Where Is All This Methane Coming From?

Stable-carbon (δ^{13}C) and naturally occurring radiocarbon (^{14}C) analyses can conclusively identify methane sources in soil gasses, groundwater, vadose soils and ambient/indoor air.

Methane in ecosystems can originate thermogenically from regions of petroleum formation deep within the earth and/or via microbial fermentation of organic carbon and microbial reduction of carbon dioxide. Because methanogens/Archaea are often the dominant microbes in reduced environments, *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 such as EHC®, Ferox-Plus®, other redox substrates (EHS) *et cetera* can generate excessive amounts of methane.

In 2014, the advent of Provectus' antimethanogenic reagents (AMRs) and their introduction to the remediation industry as constituents of Provect-IR® antimethanogenic ISCR reagent, ERD-CH4™ antimethanogenic ERD reagent, EZVI-CH4™ antimethanogenic DNAPL technology and other EHS increased awareness of potential issued associated with excessive methanogenesis during *in situ* remedial actions. Accordingly, a common question was being asked by seasoned remedial practitioners when they began looking at methane production associated with the use of conventional ERD/ISCR/EHS reagents….and finding it!

> **Where is this excessive methane coming from?**
> **Did the addition of my remedial amendment induce excessive methane production?**

Scientists now at Strategic Carbon, LLC and Texas A&M University – Corpus Christi (TAMU-CC) were among the first to utilize stable carbon isotope analysis to answers questions related to carbon forensics during environmental remediation efforts (Coffin *et al*., 1997; Hammer *et al*., 1999; Kelley *et al*., 1998; Pelz *et al*., 1998; Trust-Hammer *et al.,* 1998). More recently, they have employed these techniques on methane and other gasses to: 1) assess petroleum well casing integrity, 2) track pipeline leaks below ground or above ground, and 3) document environmental natural attenuation and health. Today, these analyses can be used to offer conclusive answers to the questions above.

For example, field monitoring of horizontal fracturing wells in southern Texas showed regions where methane production generated pressure that forced gas migration to shallow aquifers and resulted in contamination. A survey of methane δ^{13}C identified a mixture of methane that originated from both deep shale and shallow ecosystem production (**Figure 1**). At many of these sites it was believed the shallow aquifer contaminants sourced from horizontal fracturing. In this analysis δ^{13}C was measured on methane and carbon dioxide to determine the total amount gas flux from the sources; *i.e*. the fingerprint that originates from the methane is followed into the carbon dioxide.
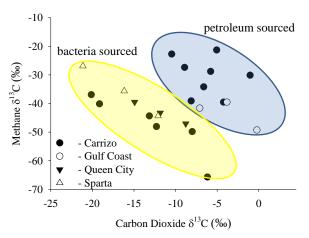

Figure 1: Methane and carbon dioxide stable carbon isotope analysis measured to distinguish between petroleum and bacterial methane near shale gas wells.

Stable carbon isotope analysis can also be applied to assess microbial degradation of organic contaminants in an ecosystem. Here, the carbon isotope ratio from the compound of interest transfers to carbon dioxide through microbial degradation and subsequently methane resulting from microbial reduction of the carbon dioxide. **Figure 2** presents data from a leaking pipeline at a Navy base and shows negative $\delta^{13}C$ in methane and carbon dioxide that confirms degradation of the petroleum. Note there are situations where $\delta^{13}C$ of the petroleum can overlap with cycling of the natural carbon. When this occurs we use radiocarbon isotope analysis to confirm that the CO_2 originated from an applied conventional ERD/ISCR/EHS remedial amendment (new or young carbon) as opposed to natural organic matter or an organic contaminant source (Coffin *et al*. 2008; Boyd *et al.*, 2013) which are typically older carbon compounds (**Figure 3**).
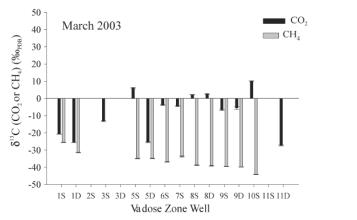

Figure 2: Stable carbon isotope analysis of carbon dioxide and methane gases taken from vadose zone wells above a leaking underground petroleum pipeline.
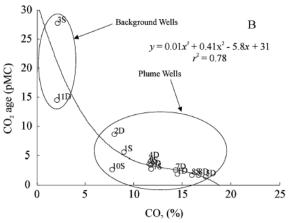
Figure 3: Radiocarbon isotope analysis of vadose zone carbon dioxide used to confirm degradation of petroleum.

Isotope biogeochemistry can provide conclusive answers at a reasonable cost.

Carbon Isotope Analysis: Light element (C, N, O, H, S) stable isotope analysis has been thoroughly developed to monitor source(s), transport, and cycling of organic and inorganic matter in complicated ecosystems. Experts at Strategic Carbon and TAMU-CC have applied isotope geochemistry to monitor environmental remediation, provide contaminant source identification, and assess deep sediment methane hydrate and petroleum deposits for >25 years. This biogeochemical approach provides thorough assessment of methane concentrations and source(s) for monitoring during environmental restoration operations, or oil and gas well operations.

Contracts can be solely for lab isotope analysis or they can include field sampling and a through ecosystem geochemical analysis. All data provided includes thorough technical interpretation. For assessment of environmental cleanup a general strategy includes: 1) analysis of background soil gas and groundwater methane and carbon dioxide concentrations, 2) measurement of contaminant concentrations, and 3) carbon isotope analysis of contaminants, background methane and carbon dioxide, and study region methane and carbon dioxide. The general approach for monitoring during oil and gas well operations includes: 1) determining background gas or hydrocarbon concentrations in groundwater, 2) establishing the source of existing gases or hydrocarbons, 3) organizing a cost effective long term monitoring plan, and 4) providing cost-effective insurance for shale play or petroleum mining operations.

The TAMU – CC Isotope Geochemistry Laboratory has developed the capability for efficient cost effective provision of these data for environmental impact assessment (http://icl.tamucc.edu/). Total cost depends on the spatial and temporal scale to address the requirement and needs for acquiring the necessary samples. If necessary there is also capability for radiocarbon isotope analysis of methane and carbon dioxide samples will be prepared by TAMU-CC. Recent analysis has been conducted at the Rafter Radiocarbon Laboratory, GNS Wellington (http://www.gns.cri.nz/Home/Services/Laboratories-Facilities/Rafter-Radiocarbon-Laboratory).

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