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Summary of the Technical Workshop on Analytical Chemical Methods

February 25, 2013

Disclaimer

This report was prepared by EPA with assistance from Eastern Research Group, Inc., an EPA contractor, as a general record of discussions during the February 25, 2013, technical workshop on analytical chemical methods. The workshop was held to inform EPA's *Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources*. The report summarizes the presentations and facilitated discussions on the workshop topics and is not intended to reflect a complete record of all discussions. All statements and opinions expressed represent individual views of the invited participants; there was no attempt to reach consensus on any of the technical issues being discussed. Except as noted, none of the statements in the report represent analyses or positions of EPA.

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Meeting Agenda

Technical Workshop on Analytical Chemical Methods
February 25, 2013

US EPA Research Triangle Park Campus
"C" Building Auditorium
Research Triangle Park, NC

8:00 am **Registration/Check-in**

8:30 am **Welcome** ..... *Glenn Paulson, Science Advisor, US EPA*

8:35 am **Purpose of Workshop and Introductions** ..... *Workshop Co-Chairs:*
Jennifer Orme-Zavaleta, US EPA
Wilma Subra, Subra Company

Session 1: Analytical Methods for Chemical Analytes

8:45 am ***Panel:***

- **EPA Analytes and Current Analytical Methods** ..... *Brian Schumacher, US EPA*
- **Analytical Considerations During Natural Gas Fracturing Activities ....** *Rock Vitale, Ruth Forman and David Thal*
  Environmental Standards, Inc.
- **Considerations for Determining the Source of Groundwater Contamination Associated with Hydraulic Fracturing** ..... *Glenn Miller, University of Nevada-Reno and Ann Maest, Stratus Consulting, Inc.*
- **Indicator Parameters** ..... *Ileana Rhodes, Shell Global Solutions (US), Inc.*
- **Alternative Methods to RSK 175 Using Purge and Trap Concentration and Automated Headspace for the Analysis of Dissolved Gases in Drinking Water** ..... *Nathan Valentine, Teledyne Tekmar*
- **Important Considerations in the Use of Carbon and Hydrogen Stable Isotopes to Determine the Origin of Hydrocarbons in Groundwater – A Case Study from Pre-Shale Gas Tioga County** ..... *Kinga Revesz, U.S. Geological Survey*

Questions of Clarification

Break (10 minutes)

Facilitated discussion among workshop participants focusing on key questions:

- What other/different/new methods should EPA consider for their analytes, and why (i.e., what limitations do these other methods overcome)?
- What other analytes should EPA be testing for, and why? What methods would we use for other analytes?
- What considerations arise relative to the differences between various matrices (injection fluids, groundwater, surface water, produced and flowback water) and the effects of high TDS, radionuclides, interference?
- What levels of sensitivity are needed for analytical methods to detect effects, serve as indicators of connection to hydraulic fracturing?

Moderator: Jennifer Orme-Zavaleta, US EPA

11:45 am **Summary of Session 1**

12:00 pm Lunch and Poster Session

Session 2: Future Trends in Hydraulic Fracturing Chemical Usage and Implications for Analytical Methods

1:30 pm ***Panel:***

- **Emerging Technologies and Increasing Data Interpretation Concerns**.....*Johnny Mitchell, TestAmerica Laboratories, Inc.*
- **Beneficial Reuse of Produced and Flowback Water**.....*David Stewart, Energy Water Solutions, LLC*
- **Monitoring Subsurface Fluid Flow Using Perfluorocarbon Tracers:**

  Another Tool Potentially Available for Subsurface Fluid Flow Assessments .....*Tommy Phelps, Oak Ridge National Laboratory*
- **New Isotopic Tracers for Shale Gas and Hydraulic Fracturing Fluids**.....*Avner Vengosh, Duke University*

Questions of Clarification

Facilitated discussion among workshop participants focusing on key questions:

- What is changing in the chemical makeup of hydraulic fracturing injection fluids, and what are the implications for chemical selection or field sample analysis?
- What has been your experience with artificial tracers for tracking hydraulic fracturing fluids? What analytical methods are suitable?

Moderator: Wilma Subra, Subra Company

3:45 pm **Summary of Session 2**

3:55 pm **Closing Remarks**..... *Ramona Trovato, US EPA*

4:00 pm Adjourn

Poster Session

Hydraulic Fracturing Fluid Analysis for Regulatory Parameters – A Progress Report
Kesavalu Bagawandoss, Accutest Laboratories, Inc.

Laser Induced Breakdown Spectroscopy (LIBS) for Rapid Monitoring of Metals in Produced Water and Its Precipitates
Helen Boylan, Westminster College

Using Integrated Noble Gas and Hydrocarbon Geochemistry to Constrain the Source of Hydrocarbon Gases in Shallow Aquifers in the Northern Appalachian Basin
Thomas Darrah, Duke University

Potential Use of Passive Sampling for Environmental Monitoring of Petroleum E&P Operations
Paul Edmiston, College of Wooster/ABS Materials, Inc.

Hierarchical Analytical Approaches for Unraveling the Composition of Proprietary Mixtures
Jennifer Field, Oregon State University

Analysis and Treatment of Waters from Hydraulically Fractured Oil and Gas Wells
Lawrence Wackett, University of Minnesota

List of Meeting Participants

Technical Workshop on Analytical Chemical Methods

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Rick Wilkin
US EPA ORD/National Risk Management Research Laboratory

Beizhan Yan
Columbia University

* Presenter

Introduction

At the request of Congress, the U.S. Environmental Protection Agency (EPA) is conducting a study to better understand the potential impacts of hydraulic fracturing on drinking water resources. The scope of the research includes the full cycle of water associated with hydraulic fracturing activities. In the study, each stage of the water cycle is associated with a primary research question:

- **Water acquisition:** What are the possible impacts of large volume water withdrawals from ground and surface waters on drinking water resources?
- **Chemical mixing:** What are the possible impacts of hydraulic fracturing fluid surface spills on or near well pads on drinking water resources?
- **Well injection:** What are the possible impacts of the injection and fracturing process on drinking water resources?
- **Flowback and produced water:** What are the possible impacts of surface spills on or near well pads of flowback and produced water on drinking water resources?
- **Wastewater treatment and waste disposal:** What are the possible impacts of inadequate treatment of hydraulic fracturing wastewaters on drinking water resources?

In 2013, EPA is hosting a series of five technical workshops related to its *Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources*. The five technical workshops include Analytical Chemical Methods (February 25, 2013), Well Construction/Operation and Subsurface Modeling (April 16–17, 2013), Wastewater Treatment and Related Modeling (April 18, 2013), and the upcoming workshops on Water Acquisition Modeling and Hydraulic Fracturing Case Studies. The workshops are intended to inform EPA on subjects integral to enhancing the overall hydraulic fracturing study, increasing collaborative opportunities and identifying additional possible future research areas. Each workshop will address subject matter directly related to the primary research questions.

For each workshop, EPA is inviting experts with significant relevant and current technical experience. Each workshop consists of invited presentations followed by a facilitated discussion among all invited experts. Participants are chosen with the goal of garnering viewpoints from a diverse set of stakeholder groups including industry; nongovernmental organizations; other federal, state and local governments; tribes; and the academic community.

The first workshop was held on February 25, 2013, and focused on Analytical Chemical Methods. The workshop was co-chaired by Dr. Jennifer Orme-Zavaleta (EPA) and Wilma Subra (Subra Company). A morning session addressed *Analytical Methods for Chemical Analytes of Interest* (Section 1 of this report), while the afternoon session focused on *Future Trends in Hydraulic Fracturing Chemical Usage and Implications for Analytical Methods* (Section 2). In addition, several experts shared technical knowledge during a poster session (Appendix C).

Summary of Presentations for Session 1: Analytical Methods for Chemical Analytes

Dr. Glenn Paulson, Science Advisor to the EPA Administrator, opened the workshop and welcomed the participants. He noted that the five technical roundtables conducted in November 2012[1] generated the ideas for the 2013 technical workshops. He emphasized that the workshop was not operating under the Federal Advisory Committee Act (FACA) and therefore was not expected to reach consensus, but rather to engage in vigorous discussion and debate. Dr. Paulson thanked the presenters for providing materials in advance, and encouraged participants to consider attending the future technical workshops.

Dr. Jennifer Orme-Zavaleta, Director of EPA's National Exposure Research Laboratory (NERL), described the purpose of the workshop. She noted that the 2012 roundtable meetings had identified a number of questions about analytical methods. She expressed the hope that information from the workshop could help EPA interpret results from the study on drinking water resources and help the Agency look to the future in determining a course of action.

Dr. Jennifer Orme-Zavaleta and **Dr. Brian Schumacher,** U.S. EPA, presented an overview of analytes and current analytical methods in EPA's study. Dr. Orme-Zavaleta noted that chemical mixing, flowback and produced water, and water treatment and waste disposal are the areas of the water cycle requiring analytical methods development. She stated that while base methods (i.e., promulgated standard EPA methods such as SW-846) are available for the majority of the analytes, EPA is working to improve the accuracy, precision, and sensitivity of methods for complex hydraulic-fracturing-related matrices. Dr. Schumacher is working to develop methods for eleven (11) key classes of chemicals. He described the challenges of methods development: lack of a validated standard method for an analyte in a specific matrix (fracturing fluid, flowback and produced water, treated wastewater); highly complicated, time-consuming existing methods; and methods that lack the sensitivity to meet the needs of the program. Dr. Schumacher described the steps involved in analytical method validation and the status of methods development for analytes of interest. He then presented examples of methods development for glycols and radionuclides.

Rock Vitale, Environmental Standards, Inc., discussed analytical considerations during hydraulic fracturing activities from an emergency response viewpoint. He presented two case studies to illustrate how natural gas companies can use method development and knowledge of sampling and analysis processes to resolve issues related to hydraulic fracturing. In the first case study, a large number of glycol detections were observed in water wells tested after a release of flowback water. An investigation revealed glycol contamination in the preserved vials used for sampling. Mr. Vitale stated that this case study showed the need for standard operating procedures with vigorous quality control practices for sample collection and analysis, such as collection of field blanks and pre-testing of bottle ware and preservatives. The second case study involved the surface release of fracturing fluid that contained compounds not routinely tested for in laboratories, so that emergency method development was required. Mr. Vitale stated that for

[1] See *Summary of Technical Roundtables on EPA's Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources* (http://epa.gov/hfstudy/pdfs/summary-of-technical-roundtables.pdf).

unusual analytes that are not routinely the subject of testing and identification robust method development is needed to ensure complete characterization, preferably before a release occurs.

Dr. Glenn Miller, University of Nevada, Reno, discussed considerations in determining the source of ground water contamination associated with hydraulic fracturing. He stated it is critical to conduct pre-fracturing sampling of ground water quality for as many additive fracturing compounds as possible. Dr. Miller described geologic and chemical issues that affect the ability to detect hydraulic-fracturing-related contamination in ground water. He stated that the presence of certain constituents in formation water (total dissolved solids [TDS], methane and sulfate) is insufficient to determine that hydraulic fracturing is the cause of ground water contamination; anthropogenic hydraulic fracturing chemicals along with produced water constituents are better possible indicators. He discussed a hypothesis that the increased presence of natural gas can increase activity of sulfate-reducing bacteria and, in turn, reduce drinking water quality. He also described the use of boron isotopes as a possible promising approach for distinguishing sources of ground water contamination at unconventional oil and gas operations.

Dr. Ileana Rhodes, Shell Global Solutions, discussed indicator parameters for baseline assessment of ground water conditions, post-drill ground water monitoring, and gas characterization. She stated that TDS, chloride and sodium are the most reliable indicator parameters for assessing potential impact to ground water from hydraulic fracturing, because they are in the highest concentrations in produced water. Dr. Rhodes noted that if these parameters are elevated above baseline conditions, further evaluation may be warranted. She stressed the importance of pre-drill baseline assessment of ground water and water supply wells, including isotopic analysis of headspace and dissolved gas. She noted that for determining gas migration sources, multiple lines of evidence and a thorough understanding of site conditions are necessary. In some areas of the country, she stated, deep gas may show "isotopic reversal" (i.e., methane is isotopically lighter than ethane above a certain depth, and heavier below a certain depth), making analysis of isotopic ratios potentially useful in some locations. Dr. Rhodes also indicated that analysis for benzene, toluene, ethylbenzene and xylenes (BTEX) may also be a useful indicator in wet gas areas.

Nathan Valentine, Teledyne Tekmar, described methods developed for determination of dissolved gases (methane, ethane, ethene and propane) in water. He stated that the currently used method, RSKSOP-175, lacks a standard calibration method, resulting in variations from lab to lab. The Pennsylvania Department of Environmental Protection (PADEP) developed a modified method (PADEP 3686) that, according to Mr. Valentine, simplified and standardized sample preparation, but still required sample manipulation for each analysis. Mr. Valentine described a new method that uses purge and trap instrumentation available in all environmental labs, automated headspace analysis, and a gas chromatogram/flame ionization detector (GC/FID) system. He stated that complete automation of sample preparation greatly increases efficiency and throughput, as well as eliminating the potential for human error by making it unnecessary to manipulate the sample. The method was approved by PADEP (PADEP 9243) in October 2012.

Dr. Kinga Revesz, U.S. Geological Survey, presented a 2005 (pre-hydraulic fracturing) case study from Tioga County, Pennsylvania, to illustrate the use of carbon and hydrogen stable isotopes to determine the source of natural gas in water wells. Dr. Revesz began by explaining the formation and isotopic signatures of thermogenic and microbial methane. In this study, Dr. Revesz identified four potential sources of the methane in water wells: native gas in the Oriskany

Sandstone (thermogenic origin), shallow native gas in Devonian bedrock (thermogenic), non-native gas from a gas-storage field (thermogenic), and microbial gas from organic debris in unconsolidated sediments. The isotopic composition of methane allowed researchers to determine whether the gas in the water wells was microbial or thermogenic in origin. By considering the isotopic composition of ethane and methane together, Dr. Revesz was able to distinguish the different thermogenic origins of the gases in water wells. In the Tioga study area, she said, almost all the thermogenic methane in the water wells matched the storage field gas. Dr. Revesz discussed the essential data needed to identify stray gas origins. She noted that the data from this study might be useful to determine if hydraulic fracturing has further impacted the aquifer system.

Summary of Discussions Following Session 1: Analytical Methods for Chemical Analytes

Participants were asked to consider the following questions during the discussion:

- What other/different/new methods or modifications should EPA consider for its analytes, and why (i.e., what limitations do these other methods overcome)?
- What other analytes should EPA be testing for, and why? What methods would we use for other analytes? Are there any that EPA should *not* be testing for?
- What considerations arise relative to the differences between various matrices (injection fluids, produced and flowback water) and the effects of high TDS, radionuclides, interference?
- What levels of sensitivity are needed for analytical methods to detect effects or serve as indicators of connection to hydraulic fracturing?
- What defines "how low is low enough" in testing for an analyte?
- What has been your experience in addressing analytical challenges?

Key themes from Session 1 discussion:

Baseline information. Participants noted the importance of collecting baseline data to understand the quality of formation water and produced water, including concentrations of organic matter and methane. Participants raised the issue of needing a robust dataset because of variability (e.g., seasonal variations, natural variability, and issues related to construction of private water supply wells). It was suggested that guidance on baseline sampling (e.g., where, when, questions to ask about well operating conditions) would be helpful.

Sampling procedures. Several participants recommended a focus on sampling, including sample collection, timing of collection, preservation, holding times and storage. The importance of developing a strategic sampling plan was discussed. One participant stated that it is not possible to identify potential contaminants in produced and flowback waters in advance, because of factors such as local geology and specific hydraulic fracturing fluids used. Therefore, it is important to take preserved and unpreserved samples, equipment blanks, and field collection blanks to maintain an archive. Field turbidity measurements before and after sampling were also recommended. It was suggested that EPA determine meaningful holding times for archiving and for regulatory acceptance. A participant also mentioned the need for certified or standard reference materials. It was noted that the U.S. Geological Survey has robust sampling protocols.

Analytical approaches. A number of participants suggested a "triage" or tiered approach, first evaluating for key indicators, such as high TDS, chlorine and sodium. If the concentrations of first-tier chemicals are significantly elevated, participants suggested performing additional (second-tier) analyses specific to conditions associated with the well, local geology, or company

practices. As possible second-tier analyses, participants suggested analyses for radionuclides, gases, and isotopic analyses to determine whether gas is of microbial or thermogenic origin. Several participants suggested that the primary purpose of analysis for additives is forensic (determining the source of contamination) rather than evaluation of toxicity or water quality impacts.

A number of participants supported the need to examine multiple lines of evidence to determine if the contamination is due to an incident or due to the natural variability of water over time. Participants suggested evaluating for chlorine, total Kjeldahl nitrogen, total organic carbon, and BTEX in some locations, in addition to TDS. Another participant described the unknown number of products in hydraulic fracturing fluids and potential barriers to reverse engineering of these fluids, especially for water-soluble products. Another participant recommended against strictly using EPA's initial list of analytes as a means for detecting a potential incident, suggesting that EPA adopt a research approach—that is, look not only at contaminants but how the water chemistry is changing (follow a tiered approach).

In discussing the use of tracers (as distinct from indicators), a participant stated that a scientific assessment is needed, e.g., what happens to tracers under high temperature/pressure conditions, before EPA incorporates them into the study. (In this discussion, participants used "tracer" to describe a compound added to the hydraulic fracturing fluid specifically designed to trace the movement of the hydraulic fracturing fluid.) The tracer would be required to be chemically stable under the high temperatures/pressures encountered during hydraulic fracturing processes. An indicator, on the other hand, is defined as a chemical (generally in the hydraulic fracturing fluid) or property used to ensure the integrity of the well construction.

Other considerations for analyte selection and methods development. Several participants discussed the need to consider lab capability and capacity, availability of equipment, and costs for specific analytical methods. For example, analyses for exotic organics are costly, requiring a low detection limit and high accuracy/precision. Another example mentioned was isotopic analysis- if everyone collected isotopic signatures as baseline data, laboratories would quickly be inundated.

Several participants supported the importance of developing and testing methods specific to the matrix of concern (i.e., determine sensitivity and detection limits based on the actual matrix and not try to make a method applicable to everything). Methods successfully developed and tested for the specific matrices will provide more reliable data.

One participant recommended analyses for disinfection byproduct precursors (not just the compounds themselves) that could render wastewater more difficult and costly to treat to meet the wastewater regulations. Another attendee discussed analyses needed for flowback and produced water reused for hydraulic fracturing, noting the lack of accurate and precise tests for polysaccharides, such as guar gum.

Several participants stated that for radionuclides analyses, radium-226 and radium-228 data could be valuable but gross alpha data are not useful. Several participants recommended against the use of the methylene blue active substances assay, a colorimetric analysis test method to detect the presence of anionic surfactants. For evaluating isotopic signatures, participants suggested considering existing information such as compound-specific isotope analysis.

Quality assurance/quality control (QA/QC). Throughout the session, the issue of needing and using appropriate QA/QC controls was discussed. For field sampling, it was suggested that both preserved and unpreserved samples be collected. It was stated that in all cases, the use of field blanks and replicate analyses was a must. In the laboratory, it was noted, contamination can come from many sources, with the example given of hydrochloric acid (HCl) used to preserve a sample causing contamination of the sample with glycol (an impurity in the acid). Because of issues like this, the use of appropriate QA/QC samples such as laboratory blanks is essential. Several participants said that the issue of instrument sensitivity should be decided based on the matrix being tested. One participant indicated that sample holding times should be revisited from a regulatory perspective, as some of the holding times could be extended with no significant loss of sample integrity. It was stated that the shorter holding times put pressure on the analytical laboratories and lead to more data flagging. The need for certified or standard reference materials was discussed for those chemicals that are not on standard EPA chemical lists.

Summary of Presentations for Session 2: Future Trends in Hydraulic Fracturing Chemical Usage and Implications for Analytic Methods

Mr. Johnny Mitchell, TestAmerica Laboratories, Inc., discussed potential data interpretation concerns associated with emerging analytical technologies. He discussed the increased risk of false positive results when using the Method Detection Limit (MDL) reporting and more sensitive analyses in forensic investigations for trace analytes. False positives are of particular concern for inorganic parameters, he stated, with potential for significant impact on the interpretation and use of analytical data. Mr. Mitchell stated that the potential for false positives for specific analytes can be estimated by evaluating the frequency of positive results above the MDL in historical laboratory blank data.

Dr. David Stewart, Energy Water Solutions, LLC, discussed analytical considerations in recovery and reuse of hydraulic fracturing fluids. Because of the large volumes of water used in hydraulic fracturing, companies are increasingly considering water recovery and reuse. Dr. Stewart discussed the contaminants of concern in produced and flowback water (both naturally occurring chemicals and those injected into the formation). He observed that guar gum, scale-forming chemicals, and hydraulic fracturing chemical accelerants in particular are difficult to remove and will be a challenge for water reuse. Dr. Stewart noted that reuse will require consideration of regulatory requirements in the Clean Water Act and water rights regulations. He emphasized that testing requirements depend on the end use of the water (Class II injection well, direct reuse, discharge to surface water) and he advocated the development of criteria for reuse/recycling and reliable field tests to control the selected treatment processes.

Dr. Tommy Phelps, Oak Ridge National Laboratory, discussed the use of perfluorocarbon tracers (PFTs) as a potential tool for subsurface fluid flow assessments. PFTs, he stated, are conservative, non-reactive, non-toxic and low-cost tracers, sensitive at the picogram to femtogram (10^{-12}–10^{-15}) level. He described the results of studies in which PFTs were used to monitor carbon dioxide plumes in carbon sequestration field demonstrations. PFTs, he stated, can complement geophysical, geochemical and modeling tools to monitor and verify plume movement and leakage to shallow aquifers or the surface. Dr. Phelps noted that while their use is not recommended in every situation (i.e., because of their greenhouse gas traits and high global warming potential), PFTs are one tool available for consideration.

Dr. Avner Vengosh, Duke University, discussed the use of new isotopic tracers for shale gas and hydraulic fracturing fluids. He described a study begun in 2010 in which more than 700 water samples from the Appalachian Basin were measured for a large spectrum of dissolved constituents. He stated that the study showed that the isotope ratios of oxygen ($\delta^{18}O$), hydrogen ($\delta^{2}H$), strontium ($^{87}Sr/^{86}Sr$), boron ($\delta^{11}B$), and radium ($^{228}Ra/^{226}Ra$) in flowback and produced waters from both conventional and unconventional oil and gas wells have distinctive fingerprints that are different from the compositions of regional ground water and surface waters in areas of shale gas exploration and waste disposal. Dr. Vengosh said that the development of combined isotopic tracers could provide a unique methodology for tracing and monitoring shale gas and hydraulic fracturing fluids in the environment.

Summary of Discussions Following Session 2: Future Trends in Hydraulic Fracturing Chemical Usage and Implications for Analytical Methods

Participants were asked to consider the following questions during the discussion:

- What is changing in the chemical makeup of hydraulic fracturing injection fluids, and what are the implications for chemical selection or field sample analysis?

- What has been your experience with artificial tracers for tracking hydraulic fracturing fluids? What analytical methods are suitable?

Key themes from Session 2 discussion:

Changes in hydraulic fracturing fluid composition and implications for chemical selection and analysis: Several participants noted that the makeup of hydraulic fracturing fluid is changing as companies learn what works best, look for more environmentally friendly chemicals with the same functionality, and strive to use less fresh water through the recycling and reuse of produced waters. Some participants stated their belief that the list of additives in use is shrinking, and is not static. The list of additives is continually evolving as new compounds are added for specific needs. A participant noted that Congress's list of chemicals used in hydraulic fracturing was based on products manufactured, not necessarily used, and a chemical on that list might be used very rarely or may no longer be a viable choice.

Several participants noted that reuse of flowback and produced water is on the rise, and the makeup of reused water can decrease the need for chemical additives. Some participants noted that there are limits regarding the quality of reused water for hydraulic fracturing purposes and treatment costs must be considered. If hydrogen sulfide levels or scaling potential are too high, it was stated, then the water cannot be reused as hydraulic fracturing fluid. When analyzing flowback and produced waters for reuse, the common issue of matrix interferences and the need for standard/certified reference materials was also raised.

Sampling for research: A participant asked about the possibility of monitoring at shale gas sites to look at water and gases in the subsurface (in addition to monitoring now being conducted at private or public wells). A participant described the possibility of monitoring wells at shale gas sites at the University of Tennessee. An EPA participant described current cooperative efforts with industry in working toward drilling monitoring wells before hydraulic fracturing begins. Ongoing sampling would help in understanding what happens in the subsurface, and in identifying best management practices. An EPA participant noted that such an effort would benefit the entire industry.

Detection limits ("How low is low enough?"). Several participants raised questions about the use of a statistically determined MDL as defined in 40 CFR Part 136. It was noted that revisions to EPA's guidance document *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods* (SW-846) recommend using the Lower Limit of Quantitation (LLOQ) rather than the MDL, the LLOQ being the lowest calibration standard that can be reliably and precisely

determined by the analytical instrument. Clean Water Act and Safe Drinking Water Act regulations, however, still specify the MDL. A participant noted that legitimate scientific methods are now available for using data below the detection limit and books have been published on the subject matter. A participant also pointed to potential migration and dilution of chemicals from flowback and suggested that EPA consider different detection limits for ground water and surface water versus flowback/produced water matrices.

Tracers and associated analytical methods: Participants discussed the difference between tracers and indicators, noting that tracers are chemicals added solely for determining the movement of fluids at well-specific locations whereas indicators are chemicals already used in fracturing fluid formulations that can be used to forensically determine movement of fluids from a more general area of wells. Attendees added that indicators may also provide information on well integrity (to be addressed in an April 2013 workshop). Current tracers described by meeting attendees include PFTs and isotopic tracers. It was observed that there are tradeoffs, such as the high global warming potential of PFTs as well as other potential health and environmental concerns that can preclude their use, and they are not suitable in every situation. A participant also noted the limited number of suppliers for radioactive isotopes.

Field sampling for methane. Participants discussed grab sampling versus capturing methane in a submerged collection system. During grab sampling, the sample is collected at the surface under different pressure and temperature regimes that lead to a potential loss of the methane when compared to the collection of the sample at depth in the well where the increased pressure and temperature help maintain the methane in the sample. It was noted that a retrospective case study in Colorado was looking at the reproducibility of the submerged method. Participants also mentioned in-line sampling at hydrostatic pressure, and laser-based devices to measure methane and carbon isotopes. Several participants recommended that EPA establish field protocols and QA/QC procedures for methane sampling. An EPA participant expressed interest in hearing what participants had learned to improve sampling integrity.

Concluding Remarks

Dr. Glenn Paulson expressed appreciation for the workshop presentations and posters, and thanked all the participants for the high-level, focused discussions throughout the day. He noted that in March 2012, the White House released a strategy to address all unconventional oil and gas resources, available at http://unconventional.energy.gov. Additionally, EPA, the Department of the Interior and the Department of Energy have signed a memorandum of agreement to begin a comprehensive study of all unconventional oil and gas resources. A framework for a multi-year study has been drafted, addressing resource estimates, seismic issues, water quality and water quantity, air quality, and effects on communities. A process will be undertaken to involve technical experts, similar to roundtables and workshops underway for the study of the potential impacts of hydraulic fracturing on drinking water resources.

Dr. Paulson noted that this workshop on analytical methods was the first in a series of five in 2013, and encouraged the attendees to nominate themselves for participation in the upcoming workshops:

- Well construction/operation and subsurface modeling (April 16–17, 2013)
- Wastewater treatment and related modeling (April 18, 2013)
- Water acquisition modeling (upcoming)
- Hydraulic fracturing case studies (upcoming)

Ramona Trovato, Associate Assistant Administrator for the EPA Office of Research and Development, provided additional information about the upcoming workshops. She encouraged the participants to submit data and scientific literature to inform the current drinking water resources study, as described in the November 5, 2012, *Federal Register* notice (see http://www.regulations.gov, Docket ID No. EPA-HQ-ORD-2010-0674). Ms. Trovato expressed appreciation to the participants for their time and expertise, and said that EPA looked forward to working with them in all of its future efforts in this area.

Appendix A.

Extended Abstracts from Session 1: Analytical Methods for Chemical Analytes

EPA Analytes and Current Analytical Methods

Brian Schumacher, Ph.D.
US EPA, Office of Research and Development, National Exposure Research Laboratory,
Environmental Sciences Division

Information presented in this abstract is part of EPA's ongoing study. EPA intends to use this, combined with other information, to inform its assessment of the potential impacts to drinking water resources from hydraulic fracturing. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Introduction

In order to determine the concentration of hydraulic fracturing (HF) related chemicals, if present, in drinking, ground, flowback and produced water, and treated wastewater, we require analytical methods that are robust and that have been properly verified. Sample analysis is an integral part of the EPA's plan to study the potential impacts of hydraulic fracturing on drinking water resources (EPA, 2011) and is clearly specified in research plans being conducted for the study's retrospective case studies, prospective case studies, and laboratory studies. Analytical methods enable accurate and precise measurement of the presence and quantities of different chemicals. The quantification of the presence or absence of chemicals in hydraulic fracturing (HF) matrices will have substantial implications on the conclusions of the study; thus, they are likely to be very contentious when results are made public. Therefore, it is of prime importance that for the chemical analytes to be identified in the study, the methods selected for their determination must be examined for the efficiency and efficacy in the wide variety of wastewaters associated with hydraulic fracturing.

EPA compiled a chemical list from publicly available sources with more than 1,000 chemicals that could potentially be used during hydraulic fracturing processes or could be present in flowback and produced water (EPA, 2012). The chemicals present in hydraulic fracturing-related waters range in properties from the inert and innocuous (e.g., sand and water) to reactive and toxic (e.g., alkylphenols and radionuclides). Little information is available on the chemicals found in flowback and produced water and treated wastewater. Of specific public health and analytical concern is the new suite of naturally occurring chemicals mobilized within the formation during injection and brought to the surface during flowback and the daughter and reaction products of the parent chemicals that are continuously forming throughout injection, flowback, storage, treatment at wastewater facilities (e.g., chlorination or bromination) and, ultimately, disposal.

Research Approach

Chemical Selection

EPA generated an initial list of 10 to 20 chemical analytes to initiate analytical method testing activities. To help prioritize chemicals for method testing, a group of EPA hydraulic fracturing researchers and EPA analytical laboratory chemists discussed which factors were most

important to the research needs of the hydraulic fracturing study. The resulting criteria for selecting these chemical analytes included, but were not limited to:

1. frequency of occurrence of the chemicals in the hydraulic fracturing fluids and waste waters,
2. toxicity of the chemical,
3. mobility in the environment (expected fate and transport), and
4. availability of instrumentation/detection systems for the chemical.

Available information was examined (chemical lists, reports, journal articles, gray literature, etc., excluding confidential business information) with these criteria in mind and a list of 10 to 20 initial chemical analytes was established. During the determination of the chemical analyte short list, a few resources in particular were especially helpful in determining the frequencies of occurrence and toxicities of the chemicals with the report on "Chemicals Used in Hydraulic Fracturing" by the U.S. House of Representatives Committee on Energy and Commerce as a key reference to determine chemicals that are used in a high number of hydraulic fracturing-related products (Waxman et al., 2011) being especially useful. In addition to the Committee Report (Waxman et al. 2011), analysis by Colburn et al. (2011) provided EPA with frequency and toxicity information. The report compiled information from MSDSs from industry and government agencies and compared the chemicals in their list with toxic chemical databases, such as TOXNET and the Hazardous Substances Database. The list of chemicals in Colburn et al. (2011) was generated by reviewing MSDSs that were provided to the Committee (Waxman et al. 2011) by the 14 leading oil and gas service companies in the U.S. (excluding confidential business information).

The initial priority list was vetted first among a small group of hydraulic fracturing analytical laboratory researchers within EPA and then to the full group of EPA HF researchers to ensure that the list was accurate, useful, and that the selected chemicals should be the first to have their methods tested, verified, and possibly validated. The final list of chemical analytes (Table 1) for analytical method testing has 14 different classes of chemicals, 44 specifically identified elements or compounds, 5 groups of compounds (e.g., ethoxylated alcohols and light petroleum distillates) and 2 related physical properties (gross α and gross β analyses associated with the radionuclides). We will continuously review the list as the study progresses, and as needs arise, new chemical analytes can and will be added to the list for analytical method testing and development.

Analytical Method Testing

Analytical method testing associated with the hydraulic fracturing study is necessary to determine if standard methods give accurate and precise measurements of a chemical in a specific matrix, if non-standard methods allow accurate and precise measurement when standard methods are unsuccessful and, in the case where no method exists, the accuracy, precision, and sensitivity of newly developed methods are established. In some cases, the chemicals of interest are elements or compounds commonly tested under different EPA regulatory programs, such as for the Resource Conservation and Recovery Act (RCRA), the Comprehensive Environmental

Response, Compensation, and Liability Act (CERCLA), the Clean Water Act (CWA) and the Safe Drinking Water Act (SDWA). These standard, promulgated methods will be used as base methods in the analytical method testing program. In each of these cases, the analytical methods were developed for a specific matrix or set of matrices and have not been tested in the particular matrices associated with hydraulic fracturing, which may have particularly high concentrations of total dissolved solids (TDS; 20,000 to greater than 100,000 mg L^{-1} TDS). Hence, the existing analytical methods need to be tested, and at times adjusted, to ensure the integrity of the data generated in conjunction with all aspects of EPA's hydraulic fracturing study. In other cases, standard, promulgated methods are non-existent. In these situations, methods that have been published in the peer-reviewed literature or developed by consensus standard organizations (e.g., American Society for Testing and Materials; ASTM) are used. However, these methods are rarely developed for or tested with matrices similar to those resulting from hydraulic fracturing so method testing is required. Finally, in rare, but existing, cases where no documented methods exist, researchers have developed new methods for use in determining the concentrations of certain chemicals analytes. For the latter two situations, the analytical methods selected for use must undergo rigorous testing, verification, and potential validation to ensure that the data generated using these analytical methods are of known and high quality.

The first step in the analytical method testing phase is to identify existing, promulgated, standard method(s) specifically developed for the priority chemical(s) of interest. Standard methods may exist for specific chemicals or for a general class of chemicals (e.g., the chemical is volatile or semi-volatile). Alternately, if an existing standard method is not available but a suitable method is published either in the peer-reviewed literature or through a consensus standard organization, then that method is selected for the base method for the initial testing of the priority chemical (Table 2).

Once a base method has been selected for testing, the method is examined to determine its feasibility and subsequent usefulness as a base method for the hydraulic fracturing study. Some of the challenges that have been identified upon examining the base methods and that need to be addressed during the method testing process include: (a) the method was developed only for a partial list of the chemicals of interest; (b) the method's sensitivity (i.e., detection limits) are too high to meet the needs of the study; (c) matrix interferences, generally due to high total dissolved solids and high salt contents may exist leading to biased results; and (d) poor extraction efficiency for the chemical(s) of interest leading to results that are typically biased low (i.e., concentrations reported are less than what is really in the sample). For several of the base methods, it is believed that the base method will work in hydraulic fracturing matrices but their effectiveness to produce accurate and precise measurements need to be confirmed.

Once an appropriate base method is selected, the next step is to analyze a batch of samples applying all the quality assurance/quality control (QA/QC) measures specified in the Quality Assurance Project Plan (QAPP). Testing will take place first using laboratory water samples containing known concentrations of an analyte (also known as spiked samples) to familiarize the analyst with the method procedure, to eliminate any potential matrix interferences, and to determine various QA/QC control parameters, such as sensitivity, bias, precision, spike recovery, and analytical carry-over (i.e., sample cross-contamination) potential. Upon completion of the analyses, the results from the QA/QC samples are examined to

determine if they met the acceptance criteria specified in the QAPP (DeArmond and Schumacher, 2011), and thus, are sufficient to meet the needs of the research study. Some of the key QA/QC samples examined include:

- standard and certified reference materials (where available) for bias;
- matrix and surrogate spikes for bias (when reference materials are not available) and matrix interferences;
- replicates for precision; and
- blanks for analytical carry-over.

If the acceptance criterion for any of the QA/QC samples is not met, typically the sample is re-run to ensure that the result is not just a random event. If the acceptance criterion is continually not met, a systematic problem is indicated and method modification is undertaken to help reduce or eliminate the problem.

The method modification process can take many forms depending on the specific circumstances and may include changing sample preparation and clean-up techniques, solvents, filters, gas flow rates, temperature regimes, injector volumes, chromatographic columns, analytical detectors, etc. Once the method modification process is complete, the analysis is repeated as described above using spiked laboratory water. If the new QA/QC sample results now meet the acceptance criterion, the method modification is deemed to have been successful for that matrix (i.e., type of hydraulic fracturing water), and an updated standard operating procedure (SOP) will be prepared followed by continued testing in more complex water matrices.

One of the essential elements during the method modification process is the need to clearly document the change(s) made to the base method. The documentation should include what was changed, why the change was made, the success of the change, and the level of success. When reporting the final modified method and associated data, the analytical method is typically reported as "modified Method XYZ in which AAA was changed to BBB to improve the CCC of the chemical(s)" where XYZ is the base method, AAA was the original condition specified in the base method, BBB is the change made, and CCC is the QA/QC parameter that the change was made to improve.

In extreme cases, if after testing and modification of the identified base methods fail to accurately and precisely quantify the chemical and/or fails to have the sensitivity required by the research program, then the last route in the methods testing program would be to undertake a new method development activity.

Table 1. Chemicals Identified for Initial Analytical Method Testing.[1]

Chemical Class	Chemical Name(s)	CASRN	Purpose in Hydraulic Fracturing	Reason Selected
Alcohols	Propargyl alcohol	107-19-7	Corrosion inhibitor	Toxicity, frequency of use
	Methanol	67-56-1		
	Isopropanol	67-63-0		
	t-Butyl alcohol	75-65-0	Byproduct of t-butyl hydroperoxide	
Aldehydes	Glutaraldehyde	111-30-8	Biocide	Toxicity, frequency of use
	Formaldehyde	50-00-0	Biocide	
Alkylphenols	Octylphenol	27193-28-8	Surfactant	Toxicity, frequency of use
	Nonylphenol	84852-15-3		
Alkylphenol ethoxylates	Octylphenol ethoxylate	9036-19-5	Surfactant	Frequency of use
	Nonylphenol ethoxylate	26027-38-3		
Amides	Thiourea	62-56-6	Corrosion inhibitor	Toxicity
	Acrylamide	79-06-1	Friction reducer	Toxicity, frequency of use, requested by EPA researchers
	2,2-Dibromo-3-nitrilopropionamide	10222-01-2	Biocide	
Amines (alcohol)	Diethanolamine	111-42-2	Foaming agent	Frequency of use
Aromatic hydrocarbons	BTEX, naphthalene, benzyl chloride, light petroleum hydrocarbons		Gelling agents, solvents	Toxicity, frequency of use, requested by EPA researchers
Carbohydrates	Polysaccharides		Byproduct	Requested by EPA researchers
Disinfection byproducts	Trihalomethanes, haloacetic acids, N-nitrosamines*		Byproduct	Toxicity
Ethoxylated alcohols	Ethoxylated alcohols, C8–10 and C12–18	68954-94-9	Surfactant	Frequency of use

Table continued on next page

Table 1. Chemicals Identified for Initial Analytical Method Testing[1] (cont.).

Table continued from previous page				
Chemical Class	**Chemical Name(s)**	**CASRN**	**Purpose in Hydraulic Fracturing**	**Reason Selected**
Glycols	Ethylene glycol	107-21-1	Crosslinker, breaker, scale inhibitor	Frequency of use
	Diethylene glycol	111-46-6		
	Triethylene glycol	112-27-6		
	Tetraethylene glycol	112-60-7		
	2-Methoxyethanol	109-86-4	Foaming agent	
	2-Butoxyethanol	111-76-2		
Halogens	Chloride	16887-00-6	Brine carrier fluid, breaker	Frequency of use
Inorganics	Barium	7440-39-3	Mobilized during hydraulic fracturing	Toxicity, frequency of use of potassium and sodium salts, mobilization of naturally occurring ions
	Strontium	7440-24-6	Mobilized during hydraulic fracturing	
	Boron	7440-42-8	Crosslinker	
	Sodium	7440-23-5	Brine carrier fluid, breaker	
	Potassium	7440-09-7	Brine carrier fluid	
Radionuclides	Gross α		Mobilized during hydraulic fracturing	Toxicity, mobilization of naturally occurring ions
	Gross β			
	Radium	13982-63-3		
	Uranium	7440-61-1		
	Thorium	7440-29-1		

1 – USEPA. 2012. Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources, US Environmental Protection Agency, Washington, DC. EPA/601/R-12/011.

Table 2. Base Methods and Analytical Challenges.

Base Method†	Chemical Name	Challenges
SW-846 Methods 8000C and 8321B + ASTM D7731-11	Glycols	No standard method available to cover all compounds; detection limits too high
ASTM D7485-09	Ethoxylated Alcohols	No standard method available to cover all compounds
No Standard Method	Alkylphenols	No Standard Method
SW-846 Methods 5030 and 8260C	Alcohols	Confirmation in hydraulic fracturing related matrices
No Standard Method	Alcohols, amine	No standard method available
SW-846 Methods 8032A	Amides	Matrix interferences; poor extractability
DWA Methods 521, 551, and 552	Disinfection Byproducts	Matrix interferences
SW-846 Method 8315	Aldehydes	Complex method; confirmation in hydraulic fracturing related matrices; detection limits too high
SW-846 Methods 5030 and 8260C	Aromatic Hydrocarbons	Confirmation in hydraulic fracturing related matrices
SW-846 Methods 3015A and 6020A	Inorganic Elements	Matrix interferences
SW-846 Method 9310	Radionuclides	Matrix interferences
SW-846 Method 9056A	Halogens	Matrix interferences

† - SDWA methods may be found at *http://water.epa.gov/scitech/methods/cwa/index.cfm*). SW-846 Methods may be found at http://www.epa.gov/epawaste/hazard/testmethods/sw846/online/index.htm. CWA methods may be found at *http://water.epa.gov/scitech/methods/cwa/index.cfm*. ASTM – American Society for Testing and Materials, International.

Analytical Method Verification Process

Upon successful testing (and modification, if needed) of the analytical method in the laboratory, analytical method verification will be performed in which the robustness of the method will be determined. Method verification involves the preparation of multiple blind spiked samples (i.e., samples whose concentrations are only known to the sample preparer) by an independent chemist (i.e., one not associated with the method under testing and verification) and the submission of the samples to the participating analytical laboratories. In general, at least three analytical laboratories will be sought to participate in the method verification process. The initial verification testing plan involves using only in-house EPA laboratories. If successful in the initial verification testing, a multi-laboratory, round-robin style testing will occur in which both EPA and non-EPA laboratories (i.e., state, county, city, or other government agency laboratories as well as commercial laboratories) will be used to test the robustness of the analytical method. Results from the method verification will be reported and the results can lead to either: (a) the acceptance of the method in the hydraulic fracturing study or (b) re-evaluation and testing of the method.

The final possible step in analytical method testing would be the validation of the method. Method validation involves large, multi-laboratory, round robin studies and is generally conducted by an EPA Program Office responsible for the publication and promulgation of standard analytical methods. It is the goal of the analytical method development research to ultimately have the modified or developed methods promulgated in the SW-846 methods manual.

The current status of methods undergoing testing for the hydraulic fracturing research study is presented in Table 3.

Table 3. Status of Analytical Method Development by Chemical.

Initial Modification/Development	Test Method in a Single Laboratory	Test Method in Multiple Laboratories	Published Method	Finalized Standard Method
Aldehydes	Ethoxylated alcohols	Glycols	Ethoxylated alcohols	
Inorganic elements	Acrylamide		Acrylamide	
Halogens	Radionuclides			
Disinfection byproducts				

Note: Future research will focus on alcohols, diethanolamine (alcohol amine), and aromatic hydrocarbons.

Examples of the method development process are presented using the analysis for glycols and radionuclides as the chemical analytes in the presentation.

References

Colborn, T., Kwiatkowski, C., Schultz, K., and Bachran, M., 2011. Natural Gas Operations from a Public Health Perspective, Human and Ecological Risk Assessment: An International Journal 17:1039-1056.

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Analytical Considerations During Natural Gas Fracturing

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The statements made during the workshop do not represent the views or opinions of EPA. The claims made by participants have not been verified or endorsed by EPA.

Introduction

Natural gas exploration and production activities are receiving intense scrutiny from the public, the media, and regulatory agencies specifically with regard to hydraulic fracturing practices. Obtaining high-quality analytical data before exploration and during and after the production processes is important to document baseline and post-drilling groundwater quality. Equally important is the ability to detect analytes that may be present in fracturing solutions and are not on usual target analyte lists for analysis.

Hydraulic fracturing solutions are typically made up of water, various sands, and chemical additives. In addition, gels, foams, and gases can also be used. Many of these additives are not routinely tested for by laboratories. When laboratory methods do not exist for unusual target analytes, a robust method development process is necessary to ensure obtain a complete characterization of groundwater. A thorough knowledge of the pre-existing conditions from review of analytical data generated from groundwater sampling is critical in identifying potential root causes when a variant result is observed once operations have commenced. Furthermore, thorough documentation of the sampling and handling processes, the bottleware used for sampling, and the instrumentation and methodology used for testing is necessary in order to properly evaluate the validity of the data and potential cause for observed variations.

Two case studies that demonstrate how method development and knowledge of sampling and analysis processes enabled natural gas companies to effectively detect and resolve issues related to hydraulic fracturing will be presented. The first case study explores the use of method development to analyze for non-routine target analytes in groundwater samples. The second case study summarizes the investigation conducted into the sampling and laboratory processes to identify the source of a suspected contaminant.

Discussion

More than 99% of the weights of the hydraulic fracturing fluids are comprised of water and proppants; the remaining percentage is made up of chemical additives such as gelling agents, friction reducers, and surfactants. Before operators commence hydraulic fracturing in a geographical area, the operator will often perform a baseline sampling of the groundwater in the area as recommended by the American Petroleum Institute guidance. It should be noted that in most geographical areas of the country, this baseline sampling is voluntary; however, the Commonwealth of Pennsylvania places the burden of proof on the operator to demonstrate that he/she has not caused any deterioration of the quality of the groundwater utilized for drinking water purposes in the vicinity of the oil and gas wells in the event of a complaint. Wherever the hydraulic fracturing operations are performed, when baseline sampling is performed, the list of target analytes that are analyzed typically include those recommended by FracFocus: major

anions and cations, pH, specific conductance, total dissolved solids, benzene, toluene, ethylbenzene, total xylenes, gasoline range organics, diesel range organics, total petroleum hydrocarbons or oil and grease by hexane extractable method, metals (including arsenic, barium, calcium, chromium, iron, magnesium, boron, sodium, chloride, potassium,), bicarbonate, and dissolved methane. Routine analytical methods exist for the analysis of these FracFocus-recommended target analytes.

Results

There are many additives in hydraulic fracturing fluid that are not in the FracFocus-recommended listing of target analytes. Moreover, routine analytical methods do not exist for the analysis of many of these additives. Furthermore, many of the additives in the hydraulic fracturing fluid become degraded, oxidized, or otherwise modified during the hydraulic fracturing process.

Case Study 1:

Environmental Standards, Inc., personnel were requested by an oil and gas operator to provide environmental chemistry and quality assurance assistance during an unplanned event in which a large volume of fracturing fluid was released at surface level and a groundwater sampling program in the vicinity surrounding the release was initiated. Based upon the material safety data sheets (MSDSs) supplied by the manufacturers of the hydraulic fracturing fluid additives, there were two analytes in the hydraulic fracturing fluid for which no US EPA published methods exist. Environmental Standards worked with the operator's contract laboratories to develop analytical methodology using available instrumentation, more specifically GC/MS and HPLC/MS, suitable for the analysis of these compounds, ensuring proper demonstration of analyte sensitivity and precision and accuracy.

Case Study 2:

Environmental Standards, Inc., personnel were requested to provide environmental chemistry and quality assurance assistance by an oil and gas operator after the operator observed an unexpected detection of a diol compound (based upon the MSDSs for the additives in the hydraulic fracturing fluid) in the majority of groundwater samples collected in the vicinity of the hydraulic fracturing activities. A similar concentration of this diol was observed to be detected across all groundwater samples (collected up and down gradient of the gas wells) and this diol was suspected to be a contaminant; a study was conducted to determine the source of the suspected contamination. A review of the analytical data revealed that the diol compound was detected in trace levels in the laboratory method blanks at sufficient concentrations that qualitatively questioned the presence of 64% of the reported diol, based upon the US EPA data validation guidelines. A review of the field notes revealed that the sample collection team had not collected any field blanks. Based upon this fact, the field team was instructed to implement the collection of blind field blanks to submit to the laboratory. Additionally, an inquiry into the bottleware utilized by the field personnel and utilized at the laboratory (for laboratory method blanks) revealed that field personnel were supplied with non-certified volatile vials containing hydrochloric acid preservation and the bottleware utilized for laboratory method blanks was a different lot of volatile vials that did not contain hydrochloric acid preservation. Based upon this fact gathering, the laboratory was instructed to analyze deionized water in preserved and

unpreserved volatile vials. Table 3 presents a summary of diol results of analysis of the deionized water in the preserved and unpreserved volatile vials. The results show evidence that the diol detections in the groundwater results are most likely attributable to the preserved volatile vials supplied to the field teams for sample collection.

Table 4. Summary of Diol Detections

Using HCl preserved VOA vials	240	27	213	89%
Using unpreserved VOA vials	69	66	3	4%

Conclusions

Routine analytical methods do not exist for many of the additives in hydraulic fracturing fluids. Robust analytical methods should be developed for the analysis of compounds for which routine analytical methods do not exist. Until published analytical methods exist, factors such as time needed for development of methods at an operator's laboratory and turn-around-time and capacity during unplanned events should be taken into consideration and are particularly important during unplanned events where the expeditious delivery of analytical results is desired.

Much emphasis is placed upon the analysis of target analytes in hydraulic fracturing fluids; however, the quality of the analytical data gathered is only as good as the quality of the collection of the samples. One of the primary issues in the collection of samples is that bottleware is certified by bottleware suppliers for routine analytes and not for additives utilized in hydraulic fracturing fluids. Laboratories should certify bottleware lots supplied to field collection personnel for all target analytes to the project reporting limits. Additionally, the same lot of bottleware should be utilized for sample collection and laboratory method blanks. Baseline sampling programs should include the collection and analysis of field blanks.

References

American Petroleum Institute Guidance (API – HF)

http://WWW.FracFocus.org

http://WWW.energydepth.org

Considerations for Determining the Source of Groundwater Contamination Associated with Hydraulic Fracturing

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The statements made during the workshop do not represent the views or opinions of EPA. The claims made by participants have not been verified or endorsed by EPA.

Introduction

In those situations where hydraulic fracturing is suspected of contaminating groundwater, determining the source is a critical aspect for protecting drinking water resources. Approaches to identifying sources have taken several forms, including the use of salts, hydrocarbons, exclusively anthropogenic chemicals, radioactive substances, and isotope characterization. Each method, by itself, may not completely indicate the source of contamination, but used together, a presumptive determination can often be made. The oil & gas industry and the public have a vital interest in determining the source of contamination.

Potential Sources and Baseline Sampling

Hydrofracking-related contamination of drinking water can potentially arise from well construction failure, migration of fracturing fluids to a drinking water aquifer, and surface spills from facilities associated with hydraulic fracturing. Additionally, migration of a carbon source (e.g., methane) for sulfate-reducing bacterial action may cause a drinking water source to be compromised. The time frame for migration of hydrofracking-related contaminants can vary from days to many years, depending on the physico-chemical properties of the analytes, the interconnectedness of induced and existing fractures, the types and characteristics of geologic formations, and the distance between the fracking operation and sampled groundwater. Gas phase transfer of the volatile hydrocarbons present in natural gas also can occur, although this process will not carry the low-volatility compounds or the salts.

A critical aspect for determining the source of contamination is obtaining pre-fracturing samples, although this is not always done. Baseline groundwater quality samples should be taken from wells near or directly over the fracturing well location. The analyte list should include as many of the additive fracturing compounds as possible, and will necessarily require a list of the compounds used in each fracturing operation.

Distinguishing Sources

Exclusive reliance on the constituents in produced water is insufficient, because those compounds are naturally occurring and contamination of drinking water cannot be proven to be associated with hydraulic fracturing, particularly when samples from the same well prior to fracturing were not collected and analyzed. The surface expression of the area of fracturing (sometimes several hundred acres) renders the likelihood of sampling each drinking water well to be small, and if constituents in produced water are present in drinking water, there is no proof that fracturing caused the groundwater contamination. Many constituents from hydrofracking additives (see EPA, 2012 and NYSDEC, 2009) and the produced water, however, will

necessarily be found in the same sample, especially in flowback water. If the water sample lacks elevated salts or some of the other mobile constituents found in produced water, it is unlikely that the measured constituents are associated with hydraulic fracturing, except potentially from a surface spill of the specific hydraulic additive.

Additionally, the presence of methane in groundwater is not sufficient for making a determination that hydraulic fracturing was the cause of groundwater contamination. Methane can originate from the hydrocarbon formation but can occur naturally through slow gas migration over the long-term. It can also result from anaerobic formation from organics present in soils, and be relatively recent. While isotopic analysis can distinguish between recent carbon and ancient carbon, it will not generally distinguish hydrofracking-released methane from naturally occurring, slowly migrating methane. Pre-fracturing groundwater gas sampling can provide strong evidence for the source of methane in drinking water samples. However, with reliable, longer-term baseline sampling of natural gas compounds in groundwater, substantial increases in concentration can be attributed to operational releases of methane.

Anthropogenic Hydrofracking Chemicals

Detection of exclusively anthropogenic hydrofracking chemicals in drinking water, in addition to produced water constituents, can provide presumptive evidence for drinking water contamination from hydraulic fracturing activities. The list of additives potentially used in hydraulic fracturing is large (US EPA, 2012, Appendix A). Determination of all of these compounds in each sample is not feasible, due to expense and the complexity of the analytical methods for complete characterization of the samples. As indicated above, disclosure of the additives used in each well is a rational approach for limiting the expense of these analyses. The list of additives often includes several that are found in both produced water and hydrofracking fluids (e.g., benzene and alkylated aromatics, PAHs). The general quantities of each hydrofracking chemical used should be estimated, because detection will be more reliable for compounds used in higher amounts.

A professional analysis should be undertaken to determine if the analytes previously found in the waters sampled are associated with hydraulic fracturing. Several of the analytes observed are unlikely to be associated with fracturing (US EPA, 2012, Table A-3). Compounds reported in produced water (US EPA, 2012, Appendix A), such as endrin, nitroso compounds, Arochlors, and hexachlorocyclohexanes are not likely used in fracturing activities and in many cases have been banned for several decades, and may well be analytical artifacts. Certain methods (e.g., Method 8015b) have been used for detection of alcohols and glycols but are severely compromised by the lack of specificity of gas chromatography/flame ionization detection.

Known hydraulic fracturing compounds that are likely strictly anthropogenic and have been detected in groundwater samples include a variety of alcohols, including glycols and glycol ethers, dioxane, acrolein, and bis-(2-chloroethyl) ether. Acrylonitrile has been detected in fracturing water and in air above flowback storage ponds but is not included in the additives list (EPA, 2012). It is, however, indicated in a Haliburton patent (Welton and Nguyen, 2010) related to an "on-the-fly" polymerization process for formation of an acrylonitrile-butadiene-styrene polymer on the surface of proppants (sand). For many of the anthropogenic compounds, the sensitivity and specificity of the analytical methods need improvement, perhaps by employing liquid chromatography – mass spectrometry (LC-MS) techniques.

Several of the detected compounds, particularly the oxygenated compounds (e.g., acetophenone, phthalates, carboxylic acids) are unlikely to be found in produced water (Orem et al., 2007; Otton, 2006) but cannot be rigorously excluded from being present naturally.

Thus, the list of strictly anthropogenic compounds that would be useful indicator or tracer compounds for hydrofracking operations is rather small, and further discussions about the best analytical candidates and perhaps additional method development are warranted. This effort should be focused on those compounds that are commonly used in hydraulic fracturing operations in easily detectable quantities.

Sulfate Reduction as a Potential Indicator of Methane Release

Another *suspected* source of drinking water contamination is caused by the increased release of methane associated with fracturing operations. Although not common, an example of this phenomenon is given by a series of samples from a well in Pennsylvania. In this case, the observed water quality is consistent with an increased carbon source that promotes sulfate reduction. As is often the case, the data are not complete and probably would have been collected differently if sulfate reduction was being studied.

Sulfate reduction is a very common anaerobic process, has long been noted in sediment systems where oxygen is completely consumed, and occurs commonly with methane generation. Sulfate reduction is also used to treat acid mine drainage (Tsukamoto, et al., 2004) because the process can remove metals through sulfide precipitation and will raise the pH of acidic drainage. Methane is a known carbon source for sulfate reduction, although the exact mode of utilization is not completely elucidated (Alperin and Hoehler, 2009; Barton and Fauque, 2009; Girguis, et al., 2005).

In this process, where methane is the carbon source, sulfate is converted to sulfide and bicarbonate is produced. Thus, the pH is expected to rise as alkalinity is increased, and soluble aluminum concentrations are expected to increase at the elevated pH produced. The oxidation-reduction potential (ORP) of the medium is shifted negative, insoluble iron oxides (various forms of ferric hydroxide) are reduced and ferrous iron (Fe^{2+}) is produced, and manganese oxide (MnO_2) is reduced and dissolved manganese (Mn^{2+}) is released.

$$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O$$

In a sulfate-reducing environment, one would expect to observe dissolved sulfide; elevated dissolved iron, manganese, and aluminum; and an elevated pH and lower ORP. This is what is observed in the well in Pennsylvania where hydraulic fracturing occurred within 1,000 feet of the domestic well (Table 5).

While the data do not "prove" a direct cause and effect, the single pre-fracturing sample met all primary and secondary drinking water standards. Within six months of fracturing, the well water became undrinkable and turbid. Unfortunately, we were unable to find any pre-fracturing methane concentrations from the well, although concentrations in the 20-35 mg/L range are high, relative to most other wells.

The chloride concentrations are a useful indicator of whether flowback or produced water have mixed with natural groundwater. While variable, the chloride concentrations do not show a distinct and consistent increase in concentration over time, which would be expected if produced water had mixed directly with the aquifer. Thus, direct contamination of the aquifer by oil & gas operations appears to be unlikely.

Increased sulfate reduction activity is likely to be observed comparatively rapidly if a migration pathway is opened during fracturing, since the rate of gas migration will likely be greater than groundwater flow.

These data also support the need for pre-fracturing groundwater quality data. For the detection of sulfate reduction, the constituents determined should include sulfide, methane, ORP, and metals, especially iron and manganese.

Table 5. A Series of Water Quality Results from a Pennsylvania Domestic Well Located within 1,000 feet of a Hydraulically Fractured Well.

Date	ORP	pH	Cl	Sulfide	TDS	Al	Fe	Mn	Methane
7/8/2008	--*	6.9	4.6	<1	151	--	0.12	--	--
1/6/2009	--	9.38	6.3	<1	290	1.03	0.354	<0.025	19
2/12/2009	--	9.39	33	<1	320	0.95	0.487	<0.01	24
4/14/2009	-73.7	9.39	11.9	<1	--	<0.1	0.318	<0.025	29
6/14/2009	-239	9.68	--	--	--	--	--	--	--
9/29/2009	1.7	9.62	5.79	5	347	0.76	7.49	0.23	25
12/3/2009	-80.6	9.59	7.88	6	308	1.06	8.88	0.23	29
2/4/2010	43.1	8.61	6.15	4	100	0.18	0.8	0.043	24
3/11/2010	-25.9	9.28	8.74	<5	270	2.36	14.5	0.63	22
4/15/2010	-116	9.42	14.5	<1	315	2.78	4.33	0.26	28
5/27/2010	-101.4	9.03	--	--	--	--	--	--	0.018
6/7/2010	-78.3	9.81	--	<1	--	--	--	--	25
1/2/2013	-23.9	9.73	8.7	0.27	303	0.438	0.381	0.0073	34

-- analyte not determined

Possible Use of Boron Isotopes to Distinguish Hydrofracking and Produced Water Sources

Boron is commonly used as a crosslinker in hydrofracturing solutions. Under high pH conditions (pH ~9-10), it attaches to guar gum, a common gelling agent. After hydrofracturing is complete, the pH is lowered and boron is released from the gelling agent. Boron is contained in approximately 70 products identified as hydrofracturing chemicals, including boric acid, potassium metaborate, sodium tetraborate, and borate salts (Ainley et al., 1993; U.S. House of Representatives, 2011; US EPA, 2012).

Boron's concentrations in hydrofracturing fluids and flowback water are less well known, although McElreach (Date Unknown) reports a value of 0.07 mg/L in hydraulic fracturing fluids. Boron occurs naturally in produced waters and derives from borosilicate minerals and hydrated

borate minerals. Concentrations of boron in produced water can be in the low to moderate mg/L range (Carty et al., 1999).

Boron isotopes have been used to distinguish waters affected by sewage effluent and to distinguish natural saline seawater from oilfield produced waters. Two isotopes of boron exist, ^{11}B and ^{10}B, and seawater has a higher proportion of ^{11}B. The ratio of ^{11}B to ^{10}B in the NBS standard and the water of interest is used to calculate $\delta^{11}B$ in per mil values, which can vary substantially between anthropogenic sources, seawater, and natural groundwater (Carty et al., 1999).

There are advantages and disadvantages to the potential use of boron isotopes to distinguish hydrofracturing fluids from produced water sources in groundwater. In general, boron is an effective tracer because it is conservative chemically (does not participate in adsorption and precipitation reactions in most natural waters) and biologically. It is detectable at low concentrations (minimum reporting limit and minimum detection limit by inductively coupled plasma-mass spectrometry are respectively 0.5 and 0.2 mg/L. In addition, the boron isotopic technique is highly precise, even though differences in $\delta^{11}B$ can be low. Possible challenges include the differences in concentrations and isotopic signature in hydrofracturing fluids and produced waters. The potential of using boron isotopes for distinguishing sources of possible groundwater contamination at unconventional oil and gas operations should be explored.

Summary

Distinguishing the sources of groundwater contamination at sites with hydrofracturing operations can be accomplished by using multiple approaches that rely on knowledge of baseline groundwater quality and the composition of hydrofracturing fluids and produced waters. In addition to the identification of anthropogenic hydraulic fracturing chemicals in groundwater, the examination of changes incurred by sulfate-reducing bacteria and the potential use of boron isotopes should be examined further as part of a program to investigate the potential effects of hydraulic fracturing on drinking water resources.

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Indicator Parameters: Pre-drill Baseline Groundwater Surveys, Post-drill Groundwater Monitoring, and Gas Analysis

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Introduction

Analysis of groundwater prior to drilling and hydraulic stimulation activities for shale gas production can help to establish baseline conditions. This presentation includes a summary of parameters commonly used in baseline assessment of groundwater quality conditions and gas characterization and provides rationale for possible selection of indicator parameters for detection of potential impact from flowback/produced water to shallow groundwater. A brief discussion on important considerations for gas analysis is also included.

It should be noted that the groundwater being monitored is typically thousands of feet above the shale being hydraulically fractured and current well construction requirements call for the installation of multiple layers of protective steel casing surrounded by cement specifically designed and installed to protect freshwater aquifers.

Groundwater Analysis

Common parameters used for establishing groundwater baseline conditions are listed below. However, several of these parameters could have limited or no relevant use for establishing a baseline in this context.

- Field Screening: pH, Temperature, Specific Conductivity, DO, Redox
- General Water Quality: Alkalinity, TDS, TSS, Hardness, Turbidity, MBAS, TOC
- Anions: Chloride, Sulfate, Bromide, Nitrates (as Nitrogen)
- Total and/or Dissolved Metals: As, Ba, Ca, Cr, Fe, K, Pb, Mg, Mn, Na, Se, and Sr
- Organics: BTEX, Dissolved Light Gases (C1-C3), glycols
    - 13δC and 2δH isotopes of Methane: Headspace or if dissolved methane exceeds a threshold value (1 to 20 mg/L, state dependent)
    - 13δC isotopes of Ethane, Propane+
- Radioactivity (less frequently tested):
    - Gross alpha, gross beta
    - Ra-226, Ra-228 may be more accurate measurements

In general, hydraulic fracture fluids are 99% water and proppant (sand) and additives are 1% volume or less. Most of the additives are common to household consumer products and pharmaceuticals. Information on stimulation date, volumes used and detailed composition of hydraulic fracturing fluids for most wells is, for the most part, listed in fracfocus.com. Detailed review of this type of information and knowledge of flowback/produced water composition

reveal that potential impact to groundwater from hydraulic fracturing can be assessed by determination of a few indicator parameters based on relative abundance of some components in produced water, the potential mobility of the indicator components in groundwater systems, as well as the ability to accurately identify and quantify the parameter in produced water and groundwater using existing EPA and/or Standard Methods.

Elevated temperatures and pressure and interactions within the fluid may change the form of some components at depths deeper than 5000 ft. Furthermore, there are interactions between the hydraulic fracturing fluid and the formation which may increase the salts content in flowback/produced water. The dissolved anions and cations can be measured using EPA and standard analytical methods.

Total dissolved solids (TDS), chloride and sodium are the most suitable indicator parameters to assess potential impact to groundwater from flowback/produced water. They are the most reliable indicator parameters for potential impact from hydraulic fracturing operations to groundwater because they are in the highest concentrations in produced water (Table 6). The concentration of TDS is predictive of the concentration of the other species. Chloride is the best key indicator parameter for evaluation of potential migration of both produced water and hydraulic stimulation fluids. Total organic carbon (TOC) is a good indicator for organics but if TDS and/or chloride are not elevated, there is no need to analyze for TOC. The concentrations of other compounds in hydraulic fracturing fluids are extremely small in produced water and if there is no elevated TDS, chloride and sodium, then there is in all likelihood no need to analyze for any other parameter.

Table 6. Comparison of Selected Parameters in Groundwater, Flowback and Produced Water

		Approximate Typical Pennsylvania Groundwater[1]	Influent[2]		5 Day Flowback[2]		Conventional Produced Water[3]
Parameter	**Units**	**Median**	**Range**	**Median**	**Range**	**Median**	**Range**
pH		7.5	6.7 - 7.4	7.2	5.8 - 7.2	6.2	5 - 8
TDS	mg/L	163	35 - 5,500	334	38,000 - 260,000	238,000	3,000 - 350,000
TOC	mg/L	<1	2 - 200	3.8	4 - 388	63	NA
O&G	mg/L	<5	19	31	<0.5 - 100	NA	3 - 100
Chloride	mg/L	5	4 - 3,000	42	26,000 - 148,000	42,000	
Sodium	mg/L	7	26 - 6,200	68	11,000 - 65,000	18,000	

[1] Pennsylvania State University, 2011, http://www.iogawv.com/Resources/Docs/Marcellus-drinking-water-2011.pdf
[2] Hayes,://www.epa.gov/hfstudy/12_Hayes_-_Marcellus_Flowback_Reuse_508.pdf
[3] IPEC, 2004 GRI, 1994

Tracers are either unstable in the downhole environment, unnecessarily costly, non-specific, or thought to be unacceptable externally. They should be used with extreme care in investigations perhaps after evaluation of indicator parameters suggest potential impacts that trigger a more focused investigation.

Gas Characterization

Gas analyses and isotopic analyses should be carefully considered using multiple lines of evidence to determine potential gas migration sources. Pre-drill groundwater headspace and dissolved gas data can be examined along with depth profiles of detailed mud gas analyses, geological information and production gas data. Pre-drill baseline assessment of groundwater and water supply wells including isotopic analyses of headspace and dissolved gas (methane, ethane, propane +) is appropriate as shallow gas can be biogenic and/or thermogenic predating any hydraulic stimulation operations. Crossplots of the ratio of methane to ethane with respect to $^{13}\delta$C-Methane and of $^{13}\delta$C-Methane to $^{2}\delta$H-Methane (deuterium in methane) of pre-drill groundwater and water supply wells are useful in the assessment of potential stray gas sources. In some areas, deep gas may exhibit "isotope reversal". This simply means that methane is isotopically lighter than ethane above a certain depth and methane is isotopically heavier than ethane below a certain depth (typically above/below a formation of different permeability). In areas with "wet" gas (C2+ >2%), ratios of isoalkanes to n-alkanes may be useful is differentiating shallow gas from deeper thermogenic gas as gas in shallower cooler zones can undergo preferential biodegradation of n-propane and n-butane.

Summary

If indicator parameters are elevated above pre-drill and/or background conditions in groundwater at a given site or well, further investigation may be appropriate. It must be noted that increases in TDS, chloride and sodium do not always imply connection to deep production water from hydraulic fracturing operations. Changes in water well operations and water table fluctuations may introduce water from restricted flow zones with relatively high salinity and not associated with hydraulic fracturing related activities.

Characterization of pre-drill groundwater and water supply wells as well as production gas and shallow mud gas are helpful in gas migration investigations. Multiple lines of evidence are needed including determination of gas composition and isotopic ratios of carbon and hydrogen (preferably methane, ethane and propane) with respect to depth, geologic zones, etc. Analysis for BTEX may also be considered.

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Alternative Methods to RSK 175 Using Purge and Trap Concentration and Automated Headspace for the Analysis of Dissolved Gases in Drinking Water

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Abstract

With the growing price of oil, many alternative energy sources are being explored. Natural gas prices are actually decreasing, in large part to the use of hydraulic fracturing in areas like the Marcellus Shale in Pennsylvania. Due to increased concern over the hydraulic fracturing process and the release of methane and other chemicals into the local drinking water, a need has developed for fast and accurate analysis of methane in water. This poster will evaluate methods developed for the determination of methane, ethane, ethene, and propane in water using a Purge and Trap concentrator and automated headspace analysis with GC/FID. Calibration curves, method detection limits (MDLs), and carryover data will be presented and comparisons between the methods will be made.

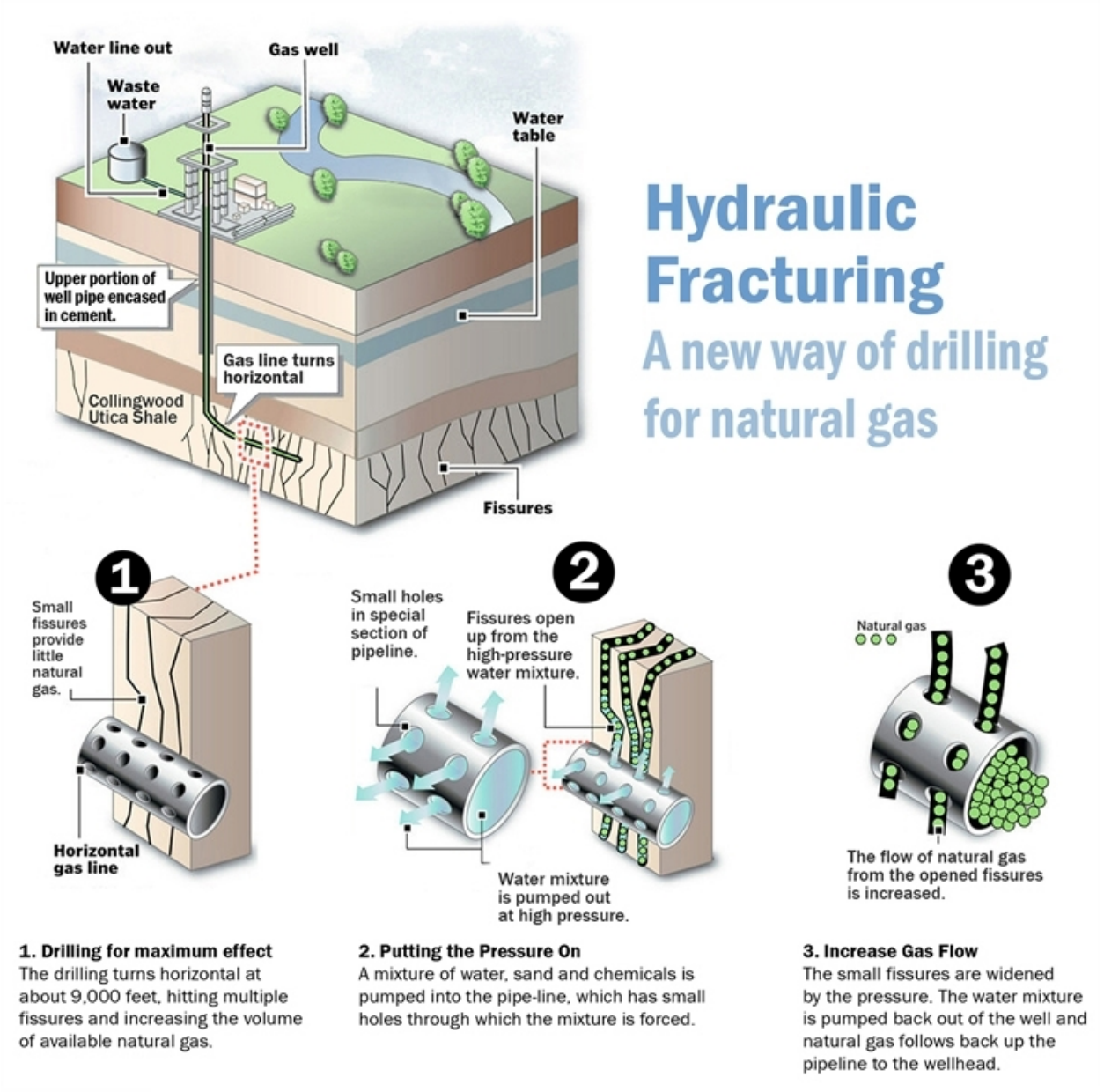
Figure 1. Examples of equipment used for analytical methods

Introduction

Hydraulic fracturing, also known as "fracking", is a drilling process currently used to recover natural gas from sources like coalbeds and shale formations. This involves injecting large amounts of water, mixed with sand and chemicals, at high pressures to break up the shale to release the gas. An outline of the hydraulic fracturing process can be found in Figure 2. Natural gas from these hard-to-extract sources is becoming increasingly popular and is projected to grow to nearly 45% of the nation's natural gas supplies by 2035.

Even though hydraulic fracturing is a relatively old practice, first employed over 60 years ago to drill for oil in Oklahoma, there has been little research into the impact of its increasing use as a drilling process for natural gas. With growing concern over the environmental effects of fracking on water quality, the United States EPA has begun studies to monitor the treatment methods and environmental impact with the goal of standardization by 2013/2014. Figure 3 shows a map of shale gas formations in the North America indicating the potential widespread environmental impact the fracking process could have.

Figure 2. Process of Hydraulic Fracturing to Drill for Natural Gas



The current method for determining natural gas constituents (methane, ethane, and ethene) in water is RSK 175. This method is employed for the analysis of dissolved gases in drinking water using a headspace equilibration technique. Propane has been added to this list in modified methods such as PA-DEP 3686, developed by the Pennsylvania Department of Environmental Protection (PADEP). This analysis also requires more modern automated headspace analyzers. A flame ionization detector (FID) will be employed for this study, although RSK 175 also allows thermal conductivity (TCD) as well as electron capture detectors (ECD) to be used. This application demonstrates alternative analyses, including purge and trap concentration and automated headspace, to create simple and efficient methods for analyzing dissolved gases.

Figure 3. Shale Gas Formations in North America

Source: U.S. Energy Information Administration based on data from various published studies. Canada and Mexico plays from ARI.
Updated: May 9, 2011

For this study, a Stratum Purge and Trap Concentrator (PTC) was used in conjunction with an AQUATek 100 Autosampler. This set-up allows for complete automation of sample preparation for the analysis of liquid samples for purge and trap. A recirculating chiller bath was also utilized to maintain a sample temperature of less than 10°C. This technique also requires a 5mL purge volume. Additionally, the HT3 and Versa Headspace analyzers, utilizing a loop sampling technique, used a 10mL sample volume for this analysis.

Utilizing a GC/FID, a linear calibration was performed and percent Relative Standard Deviation (%RSD) and Method Detection Limits (MDLs) were determined for the full list of compounds. Similarly to the PA-DEP methods, calibrations were performed on aqueous standards rather than the gaseous standards used in RSK 175. Percent carryover was also evaluated method 9243.

Experimental-Instrument Conditions

The Stratum PTC and AQUATek 100 Autosampler as well as the HT3 and Versa Headspace analyzers were coupled to a GC/FID for analysis. Teledyne Tekmar's new proprietary trap (P/N: 15-0885-403) was also utilized for the purge and trap method. The GC was configured with a Restek Rt-U-BOND 15m x 0.53mm x 20µm column. The GC/FID parameters are outlined in Table 7 and Table 8. Table 9 outlines the P&T and autosampler conditions. A recirculating chiller bath was also employed to maintain sample temperatures below 10°C. Table 10 outlines the conditions for the headspace analyses.

Table 7. GC Parameters

GC:	GC/FID
Column:	Restek Rt-U-Bond 15m x 0.53mm x 20µm, 1.0 psi constant pressure
Oven Program:	35° C for 4 min, 20° C/min to 190° C hold for 2 min
Inlet:	190° C
Gas:	Helium
Split Ratio:	20:1

Table 8. FID Parameters

Temperature:	190°C
Hydrogen Flow:	35 mL/min
Air Flow:	300 mL/min
Mode:	Constant Makeup Flow
Makeup Flow:	30 mL/min
Makeup Gas:	Helium

Table 9. Stratum PTC and AQUATek 100 Parameters (Stratum PTC Parameters are in **Blue**)

Variable	Value	Variable	Value
Pressurize Time	0.35 min	Purge Time	1.5 min
Sample Transfer Time	0.35 min	Purge Temp	20°C
Rinse Loop Time	0.30 min	Purge Flow	10mL/min
Sweep Needle Time	0.30 min	Dry Purge Time	0.0 min
Bake Rinse	On	Dry Purge Temp	20°C
Bake Rinse Cycles	1	Dry Purge Flow	100mL/min
Bake Rinse Drain Time	0.35 min	GC Start	Start of Desorb
Presweep Time	0.25 min	Desorb Preheat Temp	95°C
Water Temp	90° C	Desorb Drain	On
Valve Oven Temp	80°C	Desorb Time	2.00 min
Transfer Line Temp	80°C	Desorb Temp	100°C
Sample Mount Temp	60°C	Desorb Flow	300mL/min
Purge ready Temp	35°C	Bake Time	15.00 min
Condenser Ready Temp	40°C	Bake Temp	100°C
Condenser Purge Temp	20°C	Bake Flow	400mL/min
Standby Flow	10mL/min	Condenser Bake Temp	200°C
Pre-Purge Time	0.5 min		
Pre-Purge Flow	40.0mL/min		
Sample Heater	Off		
Sample Preheat Time	1.00 min		
Sample Temp	40°C		

Table 10. Teledyne Tekmar HT3 and Versa Automated Headspace Parameters (gray parameters were not used).

Variable	HT3	Versa
Constant Heat Time	On	N/A
GC Cycle Time	21.00 min	21.00 min
Valve Oven Temp	100°C	100°C
Transfer Line Temp	100°C	100°C
Standby Flow Rate	50 mL/min	N/A
Platen/Sample Temp	64°C	64°C
Platen Temp Equil Time	0.50 min	0.50 min
Sample Equil Time	30.00 min	30.00 min
Mixer	Off	Off
Mixing Time	5.00 min	2.00 min
Mixing Level	Level 5	Medium
Mixer Stabilize Time	0.50 min	0.50 min
Pressurize	10 psig	10 psig
Pressurize Time	2.00 min	2.00 min
Pressurize Equil Time	0.20 min	0.25 min
Loop Fill Pressure	7 psig	7 psig
Loop Fill Time	2.00 min	2.00 min
Inject Time	0.50 min	0.50 min

Calibration Data

To make the stock solutions, a 500mL volumetric flask filled with de-ionized water was placed in an ice water bath and purged with a reference gas corresponding to each of the four analytes. Each gas was bubbled through chilled water for two hours to make individual concentrated standards. Unlike in RSK 175, calibrations in PA-DEP 3686 are performed using aqueous rather than gaseous standards. This study also employs an aqueous calibration, where standards are analyzed under the same conditions as samples.

Calibration standards were made from serial dilutions of these stock standards by calculating the concentration of saturated gas solutions in water at 0°C. For example, the saturation point of methane in 0°C water is 39.59 mg/L at atmospheric pressure. Calibration standards were made in 50mL volumetric flasks filled to volume with chilled de-ionized water over a range of 7.92 ppb to 19.8 ppm. Samples were transferred to headspace free 40mL vials for analysis. These standards were additionally made for the remaining compounds of interest. Similarly, calibration standards for the headspace analysis were generated from dilutions of this stock standard, but due the fixed volumes used in the method the calibration ranges differed slightly from the purge and trap method.

The calibration data generated during this study was evaluated by linearity (r^2) and percent Relative Deviation (%RSD). Method detection limits were also established for all compounds by analyzing seven low level replicates. Calibration data and MDLs can be found in Table 11for the Stratum PTC and Table 12 for the HT3 and Versa. In addition, an example of an overlay chromatogram showing each standard can be found in Figure 4. Figure 5 presents a chromatogram of a mixed gas standard as well as an overlay showing there is no discernible difference in response between the headspace systems. A blank analyzed after the highest calibration standard was used to calculate the percent carryover for the P&T method which was less than 0.04% for all compounds.

Table 11. Calibration and MDL Data for Methane, Ethane, Ethene, and Propane using the Stratum PTC

Methane	7.92 ppb to 19.8 ppm	166	1.000	2.0	0.4 ppb	0.04%
Ethene	56.2 ppb to 281 ppm	587	0.9995	4.5	31 ppb	0.03%
Ethane	26.4 ppb to 132 ppm	621	0.9998	13.9	21 ppb	0.04%
Propane	29.4 ppb to 147 ppm	803	0.9999	12.0	18 ppb	0.04%

Figure 4. Overlay Chromatograms of Gas Standards using PA-DEP method 9243

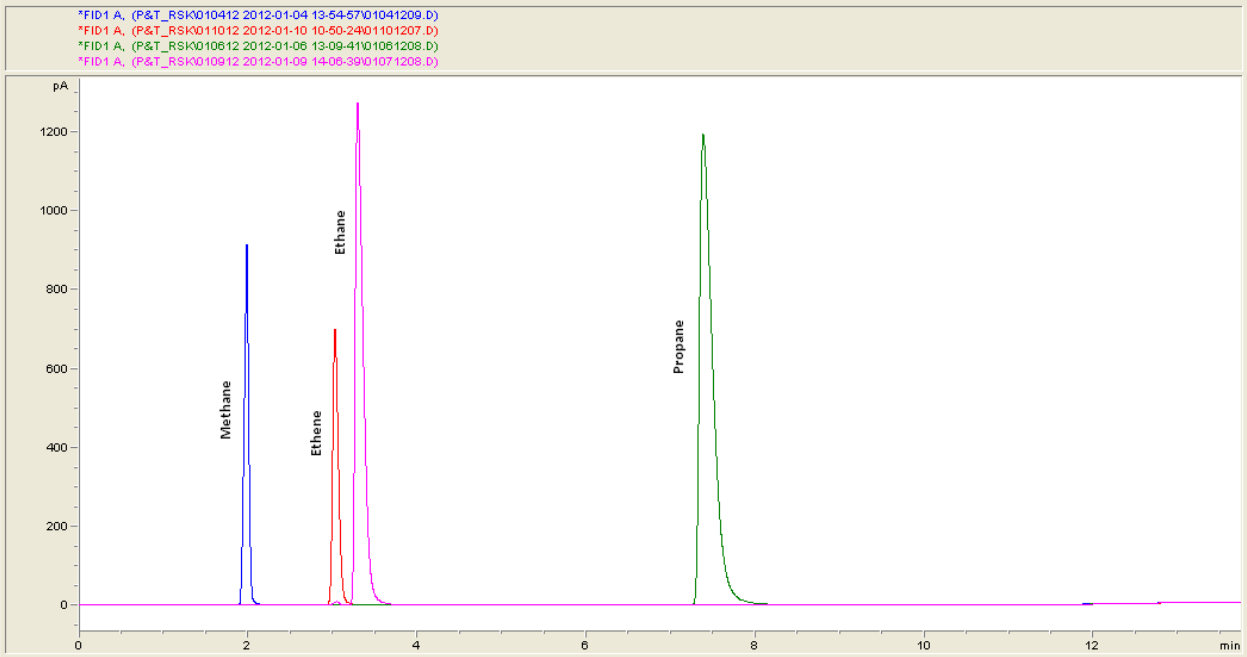
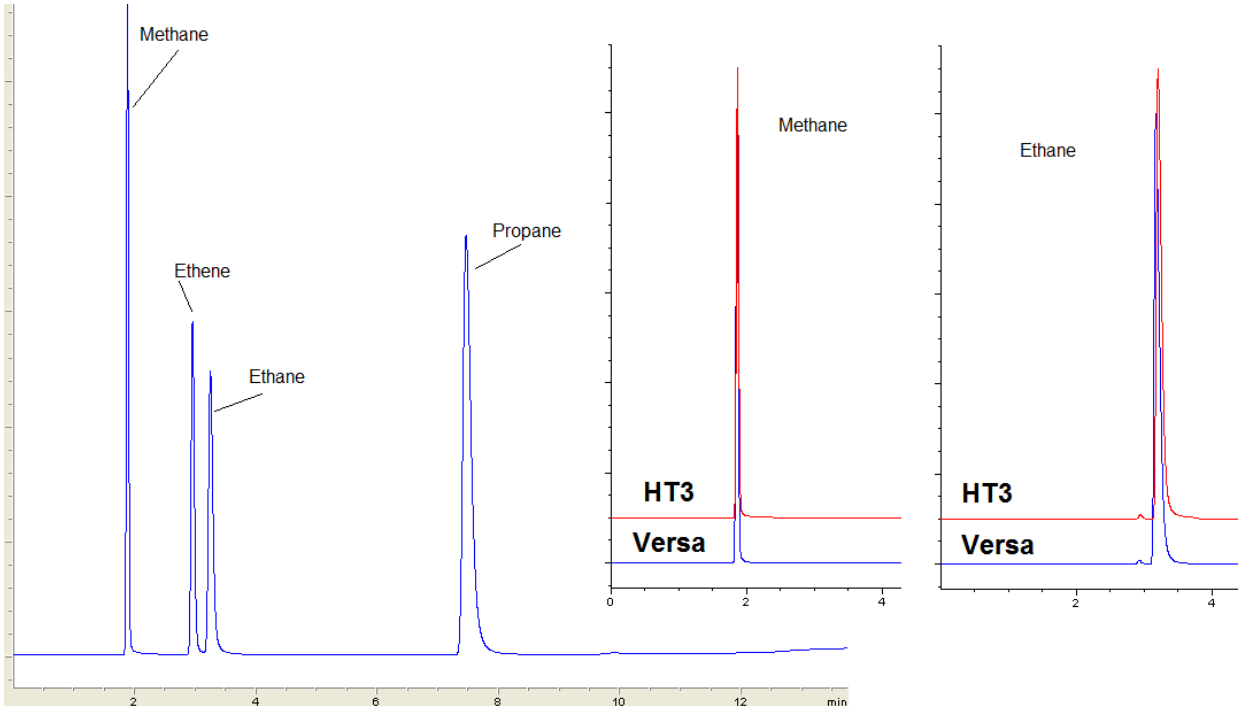


Table 12. Calibration Data for Methane, Ethene, Ethane, and Propane using the HT3 and Versa Headspace Analyzers

Compound	Calibration Range	Linearity (r2)		% Relative Standard Deviation (%RSD)		Method Detection Limit (MDL)	
		HT3	Versa	HT3	Versa	HT3	Versa
Methane	20 ppb to 24 ppm	0.9981	0.9958	3.8	7.3	2 ppb	2 ppb
Ethene	141 ppb to 169 ppm	0.9979	0.9966	6.0	11.9	25 ppb	19 ppb
Ethane	66 ppb to 79 ppm	0.9987	0.9992	6.3	7.8	5 ppb	7 ppb
Propane	74 ppb to 88 ppm	0.9989	0.9992	2.1	12.0	6 ppb	4 ppb

Figure 5. Gas Chromatogram Comparison of Methane and Ethane between the HT3 and the Versa and a Chromatogram of the Four Gases.



Conclusions

With increased interest in alternative energy sources, hydraulic fracturing has become a common practice in the extraction of natural gas from coalbeds and shale formations across the United States. Unfortunately, there has not been adequate time to measure the environmental impact of these procedures. Regulatory agencies are looking for easy and reliable testing methods to monitor these effects.

This study demonstrates methods for analyzing these gases using the Teledyne Tekmar's Stratum PTC/AQUATek 100 autosampler and HT3 and Versa Headspace analyzers coupled with a GC/FID system. These methods met all performance criteria outlined in the current headspace methods, RSK 175 and PA-DEP 3686 as well as the new purge and trap method, PA-DEP 9243. By completely automating the sample preparation, efficiency and throughput can be greatly increased while saving time and money. Using method 9243, there is no need to manipulate the samples which eliminates the potential for human error and employs instrumentation already familiar to many environmental laboratories.

Acknowledgement

Teledyne Tekmar would like to thank the Pennsylvania Department of Environmental Protection (PADEP) for all their help in developing and validating this method.

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Important considerations in the use of carbon and hydrogen stable isotopes to determine the origin of hydrocarbons in groundwater– A case study from pre-shale gas Tioga County

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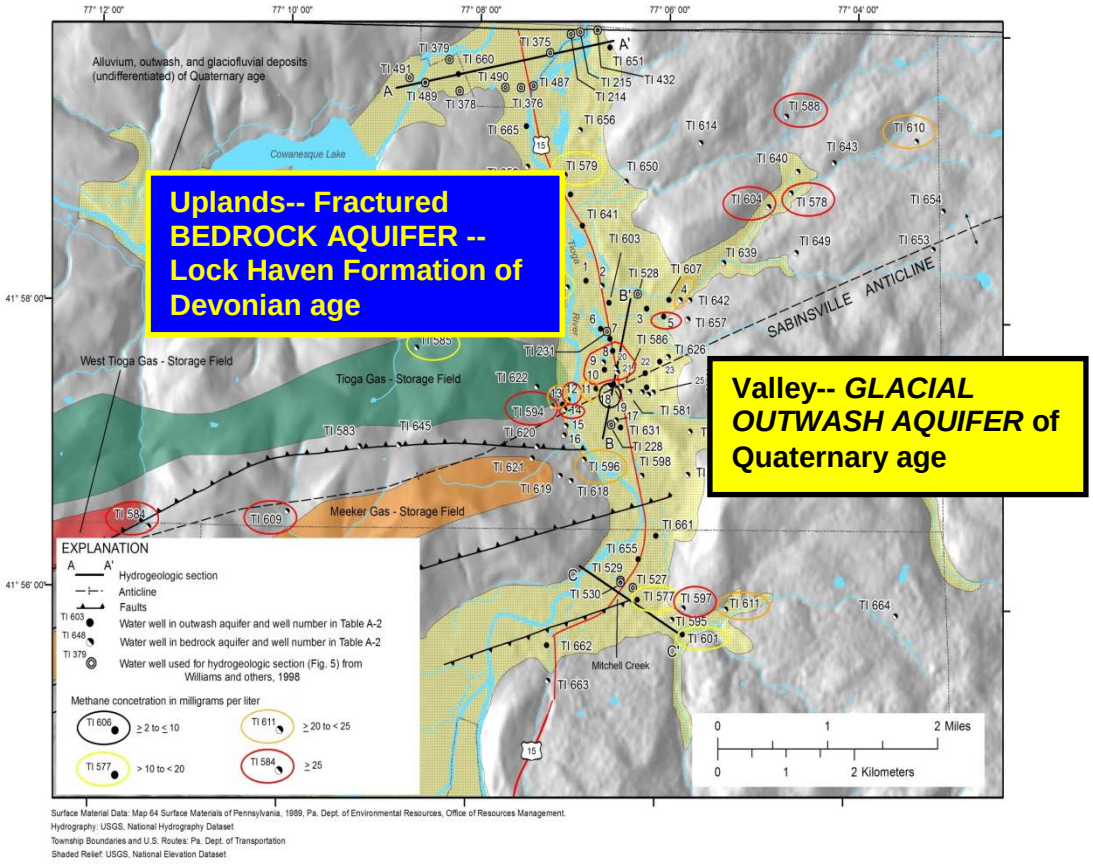
The statements made during the workshop do not represent the views or opinions of EPA. The claims made by participants have not been verified or endorsed by EPA.

Introduction

When investigating the source of stray methane gas in groundwater systems, it may not be sufficient to simply discriminate between biogenic and thermogenic geochemical origins to determine the gas source to the aquifer, as multiple plausible gas sources may be present. To illustrate this, a 2005 study of natural gas in groundwater around Tioga Junction (Tioga County, PA) is presented. In this study, dissolved gas samples were taken from water-supply wells and the isotopic and compositional characteristics of methane and ethane analyzed to determine the gas source. The wells in this study are situated in two aquifer systems in and adjacent to the Tioga River valley. An unconsolidated aquifer of outwash sand and gravel of Quaternary age underlies the main river valley and extends into the valleys of tributaries. Outwash-aquifer wells are seldom deeper than 30 m. The river-valley sediments and uplands adjacent to the valley are underlain by a fractured-bedrock aquifer in sandstones and shales of Devonian age, primarily the Lock Haven Formation. Most bedrock-aquifer wells produce water from the Lock Haven Formation at depths of 76 m or less (Figure 6). The $\delta^{13}C_{VPDB}$ and $\delta^{2}H_{VSMOW}$ (δD_{VSMOW}) values of methane in groundwater were measurable in 35 out of 91 sampled waters.

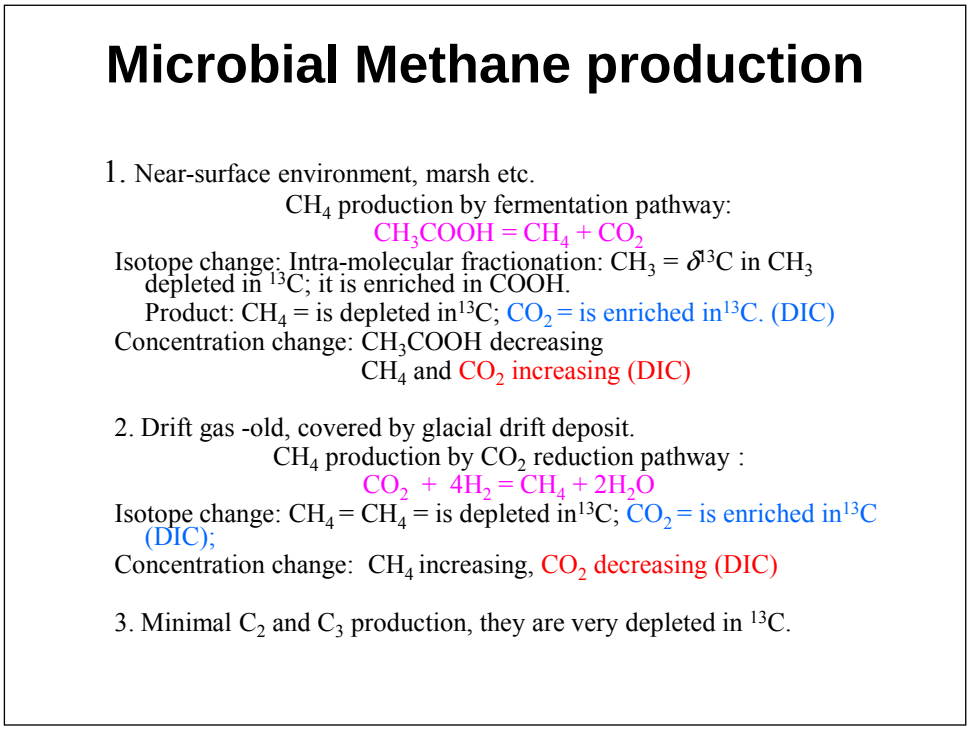
Figure 6. Study area; the circles indicate water wells where measurable natural gases were found



Isotopic Signatures of Methane in Natural Gas

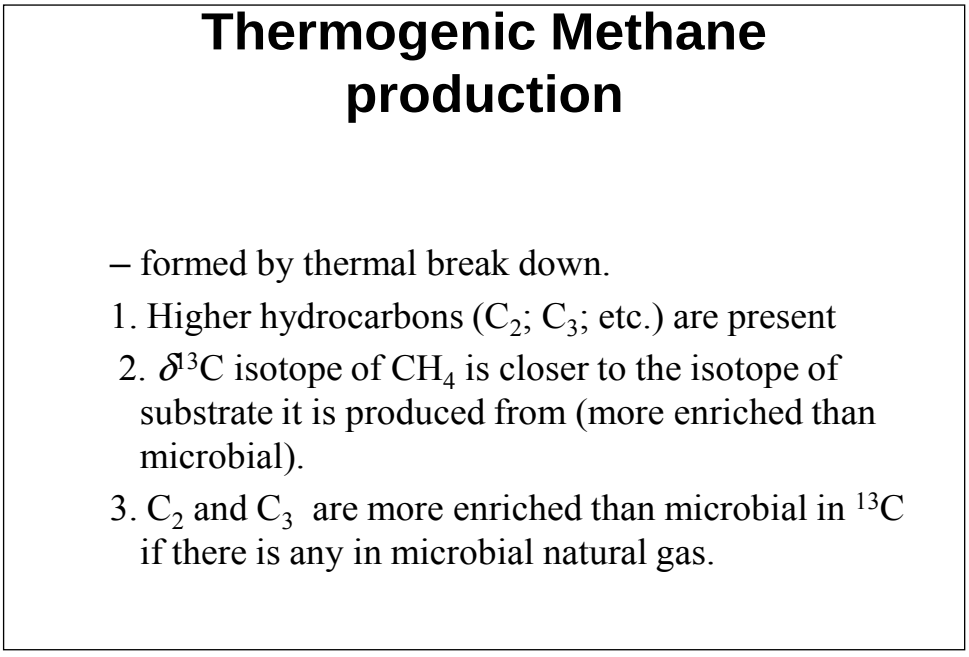
Methane is the main constituent in natural gas and anthropogenic gases, such as landfill gas. Methane is known to be formed by two major processes, microbial or thermogenic. Microbial methane is the principal product of anaerobic and bacterial decomposition of buried organic material that can be present in glacial drift or glaciofluvial deposits and in near-surface sediments and rocks. Microbial methane found in relatively low temperature, near-surface environments due to acetate fermentation is called marsh gas, swamp gas, and landfill gas (Coleman and others, 1995). In glacial-drift deposits, the product gas formed by microbial reduction of carbon dioxide (CO2) is referred to as drift gas (Figure 7).

Figure 7. Isotope Chemistry of Microbial Methane production and its effect on the dissolved inorganic carbon DIC



Thermogenic methane is formed by the thermal breakdown of organic material resulting from high temperatures created by deep burial of sediments (Schoell, 1980) (Figure 8).

Figure 8. Thermogenic Methane Production



Various researchers have determined by examination of stable hydrogen and carbon isotopes of methane that there are common hydrogen and carbon isotopic compositions for thermogenic gas associated with coal and natural gas, drift gas, and other near-surface microbial gases (Craig, 1953; Coleman and others, 1977; Deines, 1980; Schoell, 1980; Rice and Claypool, 1981; Schoell, 1983; Whiticar, 1986; Wiese and Kvenvolden, 1993; Coleman, 1994; Baldassare and Laughrey, 1997; Kaplan and others, 1997; and Rowe and Muehlenbachs, 1999). For microbial methane found in near-surface environments due to acetate fermentation (marsh gas and landfill gas), $\delta^{13}C_{CH4}$ ranges from about -40 to -62 per mil and $\delta^{2}H_{CH4}$ (δD_{CH4}) ranges from about -270 to -350 per mil. Microbial methane in outwash or "drift" gas generally has $\delta^{13}C_{CH4}$ values ranging from about -62 to -90 per mil and $\delta^{2}H_{CH4}$ ranges from about -180 to -240 per mil. Thermogenic methane has a range of $\delta^{13}C_{CH4}$ from about -28 per mil to -50 or -60 per mil and $\delta^{2}H_{CH4}$ values range from about -110 to -250 per mil. Values of $\delta^{13}C_{CH4}$ near -60 per mil associated with $\delta^{2}H_{CH4}$ values in the -160 to -260 per mil range generally are attributed to mixing of thermogenic and microbial methane (Figure 10).

Isotopic Signatures During Methane Oxidation

The combustible natural stray gas does not necessarily maintain its isotopic signature as it could travel through different redox environment, which could alter its isotopic signature. To evaluate the origin of combustible natural stray gas with isotope data, it is essential to understand the basics, not only of what is happening with the isotopes during gas productions (see above), but also during oxidation as well. Figure 9 shows the concentration and isotopic changes of methane in a system where oxidation is occurring. If only the $\delta^{13}C_{CH4}$ of a stray gas sample is measured, a microbial methane could easily be mistaken for a gas having a thermogenic origin (Figure 10).

Figure 9. Isotope Chemistry of Methane Oxidation

Methane oxidation

independent from production pathways

$$2CH_4 + 4O_2 = 2CO_2 + 4H_2O$$

Concentration change:

CH_4 decreasing, CO_2 (DIC) increasing.

^{13}C isotope change:

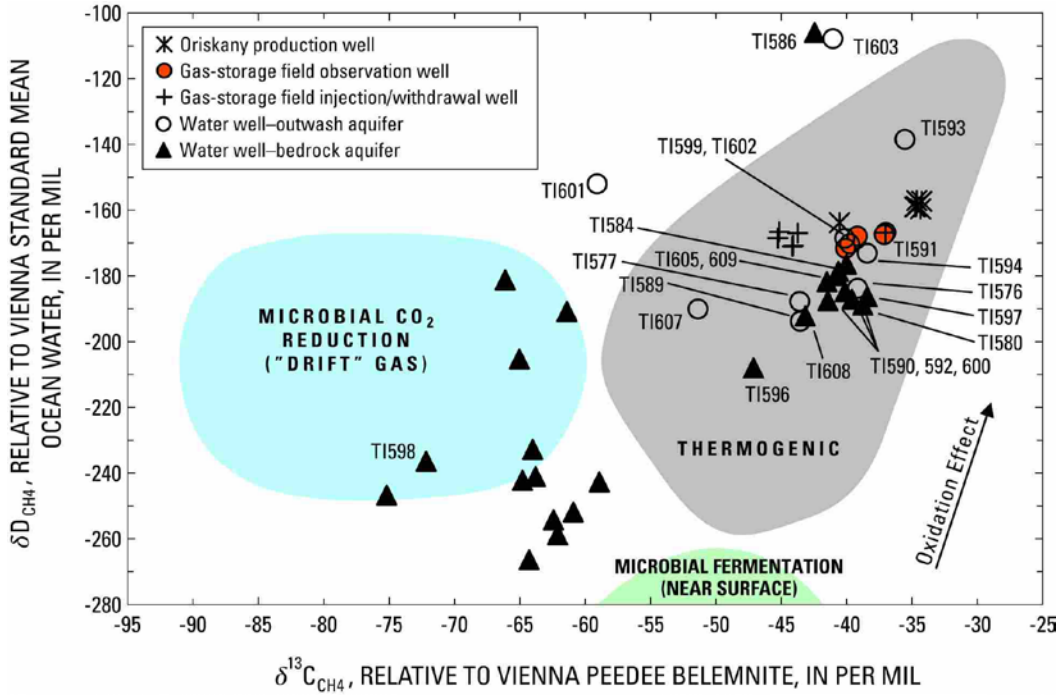
CH_4 becomes enriched ; CO_2 (DIC) becomes depleted in ^{13}C.

Results and Discussion

There are four plausible origins for natural gas in the water wells at Tioga Junction: (1) deep native gas in the Oriskany Sandstone (thermogenic), (2) shallow native gas in Devonian shale

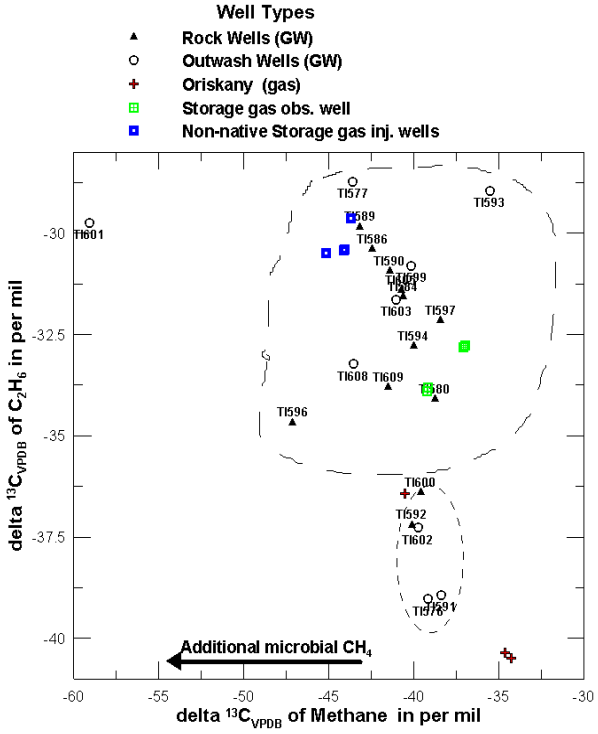
bedrock (thermogenic), (3) non-native gas from a gas-storage field (thermogenic) and (4) microbial gas from organic debris (drift gas) in unconsolidated sediments. Gases from the Oriskany Sandstone and the gas-storage field were similar in chemical composition, with methane and ethane being predominant; stable isotopic compositions however were sufficiently different to distinguish between all these sources with a high degree of certainty.
The isotopic composition of methane in water samples from 14 wells reflected a microbial origin, while the composition of the other 21 wells was representative of a thermogenic origin (Figure 9).

Figure 10. $\delta^{13}C$ and $\delta^{2}H$ (D) of methane, relative to VPDB and VSMOW international standard respectively, in water wells showing on Coleman – Schoell graph. The natural gas sampled in water wells clearly separated out the two type of gases; microbial and thermogenic.



The $\delta^{13}C$ values of ethane, however, could further distinguished between different thermogenic gas origins. Thus, the $\delta^{13}C$ values of both methane and ethane from water wells either matched or were intermediate between the values measured from the samples of non-native storage-field gas from injection wells and the samples of gas from storage-field observation wells (Figure 8).

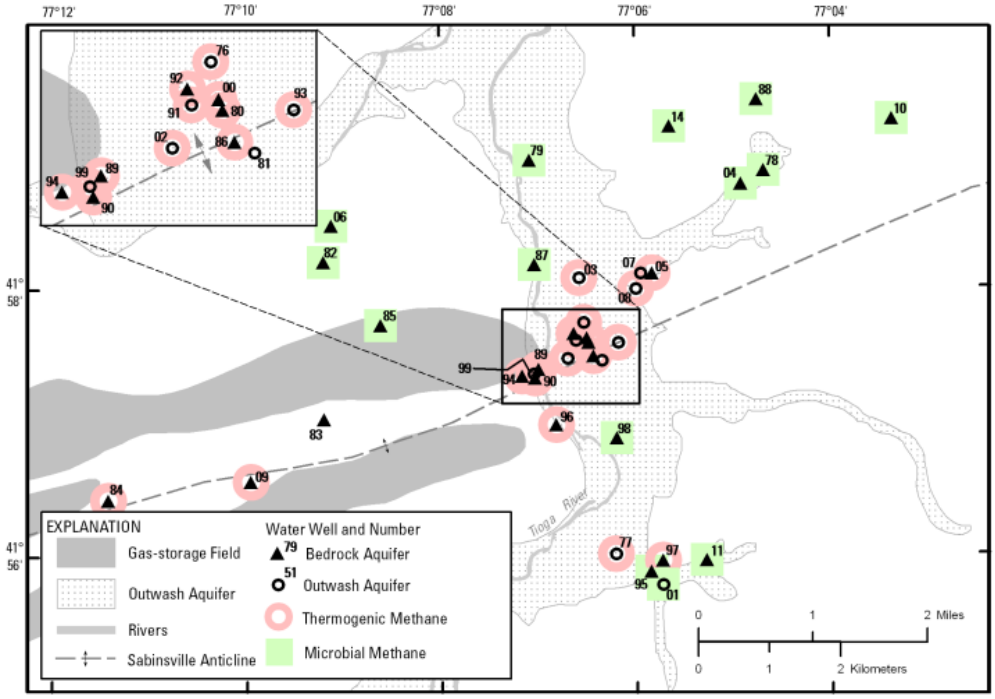
Figure 11. δ13C of ethane with the δ13C of methane could further distinguish between the different thermogenic gas origins.



Conclusions

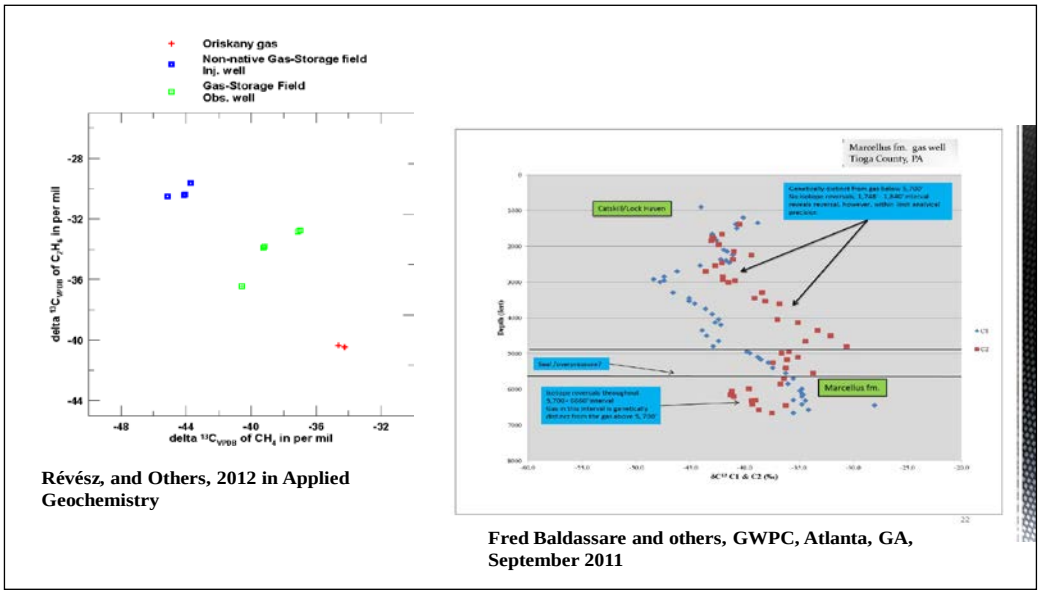
The carbon and hydrogen stable isotopes of methane in natural gases only allowed the origin of the gas (either microbial or thermogenic) to be determined (Figure 10 and Figure 12). By including the carbon isotope composition of ethane and methane together, definitive characteristics of thermogenic gases could be distinguished (Figure 11).

Figure 12. Location of thermogenic and microbial methane



There is a strong possibility for identifying Shale Gas contamination in aquifer by applying stable isotopic technique because the ethane in Shale Gas has a unique stable carbon isotopic signature as compared to that of methane in the same gas (reverse isotope signature) (Figure 13).

Figure 13. Isotope results from Révész et al. and Baldassare et al.



Révész, and Others, 2012 in Applied Geochemistry

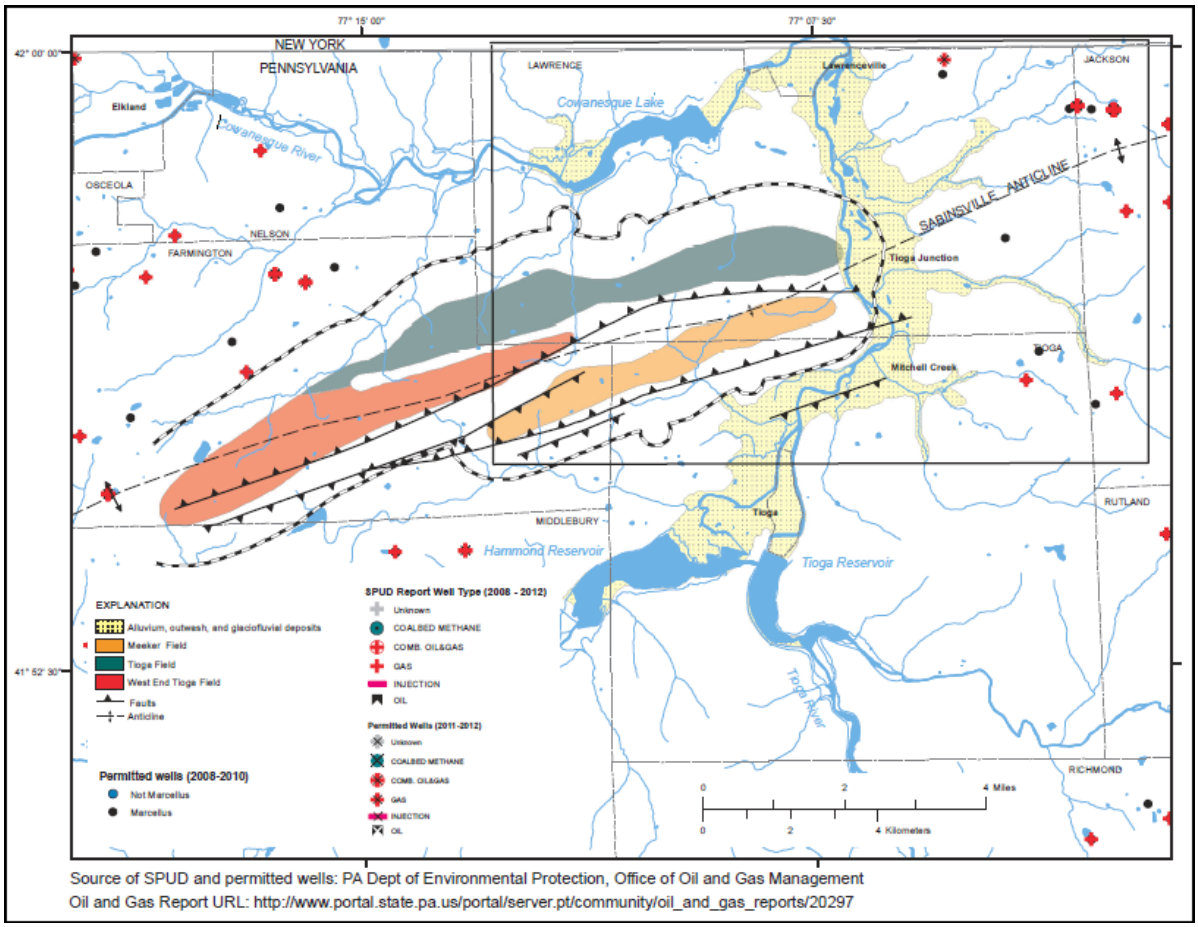
Fred Baldassare and others, GWPC, Atlanta, GA, September 2011

<u>Essential data</u> to identify stray natural gas origins:

1. **Identify possible gas sources.**
2. **Create a baseline gas signature library.** Determine concentrations and $\delta^{13}C$ - $\delta^{2}H$ of CH_4; and $\delta^{13}C$ of higher hydrocarbons across the play from various source units.
3. **Carry out site specific monitoring of natural gas and dissolved inorganic carbon DIC) in groundwater before (baseline), during and after drilling.** (Concentrations and $\delta^{13}C$ - $\delta^{2}H$ of CH_4; and $\delta^{13}C$ of higher hydrocarbons $\delta^{13}C$ of DIC). Determine the source(s) of stray gas in domestic-supply wells and identify gases from major and minor gas production zones across the play.
4. **Monitor longer-term changes** in methane presence/concentration as play develops (well density), and as the play ages (leakage from casing/grout seals) **during and following gas production (decades).**

Since this study finished in 2005, there has been extensive construction of new gas wells using hydraulic fracturing technology (see red symbols in Figure 14). The Marcellus Shale gas has a unique isotopic signature compared to the gases analyzed in this study; therefore, this study could serve as a background data set to check if the recent drilling has further impacted the aquifer system.

Figure 14. Map showing the 2005 study area (square in the map), and the hydraulic fractured drilling sites (red symbols).



Source of SPUD and permitted wells: PA Dept of Environmental Protection, Office of Oil and Gas Management
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Appendix B.

Extended Abstracts from Session 2: Future Trends in Hydraulic Fracturing Chemical Usage and Implications for Analytical Methods

Emerging Technologies and Increasing Data Interpretation Concerns

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The statements made during the workshop do not represent the views or opinions of EPA. The claims made by participants have not been verified or endorsed by EPA.

Introduction

Environmental testing laboratories have historically focused on development of more sensitive or specific technologies for analysis and the generation of large volumes of analytical data, with limited involvement in the interpretation of that data for decision making. As technologies improve and more data are made available, there is an increasing disconnect in turning the data into useful information for that decision making process. Despite the best intentions of all involved, there are increasing concerns related to false positives, false negatives, poor accuracy, and an increasing lack of understanding of the limitations of a data set that can lead to erroneous decision making. This presentation will examine some of the emerging technologies for use in the analysis of samples from oil and gas exploration or production sites and the pitfalls to avoid in the interpretation of the data, providing suggestions for a more accurate interpretive path forward.

Background

With the increasing improvement in analytical methodologies and instrumental analytical technologies, commercial laboratories are routinely providing more detailed analytical data to end users. As these technological capabilities improve, such requests often include requirements for lower limits of reporting, or for reporting of data to the limit of detection for the analytical method and instrumentation utilized for the testing. This is typically defined in the industry as the Method Detection Limit (MDL) and is generally defined using the procedures outlined in 40 CFR part 136(1). As defined in this procedure, the MDL is the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. The procedure typically involves the measurement of the concentration of seven replicate analyses of an analyte spiked into reagent water at a level at or near the estimated MDL. The Standard deviation of the results is used to calculate the MDL at the 99%confidence interval for that analyte. This procedure, however, does not account for bias that may be introduced in the measurement from the blank water used in spiking to calculate the MDL. A procedure for determining the minimum detection limit that does not adjust for bias in the blank will underestimate the minimum concentration at which there is 99% confidence that a result from the analysis of a sample can be distinguished from that of a blank. The procedure also assumes that the standard deviation does not change between the calculated MDL and the spike concentration used for determination. Because the standard deviation cannot be assumed to be constant over varying concentrations, the calculated MDL may vary based only on the concentration used in spiking the replicates for the determination. The procedure outlined in 40 CFR part 136 also provides no ongoing measure of the precision associated with the reporting of results at the calculated MDL, and does not account for normal instrument and method variability over time. MDL studies are usually performed once at the initial set up of a new instrument, and then yearly as required by many regulatory agencies. These studies are typically

performed on a single day on a freshly cleaned and calibrated instrument, and the values obtained represent an ideal situation not reflective of normal operating conditions.

Evaluation of Blank Data

Data used for risk evaluation should provide a level of certainty that the values obtained are distinguishable from method blank results. When evaluating data for metals analysis, it is often observed that method blank analyses are positive for the target analytes at levels greater than the MDL determined statistically using the procedures outlined in 40 CFR part 136, making it difficult to ascertain whether the results obtained on surface water samples can be distinguished from Laboratory blank levels. This suggests that levels of some metals reported to the MDL may be false positive results when compared to the method blank data pool. Data presented in this discussion evaluated historical method blanks for metals analyses generated over time to estimate the frequency of detections at values greater than the MDL for analytes of concern. This frequency may suggest that similar detections in environmental samples may be considered false positive results. Analyses were conducted using the procedures defined by EPA Method 200.8, and were performed on a single Agilent 7500ce ICP-MS instrument. In this study, 21 method blanks analyzed on different days were evaluated for a list of metals. As shown in Table 13, several elements analyzed in the study gave an average method blank result greater than the calculated MDL, including arsenic and manganese, which have been analytes of particular concern in oil and gas operations in several geographical regions. Additionally, the average method blank results for thallium, copper, chromium, and cadmium were all within 1 standard deviation of the calculated MDL. Defined as the detection of an analyte at a level above the MDL value used for reporting, false positive results for antimony, arsenic, molybdenum, and vanadium were reported in 80% or more of the method blanks analyzed. The frequency of positive blank results compared to the MDL make it improbable to state with analytical certainty that similar results obtained in the surface water samples analyzed are actual detections suitable for risk evaluation.

In a larger evaluation of reported data, Dr. Richard Burrows (2) evaluated reported data from 19 laboratories to determine the potential for false positive results based on the use of the MDL for reporting. Included in the evaluation were 138,212 actual reported results for an assortment of analytical methods from actual environmental samples based on requirements from customers or regulatory authorities to report data to the MDL as defined by 40 CFR Part 136. In evaluating the reported data, 5,043 of these reported results were actually between the MDL and the calibrated reporting limit for the Laboratory, or 3.6 %. Based frequency of detection of the analytes in the associated Method Blanks, it was estimated that the anticipated frequency of false positive results in this total population would be 2.3 %. That implies that 3,511 of the reported results above the MDL but less than the calibrated reporting limit (70 % of the population of results reported between the MDL and the calibrated lower limit of reporting) are potentially false positive results based on the frequency implied by the method blank results.

Summary

There are multiple opportunities available to the data user and analytical community in light of this information. Although newer methods and instrumental technologies allow for analysis at lower levels of sensitivity, the data must be evaluated with respect to all available information including a full understanding of the limitations of the detection limits and the MDL procedures

as generally applied in the commercial laboratories. Historical laboratory blank data should be evaluated with respect to frequency of detections above the MDL to determine the potential for false positive results for specific analytes. For most organic analyses, where instrument and method blank data is expected to return a zero result, the frequency of false positive results using the traditional MDL procedures as defined by 40 CFR Part 136 is not anticipated to be of primary concern, but for inorganic parameters, many of which are of particular interest in the oil and gas exploration arena today, that potential may have a significant impact on the interpretation and use of analytical data. An alternative procedure for determining the MDL that considers laboratory statistical blank data may be a more reliable indicator of the true detection limit for data evaluation.

Resources

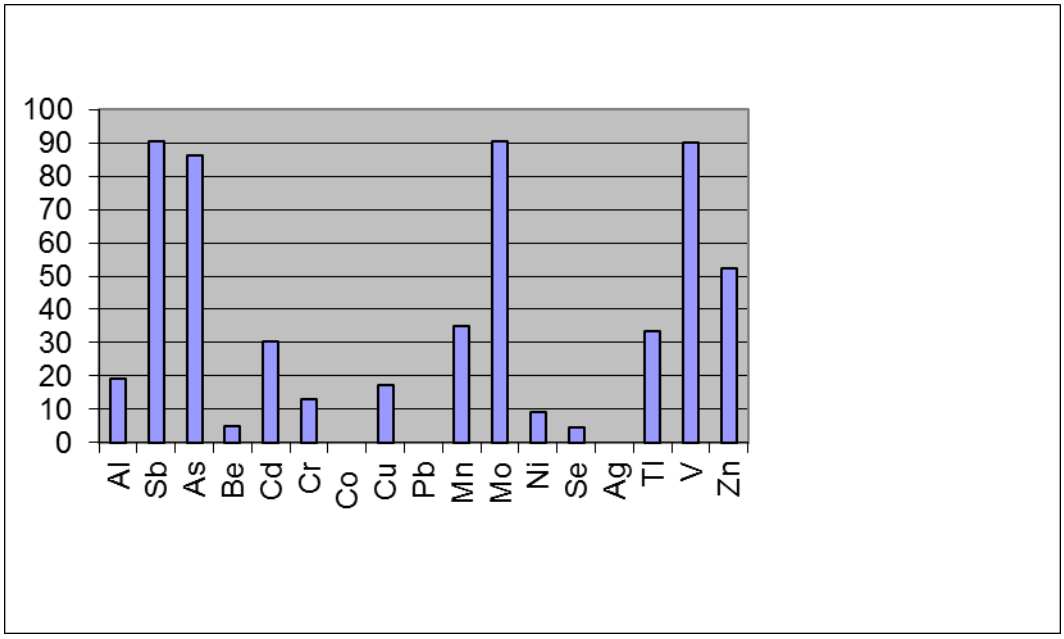
Code of Federal Regulations - Title 40: Protection of Environment 40 CFR Appendix B to Part 136 - Definition and Procedure for the Determination of the Method Detection Limit - Revision 1.11 December 30, 2005

Burrows, Richard, Proceedings of FSEA, December, 2008

Table 13. Comparison of Calculated MDL values using 40 CFR Procedures with Average Method Blank Results

Analyte	40 CFR Determined MDL	Average Blank Concentration	Standard Deviation of Blank Concentration
Aluminum	10.23	4.7	5.23
Antimony	0.0168	0.109	0.0886
Arsenic	0.0168	0.0292	0.0971
Beryllium	0.0613	0.0105	0.0339
Cadmium	0.0153	0.00591	0.023
Chromium	0.25	0.138	0.276
Cobalt	0.1057	0.0065	0.0254
Copper	0.2497	0.102	0.196
Lead	0.0819	0.0141	0.0238
Manganese	0.1109	0.185	0.442
Molybdenum	0.047	0.373	0.513
Nickel	0.0819	0.0157	0.034
Selenium	0.0382	0.0045	0.0274
Silver	0.1023	0.0141	0.0313
Thallium	0.0153	0.00714	0.0318
Vanadium	0.13	0.311	0.193
Zinc	0.61	1.26	2.01

Figure 15. Percent False Positive Results for Method Blank Analyses



Analytical Testing for Hydraulic Fracturing Fluids Water Recovery and Reuse

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The statements made during the workshop do not represent the views or opinions of EPA. The claims made by the participants have not been verified or endorsed by EPA.

Introduction

Water reuse and recycling in hydraulic fracturing operations will be a significant issue as the United States develops their oil and gas shale plays. Water is an essential component of the development of oil and gas wells, both in the development of the well and through the increased use of the hydraulic fracturing techniques. Well development typically utilizes 60,000 to 650,000 gallons for the use of cuttings control and lubrication of the drill bit. Currently, 3 to 5 million gallons of water is utilized per hydraulic fracturing event per well.[1] As part of the desire by energy companies to conserve and reuse water, there will need to be a method to determine what analytes will be needed to allow for reuse and recycling. This abstract will discuss the potential reuse of produced and flowback water and what considerations are important in the feasibility of this water reuse opportunity.

When discussing water reuse of produced water or hydraulic fracturing fluids, it is very important to define these terms. Produced water is the water that originates in an oil or gas well and is developed with the oil and/or gas resource. Hydraulic fracturing flowback (flowback) water is defined as the water that is released from the well after a hydraulic fracturing process. This flowback water normally will return between 50 to 80 percent of the water that was originally used in the hydraulic fracturing process and is returned over a 60 to 90 day period. Produced water will follow the flowback water after the initial 60 to 90 day period. Therefore, if 5 million gallons are used in the hydraulic fracturing process, then 2.5 to 4 million gallons will be returned as flowback water.

Another important issue of water reuse of produced and flowback water are the water quality aspects. Water quality will be discussed in detail, but this characteristic is important due to the water quality components of the produced or flowback water and the interacting of these fluids with either the hydraulic fracturing fluids or the formation water. In addition, the water quality components are important for the ability to treat and eventually discharge produced or flowback water to the surface. The regulations that affect these water quality components are also discussed.

The last aspect is the actual testing criteria and how these criteria interact with the final reuse of the water.

Water Quality

Produced and flowback water include water naturally occurring alongside hydrocarbon deposits as well as constituents injected into the formation. The following are the main contaminants of concern in produced and flowback water:[2]

- Total Dissolved Solids – ranging from brackish water (>1,000 mg/l) to saturation levels (>300,000 mg/l)
- Oil and Grease
- Suspended solids
- Dispersed oil
- Dissolved and volatile organic compounds
- Heavy metals
- Radionuclides
- Dissolved gases and bacteria
- Chemical additives, such as biocides, scale and corrosion inhibitors, guar gum and emulsion/reverse-emulsion breakers

The amount of these constituents vary considerably from both the formation water as well as the mixture of chemical additives (Refer to Table 14 and Table 15). In the early development of the production well, there will be higher concentrations of the chemical additives and later in the well development, the produced water will be closer to the formation water. A more detailed listing of the typical flowback water chemical additives is found in Figure 16.[3]

Table 14. Flowback Chemistry Example

Parameter	Feed Water	Flowback
pH	8.5	4.5 to 6.5
Calcium	22	22,200
Magnesium	6	1,940
Sodium	57	32,300
Iron	4	539
Barium	0.22	228
Strontium	0.45	4,030
Manganese	1	4
Sulfate	5	32
Chloride	20	121,000
Methanol	Neglible	2,280
TOC	Neglible	5,690
TSS	Neglible	1,211

Table 15. Wide Variation of Flowback Chemistry (mg/l)

Parameter	Frac 1	Frac 2	Frac 3	Frac 4
Barium	7.75	2,300	3,310	4,300
Calcium	683	5,140	14,100	31,300
Iron	211	11.2	52.5	134.1
Magnesium	31.2	438	938	1,630
Manganese	16.2	1.9	5.17	7.0
Strontium	4.96	1,390	6,830	2,000
TDS	6,220	69,640	175,268	248,428
TSS	490	48	416	330
COD	1,814	567	600	2,272

Ref: ProChemTech International, Inc.

One of the most significant issues in water reuse of produced water and especially flowback water is guar gum. The values that we have seen in the field range from 100 mg/l to over 20,000 mg/l of guar gum. Guar gum is a thixotrophic material that is used to move the silica sand or propant to the end of the fracture zone. This material is a significant hindrance to any filtration of this water. Treatment of the guar gum, which is a polymer, will require either breakdown of the polymer by enzyme chemistry or for the polymer to react with a cation, such as iron. Therefore it is extremely important to understand the levels of guar gum in the flowback water, how these different concentrations react to filtration and to be able to test for this chemical additive in the field as well as the laboratory.

The other issue of concern is the scale formation chemistry. As shown in Table 14 and Table 15, there are significant scale formation constituents. These include barium sulfate, silicates, calcium, and magnesium. Therefore, if reuse is a consideration, you need to remove the constituents which could form scales in the formation, which will impact the production well.

In addition to the above issues, it is important to consider which compounds can lead to interference issues with the hydraulic fracturing chemistry. An example of this is boron, which is an accelerant of the fracturing fluids. Therefore, you need to reduce boron below 1 mg/l in the hydraulic fracturing fluid makeup water.

These three components of guar gum, scale forming chemistry and hydraulic fracturing chemical accelerants are very difficult items to remove and will be a challenge as the industry moves forward with water recycling and reuse.

An example of the water quality goals for hydraulic fracturing fluid makeup water is provided in Table 16.

Table 16. An Example of Water Quality Goals for Hydraulic Fracturing Fluids

Bacteria	100,000 per 100 ml
Barium (mg/l)	< 2
Bicarbonates (mg/l)	250 to 100,000
Calcium (mg/l)	300
Chlorides (mg/l)	2,000 to 40,000
Iron (mg/l)	10
Hydrogen Sulfide (mg/l)	ND
Magnesium (mg/l)	100
pH	6.5 to 8.0
Phosphates (mg/l)	10
Radionuclides (pCi/l)	<15
Reducing agents (mg/l)	ND
Silica (mg/l)	<20
Strontium (mg/l)	<10
Sulfate (mg/l)	400 to 1,000
Total Dissolved Solids (mg/l)	500 to 5,000

Regulatory Issues

One of the driving forces for water quality issues in hydraulic fracturing are the environmental regulations. Typically, past operations in the energy industry have utilized Class II injection wells for the disposal of produced and flowback water. This process of injection wells are currently regulated under the Safe Drinking Water Act. However, if a company is looking to reuse produced or flowback water, then there will be other regulatory issues to consider.

One of the issues is the movement of the water. There are two issues to consider: (1) the Clean Water Act for discharge of water to a surface stream and (2) Water Rights regulation. Both of these issues will force the industry to handle the salt loading associated with produced and flowback water. An example of this is discharge to the Colorado River basin. The water quality standards in the Colorado River basin will require the control of sodium as it relates to salt loading. This will require advanced treatment technologies.[4]

In addition, the Clean Water Act will require the control of radionuclides. In the eastern US, it was typical for produced water to be treated utilizing a Publically Owned Treatment Works (POTW). However, a typical POTW cannot remove radionuclides and therefore prevents the discharge of produced water to this type of treatment facility.[1]

An example of water quality goals on a state wide basis is the Colorado State Wide permit system for produced water. These goals are very tight, but allow for the same treatment of the discharge of produced water throughout the state.[5] The discharge standard for TSS is 30 mg/l, the BOD is 30 mg/l, the TDS is 500 and the Sodium Absorption Ratio is less than 5. There are additional limits listed in Figure 17 which require very highly treated water. However, this allows for discharge of the water which is some cases are less expensive than the injection of the produced water into a Class II injection well.

Another example of a regulatory issue is the requirement in Colorado and Pennsylvania of groundwater prior to the hydraulic fracturing of an oil or gas well. In Colorado, this is under the purview of the Colorado Oil and Gas Conservation Commission. Under Rule 609, energy companies are required to obtain a baseline of the groundwater surrounding the oil or gas well. This background testing normally incorporates a relatively small suite of analytes. However, in our work, we have found that other considerations, such as radioisotopes should be included to insure the identification of hydraulic fracturing fluid separation from groundwater samples. A statistically significant sampling program will assist the energy company in proving that the hydraulic fracturing of a well in not interacting with the surface or ground waters.

Testing Requirements

The testing requirements for produced water and flowback water are similar but in almost all cases, the requirements for reuse are set by the end use of the water. If the water is being injected into a Class II injection well, then the testing requirements are reduced significantly. The main issue is to remove constituents such as TSS and Oil/grease to make sure that they do not interfere with the formation water. In most cases, the formation chemistry interaction can be controlled by sequestering agents.

The testing requirements for direct reuse will require additional characterization of the water. It is important to understand the chemical additives along with the interaction of chemistry in the hydraulic fracturing fluid. In this case, you will likely be starting to control salts, which require additional testing to dictate the treatment technology.

The highest testing requirements arise when the produced water is to be discharged to surface water. This will require the control of salts, radionuclides, organic compounds, etc.

Field Testing

At the present time, field testing technology is very limited. The industry is in need of quick and reliable field tests which will provide the information needed to control the selected treatment processes. The current technologies of UV-Vis colormetric tests need to be developed to provide reliable tests for the constituents of concern.

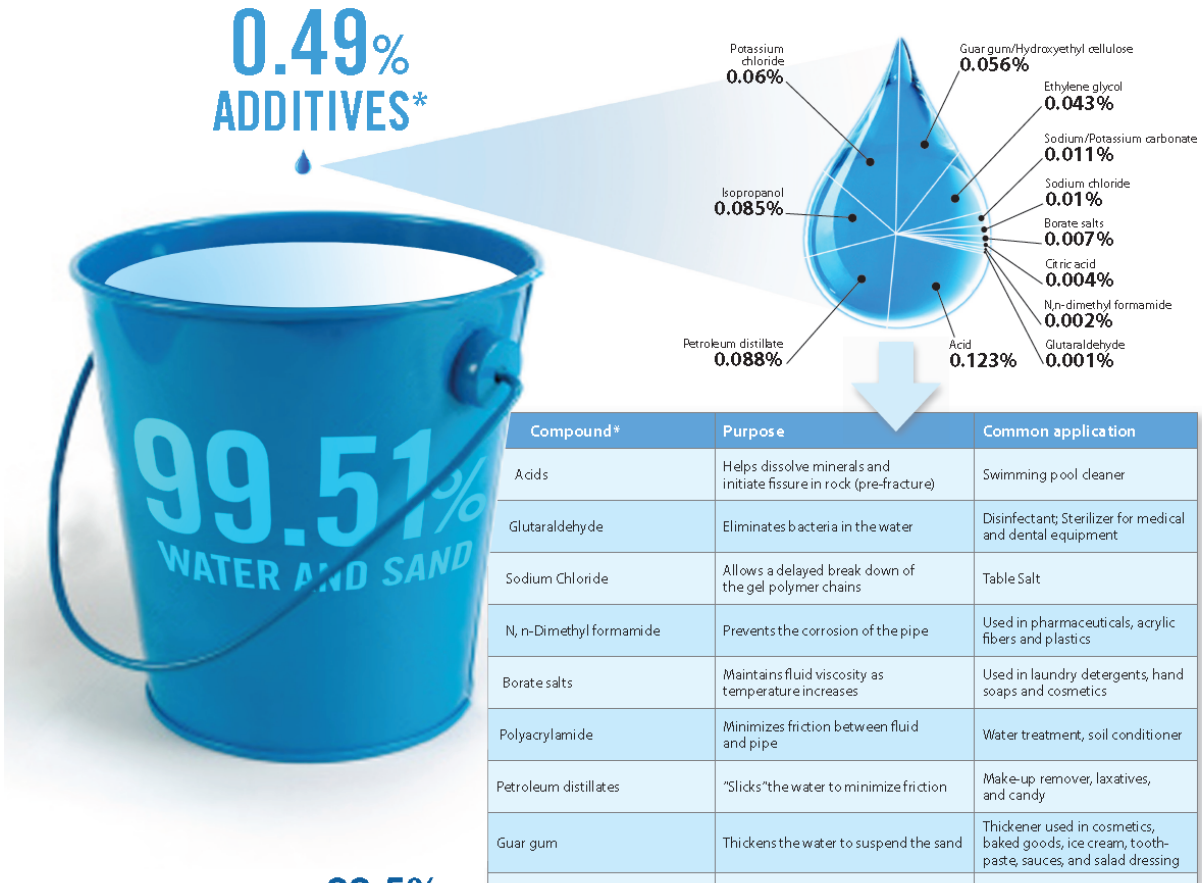
Conclusions

Water reuse and recycling will become one of the controlling factors for hydraulic fracturing of oil and gas wells in the United States. It will become very important for the energy industry to develop the criteria for water recycling and reuse and then develop the treatment technologies and testing techniques to implement these recycling and reuse projects.

Figure 16. Typical Solution Used in Hydraulic Fracturing

A FLUID SITUATION:

TYPICAL SOLUTION* USED IN HYDRAULIC FRACTURING



Compound*	Purpose	Common application
Acids	Helps dissolve minerals and initiate fissure in rock (pre-fracture)	Swimming pool cleaner
Glutaraldehyde	Eliminates bacteria in the water	Disinfectant; Sterilizer for medical and dental equipment
Sodium Chloride	Allows a delayed break down of the gel polymer chains	Table Salt
N, n-Dimethyl formamide	Prevents the corrosion of the pipe	Used in pharmaceuticals, acrylic fibers and plastics
Borate salts	Maintains fluid viscosity as temperature increases	Used in laundry detergents, hand soaps and cosmetics
Polyacrylamide	Minimizes friction between fluid and pipe	Water treatment, soil conditioner
Petroleum distillates	"Slicks" the water to minimize friction	Make-up remover, laxatives, and candy
Guar gum	Thickens the water to suspend the sand	Thickener used in cosmetics, baked goods, ice cream, tooth-paste, sauces, and salad dressing
Citric Acid	Prevents precipitation of metal oxides	Food additive; food and beverages; lemon juice
Potassium chloride	Creates a brine carrier fluid	Low sodium table salt substitute
Ammonium bisulfite	Removes oxygen from the water to protect the pipe from corrosion	Cosmetics, food and beverage processing, water treatment
Sodium or potassium carbonate	Maintains the effectiveness of other components, such as crosslinkers	Washing soda, detergents, soap, water softener, glass and ceramics
Proppant	Allows the fissures to remain open so the gas can escape	Drinking water filtration, play sand
Ethylene glycol	Prevents scale deposits in the pipe	Automotive antifreeze, household cleansers, deicing, and caulk
Isopropanol	Used to increase the viscosity of the fracture fluid	Glass cleaner, antiperspirant, and hair color

On average, **99.5%** of fracturing fluids are comprised of freshwater and compounds are injected into deep shale gas formations and are typically confined by many thousands of feet or rock layers.

Source: DOE, GWPC: Modern Gas Shale Development In the United States: A Primer (2009)

*The specific compounds used in a given fracturing operation will vary depending on source water quality and site, and specific characteristics of the target formation. The compounds listed above are representative of the major material components used in the hydraulic fracturing of natural gas shales. Compositions are approximate.

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Figure 17. Statewide Limits for Discharge of Produced Water in Colorado

Appendix A. Inventory of Statewide Limits and Site-Dependent Limits, Based on Receiving Water Features , for Surface Waters.

This overview (July 9, 2009) is based on current versions of regulations and practices of implementing narrative standards for protection of livestock watering, crop irrigation of crops, and aquatic biota. While key information is provided in the table and associated notes for each entry, more detailed information is available in the regulations and policies and will be utilized by the permit writer when monitoring requirements and limits are selected. The notes are provided on the pages after the table and indicate the method to calculating the limits that are based on receiving water chemistry and other parameters.

PARAMETER			REGULATORY BASIS FOR LIMITS (ug/l unless noted otherwise)								
			Beneficial Uses and Water Quality Standards (Regulation No. 31)								Other Regulations or Policies
			All Waters	Aquatic Life				Agriculture	Domestic Water Supply	Recreation	
				All Classes	Class 1		Class 2				
				Acute	Chronic	Cold	Warm				
Radionuclides (Picocuries/l, pCi/l)											
Americium 241			0.15								
Cesium 134			80								
Plutonium 239 and 240			0.15								
Radium 226 and 228			5								
Strontium 90			8								
Thorium 230 and 232			60								
Tritium			20,000								
Regulation No. 62 (mg/l except pH)											
Total Suspended Solids (TSS)											30
Total Residual Chlorine (TRC)											0.5
Total Residual Chlorine (TRC)	1-Day					0.019	0.019	--			
	30-day					0.011	0.011	0.011			
Oil and Grease	Reg. No. 62										10
	40 CFR 435.E ELG										35
BOD-5 day											30
CBOD-5 day											25
pH, su						6.5 – 9.0	6.5 – 9.0	6.5 – 9.0		5.0-9.0	6.5 – 9.0	6.0 – 9.0
Physical Parameters											
Dissolved Oxygen, mg/l	No spawning					6.0	6.0	5.0			3.0	
	Spawning					7.0	7.0	--				
Temperature, degrees Centigrade						Note 1	Note 1	Note 1				
Total Dissolved Solids (TDS), mg/l	Reg. No. 61	Concentration										500
		Load, Ton/Day										1.0
	Livestock Watering, BPJ								3,5000			
Biological Parameters (#/100 ml)											
E. coli										630		
E. coli	Class E and U										126	
	Class P										205	
	Class N										630	
Inorganic Chemicals -Nonmetals (mg/l)											
Total Ammonia (as nitrogen)						Note 2	Note 2	Note 2				
Cyanide - Free						0.005	0.005	0.005	0.2	0.2		
Fluoride										2.0		
Nitrate (as nitrogen)									100	10		
Nitrite (as nitrogen)						Note 3	Note 3	Note 3	10	1.0		
Sulfide (as hydrogen sulfide), undissociated						0.002	0.002	0.002		0.03		
Boron									0.75			
Chloride										250		
Sulfate										250		
Asbestos, fibers/liter										7,000,000		
Phosphorus (as phosphate)	Reg. No. 71 Dillon											Note 4
	Reg. No 72 Cherry Creek											Note 5
	Reg. No 73 Chatfield											Note 6
	Reg. No. 74 Bear Creek											Note 7
	Reg. No. 75 Cheraw											Note 8
Inorganic Chemicals – Metals (ug/l)												
Aluminum , Total Recoverable				750	87							
Antimony										6.0 (30-day)		
Arsenic				340	150					0.02 (30-Day)		
Barium	1-Day									1,000		
	30-Day									490		
Beryllium									100 (30-Day)	4.0 (30-Day)		
Cadmium				Note 9	Note 9				10 (30-Day)	5.0 (1-Day)		
Chromium	III (+3)			Note 10	Note 10				100 (30-Day)	50 (1-Day)		
	VI (+6)			16	11				100 (30-Day)	50 (1-Day)		
Copper				Note 11	Note 11				200	1,000 (30-Day)		
Iron	Total Recoverable			--	1000							
	Dissolved									300 (30-Day)		
Lead				Note 12	Note 12				100 (30-Day)	50 (1-Day)		
Manganese				Note 13	Note 13				200 (30-Day)	50 (1-Day)		
Mercury, Total				1.4	Note 14					2.0 (1-Day)		
Nickel				Note 15	Note 15				200 (30-Day)	100 (30-Day)		
Selenium				16.4	4.6				20 (30-Day)	50 (30-Day)		
Silver				Note 16	Note 16					100 (1-Day)		
Thallium				--	1.5					0.5 (30-Day)		
Uranium				Note 17	Note 17					30		
Zinc				Note 18	Note 18				2000 (30-Day)	5,000 (30-Day)		
Organic Chemicals (CAS Number)												
Acenaphthene (83-32-9)				1,700	520					420		
Acetochlor (34256-82-1)				---	---					140		
Acrolein (107-02-8)				68	21					3.5		
Acrylamide (79-06-1)				--	--					0.0078		
Acrylonitrile (107-13-1)				7,500	2,600					0.065		
Alachlor (15972-60-8)				---	---					2		
Aldicarb (116-06-3)				---	---					7		
Aldicarb Sulfone (1646-88-4)				---	---					7		
Aldicarb Sulfoxide (1646-87-3)				---	---					7		
Aldrin (309-00-2)				1.5	---					0.0021		
Aniline(62-53-3)				---	---					6.1		
Anthracene (120-12-7)				---	---					2,100		
Aramite (140-57-8)				---	---					1.4		
Atrazine (1912-24-9)				---	---					3		
Azobenzene (103-33-3)				---	---					0.32		
Benzene (71-43-2)				5,300	---					2.2		
Benzidine (92-87-5)				2,500	---					0.00013		
Benzo(a)anthracene (PAH) (56-55-3)				---	---					0.0048		
Benzo(a)pyrene (PAH) (50-32-8)				--	--					0.0048		
Benzo(b)fluoranthene (PAH) (205-99-2)				---	---					0.0048		
Benzo(g,h,i)perylene (PAH) (191-24-2)				---	---					---		
Benzo(k)fluoranthene (PAH) (207-08-9)				---	---					0.0048		

Benzotrichloride (98-07-7)			---	---					0.0027		
Benzyl chloride (100-44-7)			---	---					0.21		
Bis(chloromethyl) ether (BCME) (542-88-1)			---	---					0.00016		
Bromate (15541-45-4)			---	---					0.050		
Bromodichloromethane (HM) (75-27-4)			11,000	---					---		
Bromoform (HM) (75-25-2)			---	---					---		
Butyl benzyl phthalate (85-68-7)			---	---					1,400		
Carbofuran (1563-66-2)			---	---					35		
Carbon tetrachloride (56-23-5)			35,200	---					0.27		
Chlordane (57-74-9)			1.2	0.0043					0.10		
Chloroethyl ether (BIS-2) (111-44-4)			---	---					0.032		
Chlorobenzene (108-90-7)			---	---					100		
Chlorodibromomethane (HM) (124-48-1)			---	---					---		
Chloroform (HM) (67-66-3)			28,900	12,40					---		
Chloroisopropyl ether (BIS-2) (108-60-1)			---	---					280		
4-Chloro-3-methylphenol (59-57-8)			30	---					210		
Chloronaphthalene (91-57-7)			2,300	620					560		
Chlorophenol or (2-Chlorophenol) (95-57-8)			4,380	2,000					35		
Chlorpyrifos (2921-88-2)			0.083	0.041					21		
Chrysene (PAH) (218-01-9)			---	---					0.0048		
DDD (72-54-8)			0.6	---					0.15		
DDE (72-55-9)			1,050	---					0.1		
DDT (50-92-3)			0.55	0.001					0.1		
Dalapon (75-99-0)			---	---					200		
Demeton (8065-48-3)			---	0.1					---		
Diazinon (333-41-5)			0.17	0.17					---		
Dibenzo(a,h)anthracene (PAH) (53-70-3)			---	---					0.0048		
1,2 Dibromo-3-Chloropropane (DBCP)			---	---					0.2		
Dicamba (1918-00-9)			---	---					210		
Dichloroacetic acid (79-43-6)			---	---					0.7		
Dichlorobenzene 1,2 (95-50-1)			---	---					600		
Dichlorobenzene 1,3 (541-73-1)			---	---					94		
Dichlorobenzene 1,4 (106-46-7)			---	---					75		
Dichlorobenzidine (91-94-1)			---	---					0.078		
Dichloroethane 1,2 (107-06-2)			118,000	20,000					0.38		
Dichloroethylene 1,1 (75-35-4)			---	---					7		
Dichloroethylene 1,2 cis (156-59-2)			---	---					2		
Dichloroethylene 1,2 trans (156-60-50			---	---					100		
Dichlorophenol 2,4 (120-83-2)			2,020	365					21		
Dichlorophenoxyacetic acid (2,4-D) (94-75-7)			---	---					70		
Dichloropropane 1,2 (78-87-5)			23,000	5,700					0.52		
Dichloropropylene 1,3 (542-75-6)			6,060	244					0.35		
Dichlorvos (62-73-7)			---	---					0.12		
Dieldrin (60-57-1)			0.24	0.056					0.002		
Diethyl phthalate (84-66-2)			---	---					5,6000		
Diisopropylmethylphosphonate (DIMP) (1445-75-6)			---	---					8		
Dimethylphenol 2,4 (105-67-9)			2,120	---					140		
Dimethyl phthalate (131-11-3)			---	---					70,000		
Di-n-butyl phthalate (84-74-2)			---	---					700		
Dinitrophenol 2,4 (51-28-5)			---	---					14		
Dinitro-o-cresol 4,6 (534-52-1)			---	---					0.27		
Dinitrotoluene 2,4 (121-14-2)			---	---					0.11		
Dinitrotoluene 2,6 (606-20-2)			330	230					---		
Dinoseb (88-85-7)			---	---					7		
Dioxane 1,4 (123-91-1)	Through 03/21/10		---	---					6.1		
	Effective 03/22/10		---	---					3.2		

Dioxin (2,3,7,8 TCDD) (1746-01-6)		0.01	0.00001					2.2 x 10-7		
Diphenylhydrazine 1,2 (122-66-7)		270	---					0.044		
Di(2-ethylhexyl) adipate (103-23-1)		---	---					400		
Diquat (85-00-7)		---	---					15		
Endosulfan (115-29-7)		0.11	0.056					42		
Endosulfan, alpha (959-98-8)		0.11	0.056					42		
Endosulfan, beta (33213-65-9)		0.11	0.056					42		
Endosulfan, sulfate (1031-07-8)		0.11	0.056					42		
Endothall (145-73-3)		---	---					100		
Endrin (72-20-8)		0.086	0.036					2		
Endrin aldehyde (7421-83-4)		---	---					2.1		
Epichlorohydrin (106-89-8)		---	---					3.5		
Ethylbenzene (100-41-4)		32,000	---					700		
Ethylene dibromide (106-93-4)		---	---					0.2		
Ethylhexyl phthalate (BIS-2)(DEHP)(117-81-7)		---	---					2.5		
Fluoranthene (PAH) (206-44-0)		3,980	---					280		
Fluorene (PAH) (86-73-7)		---	---					280		
Folpet (133-07-3)		---	---					10		
Furmecyclox (60568-05-0)		---	---					1.2		
Glyphosate (1071-83-6)		---	---					700		
Guthion (86-50-0)		---	0.01					---		
Heptachlor (76-44-8)		0.52	0.0038					0.008		
Heptachlor epoxide (1024-57-3)		0.52	0.0038					0.004		
Hexachlorobenzene (118-74-1)		---	---					0.022		
Hexachlorobutadiene (87-68-3)		90	9.3					0.45		
Hexachlorocyclohexane, alpha (319-84-6)		---	---					0.45		
Hexachlorocyclohexane, beta (319-85-7)		---	---					0.019		
Hexachlorocyclohexane, gamma (58-89-9)		0.95	0.08					0.2		
Hexachlorocyclohexane, technical (608-73-1)		100	---					---		
Hexachlorocyclopentadiene (HCCPD) (77-47-4)		7	5					42		
Hexachlorodibenzo-p-dioxin (19408-74-3)		---	---					5.60E-06		
Hexachloroethane (62-72-1)		980	540					0.7		
Hydrazine (302-01-2)		---	---					0.012		
Indeno(1,2,3-cd)pyrene (PAH) (193-39-5)		---	---					0.0048		
Isophorone (78-59-1)		---	---					140		
Malathion (121-75-5)		---	0.1					140		
Methoxychlor (72-43-5)		---	0.03					35		
Methyl Bromide (HM) (74-83-9)		---	---					---		
Methylene chloride (HM) (74-87-3)		---	---					---		
4,4- Methylene bis (N,N'-dimethly)aniline (101-61-1)		---	---					0.76		
Methylene chloride (75-09-2)		---	---					4.7		
Metribuzin (21087-64-9)		---	---					180		
Mirex (2385-85-5)		---	0.001					1.4		
Naphthalene (PAH) (91-20-3)		2,300	620					140		
Nitrobenzene (98-95-3)		27,000	---					3.5		
Nitrophenol 4 (100-07-2)		---	---					56		
Nitrosodibutylamine N (924-16-3)		---	---					0.0065		
Nitrosodiethylamine N (55-18-5)		---	---					0.00023		
Nitrosodimethylamine N (62-75-9)		---	---					0.00069		
N-Nitrosodiethanolamine (1116-54-7)		---	---					0.013		
Nitrosodiphenylamine N (86-30-6)		---	---					7.1		
N-Nitroso-n-methylethylamine (10595-95-6)		---	---					0.0016		
Nitrosopyrrolidine N (930-55-2)		---	---					0.017		
N-Nitrosodi-n-propylamine (62-64-7)		---	---					0.005		
Nonylphenol (84852-15-3 and 25154-52-3) Eff 07/01/10		28	6.6					---		
Oxamyl (vydate) (23135-22-0)		---	---					175		

PCBs (1136-36-3)		2.0	0.014					0.0175		
Parathion (56-38-2)		0.065	0.013					---		
Pentachlorobenzene (608-93-5)		---	---					5.6		
Pentachlorophenol (87-86-5)		19	15					0.29		
Phenol (108-95-2)		10,200	2,560					2,100		
Picloram (1918-02-1)		---	---					490		
Prometon (1610-18-0)		---	---					100		
Propylene oxide (75-56-9)		---	---					0.15		
Pyrene (PAH) (129-00-0)		---	---					210		
Quinoline (91-22-5)		---	---					0.012		
Simazine (122-34-9)		---	---					4		
Styrene (100-42-5)		---	---					100		
Tetrachlorobenzene 1,2,4,5 (95-94-3)		---	---					2.1		
Tetrachloroethane 1,1,2,2 (79-34-5)		---	2,400					0.18		
Tetrachloroethylene (PCE) (127-18-4)		5,280	840					5		
Toluene (108-88-3)		17,500	---					560		
Toxaphene (8001-35-2)		0.73	0.0002					0.032		
Tributyltin (TBT)(56573-85-4)		0.46	0.072					---		
Trichlorobenzene 1,2,4 (120-82-1)		250	50					70		
Trichloroethane 1,1,1 (1,1,1-TCA) (71-55-6)		---	---					200		
Trichloroethane 1,1,2 (1,1,2-TCA) (79-00-5)		9,400	---					2.8		
Trichloroethylene (TCE) (79-01-6)		45,000	21,900					5		
Trichlorophenol 2,4,5 (95-95-4)		---	---					700		
Trichlorophenol 2,4,6 (88-06-2)		---	970					3.2		
Trichlorophenoxypropionic acid (2,4,5-tp) (93-72-1)		---	---					50		
Trihalomethanes, total (sum of sveveral compounds)		---	---					80		
Vinyl chloride (75-01-4)		---	---					0.023		
Xylenes (total) (1330-20-7)		---	---					1,400		
Toxicity										
Whole Effluent Toxicity (WET)		Note 19	Note 19							
WQP #24 (Protection of Irrigated Crops)										
Electrical Conductivity (EC)										Note 20
Sodium Absorption Ratio (SAR)										Note 20
Sodium										Note 20
Calcium										Note 20
Magnesium										Note 20

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Appendix A for Produced Water Colorado Discharge Permit System, 2009

Beneficial Use of Produced Water – Considerations for Projects Along the Colorado River, International Petroleum Environmental Conference, 2010

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Monitoring Subsurface Fluid Flow using Perfluorocarbon Tracers:
Another potential tool available for subsurface fluid flow assessments

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Introduction

Perfluorocarbon tracers (PFTs) are volatile to semi-volatile conservative tracers that are non-depositing, non-scavenged, non-reactive, have low atmospheric background and detectable at the pictogram to femtogram level (Senum et al, 1990; Straume et al, 1998). Due to their properties PFTs they have been used extensively for atmospheric and subsurface studies (Senum et al, 1990; McKinley and Colwell, 1996; Sullivan et al, 1998; Freifeld et al, 2005; Wells et al, 2007; Kieft et al, 2007; Kharaka et al, 2009; Siriwardane et al, 2012 and Lu et al, 2012). Also included in this group of tracers is sulfur-hexafluoride (SF_6), though not a fluorocarbon, it otherwise behaves similarly to PFTs (Freifeld et al, 2005 and Lu et al, 2012). These tracers are unusual in that they are not naturally occurring, are relatively inexpensive costing a few hundred dollars per kg, and when added to a fluid at near ppm levels may be detectable at a further 5-6 orders of magnitude using a gas chromatograph (GC) equipped with an electron capture detector (ECD). Two or more order of magnitude improvement in detection can be achieved by sample concentration prior to the GC. As such PFTs may be considered as another potential tool for verifying or assessing flow of subsurface fluids from an injection point to a distant monitoring point as part of an integrated site monitoring program where PFTs can complement geophysical, geochemical or modeling tools. Importantly, due to their not occurring naturally coupled with their extremely low detection limits of pg-fg, PFTs may be more sensitive than typical geochemical tracers such as anions, cations, organics, or stable isotopes (Table 17). Use of PFTs should complement the typically used tracer techniques rather than displace them. For example, in carbon sequestration studies where movement of subsurface CO_2 plumes are monitored fluorinated tracers may signal a soon-to-arrive decrease in pH form the arriving CO_2.

In recent years a background level of PFTs has been observed in the atmosphere requiring care whenever they are used at or above ground (Watson and Sullivan, 2012). They suggested that background atmospheric concentration renders PFTs less than ideal for assessing leakage from the subsurface. Importantly, PFTs are not readily detected in potable aquifers making their use particularly useful if deeper fluids migrate to shallower potable supplies. While atmospheric background is problematic for total PFT detection at the ground surface by pyrolysis detection it may not interfere with chromatographic separation and detection of discrete PFT suites used at identified ratios at specific sites.

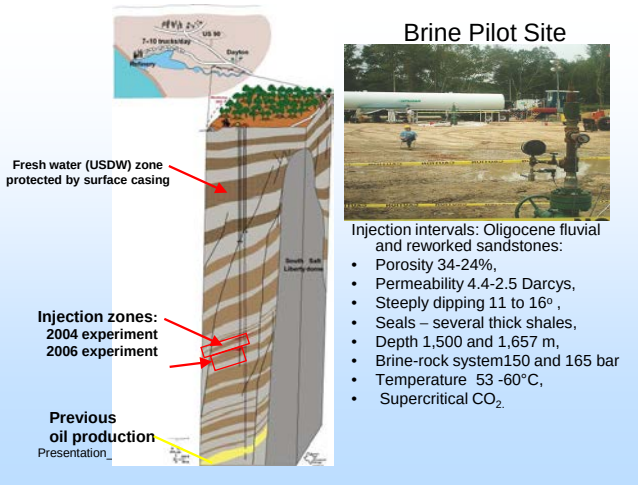
The objective of our multi-field site research has been to track the plume from injected fluids using suites of perfluorocarbon tracers (PFTs). In some cases PFTs were added as a conservative tracer in drilling fluids examining its occurrence in recovered core materials as a QA/QC tool for core recovery (McKinley and Colwell, 1996; Kieft et al, 2007). In later studies PFTs were used to monitor CO_2 plumes in carbon sequestration field demonstrations (Freifeld et al, 2005; Kharaka et al, 2009; and Lu et al, 2012) where the PFTs were used to identify CO_2 plume

breakthrough, added value to model validity testing, and provided insight into the saturation behavior of CO_2 (Figure 18). This paper describes the methods used to inject, collect, and analyze PFTs to facilitate technology transfer for their potential employment complementing geophysical and geochemical techniques during the assessment, verification or modeling of other environmentally relevant subsurface flows.

Materials and Methods

PFTs were procured from F2 Chemicals (England). The company web site provided a thorough listing of potential tracers along with detailed characteristics and material safety data sheets. PFTs typically used to monitor subsurface fluid transport include: perfluoromethylcyclopropane (PMCP), perfluoroethylcyclohexane (PECH), perfluorodimethylcyclohexane (PDCH), perfluporotrimethylcyclohexane (PMCH), perfluorotrimethylcyclohexane (PTCH). Compressed gas cylinders of SF6 were procured from local gas distributors.

Figure 18. Site where PFTs were used to monitor a subsurface CO2 plume as part of a carbon sequestration project.

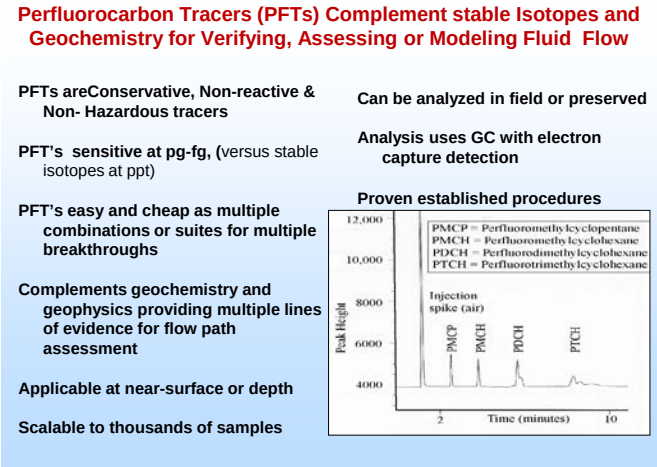


These and similar fluorinated tracers are volatile to semi-volatile with boiling points generally below 100°C. Fluorinated tracers are not naturally occurring and exhibit low detection limits making them more sensitive than cation, anion, organic or stable isotope tracers thereby serving as a complement to more typical geochemical monitoring (Table 18).

Table 17. Candidate Tracers for Verification or Assessment (complementing geophysics)

Brines	Native non-conservative tracers that respond to changes pH, alkalinity, electrical conductivity Cations: Na, K, Ca, Mg, ΣFe, Sr, Ba, Mn Major anions: Cl, HCO_3, SO_4, F Organics: DOC, acetate, methane, benzene, toluene
Gases	Native conservative tracers or added conservative tracers Ions: Br, I (*Na, K*) Gases: CO_2, N_2, H_2, CH_4, $C_2 - C_n$ Noble gas tracers: Ar, Kr, Xe, Ne, He (and their isotopes) Perfluorocarbon tracers (PFT's): PMCP, PECH, PMCH, PDCH, PTCH (also SF_6)
Isotopes	D/H, $^{18}O/^{16}O$, $^{87}Sr/^{86}Sr$ in water, DIC, minerals $^{13}C/^{12}C$ in CH_4, CO_2, DIC, DOC, carbonate minerals

Figure 19. Gas chromatograph showing PFTs and their relative elution times.

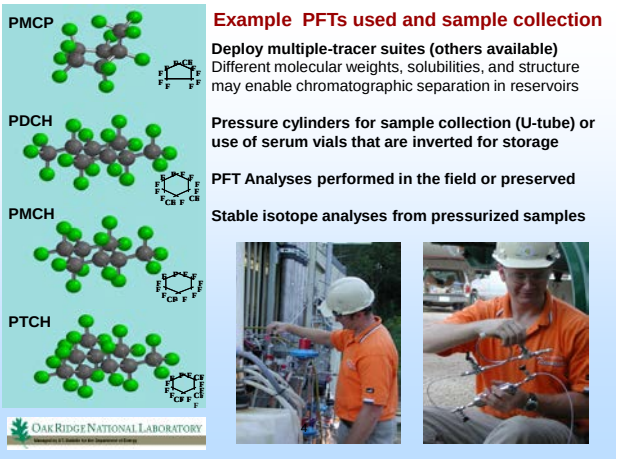


Suites and combinations of PFTs can be selected because of their volatility and their favorable gas chromatographic (GC) separation and elution time (Figure 19). Using PFTs with spaced elution times allowed multiple PFTs to be examined in a single GC injection. Detection of the PFTs was sensitive to the sub-picogram level when using an Agilent gas chromatograph equipped with an electron capture detector (ECD) with a 50 m RT-Alumina (Restek Corporation, Bellefonte, PA) capillary column.

After selecting PFTs for a particular project an injection scenario was devised. In most instances a high performance liquid chromatography pump (HPLC) that operated at pressures in excess of the formation pressure was used. Tracers were added to injected fluids at a level of 0.01-10mg/L over a period of a few hours. Quantities of 0.2-2kg over 0.5-5 hr typically at rates of a few ml/min entered the downhole stream. In most projects a ½" NPT fitting was provided by the contractor to which we connected a 1/8" Swagelok high pressure connection. When injecting into clathrate-forming fluids such as CO_2 or CH_4 care needs was taken to insure no water condensate developed in the injection supply line, otherwise a clathrate plug may develop. It was found that pumping 10 ml of methanol through the lines immediately prior to hooking them to the delivery system avoided clathrate formation. High frequency samples could be collected at monitoring wells using a U-tube, described in detail by Freifeld et al. (2005) (Figure 20). The U-tube was a 'U' shaped tube that was inserted in a monitoring well casing to the sampling depth. The U-tube was equipped with a series of one way check valves at the cusp of the 'U' bend in the tube. The pressure in the U-tube could be decreased below formation pressure which would permit sample fluids to enter the tube through the check valves. The U-tube pressure would then be increased with nitrogen gas propelling samples from the monitoring well screen zone to the surface at near in situ pressure. U-tube installations were ideal for long term high frequency sampling. Conventional grab samples were more economical during low resolution sampling.

Samples transported to the surface by the U-tube system were subsampled by filling 150 mL high pressure cylinders (Hoke Incorporated, Spartanburg, SC) with formation fluid (brine, and gas). The cylinders remained pressurized and were further subsampled using a sample loop (Figure 20), which also remained pressurized. At each sampling time point replicate serum vials (15-58 mL) were injected with 0.4 - 10 mL of formation fluids from pressurized sample loops. The fluid was introduced to each serum vial alongside a Teflon septa. The sample loop would be vented into a 58 mL into glass serum vials that also contained 2 mL of water. Vials were sealed with an aluminum crimp seal and stored inverted until analysis. Samples were analyzed by a GC-ECD using duplicate 50 µL injections. Standards were analyzed at the beginning and end of each GC working day.

Figure 20. Pressure vessels and sample loop for subsampling into Teflon-sealed vials for transport, storage and analysis.



Results and Discussion

Breakthrough times for the 3 PFT injections in a field project are summarized in Table 18. Multiple PFT tracer suites were introduced via an injection well at three separate times. The PFTs were then sampled at a monitoring well 30 meters away. The use of PFT suites provided data for identification of multiple breakthroughs. Travel times for each injection varied between 50.3 and 51.7 hours. The variability in breakthrough times was minimal for all three injections. Breakthrough of injection 2 (PMCP/PDCH) appeared as a well defined peak that spanned less than 20 hours.

The 3rd injection breakthrough was partially overlain by the PFTs of injection 2, but also spanned approximately 20 hours. The lack of variability in CO_2 saturation from the first to third injection implied that saturation and CO_2 flow paths were rapidly established and persisted.

Table 18. Results from PFT tracer test.

PFT injection results

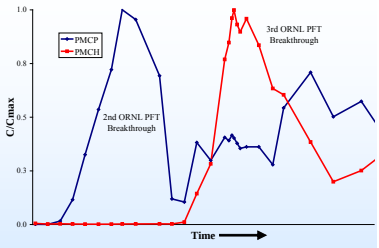
PFT Travel Time

- **Travel time nearly constant (50 ±1.6 hr)**
- **Well developed CO_2 flow path**

Peaks Broadened with time implying;

PFTs were dispersing in the CO_2 throughout the experiment

Flow paths continued to develop as the CO_2 injection progressed



Injection #	Injection time (hours after CO_2 start)	Injection Duration (hours)	Peak Arrival Time (hours)	PFT Travel Time (hours) (GC)	PFT Travel Time (hours) (MS)	PFT Peak Broadness (hours) (GC and MS)
#1 PMCH/PTCH	2	4	54	50	49	14
#2 PMCP/PDCH	103	0.6	157	52	49	20
#3 PMCH/PTCH	120	0.5	173	51	53	24

Table 19 shows results from another field campaign where two monitoring wells were located 68 and 112m downgradient from the CO_2 injection well. One tracer injection campaign was initiated in December and a second the following April. Within an individual campaign the initial breakthroughs and maximum peak at each monitoring well were similar. Between December and April it appeared the flow field further developed in that it took longer for the peaks to arrive at respective monitoring wells. In late December rate of CO_2 injection was nearly doubled resulting in a pressure front arriving at each monitoring well, exhibited by an abrupt increased concentration of all PFTs within the system at a time considerably faster than plume migration. Other interesting features included the arrival of a small fraction of the plume at the further sampling well in the April scenario before tracers contacted the closer monitoring well. Importantly though, the maximum peak took nearly twice as long to arrive at the distal monitoring well in both the December and April experiments.

Table 19. Travel Times of Tracer Breakthroughs and major Peaks (2nd site)

December			**April**	
Breakthrough/Maximum Peak			**Breakthrough /** Major Peaks**, Maximum**	
(Travel time in hr after injection)				
		Monitoring Well ~ 50m		
PMCH	-/ **182**		PMCP	288/ 360, **530,** 861
PTCH	-/ **177**		PDCH	288/ 359, **497**, 861
Increased flow front 35/ 38[b]			PECH	284/ 357, **423,** 446,810
			SF6	284/ 370[a,] **405,** 426, 841
			PTCH/PMCH	>150/ *
		Monitoring Well ~100m		
PMCH		-/ **238**	PMCP	240/ 313, 470, **808**
PTCH	214/ **277**		PDCH	262/ 327, 477, **793**
Icreased flow front 140/ 158[b]			PECH	262/ **419,** 787, **880**
			SF6	299/ 402, **803**
			PTCH/PMCH	169/ 197 *

In April 2010 tracers were added at the following hours: PMCP & PDCH = hr 1; PECH = hr 52; SF6 = hr 54; PTCH & PMCH = hr 693

Missed result due to U-tube issues.*.

Experiment ended at hr 906.

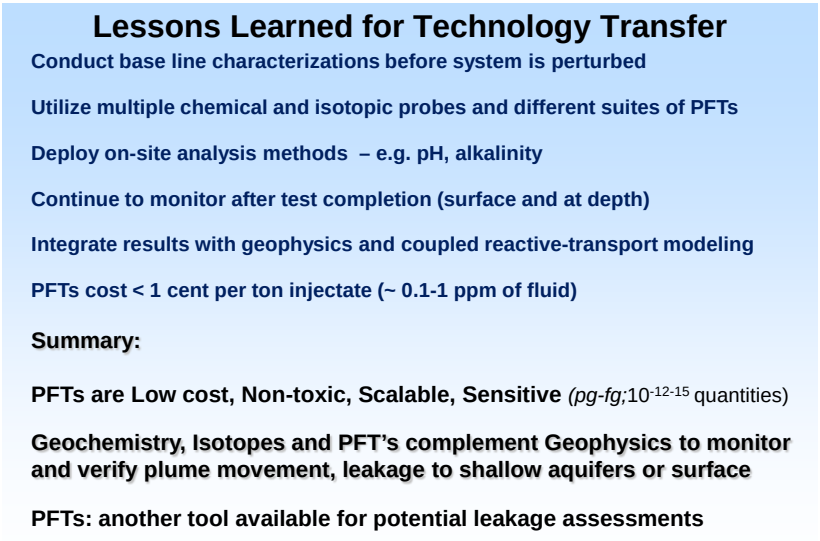
a. SF6 peak was >10 times larger exhibiting larger and longer peaks.

b. After 30 days the flow into the formation was nearly doubled.

Summary:

As summarized in Figure 21 PFTs complement geophysical and geochemical strategies for monitoring, verifying and assessing subsurface fluid flow. PFTs cannot replace more traditional measures but because of their non-native and low detection attributes they can be detected before more conventional tracers and have less confusing backgrounds thereby providing excellent lines of evidence for flow verification. While the absence of PFTs may not ensure a lack of fluid transport to a designated point, the presence of PFT suites is verifiable evidence of flow, given the safeguards of adequate QA/QC. For example if a PFT were used nearby for atmospheric tests then detection of different discrete PFT suites at proper ratios from multiple subsurface samples over time may be used to substantiate the notion of subsurface flow.

Figure 21. Lessons learned during PFT field implementation



PFTs are non-toxic, and if added to subsurface flows at 1ppm or less for defined periods of time are relatively low cost. Samples can be stored for months in Teflon-septa sealed vials if stored inverted with a blanket of water. The described methods could readily be scaled from the hundreds of samples collected in the described tests to handle larger sampling scenarios. PFTs have successfully been employed in numerous subsurface projects to monitor migration of drilling fluids, process fluids or injected fluids including CO_2 plumes during pilot scale carbon sequestration experiments. PFTs may be considered as another potential tool for verifying or assessing flow of subsurface fluids from an injection point to a distant monitoring point as part of an integrated site monitoring program where PFTs can complement geophysical, geochemical and modeling tools.

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New Isotopic Tracers for Shale Gas and Hydraulic Fracturing Fluids

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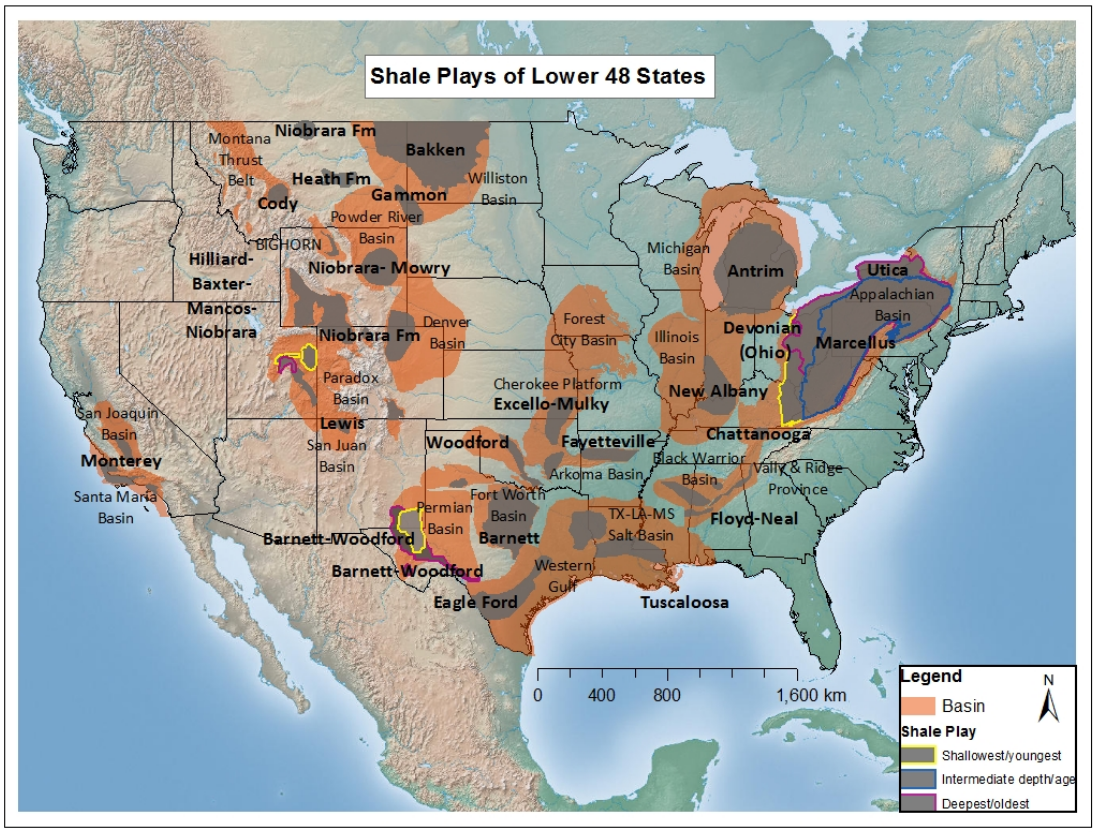
Introduction

Advances in drilling technologies and production strategies such as horizontal drilling and hydraulic fracturing have significantly improved the production of hydrocarbons by stimulating the flow of gas and liquids from impermeable geologic formations (Pacala and Socolow, 2004; Kargbo et al., 2010; Kerr, 2010). These technological improvements have increased oil and gas exploration in numerous unconventional fields across the U.S., particularly in the Barnett, Haynesville, Bakken, Fayetteville, Woodford, Utica, and Marcellus shale formations (Figure 22). The U.S. Department of Energy Information Agency (EIA) projects that by 2035 shale gas production will increase to 340 billion cubic meters per year, about 50% of the total projected gas production in the USA. (U.S. Energy Information Agency, 2012).

Figure 22. Map of shale gas basins in the USA. Map was prepared by Cidney Christie (Duke University), based on data from U.S. Energy Information Administration (EIA).



The increased extraction of natural gas resources from the shale gas basins in the U.S. has increased awareness for possible environmental consequences, particularly contamination of shallower drinking water aquifers and river systems. The debate surrounding the safety of shale

gas extraction and hydraulic fracturing has focused on stray gas migration to shallow groundwater (Osborn et al., 2011) and to the atmosphere (Howarth et al., 2010), possible hydraulic connectivity between deep shale formations and shallow aquifers (Warner et al., 2012), water use (Nicot and Scanlon, 2012), air quality (Colborn et al., 2012), as well as the potential for contamination from hydraulic fracturing fluid and/or produced brines containing toxic substances during drilling, transport, and disposal (Dresel and Rose, 2010; Rowan et al., 2011; Gregory et al., 2011; Haluszczak et al., 2012).

Since 2010, Duke University has engaged in testing the quality of groundwater and surface waters in areas associated with shale gas exploration in the United States. In addition, we have measured produced waters, flowback waters, and disposed effluents associated with conventional and unconventional oil and gas wells. We have collected over 700 water samples from Pennsylvania, New York, West Virginia, North Carolina, Arkansas, and Texas. We measured a large spectrum of dissolved constitutes, including major and trace inorganic elements, hydrocarbons and noble gases, stable isotopes of hydrocarbons, stable isotopes in water and dissolved inorganic carbon, isotopes of dissolved salts in water (boron and strontium), and naturally occurring radioactivity (radium isotopes). Here we show that the isotope ratios of oxygen ($\delta^{18}O$), hydrogen ($\delta^{2}H$), strontium ($^{87}Sr/^{86}Sr$), boron ($\delta^{11}B$), and radium ($^{228}Ra/^{226}Ra$) in fluids associated with shale gas and hydraulic fracturing (i.e., flowback and produced waters) have distinctive fingerprints that are different from the compositions of regional groundwater and surface waters in areas of shale gas exploration and waste disposal.

Analytical Techniques

Major anions were determined by ion chromatography (IC), major cations by direct current plasma optical emission spectrometry (DCP-OES), and trace-metals by inductively-coupled plasma mass spectrometry (ICP-MS) on a VG PlasmaQuad-3 at Duke University. Stable oxygen and hydrogen isotopes were determined by thermochemical elemental analysis/continuous flow isotope ratio mass spectrometry (TCEA-CFIRMS), using a ThermoFinnigan TCEA and Delta+XL mass spectrometer at the Duke Environmental Isotope Laboratory (DEVIL) at Duke University. $\delta^{18}O$ and $\delta^{2}H$ measured isotopic values were normalized to V-SMOW and V-SLAP. *Strontium isotopes:* Aqueous samples were treated by hydrogen peroxide and evaporated to total dryness in HEPA filtered clean hood. The dried sample was then digested in 8 N ultra-pure HNO_3 and extracted using Teflon micro columns containing Eichrom Sr-specific ion-exchange resin. The resin was pretreated with 8 N HNO3 prior to the addition of the sample. Following the sample flow through the ion-exchange resin, an additional 8 1-mL aliquots of 8 N nitric acid was applied to the column to remove other cations, including calcium and magnesium. Strontium was released from the resin with 2 mL of dionized water (>17.8 ohms). The extracted Sr was treated with phosphoric acid then dried again before digestion with TaCl solution and loaded onto outgassed rhenium filaments for a final dry-down and deposition on the center of the filament. Strontium isotopes were analyzed by thermal ionization mass spectrometer (TIMS) using a *ThermoFisher Triton* at Duke University. Approximately 1 to 10µg Sr was loaded onto out-gassed single rhenium filaments along with TaO activator solution. Samples and standards were gradually heated to obtain a ^{88}Sr beam intensity of ~3V, after which 300 cycles of data were collected, yielding a typical internal precision of ~ 0.000004 for $^{87}Sr/^{86}Sr$ ratios (1 sd). External reproducibility on standard NIST987 yielded a mean $^{87}Sr/^{86}Sr$ ratio of 0.710260 +/-0.000009 (1-SD) (n=98).

Boron isotopes: Aqueous samples were treated by hydrogen peroxide (H_2O_2) prior to directly loading (for boron-rich samples) or preconcentrated (for low-boron samples) via low-temperature, partial evaporation in an oven located in a vertical laminar flow clean hood, equipped with boron-free PTFE HEPA filtration. Approximately 4 ug of boron was loaded directly onto outgassed single rhenium filaments along with 2 µL of activator solution containing Na, Mg, Ca, and K (roughly in proportions of seawater), mixed from high-purity single-element standard solutions in 5% HCl matrix. The load solution delivers ionization efficiency similar to seawater and has negligible CNO- (mass 42) interference, based on negligible signal at proxy mass 26 (CN^-). Loads on the filaments were evaporated to dryness at low current (~0.4A), typically taking 8 to 15 minutes depending on sample volume. Boron isotopes were analyzed by thermal ionization mass spectrometer (TIMS) using a *ThermoFisher Triton,* converted to negative polarity at Duke University. Samples and standards were gradually heated to obtain a $^{11}B^{16}O_2^-$ (mass 43) beam intensity range from 0.3V to 3V, after which 60 cycles of data were collected. CN mass was monitored during the measurements and was used to detect samples with possible CNO interference. Boron isotope ratios in samples with excessive CN (>5,000 counts per second) were rejected. $^{11}B/^{10}B$ ratios were reported in the conventional $\delta^{11}B$ notation, normalized to the NBS Standard Reference Material (SRM) 951 boric acid standard. The average ratio measured for the SRM-951 standard was 4.0057 +/-0.0015 (1-SD) (n=210).

Select samples were processed through cation-exchange resin (AG® 50W-x8 Resin) to remove cations (mostly calcium) and then treated with hydrogen peroxide to remove organic matter including CNO complexes (that might interfere with ratio collection at mass 42 which would interfere with $^{10}B^{16}O^{16}O$ species). Data from replicate external standards (NIST-951, OISL Atlantic seawater, and IAEA Groundwater B-3) loaded using this method yielded external precision of approximately 0.5‰ $\delta^{11}B$. The variability within replicates of brine samples was ±1.5‰. Total loading blank was <15pg B as determined by isotope dilution (NBS 952).

Radium isotopes: For lower-activity samples (<100 pCi/L), between 1 and 50 liters of water samples were filtered through two plastic columns each containing 10 grams dry-weight of Mn-oxide covered acrylic fibers in sequence. The Mn-oxide efficiently adsorbs the radium isotopes and pre-concentrate the radium prior to analysis. Flow rates were less than 1 liter per minute. The fibers were transported to the Laboratory of Environmental RadioNuclides (LEARN) at Duke University rinsed with dionized water to remove any possible sediment contamination and then hand-squeezed to remove excess water. The fibers were then incubated in a sealed glass cylinder for 3 weeks and measured ^{222}Rn as a proxy for ^{226}Ra, using a Radon-in-Air monitor (RAD7, Durridge Inc.), following the method of Kim et al. (2001). All the fibers were then smashed and sealed in 90 mL tin cans. Each sample was counted in a Canberra DSA2000 broad energy germanium (BEGe) gamma detector at LEARN in Duke University to measure all nuclides from the U-Th series (for more details see Vinson et al., 2009).

For samples with greater than 100 pCi/L activity, pre-concentration of radium was not necessary. Instead, 60 mL of sample is placed in a sediment 4 ounce HDPE sediment jar and sealed. The sealed jars were then incubated for at least 3 weeks to allow ^{226}Ra to reach secular equilibrium with its ^{214}Bi granddaughter. The ^{226}Ra activities were then obtained through the 609keV energy line of its radioactive granddaughter, ^{214}Bi assuming secular equilibrium. ^{228}Ra activities were obtained through the 911keV energy line of ^{228}Ac. The counting efficiency of both ^{228}Ra and ^{226}Ra were calibrated using standards that were measured under physical conditions identical to the samples (e.g., jar or can size, material type). The counting statistics were calibrated using a

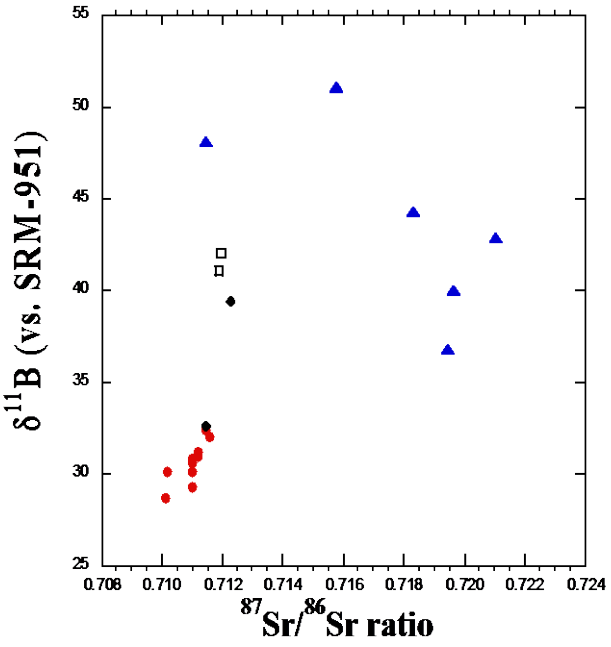
^{226}Ra solution (National Institute for Standards and Technology) transferred into a radium free seawater matrix or Mn-oxide fibers.^{228}Ra was calibrated using DL-1a ore (Canadian Certified Reference Materials Project), GSP-2 rock standard (USGS), and an aged ^{232}Th solution on compressed fibers in matching geometry.

Results

The chemical and isotopic characterization of shale gas fluids is based on measurements of flowback waters (i.e., water collected from shale gas wells following fracturing) and produced waters (water collected during gas production) from conventional oil and gas wells in New York and Pennsylvania as well as Marcellus shale gas wells in Pennsylvania. Results show that high levels of salinity characterize the Appalachian brines, with total dissolved salts up to 350,000 mg/L. The salinity of produced waters from conventional oil and gas wells in New York were similar, and in some cases even exceeded the salinity of the Marcellus brines, particularly for formation waters from the Lower Silurian Oneida and Lower Silurian Medina formations.

Oxygen and hydrogen isotopes: Results from flowback waters in two shale gas wells in Pennsylvania show a clear distinction between the source(s) of the injected waters; in case A the injected hydraulic fracturing water was composed of fresh water (i.e., surface water) and thus the $\delta^{18}O$ and $\delta^{2}H$ values of the flowback waters progressively increase with time, reflecting a mixture between the freshwater source with depleted ^{18}O and ^{2}H composition and the composition of the original Marcellus brine with higher $\delta^{18}O$ and $\delta^{2}H$ values. In contrast, in case B the original injected water was flowback water recycled from previous hydraulic fracturing activities, and thus the $\delta^{18}O$ and $\delta^{2}H$ values were much higher and similar to the composition of the Marcellus brines even in early (i.e., days 0-5) flowback samples. These distinctions provide a method to identify the relative mixing proportion between injected water and the original formation water in cases where fresh water is used for injection. In addition, the elevated $\delta^{18}O$ and $\delta^{2}H$ values and their relationships (i.e., slope < 8) measured in oil and gas waste waters are different from regional groundwater and surface waters that are typically characterized by

Figure 23. Boron isotopes (δ^{11} B, normalized to SRM-951 standard) versus $^{87}Sr/^{86}Sr$ ratios measured in flowback and produced water from the Marcellus brines (red circles) as compared to produced water from conventional oil and gas wells including the Upper Devonian formations (blue triangles), the Silurian Herkimer Formation (black diamond), and Lower Silurian Medina Formation (open squares). Note the relatively low δ^{11} B and $^{87}Sr/^{86}Sr$ ratios of the Marcellus brines as compared to other formation waters from the Appalachian basin.

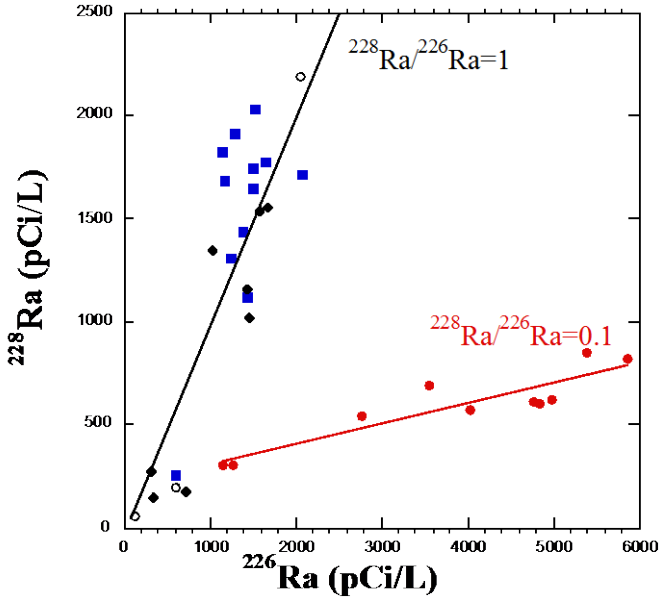


significantly more depleted ^{18}O and ^{2}H composition and a $\delta^{2}H$ /$\delta^{18}O$ slope ~8.

Strontium isotopes: Results from $^{87}Sr/^{86}Sr$ data measured in produced waters from the Marcellus Shale and conventional oil and gas wells in the Appalachian Basin show a distinctive lower $^{87}Sr/^{86}Sr$ imprint of the Marcellus brines relative to produced waters from other formations, particularly from the Upper Devonian formations (Figure 24). The mean $^{87}Sr/^{86}Sr$ ratio of flowback and produced waters from the Marcellus shale was 0.71095±0.00015 (n=18), while the Upper Devonian brines had typically higher $^{87}Sr/^{86}Sr$ ratios (Warner et al, 2012). This isotopic difference provides a new methodology to delineate possible migration of the Marcellus brines in the subsurface in areas of shale gas exploration (Warner et al., 2012) and also to identify the specific origin of oil and gas wastewaters upon disposal or spills, in particular the distinction between liquid wastes that originated from conventional and unconventional gas wells.
Boron isotopes: Results from boron isotope data measured in produced waters from the Marcellus Shale and conventional oil and gas wells in the Appalachian Basin show a distinctive lower $\delta^{11}B$ imprint of the Marcellus flowback water relative to produced waters from other formations, particularly from the Upper Devonian formations. The mean $\delta^{11}B$ value of flowback and produced waters from the Marcellus shale was 30.9±0.3‰ (n=19) while other produced waters had typically higher $\delta^{11}B$ values (Figure 24). This isotopic difference provides a new methodology to delineate possible migration of the Marcellus brines in the subsurface in areas of shale gas exploration. The combined utilization of $\delta^{11}B$ and $^{87}Sr/^{86}Sr$ (Figure 24) provides a unique tool to distinguish between liquid wastes that originated from conventional and unconventional gas wells.

Radium isotopes: Results from radium isotope data measured in flowback waters from the Marcellus Shale and conventional oil and gas wells in the Appalachian Basin show that the Marcellus brines had typically higher activities, particularly for the long half-life ^{226}Ra nuclide, up to 6,000 pCi/L (Figure 25). The Marcellus brines had a distinctive lower $^{228}Ra/^{226}Ra$ ratio relative to produced waters from other formations. The $^{228}Ra/^{226}Ra$ ratios measured in flowback and produced waters from the Marcellus shale was 0.1 (n=10), while produced waters from other formations in the Appalachian Basin had much higher $^{228}Ra/^{226}Ra$ ratios, close to unity (Figure 25). Given the high reactivity of radium nuclides with sediments in many environmental conditions (e.g., low salinity), this isotopic difference provides a new methodology to delineate the impact of the disposal of

Figure 24. Radium-228 versus radium-226 (in pCi/L unit) in flowback and produced water from the Marcellus brines (red circles) as compared to produced waters from conventional oil and gas wells including the Lower Silurian Oneida Formation (blue squares), the Silurian Herkimer Formation (black diamond), and Silurian Vernon Formation (open circles). Note the low $^{228}Ra/^{226}Ra$ ratios of the Marcellus brines relative to the other formation waters.



shale gas liquid wastes on the environment, in particular to evaluate the long-term environmental legacy of gas and oil wastes disposal sites.

Discussion

The high levels of salinity (TDS up to 350,000 mg/L), toxic elements (e.g., barium), and naturally occurring radioactivity in produced and flowback waters from the Marcellus Shale reported here and in previous studies (Dresel and Rose, 2010; Rowan et al., 2011; Gregory et al., 2011; Haluszczak et al., 2012; Chapman et al., 2012; Warner et al., 2012) and in other shale gas basins such as the Fayetteville Shale (Kresse et al., 2012) present new challenges for handling the large volume of wastewaters that are generated together with extraction of natural gas. At the same time, the salinity and radioactivity of produced water generated from conventional oil and gas wells in the Appalachian Basin are also high. Flowback and produced waters from both conventional and unconventional oil and gas wells require adequate regulations for safe disposal. However the recent increase in the use of hydraulic fracturing and the volume of flowback and produced water that requires disposal/treatment is an ever-increasing issue of environmental concern.

This study presents several isotopic tracers (oxygen, hydrogen, strontium, boron, and radium) in flowback and produced water generated through conventional oil and gas and unconventional shale gas exploration in the Appalachian Basin. The development and utilization of multiple isotopic tracers provide a novel methodology for robust assessment of the sources and magnitude of contamination of surface water, groundwater, as well as river and lakes sediments that could be affected by disposal or spills of oil and gas liquid wastes. Furthermore, the combined isotopic tracers enable researchers and regulatory agencies to monitor the effect of the long-term disposal of liquid oil and gas wastes. The distinct isotopic fingerprints of the Marcellus brines and flowback waters associated with shale gas exploration also provide a unique tool to delineate the possible migration of hydraulic fracturing fluids in the subsurface that could possibly contaminate shallow groundwater resources.

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Appendix C.

Poster Abstracts

Hydraulic Fracturing Fluid Analysis for Regulatory Parameters – A Progress Report

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Accutest Laboratories, Inc.

The statements made during the workshop do not represent the views or opinions of EPA. The claims made by participants have not been verified or endorsed by EPA.

Introduction

This presentation is a progress report on the analysis of Hydraulic Fracturing Fluids for regulatory compounds outlined in the various US EPA methodologies. Fracturing fluids vary significantly in consistency and viscosity prior to fracturing. Due to the nature of the fluids the analytical challenges will have to be addressed. This presentation also outlines the sampling issues associated with the collection of dissolved gas samples.

Discussion

Hydraulic Fracturing Fluid Analysis:
Fracturing Fluids vary in consistency and viscosity. Methods employed for the analyses of the fracturing fluids include US EPA 500 and 600 series methods and Standard Methods for Water and Wastewater in combination with SW846 methods. Samples were analyzed for the constituents of the methods outlined. Sample preservation consisted of those outlined in the appropriate methods. No issues were encountered upon preservation of the fluids. Analytical challenges were encountered during analyses due to the matrices and the viscosity of the samples. The matrices and viscosity issues were alleviated by performing dilutions and utilization of smaller aliquots of samples. Recoveries of surrogates and spikes were affected in the viscous samples. The parameters of interest would be outlined in the presentation.

Dissolved Gas Sampling:
Sample collection for dissolved gases must be precise in order to determine the gaseous components present. This discussion focuses on sample collection using traditional techniques in comparison to samples collected in a pressurized piston sampling device as outlined in GPA method 2174-93. This presentation focuses on a real world sampling episode collected using a pressurized piston sampling device. Samples were collected in Tedlar bags utilizing various techniques in the field, however, the gases present in the aqueous samples could not be detected or quantified. Upon utilizing the pressurized piston sampling device, as outlined in GPA 2174-93, the gaseous components were identified and quantified. The sampling device can be utilized to collect samples at the wellhead to determine gaseous components in the flow back water after the fracture job is complete to account for emissions.

Conclusion

Viscous fracturing fluids required dilutions due to the matrix. Quality control limits were achieved for non viscous samples. Sample aliquot reduction in some cases without matrix

interferences yielded adequate recoveries. Even though smaller aliquots were used in the extraction process dilutions were still required to suppress matrix interferences.

Utilization of the pressurized piston sampling device provided meaningful data and detection of gaseous components. The concentration of the gaseous component was measurable whereas samples collected in Tedlar bags did not yield any meaningful data.

Laser Induced Breakdown Spectroscopy (LIBS) for Rapid Monitoring of Metals in Produced Water and Its Precipitates: A Preliminary Report

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The statements made during the workshop do not represent the views or opinions of EPA. The claims made by participants have not been verified or endorsed by EPA.

Background

Major challenges exist for the rapid analysis of produced and flowback water with traditional analytical approaches, especially in the context of on-site treatment and/or reuse of the water. Laser induced breakdown spectroscopy (LIBS) is one approach with the potential to overcome many of these challenges because of its transportability, no need for sample preparation, and semi-quantitative results. LIBS is a form of emission spectroscopy in which a high energy laser ablates a small portion (ng or less) of a sample, creating a high temperature plasma. As the continuum radiation of the plasma cools, light from atomized and ionized species at characteristic frequencies can be detected for both qualitative and semi-quantitative results.

We are developing LIBS methodology for the rapid characterization of barium and strontium in produced water and its precipitates. Treatment of produced or flowback water often involves precipitation to remove corrosives prior to reuse. The ability to rapidly characterize the produced water and/or its precipitates on-site would mean less downtime and improved treatment control. Our research applies the LIBS methodology in conjunction with a Sequential Precipitation Fractional Crystallization Process (SPFCP), technology developed by ProChemTech International, Inc. However, LIBS can be broadly applied for the analysis of metals associated with any treatment process.

Discussion

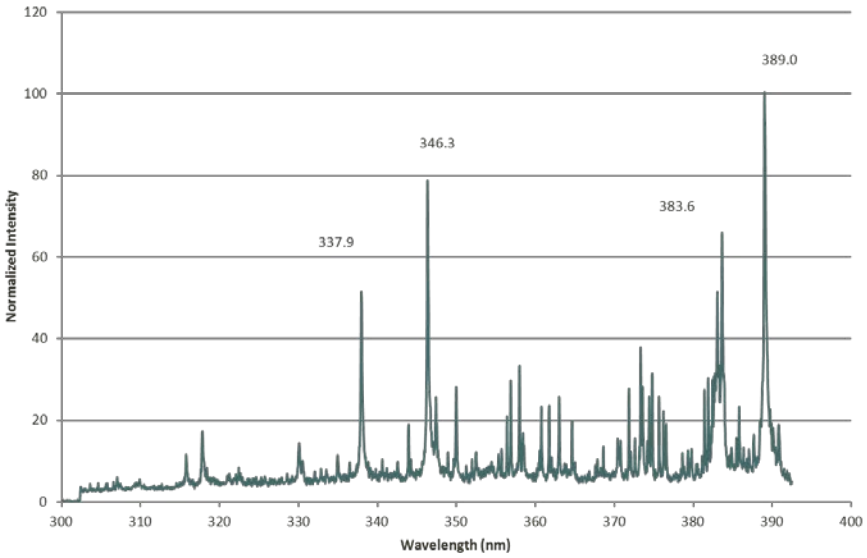
In the process of SPFCP, the goal is water treatment and resource recovery. The first step of SPFCP involves the precipitation of barium as the insoluble sulfate. The challenge lies in minimizing the co-precipitation of strontium. In typical produced water samples, up to 50% of the strontium is pulled out in the barium precipitation step. Our research focuses on optimizing the barium precipitation to improve purity of the resulting barite and thus improve marketability of this chemical commodity.

LIBS offers a quick and easy way for us to analyze the solid products resulting from our precipitation studies. No sample preparation is required; the solid precipitates can be analyzed directly in a matter of seconds. Despite the ease of analysis, LIBS suffers from challenging data analysis. Quantification with LIBS is not straightforward. The resulting emission spectra are quite complex (Figure 25), and matrix interferences and plasma heterogeneity result in variable peak intensities. We have explored several quantification strategies to overcome these limitations.

Results

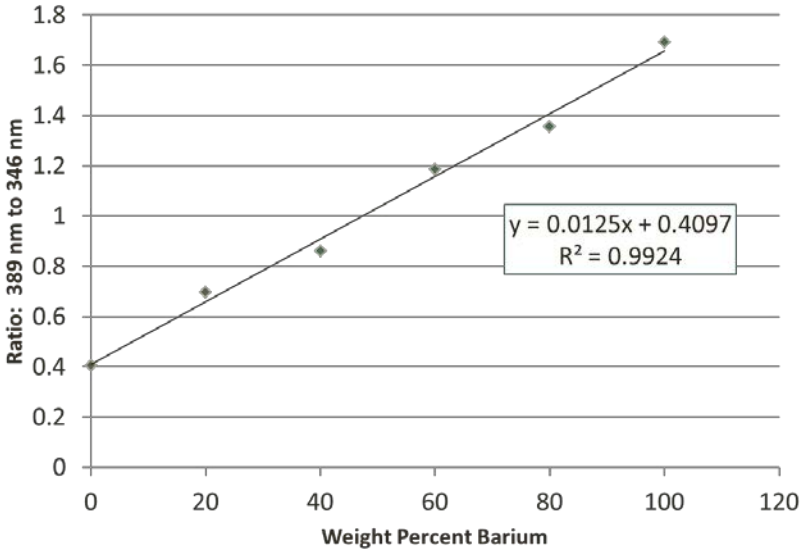
Figure 25 demonstrates the complex spectra that are typical with LIBS analysis. Multiple atomic and ionic emission transitions occur in the high temperature plasma from the laser ablation process. The transition at 389 nm is an intense, characteristic barium emission line.

Figure 25. LIBS spectrum resulting from the analysis of produced water precipitates.



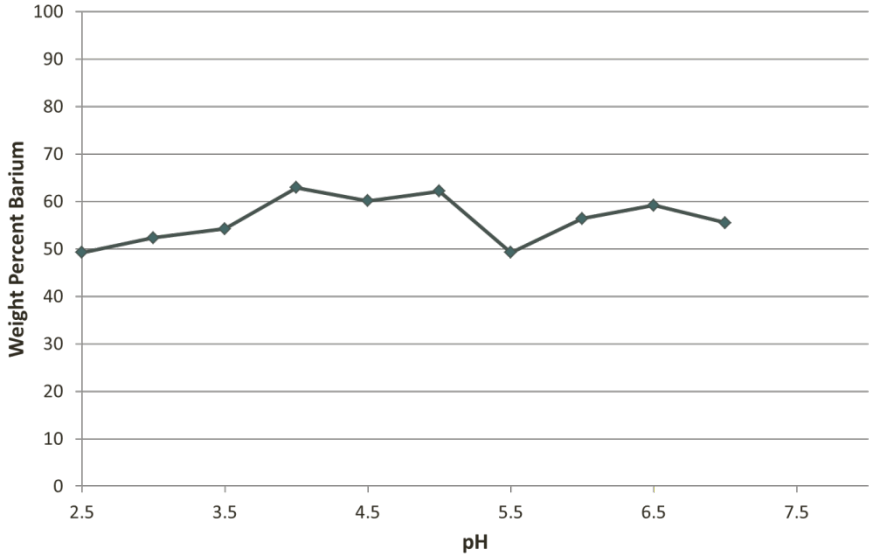
The ratio of a characteristic analyte emission line to that of a non-analyte can be used in quantification to mitigate the issues associated with matrix and plasma variability. We have successfully quantified barium in precipitates using a ratio of 389 to 346 nm. A calibration curve for barium is provided in Figure 26.

Figure 26. Calibration curve used for barium quantification.



A preliminary optimization strategy that we tested was the investigation of barium sulfate precipitation from produced water at various pH levels. The results in Figure 27 confirm that significant co-precipitation occurs regardless of pH. We are currently testing other approaches.

Figure 27. Barium sulfate concentration in produced water precipitates at various pH levels.



Conclusions

This preliminary work done at an undergraduate institution demonstrates the potential for LIBS in the analysis of precipitates from produced water. The lack of sample preparation is the clear advantage to this approach. Our results indicate that the challenges associated with quantification can be overcome, and we have established quality results for the analysis of barium.

Current work is focused on the quantification of strontium and optimization of the barium sulfate precipitation in the SPFCP process. We are exploring chemometrics for more sophisticated data analysis and experimenting with the direct analysis of produced water samples.

Acknowledgments

We would like to thank Timothy Keister of ProChemTech International, Inc., for provision of samples and an interesting project idea. We are grateful to Dan Willoughby of D&N Scientific for use of the LIBS system. We thank Gavin Steadman, Brittany Majors, Tyler Umstead, and Lance Jubic for providing complementary analysis of produced water by GC-MS and FAAS.

Using Integrated Noble Gas and Hydrocarbon Geochemistry to Constrain the Source of Hydrocarbon Gases in Shallow Aquifers in the Northern Appalachian Basin

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Recent advances in horizontal drilling and hydraulic fracturing technologies have substantially increased the potential for the recovery of natural gas and oil from unconventional energy resources (e.g. organic-rich black shales). Rising demands for domestic energy sources, mandates for cleaner burning fuels for electricity generation, and the approach of peak global hydrocarbon production are also driving this transformation. Nonetheless, public and political enthusiasm and consent is tempered by various concerns regarding the environmental risks associated with shale gas development, specifically drinking-water quality (e.g. contamination from hydraulic fracturing fluids, production/flow back waters, and/or stray combustible gases).

Questions and concerns regarding the significance of elevated levels of combustible gas in shallow aquifers has been at the forefront of these concerns. Previously, Osborn et al 2011 identified higher concentrations of thermally mature methane (CH4) and aliphatic hydrocarbons (e.g. ethane (C2H6)) in drinking water wells within 1km of shale gas development sites producing from the Marcellus Shale in northeastern Pennsylvania (Osborn et al., 2011). While these findings suggest a correlation between areas of shale gas development and elevated methane concentrations in shallow aquifers, others suggest that the presence of methane in shallow groundwater aquifers is common, natural, and unrelated to shale gas development (Baldassare, 2011; Baldassare et al., 2012; Molofsky et al., 2011). Indeed, examples of natural methane seeps are identified in the northern Appalachian Basin (e.g. Salt Spring State Park, Montrose, PA) (Warner et al., 2012).

The occurrence, distribution, and composition of hydrocarbons in the Earth's crust, including Devonian hydrocarbon-bearing formations in the NAB (Figure 29), result from the complex interplay between the hydrologic and tectonic cycles (e.g., Ballentine et al., 1991; Bethke and Marshak, 1990; Cathles, 1990). Efforts to utilize unconventional hydrocarbon deposits and evaluate the environmental implications of shale gas development (Jackson et al., 2012; Molofsky et al., 2011; Osborn et al., 2011; Warner et al., 2012) require an in-depth understanding of the geological history and modern geological setting (Darrah et al., 2013; Darrah et al., 2012). These demands have catalyzed the need to understand crustal fluid

migration in greater detail. In complex tectonic regimes such as the NAB, hydrological, geophysical, and geochemical techniques are all helpful in evaluating the distribution of hydrocarbons in UD aquifers and elsewhere in the Earth's crust (Ballentine et al., 1991; Pepper and Corvi, 1995; Warner et al., 2012; Zhou and Ballentine, 2006). One technique that traditionally links these disciplines is the analysis of gas geochemistry, specifically noble gas and stable isotopic compositions (e.g., $\delta^{13}C$ and $\delta^{2}H$) of hydrocarbon gases or CO2 (e.g., Ballentine et al., 1991; Craig, 1953; Gilfillan et al., 2009; Jenden et al., 1988; Lollar and Ballentine, 2009; Poreda et al., 1992).

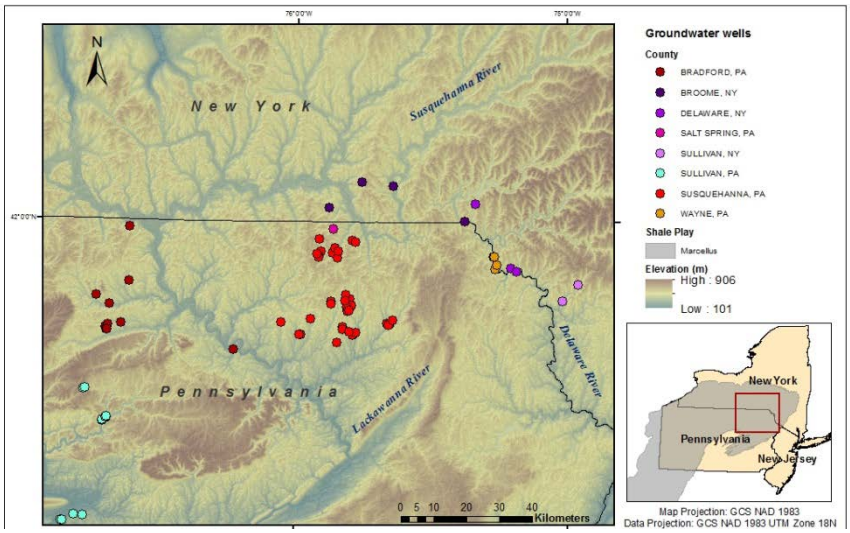
The potential for elevated methane concentrations from both natural geological migration and anthropogenic activities highlights the need to develop and validate advanced geochemical systematics (e.g. integrated noble gas and hydrocarbon molecular and isotope geochemistry) capable of evaluating the source, timing, and migration history of hydrocarbon gases currently present within shallow aquifers (Darrah et al., 2013; Darrah et al., 2012). Herein, we present our initial assessment of the noble gas and hydrocarbon molecular and isotope geochemistry of shallow aquifers in the northeastern tier of Pennsylvania and southeastern tier of New York State.

Within the context of petroleum geochemistry, gases are often classified as thermogenic, biogenic, or "mixed" based on molecular ratios (e.g., wetness: $C2^{+}/C1$) and C and H isotopic composition (e.g., Bernard et al., 1976; Clayton, 1991; Rice and Claypool, 1981; Schoell, 1980; Schoell, 1983; Schoell, 1988). The composition of thermogenic gases evolves as the organic source (i.e., kerogen or liquid hydrocarbons) degrades, producing diagnostic geochemical fingerprints (i.e., δ^{13}C-CH4, δ^{2}H-CH4, and C1/C2+; (e.g., Schoell, 1983). Conversely, "biogenic" gas is generated at low temperature ($<<100^{o}C$) in anoxic conditions from the microbial decomposition of organic matter or the reduction of CO2 (e.g., Rice and Claypool, 1981; Schoell, 1980; Whiticar et al., 1986). Under these conditions, microbes produce almost exclusively CH4 (>>99%; C2+/C1 $\leq 1x10^{-4}$) with a typically light δ^{13}C-CH4< -60 to -70 $^{o}/oo$ (Schoell, 1983; Whiticar et al., 1985). In addition to these genetic fingerprints, the original composition of natural gas can be altered by post-genetic fractionation (e.g., diffusion) where migrating gases are selectively enriched in ^{12}C and ^{1}H relative to their original composition (e.g., Craig, 1968; Prinzhofer and Pernaton, 1997; Prinzhofer and Huc, 1995; Xia and Tang, 2012).

The elemental and isotopic compositions of noble gases (e.g., helium (He), neon (Ne), argon (Ar), etc.) provide a suite of inert geochemical tracers that are unaffected by chemical reactions or microbial activity (Ballentine et al., 1991; Lollar and Ballentine, 2009). Their inert nature, low terrestrial abundance, and well-characterized isotopic composition in the mantle, crust, hydrosphere, and atmosphere enhance their utility as conservative geochemical tracers of crustal fluids. In most groundwaters, the noble gas isotopic composition reflects a binary mixture of inert gases from two distinct sources: the atmosphere (air-saturated water (ASW): ^{20}Ne, ^{36}Ar, ^{84}Kr) and the crust (U + Th• ^{4}He and ^{21}Ne* and K• ^{40}Ar*) (e.g., Ballentine et al., 2002). These distinct signatures can be resolved in either groundwater or natural gases and are only fractionated by well-constrained physico-chemical mechanisms such as diffusion and solubility-driven phase partitioning (e.g., Gilfillan et al., 2009; Zhou et al., 2012).

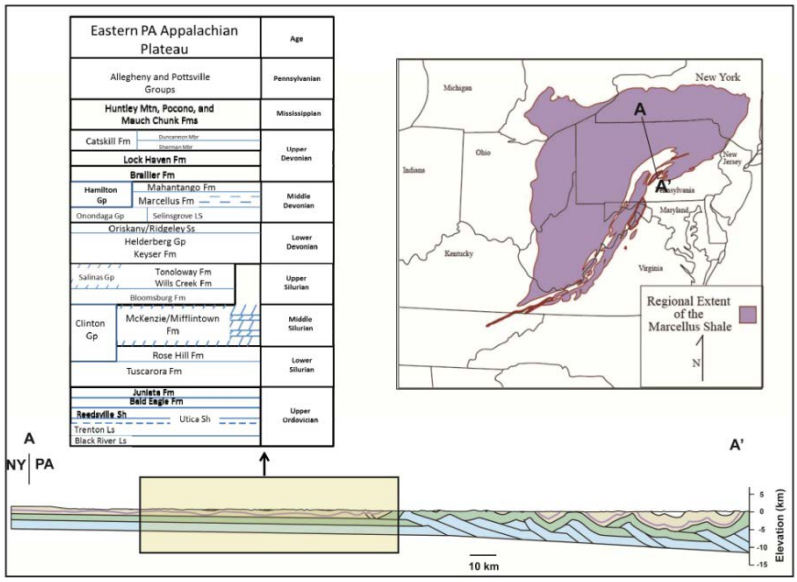
When paired with hydrocarbon composition, noble gases can provide particularly valuable insights into the source, migrational history, and residence time of crustal fluids (e.g., Darrah et al., 2013; Gilfillan et al., 2008; Gilfillan et al., 2009; Hunt et al., 2012; Lollar and Ballentine, 2009; Zhou and Ballentine, 2006). Here, we demonstrate that noble gas geochemistry in combination with hydrocarbon geochemistry helps to constrain the geological history of "background" methane naturally present in the NAB (Darrah et al., 2013; Darrah et al., 2012). By understanding the geochemical signatures imparted on a fluid as it migrates through the crust, researchers will have a more robust geochemical framework for differentiating gases found naturally compared to those arising from fugitive gases (e.g., CH4 or CO2) related to shale gas development, gas storage fields, enhanced oil recovery, coalbed methane, and/or carbon capture and storage.

Figure 28. Digital elevation map of groundwater samples (n=72), sorted by location (county).



Shaded brown areas represent higher elevations, while the blue-green demarks lower lying areas (valleys). All samples from this study were collected at distances >1 km from active shale gas development at the time of sample collection across four counties in Pennsylvania (Bradford, Susquehanna, Wayne, Sullivan) and 3 counties (Delaware, Sullivan, Broome) in New York (Darrahetal.,2013).Previous work identifies increasing [CH4] and salt concentrations in valley bottoms (Warneretal, 2012, Molofskyetal, 2011).

Figure 29. A generalized stratigraphic column (left), areal extent of the Marcellus Formation (right), and a simplified structural cross-section (reproduced from Sak et al, 2012) of the northern Appalachian Basin (NAB) plateau in northeastern PA and southeastern NY (bottom, see cross-section A-A' on map) (Darrah et al., 2013). The Marcellus Formation out crop belt (upper right) is highlighted in red and the areal extent of the Marcellus Formation is shown in purple.



The three principal shallow Upper Devonian aquifers include the Catskill, Lock Haven, and surficial alluvium. The generalized structural cross-section (bottom right) spans from the intensely deformed Valley and Ridge (southeast) to the Appalachian Plateau (to the north and west) across the Appalachian Structural Front (ASF). Samples in this study were collected within the yellow box at distances ranging from ~20-80 km from the ASF.

Figure 30. Variations of [Cl], [Ba], [CH4], and [He] in ground water and natural salt-rich spring located >1 km from active shalegas drilling in Pennsylvania and New York. Sample colors indicate the county where samples were located. CH4 and 4H econcentrations increase with Cl and Ba across the study area (Darrahetal., 2013; Darrahetal., 2012). The Cl-rich fluids contain elevated Br-/Cl- and Ba/Sr, as well as 87 Sr/86 Sr consistent with Middle Devonian Formation brines (i.e., Marcellus-type) (Warner et al, 2012). The upper limit (solubility saturation = 40cc/Lat 1 atm) for [CH4] demonstrates how ground water solubility limits the maximum dissolved gas concentrations. The positive correlations of [4He] with [Cl], [Ba], and [CH4] suggests previous migration of a gas-rich, saline fluid from deeper formations into Upper Devonian aquifers across the region. The coexistence of CH4 and [4He] suggests a thermogenic source of methane (Darrahetal., 2013; Hunt et al., 2012).

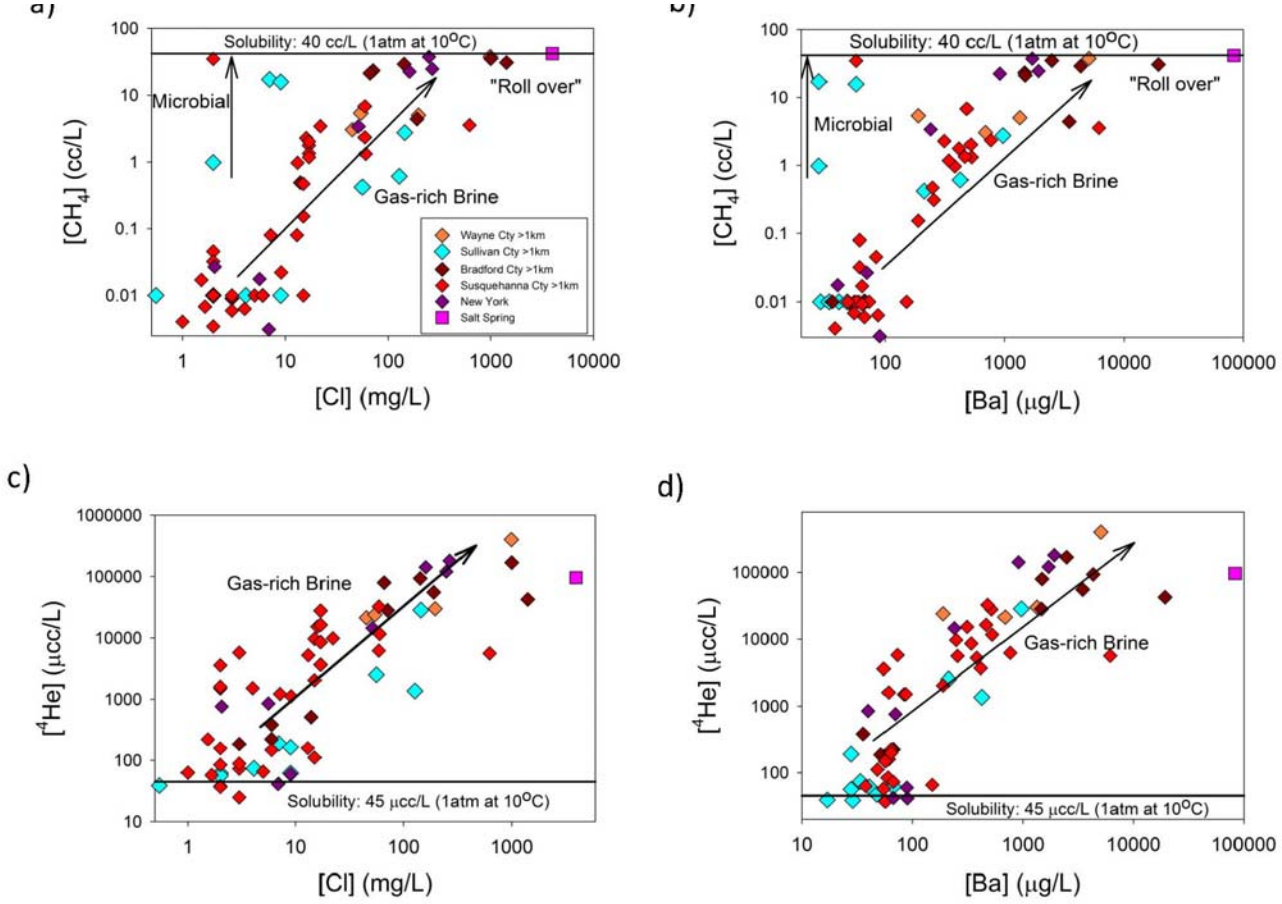
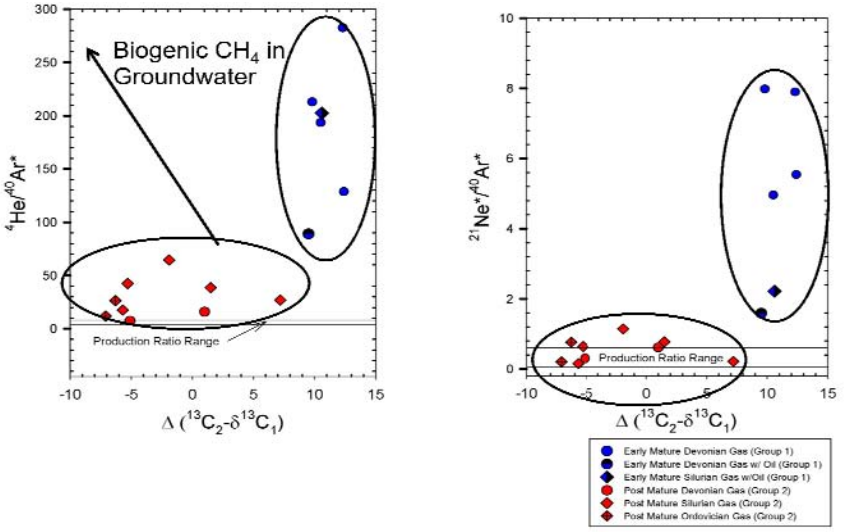


Figure 31. An example of how paired noble gas and radio genicisotopes can be used to fingerprint the genetic source and post-genetic migrational history of natural gases (Darrahetal., 2013; Hunt et al., 2012). The release of radio genicisotopes (4He, 21Ne*, and 40Ar*) is a function of temperature. As a result, radio genic noble gases provide conservative tracers of gas source that are unaffected by microbial activity or subsequent chemical reactions.



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Potential Use of Passive Sampling for Environmental Monitoring of Petroleum E&P Operations

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The statements made during the workshop do not represent the views or opinions of EPA. The claims made by participants have not been verified or endorsed by EPA.

Abstract

Reliance on grab samples generally captures limited "snapshots" of environmental contaminant concentrations, is time intensive, costly, and generates residual waste from excess sample and/or reagents used in the analysis procedures. As an alternative to the standard methods, swellable organosilica is being evaluated as an alternative capture media for passive sampling systems that can be used to measure a wide variety of water contaminants. Swellable organosilica materials have been successfully developed and tested for solvents, chlorinated solvents, endocrine disruptors, explosives, pesticides, fluorinated chemicals, and metals including Ba, Sr, Hg, Pb, Fe, Cu, and Zn. The advantages are that the material can capture target compounds for an extended periods of time, does not absorb natural organic matter, and resists biofilm formation since the sorbent possesses an animated surface morphology. Laboratory measurements for a wide variety of analytes relevant to petroleum E&P operations including hydrocarbons, surfactants, and process chemicals have shown that the sorbents have wide specificity. Initial field trials for environmental monitoring in Ohio have shown that data can be achieved at after 16 days with minimal biofilm formation.

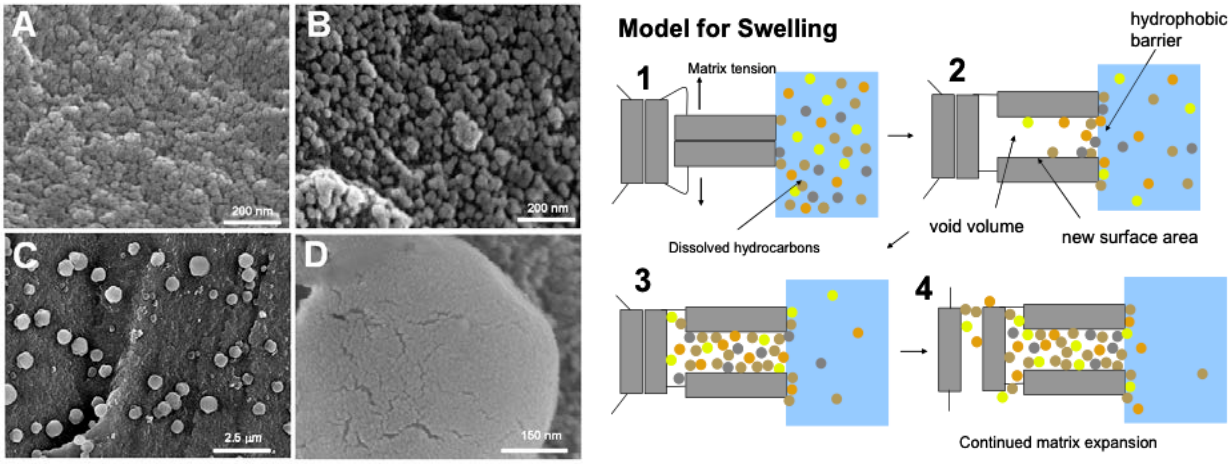
Introduction

When monitoring E&P operations for environmental compliance sampling time is a significant variable to achieving accurate results as discharges may have a high degree of temporal variance. Passive sampling may be a useful tool in identifying contaminants that are present in discrete, random intervals. Although the development of passive sampling has been ongoing for some time, widespread use of solid sampling systems has been limited due to the inherent challenges of calibration. (For reviews on passive sampling for water monitoring see: [1-14]) Specifically, sorbents are currently able to collect analytes during sampling, but accurately relating sampling data to concentrations in situ can be challenging. The typical approach currently employed is to compare data from passive sampling to laboratory experiments that measure the kinetics and equilibrium of binding under a standard set of conditions. Reliance on comparative data sets may be prone to error if field conditions (temperature, flow rate, presence of mixed contaminants) differ from the protocols used to calibrate in the laboratory.

Swellable organically modified silicas are chemically inert, nano-engineered materials that swell up to eight times their dry mass in the presence of organic liquids [15,16]. Synthesis of the sorbent is based on sol-gel derived, hybrid organic-inorganic structures that have appropriate pore size and chemical functionality to absorb organic molecules from air and water with high affinity and capacity. Swellable organosilica is hydrophobic and does not absorb water, but is

effective at absorbing a wide range of organics from aqueous solution and gas streams. Swelling is reversible and occurs in less than one second when exposed to neat organic liquids. The swelling process is reversible if absorbates can be evaporated from the material thus allowing recovery by thermal evaporation. No loss in the swelling behavior is observed after repeated use, thus swellable organosilica can be considered a nano-mechanically actuated sponge to remove and recover organic compounds from water and air. A substantial amount of data (absorption isotherms, equilibrium binding, and breakthrough curves) has been measured for swellable organosilica [17]. In total, the absorption of ~100 individual substances have been measured. The data indicate that a dynamic absorption behavior results from animation of the swellable organosilica matrix leading to the non-selective capture of organics beyond what could only be attributed to physisorption. Once a particular amount of target species is adsorbed, it "unlatches" the matrix to yield void volume for subsequent absorption events, further drawing the target molecules into the open pores (Figure 32). As the matrix relaxes to the expanded state, i.e. the initial gel-state configuration prior to drying, new surface area and volume is created for molecules that have properties which allow them to permeate through the micropores. Based on current evidence, it appears that a sub-monolayer coverage is sufficient to lead to the unlatching mechanism.

Figure 32. **(Left)** Electron micrographs of: A. Unswollen swellable organosilica (1 polymerized in THF using TBAF catalysis). B. swellable organosilica swollen in a solution of poly (2,2,3,3, 4,4,4-heptafluorobutyl-methacrylate) and dried to leave entrapped polymer. C & D. swellable organosilica swollen in ethanol followed by critical point drying showing the fully expanded state. Proposed model for absorption of dissolved organics by swellable glass media. **(Right)** 1. Initial adsorption to the surface of the material. 2. Sufficient adsorption occurs to trigger matrix expansion leading absorption across the sorbent-water boundary. 3. Pore filling leading to further percolation into the nanoporous matrix. 4. Continued matrix expansion increases available void volume.



Using the unique property of swellable organosilica to reversibly desorb specific compounds, multi-functional passive samplers are being developed that will account for time in the field and differences in conditions. The resulting device is a single system that can be deployed, sample for a variable amount of time, and then will be tested using a single analytical method to determine average concentration of the target during sampling. Overcoming the challenge of calibration will allow the inherent advantages (i.e. sample pre-concentration, reduction in waste)

to be realized. The goal is to develop systems that can be integrated with standard laboratory equipment and allow for analysis by a suitable analytical technique such as gas chromatography, liquid chromatography, or elemental analysis. Use of the sampling systems for field analysis, such as hand-held x-ray fluorescence, may also be possible with passive sampling devices.

Absorption of Dissolved Organics

The ability of swellable organically modified silica (SOMS) to capture dissolved organic species has been evaluated using a wide range of compounds including trichloroethylene (TCE), perchloroethylene (PCE), methyl *t*-butyl ether (MTBE), toluene, naphthalene, acetone, phenol, 1,4-dioxane, and 1-butanol from water (REF). Partition coefficients for the absorption of organic species from water by swellable organosilica range from $2.8\times10^5 - 1.0\times10^2$

Table 20. Absorption Data for Toluene*

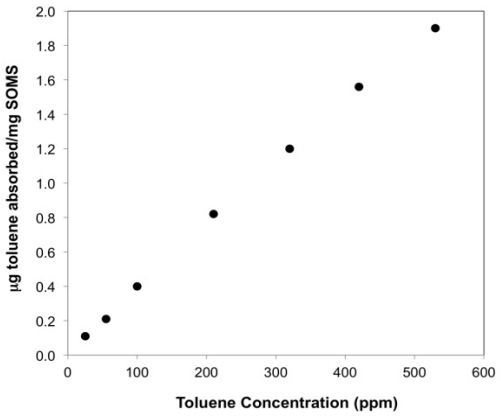
Concentration (ppm)	Percent Extraction[§]	Partition Coefficient[#] /10[3]	µg toluene abs/ mg SOMS
25	99.8	285	11
55	98.2	21.8	21
100	95.9	9.4	40
210	96.1	9.8	82
320	94.4	6.7	120
420	91.9	4.5	156
530	89.6	3.4	190

* Mass SOMS/volume solution = 0.25% *w/v*. Temperature = 25°C

§ Relative standard deviation < ±2% for all measurements (n=3).

Relative standard deviation < ±6% for all measurements (n=3)

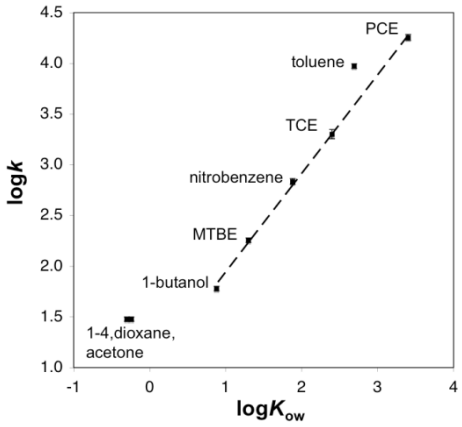
Figure 33. Adsorption isotherm for toluene (0.5% *w/v*)



Equilibrium binding measurements indicate that absorption to swellable organosilica appears to be facilitated by a step-wise process that involves initial physisorption events which trigger matrix expansion leading to new surface area/void volume. The absorption behavior for a number of dissolved organic species has been studied, although for brevity the absorption characteristics of toluene which is highly representative of swellable organosilica's characteristics are given here. Equilibrium absorption measurements for toluene across a range of concentrations (Table 20), indicate that the partition coefficients tend to reach a maximum value or series of maximum values at a particular concentration(s). For instance, $k_{toluene}$ when measured at 35 ppm (2.85×10^5) was greater than that observed at all higher concentrations. The difference implies that the absorption is not due to toluene binding to a homogeneous surface in a uniform manner. The adsorption isotherm is linear for toluene (Figure 33) and all other organic species tested (data not shown). The linear absorption isotherm indicates that even at high concentrations and loadings saturation is not reached which is attributed the high capacity of the swellable organosilica matrix. Understanding these relationships will be important for understanding solid sampling.

The magnitude of the observed partition coefficients, *k*, followed absorbate polarity as assessed by K_{OW} (Figure 34) except for the most polar species. Another exception to this trend was toluene which had a slightly higher partition coefficient than predict by a direct relationship upon K_{OW}. Toluene exhibited the strongest binding affinity ($k = 2.85 \times 10^5$) when the concentration of toluene was 25 ppm. At high toluene concentrations (530 ppm) swellable organosilica absorbed 190 µg of toluene per mg of material. Based on surface area measurements of the dry material using BET nitrogen absorption, we have estimated that the packed monolayer is be achieved at 150 µg/mg (toluene/swellable organosilica), thus expansion of the matrix must play a role in the absorption under conditions of high loading. The partition coefficients for absorption of water miscible organic solvents such as acetone and 1,4-dioxane do not follow a relationship as predicted by K_{OW} and exhibit a higher degree of absorption than expected based on polarity. Matrix expansion may also aid binding of these polar species even though they are fully soluble in water.

Figure 34. Plot of partition coefficient, logk, for binding of various contaminants in water by swellable organosilica vs. logKow. Conditions: contaminant concentration 100 ppm, 0.5% w/v swellable organosilica per volume of solution, T=25°C.



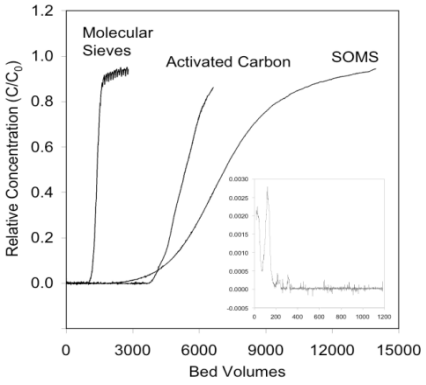
Measurement of breakthrough curves is a common approach to evaluate a material's ability to remove a substance from a flowing fluid. Absorption of contaminants in a flowing stream by stationary beds of swellable organosilica were measured for saturated solutions of PCE, toluene, TCE, MTBE, and naphthalene (Table 21). Swellable organosilica was packed into a loose bed of ground glass to provide volume for swelling. Both DARCO G-60 activated carbon and organophilic molecular sieves were also tested to compare swellable organosilica to these widely studied adsorbents. Swellable organosilica had higher capacity for PCE compared to activated carbon. However, the breakthrough times for activated carbon are in all cases longer than those corresponding to the swellable organosilica. This can quantitatively assessed by the total amount of contaminant absorbed when the elution concentration, *C*, is 10% and 90% of the concentration entering the bed, C_0: C/C_0=0.1 and C/C_0=0.9, respectively. The high degree of absorption allowed for the mass gain to be confirmed by weighing the material post-absorption. As noted above, variation in partition coefficients measured by equilibrium binding are suggestive that matrix expansion enhances affinity. This behavior was observed when contaminant was captured from a flowing stream. Small oscillations in the elution concentration (C/C_0) of PCE when aqueous solution was passed through a bed of swellable organosilica occurred during the initial stages of absorption (Figure 35, *inset*).

Table 21. Mass of Contaminants Absorbed by Stationary Beds

	(Mass bound contaminant)/(Dry bed mass) (µg/mg)					
Dissolved	**swellable organosilica**		**Activated Carbon**		**Molecular Sieves**	
Contaminant	C/C_0=0.1	C/C_0=0.9	C/C_0=0.1	C/C_0=0.sure9	C/C_0=0.1	C/C_0=0.9
MTBE	~5	720	no absorption		no absorption	
TCE	300	920	930	1500	20	135
toluene	350	870	440	480	65	66
PCE	660	1080	620	780	170	204
naphthalene	149	365*	160	185	n.p.**	

* mass bound/bed mass at C/C_0=0.8 (50,000 bed volumes). ** not performed

Figure 35. Breakthrough curves for 145 ppm aqueous PCE when applied to columns containing swellable organosilica, activated carbon, or molecular sieves. (Inset: Expanded swellable organosilica curve during the initial time.)

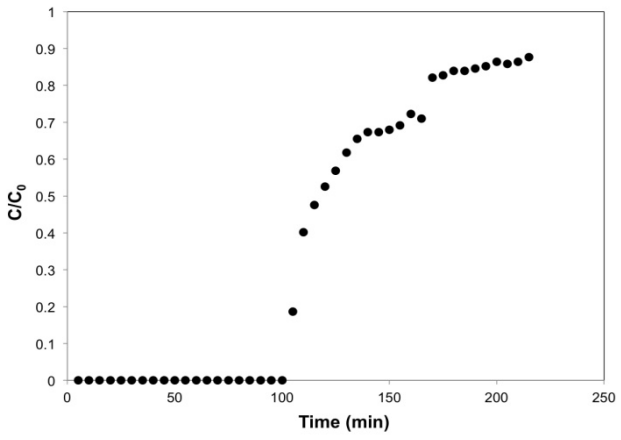


Binding Metal Ions, Polar Organics, and Fluorinated Compounds

Various functional groups can be added to the swellable organosilica matrix through the use of mixed alkoxysilane precursors or modification of the organosilica surfaces post-gelation. Covalently bound ligands have already been developed for swellable organosilica and tested for the absorption of metal ions. Recently, we have determined that swellable organosilica can be prepared from formulations containing up to 60% of other alkoxysilane precursors of any type including silanes that have organic ligands. Formulations that have metal ion binding ligands have been tested and achieve such functionality for Group II and transition metals. To date, we have shown that we extract >99% of Ba^{2+}, Zn^{2+}, Cu^{2+}, Fe^{3+}, Pb^{2+}, and Hg^{2+} from water and brines. Ligands that have been successful introduced to swellable organosilica particles include pyridine, imidazole, and mercapto (thiol) functional groups. The binding capacity of an material synthesized using 5% mercaptopropyltrimethoxysilane for Fe^{3+} is ~5.5 mg/g (Figure 36). In addition to functionalizing the surface of swellable organosilica, the matrix can be preloaded with extractants that have selective affinities for various metal ions or oxyanions.

Surface chemistry on the interior surfaces of swellable organosilica can be modified with polymers to change the hydrophobicity and allow for the capture of non-volatile polar organics. For instance, polyethylenimine has can be tethered to the interior pores of swellable organosilica which imparts the surface with multiple amine groups. The combination of the hydrophobic matrix and polar polymer modifying layer creates a mixed mode surface that has high affinity for polar analytes dissolved in natural waters including as phenols, caffeine, sulfamethoxazole, and coumatetralyl similar to high end sorbents such as Oasis HLB. Fluorinated

Figure 36. Breakthrough curve for thiolylated-swellable organosilica, 1 ppm Fe3+

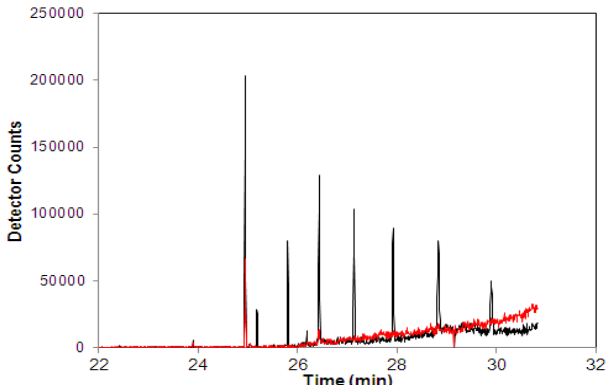


species can be captured by modifying the swellable organosilica either by the use of commercially available fluorinated precursors or by using a fluorinated derivatization agent during manufacturing. The resulting swellable organosilica with fluorinated groups has the ability to swell with liquid fluorous solvents and remove >99% of perfluorooctanoic acid from creek water when the nominal concentrations are in the ppb range.

Extraction of Flow Back Water

A sample of late stage flow back water was obtained from the Department of Energy National Energy Technology Laboratory. Gas chromatographic analysis indicated that the water sample had appreciable amounts of hydrocarbons due to the length of time spent in the formation. Semi-volatile slicking agent was also detected. Extraction with swellable organosilica led to >98% extraction of the hydrocarbons and 65% extraction of the slicking agent using 0.2% *w/v* sorbent in 30 s. Data indicate that multiple types of contaminants can be sampled simultaneously from water to monitor water quality even when events are short in duration.

Figure 37. (black) Untreated late stage flow back water. First major peak at retention time ~ 25 min is a slicking agent. The other major peaks are alkane formation hydrocarbons (red). Water after being sampled by 0.2% w/v swellable organosilica. Extensive removal of all organic contaminants was noted.



Absorption from Natural Waters

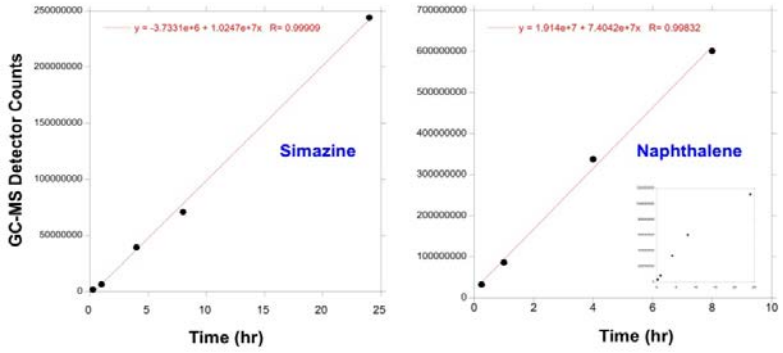
Absorption of organics is equally effective in salt water and water containing an abundance of natural organic matter. Water fully saturated with organic rich topsoil was used to test the absorption of environmentally relevant concentrations of TCE from a natural matrix. TCE (100 ppb) was spiked into a water/topsoil to which 0.0025% *w/v* swellable organosilica was applied where the volume included both the soil and water (~50% of each). The mixture was incubated for 48 hr and tested over 5 days to ensure complete equilibrium. swellable organosilica extracted 64 ± 12% (n=5) of the TCE from the soil/water mixture with a corresponding partition coefficient of $k_{TCE} = (1.8 \pm 0.4)\times10^4$. The partition coefficient was reduced approximately 25% compared to TCE in pure water. Thus, the large amount of organic matter had a measurable, but relatively minor affect on the absorption of TCE. This is likely due to the fact that much of the natural organic matter consists of high molecular weight species that are excluded by the nanoporous swellable organosilica matrix. Such behavior would indicate that swellable organosilica would be useful to remove low molecular weight contaminants from natural waters.

In addition to excluding particles and other soil components, swellable organosilica is also resistant to binding humic acids and other large organic polymers such as protein and DNA. Humic acids are physically too large and too polar to enter the nanoporous matrix. Initial pilot testing of swellable organosilica passive samplers have shown that the surface is highly resistive to biofilm formation. swellable organosilica has been stored in creek water for over 3 years and maintains its general properties of being physically unchanged and not leaching any breakdown contaminants. Although the storage jars are filled with biological dentritis the swellable organosilica remains hydrophobic with little if any biofilm growth. Recently, we have mixed swellable organosilica into bacterial culture media and algae lysate solutions and have observed little if any decrease in absorptive properties of the swellable organosilica. The reason for the lack of film grow is that the surface of the swellable organosilica particles is hydrophobic and animated which appears to prevent protein adhesion on the nanoscale. The biocompatibility and resistance to film formation makes swellable organosilica an interesting candidate for passive sampling, especially in water containing high levels of natural organic matter.

Preliminary Passive Sampling Results

Preliminary experiments testing swellable organosilica passive sampling devices both in the laboratory and in the field. Bench-scale work has involved the capture of naphthalene and simazine (a pesticide) by a sampler containing standard granular swellable organosilica housed in a stainless steel mesh pouch ($1cm^3$). Various concentrations of natural creek water were spiked with environmentally relevant concentrations of both compounds. The samplers were placed in 5 gallon buckets of spiked creek water which was slowly mixed with a stirbar. The amount of captured targets was linear with time even when exposed to relatively high concentrations (1 ppm) indicating that capacity may be acceptable for long-term monitoring (Figure 38). The concentration of simazine was varied for a given absorption time of 24 hr which gave a linear response. For a 24 hr sampling time the limit of detection for a 100 mg swellable organosilica sampler was found to be ~0.2 ppb for simazine and 0.05ppb for naphthalene. One of the observations made through tis work is that the affinity for naphthalene is very high and response can be non-linear at concentrations <10 ppb where most of the molecules are removed from the 5 gal test sample in a few hours. These data suggest an integrative mode of sampling.

Figure 38. Concentration response of swellable organosilica passive samplers to 1.0 ppm simazine (left) and 1.0 ppm naphthalene (right) over 8 hrs. Each data point was obtained from a different sampler.

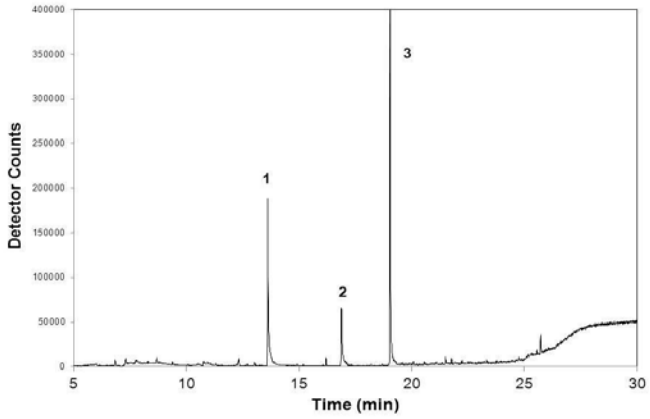


A field test of the passive sampler was done at Chippewa Lake which at 324 surface acres, is Ohio's largest natural inland lake, located in Medina County in Northeast Ohio. The lake is at the

headwaters of Chippewa Creek, and has historically been bordered by large areas of wetland on the north and south. However, these wetlands have largely been eliminated today, which may be a contributing factor to increased flooding and poor water quality. The Chippewa Lake watershed, largely located within Lafayette Township, is mostly rural and contains woodlands, farmland, residential areas, and limited urban development. The area also contains significant industrial development, particularly construction and metal fabrication. Chippewa Lake was selected because it the proximity to campus and because the water body has a very limited number of inflow sources. Other agencies profile the lake for comparison. Although hydrofracking operations have been done in Medina County (Utica Shale), the number of wells has been limited to date.

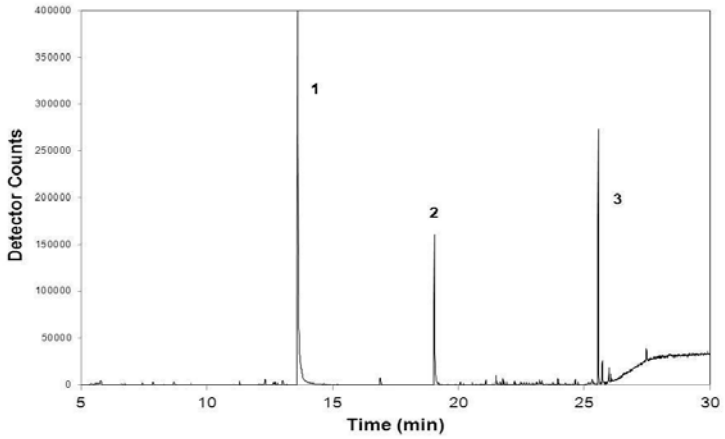
Three swellable organosilica passive water samplers were suspended from the sailing dock at the Chippewa Sailing Club with permission. The sailing dock is used solely by club members who race non-motorized racing sailboats. The three samplers were suspended by a cord 3' below the surface of the water and approximately 4' from the bottom about 50' from the shoreline. This depth was selected to ensure that only fully soluble species would be captured and prevent sheens or surface events from blinding or skewing the results. Sampler #1 was removed after two hours, providing the equivalent of a snapshot sample (Figure 39). Sampler #2 was removed after two days (50 hours), providing a short profile of the site (Figure 40). Sampler #3 was removed after 16 days, providing an extremely detailed portrait of the lake organic contaminants (Figure 41).

Figure 39. The 2 hr swellable organosilica passive water sampler results from Chippewa Lake, Ohio. Extracted compounds analyzed by GC-MS. Major compounds detected: 1. Gasoline surfactant; 2. Unidentified hydrocarbon - possibly a cooking oil or other organic oil; 3. Algae fatty acid.



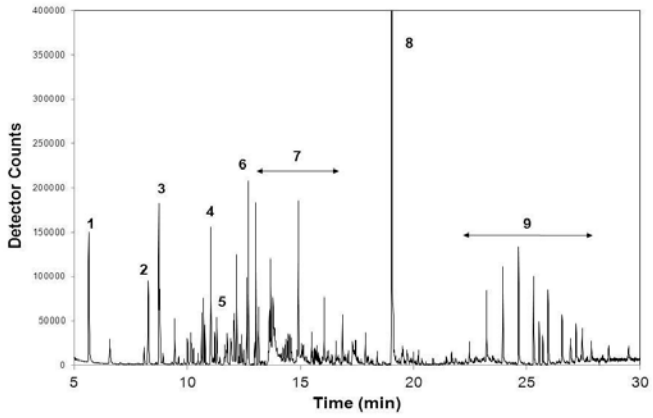
This snapshot, taken on a Sunday afternoon with moderate boating in the lake and two jet skis passing back and forth within 100' of the sampling site, indicates a relatively healthy boating lake. The largest peak during the two hour window is a fatty acid generated by lake algae. This naturally occurring fatty acid is at least three times more common than human activity spillage of hydrocarbons. There are also many very small, difficult to fully profile peaks in the low detector count ranges. A probable motor oil peak at approximately 25 minutes on the GC-MS detection process is already apparent, but still only at a trace level.

Figure 40. The two day swellable organosilica passive water sampler results from Chippewa Lake, Ohio. Extracted compounds analyzed by GC/MS. Major compounds detected: **1.** Gasoline surfactant. **2.** Algae fatty acids. **3.** High molecular weight polycyclic organic of unknown origin (synthetic oil).



Based on the two day sample, additional chemical compounds are being detected including aromatic hydrocarbons. The gasoline-surfactant spike and motor oil spike is so pronounced they are at least three times greater than the naturally occurring algae fatty acids. As it is autumn, many people were likely beginning to pull boats from the lake for the winter, and it would appear there has been a substantial fuel-motor oil incident on or in the lake. The 16-day swellable organosilica passive water sample indicates the lake water continues to be contaminated with both gasoline and motor oils associated with boating activity. The chromatogram indicates numerous hydrocarbons associated with gasoline engines, and three new spills (peaks 1-2, 4 and 6) indicate the lake has other substantial and biologically dangerous impacts during this period. The presence of limonene indicates that a boater may have rinsed out their engine compartment with a consumer soap product.

Figure 41. The 16 day swellable organosilica passive water sampler results from Chippewa Lake, Ohio. Extracted compounds analyzed by GC-MS. Major compounds detected: **1.** toluene; **2.** *p*-xylene; **3.** styrene; **4.** *p*-dichlorobenzene; **5.** limonene; **6.** methyl-ethyl-benzene; **7.** BTEX and gasoline hydrocarbons; **8.** algae-derived fatty acid; **9.** several common motor oil hydrocarbons from both 2 stroke and 4 stroke engines.



Summary

Initial work studying the use of swellable organosilica for passive sampling applications has shown that the materials have the ability to absorb a wide number of chemical species. Extraction of organic compounds is most pronounced due to the hydrophobic expandable matrix. The silica matrix can be functionalized with ligands that bind metals or be tailor to bind fluorinated compounds. Preliminary field testing shows sampling can be done for at least 16 days with minimal biofilm formation.

Acknowledgements

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Hierarchical Analytical Approaches for Unraveling the Composition of Proprietary Mixtures

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The statements made during the workshop do not represent the views or opinions of EPA. The claims made by participants have not been verified or endorsed by EPA.

Background

Identifying the chemical components of complex, propriety mixtures is the requisite first step towards understanding the occurrence, fate, and transport of the components in the environment. Hydraulic fracturing fluids are examples of proprietary mixtures containing chemicals, the identities of which are regarded as confidential business information. Other examples of proprietary mixtures include pesticide inert ingredients and aircraft deicers, oil dispersants, and aqueous film-forming foam (AFFF) formulations. Fully quantitative analytical methodologies can only be developed for mixture components once their identities are known. Because proprietary mixtures may contain volatile and non-volatile components, a hierarchy of analytical methods is often required for the full identification of all proprietary mixture components. Analytical strategies for identifying non-volatile mixture components are needed and ideally include approaches that require the least amount of sample preparation because sample preparation requires time, is expensive, and generates chemical and solid waste. Sample preparation also requires *a priori* knowledge of a chemical's structure and properties in order to avoid possible bias (artifacts)/sample discrimination.

Gas chromatography mass spectrometry (MS) is ideal for identifying volatile chemicals because searchable libraries are well established. In contrast, for polar non-volatile chemicals, liquid chromatography-tandem mass spectrometric (LC-MS/MS) methods are ideal. However, there are no reliable libraries that can be used for screening samples by LC-MS/MS. Alternatively, high mass accuracy measurements can be used to identify unknowns. One challenge to high mass accuracy measurements is that the very large amount of data generated requires time-intensive and sophisticated data-mining techniques. Simple, screening (targeting) techniques such as fast-atom bombardment (FAB) MS can be used to efficiently target masses for identification by high mass accuracy mass spectrometric approaches or to direct the development of quantitative LC-MS/MS methods.

Pesticide (and their inert ingredient packages) and deicer formulations are applied in the environment for weed control[1] and for purposes of ensuring air safety during times of inclement weather, respectively.[2] However, these applications raise questions regarding the environmental safety of the chemicals contained in these formulations. Investigations aimed at understanding the fate and potential effects of these proprietary formulation ingredients often begin with the identification of chemical classes in the formulations. Once classes are identified, sensitive and selective analytical methods can be developed for monitoring the chemicals' fate and potential effects at the trace level concentrations that are found in the environment. Oil dispersants are

complex, proprietary mixtures that contain numerous components including surfactants, corrosion inhibitors, and solvents.[3] Understanding the proprietary composition of the Corexit dispersant formulations used during the recent Gulf of Mexico oil spill was the first barrier that had to be overcome before setting up analytical methods to monitor for dispersant components in seawater and seafood. Finally, AFFF have come under increasing scrutiny due to their large-scale and repeated use at former fire-training sites located at military, industrial, and civilian sites.[4] Full identification of all the major and minor surfactant components of AFFF formulations was needed to fully characterize the fluorochemical inputs and to guide subsequent efforts to fully characterize all intermediate and persistent degradation products at these sites.

Experimental Approach

Complex, proprietary mixtures were analyzed for their polar, non-volatile components with a combination of approaches including FAB/MS, LC-MS/MS, and high mass accuracy (in the case of AFFF formulations). Proprietary mixtures included pesticide inert packages, aircraft deicers, oil dispersants, and AFFF formulations. Major surfactant classes were first identified by FAB/MS analysis and detailed information was obtained on alkyl chain lengths or ethoxylate oligomers. Information on minor components was obtained by infusing standard reference materials and authentic analytical standards into a LC-MS/MS system. In the case of AFFF formulations, target masses of unknowns identified by FAB/MS were then identified by high mass accuracy measurements.

Results

Pesticide inert ingredient packages and deicer formulations were qualitatively identified as containing linear alcohol ethoxylate and branched alkylphenol polyethoxylates.[5,6] The homologous series of carbon-chain lengths as well as the ranges of ethoxylated oligomers were readily identified by FAB/MS. Once identified, a sensitive analytical method was developed for environmental samples in order to understand the fate and potential impacts of these nonionic surfactants on estuarine biota when pesticides are applied to reduce invasive plant species and on biota near airports where deicers were used. Linear alkylbenzene $_{(C10\text{-}C14)}$ sulfonates also were identified in pyrethroid pesticide formulations.[1]

FAB/MS required no sample preparation yet provided *qualitative* information on the major classes of non-ionic (Span and Tweens) and anionic surfactants (sodium dioctylsulfosuccinate or DOSS) present in Corexit oil dispersant formulations.[3] In addition, LC-MS/MS provided *quantitative* information that was complementary to that obtained by FAB/MS but that required additional laboratory personnel expertise and instrument time. LC-MS/MS also was used to identify the á- and â-ethylhexyl sulfosuccinates that were present in Corexit formulations, which indicates that low levels of these related products also were applied to the oil spill in the Gulf of Mexico. Given the background presence the ethylhexyl sulfosuccinates in Corexit formulations, they are not unambiguous indicators of DOSS transformation if found in seawater or marine sediments.

FAB/MS and high mass accuracy mass spectrometry were combined to identify nine new classes of fluorinated chemicals in AFFF formulations used at US military sites.[6,7] FAB/MS also was sufficiently sensitive to identify fluorinated surfactants at mg/L levels in groundwater.[8] New

classes of fluorochemicals include cationic and zwitterionic species, which indicate that these chemicals may cation exchange onto sediments at contaminated sites and serve as long-term source zones. A sensitive LC-MS/MS-based analytical method was then developed and is being applied to groundwater, sediment, and soil at military sites to aid in more fully charactering the fluorochemical contamination at these sites.

Conclusions

FAB/MS is a lesser known, qualitative technique that is well-suited for the characterization of non-volatile surfactants in proprietary mixtures such as pesticide inert ingredient packages, aircraft deicer formulations, oils dispersants, and fire fighting foams. By analogy, FAB/MS can be used to identify the surfactant mixtures present in fracking fluids. Once mixture components are identified by FAB/MS, LC-MS/MS methods can be developed for analyte quantification. The use of FAB/MS also can be used to target masses of interest for identification by high mass accuracy mass spectrometry. Additional information, such as patents, can then be used to further validate the mixture components identified.

Acknowledgments

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Analysis and Treatment of Waters From Hydraulically Fractured Oil and Gas Wells

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The statements made during the workshop do not represent the views or opinions of EPA. The claims made by participants have not been verified or endorsed by EPA.

Introduction

Hydraulic fracturing of shale formations is an important and expanding process used for unconventional oil and natural gas extraction.[1] The process has contributed to an increase in gas and oil production within the United States and it is predicted that the U.S. will be world's leading producer by 2020. Each hydraulic fracturing, or fracking, event uses millions of gallons of water and wells can be fracked multiple times. On the order of thirty to forty percent of the water comes back to the surface as flowback or produced water. Many users are seeking innovative methods to handle the returned waters since conventional approaches, that include evaporation, filtration and landfilling, are expensive. The waters contain suspended solids, inorganic compounds, organic compounds, and microorganisms. Our research is largely focused on analyzing the chemical and microbiological components of the waters. In addition, we are conducting studies to biodegrade the organic pollutants within flowback and produced waters to develop the potential for inexpensive bioremediation technologies. We have explored a process of encapsulating biodegrading bacteria within silica spheres and showed that the biosilica catalysts extensively degrade organic contaminants and demonstrate long catalyst lifetimes.

Materials and Methods

Fracking fluid, flowback, and produced waters have been obtained from gas and oil wells from the Marcellus and Bakken shale regions, respectively. The waters were characterized with respect to dissolved solids, total organic carbon, salinity, hardness, elemental composition, and organic compound composition. TOC was determined by colorimetric assay using HACH Method 10173 and a DRB200 Reactor (HACH Company, Loveland CO). Salinity was measured with a portable probe, ULTRAPEN^{TM} PT1 (Myron L Company, Carlsbad CA). Elemental analysis was also used to determine chloride by inductively coupled plasma-mass spectrometry on a XSERIES 2 ICP-MS with PC3 Peltier cooled spray chamber (Elemental Scientific, Omaha, NE), SC-FAST injection loop, and SC-4 autosampler (Thermo Scientific Waltham, MA).

Organic content was analyzed by GC × GC–TOF-MS after extraction with a conditioned Gerstel stir bar (Twister, 0.5 mm film thickness x 10 mm, Gerstel Inc., Baltimore, MD) at room temperature at 140 rpm for 1 h.[2] After extraction, the organics were desorbed and injected onto a Pegasus-4D GC × GC–TOF-MS (LECO, St. Joseph, USA) equipped with a cryogenic inlet system (CIS-4) injector and a Thermal Desorption Unit (TDU) (both from Gerstel Inc., Baltimore, MD) and controlled by LECO ChromaTOF software version 4.50. The desorbed compounds were cryofocused within the cryogenic injector (CIS) at −125°C. The CIS temperature was then ramped at 12 °C/s to 300 °C and held for 5 min to vaporize the trapped compounds in the injector. The column set comprised a non-polar primary column

(30 m × 0.25 mm × 0.25 μm DB-5 (95% dimethylpolysiloxane, Agilent, Santa Clara, CA)) and a mid-polarity secondary column (1.69 m × 0.10 mm × 0.1 μm BPx50 (50% phenyl polysilphenylene-siloxane, SGE Analytical Science, Austin Texas). Ultrapure helium (99.9999%) was used as the carrier gas and was maintained at a constant flow rate of 1 mL/min. The temperature program of the first column (main GC oven) was: 40 °C (2min) → 120 °C (at 5°C/s) → 250 °C (at 6°C/s) → 280°C (at 7°C/s) (3min). The temperature of the second oven was offset by 15°C, and the modulator temperature offset was 30 °C, both relative to the first GC oven temperature. The second-dimension separation time (modulation time) was 4 s divided into a hot pulse time of 1.0s and a cold pulse time between the stages of 1.0 s. The transfer line from the secondary oven into the mass spectrometer was maintained at 270 °C. The ion source was operated at 200 °C. The electron energy was −70 eV. The detector voltage was set at −1750 V. The data acquisition rate was 200 scans/s covering a mass range of 5–500 m/z. The pressure inside the flight tube was about 1E-7 Torr. A typical analysis run time was 47 min. For analyzing peaks, LECO's ChromaTOF Data analysis software integrates preprocessing tools to correct for instrumental fluctuations and noise, followed by mathematical resolution of overlapping peaks. Automated mass spectral matching was used to identify compounds in the sample. Mass spectra were matched with a combination of NIST 2008 library and individual authentic standars run on our instrument.

Microbial composition of the waters was determined by total metagenomic DNA sequencing of amplified 16S rRNA genes. DNA was extracted and purified using MOBIO PowerSoil DNA extraction kits (MOBIO, Carlsbad, CA), according to the manufacturer's instructions. DNA concentrations were measured using a QuBit DNA quantification system (Invitrogen, Carlsbad, CA) with QuBit high sensitivity assay reagents. The V6 region of 16S rDNA was amplified by PCR and amplified DNA from each site was paired-end sequenced (2 × 150) on an Illumina MiSeq platform at the University of Minnesota BioMedical Genomics Center (St. Paul, MN) as previously described.[3]

Bacteria were extracted from flowback and produced waters by mixing with 0.1% hydrolyzed gelatin and agitated with 3mm glass beads for 30 min at 250RPM, then filtered through sterile size 047 glass fiber pre-filter (type SM 13430A, Whatman). The flitrate was centrifuged at 5000 x g for 20 min and the pelleted bacteria were encapsulated into a silica gel at 0.08 g bacteria per ml gel solution as previously described.[4] Bacteria in encapsulated gels were incubated with flowback waters with shaking at 25^{o}C and analyzed for the extent of their biodegradation of compounds in the waters by TOC determination and by GC × GC–TOF-MS as described above.

Results

General characteristics of waters

The waters were obtained from hydraulic fracturing production wells in the Marcellus (M) and Bakken (B) shale regions and represent fracturing fluid (FF), a produced water (PW) obtained 18 months after hydraulic fracturing, an oil shale water (Bakken) broken gel (BG) water, and a separation tank bottom (TB) water sample. The general properties of the waters are as described in Table 22.

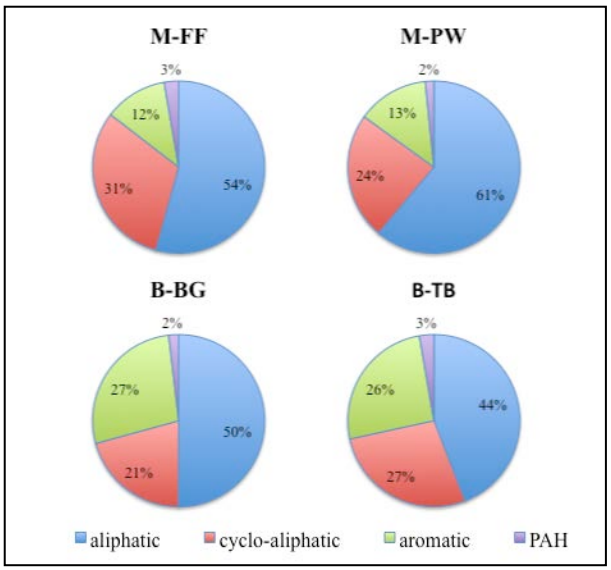
Table 22. Properties of waters from fracturing operations in Marcellus and Bakken shale regions.

Waters	pH	TOC (mg/L)	Salinity, NaCl (M)
M-FF	7.1	990	0.47
M-PW	7.0	1112	0.89
B-BG	8.0	4589	3.55
B-TB	6.5	1741	0.03

Organic components in waters

Analysis of the organic chemical composition of the waters by GC x GC-TOF-MS revealed on the order of one thousand total distinguishable compounds that were identified and binned as shown in Figure 42.

Figure 42. Major classes of organic chemicals found in waters from Marcellus (M) and Bakken (B) wells.



Microbiological composition of waters

The fracking fluid and recovered waters contained complex communities of microorganisms as revealed from deep DNA sequencing that produced 684,224 to 983,600 reads for each water sample (Table 23). Greater than 1800 distinct bacterial types were detected in each 50 ml water sample, consistent with the idea that these water samples are teeming with microbial life.

Table 23. Major genera of bacteria in each water as determined by DNA sequencing. Numbers in parentheses represent the number of individual DNA reads determined for each bacterial genus.

Waters	Genus 1	Genus 2	Genus 3	Genus 4	Genus 5
Marcellus - FF (684,224)	*Thauera* (269,602)	*Sporolacto-bacillaceae* (178,956)	*Prostheco-microbium* (53,517)	*Auraticoccus* (50,814)	*Colwellia* (47,651)
Marcellus - PW (983,600)	*Thauera* (195,810)	*Prostheco-microbium* (129,124)	*Auraticoccus* (52,016)	*Streptohalo-bacillus* (46,784)	*Gibbsiella* (35,470)
Bakken - BG (839,621)	*Halanaero-bium* (398,756)	*Marinobac-terium* (206,787)	*Enterobacter* (61,898)	*Oceanimonas* (26,221)	*Pseudomonas* (18,906)
Bakken - TB (836,214)	*Pseudo-monas* (242,631)	*Jishengella* (108,667)	*Malikia* (61,694)	*Wlliamsia* (47,105)	*Mitsuaria* (39,325)

Biodegradation in flowback waters

A direct experiment was conducted to determine if the Bakken broken gel (B-BG) and tank bottom (B-TB) waters contained bacteria that were capable of degrading compounds derived from the shales and fracking fluid additives. Two treatments were examined: (1) the waters with their bacterial populations and (2) the waters with the addition of bacteria that had been harvested and encapsulated. Previously described procedures were used to put the harvested bacteria into a silica gel matrix, a process that is shown to preserve bacteria and enhance their abilities for biodegradation.[4]

Table 24. Total organic carbon (TOC) after treatment with native bacteria or silica-encapsulated bacteria.

Waters	TOC, Starting (mg/L)	TOC, Free cells (mg/L)	TOC, Cells in silica (mg/L)	% TOC removed by cells in silica
B-BG	4589	3134	1833	60%
B-TB	1741	1600	790	55%

Biodegradation was first demonstrated by analysis of total organic carbon, or TOC (Table 24). The free cells in the waters showed some biodegradation, but that was greatly enhanced by using bacteria that were harvested and encapsulated in silica gel beads. This is consistent with previous observations in which biodegradation of atrazine was greatly enhanced by encapsulating the bacteria within silica gels.[4] The decline in TOC of 55-60% in each water indicated that many compounds are undergoing complete biodegradation to carbon dioxide that is being lost from the aerated cultures. The amount of total organic carbon left in the waters treated with the silica-encapsulated cells was approximately one-half of that remaining with free bacteria that were natively found in the waters. The waters incubated at 4^{o}C show negligible biodegradation, indicating that sorption or evaporation could not explain the results. Moreover, analysis by GC x GC-TOF-MS showed selective biodegradation of specific compounds, consistent with biological

processing. In total, these data show that the native bacterial populations within the Bakken waters had the potential for extensive levels of biodegradation when incubated with shaking at 25°C.

Conclusions

Water from hydraulic fracturing operations for oil (Bakken) and natural gas (Marcellus) have been analyzed for chemical and microbiological content. The natural microbial flora in the waters are from genera (classifications) of bacteria that are known to have the ability to biodegrade the types of chemicals found within the waters, specifically: alkanes, cycloalkanes, aromatics, and polycyclic aromatic compounds.[5] A novel encapsulation process has been investigated and shown to have the potential for development into a bioremediation tool to remove all classes of chemicals found within waters derived from hydraulic fracturing operations.

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