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## 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.



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

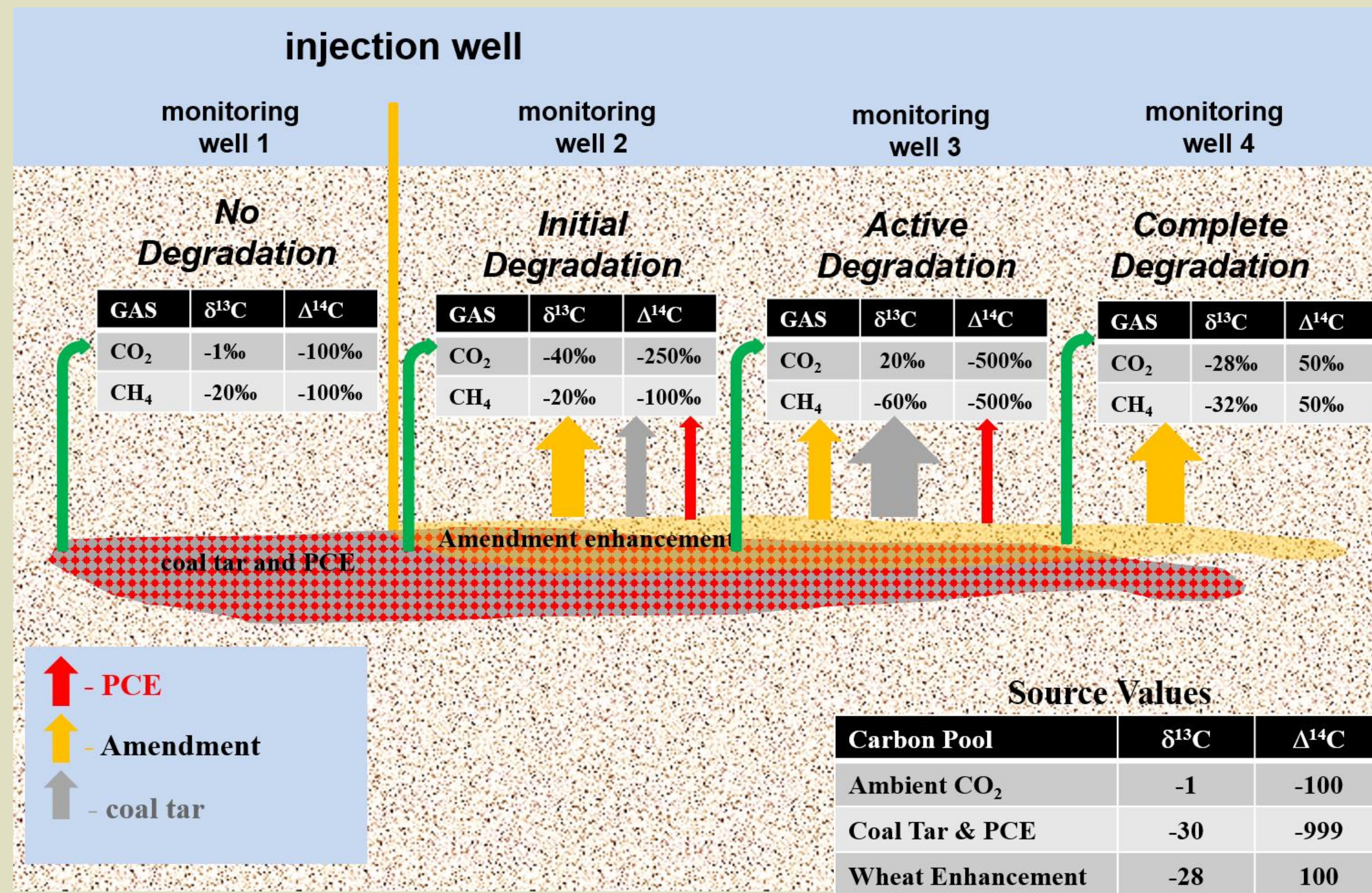
Hence, the origin of methane is not always clear.

CH4 production >12 months Post EVO (Newman Zone®) Application  
Source US DOD 2017

## WHERE DID ALL THIS METHANE COME FROM?

This question can be answered conclusively using carbon isotope analyses - radiocarbon ( $\Delta^{14}\text{C}$ ) and stable carbon ( $\delta^{13}\text{C}$ ). When coupled with methane ( $\text{CH}_4$ ) and carbon dioxide ( $\text{CO}_2$ ) data from groundwater samples the origin of the respired carbon is often clearly determined.

For water  $\text{CO}_2$ , dissolved inorganic carbon can be converted to  $\text{CO}_2$  and concentrations determined with a coulometer. For water  $\text{CH}_4$ , the concentration is measured via GC-FID. This combination of both gasses provides an estimate of total degradation by assuming microbial degradation to  $\text{CO}_2$  and, when there is active anaerobic degradation,  $\text{CO}_2$  is further reduced to  $\text{CH}_4$ .



### Isotope Data Interpretation

- ◆ Contaminant Degradation ( $\text{CO}_2$  source) =  $\Delta^{14}\text{C}_{\text{well1}} - \Delta^{14}\text{C}_{\text{well2-4}}$
- ◆ PCE vs Coal Tar Contribution ( $\text{CO}_2$  source) = (Chlorine/PCE)  $(\Delta^{14}\text{C}_{\text{well1}} - \Delta^{14}\text{C}_{\text{well2-4}} / \Delta^{14}\text{C}_{\text{well1}})$
- ◆ Stable carbon isotope analysis is used to calibrate and confirm radiocarbon

For Technical Support and Proposals

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