Baseline Methane Concentrations in Drinking-Water Wells in the Appalachian Plateau Province of Western Maryland

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Introduction

What is methane?

- **Chemical properties**
  - No color, odor, or taste
  - Lighter than air
  - Highly flammable
  - \( \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \)
  - Water solubility \(~28\text{ mg/L}\)

- **Accumulation in confined areas**
  - Asphyxiation
  - Explosive conditions
  - Recommended action level of 10 mg/L (Eltschlager and others, 2001)
  - Mitigation using vented well cap or aeration systems
Origin of methane in ground water

- Thermogenic
- Biogenic

Sources of methane

- Organic-rich rocks
- Abandoned or leaking gas wells
- Coal seams; abandoned/active coal mines
- Landfills
- Swamps and marshes
Appalachian Plateau Province

Physiographic Provinces and Their Subdivisions in Maryland

Maryland Geological Survey
January, 2001
http://www.mgs.md.gov
Geology of Appalachian Plateau Province

Source: Maryland Geological Survey
Geologic cross section of Garrett County

Source: Maryland Geological Survey
Study Objectives

- **Background**
  - Methane in well water has been reported anecdotally
  - Methane is not routinely tested for in well water
  - No systematic study of well-water methane has been conducted in Maryland

- **Goals**
  1. Evaluate ambient methane concentrations in water wells in the Appalachian Plateau Province of Maryland
  2. Obtain a general understanding of the occurrence and distribution of methane
  3. Evaluate source(s) of methane in well water
  4. Determine methane variability at individual wells
Methods

Well selection process

- **Geology**
  - Coal basins (36 wells)
  - Non-coal regions (42 wells)

- **Topography**
  - Valleys (32 wells)
  - Hilltops/Hillsides (46 wells)

- **Other well criteria**
  1. Well permit number
  2. Submersible pump; well in use
  3. Access to untreated well water
  4. Reasonable spatial distribution
  5. No obvious or potential sources of contamination

<table>
<thead>
<tr>
<th></th>
<th>Coal</th>
<th>Non-coal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Valley</td>
<td>15</td>
<td>17</td>
</tr>
<tr>
<td>Hilltop+ Hillside</td>
<td>21</td>
<td>25</td>
</tr>
</tbody>
</table>
Methods

- **Sampling procedures**
  1. **Well purge**
     - pH, specific conductance, dissolved oxygen, temperature
     - 5-minute intervals until stabilization
  2. **Sample collection**
     - Methane sample collected using inverted bottle technique
     - Two 40mL glass vials per well site
     - Field measurements of alkalinity, chloride, and total hardness
  3. **Preservation and storage**
     - HCl drops added to glass vials (pH<2)
     - Vials stored on ice
Methods

Purge bucket with probes

Sampling bucket
Methods

- Inverted Bottle Technique
Results

- Dissolved methane concentrations ranged from less than 1.5 to 8,550 micrograms per liter (µg/L).

- 44 percent of wells (34 of 78) had methane detections (>1.5 µg/L).

- 56 percent of wells (44 of 78) had no methane detections (<1.5 µg/L).

- 4 wells exceeded 1,000 µg/L of dissolved methane. No wells exceeded the 10,000 µg/L (10 mg/L) recommended action level for dissolved methane.
Methane distribution
Methane in relation to topographic position and geologic setting

- **Hilltop/hillside**
  - n=46
  - 30<RL
  - 14<RL

- **Valley**
  - n=32

- **Coal basin**
  - n=36
  - 16<RL

- **Non-coal basin**
  - n=42
  - 28<RL
Results
Methane vs. age of geologic formation

Devonian

Mississippian

Pennsylvanian

Methane (micrograms per liter)

n=23

17<RL

n=19

11<RL

n=36

16<RL
Other water-quality data

<table>
<thead>
<tr>
<th>Category</th>
<th>Number of wells</th>
<th>Dissolved methane (µg/L)</th>
<th>pH</th>
<th>Specific conductance (µS/cm)</th>
<th>Dissolved oxygen (mg/L)</th>
<th>Alkalinity (mg/L as CaCO₃)</th>
<th>Chloride (mg/L)</th>
<th>Total hardness (mg/L as CaCO₃)</th>
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</thead>
<tbody>
<tr>
<td>Coal / Valley</td>
<td>15</td>
<td>6.7</td>
<td>7.5</td>
<td>297</td>
<td>&lt;1</td>
<td>139</td>
<td>&lt;10</td>
<td>130</td>
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<tr>
<td>Coal / Hilltop+Hillside</td>
<td>21</td>
<td>&lt;1.5</td>
<td>7.0</td>
<td>251</td>
<td>&lt;1</td>
<td>109</td>
<td>&lt;10</td>
<td>124</td>
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<tr>
<td>Non-Coal / Valley</td>
<td>17</td>
<td>&lt;1.5</td>
<td>7.9</td>
<td>172</td>
<td>1.4</td>
<td>58</td>
<td>&lt;10</td>
<td>50</td>
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<tr>
<td>Non-Coal / Hilltop+Hillside</td>
<td>25</td>
<td>&lt;1.5</td>
<td>7.3</td>
<td>181</td>
<td>&lt;1</td>
<td>72</td>
<td>&lt;10</td>
<td>68</td>
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<tr>
<td>ALL WELLs</td>
<td>78</td>
<td>&lt;1.5</td>
<td>7.4</td>
<td>218</td>
<td>&lt;1</td>
<td>88</td>
<td>&lt;10</td>
<td>80</td>
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</tbody>
</table>
Monthly methane concentrations
Thermogenic vs Biogenic?

(modified from Molofsky and others, 2011)
West Virginia study (Mathes and White, 2006)

- 170 water wells
- Sampled from 1997 to 2005

Main Findings

Methane concentration ranged from <1 to 68.5 mg/L.

Higher CH₄ levels (>10,000 µg/L):
- Wells completed in Pennsylvanian-age rock formations
- Wells located in low-sulfur coal areas
Pennsylvania study (Molofsky and others, 2011)

- +1,700 water wells
- Sampled from 2008 to 2011

Main Findings

Concentration of methane ranged from <0.1 to 43,000 µg/L.

Elevated CH$_4$ levels are:

- Common in Susquehanna County, PA
- The authors correlated with topography rather than proximity to oil and gas operations
New York study (Kappel and Nystrom, 2012)

- 239 water wells
- Sampled from 1999 to 2011

Main Findings

Methane detected in unconsolidated and bedrock aquifers.
Methane concentration ranged from <1 to >28,000 µg/L.
91% of wells ≤ 10,000 µg/L.
5 samples with methane level >28,000 µg/L.
Methane was detected in 34 of 78 wells tested (~44 percent). 44 of the wells (~56 percent) had no reported methane (less than 1.5 µg/L). Methane concentrations ranged from less than 1.5 to 8,550 µg/L.

4 wells exceeded 1,000 µg/L of dissolved methane. No wells exceeded the 10,000 µg/L (10 mg/L) recommended action level for dissolved methane.

Methane from wells in coal basins tended to be higher than from wells in non-coal basins. Methane from wells in valleys tended to be higher than from wells located on hilltops or hillsides. However, in both cases the overall concentrations were very low.

Monthly methane concentrations were quite variable.

δ^{13}C-CH_{4} and δ^{2}H-CH_{4} values from two samples indicate thermogenic origin for methane.
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Questions?

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