estimate CO_2 flux due to LNAPL degradation (Sihota et al, 2012). This is known as the “background correction” and assumes that the rates of natural soil respiration (i.e., modern carbon CO_2 fluxes) are similar for both impacted and unimpacted locations.

The difficulties of this approach are: a) at many industrial facilities it is difficult to find unimpacted locations, and b) the unimpacted locations have very different vegetation to that at the impacted locations. This document provides the basis to use carbon isotope analysis as a location specific correction to the total carbon CO_2 fluxes, designed to overcome the limitations of the background correction.

Carbon Isotope Analysis Methodology

Upon sampling and analysis of the samples by the methods described before (McCoy et al, 2015), the analysis for carbon isotopes is conducted on the homogenized solid samples from the CO_2 flux traps.

Unstable isotopic analysis has been previously used to differentiate anthropogenic (due to fossil fuel-burning) and natural sources of atmospheric CO, CO_2 and methane (for example, Klouda and Connolly, 1995; Levin et al, 1995; Avery et al, 2006). Such findings are the basis of ASTM Method D6686-12, Determining the Biobased Content in Solids, Liquids and Gases Using Radiocarbon Analysis (ASTM, 2012). The technique relies on the analysis of ^{14}C, an unstable carbon isotope (with a half-life of approximately 5600 years) that is generated by cosmic rays in the atmosphere. Thus, contemporary (modern) organic carbon is ^{14}C-rich, while fossil fuel carbon is completely ^{14}C-depleted. Furthermore, contemporary samples and atmospheric samples have the same characteristic amount of ^{14}C. The detection limit of ^{14}C by accelerator mass spectrometry enables dating of samples younger than 60,000

years, while older samples (such as fossil fuels) have non-detectable ^{14}C activity (Stuiver and Polach, 1977).

For a sample that contains carbon from both modern and fossil fuel carbon sources, measurement of the ^{14}C enables quantitation of both source contributions. The fossil fuel fraction of the sample, ff_{sample}, and the remaining non-fossil fuel or contemporary fraction ($1- ff_{sample}$), are related by the following two-component mass balance:

$$Fm_{sample} = ff_{sample}\left(Fm_{ff}\right)+\left(1- ff_{sample}\right)\left(Fm_{atm}\right)$$

In this formula, Fm_{sample} is the measured modern fraction of the sample, Fm_{ff} is the fraction of modern carbon in fossil fuel ($Fm_{ff} = 0$), and Fm_{atm} is the fraction of modern carbon in contemporary living material ($Fm_{atm} = 1.05$) (Hua et al., 2013). By convention, the reporting of carbon isotope analysis is based on a 1950 NBS oxalic acid standard, synthesized when the ^{14}C atmospheric levels were lower than current ones due to nuclear tests. Thus, Fm_{sample} is reported as if the analysis was done in 1950, and Fm_{atm} is counter-intuitively larger than 1.

Expected Results and Recommendations

Our results suggest that the ^{14}C-based technique offers a built-in, location specific correction for fossil fuel as an alternative to the background correction often done at these sites. Earlier data on a limited amount of samples suggested that results using the ^{14}C-correction were equivalent to the background correction (McCoy et al, 2015; Sihota et al, 2012). However, a recent compilation at 4 sites comparing results from the background correction to the ^{14}C-correction suggests that modern carbon fluxes can vary over a factor of 5x for different locations within the same site (Zimbron and Kasyon, 2015). The resulting difference between the background-corrected estimates and the fossil-fuel carbon corrected data can be up to one order of magnitude (depending on the location).

This finding suggests that the assumption implied by the background correction that the modern carbon flux is constant for an entire site might introduce large errors in the correction for petroleum-biodegradation derived CO_2 fluxes. Contrary to the background correction, the ^{14}C-based correction is collocated with the measurement, and thus spatially unbiased by uncertainties related to differences with respect to background location(s) (i.e., due to different vegetation and lithology, unknown impacts, different gas transport regimes, high sensitivity to soil moisture, etc).

The fossil-fuel carbon content on the unexposed sorbent is non-zero (typically around 30%). This might be the result of either a background fossil fuel signature of the sorbent (due to processing of the chemical or mineral sources), or due to material handling (i.e., exposure to fossil fuel fumes). Although the fossil fuel CO_2 mass is very small, this error is adjusted by a travel blank correction procedure. This consists of subtracting the fossil fuel CO_2 mass from an unexposed trap (a travel blank) from those measured on the traps deployed in the field. The ^{14}C analysis is done on CO_2 sorbent subsamples, after homogenization.

Study Results

The report and results below are based on proprietary technology to measure the soil gas efflux. All information contained in this report is strictly confidential to the customer. The chemical analysis is based on methods ASTM 4373-02 (Rapid Determination for Carbonate Content in Soils) and ASTM D6686-12 (Determining the Biobased Content in Solids, Liquids and Gases Using Radiocarbon Analysis).

The site specific results and interpretation are as follows:

EOFLUX
Easy set-up. Expert results.

Project: Brooklyn, NY

Customer: McCusker, Anselme, Rosen and Carvelli, P.C.

Customer Contact: Tali Mousserie

Report Date: 17-Nov-16

Sample ID	Deployment Dates			Raw Results (not blank corrected)					Blank Corrected Results[a] and ^{14}C Analysis (Fossil Fuel)								
	Deployed	Retrieved	Days	Moisture	Dry Sorbent Mass (g)	Num. of Reps.	Avg CO_2[b]	CV CO_2[c]	Carbon Content[d] %	Carbon Content[d] (g)	CO_2 Flux[e] (microM/ m^2.sec)	Modern Carbon, As Reported[g]	Std. Dev. Modern	Modern CO_2 Flux (microM/ m^2.sec)	Contemporary Fossil Fuel Carbon	Grams Of Fossil Fuel CO_2 (g)	Fossil Fuel CO_2 Flux (microM/ m^2.sec)	Equivalent Fossil Fuel-Based NAPL Loss Rate (gallons/ acre.yr)
BROO-R8-CO2-TB	NA	NA	-	16.8%	42.905	2	1.09%	1.12%	-	-	-	76.7%	0.45%	-	27.0%	-	-	-
BROO-R8-CO2-01	10/3/16 8:39	10/17/16 12:36	14.16	35.5%	43.310	2	2.69%	1.75%	1.6%	0.70	0.40	82.4%	0.34%	0.33	21.5%	0.12	0.07	44
BROO-R8-CO2-02	10/3/16 8:44	10/17/16 12:38	14.16	22.5%	45.399	2	4.15%	0.97%	3.1%	1.39	0.80	74.0%	0.30%	0.56	29.5%	0.42	0.24	152
BROO-R8-CO2-03	10/3/16 8:48	10/17/16 12:41	14.16	16.3%	47.888	2	16.23%	1.80%	15.1%	7.25	4.15	65.6%	0.30%	2.56	37.5%	2.78	1.59	994
BROO-R8-CO2-04	10/3/16 9:08	10/17/16 14:26	14.22	18.7%	44.686	2	5.32%	0.22%	4.2%	1.89	1.08	67.7%	0.26%	0.67	35.6%	0.71	0.41	255
BROO-R8-CO2-05	10/3/16 9:11	10/17/16 14:24	14.22	25.5%	46.005	2	4.76%	0.68%	3.7%	1.69	0.96	73.5%	0.46%	0.67	30.0%	0.52	0.30	186
BROO-R8-CO2-06	10/3/16 9:43	10/17/16 13:53	14.17	15.5%	52.266	2	31.69%	0.44%	30.6%	16.00	9.16	99.3%	0.37%	8.73	5.4%	0.75	0.43	267*
BROO-R8-CO2-07	10/3/16 9:46	10/17/16 13:52	14.17	12.3%	55.857	2	38.55%	0.98%	37.5%	20.93	11.98	99.3%	0.31%	11.40	5.4%	1.01	0.58	361*
BROO-R8-CO2-08	10/3/16 11:05	10/17/16 14:50	14.16	18.1%	44.066	2	4.91%	0.31%	3.8%	1.69	0.97	79.4%	0.70%	0.74	24.4%	0.40	0.23	143
BROO-R8-CO2-09	10/3/16 11:10	10/17/16 14:51	14.15	19.1%	44.523	2	5.46%	0.08%	4.4%	1.95	1.12	65.5%	0.24%	0.67	37.6%	0.78	0.45	281

This report contains Confidential Information and is to be delivered only to the Customer indicated above.

See following page for assumptions, project specific quality assurance/quality control information, and notes.

The Following Assumptions and General Notes apply:

a. Results are travel blank corrected but not background location corrected.
Blank Corrected Results = Raw Results - Travel Blank

b. Number of Replicates: Carbon analysis was conducted in duplicate if CV ≤ 5%. If CV > 5%, carbon analysis was conducted with triplicates. Avg % refers to the percent of CO2 in the dry sorbent mass before blank corrected.

c. CV is coefficient of variation, equal to the ratio of the standard deviation over the average.

d. If trap carbon content is not larger than travel blank, results are reported as ND.

e. Trap cross sectional area is 3.24 x 10^{-2} m^2 (i.e., equivalent to an 8in receiver pipe).

f. The flux equivalence is 1 microMole/(m^2.sec) equals 625 gallons/(acre.yr). This assumes a hydrocarbon density of 0.77 g/mL and a formula of C_8H_{18}.

g. "As reported" refers to % modern carbon at the time of development of the test (1950).

h. Adjusted fossil fuel carbon has been transformed from the "As reported" basis (1950) to present ^{14}C levels.

NA means Not Applicable.

*Traps were above typical saturation limits (30%). Actual results may be higher than reported.

Quality Assurance / Quality Control Notes:

- The Travel Blank (TB) concentration for this report was 1.09%. Typical Travel Blank concentration is <2%.
- Trap tops were not saturated with CO_2. Maximum measured top concentration was *7.5%* (sample BROO-R8-CO2-07). Sorbent saturation is 30%.
- Modern carbon fluxes represent the contribution of plant and microbial activity to the total carbon flux that the ^{14}C analysis corrects for. Average modern CO_2 flux was 2.92 microMole/m^2.s, with a coefficient of variation of 142%.
- ASTM 4373-02 QA/QC criteria does not provide acceptable variability (CV) standards. Similar methods (for example the carbonates in water, such as ASTM 513.02) provide typical error ≤20%. E-Flux practice is that a CV ≤5% is acceptable.

Calculation Explanations

Conversion of grams CO_2 to CO_2 Flux

Calculating the CO_2 flux from grams of CO_2 involves the cross-sectional area of the trap as well as the number of days that the trap was deployed in the field. The cross-sectional area of the trap is 8.11 x 10^{-3} m^2 (for a 4in receiver). The molecular weight of CO_2 is 44 g/mol. Converting g of CO_2 to CO_2 flux is as follows:

$$\frac{\left(g\ CO_2 * \left(\frac{1\ mol\ CO_2}{44\ g\ CO_2}\right) * \left(\frac{1{,}000{,}000\ micromol\ CO_2}{mol\ CO_2}\right) * \left(\frac{1}{8.11 * 10^{-3}\ m^2}\right)\right)}{days\ in\ the\ field * \frac{24\ hr}{day} * \frac{3600\ sec}{hr}} = \frac{micro\ mol\ CO_2}{m^2 * sec}$$

Conversion of Modern C to Fossil Fuel C

Reported modern carbon content (from carbon dating or ^{14}C analysis) is by convention at the ^{14}C levels as of the time of development of the test (1950). Due to higher current levels of ^{14}C in the environment resulting from atomic testing, current (contemporary) levels are approximately 5% higher than in 1950 (Hua et al., 2013). Thus, fossil fuel C can be found with the following conversions:

$$\%\ Modern\ C_{contemporary} = \frac{\%\ Modern\ C_{1950}}{1.05}$$

$$Contemporary\ fossil\ fuel\ C\ \% = 1 - \%\ Modern\ C_{contemporary} = 1 - \frac{\%\ Modern\ C_{1950}}{1.05}$$

Calculating Grams of Fossil Fuel CO_2

Calculating grams of fossil fuel (ff) CO_2 is based on the travel blank corrected percent fossil fuel carbon in the sample (the difference between total fossil fuel CO_2 in the sample and that of the travel blank). This is done as follows:

$$g\ CO_{2(ff)} = g\ sorbent * \left((Avg\ sample\ \%\ CO_2 * ff\ sample\ \%\ C) - (Avg\ TB\ \%\ CO_2 * ff\ TB\ \%\ C)\right)$$

Calculation to Convert Carbon Flux to Equivalent LNAPL Loss Rate

The intermediate reactions for LNAPL mineralization include methanogenesis (production of methane and CO_2) and the subsequent aerobic oxidation of methane (into CO_2):

$$C_8H_{18} + 3.5\ H_2O \rightarrow 6.25\ CH_4 + 1.75\ CO_2$$

$$6.25\ CH_4 + 12.5\ O_2 \rightarrow 6.25\ CO_2 + 12.5\ H_2O$$

The overall reaction (the summation of both reactions), is:

$$C_8H_{18} + 12.5\ O_2 \rightarrow\ 9H_2O + 8\ CO_2$$

For C_8H_{18}, the molecular weight is 114.23 g/mole. Assuming an LNAPL density of 0.77 g/mL (in the upper range of gasoline, for a conservative estimate), the following unit conversion results:

$$1\frac{\mu Mole\ CO_2}{m^2\ s}$$
$$= \frac{\mu Mole\ CO_2}{m^2\ s} \times \left(\frac{1\ \mu Mole\ C_8H_{18}}{8\ \mu Mole\ CO_2}\right) \times \left(\frac{Mole}{1 \times 10^6 \mu Mole}\right) \times \left(\frac{4{,}046\ m^2}{1\ acre}\right) \times \left(\frac{3600\ s}{1\ h}\right) \times \left(\frac{24\ h}{1\ d}\right) \times \left(\frac{365\ d}{1\ yr}\right)$$
$$\times \left(\frac{114\ g\ C_8H_{18}}{1\ Mole\ C_8H_{18}}\right) \times \left(\frac{1\ mL\ C_8H_{18}}{0.77\ g\ C_8H_{18}}\right) \times \left(\frac{1\ L}{1000 mL}\right) \times \left(\frac{1\ gallon}{3.785\ L}\right) = 625\frac{gallon\ C_8H_{18}}{acre.yr}$$

Note that both the LNAPL formula and its density are assumed, and thus subject to uncertainty. If available, site specific data can be used.

Alternative assumptions on the LNAPL formula and its corresponding density generally result in slightly different conversion factors, within 10-15% of the value shown here. Thus, such uncertainty still results in an acceptable estimate.

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