

# **Protocol for Water Monitoring at Oil and Gas Exploration and Production Sites**

## **Final Report, Prepared for EBSI**

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### **Introduction**

There is a compelling need for municipal and county governments to have requirements in place that help assure that oil and gas exploration and production are done in a way that are protective of local water resources and ecosystems while at the same time allowing for the economic benefits that such activities provide. Unfortunately, there is not a clear set of guidelines on where monitoring should occur, at what frequency, nor what kinds of geochemical analyses should be conducted. Different protocols have been proposed by various organizations or researchers, but these are not well vetted nor has a consensus emerged about which approaches are best. This makes it difficult for governments and policy makers to decide on what the best approaches are which can easily result in overly conservative and wasteful requirements, or even worse, inadequate or poorly protective requirements. This document is a first attempt to suggest options that would be appropriate for the monitoring of oil and gas operations in northeastern, New Mexico. The protocol breaks the issue down into four areas: (1) general comments about monitoring; (2) monitoring for impacts on surface waters during drilling and production; (3) monitoring for impacts on groundwaters during drilling and production; and (4) monitoring for hydraulic fracturing impacts. There is significant overlap between these areas, but there are unique aspects to each which are discussed below. The reader must also keep in mind that much of what is discussed here is based on scientific opinion because of a limited amount of testing and real world study of oil and gas impacts (especially with hydraulic fracturing) by regulatory and scientific bodies. Much of this uncertainty arises from the fact that there are many exemptions from federal environmental legislation for oil and gas development and because new and rapidly evolving enhanced production methods are emerging especially in the case of hydraulic fracturing. Recommendations are also based on existing protocols (e.g., EPA) related

to groundwater and surface water contamination in general and transferring these approaches to oil and gas exploration and production monitoring does have the benefit of decades of regulatory experience from similar water quality perspectives. Major sources of potential surface water and groundwater contaminants during exploration and production include drilling muds and fluids (e.g., lubricants and surfactants), hydraulic fracturing fluids (discussed further below), recovered fluids including a variety of hydrocarbons and organic compounds, formation waters and brines, and naturally occurring radioactive material (NORM). Although this protocol does not discuss a formalized environmental and human health risk assessment, it is adaptable to one and it should be noted that though the various chemicals and fluids used in exploration and production are potential hazards, there must be a route or pathway for the chemicals to the accessible environment (e.g., surface water or groundwater) before there is a real risk or impact. Therefore, one of the main goals of monitoring is to be able to detect connections between source or release areas to nearby surface waters or local groundwaters. Thus, monitoring does not necessarily need to include analyses of every potential contaminant, which would be cost prohibitive and wasteful given the hundreds of possible chemicals used during drilling and production, nor does it have to focus on hazardous chemicals. A way of thinking about monitoring is that we want to analyze for chemicals that are good tracers of drill site releases. What is desirable is to monitor for chemicals which have the greatest mobility to try and catch problems early, have low environmental background values, are specific to oil and gas development and production, have straightforward sampling and analysis requirements, and are low cost. There are currently no ideal analytes that meet all of these requirements, so multiple analytes are required. The question is which ones are most appropriate? Roback et al. (2011) reviewed multiple sources about what would be the most appropriate analyte list for monitoring and derived a list of recommended analytes (Table 1). Their list was based on recommendations by a variety of government agencies, and independent water quality testing firms and laboratories. Analytes selected were based on frequency of recommendations by these various entities.

Table 1. Recommended Analytes for Monitoring from Roback et al., (2011).

Alkalinity  
Arsenic  
Barium  
Calcium  
Chloride  
Gross Alpha/Beta (for all radioactivity, including Thorium, Potassium-40, Uranium-series decay products (e.g., Radon)  
Hardness  
Iron  
Magnesium  
Manganese  
Methane/Ethane  
Nitrate  
Oil/Grease (HEM)  
pH  
Selenium  
Sodium  
Strontium  
Sulfate  
Total Dissolved Solids  
Uranium  
Volatile Organic Compounds (VOCs, i.e., BTEX)

It is also useful to consider the kinds of chemical additives that are commonly used at the well site. Colborn et al. (2011) reviewed chemical additive information from eight different states including New Mexico and published a list of chemicals that are used most often as additives in different products. This list provides insights on what is likely to be used at a site keeping in mind that each well site can have different or new products and additives than what was listed by Colborn et al. (2011). There are additional complications in that many of these substances are introduced as solids or are not very mobile in the subsurface, so they would generally make poor choices as tracers of oil and gas impacts on water quality. We also do not know what

concentrations of additives are being used and there is a natural tendency for concentrations to decrease along flow paths because of mixing with unimpacted water.

Table 2 Chemicals found in the highest number of products used in natural gas drilling and development (from Colborn et al., 2011).

Crystalline silica, quartz

Methanol

Isopropanol (propan-2-ol)

Petroleum distillate, hydrotreated light

(2-BE) Ethylene glycol monobutyl ether

Bentonite

Diesel

Naphthalene

Aluminum oxide

Ethylene glycol

Sodium hydroxide

Barite (BaSO<sub>4</sub>)

Heavy aromatic petroleum naphtha

Crystalline silica, cristobalite

Mica

Sodium chloride

Crystalline silica, tridymite

Hydrochloric acid (HCl)

Glutaraldehyde

Xylene

Guar gum

Iron oxide (ferric oxide)

Potassium chloride

Table 2 (continued)

Potassium hydroxide

Xanthan Gum  
Fuel oil  
Hydrotreated heavy petroleum naphtha  
Limestone (calcium carbonate)  
Polyacrylamide/polyacrylate copolymer  
Sodium carboxymethylcellulose (polyanionic cellulose)  
Calcium hydroxide  
Crystalline silica (silicon dioxide)  
Ethanol  
Formic acid  
Graphite  
2-Ethylhexanol  
Acetic acid  
Asphaltite (gilsonite, hydrocarbon black solid)  
Butanol (n-butyl alcohol, butan-1-ol, 1-butanol)  
Calcium carbonate  
Calcium chloride  
Ethoxylated nonylphenol  
Ethylbenzene  
Petroleum distillate naphtha  
Propargyl alcohol (prop-2-yn-1-ol)  
Tetramethylammonium chloride

Quite a few of the more mobile chemicals of Colborn et al. (2011) are covered by the recommended list of Roback et al. (2011) in Table 1. Note that the VOC and Oil/Grease analyses in Table 1 would cover many of the organic solvent/hydrocarbon entries on Table 2. Table 1 also includes methane/ethane, gross alpha/beta, and uranium which Table 2 does not. These analyses are essential given that methane/ethane are mobile gases and that NORM is a relatively common byproduct of exploration/production.

As indicated earlier, monitoring can be initiated using a suite of tracers concept. However, if unexpected detections, or elevated concentrations are observed sometime during the monitoring schedule which point to a possible release or impact, then a more complete analytical protocol is warranted. More sampling and expanded analysis is needed so that the environmental and human health risks and general impacts to surface water or groundwater can be better understood. Such an enhanced sampling and analysis protocol should proceed in an expedited way. The expanded analyte suite will need to be determined based on the known or potential type of release and suspected pathway for the particular location/situation.

### **General Comments**

A detailed surface water/groundwater monitoring plan should be required for each drilling or production site. The plan should identify specific sampling locations, frequency of sampling, and the specific analytes that should be sampled for and measured. It should also include contingencies if a known or suspected release occurs. Baseline measurements before activities commence are absolutely critical because it is very difficult to assess potential impacts without a background reference condition. Establishing a pre-activity baseline is essential because most of the chemicals used in exploration and production are also used in other industries, in agriculture, or are naturally occurring. Multiple rounds of baseline measurements are needed especially for surface and shallow groundwaters (e.g., < 50 ft) where temporal variability in chemistry can be pronounced. A minimum of 1 year of quarterly sampling should be required. A single baseline sample collected within one year before site activity is appropriate for deeper groundwater systems. If funding can be obtained, a county-wide baseline survey can be a valuable supplement and reference point prior to active exploration and such surveys have the added benefit of independence since there is no relationship to a particular oil or gas company. Such a baseline survey can also be used to help establish other potential water quality impacts (i.e., those not related to oil and gas exploration and development) that have occurred or may occur in the future. Aside from field measured parameters (e.g., temperature, pH, Eh, alkalinity), analyses should be conducted using a certified laboratory following proper sampling and chain of custody procedures to reduce the risk of analysis quality being challenged. Where possible using EPA approved sampling and analysis protocols for RCRA/CERCLA/Clean Water Act type monitoring should provide the most defensible data sets. Roback et al. (2011) provide a good

overview of testing protocols and sources of such information. Approved sampling and analytical procedures for surface water and groundwater can be found at the U.S. Environmental Protection Agency web site ([www.epa.gov](http://www.epa.gov)).

While baselining provides an essential reference point, additional monitoring during and post-operation is also required to actually assess potential impacts. Threshold or trigger values for certain analytes can be used as decision points to drive further investigative actions or remediation activities. For example, the state of Colorado has issued orders that stipulate that if groundwater monitoring samples exceed 2 mg/L methane then compositional analysis and carbon isotope analysis (discussed later) is required to determine the gas type. If the gas is indicated as thermogenic (which implies a possible connection to oil and gas production) or if an intermediate signature between thermogenic and biogenic gas is found, then annual isotope testing is required. In addition, if methane concentrations increase by more than 5 mg/L between sampling periods or increases to more than 10 mg/L then actions must be taken to determine the source of the gas. An additional way of evaluating monitoring data for decision making is trend analysis (i.e., are concentrations of analytes that could be related to oil and gas production increasing?). Proper trend analysis goes well beyond simple visual inspection of a concentration time series and gets into a quantitative determination of whether a possible trend is statistically significant or not. If statistically significant increasing trends are found, then these can be triggers for action. Non-parametric (i.e., non-Gaussian or non-“bell-curve”) approaches such as the “Mann-Kendall” test are preferred ways to assess significance because these tests do not have as restrictive assumptions as more traditional parametric tests (which if used in the wrong situation can lead to misleading results). Helsel and Hirsch (2002) is an excellent reference on water chemistry trend analysis and geochemical statistical methods in general and is available through <http://water.usgs.gov/pubs/twri/twri4a3>. Specifying specific analyte triggers/thresholds and trend actions is beyond the scope of this report, but is a worthy area of future investigation.

### **Monitoring for Impacts on Surface Waters**

If surface waters are present near a well site then they should be monitored because the potential for surface water impacts are at least as large, and possibly larger, than the potential for groundwater impacts. The importance of surface water monitoring is demonstrated by a recent

finding in Colorado where 17% of the 2078 spills and slow releases that oil and gas companies have reported to state regulators over the past five years have contaminated groundwater (as reported by Finley, 2012). These spills and leaks were from surface and shallow sources which likely impacted the land surface and possibly surface waters before they contaminated groundwater. The type of monitoring discussed in this section focuses on surface based activities at a drilling or production site and the detection of impacts on nearby surface water bodies. Impacts on surface water related to the subsurface (e.g., groundwater discharges into surface water) are covered in later. There are typically large volumes of containerized liquids and open pits or ponds at a site which can potentially leak or spill and drain into a surface water body such as a pond, stream, or arroyo. Colborn et al. (2011) analyzed results from a study of six evaporation pits at well sites in New Mexico and found they contained forty different chemicals that carry some type of health hazard, and almost all of these were on the 2005 EPA CERCLA list and nearly 75% were on the 2006 EPCRA Lists of Reportable Toxic Chemicals. Colborn et al. (2011) did not report on the concentrations and risk levels of these chemicals, but their work does show there is a real potential for water quality impacts to surface waters (and groundwaters) through leaky pits or drill site spills. By having baseline (pre-activity) data from these surface water systems and monitoring during and after activities are completed detection of problems can be made. Note that because streams often flow across different properties and types of land, monitoring may need to be done at multiple locations along the stream channel (above and below the site). It is important to conduct a visual inspection of the site and determine if there are erosional or gully features connecting the site to the surface water bodies and to note if new ones have developed since last sampling. Such features can be used to help establish where to monitor and newly developed features are an indicator of possible impacts. Like the analyte list mentioned earlier there is no clear guidance about where surface waters should be sampled or how frequently. Santa Fe County Ordinance 2008-09 covering oil and gas development requires monitoring (including baseline monitoring) from all surface water locations within a three mile radius of the well site. Note that the Santa Fe ordinance does not specify whether surface water bodies are perennial or ephemeral. Three miles is somewhat arbitrary, but seems appropriate given the use of directional drilling and potential extent of induced fractures away from a well site. The ordinance recommends a frequency of annual sampling. However, surface water chemistry can vary significantly in time and thus annual sampling does not allow for

development of a proper baseline. In addition, should an unreported spill or leak happen it could go untreated for up to a year. Quarterly sampling is often recommended as a starting point for sites with established surface water contamination issues because it is frequent enough to capture much of the natural variability in chemistry to establish a good baseline and frequent enough to detect spill or pulse release events that mitigation can be implemented in a reasonable time. Therefore, this protocol suggests that all perennial surface water bodies within a three-mile radius of the well site be sampled quarterly as part of the preactivity baseline and that a minimum of three of these bodies or locations be sampled every six months while the well site is active. The three locations should be selected based on the site conditions and topography, and should be at locations which appear to be most vulnerable should a spill or leak occur. It is appropriate to sample multiple locations along the same stream if there appear to be multiple routes of surface flow from the well site. If there are insufficient numbers of perennial surface water bodies then sampling seasonal/ephemeral runoff in arroyos can be appropriate. Thus, arroyo sampling of flows can, and in some cases probably should, be included as part of the group of primary monitoring locations if the site conditions suggest that surface flows from the well site are most likely to enter an arroyo system. However, monitoring of ephemeral flows in systems like arroyos does present a challenging logistical problem. For example, does the Santa Fe ordinance imply that all arroyos in a 3 mile radius must be sampled? This kind of stipulation could be difficult to implement if there are many arroyos in the area. Also, given the climate of New Mexico, it is never a sure thing when an arroyo might flow enough for sampling and flow durations can be short. The variable nature of arroyo flows also suggests that baseline sampling might best be initiated two years before site activity, although this may not be possible in practice. Despite these difficulties, arroyos may be the main route for surface water contamination to travel off-site at many locations in north-eastern New Mexico and are known to be pathways for groundwater recharge. Identifying the best approach for addressing the arroyo monitoring issue requires additional discussion and investigation than can be done here. However, a strawman proposal would be to time arroyo sampling during two periods when flow is most likely, such as during spring flows and late summer thunderstorm periods, and to select up to three of the most vulnerable arroyos (based on surface topography) as monitoring locations. Thus, this report recommends what amounts to a 6 month surface water sampling protocol during drilling and production (assuming there is surface water present to sample). The

water monitoring plan should also contain a requirement for a final round of surface water sampling after a well has been plugged and abandoned. It is recommended that this round of monitoring should be conducted within 6 months after termination of activities at the well.

### Monitoring for Impacts on Groundwaters

As noted above, a significant percentage of oil and gas related spills and shallow releases in Colorado have contaminated groundwater. In one county, 40% of spills reached groundwater (Finley, 2012). If the additional possibility of groundwater impacts through deeper subsurface sources (e.g., through leaky casings, etc.) is considered, then the potential pathways for groundwater contamination increases further. Thus, monitoring plans need to be comprehensive and include both surface water and groundwater sampling. Mutz, (2012) compiled a review that shows the variety of groundwater (and surface water) monitoring approaches that various states are either implementing or proposing. None of these approaches are considered to be totally protective of groundwater resources and are best viewed as “hopefully sufficient” to detect most of the potential groundwater contamination problems related to oil and gas development. Implementation of something substantially more protective is likely to be cost-prohibitive. In other words, all of the current and proposed schemes for groundwater monitoring carry some risk that contaminants will not be detected by the particular approach. This partial protection situation thus places a premium on being smart about the kinds of tracers/analytes used and about where and when groundwater is sampled.

Specified groundwater monitoring areas described in Mutz (2012) range from 1,500 ft to 3 miles from the well site depending on the particular state or locality. Hydraulic fracturing zones and directionally drilled wells can be laterally extensive, and thus a 3 mile radius is not unreasonable. The typical RCRA approach of one up gradient and two downgradient wells/and or spring locations would be a minimum approach. Santa Fe county has taken a more protective approach in that all wells within a 3 mile radius should be sampled for baselining and at least 3 monitoring must be constructed. In the case of northeastern New Mexico the 3 mile radius makes sense given the fact that there may not be very many places where groundwater could be sampled. The stipulation of constructing new monitoring wells is also an interesting aspect because it acknowledges the fact that existing drinking water or other wells, while being of use for

baselining, are often poor wells for long-term monitoring. Not only might existing wells be in the wrong locations, such wells are often poorly constructed, have inadequate well-head protection, and it may not even be known how they were built, what the geology is like, or where the water is actually coming from. A modern monitoring well is generally superior in construction and there will be much more information about the well hydrogeology than is typical for an existing well. The problem with installing monitoring wells is expense. According to examples provided by Florentino (2012) a pair of shallow (< 25 ft) wells can cost between \$13K-\$15K, while a pair of deep wells (~300 ft) can cost \$80-\$100k. In New Mexico some aquifers are deep and a 300 ft well may not even reach important aquifer zones. From a technical standpoint, this report recommends construction of proper monitoring wells if none exist in the area. However, the cost issue is an important consideration and any decision about requiring new wells needs to be made at the local government level with appropriate stakeholder involvement.

A related and complicating issue is that multiple- or layered-aquifer systems are common in New Mexico. Examination of the available information on groundwater monitoring for oil and gas impacts suggests that this issue is an unaddressed gap. Most private rural wells are drilled into shallow aquifer systems that would be the first impacted by surface/shallow contamination, but would probably be poor locations to monitor deeper groundwaters that could be impacted by deeper sources of contaminants. Municipal and industrial wells (as well as some private wells) can utilize deeper groundwater and it is important to protect all fresh groundwaters. Thus, a prudent groundwater monitoring plan should include sampling from all of the major aquifer systems that are currently being utilized for water supply. This is another reason why a 3-mile radius is beneficial, because it provides increased opportunity that there may be wells in different aquifers. Another complication is whether saline/brackish aquifers should be monitored. These systems are common in New Mexico, though they are not typically currently utilized in any great way. They also likely lack existing wells for monitoring (completing wells in saline aquifers is generally avoided) and the already low water quality conditions suggests that a focus on fresh systems is most appropriate. However, if saline aquifer waters are being utilized or there are plans to do so, then monitoring of these systems can make sense.

Groundwater sampling schedules during drilling and production by various states and the proposed Environmental Defense Fund/Shell protocol are often dependent on drilling schedule/completion, and/or when stimulation procedures such as hydraulic fracturing are used (Mutz, 2012). Generally, sampling is required some months after completion/restimulation and one to five years after completion of the well. Others such as Santa Fe county specify annual sampling. This report recommends either annual sampling because of its simplicity, or sampling within one year of completion or any restimulation activity, and at least every 5 years while the well is still active. Groundwater flows are generally slow (especially compared to surface water) and a longer duration between monitoring periods seems appropriate for the majority of situations in northeastern New Mexico.

A final recommendation is that monitoring needs to continue after oil and gas wells are abandoned. This is especially important for groundwater because flow rates are generally slow and it may take years before contaminants reach a monitoring location. It is difficult to know how long monitoring should be done after the well has been abandoned because it greatly depends upon the flow rate to the monitoring well. In some aquifers appearance of contamination may take decades or more if the monitoring well is far from the drill site. Monitoring one year after abandonment should be a minimum, but to be more protective, monitoring after five or ten years would not be inappropriate for some aquifer systems. Therefore, the best approach would be to have, for example, the county hydrologist stipulate the post-monitoring protocol after consideration of the particular site/aquifer conditions/flow rates.

There does not appear to be a compelling reason to have a different analyte suite for groundwater than was proposed for surface water. One recommended addition to the analyte list in Table 1 would be ferrous iron ( $\text{Fe}^{2+}$ ). Ferrous iron is the reduced form of iron and there are many drilling additives which would impact the oxidation/reduction potential of the local groundwater (this condition is often described using terms such as redox, Eh, or ORP). Ferrous iron can be measured in the field using a simple field kit and field measurement is preferred because redox conditions can change quickly after sampling. Measuring ferrous and total iron in a sample gives a more useful picture of redox state than a measurement of Eh or ORP. A revised version of Table 1 is provided later in this report.

### Monitoring Hydraulic Fracturing Sites

This section focuses on water quality impacts as a result of the fracturing process and extends the monitoring required for surface water and groundwater discussed above. Substantial amounts of water are typically used during hydraulic fracturing which could potentially affect local water supplies. However, the water supply impact issue is beyond the scope of this protocol. One of the most visible water quality considerations at hydraulic fracturing sites is the release of natural gas (methane) into drinking water aquifers and surface waters. This is a controversial topic and it is not yet known how frequently this kind of problem occurs. Unfortunately, because methane is a dissolved gas it is much more difficult and expensive to sample and analyze than most other geochemical indicators. However, it is such a key potential contaminant and indicator of subsurface transport that it must be a priority analyte at hydraulic fracturing sites. One problem with methane is that there are many potential sources including wetlands, dairy farms, coal beds, and landfills. The multiple source issue means that a well-established methane baseline is critical. One related gas that occurs in the thermogenic methane deposits that are now being exploited through hydraulic fracturing is ethane and ethane/methane ratios can help determine which methane source is responsible for a detection or increase during monitoring (e.g., Aydin et al., 2011). Therefore, it is recommended that both methane and ethane be part of any hydraulic fracturing monitoring plan. The stable isotopes of methane can also be used to help differentiate between methane sources and could be considered as a supplementary analyte should elevated methane detections or concentration increases occur (see previous discussion regarding trigger examples for Colorado). Methane from natural gas (thermogenic) deposits have a different stable isotope composition than other sources which are generally of biogenic origin (Figure 1). Thus, the isotopes can be used as a way of “fingerprinting” methane to determine if the methane came from drilling/production or not. Two problems are that there are only a few laboratories capable of analyzing methane isotopes and analysis is expensive. Therefore, these analyses should be restricted to instances where source attribution is critical.

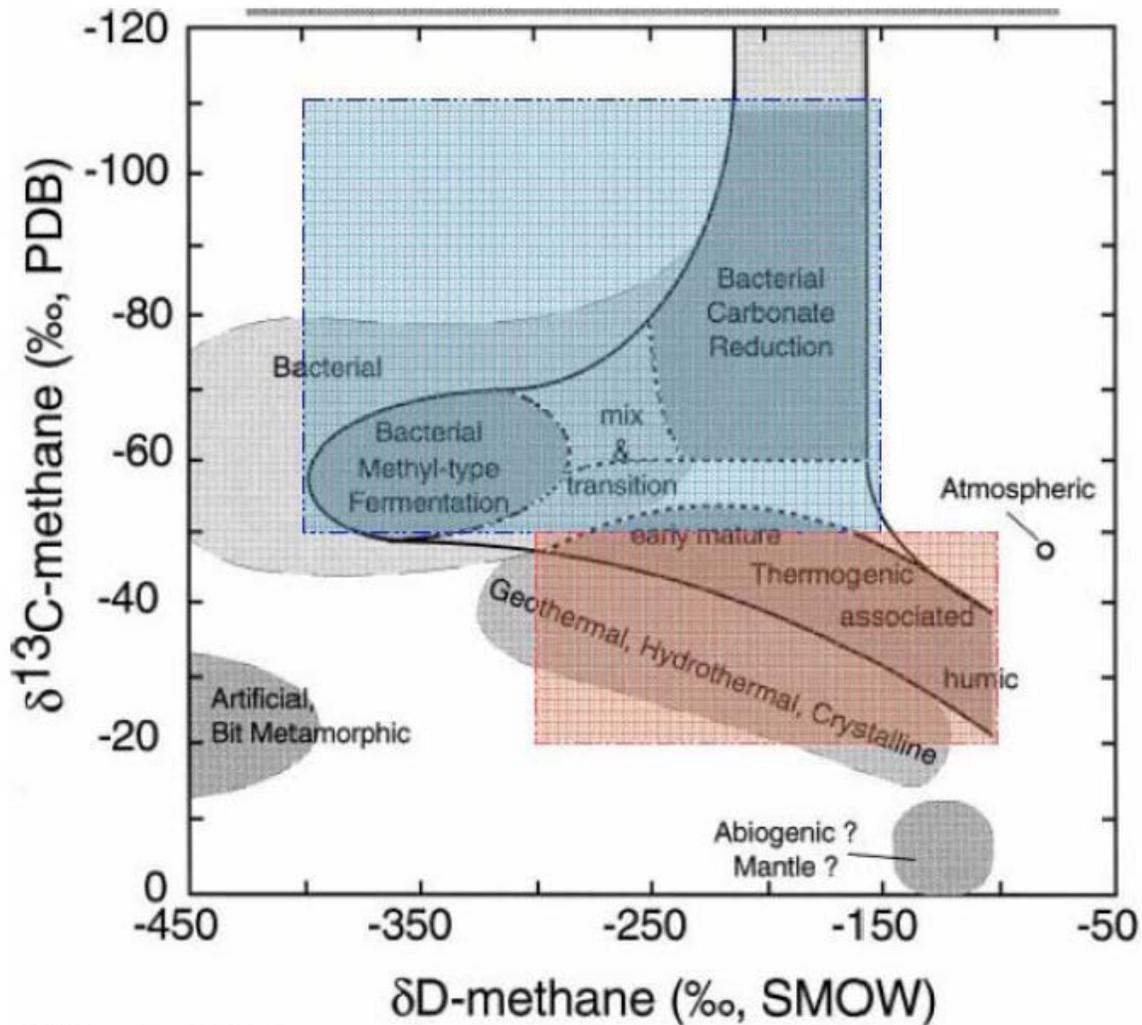


Figure 1. Isotope compositions of different methane sources. Biogenic methane tends to have more negative  $\delta^{13}\text{C}$  values compared to thermogenic methane. From Whiticar et al., 1999.

In addition to the release of methane and ethane, the fluids used for fracturing pose a water quality hazard. “Fracking” fluid is pumped down a well under high pressures in order to break the reservoir rocks so that natural gas can flow more freely to the well. Fracking fluids are generally about 99% water and sand and about 1% chemical additives. These additives can potentially impact groundwater through leaky casings or if upward gradients somehow cause the fracturing fluids to mix with an aquifer system. They can also potentially impact surface water through spills and pit leaks or if contaminated groundwater discharges into a surface water body. Therefore, it is prudent to also include analytes that can be used as indicators of fracturing fluid impacts. Some of these chemicals are included in Tables 1 and 2. Fracking fluids vary greatly in

chemistry, are adjusted based on the conditions of a particular well and may be proprietary mixtures. If the drilling company provides information about what the fracking fluids are then appropriate analytes can be selected based on that information. Some companies are voluntarily disclosing their fracking fluid components on FracFocus.org. An example is shown from a well in southwestern New Mexico in Table 3.

Hydraulic Fracturing Fluid Product Component Information Disclosure							
Fracture Date:	3/1/2012						
State:	New Mexico						
County:	Chaves						
API Number:	32-065-29186						
Operator Name:	Climarex Energy Co of Colorado						
Well Name and Number:	Boxer 3 Fed Com #1H						
Longitude:	-103.80160620231						
Latitude:	33.3484711488204						
Long/Lat Projection:	NAD83						
Production Type:	Oil						
True Vertical Depth (TVD):	8,782						
Total Water Volume (gal)*:	1,772,439						
Hydraulic Fracturing Fluid Composition:							
Trade Name	Supplier	Purpose	Ingredients	Chemical Abstract Service Number (CAS #)	Maximum Ingredient Concentration In Additive (% by mass)**	Maximum Ingredient Concentration In HF Fluid (% by mass)**	Comments
Fresh Water	Operator				100.00%	87.53621%	Density = 8.340
Ferchek 3C Acid	Halliburton				100.00%	1.63274%	Density = 8.970
15% ZCA Acid	Halliburton				100.00%	2.47385%	Density = 8.970
Premium White 20140	Halliburton				100.00%	5.22621%	Not Found in DB
Super LC - 20140	Halliburton				100.00%	2.76161%	Not Found in DB
LoSurf-300D	Halliburton	Non-ionic Surfactant	1,2,4 Trimethylbenzene	95-63-6	1.00%	0.00083%	
			Ethanol	64-17-5	60.00%	0.04986%	
			Heavy aromatic petroleum naphtha	64742-94-5	30.00%	0.02493%	
			Naphthalene	91-20-3	5.00%	0.00415%	
			Poly(oxy-1,2-ethanedyl), alpha-(4-nonylphenyl)-omega-hydroxy-, branched	127087-87-0	5.00%	0.00415%	
BE-9	Halliburton	Biocide	Tributyl tetradecyl phosphonium chloride	81741-28-8	10.00%	0.00207%	
FR-66	Halliburton	Friction Reducer	Hydrotreated light petroleum distillate	64742-47-8	30.00%	0.00521%	
SUPERSET W	Halliburton	Activator	Methanol	67-56-1	60.00%	0.01445%	
			Ethoxylated nonylphenol	Confidential Business Information	60.00%	0.01445%	
BC-140 X2	Halliburton	Initiator	Ethylene glycol	107-21-1	30.00%	0.01612%	
			Monoethanolamine borate	26038-87-9	100.00%	0.05374%	
D-AIR 1	Halliburton				100.00%	0.00000%	Not Found in DB
BP BREAKER	Halliburton	Breaker	Sodium persulfate	7775-27-1	100.00%	0.00034%	
OPTIFLO-HTE	Halliburton	Breaker	Crystalline silica, quartz	14809-60-7	30.00%	0.00116%	
			Walnut hulls	Mixture	100.00%	0.00386%	
WG-36 GELLING AGENT	Halliburton	Gelling Agent	Guar gum	9000-30-0	100.00%	0.16624%	
Ingredients Listed Below This Line Are Part of the Fluid Composition Provided by Halliburton Which Do Not Appear On the Material Safety Data Sheets (MSDS)							
			2,7-Naphthalenedisulfonic acid,	915-67-3			

		2-hydroxy-4-[[4-sulfon-1-naphthalenyl]azo] - sodium salt				
		Alcohols, C12-16, ethoxylated	68551-12-2			
		Ammonium chloride	12125-02-9			
		Bentonite, benzyl(hydrogenated tallow alkyl) dimethylammonium stearate complex	121888-68-4			
		C.I. Pigment Red 5	6410-41-9			
		Crystalline Silica, Quartz	14808-60-7			
		Cured Acrylic Resin	Confidential Business Information			
		Cured Acrylic Resin	Confidential Business Information			
		Enzyme	Confidential Business Information			
		Oxyalkylated Phenolic Resin	Confidential Business Information			
		Oxyalkylated Phenolic Resin	Confidential Business Information			
		Polyacrylamide Copolymer	Confidential Business Information			
		Silica gel	112926-00-8			
		Sodium chloride	7647-14-5			
		Sodium sulfate	7757-82-6			
		Sorbitan monooleate polyoxyethylene derivative	9005-65-6			
		Sorbitan, mono-9-octadecenoate, (Z)	1338-43-8			
		Surfactant Mixture	Confidential Business Information			
		Surfactant Mixture	Confidential Business Information			
		Tall oil acid diethanolamide	68155-20-4			
		Water	7732-18-5			
<p>* Total Water Volume sources may include fresh water, produced water, and/or recycled water  ** Information is based on the maximum potential for concentration and thus the total may be over 100%</p> <p>Ingredient information for chemicals subject to 29 CFR 1910.1200(i) and Appendix D are obtained from suppliers Material Safety Data Sheets (MSDS)</p>						

Table 3. Hydraulic fracturing fluid description from a Chavez County, New Mexico well. Downloaded from FracFocus.org 11/9/2012.

Typical hydraulic fracturing fluid additives include various acids, sodium chloride, polyacrylamide, ethylene glycol, borate salts, sodium/potassium carbonate, glutaraldehyde, guar gum, and isopropanol (DOE and GWPC, 2009). Some of these have attributes that make them good candidates for indicating hydraulic fracturing impacts. For example, according to Table 2, potassium is commonly used in drilling fluids and is a relatively easy chemical to sample and analyze. Borate salts are also included in Table 2. These salts are typically soluble which increases boron concentrations in solution. Most natural waters have low boron concentrations and thus, boron along with potassium would be good to add to those in Table 1 when monitoring sites where hydraulic fracturing is being done. Because a well can be used for fracturing multiple times, the monitoring schedule would need to be modified to account for multiple hydraulic fracturing jobs.

There are other potential tracers/analytes that could be of use for monitoring hydraulic fracturing sites. Radon-222 is a naturally occurring noble gas isotope that can co-migrate with methane and can be analyzed in water or in air. However, additional research is required to establish how

useful radon might be. Another potentially useful tracer pair includes the stable isotopes of water ( $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ ). Very large volumes of water are often pumped into the subsurface as part of the hydraulic fracturing process. If this water has different  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values than the local groundwater and dilution is not too extreme, then the hydraulic fracturing related water could be detected in an aquifer. These stable isotopes have minimal preservation requirements and are relatively inexpensive to analyze. Some organizations do include them as part of their general water quality analyte list.

### Summary

Until better guidance on surface water and groundwater monitoring at oil and gas exploration and production is developed the best course of action appears to be to follow EPA protocols for contamination monitoring under RCRA/CERCLA. The establishment of monitoring wells at one location upgradient and two locations downgradient of the well site approach appears to be a good protocol for groundwater monitoring (although the number of monitoring wells may need to be increased to address layered aquifer systems). Likewise, where possible, having three surface water sampling locations is recommended. One full year of quarterly baseline measurements should be included in the site monitoring plan for surface water and shallow groundwater. One baseline sample from any deeper groundwater monitoring locations within one year prior to the start of drilling should also be included. The choice of analytes is a difficult one given the wide range of chemicals that are used or present in drilling fluids and produced fluids. A reasonable starting place is Table 1 with a few additions. The full suite of recommended analytes is provided below in Table 4. This would be a minimum suite and additions to the Table 1 list are noted in Table 4. The cost of conducting a round of sampling using a list such as this is not trivial. Florentino (2012) estimated laboratory and labor costs based on the proposed new Colorado protocol (see Mutz, 2012) to be around \$4,200 per production well. This estimate is based on only two groundwater monitoring locations and does not include surface water monitoring. As more information and knowledge is gained about the risks of oil and gas contamination, the target analyte list in Table 4 could be significantly reduced which would moderate implementation costs substantially.

Table 4. Expanded list of analytes for surface water and groundwater monitoring. Additions to the Table 1 list are highlighted by an \*.

Alkalinity

Arsenic

Barium

\*Boron

Calcium

Chloride

Eh/ORP

Gross Alpha/Beta (for all radioactivity, including Thorium, Potassium-40, Uranium-series decay products (e.g., Radon))

Hardness

Iron Total

\*Ferrous Iron

Magnesium

Manganese

Methane/Ethane

Nitrate

Oil/Grease (HEM)

\*Potassium

pH

Selenium

Sodium

Strontium

Sulfate

Total Dissolved Solids

Uranium

Volatile Organic Compounds (i.e., BTEX-Benzene, Toluene, Ethylbenzene, Xylenes)

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