



Confidential Report
CO₂ Flux and NSZD Rate Results

AMAYA SAYAS
AECOM
PROJECT: ALCANIZ, SP
UNDER CONCRETE
SAMPLING DATES:
9/28/2017-10/6/2017

For technical support questions contact:

Julio Zimbron, Ph.D.
E-Flux, LLC
3185-A Rampart Road, Room D214
Fort Collins, CO 80521
o: (970) 492-4360 c: (970) 219-2401
jzimbron@soilgasflux.com

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 CO₂ (i.e., fossil fuel CO₂) from modern CO₂ interferences. The following topics are addressed:

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

The Value of the ¹⁴C Analysis

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

Unimpacted soils have natural CO₂ flux generation rates, due to microbial root zone activity and/or the degradation of natural organic matter (NOM). Thus, the total CO₂ 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 CO₂ flux due to natural soil respiration can be estimated by measuring CO₂ fluxes at unimpacted locations, and subtracting such rates from the total CO₂ fluxes at LNAPL impacted locations in order to estimate CO₂ 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 CO₂ 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 CO₂ 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 CO₂ flux traps.

Unstable isotopic analysis has been previously used to differentiate anthropogenic (due to fossil fuel-burning) and natural sources of atmospheric CO, CO₂ 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 ¹⁴C, 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 ¹⁴C-rich, while fossil fuel carbon is completely ¹⁴C-depleted. Furthermore, contemporary samples and atmospheric samples have the same characteristic amount of ¹⁴C. The detection limit of ¹⁴C 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 ($1 - ff_{\text{sample}}$), are related by the following two-component mass balance:

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

In this formula, Fm_{sample} is the measured modern fraction of the sample, Fm_{ff} is the fraction of modern carbon in fossil fuel ($Fm_{\text{ff}} = 0$), and Fm_{atm} is the fraction of modern carbon in contemporary living material ($Fm_{\text{atm}} = 1.05$) (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:



Easy set-up. Expert results.

Project:

Alcaniz, Spain

Customer:

AECOM

Customer Contact:

Amaya Sayas

Report Date:

20-Nov-17

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. ^b	Avg CO ₂ ^b	CV CO ₂ ^c	Carbon Content ^d		CO ₂ Flux ^e (microM/ m ² .sec)	Modern Carbon, As Reported ^g	Std. Dev. Modern	Modern CO ₂ Flux (microM/ m ² .sec)	Adjusted Fossil Fuel Carbon ^h	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)
									%	(g)								
AZES-R1-CO2-TB	NA	NA	0.00	17.4%	42.421	2	0.93%	0.83%	-	-	-	79.9%	0.24%	-	23.9%	-	-	-
AZES-R1-CO2-01*	9/28/17 15:45	10/6/17 10:12	7.77	27.8%	40.636	2	1.10%	1.30%	0.2%	0.07	0.3	77.1%	0.25%	0.2	26.6%	0.03	0.1	74
AZES-R1-CO2-02	9/28/17 17:24	10/6/17 10:18	7.70	24.4%	42.096	2	1.36%	0.01%	0.4%	0.18	0.8	80.4%	0.32%	0.6	23.4%	0.04	0.2	108
AZES-R1-CO2-03	9/28/17 15:56	10/6/17 9:56	7.75	24.3%	44.358	2	10.40%	1.91%	9.5%	4.20	17.6	32.2%	0.17%	4.6	69.4%	3.10	13.0	8,113
AZES-R1-CO2-04	9/28/17 16:29	10/6/17 10:04	7.73	22.4%	45.141	2	14.85%	2.34%	13.9%	6.28	26.4	21.8%	0.14%	4.5	79.2%	5.21	21.9	13,663
AZES-R1-CO2-05*	9/28/17 15:35	10/6/17 9:50	7.76	26.3%	44.467	2	5.53%	0.83%	4.6%	2.05	8.6	68.0%	0.23%	5.3	35.2%	0.77	3.2	2,006

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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 $CV \leq 5\%$. If $CV > 5\%$, carbon analysis was conducted with triplicates. Avg % refers to the percent of CO_2 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. Expressed as CO_2 not pure carbon.
 - e. Trap cross sectional area is $8.11 \times 10^{-3} \text{ m}^2$ (i.e., equivalent to a 4in receiver pipe).
 - f. The flux equivalence is 1 microMole/($\text{m}^2 \cdot \text{sec}$) 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.
- * Caps for trap 1 (top) and trap 5 (top) were cracked upon arrival.

NA means Not Applicable.

Quality Assurance / Quality Control Notes:

- o The Travel Blank (TB) concentration for this report was **0.93%**. Typical Travel Blank concentration is $<2\%$.
- o Trap tops were not saturated with CO_2 . Maximum measured top concentration was **1.15%** (sample AZES-R1-CO2-02.1). Sorbent saturation is 30%.
- o 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 **3.04** microMole/ $\text{m}^2 \cdot \text{s}$, with a coefficient of variation of **81%**.
- o 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 $\leq 20\%$. E-Flux practice is that a CV $\leq 5\%$ is acceptable.

Calculation Explanations

Conversion of grams CO₂ to CO₂ Flux

Calculating the CO₂ flux from grams of CO₂ 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 $8.11 \times 10^{-3} \text{ m}^2$ (for a 4in receiver). The molecular weight of CO₂ is 44 g/mol. Converting g of CO₂ to CO₂ flux is as follows:

$$\frac{\left(g \text{ CO}_2 * \left(\frac{1 \text{ mol CO}_2}{44 \text{ g CO}_2} \right) * \left(\frac{1,000,000 \text{ micromol CO}_2}{\text{mol CO}_2} \right) * \left(\frac{1}{8.11 * 10^{-3} \text{ m}^2} \right) \right)}{\text{days in the field} * \frac{24 \text{ hr}}{\text{day}} * \frac{3600 \text{ sec}}{\text{hr}}} = \frac{\text{micro mol CO}_2}{\text{m}^2 * \text{sec}}$$

Conversion of Modern C to Fossil Fuel C

Reported modern carbon content (from carbon dating or ¹⁴C analysis) is by convention at the ¹⁴C levels as of the time of development of the test (1950). Due to higher current levels of ¹⁴C 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:

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

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

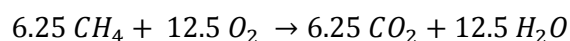
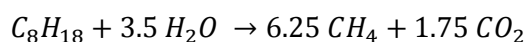
Calculating Grams of Fossil Fuel CO₂

Calculating grams of fossil fuel (ff) CO₂ is based on the travel blank corrected percent fossil fuel carbon in the sample (the difference between total fossil fuel CO₂ in the sample and that of the travel blank). This is done as follows:

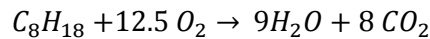
$$g \text{ CO}_{2(\text{ff})} = g \text{ sorbent} * ((\text{Avg sample \% CO}_2 * \text{ff sample \% C}) - (\text{Avg TB \% CO}_2 * \text{ff TB \% C}))$$

Calculation to Convert Carbon Flux to Equivalent LNAPL Loss Rate

The intermediate reactions for LNAPL mineralization include methanogenesis (production of methane and CO₂) and the subsequent aerobic oxidation of methane (into CO₂):



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



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:

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

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.

References

ASTM (2012), Method D6686-12, Determining the Biobased Content in Solids, Liquids and Gases Using Radiocarbon Analysis.

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Confidential Report
CO₂ Flux and NSZD Rate Results

CARLOS MAGARZO
AMAYA SAYAS
AECOM
PROJECT: ALCANIZ, SPAIN
UNDER CONCRETE
SAMPLING DATES:
4/20/2018-5/3/2018

For technical support questions contact:

Julio Zimbron, Ph.D.
E-Flux, LLC
3185-A Rampart Road, Room D214
Fort Collins, CO 80521
o: (970) 492-4360 c: (970) 219-2401
jzimbron@soilgasflux.com

The purpose of this document is to provide sample calculations for the reported results, and to explain the method for differentiating petroleum hydrocarbon-derived CO₂ from that produced from natural soil respiration processes. The value of the ¹⁴C analysis, site-specific study results and applicable notes, calculation explanations, and references are included.

The Value of the ¹⁴C Analysis

How to differentiate between petroleum hydrocarbon-derived CO₂ and natural process-derived CO₂ using CO₂ flux traps:

Unimpacted soils naturally produce CO₂ fluxes due to microbial root zone activity and/or the degradation of natural organic matter (NOM). Thus, the total measured CO₂ flux at an impacted location is the sum of both natural soil respiration processes and those related to LNAPL degradation (Sihota and Mayer, 2012). The CO₂ flux caused by LNAPL degradation can be estimated by subtracting measured CO₂ fluxes at unimpacted locations from the total measured CO₂ fluxes at LNAPL impacted locations (Sihota and Mayer, 2012). This process is a spatial “background correction,” and assumes that the rates of natural soil respiration (i.e., present-day, bio-based CO₂ fluxes) are similar for both impacted and unimpacted locations. This approach is complicated to implement, given that at many industrial facilities it is difficult to find unimpacted areas, and that vegetation is different between impacted and unimpacted locations. Alternatively, carbon isotope analysis can be used as a location-specific correction for total measured carbon CO₂ fluxes, and effectively overcomes the limitations of the background correction.

Carbon Isotope Analysis Methodology:

Isotopic analysis has been previously used to differentiate between anthropogenic (due to fossil fuel-burning) and natural sources of atmospheric CO, CO₂, and methane (for example, Klouda and Connolly, 1995; Levin et al., 1995; Avery et al., 2006). These findings form the basis of ASTM Method D6686-12, “Determining the Biobased Content in Solids, Liquids and Gases Using Radiocarbon Analysis” (ASTM, 2012). This technique relies on the analysis of ¹⁴C, an unstable carbon isotope with an absolute half-life of 5,730 years, which is generated by cosmic rays in the atmosphere. Thus, living and bio-based organic carbon is ¹⁴C-rich, while fossil fuel carbon is completely ¹⁴C-depleted. Furthermore, bio-based organic carbon and atmospheric samples have the same characteristic amount of ¹⁴C. Despite the use of highly sensitive accelerator mass spectrometry (AMS), the short isotopic half-life of ¹⁴C only allows for dating of samples younger than 60,000 years, while older samples (such as fossil fuels) contain non-detectable amounts of ¹⁴C and thus cannot be dated using this method (Stuiver and Polach, 1977).

For samples that contain both contemporary and fossil fuel carbon, such as E-Flux’s fossil fuel traps, measurement of ¹⁴C enables quantitation of *both* source contributions. The fossil fuel-derived fraction of the sample (ff_{sample}) and the remaining non-fossil fuel fraction ($1 - ff_{sample}$) are related by the following two-component mass balance (modified from Avery, Jr. et al., 2006):

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

Here, Fm_{sub} represents the fraction of modern, a measure of how close the present ¹⁴C/¹²C ratio of the sample is to the ratio from 1950, which is derived from a pre-industrial era standard. Fm_{sample} is the total measured fraction of modern of the sample, which takes all ¹⁴C from the sample into account. Fm_{ff} is the fraction of modern of only the fossil fuel portion of the sample; this number is 0, as there is no ¹⁴C in fossil fuel-derived

CO₂. Fm_{atm} is the fraction of modern of the part of the sample derived from living material and natural soil respiration processes; this value has been experimentally determined and is considered a fixed value at each point in time, and is currently equal to 1.05 (Hua et al., 2013). By convention, the results of carbon isotope analysis are reported based on a 1950 NBS oxalic acid standard, and so Fm_{sample} is reported as if the analysis was done in 1950. However, current ¹⁴C atmospheric levels are now higher than in 1950 due to nuclear testing, meaning that Fm_{atm} is counter-intuitively larger than 1 (as the ¹⁴C/¹²C sample ratio is higher now than it would have been in 1950).

Expected Results and Recommendations:

Recent work suggest that the ¹⁴C-based technique offers a built-in, location-specific correction as an alternative to a background correction, as is often done for contaminated sites. Earlier work on a limited amount of samples suggests that ¹⁴C-corrected results are equivalent to background-corrected results (McCoy et al., 2015; Sihota and Mayer, 2012). However, a recent compilation of 4 sites comparing results from the background correction to the ¹⁴C correction suggests that measured carbon fluxes are highly variable and can differ by up to five times among different locations within the same site (Zimbron and Kasyon, 2015). Depending on the location, the resulting difference between background-corrected and ¹⁴C-corrected estimates can be up to one order of magnitude.

This suggests that the assumption implied by the background correction (that the non-fossil fuel carbon flux is constant for an entire site) might introduce large errors in the background correction of petroleum biodegradation-derived CO₂ fluxes. Contrary to the background correction, the ¹⁴C correction is co-located with the measurement, and thus is spatially unbiased by uncertainties related to differences with respect to the background location(s) (i.e., different vegetation and lithology, unknown impacts, different gas transport regimes, high sensitivity to soil moisture, etc).

The fossil-fuel carbon content of unexposed CO₂ sorbent as used in the traps is non-zero (typically around 30%). This might be the result of processing of the chemical or mineral sources, or of material handling (e.g., exposure to fossil fuel fumes). Although this fossil fuel CO₂ mass is very small, its effects on the results are removed by carrying out a travel blank correction: the mass of fossil fuel CO₂ from an unexposed trap (a travel blank) is subtracted from the masses of fossil fuel CO₂ from field-deployed traps. The ¹⁴C analysis is then performed on CO₂ sorbent sub-samples after homogenization of the entire bottom layer of sorbent, which follows sampling and sample analysis procedures from McCoy et al. (2015).

Study Results

The reported results below are based on proprietary technology used to measure 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; ASTM, 2002) and ASTM D6686-12 (Determining the Biobased Content in Solids, Liquids and Gases Using Radiocarbon Analysis; ASTM, 2012).

The site-specific results and interpretation are as follows:



Easy set-up. Expert results.

Project:
Alcaniz, Spain

Customer:
AECOM

Customer Contact:
Carlos Magarzo / Amaya Sayas

Report Date:
20-Jun-18

Sample ID	Deployment Dates			Raw Results (not blank corrected)				¹³ C Results ^a	Blank Corrected Results ^b			Blank Corrected ¹⁴ C Analysis Results (Fossil Fuel) ^c						
	Deployed	Retrieved	Days	Dry Sorbent Mass, g	Num. of Reps. ^d	Avg. CO ₂ ^e , %	CV CO ₂ ^f , %	Results (Not Travel Blank Corrected)	Carbon Content ^g		CO ₂ Flux, $\mu\text{mol m}^{-2} \text{s}^{-1}$	Fraction of Modern Carbon, As Reported ^h	Std. Dev., 1 σ	Contemporary CO ₂ Flux, $\mu\text{mol m}^{-2} \text{s}^{-1}$ ⁱ	Adjusted Fossil Fuel Carbon ^j	Grams Of Fossil Fuel CO ₂ , g	Fossil Fuel CO ₂ Flux, $\mu\text{mol m}^{-2} \text{s}^{-1}$	Equivalent Fossil Fuel-Based NAPL Loss Rate, gal. acre ⁻¹ yr ⁻¹
									%	g								
TB AVERAGE	NA	NA	NA	41.903	2	1.45%	NA	0	0.00%	0.00	NA	67.6%	0.31%	NA	35.7%	0.00	NA	NA
AZES-R2-CO2-TB	NA	NA	NA	41.454	2	1.36%	2.50%	4	-0.09%	-0.04	NA	68.1%	0.36%	NA	35.2%	-0.02	NA	NA
AZES-R2-CO2-TB2	NA	NA	NA	42.351	2	1.55%	4.74%	-3	0.09%	0.04	NA	67.0%	0.25%	NA	36.2%	0.02	NA	NA
AZES-R2-CO2-01	4/20/18 11:42	5/3/18 13:58	13.09	41.119	2	1.83%	0.77%	-9	0.38%	0.16	0.38	73.8%	0.25%	0.36	29.7%	0.01	0.03	16
AZES-R2-CO2-02	4/20/18 11:32	5/3/18 13:55	13.10	40.879	2	1.33%	2.29%	24	ND	ND	ND	65.7%	0.43%	ND	37.4%	ND	ND	ND
AZES-R2-CO2-03	4/20/18 11:18	5/3/18 13:45	13.10	42.457	2	5.67%	2.62%	-25	4.22%	1.79	4.44	43.4%	0.17%	1.48	58.7%	1.19	2.96	1848
AZES-R2-CO2-04	4/20/18 11:25	5/3/18 13:50	13.10	37.869	2	5.17%	4.87%	-21	3.71%	1.41	3.48	30.7%	0.18%	0.54	70.7%	1.19	2.94	1839
AZES-R2-CO2-05	4/20/18 11:05	5/3/18 13:40	13.11	42.340	2	3.56%	1.83%	-16	2.10%	0.89	2.20	64.2%	0.23%	1.30	38.8%	0.37	0.90	566

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

General notes:

- Trap cross sectional area is $8.11 \times 10^{-3} \text{ m}^2$ (i.e., equivalent to a **4-inch** receiver pipe).
- The flux equivalence is $1 \text{ } \mu\text{mol m}^{-2} \text{ s}^{-1}$ equals **625.2** gallons acre⁻¹ yr⁻¹. This assumes a representative hydrocarbon density of 0.77 g mL^{-1} with the formula C_8H_{18} .
- NA = Not Applicable
- ND = Not Detectable
- Italicized values are calculated averages of the two travel blanks

Results Report Notes:

- ¹³C results are as reported by the carbon isotope lab (not travel blank corrected).
- Results are travel blank-corrected (using the average of the two travel blanks) and are not yet ¹⁴C-corrected. Blank Corrected Results = Raw Results - Travel Blank (average)
- Results have been both travel blank- and ¹⁴C-corrected.
- Number of Replicates: Carbon analysis of each trap/sample is conducted in duplicate if the coefficient of variation (CV) of the duplicates is $\leq 5\%$. If $\text{CV} > 5\%$, duplicate analyses are repeated until $\text{CV} \leq 5\%$.
- "Avg. CO₂" refers to the measured (not blank corrected) % CO₂ of the dry sorbent mass.
- CV is the coefficient of variation, the ratio of the standard deviation of the % CO₂ to the average % CO₂.
- If the travel blank contains more carbon than a trap, carbon content results (expressed as CO₂, not pure carbon) are generally reported as ND (note that negative numbers are shown for clarity for sample TB).
- "As reported" refers to the total measured fraction of modern ($F_{m\text{sample}}$) as it would have been at the time when ¹⁴C testing was developed (1950). This number is reported as pMC (percent of modern carbon) and is converted into F_m for our calculations using the relation $100.0 \text{ pMC} = 1.0 F_m = 100\% F_m$. This value has not been corrected to account for present-day ¹⁴C atmospheric levels.
- "Contemporary" indicates a correction has been applied which accounts for the difference between 1950's and present-day ¹⁴C levels (Stenström et al., 2011). This value is the portion of the total carbon flux derived from present-day (non-fossil fuel) sources.
- "Adjusted fossil fuel carbon" refers to the percentage of carbon in a sample that is derived from fossil fuel CO₂ according to ambient levels of ¹⁴C at the time of sampling. This number is adjusted to account for the increase in atmospheric ¹⁴C levels since 1950.

Quality Assurance / Quality Control Notes:

- The concentrations of the travels blanks are **1.36%** (TB) and **1.55%** (TB2), with an average of **1.45%**; typical TB concentration is $< 2\%$.
- Trap tops are not saturated with CO₂ (sorbent saturation is 30%). The maximum measured (not blank-corrected) top concentration is **1.75%** (sample 4).
- Contemporary carbon fluxes represent the CO₂ contributions from natural soil respiration processes (bio-based CO₂ production) to the total carbon flux; the ¹⁴C analysis corrects for this contribution. Average contemporary CO₂ flux is $0.92 \text{ } \mu\text{mol m}^{-2} \text{ s}^{-1}$, and the coefficient of variation is **60%**.
- **Sample 2** shows non-detectable (ND) fossil fuel CO₂ flux. This sample is not included in the contemporary CO₂ flux average or CV calculations. This sample was also saturated with water upon arrival, and had less total CO₂ than the travel blank(s).
- ASTM 4373-02 QA/QC criteria does not provide acceptable variability (CV) standards. Similar methods (e.g., ASTM 513.02, Analysis of Carbonates in Water) allow typical errors of $\leq 20\%$. E-Flux practice is that a $\text{CV} \leq 5\%$ for duplicate analyses is acceptable.

Calculation Explanations

Conversion of grams CO₂ to CO₂ Flux:

Calculating the CO₂ flux from grams of CO₂ involves the cross-sectional area of the trap ($8.11 \times 10^{-3} \text{ m}^2$ for a 4-inch receiver), the number of days that the trap was deployed in the field, and the molecular weight of CO₂ (44 g mol^{-1}). Grams of CO₂ is converted to CO₂ flux according to the following equation:

$$\frac{\text{g CO}_2 \cdot \frac{1 \text{ mol CO}_2}{44 \text{ g CO}_2} \cdot \frac{1,000,000 \text{ } \mu\text{mol CO}_2}{\text{mol CO}_2}}{\text{days in the field} \cdot \frac{24 \text{ hr}}{\text{day}} \cdot \frac{3600 \text{ s}}{\text{hr}} \cdot (8.11 \times 10^{-3} \text{ m}^2)} = \frac{\mu\text{mol CO}_2}{\text{m}^2 \cdot \text{s}}$$

Conversion of Fraction of Modern Carbon to Fossil Fuel Carbon:

Fraction of modern (Fm_{sample} , from ^{14}C analysis) is reported by convention based on ^{14}C levels from 1950. Because of atomic testing, current environmental ^{14}C levels are approximately 5% higher than they were in 1950 (Hua et al., 2013). Thus, the equation for calculating the fraction of fossil fuel carbon (ff_{sample}) is derived from the following mass balance:

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

Solving for ff_{sample} yields:

$$ff_{\text{sample}} = 1 - \frac{Fm_{\text{sample}}}{Fm_{\text{atm}}}$$

As Fm_{atm} is equal to 1.05, this equation becomes:

$$ff_{\text{sample}} = 1 - \frac{Fm_{\text{sample}}}{1.05}$$

The fraction of contemporary carbon (cc_{sample}) can then be calculated using the relation:

$$cc_{\text{sample}} = 1 - ff_{\text{sample}} = 1 - \left(1 - \frac{Fm_{\text{sample}}}{1.05}\right) = \frac{Fm_{\text{sample}}}{1.05}$$

Calculating Grams of Fossil Fuel CO₂:

Grams of fossil fuel CO₂ ($\text{g CO}_{2(\text{ff})}$) is calculated by subtracting the total fossil fuel CO₂ in the travel blank (TB) from the total fossil fuel CO₂ in the sample:

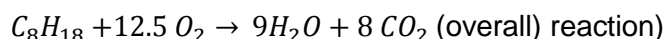
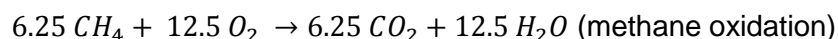
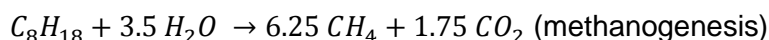
$$\text{g CO}_{2(\text{ff})} = \text{g}_{\text{sorbent}} \cdot [((\% \text{ CO}_2)_{\text{sample}}(ff_{\text{sample}})) - ((\% \text{ CO}_2)_{\text{TB}}(ff_{\text{TB}}))]$$

Here, $\text{g}_{\text{sorbent}}$ is the mass of sorbent used in the bottom layer of a trap, $(\% \text{ CO}_2)_{\text{sample}}$ is the average weight percent of CO₂ in the sample, ff_{sample} is the percent of carbon in the sample derived from fossil fuels,

$(\%CO_2)_{TB}$ is the average weight percent of CO_2 in the travel blank, and ff_{TB} is the percent of carbon in the travel blank derived from fossil fuels.

Converting 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):



Assuming a conservative LNAPL density of 0.77 g/mL (upper range of gasoline) and using the molecular weight of C_8H_{18} (octane, 114.23 g/mole), $\mu\text{mol m}^{-2} \text{ s}^{-1}$ of CO_2 can then be converted into $\text{gal. acre}^{-1} \text{ yr}^{-1}$:

$$1 \frac{\mu\text{mol } CO_2}{\text{m}^2 \text{ s}} \cdot \left(\frac{1 \mu\text{mol } C_8H_{18}}{8 \mu\text{mol } CO_2} \right) \left(\frac{\text{mol}}{1 \times 10^6 \mu\text{mol}} \right) \left(\frac{4,046 \text{ m}^2}{1 \text{ acre}} \right) \left(\frac{3600 \text{ s}}{1 \text{ h}} \right) \left(\frac{24 \text{ h}}{1 \text{ d}} \right) \left(\frac{365 \text{ d}}{1 \text{ yr}} \right) \cdot$$

$$\left(\frac{114 \text{ g } C_8H_{18}}{1 \text{ Mole } C_8H_{18}} \right) \left(\frac{1 \text{ mL } C_8H_{18}}{0.77 \text{ g } C_8H_{18}} \right) \left(\frac{1 \text{ L}}{1000 \text{ mL}} \right) \left(\frac{1 \text{ gal.}}{3.785 \text{ L}} \right) = 625 \frac{\text{gal. } C_8H_{18}}{\text{acre} \cdot \text{yr}}$$

Note that both the LNAPL formula and its density are assumed, and thus this conversion is subject to uncertainty; however, site specific data can be used if available. Using alternative representative hydrocarbon formulas and densities generally results in conversion factors that are within 10-15% of 625 $\text{gal acre}^{-1} \text{ yr}^{-1}$. Therefore, the uncertainty associated with these values does not preclude an acceptable estimate.

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