RECOMMENDED PRACTICES FOR BASELINE SAMPLING OF DISSOLVED GASES AT WATER WELLS IN AREAS OF SHALE OIL & GAS DEVELOPMENT

NEMC

GSI ENVIRONMENTAL

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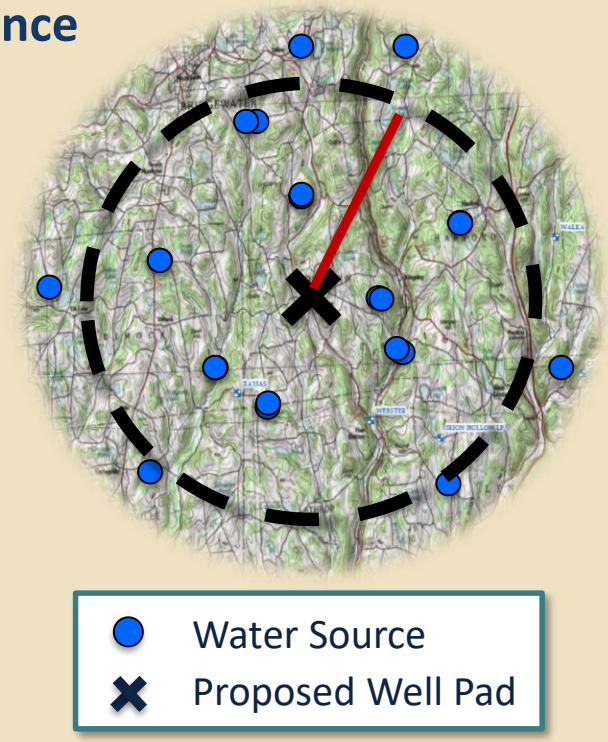
BASELINE SAMPLING OF WATER SOURCES
What is it?

What is Baseline Sampling?

- Sampling of water sources within a defined distance from the proposed location of oil and gas development
- Residential water wells, surface waters, springs



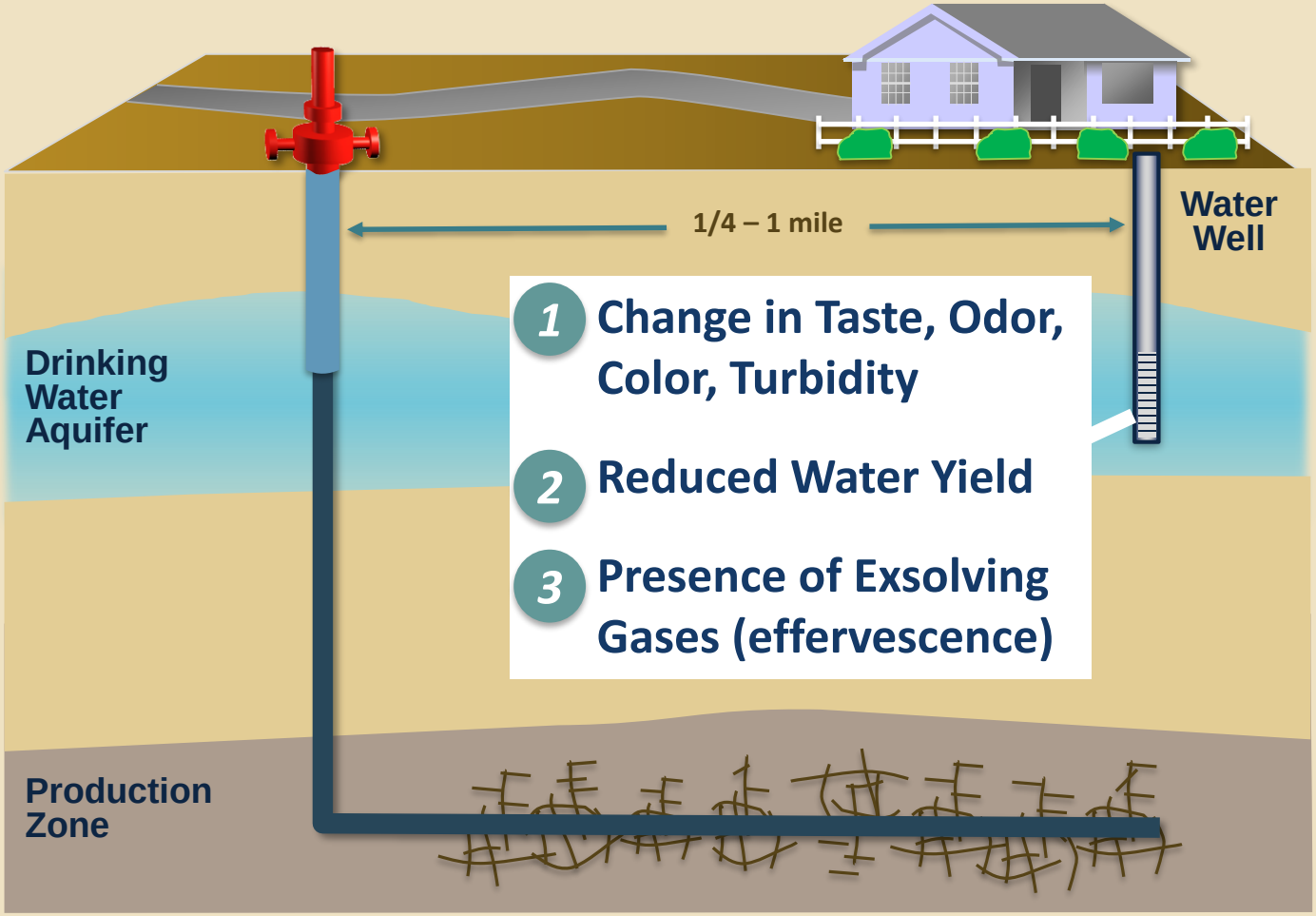
Why Collect Baseline Samples?

- Evaluate whether reported changes in local water quality are naturally occurring or the result of stray gas migration
- Many state agencies require pre-drill and post-drill sampling to obtain drilling permits

KEY POINT: **Baseline sampling is a *critical* line of evidence to investigate well owner complaints**

BASELINE SAMPLING OF WATER SOURCES

What's the Driver?



KEY POINT: **Pre- and post-drill monitoring of dissolved methane is a primary metric for investigating well owner complaints**

BASELINE SAMPLING CHALLENGES

Methane in Groundwater: Natural or Impact?

Naturally Occurring

Eternal Flame Falls, NY

- Thermogenic and biogenic
- Natural seeps
- Effervescing wells

Gas Well Migration

House Explosion, Western PA

- Casing leak or cement failure
- Creates pathway for deeper methane into shallow aquifers

KEY POINT:

A baseline study in NE Pennsylvania reported (Baldassare et al., 2014):

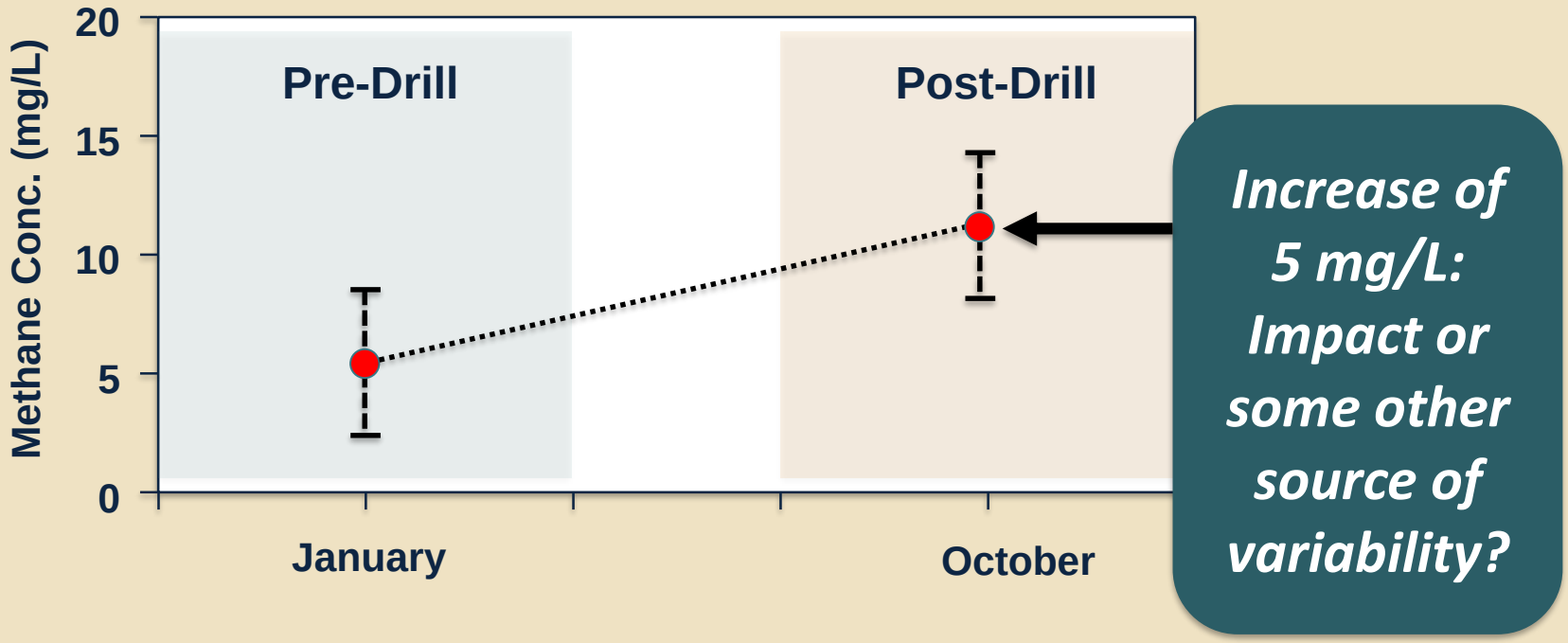
- **24% of water wells with detectable levels of dissolved methane**
- **12% of wells contained dissolved methane > 7 mg/L**

BASELINE SAMPLING CHALLENGES

Pre-drill vs. Post-drill Methane

Challenge:

Differentiating *natural* variability in groundwater quality from *induced* variability (i.e., stray gas impacts).



KEY POINT: **There are factors unrelated to unconventional oil and gas development that can affect residential water quality results**

BASELINE SAMPLING CHALLENGES
Sources of Variability

Sampling Variability

- Purge volume
- Sampling methods
- Sample containers
- Sample location

Temporal Variability

- Seasonality
- Aquifer dynamics
- Precipitation
- Water use

Lab Variability

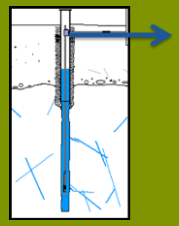
- Sample preparation
- Calibration
- Sample Analysis

BASELINE SAMPLING OF WATER WELLS
Key Questions

Sampling Methods

What is the effect of *sample collection methods* on dissolved methane concentrations?

Well Purging

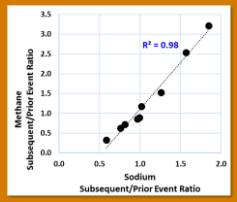


What is the effect of *purging practices* on dissolved methane concentrations?

Temporal Variability

What is the *magnitude of variability* in dissolved methane concentration and isotopic composition over time?

Key Factors



What are the *key relationships* that can help us better understand the occurrence of natural methane?

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 pre-treatment devices

STUDY DESIGN
Effect of Sample Collection Methods

Of the three common sampling collection methods used for dissolved gases, which produces the most reliable results?

1

Open System
Direct Fill Method
(40 ml VOA vials)

2

"Semi-closed" System
Inverted Bottle Method
(40 ml VOA vials)

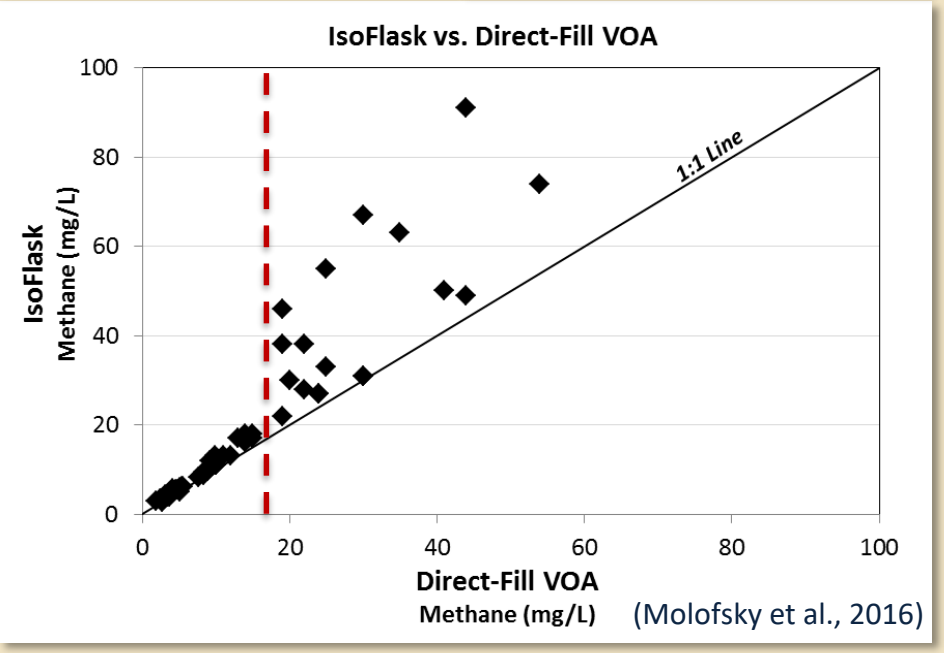
3

Closed System
In-Line Sampling Device
(IsoFlask)

RESULTS
Effect of Sample Collection Methods

Open System
Direct Fill Method
(40 ml VOA vials)

Closed System
In-Line Sampling (IsoFlask)



(Molofsky et al., 2016)

RESULTS
Effect of Sample Collection Methods

Open System
Direct Fill Method
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Closed System
In-Line Sampling (IsoFlask)

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"Semi-closed" System
Inverted Bottle
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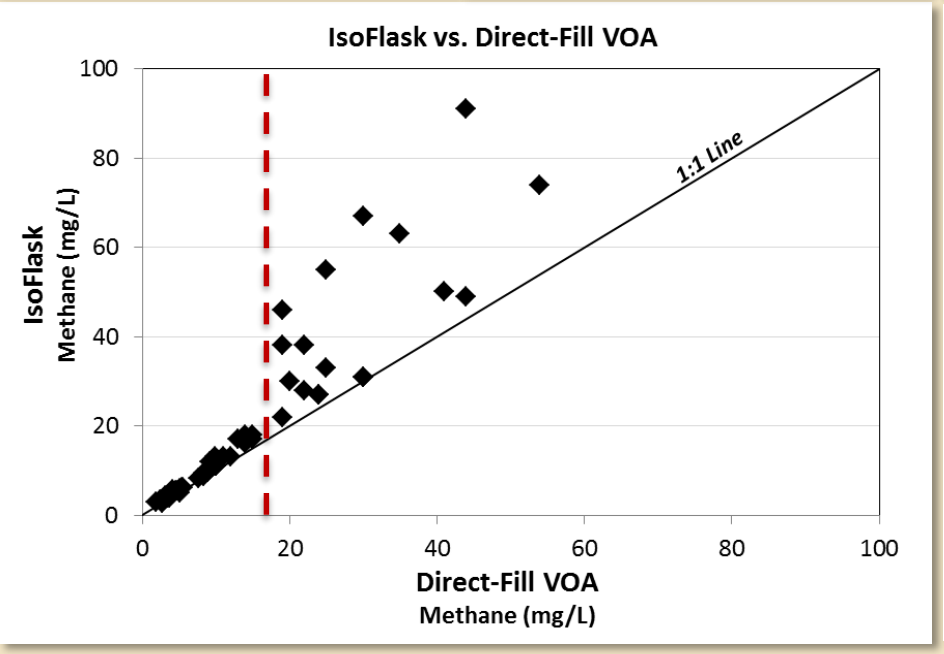
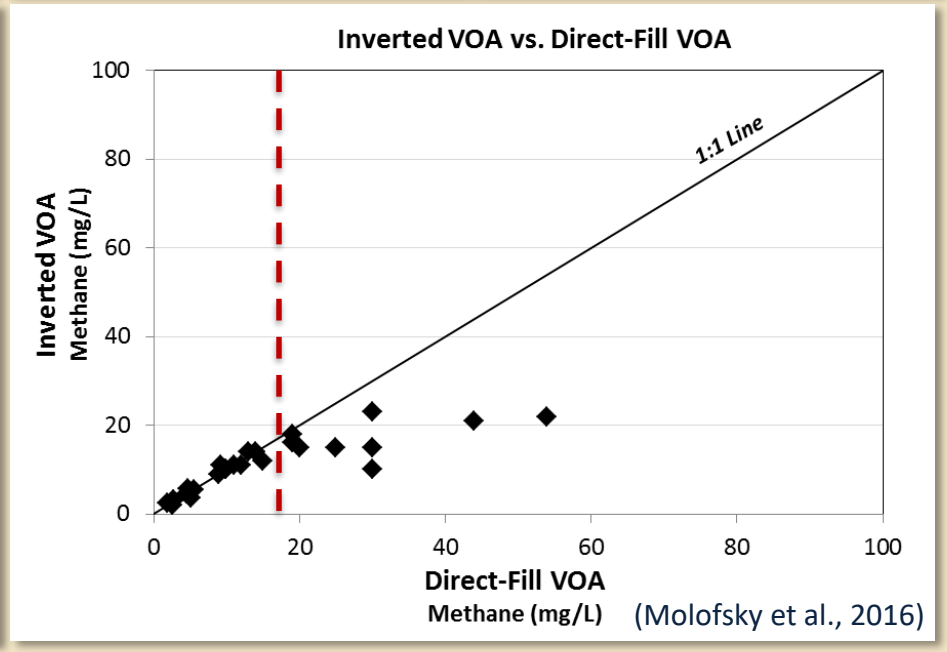




(Molofsky et al., 2016)

RECOMMENDATIONS
Effect of Sample Collection Methods

Open System
Direct Fill Method

Loses effervescing gases to atmosphere during sample collection

"Semi-closed" System
Inverted Bottle Method

Traps effervescing gases as a bubble in the vial – but lab only analyzes the dissolved phase

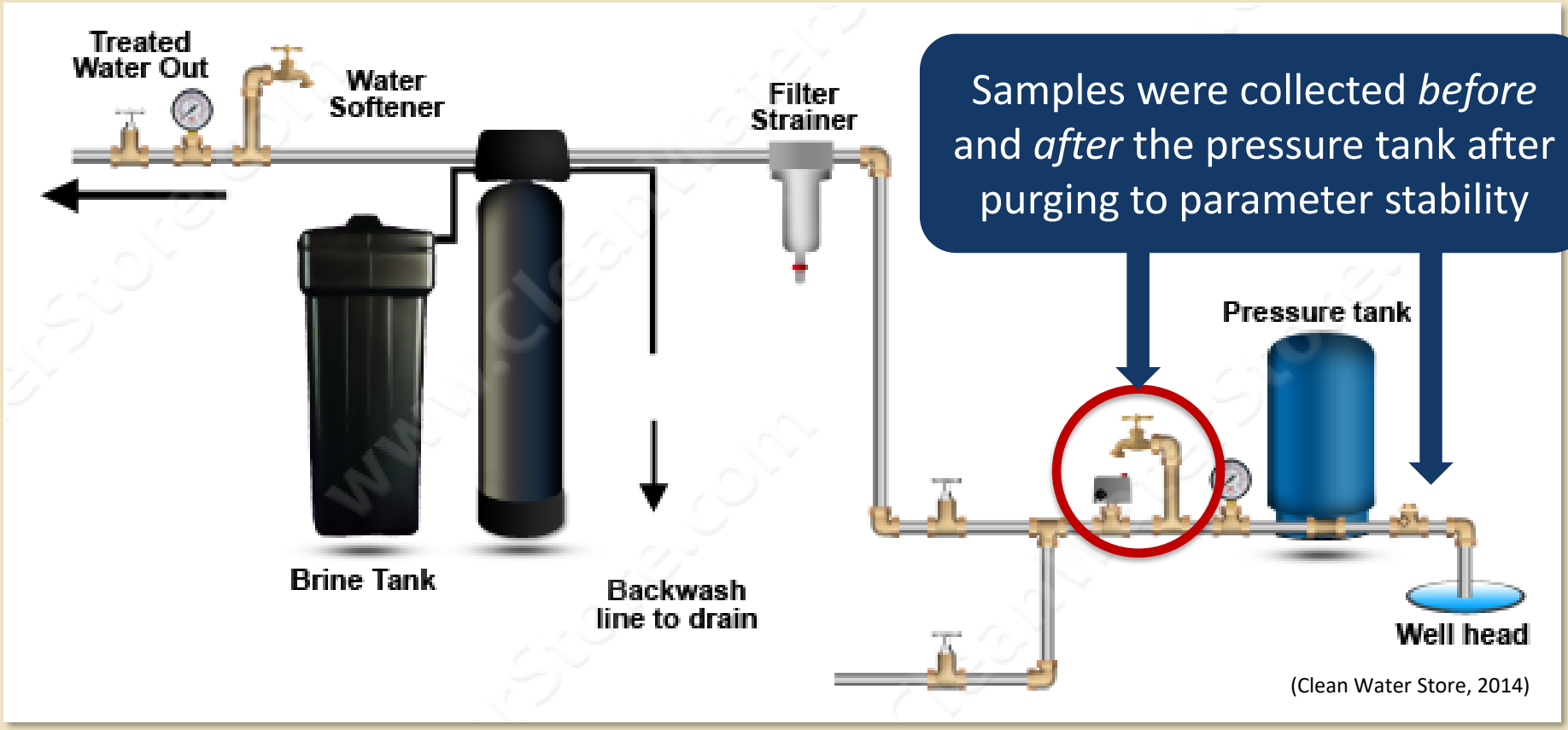
Closed System
IsoFlask

Traps effervescing gases in container. Lab analyzes mass of methane in headspace and water

KEY POINT: **If elevated methane concentrations or effervescence is observed, collect samples using a closed-system method**

STUDY DESIGN
Effect of Sample Location

Does water lose dissolved methane as it moves through the pressure tank of the water system?



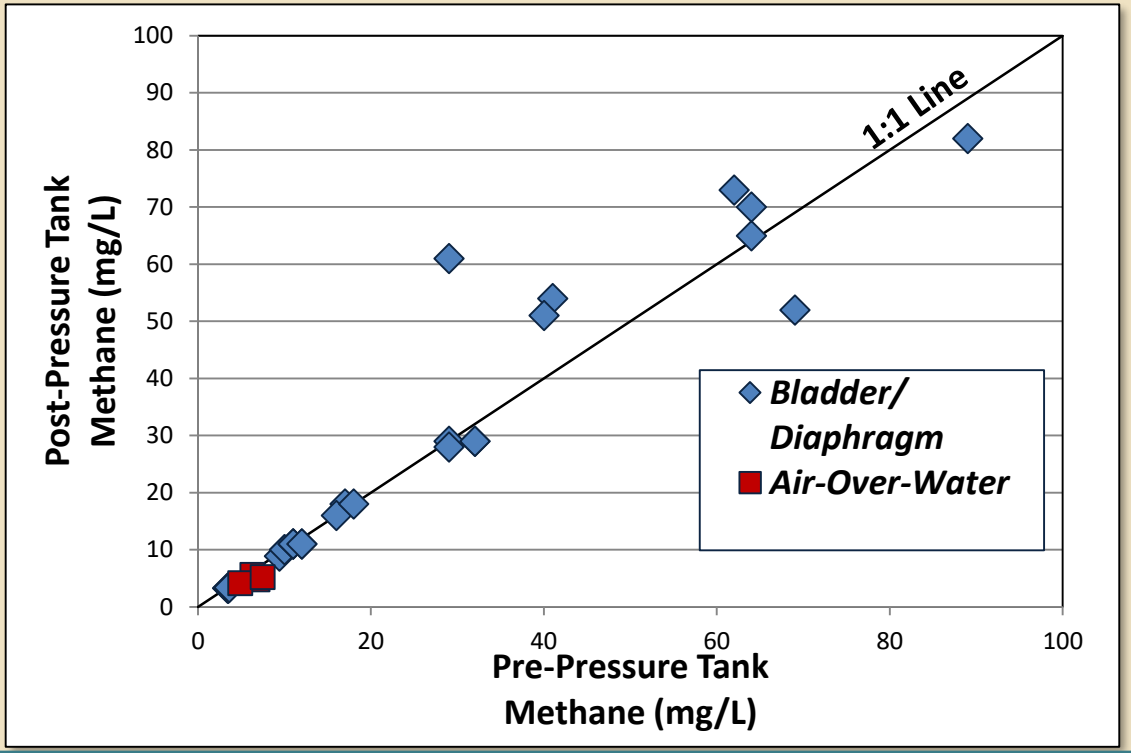
RESULTS
Effect of Sample Location

Does water lose dissolved methane as it moves through the pressure tank of the water system?

Key Findings

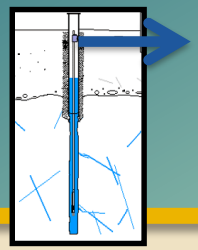
No pattern in methane concentration between samples collected before and after the pressure tank.

For air-over-water tank, lower concentrations were consistently observed post pressure tank (13 – 44%)



KEY POINT: As a precautionary measure, we recommend sampling *pre-pressure* tank when possible particularly for less common pressure tank configurations that can result in methane loss.

STUDY DESIGN
Effect of Well Purging



How much water should be purged before collecting a sample for analysis of dissolved methane concentration?

Procedure

At multiple events, Isoflask samples were collected after 3 successive purge volumes:

- **Minimal purge (1 min = ~0.5 gallons)**
- **Purge to parameter stability**
- **3 casing volumes (high-volume purge)**

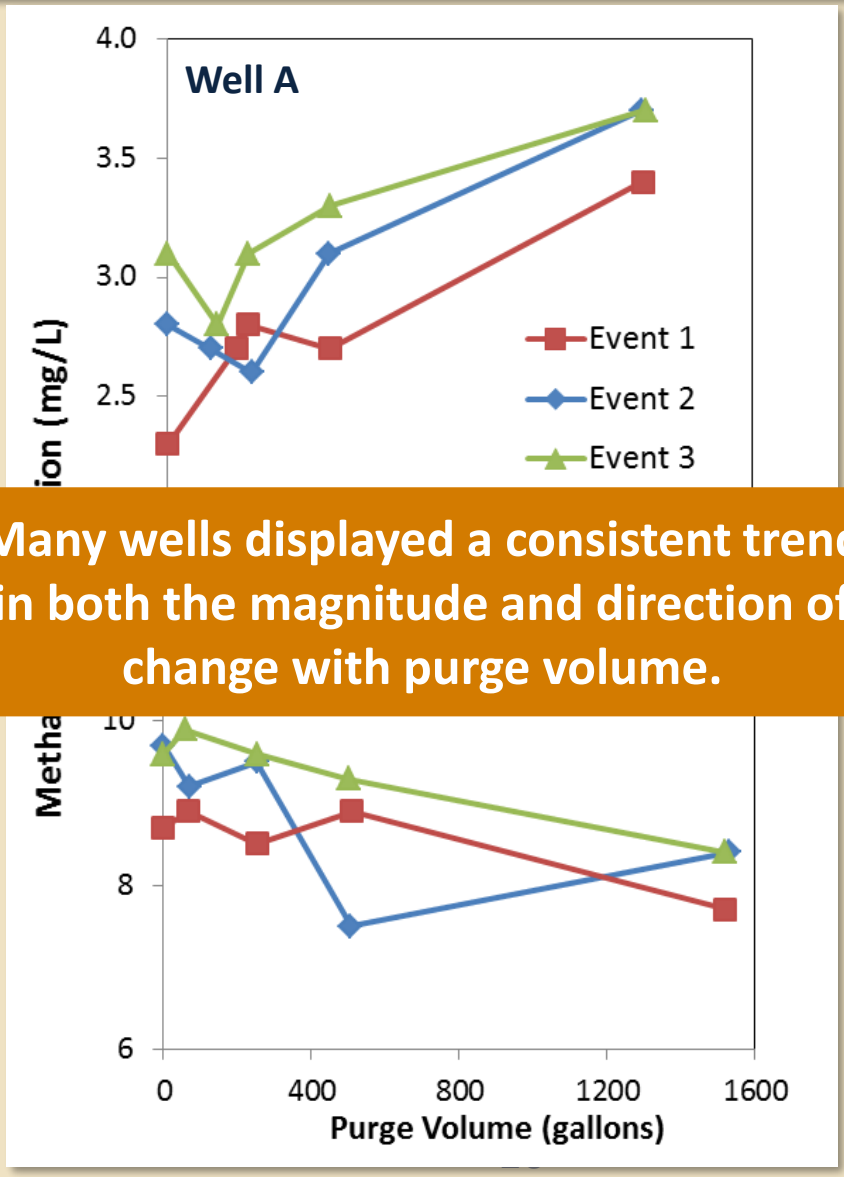
3 consecutive readings of:

- **pH = ± 0.2 SU**
- **Spec. Cond = ± 5%**
- **Temp. = ± 0.2 °C**

RESULTS
Effect of Well Purging

Key Findings

1. ***Population*** **of wells did not exhibit a predictable relationship between methane conc. and purge volume.**

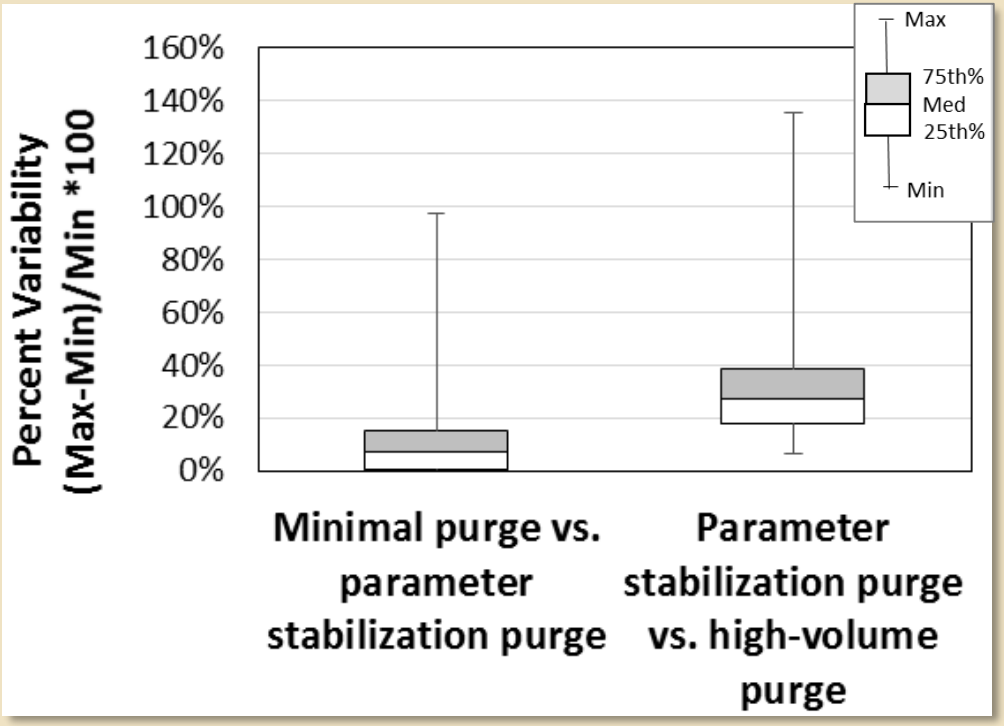


Many wells displayed a consistent trend in both the magnitude and direction of change with purge volume.

RESULTS
Effect of Well Purging

Key Findings

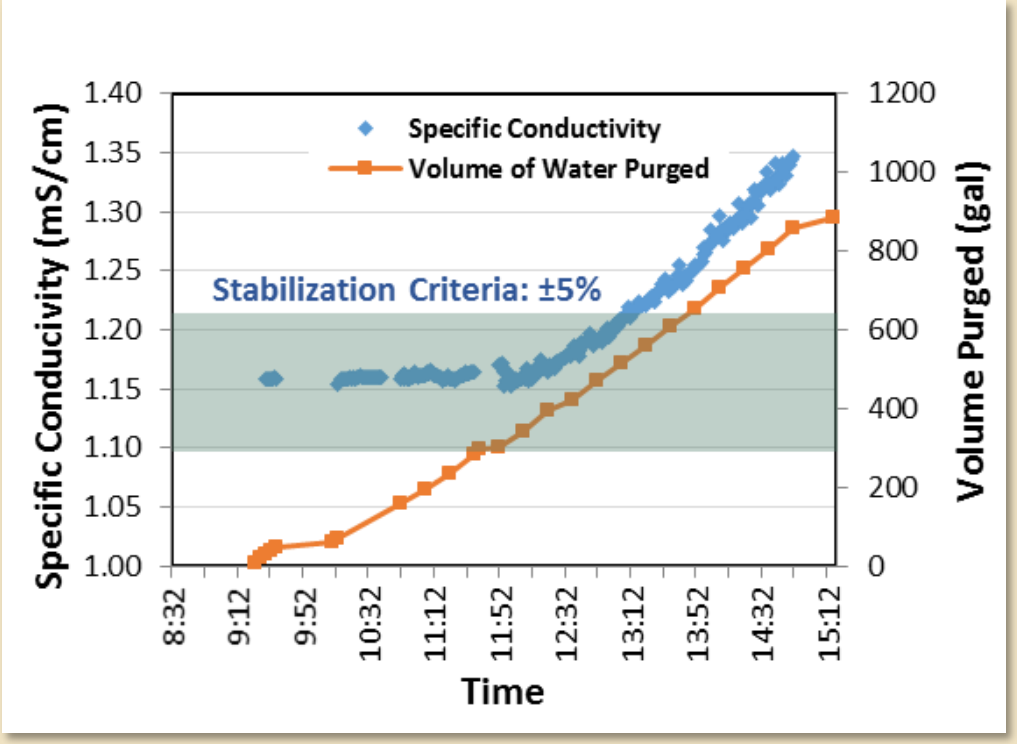
1. ***Population*** **of wells did not exhibit a predictable relationship between methane conc. and purge volume.**
2. **Methane concentration did not typically stabilize after parameter stability achieved.**



RESULTS
Effect of Well Purging

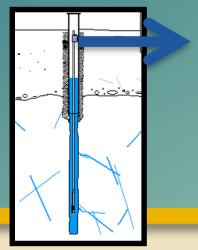
Key Findings

1. ***Population*** **of wells did not exhibit a predictable relationship between methane conc. and purge volume.**
2. **Methane concentration did not typically stabilize after parameter stability achieved.**
3. **Field parameters often did not remain stable after initial parameter stability achieved.**



KEY POINT: **These results point to changes in mixing dynamics within the well as purging continues.**

RECOMMENDATIONS
Effect of Well Purging



Key Findings on Well Purging

1. No clear advantage to tracking field parameter stability as a metric for sample collection.

2. No clear advantage to purging larger volumes of water (i.e., at any given well, methane concentration may increase or decrease due to changes in mixing dynamics).

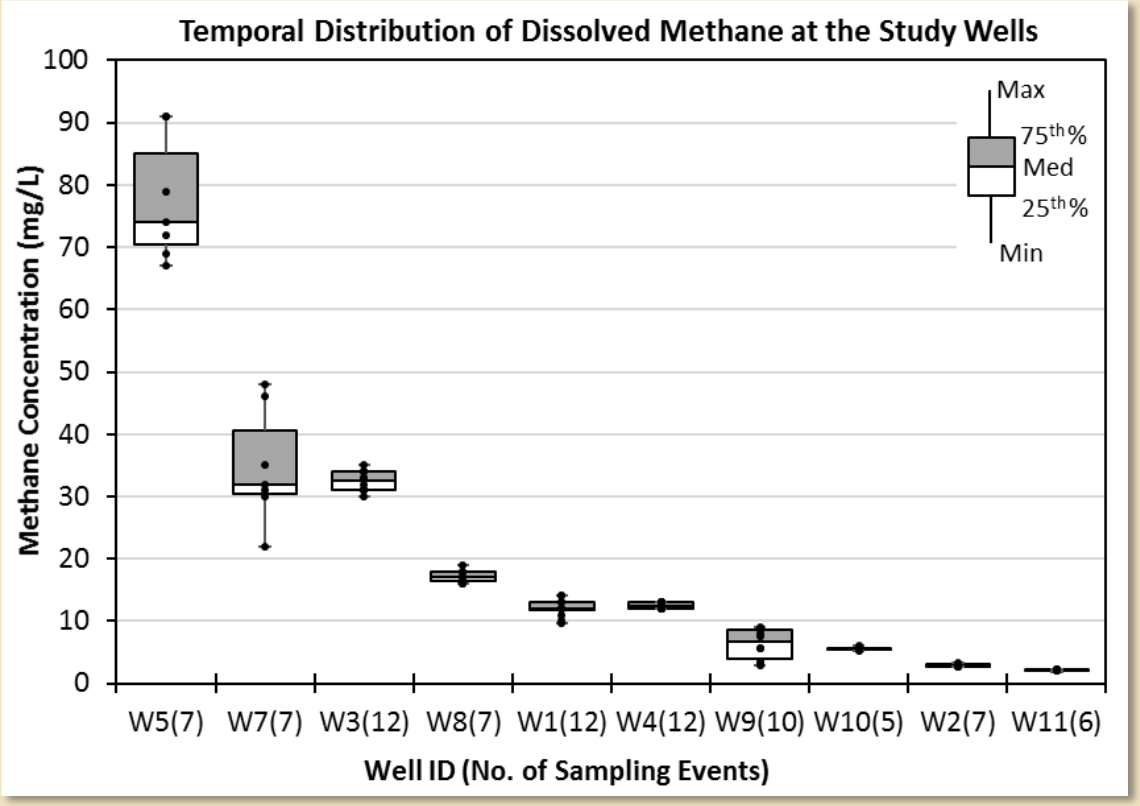
3. We recommend using a consistent purge volume prior to sample collection. Purging of 2 pressure tank volumes should be adequate to remove standing water from the tank and lines at most wells.

RESULTS
Temporal Variability

What is the degree of variability in methane concentrations and isotopic signature over time at the wells tested?

11 wells sampled after purging to parameter stabilization over a 2-year period

- **Event-to-event variability commonly less than 20%.**
- **Majority of wells showed less than a 2-fold max change.**



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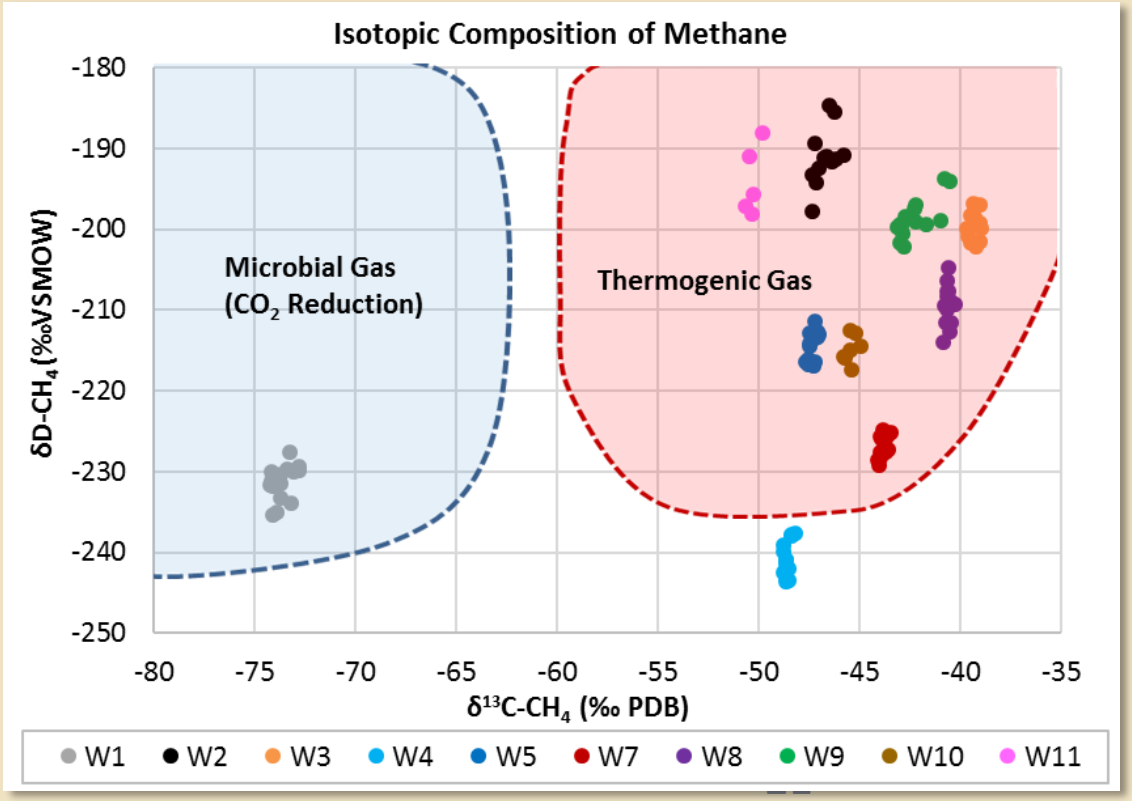
- Majority of wells showed less than a 2-fold max change.
- Relatively constant sources of methane at each well.



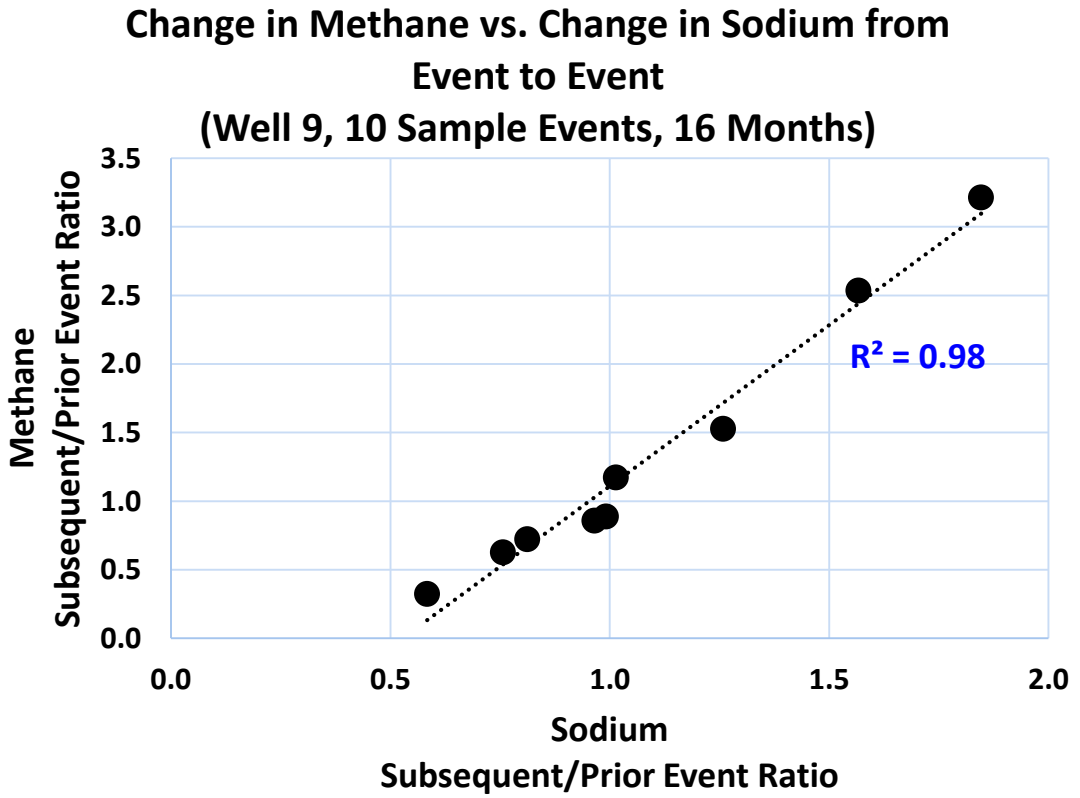
RESULTS
Key Relationships with Methane

What factors can help understand variability of methane concentration over time?

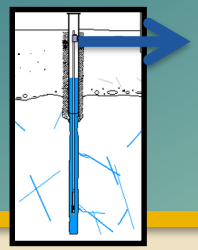
Water Quality Parameters

We observed a strong correlation between methane and salt indicator parameters:

- Sodium
- Chloride
- Total Dissolved Solids (TDS)
- Bromide
- Specific Conductivity



RECOMMENDATIONS
Key Relationships with Methane



Key Findings

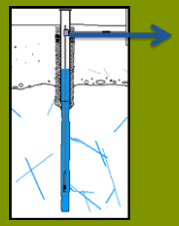
1. Strong correlation between methane and parameters associated with sodium-rich water types (e.g., sodium, chloride, TDS).
2. Evidence for natural variability driven by changes in mixing dynamics.
3. Large changes in methane concentration (i.e., 2x) accompanied by large changes in sodium and others can be strong evidence for natural variation.

BASELINE SAMPLING OF WATER WELLS
Recommended Practices

Sampling Methods

Use a fully closed sampling system for collecting effervescing samples; Inverted Bottle provides no advantage relative to Direct-Fill method.

Well Purging

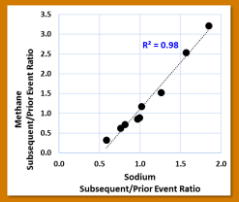


Purge a consistent volume prior to each sampling event (e.g., 2 pressure tank volumes).

Temporal Variability

For the study wells, change in methane concentrations greater than 2-fold may warrant further investigation.

Key Factors



Large changes in methane concentration should be compared to changes in concentrations of sodium and other indicator parameters.

BASELINE SAMPLING OF WATER WELLS

For more information…

REDUCING THE ENVIRONMENTAL IMPACT OF SHALE GAS DEVELOPMENT

ADVANCED ANALYTICAL METHODS FOR AIR AND STRAY GAS EMISSIONS AND PRODUCED BRINE CHARACTERIZATION

RPSEA Research Partnership to Secure Energy for America

DRAFT FINAL TECHNICAL REPORT

RPSEA PROJECT 11122-45

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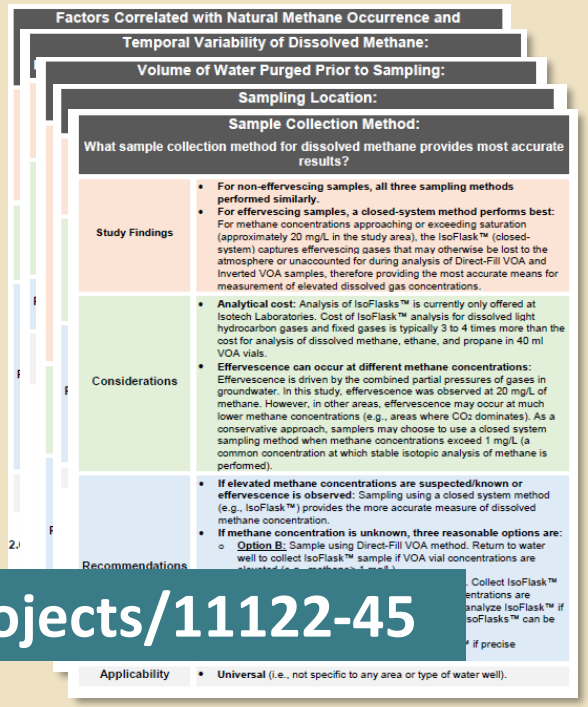

Factors Correlated with Natural Methane Occurrence and Temporal Variability of Dissolved Methane:

Volume of Water Purged Prior to Sampling:

Sampling Location:

Sample Collection Method:

What sample collection method for dissolved methane provides most accurate results?

Study Findings	• **For non-effervescing samples, all three sampling methods performed similarly.** • **For effervescing samples, a closed-system method performs best:** For methane concentrations approaching or exceeding saturation (approximately 20 mg/L in the study area), the IsoFlask™ (closed-system) captures effervescing gases that may otherwise be lost to the atmosphere or unaccounted for during analysis of Direct-Fill VOA and Inverted VOA samples, therefore providing the most accurate means for measurement of elevated dissolved gas concentrations.
Considerations	• **Analytical cost:** Analysis of IsoFlasks™ is currently only offered at Isotech Laboratories. Cost of IsoFlask™ analysis for dissolved light hydrocarbon gases and fixed gases is typically 3 to 4 times more than the cost for analysis of dissolved methane, ethane, and propane in 40 ml VOA vials. • **Effervescence can occur at different methane concentrations:** Effervescence is driven by the combined partial pressures of gases in groundwater. In this study, effervescence was observed at 20 mg/L of methane. However, in other areas, effervescence may occur at much lower methane concentrations (e.g., areas where CO_2 dominates). As a conservative approach, samplers may choose to use a closed system sampling method when methane concentrations exceed 1 mg/L (a common concentration at which stable isotopic analysis of methane is performed).
Recommendations	• **If elevated methane concentrations are suspected/known or effervescence is observed:** Sampling using a closed system method (e.g., IsoFlask™) provides the more accurate measure of dissolved methane concentration. • **If methane concentration is unknown, three reasonable options are:** ○ **Option B:** Sample using Direct-Fill VOA method. Return to water well to collect IsoFlask™ sample if VOA vial concentrations are
Applicability	• **Universal** (i.e., not specific to any area or type of water well).

www.rpsea.org/projects/11122-45

1. Molofsky, L.J., Richardson, S.D., Gorody, A.W., Baldassare, Connor, J.A., McHugh, T.E.; Smith, A.P., Wylie, A.S., and Wagner, T. (*accepted*). Purging and Other Sampling Variables Affecting Dissolved Methane Concentration in Water Supply Wells. *Science for the Total Environment*.

2. Molofsky, L.J., Richardson, S.D., Gorody, A.W., Baldassare, F.; McHugh, T.E.; and J.A. Connor (2016). Effect of Different Sampling Methodologies on Measured Methane Concentrations in Groundwater Samples, *Groundwater*, 54(5): 669-680.

3. Molofsky, L.J., Connor, J.A., McHugh, T.E., Richardson, S.D., Woroszlyo, C., P.A. Alavarez (2016). Environmental Factors Associated with Natural Methane Occurrence in the Appalachian Basin, *Groundwater*, 54(5):656-668

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