SCRUBBING BUBBLES: THE IMPORTANCE OF SAMPLE COLLECTION METHOD FOR MEASURING METHANE IN GROUNDWATER



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INTRODUCTION

HOW DOES PETROLEUM NATURAL ATTENUATION WORK?

Evolving Understanding of Natural Source Zone Depletion

Technology Overview

Evaluating Natural Source Zone Depletion at Sites with LNAPL



<u>1990s</u>

- Dissolution into groundwater
- Degradation within the dissolved plume.

<u>2000s</u>

- Volatilization
- Degradation within the vadose zone.





Natural Source Zone Depletion (NSZD): 2010s – Methanogenisis





NSZD: CURRENT CONCEPTUAL MODEL



OTHER SOURCES OF METHANE IN GROUNDWATER

Naturally Occurring



- Thermogenic gases that are naturally present in aquifers
- Microbial gases that form from the biodegradation of organic materials

Stray Gas Migration



- Oil or gas wells
- Coalbed methane
- Gas storage reservoirs
- Pipelines
- Landfills

RESEARCH STUDY

WHAT IS THE BEST WAY TO MEASURE DISSOLVED METHANE CONCENTRATIONS IN GROUNDWATER?

DISSOLVED METHANE SAMPLE COLLECTION: How do we do it?



Sample Collection Method

Sampling for Dissolved Methane:

- Samples collected at the surface
- Downhole techniques are complicated, expensive, and not widely available.

Objective:

Determine how common sampling methods affect dissolved methane concentrations







Open System: Direct-Fill VOA

Who Uses It:

- Most common method.
- Adapted from the method for collecting samples for EPA Method 8260 (measuring of VOCs in groundwater).
- For methane, it is recognized that there may be loss of gas to atmosphere.



Semi-Closed System: Inverted VOA

Who Uses It:

- Marcellus Shale Coalition
- Ohio Department of Natural Resources (Ohio DNR)
- For methane, it is intended to prevent the loss of gases to the atmosphere during sample collection.



Who Uses It:

- Researchers
- A truly closed system prevents any loss of gases during sample collection.



STUDY DESIGN *Residential Water Wells in NE Pennsylvania*

Residential Well Details

- 12 residential water wells in Bradford and Susquehanna Co., NE Pennsylvania
- All wells were >2,500 ft. from the nearest existing or proposed gas well location

Well Completion	Open hole; completed in Catskill and Lock Haven Formations, and glacial till
Well Depths	25 - 438 ft. btoc
Casing Volumes	30 - 388 gallons
Methane Concentrations	Low: < 5 mg/L Medium: 5 – 15 mg/L High: > 15 mg/L

Sampling Procedures

- Wells were purged at a flowrate of ~3 gpm
- Field parameters (temp., pH, and spec cond.) were monitored during purging
- Flowrate was reduced to <0.5 gpm to sample
- Samples were collected after the pressure tank and prior to any pretreatment devices



Question

How does Inverted VOA Compare to Direct-Fill VOA?



Question

How does Direct-Fill VOA Compare to IsoFlask?



Key Findings:

Below 20 mg/L:

No significant difference between sample collection methods.

> At or above 20 mg/L:

IsoFlask reports higher methane concentrations than Direct-Fill VOA, and Inverted VOA reports lower concentrations.

What's Happening at 20 mg/L of Methane?

Effervescence: Bubble formation





Loses effervescing gases to atmosphere during sample collection.



Loses effervescing gases to atmosphere during sample collection. Traps effervescing gases as a bubble in the vial – but lab only analyzes the dissolved phase.



Loses effervescing gases to atmosphere during sample collection. Traps effervescing gases as a bubble in the vial – but lab only analyzes the dissolved phase. Traps effervescing gases in container. Lab analyzes mass of methane in both headspace and water to get an original dissolved gas concentration.



FINDING

IF EFFERVESCENCE IS POSSIBLE, USE A TRULY CLOSED SAMPLE COLLECTION METHOD

APPLICATION TO NSZD

DO WE NEED CLOSED SAMPLING SYSTEMS IN LNAPL SOURCE AREAS?



Application: Dissolved Methane in LNAPL Area

- Two Background Locations
- Four Impacted Locations

<u>Results from</u>: Current Developments in Thermal NSZD Monitoring – Application at an LNAPL Research Site

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Methane in GW: Results

Location	CH ₄	CO ₂	
Background Wells			1
BK-1	<0.01 mg/L		
BK-2	<0.01 mg/L		2



Results: Lots of Methane, CO₂ in Groundwater

Location	CH ₄	CO ₂	
	Background Wells	S	
BK-1	<0.01 mg/L (0.01%)		
BK-2	<0.01 mg/L (0.01%)		5
	Impacted Wells		
T-1	5.5 mg/L		ISOF SK
T-2	11 mg/L		
T-4	7.6 mg/L		

Results: Lots of Methane, CO₂ in Groundwater

		CO ₂	
	Background Wells		
BK-1	<0.01 mg/L (0.01%)	23%	
BK-2	<0.01 mg/L (0.01%)	19%	
	Impacted Wells		
T-1	5.5 mg/L (19%)	55%	BOPLSK
T-2	11 mg/L (30%)	36%	
T 4	7.0	07 0/	

LNAPL source area may result in effervescing during sample collection.

CONCLUSIONS

- For effervescing samples:
 - IsoFlask is truly closed system you never lose methane.
 - Direct-Fill VOA is an open system you lose methane during sample collection but not during transport.
 - Inverted VOA is a semi-closed system –you continue to lose methane after sample collection to bubbles in vial.



Note: Effervescence rarely driven just by methane.

MORE DETAILS

Groundwater

Effect of Different Sampling Methodologies on Measured Methane Concentrations in Groundwater Samples

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Abstract

Analysis of dissolved light hydrocarbon gas concentrations (primarily methane and ethane) in water supply wells is commonly used to establish conditions before and after drilling in areas of shale gas and oil extraction. Several methods are currently used to collect complex for discolved gas analysis from water supply wells; however, the reliability of results obtained from these

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