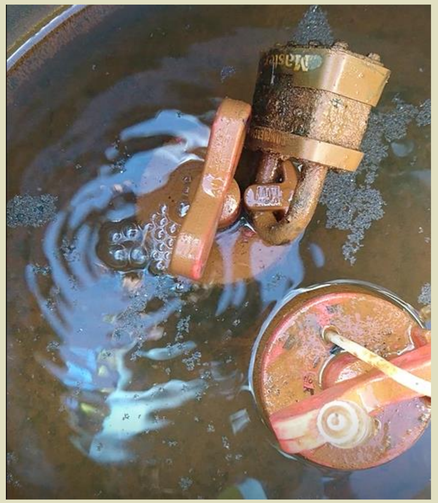
Did My Remedial Amendment Produce All That Methane?

Rick Coffin (Strategic Carbon, LLC), James Peale (MFA, Inc.), Tom Boyd (NRL) and Jim Mueller (Provectus Environmental Products, Inc.)

PROBLEM STATEMENT

Methanogens/Archaea produce methane. They are often the dominant microbes in reduced environments. Methanogenesis is a requisite component of conventional anaerobic bioremediation.

If Archaea are not controlled, then *in situ* remedial actions employing conventional (*i.e.*, no active control of Archaea) ERD amendments such as [emulsified] oils/lecithins, lactates/sugars, simple hydrogen release compounds or conventional ISCR reagents can generate excessive amounts of methane. At several sites where these conventional ERD/ISCR remedial amendments have been applied excessive methanogenesis (some yielding effervescent samples as shown below) has been observed, sometimes for many months - even years - after the amendments were applied.



CH4 production >12 months Post EVO
Source US DOD 2017

Methane in ecosystems can originate:

- **Thermogenically from regions of petroleum formation deep within the earth**
- **Via microbial fermentation of indigenous organic carbon and subsequent microbial reduction of carbon dioxide**
- **Via fermentation of an added carbon source, and /or**
- **Via catabolism of contaminant carbon**

Hence, the origin of methane is not always clear.

WHERE DID ALL THIS METHANE COME FROM?

This question can be answered conclusively using carbon isotope analyses - radiocarbon ($\Delta^{14}C$) and stable carbon ($\delta^{13}C$). When coupled with methane (CH_4) and carbon dioxide (CO_2) data from groundwater samples the origin of the respired carbon is clearly determined.

For water CO_2, dissolved inorganic carbon can be converted to CO_2 and concentrations determined with a coulometer. For water CH4, the concentration is measured via GC-FID. This combination of both gasses provides an estimate of total degradation by assuming microbial degradation to CO_2 and, when there is active anaerobic degradation, CO_2 is further reduced to CH_4

STUDY LOCATION

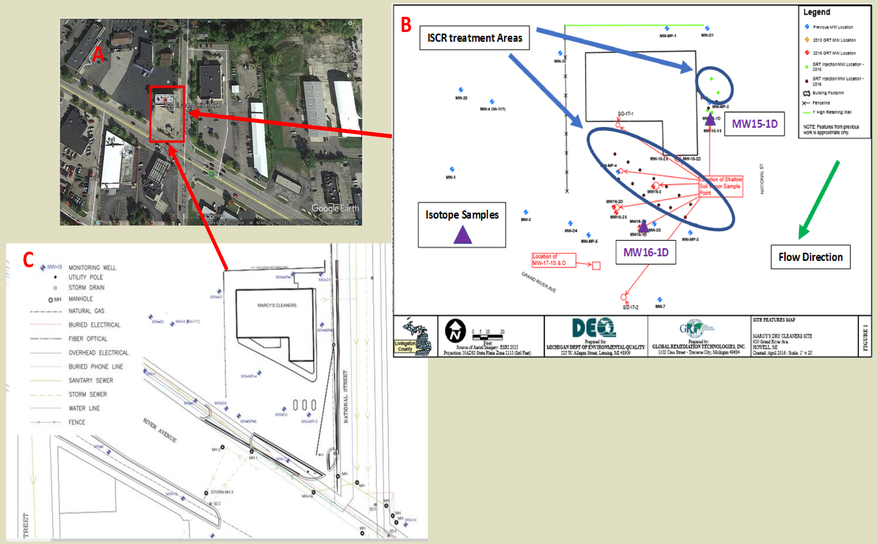


Figure 1: An overview of the sample location including; A) location of the dry cleaning facility; B) location of the monitoring wells including the sample wells reviewed in this study (purple triangles); C) distribution of sewer lines, storm water drains and utilities below ground in the study area.

CONCLUSIONS

These data show with strong certainty two distinct sources of CH_4 at MW15-1D and MW16-1D (Figure 1). This statement is based on the following points.

1. **$\Delta^{14}C$ CH_4 and CO_2 data are modern; there is no contribution from petroleum gas or microbial degraded petroleum.**
2. **$\delta^{13}C$ CH_4 shows the gas source at both sampling locations is biogenic, produced from organic carbon degradation.**
3. **Data suggested that each source is focused within its region, and there was little mixing of sources between the two wells, approximately 200 ft apart.**
4. **The most modern CH_4 ^{14}C signature was observed at well MW16-1D and the gas was produced from microbial reduction of CO_2 during the degradation of sewage (very young carbon) and/or subsequent leakage from the sewage lines.**
5. **The ISCR amendment was the primary source of carbon for CH_4 production at MW15-1D.**

DATA INTERPRETATION

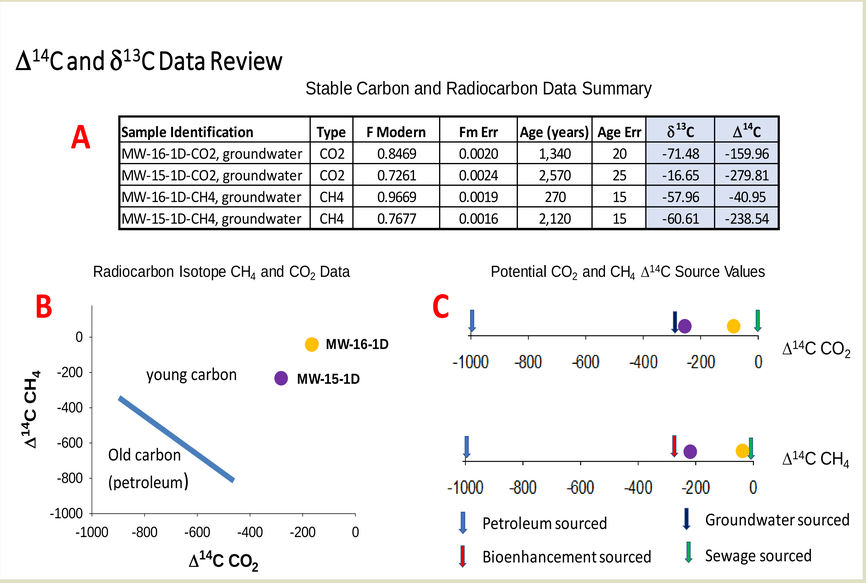


Figure 2: This figure provides an overview of our data interpretation. A) $\Delta^{14}C$ and $\delta^{13}C$ for CH_4 and CO_2 samples taken at the well locations and discussed in this summary are highlighted in blue. Radiocarbon data are listed as fraction modern and error, carbon age and error [for external reference], and $\Delta^{14}C$ to provide capability to compare these data with other studies. B) Radiocarbon ($\Delta^{14}C$) is compared for CH_4 and CO_2 samples taken from MW-16-1D and MW-15-1D (Figure 1). C) $\Delta^{14}C$ CO_2 and CH_4 data (section B in this figure) are compared with potential endmembers from this study site. Petroleum carbon $\Delta^{14}C$ will be -999‰, with no measureable ^{14}C present. Groundwater CO_2 will be moderately depleted in^{14}C with a value of -279.81‰; this value varies between ecosystems, depending on pavement capping vs gas flux from the atmosphere and plant growth vs. industrial activity. Sewage CH_4 and CO_2 found in the groundwater wells would come from leaking pipelines and $\Delta^{14}C$ would be modern, originating from recent carbon production.

For Technical Support and Proposals:

Dr. Rick Coffin, Strategic Carbon, LLC
20 Ladd St., Suite 200, Portsmouth, NH 03801
Phone: (301) 404-2364
rcoffin@strategic-carbonllc.com