SOURCES OF VARIABILITY IN DISSOLVED METHANE CONCENTRATIONS AT RESIDENTIAL WATER WELLS

Lisa J. Molofsky, Stephen D. Richardson, Thomas E. McHugh, John A. Connor; GSI Environmental Inc.
Anthony W. Gorody, Universal Geoscience Consulting, Inc.
Fred Baldassare, Echelon Applied Geosciences
June A. Black, Pennsylvania Department of Environmental Protection
ADVANCED ANALYTICAL METHODS
RPSEA 11122-45

- 3-Year project in 2 phases (currently in Phase II)
- $3.5M from DOE/RPSEA, $900k in cost share

RESEARCH FOCUS ON THREE KEY ENVIRONMENTAL ISSUES:

Baseline Sampling and Stray Gas Investigation

Advanced Analytics for Air Emissions

Produced Water Characterization
What's the Goal?

Baseline Sampling of Water Sources

- Surface Water
- Water Wells
- Springs/Seeps

Develop a practical protocol for improved sample collection methods and data interpretation for pre-drill and post-drill sampling programs.

1. Regulations & Guidance
2. Information Resources
3. Sample Collection & Analyses
4. Data Analysis & Management
5. Implications & Case Study
What’s the Goal?

Develop a practical protocol for improved sample collection methods and data interpretation for pre-drill and post-drill sampling programs.
What is Baseline Sampling?

- aka: Pre-drill sampling or Pre-alteration survey
- Sampling of water sources within a defined distance from the proposed location of oil and gas development

Why Collect Baseline Samples?

- Establish water quality of drinking water sources
- Evaluate whether reported changes in local water quality are naturally occurring or the result of nearby drilling

What Water Sources?

- Residential water wells, springs, and/or surface waters that are intended for human or livestock consumption
**Challenge:**
Differentiating *natural* variability in groundwater quality from *induced* variability (i.e., impacts).

**KEY QUESTION:**
Are observed changes in residential water quality within the range of expected variability or suggestive of an impact?
There are factors unrelated to shale gas extraction that can influence residential water quality results.
BASELINE SAMPLING CHALLENGES

Key Sources of Variability

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

**Temporal Variability**
- Seasonality
- Aquifer dynamics
- Precipitation
- Water use

**Lab Variability**
- Sample preparation
- Calibration
- Sample Analysis
BASELINE SAMPLING CHALLENGES

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STUDY GOAL:
Quantify the degree of variability in dissolved gas concentrations, isotopic composition, and water quality parameters due to sampling, temporal and analytical sources of variability.
STUDY DESIGN

Residential Water Wells

- 12 residential water wells in Susquehanna and Bradford Counties, NE Pennsylvania

**Sampling Var:** 9 wells

**Temporal Var:** 6 wells

- All wells were >2,500 ft from the nearest existing or proposed gas well location

<table>
<thead>
<tr>
<th>Well Completion</th>
<th>Open hole; completed in Catskill Formation, Lock Haven Formation, and glacial till</th>
</tr>
</thead>
<tbody>
<tr>
<td>Well Depths</td>
<td>25 - 438 ft btoc</td>
</tr>
<tr>
<td>Casing Volumes</td>
<td>30 - 388 gallons</td>
</tr>
</tbody>
</table>
| Methane         | Low: < 5 mg/L
                  | Medium: 5 – 15 mg/L
                  | High: > 15 mg/L                                                                   |
STUDY DESIGN
Monitoring & Sample Collection

General Sampling Procedures

- Wells were purged at a flowrate of ~3 gpm
- Field parameters (temperature, pH, and specific conductivity) were monitored during purging
- Flowrate was reduced to <0.5 gpm prior to sampling
- Samples were collected from a faucet after the pressure tank and prior to any pre-treatment devices
- Duplicates samples were collected immediately after first sample (no splits)
STUDY DESIGN

Effect of Sample Collection Methods

**Challenge**
Determine how common sampling methods affect dissolved gas concentrations at domestic water wells

**Procedure**
Samples were collected using three common methods:

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

**Open System**
- **Direct Fill Method**
  - (40 ml VOA vials)

**Closed System**
- **In-Line Sampling Device**
  - (IsoFlask™)

![Graph](IsoFlask vs. Direct-Fill VOA)
**Question**

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

**RESULTS**

**Effect of Sample Collection Methods**

- **Open System**
  - Direct Fill Method (40 ml VOA vials)

- **“Semi-closed” System**
  - Inverted Bottle Method (40 ml VOA vials)

**KEY POINT:**

Sampling method can impact resulting dissolved methane concentrations, particularly at higher methane wells.
**STUDY DESIGN**

**Effect of Well Purging**

**Challenge**
Determine how purge volume affects variability in dissolved gas concentrations and water quality at domestic water wells.

**Procedure**
At three events, samples were collected after 5 successive purge volumes:

- “Zero” purge (1 min = ~0.5 gallons)
- Purge to parameter stability
- 0.5 casing volumes
- 1 casing volume
- 3 casing volumes

3 consecutive readings of:
- pH = ± 0.2 SU
- Spec. Cond = ± 5%
- Temp. = ± 0.2 °C
Question

What is the effect of purge volume on dissolved methane concentrations?

KEY POINT:
No clear advantage to purging larger volumes of water to produce more consistent dissolved gas concentration results.

Change from “No Purge” to “3 Casing Volumes Purged” typically ≤ 30%
What is the degree of variability in dissolved gas concentrations over time at the wells tested?

**KEY POINT:** Dissolved methane concentrations varied by a factor of 1.4 to 2.9 over 18 months.
What is the effect of different laboratories on dissolved methane concentrations?

**PADEP BOL: 3868 Ver. 1**

1. Transfer 10 ml sample aliquot to a 20 ml headspace vial by volumetric pipette at 4°C
2. Agitate headspace vial at constant temperature
3. Inject 1 ml of equilibrated headspace into a GC-FID
4. Results are referenced to aqueous calibration standards
RESULTS

Effect of Laboratory Procedures

Question
What is the effect of different laboratories on dissolved methane concentrations?

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3. Inject 1 ml of equilibrated headspace into a GC-FID
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Lancaster: Modified RSK-175

1. Transfer 5 ml sample aliquot to a 10 ml headspace vial by helium displacement
2. Agitate headspace vial at constant temperature
3. Inject 1 ml of equilibrated headspace into a GC-FID
4. Results are referenced to aqueous calibration standards
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**RSK-175**
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2. Agitate headspace vial at constant temperature.
3. Inject 1 ml of equilibrated headspace into a GC-FID.
4. Results are referenced to aqueous calibration standards.

**KEY POINT:**
Despite differences in sample transfer techniques, good agreement was observed between these two laboratories.
BASELINE SAMPLING CHALLENGES

Effect of Laboratory Procedures

**Challenge**
Variations in analytical procedures between labs can impact resulting dissolved methane concentrations

**Variables**
- Sample transfer
- Prep of Calibration Standards
- Calibration Range
- Sample Temperature
- Sample Analysis
- Others?

**Research Question:** What is the effect of variations in analytical procedures on dissolved methane concentrations?
**Sample Collection Methods**

- At dissolved methane concentrations below 20 mg/L, the three sample collection methods provide comparable results.
- A fully closed sampling system is best for collecting effervescing samples.
- Inverted VOA sampling method provides no advantage relative to Direct-Fill VOA sampling method in non-effervescing conditions.
- Dissolved gas concentration data previously obtained using the Direct-Fill VOA or Inverted VOA sample collection methods should be considered valid unless effervescence is known or suspected.
SOME TAKE-HOME MESSAGES...

2. **Effect of Well Purging**
   - Based on the wells tested, there appears to be no real benefit to purging larger volumes of water.

3. **Temporal Variability**
   - For some wells, large variability was observed. Methane concentrations varied by a factor of 1.4 to 2.9 over 18 months.

4. **Effect of Laboratory Methods**
   - Despite differences in sample transfer techniques, good agreement was observed between two laboratories.


Stephen D. Richardson, Ph.D, P.E.
GSI Environmental Inc.
(512) 346-4474
sdrichardson@gsi-net.com