

Unconventional Oil and Gas Drilling and Water Quality Assessment

Analysis Parameters and Methods

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UNCONVENTIONAL OIL AND GAS DRILLING AND WATER QUALITY ASSESSMENT

This document addresses, through a limited literature review, methods for testing water quality near unconventional oil and gas development (UOGD) sites. During the six month fellowship I reviewed several relevant documents and recent studies that provide detailed information on chemicals used in UOGD, methods for collecting water samples and how to perform analyses. While not exhaustive in scope, this review covers a number of issues associated with UOGD water impacts near well pad development sites and suggests methods for water quality assessment. Contact EHP for updates or further information.

Approximately 44 million Americans rely on private water supplies [7], of which more than 3 million are residents of Pennsylvania [17].

Unconventional oil and gas drilling (UOGD), which involves both horizontal drilling and hydraulic fracturing with high pressure and fluids, can produce over 1 million gallons of wastewater during the first month of drilling and production alone [7]. This wastewater creates a potential threat of contamination to surface and ground water sources, both of which can affect private well water quality. UOGD wastewater is highly saline, and contains toxic trace elements as well as naturally occurring radioactive materials [3]. There are various pathways by which contamination can occur to surface or groundwater during well site development and production including transportation spills, stray gas contamination, well casing leaks, leaks from fractured rocks, site discharges, accumulation of radioactive materials in sediments, and wastewater disposal [4].

Elevated levels of contaminants have been detected after documented spills. Various studies have found that contaminated stream waters can exhibit contamination levels exceeding the federal standards set for safe drinking and environmental health [3]. The list of contaminants that reach these exceeding levels is extensive, some of the most common being ammonium, selenium, thallium, radium, chloride, iron and manganese [9].

There remains a significant lack of water quality data relating to UOGD activity. This void leaves public officials and the general public uninformed, which can create conflict within communities [2]. The effects of hydraulic fracturing on groundwater and surface waters is not well understood and has been referred to as an uncontrolled science experiment on groundwater [11]. Thus collecting, analyzing and compiling water quality data is a priority research topic. Legislators need this information to make scientifically sound decisions concerning UOGD and water sources in a timely manner. In order for policy makers to receive the information they need, researchers and citizen scientists need to know how to best collect and analyze samples to detect possible contamination events.

LIMITATIONS OF TESTING

In order to determine the extent of water source impact, contaminant sources and contamination trends, it is necessary to establish long-term and comprehensive data collection. Baseline measurements allow for proper insight to water quality trends, so the presence and magnitude of a contamination event can be adequately evaluated.

Current water quality monitoring efforts are insufficient for accurately identifying surface or ground water impacts. Measuring water quality in areas of UOGD is a complex, technical challenge. While there are many lists of chemicals that can potentially contaminate these waters, collection and analysis can be expensive. First, one must define the purpose for testing, then answer the questions of what to test for where, and determine which chemicals would be most important to sample for, based on funding restraints.

Once the reason for sampling is defined and the location for monitoring is selected (this could be streams, lakes, private wells or spill runoffs), the appropriate monitoring parameters can be identified. Addressing temporal variation through frequent monitoring is vital to determining trends and impacts where possible[2]. So far, few studies show how water chemistry impacts due to UOGD activity change over time [5, 11]. This change over time is important information for researchers to detect trends, and to precisely determine which water parameters to focus on for the particular time in which the sample collection process is being conducted.

Researchers also have a difficult time defining the source of contamination due to lack of chemical disclosure by industry [5, 11]. The chemicals used throughout hydraulic fracturing process are diverse and numerous, so determining which to sample and analyze is a problematic task. Many of the chemicals are also used in other industrial, agricultural and residential activities. Without baseline tests and chemical disclosure, it is difficult to conclude whether the presence of a chemical is naturally occurring or the result of industrial activity (e.g., mining or fracking).

There are several groups of chemicals used for drilling and hydraulic fracturing including lubricants, corrosion inhibitors, biocides, and emulsifiers [4]. The chemical composition of the different fluids used throughout the process can be very complex, and vary based on local geology. Each site may require a different mixture [4].

PURPOSE OF DOCUMENT

This document was created for use by the public and researchers who are looking for information about water collection and analysis of water chemistry parameters concerning contamination by UOGD activity. It describes the various groups of chemicals used throughout the hydraulic fracturing process, identifies numerous specific compounds that are commonly used, and assigns a collection and analysis method for each compound. The document also includes recommendations for monitoring water source impacts by UOGD for the government, researchers and individuals.

FRACTURING FLUID COMPONENTS

The following information comes from Ferrer and Thurman, in their paper, “Chemical constituents and analytical approaches for hydraulic fracturing waters” [4]. The information provided is a breakdown of the different groups of chemicals used for hydraulic fracturing purposes, and includes a description of the uses of each group as well as examples of specific compounds. Water makes up 90.80% of the fracturing fluid and sand, a propping agent used to hold open fractures to allow gas to escape, makes up 8.50%.

Gels (0.050%):

Gels are used to increase the viscosity of the fracturing fluid, which helps to deliver the proppant into the fractures. The most commonly used gelling agent is guar gum and its carboxylated derivatives; others are cellulose-based. Organic solvents (methanol, ethanol, isopropanol, ethylene glycol) are used as gel stabilizers.

Crosslinkers (0.007%):

These compounds are used to chemically bind individual gel polymer molecules to maintain the viscosity of the fracturing fluid. Commonly used crosslinkers are borate salts, inorganic complexes with zirconium or aluminum, monoethanolamine, monoethylamine, ammonium chloride, ethylene glycol and potassium hydroxide.

Friction reducers (0.070%):

Friction reducers are used to reduce the interfacial tension between the fracturing fluid and pipe. They are also used to maintain the laminar flow during the pumping process. The main active ingredient is usually polyacrylamide dispersed in a hydrocarbon carrier. Sometimes friction reducers are used instead of gels and have proven to be more effective by reducing fracture plugging.

Breakers (0.060%):

Breakers are used after the fracturing occurs to reverse the crosslinking. This allows the gas to flow and increases productivity. There are two types of breakers: enzyme and inorganic. The enzyme breakers are mainly proteins that degrade cellulose polymers into smaller sugars. Inorganic breakers are common salts (calcium chloride, sodium chloride, potassium chloride or ammonium sulfate).

pH adjusters (0.010%):

Acids or bases are added to the fracturing fluids to increase the effectiveness of the polymers and crosslinkers. The pH adjusters used depend upon whether a low or high pH is necessary, which depends upon the polymers and crosslinkers used. Examples of pH adjusters used are: acetic acid, sodium hydroxide, potassium hydroxide, sodium carbonate or potassium carbonate.

Acids (0.050%):

Acids are used to clean the wellbore and to dissolve the minerals present in the geological formation, prior to the injection of hydraulic fluids, in order to clear flow paths for the gas and ultimately increase well production. The most common acid for this purpose is hydrochloric acid.

Corrosion inhibitors (0.002%):

Corrosion inhibitors are used to prevent casing corrosion, which can occur from the acids and salts. They form a protective layer on metal well casings. Chemically, they consist of acetaldehyde, acetone, formic acid, thiourea, amines, amides or amido-amines.

Scale inhibitors (0.090%):

These inhibitors are used to prevent mineral precipitation when formation waters come in contact with injection fluids. The most common compounds are carboxylic acids, acrylic acid polymers and phosphonic acid salts.

Iron control (0.006%):

These compounds are used to prevent iron precipitation in the wellbore as well as potential dissolving of iron from the well casing. The most common iron control compounds are citric acid, acetic acid, thioglycolic acid and EDTA.

Clay stabilizers (0.120%):

Clay stabilizers prevent the swelling of clays in the shale formation, which can reduce permeability and overall well productivity. Clay stabilizers are usually ion exchange compounds such as choline chloride, tetramethylammonium chloride, potassium and sodium chloride.

Biocides (0.060%):

Biocides are used in fracturing fluid to sanitize and reduce the number of bacteria in the water that is used in the fluid. The bacteria can cause wellbore clogs, corrosion of the equipment and degrading of the chemicals used. Historically, the compound most generally used has been glutaraldehyde and its derivatives. Other compounds used as biocides are tetrakis hydroxymethyl phosphonium sulfate, 2,2-dibromo,3-nitrilopropionamide (DBNPA), quaternary ammonium compounds and common sodium hypochlorite or bleach.

Surfactants (0.075%):

Surfactants are used to reduce interfacial tension between the hydraulic fluids and the shale. They are also used to remove possible emulsions formed by the mix of oil and water in the well. Surfactants can also be used as gelling agents, crosslinkers, corrosion inhibitors or biocides. Their wide range of usage means they fall into various chemical categories. They can be divided mainly into 4 group classes: nonionic, anionic, cationic and amphoteric compounds. The most commonly used are lauryl sulfates.

PARAMETERS FOR ANALYSIS

This section addresses groups of chemicals to focus on when deciding which analytes to collect for the study of water source impacts by UOGD. According to the literature reviewed for this paper, the groups that are most commonly used and therefore should be considered for monitoring are:

Cations and metals
Anions
Radioactive material
Alcohols and solvents
Hydrocarbons
Geologic isotopes

Specific Compounds

Of the groups listed above, there are 44 specific compounds that the literature describes as either commonly used by the industry, or frequently detected in UOGD contaminated waters. Those compounds are listed here:

2-butoxyethanol	Magnesium
Acetaldehyde	Manganese
Ammonium	Methanol
Arsenic	Methane
Barium	Molybdenum
Benzene	Nickel
Boron	Potassium
Bromide	Radium
Calcium	Selenium
Chloride	Sodium
Chromium	Stable oxygen isotope
Cobalt	Stable hydrogen isotope
Copper	Strontium
Cyclohexane	Sulfate
Dichloromethane	Titanium
Ethanol	Toluene
Ethyl Benzene	Total Nitrogen
Ethylene Glycol	Total Organic Carbon
Fluoride	Vanadium
Hydrotreated light petroleum distillates	Xylene
Isopropanol	Zinc
Lead	Zirconium

Collection Methods

General

When performing any sort of water chemistry analysis, it is good practice to collect on site readings for basic parameters such as pH and conductivity, using a Yellow Springs Instrument (YSI) multi-meter probe. A YSI multi-meter can obtain several different readings simultaneously depending on what specific probes are on the device, but temperature, dissolved oxygen, pH and conductivity can provide an initial assessment of the overall water quality. It is important to begin the process by purging the source (e.g., well) for at least 10-20 minutes depending on the flow. In some extreme cases where flow and volume are an issue, this may not be possible.

The following collection methods are documented in the references provided, where further details can be found as needed.

Anions, Sr Isotopes, Dissolved Organic Carbon

Purge the source for 10-20 minutes. Use a high-density polyethylene sample bottle for collection and filter in the field using 0.45µm syringe filters. Store samples in the dark and on ice during transport [1,10].

Cations and Metals

Purge the source for 10-20 minutes. Use a high-density polyethylene sample bottle for collection. Bottles should be acid washed prior to use for collection. "Trace metal clean" containers can also be used. Filter in the field using 0.45µm syringe filters. Preserve samples with 10% high purity nitric acid. Store samples in the dark and on ice during transport [1,10].

Alkalinity, Oxygen/Hydrogen Isotopes

Purge the source for 10-20 minutes. Use a high-density polyethylene sample bottle for collection. Do not filter. Leave no headspace in the container. Store samples in the dark and on ice during transport [1,10].

Hydrocarbons

Purge the source for 10-20 minutes. Use amber septum vials (100mL) for collection, do not filter and leave no headspace. Store samples in the dark and on ice during transport [1].

Radioactive Material

Purge the source for 10-20 minutes. Use a plastic container for sample collection and filter on site using 0.45µm pore size filters. Bring the pH of the sample to ≤ 2 by using hydrogen chloride or nitric acid. This inhibits biological growth and prevents radium from adsorbing to the wall of the container [8].

Organics

Purge the source for 10-20 minutes.

Hydrophilic: Collect sample using a pre-combusted amber glass container and a Teflon cap. Fill container about halfway and freeze sample to preserve prior to analysis.

Hydrophobic: Collect sample using a pre-combusted amber glass container. Minimize the headspace in the container and freeze sample to preserve prior to analysis.

Lighter hydrophobic: Collect sample using a pre-combusted amber glass container. Do not use a Teflon cap, as heavier hydrocarbons will adsorb to the Teflon polymers over time. Minimize the headspace in the container and freeze sample to preserve prior to analysis [12].

Analysis Methods

These are general guidelines, and the full references provided should be consulted. The details of the method used may need to be varied based on the instrumentation and the solvent used.

Anions

Method: Ion chromatography

Equipment: ThermoFisher Sionex IC, ThermoFisher Dionex ICS-1100

Protocol: Concentrations of selected anions are measured using an ion chromatography system equipped with a conductivity cell and UV/VIS detector using EPA Method 300.0. Five-point calibrations, in triplicate, are done with standards for each anion. Use the following, all from ThermoFisher/Dionex, to quantify anions: an IC-25 isocratic pump with an EG40 electrochemical eluent generator, AG20/AS20 guard and separation column (2 mm bore) sets housed in a LC30 temperature controlled oven (30°C), ASRS-Ultra II anion suppressor in external water mode, and a CD-25 conductivity detector. Electrochemically generated high purity KOH eluent is used at a flow rate of 0.25 mL/min with the gradient: 4 mM for 3 min to 10 mM at 15 min, then to 40 mM at 19 min until 27 min, and re-equilibrating at 4 mM for 27.50 min to 30 minutes. Eluent generation, sample injection (2 μ L), electrochemical suppression, auto-ranging conductivity detection and data acquisition are conducted under Excalibur/Chromleon software control [1,6].

Cations

Method: Direct current plasma optical emission spectrometry, inductively coupled plasma-optical emission spectrometry

Equipment: Perkin-Elmer NexION 300X ICP-MS, Shimadzu ICPE-9000 OES

Protocol: Analysis for selected cations is done using EPA Method 200.8. Samples should be introduced with a Mini Torch nebulizer, ionized with argon plasma, and introduced into the spectrometer in the axial view.

Quantitation is performed using the standard addition method with 100 and 200 µg/L analyte spikes. An average of three measurements per acquisition is used for signal intensity at each spiked level. Spectral line intensities for all elements are recorded simultaneously with the large-scale charge-coupled device detector, which is characterized by a resolution of < 5 pm at 200 nm in the instrument [1,6,10].

Total Nitrogen and Total Organic Carbon

Method: Total nitrogen and total organic carbon analysis

Equipment: Shimadzu TOC-L/TN

Protocol: Sampled water is introduced into 40 mL septum-top VOA vials (and may be loaded into an ASL autosampler). Standards and calibration curves for total organic carbon, inorganic carbon, and total nitrogen are generated using the manufacturer's recommendations [6].

Oxygen/Hydrogen Isotopes ($\delta^{18}\text{O}/\delta^2\text{H}$)

Method: Continuous flow isotope ratio mass spectrometry

Equipment: ThermoFinnigan TCEA and Delta + XL mass spectrometry [9]

Strontium Isotopes ($^{87}\text{Sr}/^{86}\text{Sr}$)

Method: Thermal ionization mass spectrometry

Equipment: ThermoFisher Triton [9]

Alcohols, Aromatics, Aldehydes

Method: Gas chromatography-mass spectrometry

Equipment: GCMS-QP2010 Ultra

Protocol: The compounds (all alcohols, aromatics and aldehydes) are all separated on a Rxi-5ms column (30m x 0.25mm; 0.25µm df). Oven programming and detection should be performed using a GCMS-QP2010 Ultra.

Temperature programming is as follows: 40°C for 3 minutes, increased at 20°C/min to 70°C, then 40°C/min to 330°C, held for 2 minutes. The GC split inlet, MS interface, and MS temperatures are set to 300°C, 260°C and 260°C, respectively [6].

Solvents

Method: Headspace gas chromatography

Equipment: AOC-5000 Plus headspace autosampler

Protocol: Solvent detection is performed using static headspace-GC with a flame ionization detector. Headspace operations are controlled with the AOC-5000 Plus headspace autosampler. 5ml of sample is mixed with 1ml of 0.25M NaCl (aq) in a 20ml screw-top headspace vial. Automated incubation at 90°C for 15 minutes and agitation is performed before 750µL of headspace was sampled. Separation and detection is achieved using a Shimadzu GC-2010 Plus equipped with a Phenomenex ZB-BAC2 column (30m x 0.32mm; 1.2µm df) held at 40°C for 4.5

minutes, then increased to 130°C at 30°C/minute, held for 2 minutes. Inlet and detector temperatures are set to 200°C, in which the injector is set for a 5:1 split ratio [6].

Metals

Method: Inductively coupled plasma-mass spectrometry

Equipment: Varian 820 ICP-MS coupled with an SPS 3 Varian autosampler

Protocol: Elemental analysis of the heavy metal ions is conducted using a Varian 820 ICP-MS coupled with an SPS 3 Varian autosampler using Argon as the plasma source. Mass Spectrometry data acquisition is performed in scan mode with 5 replicates, 30 scans per replicate [6].

Radium (^{226}Ra and ^{228}Ra)

Method: Gamma spectrometry, Alpha spectrometry

Protocols:

Gamma spectrometry – Pre-concentration can be done via evaporation. For sample volumes between 0.1-20L, place sample in a 70-100°C environment at atmospheric pressure. The process takes anywhere from less than 1 hour to 3 days, depending upon conditions and sample size. Other effective preconcentration procedures include: MnO_2 adsorption, $\text{Ba}(\text{Ra})\text{SO}_4$ and/or $\text{Pb}(\text{Ra})\text{SO}_4$ coprecipitation, cation-exchange resin adsorption, and Radium Rad Disc adsorption. For Ra purification, crystallization as BaSO_4 , anion- or cation-exchange resin chromatography, solvent extraction with HDEHP, TBP, HMHN and Cy221C7, and extraction chromatography with Microthene-TOPO, can be used. Then low-background HPGe gamma spectrometry technique can be used for determination of ^{228}Ra and ^{226}Ra in environmental samples [8,9].

Alpha spectrometry – Samples can commonly be prepared either in the form of micro-precipitation of BaSO_4 or of electrodeposition in the media of oxalate or ethanol. Due to better energy resolution and effective decontamination, electrodeposition is recommended. Then alpha spectrometry technique can be used for determination of ^{228}Ra and ^{226}Ra in environmental samples.

The alpha spectrometry is a better option over gamma spectrometry because it allows for higher sensitivity resulting from the observation of the high-yield alpha decay process, low intrinsic detector background and the elimination of competing radionuclides by chemical separation; the ability to measure concentration of ^{226}Ra without an ingrowth period for ^{222}Rn and daughters; and the ability to measure activity concentrations of all the naturally occurring Ra isotopes (^{226}Ra and ^{228}Ra included) on a single source [8].

Quick Reference Guide

The chart below was developed as a quick reference guide. It includes each of the specific compounds mentioned previously, and includes the corresponding collection and analysis methods that should be used.

Compound	Collection Method*	Analysis Method**
2-butoxyethanol	Organics	Alcohols/Solvents
Acetaldehyde	Organics	Aldehydes
Ammonium	Cations	Cations
Arsenic	Metals	Metals/Cations
Barium	Metals	Metals/Cations
Benzene	Hydrocarbons	Aromatics
Boron	Metals	Metals/Cations
Bromide	Anions	Anions
Calcium	Metals	Metals/Cations
Chloride	Anions	Anions
Chromium	Metals	Metals/Cations
Cobalt	Metals	Metals/Cations
Copper	Metals	Metals/Cations
Cyclohexane	Hydrocarbons	Solvents
Dichloromethane	Organics	Solvents
Ethanol	Organics	Alcohols/Solvents
Ethyl Benzene	Hydrocarbons	Aromatics
Ethylene Glycol	Organics	Alcohols/Solvents
Fluoride	Anions	Anions
Hydrotreated light petroleum distillates	Hydrocarbons	Solvents
Isopropanol	Organics	Alcohols/Solvents
Lead	Metals	Metals/Cations
Magnesium	Metals	Metals/Cations
Manganese	Metals	Metals/Cations
Methane	Hydrocarbons	Hydrocarbons
Methanol	Organics	Alcohols/Solvents
Molybdenum	Metals	Metals/Cations
Nickel	Metals	Metals/Cations
Potassium	Cations	Cations
Radium	Radioactive materials	Radioactive materials
Selenium	Cations	Cations
Sodium	Cations	Cations
Stable hydrogen isotopes	$\delta^{18}\text{O}/\delta^2\text{H}$	$\delta^{18}\text{O}/\delta^2\text{H}$
Stable oxygen isotopes	$\delta^{18}\text{O}/\delta^2\text{H}$	$\delta^{18}\text{O}/\delta^2\text{H}$
Strontium	Metals	$^{86}\text{Sr}/^{87}\text{Sr}$
Sulfate	Anions	Anions
Titanium	Metals	Metals/Cations
Toluene	Hydrocarbons	Aromatics
Total Nitrogen	Organics	TN
Total Organic Carbon	Organics	TOC
Vanadium	Metals	Metals/Cations
Xylene	Hydrocarbons	Aromatics
Zinc	Metals	Metals/Cations
Zirconium	Metals	Metals/Cations

* See Collection Methods section; See Analysis section: these methods are specific to the research articles referenced in these sections

RECOMMENDATIONS

Government

There is a need for a national database of compounds (particularly those related to hydraulic fracturing) found in surface and ground water sources [7]. Comprehensive water chemical composition data would allow the public, researchers and policy makers to use this database as a reference tool so that water quality changes could be tracked over time, particularly before, during and after hydraulic fracturing activities. Researchers could better determine if and when a contamination event occurred, and it would make collection and analysis more efficient in that researchers could look at the database and know when a site was last sampled. The US Environmental Protection Agency and the US Geological Survey would be appropriate entities for database development. This database should focus on collecting baseline measurements before hydraulic fracturing activities, and continue to collect data long-term in order to provide an accurate assessment of how water chemistry changes over time and during well development. The National Park Service and USGS Water Quality Partnership Program has a baseline water quality testing program for private wells, monitoring water quality in national parks to provide park resource managers with data to make scientifically sound decisions. This program could be used as a guide for the development of this database [7].

Thorough evaluation of the mechanisms of methane contamination (as well as other compounds) in drinking water should be a priority concern [6]. It is often said that methane contamination of private well water is impossible due to the distance between the shale deposits and water sources. Conducting field and modeling studies would confirm whether or not this is the case, and could help determine the mechanism(s) of potential contamination. This would also support the development of more precise preventative measures and regulations. The evaluation could be conducted by a federal agency, such as the US Geological Survey or the US Department of Energy [7].

There is also a need for greater focus on the legacy of hydraulic fracturing wastewater disposal. The current methods of wastewater disposal are: transport to wastewater and/or brine treatment centers, injection into deep geological formations, recycling using a variety of treatment technologies and reuse as fracturing fluid, and spreading on local roads for dust suppression. There is no comprehensive evaluation of the long-term health and environmental impacts of wastewater disposal methods. The wastewater from the Marcellus shale region is of particular concern because it is more saline and more radiogenic than other sedimentary basins where high volume fracturing is occurring [18].

In much of the US, UOGD wastewater is disposed of by deep well injection, but Pennsylvania currently has only seven injection wells [19]. The main wastewater disposal methods in PA are reuse and transportation to Ohio and West Virginia, though transportation is limited due to high costs. The reuse of UOGD wastewater also raises concerns about the compatibility of the chemical composition of the wastewater mixed with the fracturing fluid. A better understanding of wastewater composition would allow for improved assessment of this disposal method. Furthermore, the reuse program is only a temporary solution. There is a need to develop an alternative disposal method for the wastewaters that can no longer be reused. Treatment technologies and management strategies for this wastewater are constrained by regulations, economics of implementation, technology performance, geologic setting, and final disposal alternatives [7,15].

Research Considerations

When conducting analyses to determine the presence or absence of water contamination due to UOGD activity, we recommend determining the specific isotopic signature of the geologic region in which the studies are being conducted. For example, researchers from Duke University used Br/Cl and $^{87}\text{Sr}/^{86}\text{Sr}$ tracers to compare the geochemical and isotopic profiles of water samples in North Dakota. By using these tracers, they were able to determine the source of contamination [9]. Additionally, the use of isotopic and geochemical analyses is beneficial when analyzing water sources for methane. Methane can be either biogenic or thermogenic in origin. Biogenic sources may be distinguished from thermogenic sources through isotopic ($\delta^{13}\text{C}-\text{CH}_4$ and $\delta^2\text{H}-\text{CH}_4$) and geochemical analyses (propane/methane ratios). The presence of associated hydrocarbons (ethane, propane, propylene, butane) may be an indication that the source of methane is thermogenic. Definitive determination of the thermogenicity will require isotopic analyses. It is important to identify the origin of the methane in order to determine whether the contamination occurred naturally or from UOGD activity [1].

The chemical composition of contamination depends upon the point in the process when the contamination event occurs, as well as the geologic composition of the area. It is helpful to check for chemical disclosure from the industry, based on the type of fluids in use, to assess which chemicals to analyze for (see [FracFocus Chemical Disclosure Registry](https://fracfocus.org) <https://fracfocus.org>). Fracturing fluids have a different chemical composition than flowback and produced water. Treated wastewaters may also have a different composition as the sludges have removed some of the barium and strontium. Flowback water and produced water typically contains total dissolved solids, organics, metals and radioactive material. Wastewater tends to be high in hydrocarbons, salts and total dissolved solids [14].

A good example of identifying differences in water samples is demonstrated by Lauer et al. [9]. Their study of hydraulic fracturing contamination in North Dakota identified two water sample sources, Type A and Type B.

Type A samples were from spills of mixed brine water and background waters. Type B samples were of different chemical composition caused by chemical precipitation due to isolation and sequential partial evaporation. In order to accurately determine which water chemistry parameters to analyze and compare, it is necessary to identify the specific chemical composition of the waters sampled.

Repeated measures would provide valuable information about changes over time. One study found that as more unconventional wells were drilled and began the production process, more contaminants were found in the water sources [5]. The study also found that heavy metal and toxic chemical contamination levels fluctuated over time. The authors collected and analyzed samples at four different time periods, and found that certain compounds displayed significant quantitative changes between phases. Those compounds were: TDS, pH, total organic carbon, total nitrogen, ethanol, chloride, bromide, dichloromethane, toluene, selenium, barium, strontium, iron. Focusing on temporal variation will allow for the determination of trends and provide information on which parameters to analyze for and when.

Non-profit organizations

Grassroots organizations that do not have extensive resources and are interested in monitoring water sources for potential UOGD contamination near well pads could focus on the following compounds:

Methanol
Isopropanol
2-butoxyethanol
Ethylene glycol
Hydrotreated light petroleum distillates

The above compounds were selected because they are commonly used by the hydraulic fracturing industry. Collection and analysis methods have been assigned to each of these compounds (see page 13) [13].

The Pennsylvania Department of Environmental Protection (DEP) provides a valuable resource of accredited labs to carry out analyses. Another option is to refer to the literature, and to use the specific labs referred to in the protocols if possible. Some relevant examples are listed below:

Compound: light hydrocarbons, lab: VaporTech Analytical Laboratory, Valencia PA [1]

Compound: cations, lab: University of Pittsburgh [1]

Compound: stable oxygen and hydrogen isotopes, lab: Duke Environmental Isotope Lab (DEVIL) [9]

Compound: 226Ra and 228Ra, lab: Duke Lab for Environmental Analysis of Radionuclides (LEARN) [9]

Individuals

For individuals or residents who are interested in monitoring their water quality, we highly recommend having a water chemical analysis done prior to drilling, to provide baseline measurements. Throughout the drilling and production process, pH and conductivity should be continuously monitored. Changes in these parameters may indicate water contamination from UOGD fluids which are often highly saline. This can be done relatively inexpensively, or (or free of cost if within EHP's service area) through EHP's CATTfish monitor project. CATTfish monitors (also available commercially from <http://store.cattfish.com/about-us.aspx>) measure water temperature and conductivity. These parameters will allow a resident to monitor their water for changes in water quality relatively easily and inexpensively (note that the CATTfish is a general screening tool and does not detect changes in other parameters). If a change occurs, then another complete chemical analysis can be conducted, to compare with the baseline measurements. Individuals can find appropriate laboratories through the Pennsylvania Department of Environmental Protection Accredited Lab Database, located on the website or at:

http://www.depreportingservices.state.pa.us/ReportServer/Pages/ReportViewer.aspx?/LABS/LAB_CERTIFICATION.

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