Simple and economical testing of groundwater for contamination due to nearby drilling activities

White Paper

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Abstract

This project defines a simple water analysis kit suitable for ground water measurements of possible residuals caused by the hydraulic fracturing process or other industrial or agricultural operations in the area. The portable laboratory kit will be customized for Texas A&M county extension agents located in the Eagle Ford shale region in Texas. It will be a simple, portable method for the agents to analyze surface and ground water and obtain instant data about the water quality. The test kit will analyze between 15 to 19 parameters that could potentially determine groundwater contamination due to hydraulic fracturing. The estimated cost per test, which includes the 15 to 19 parameters, is approximately $6 to $10 per test after the initial capital equipment is purchased

The test kit is not intended to pinpoint the source of any contamination. Rather it is intended to be a screening tool for further, more quantitative analysis. It is envisioned, that based on the results of the test kit, the landowner will have information necessary to determine if additional testing is required. It is also designed to allow the land owner or extension agent to perhaps narrow the range of parameters that may need to be investigated.

Introduction

The rapid expansion of gas shale drilling in the U.S. has created public concerns Regarding potential contamination of ground water resources. High performance completion employing multi-stage hydraulic fracturing process requires large quantities of water mixed with chemical additives to enhance the production of oil and gas from underground reservoirs. After fracturing, much of the fluid that returns to the surface is referred to as either “produced water” or “flow back fluid”. Flow back brines may contain a portion of the final volume of injection brine used to place fracturing fluids while produced water is the brine water naturally occurring in the reservoir.

Because concerns have been raised regarding the release of these fluids into the environment, GPRI has set out to identify a simple water analysis kit for Agrilife Extension agents to evaluate

their constituent's ground water for any possible residuals caused by the hydraulic fracturing process or any other industrial operation or management practice. Analytical data generated by the water analysis kits should allow Agrilife Extension agents to make informed decisions on possible relationships between the water quality and hydraulic fracturing operations in the area, if any, and to make informed decisions on what action is required to address contamination, including further analysis to determine the source of the contamination.

Process

Hydraulic fracturing utilizes fluids to create or restore small fractures in a hydrocarbon bearing formation in order to stimulate production from new and existing oil and gas wells. These fractures create paths that increase the rate at which gas and fluids can be produced from the reservoir formations, in some cases by many hundreds of percent. Great efforts are taken to ensure that neither the fluid pumped through the well, nor the oil or gas that will be collected, enters a potential water supply. To accomplish this, steel surface or intermediate casings are inserted into the well to depths of between 1,000 and 4,000 feet. Protection of aquifers as sources of usable water is the main objective of casing and cementing requirements. Such protection is provided from drilling fluids, methane leakage during drilling, and fracturing fluids during hydraulic fracturing. The space between these casing (strings) and the drilled hole (wellbore) is called the annulus and is filled with cement to prevent migration of fluids into unintended subsurface areas. After the casing is set and analytical measurements are taken to ensure the integrity of the casing, high volumes of fracturing fluids are pumped deep into the well at pressures sufficient to create or restore the small fractures in the reservoir rock needed to make production possible (Fracfocus.org).

It should be noted that previous investigations have suggested that water quality changes observed in water wells during nearby shale gas operations may be due to mobilization of constituents that were already present in the wells. Seismic pulses and vibrations due to drilling machinery often disturb the well and as a consequence, accumulated particles of iron as well as other materials on the casing wall and well bottom may become agitated into suspension causing changes in color (red, orange or gold), increasing turbidity, and release of odors in the water.

The Texas County Extension Agents are a group of professionals employed by the state and have the primary responsibility of educating the agricultural community on various issues in the community. Their mission has remained unchanged for almost a century and is to serve state residents through community-based education. Their goal is to define specific concerns of the residents of their regions and to collect and disseminate available information to the community so that they are better prepared to make informed decisions to address those issues . To accomplish their goals, County extension agents have offices in over 250 counties in Texas and work hand-in-hand with its Texas A&M System partners, the State Legislature, and local communities. The agents depend on the residents for input and program delivery and custom-design their programs for specific areas of the state.

The county extension agents of the Eagle Ford Shale area are currently responding to the residents' concerns of drilling and hydraulic fracturing and the potential effect these processes have on the groundwater they rely on for agricultural purposes. It is also important to note that a water's taste, smell, or color is not necessarily an indicator of water quality. Many of the most hazardous contaminants are undetectable to the senses. The only way to detect most pollutants is by testing for them" (Fracfocus.org). Historically the extension agents often assisted residents with water quality issues by having them collect water samples in an easily acquired sterile baby bottle and refer landowners to laboratories to test their water. The land owners are assessed a a small partial recovery fee such as $10 per test, help defray the costs of the analysis. However, because of the expense of these analytical tests by commercial laboratories, only a limited number of parameters were investigated limiting the effectiveness and usefulness of the testing program. In addition, many counties currently do not have access to adequate and affordable testing services.. If the Extension Agents had access to a relatively simple and inexpensive water quality testing kit, this could function as an analytical tool for them to utilize to gather water quality information and assist their constituents to make informed decisions in a reasonable time frame and at an affordable cost. The portable laboratory kit would be customized for extension agents located in the Eagle Ford shale region in Texas. It would need to be a simple, portable method for the county extension agents to analyze surface and ground water and obtain instant data about the water quality.

Ideally, the proposed test kit will analyze between 15 to 19 parameters that could potentially determine groundwater quality. The estimated cost per test is approximately $6 to $10 per test after the initial capital equipment is purchased. This portable water kit is designed to be used by county extension agents either in the field or in the office. An elevated test result for a single parameter would not necessarily mean a positive association with drilling or hydraulic fracturing because agricultural runoff or other chemicals may naturally occur in the water. However, an elevated test result for several parameters may suggest that further testing may be appropriate. Additionally, the collection of baseline data before production activities commence should strengthen any correlation analysis if there is a concern that future activities are affecting the water quality.

It is important to note, that the test kit is not intended to determine, with any degree of certainty, the source of any contamination. Rather it is intended to be a screening tool for further, more robust quantitative analysis. It is envisioned, that based on the results of the test kit, the landowner will have information necessary to determine if additional testing is required. It is also designed to allow the land owner or extension agent to perhaps narrow the range of parameters that may need to be investigated.

The following testing parameters should be tested using this kit:

Acidity – High measurements of acidity in the water may indicate a connection to Oil and Gas drilling or other agricultural activity. High acidity may be due surface spills of chemicals as groundwater contamination would be diluted and not easily detectable. Pesticide sprays, fertilizer runoff, acid rain, and rock formations such as limestone are among other causes of high acidity in water.

Alkalinity – Alkalinity is a measure of the capacity of water to neutralize acids, low measurements of alkalinity may be caused by industrial waste. Alkalinity may also deplete due to acids from de-nitrification.

Ammonia – Ammonia is used in hydraulic fracturing as a breaker to make it easier for the fluid to flow to the borehole. The reaction between the breaker in the formation produces ammonia which is sometimes found in produced water. Ammonia is a product of the microbiological decay of animal and plant protein and may also be products of agricultural activities such as fertilizers.

Barium – Barium is sometimes found in produced water because drilling mud sometimes contains barium as weighting agents. Trace amounts of barium could also be naturally occurring in groundwater. Barium and its compounds can be found in pigments, rat poisons, fireworks, and are used in rubber making, and x-ray photography.

Chlorides – Chlorides (Cl^{-}) commonly found as sodium chloride or "salt" is always present in oil field brine at higher concentrations than a potable water supply. . Chloride is also found in flow back fluid. Spills of flow back fluid in the surface are often the cause of high amounts of chloride in the soil and ground water surrounding the spill. Almost all natural water contains some amount of chlorides. Other causes of chloride getting into water include agricultural runoff, rocks containing chloride, and effluent water from wastewater plants.

Chromium – Chromium is sometimes found in flow back fluid and is sometimes used in drilling mud. Chromium occurs in nature mostly as chrome iron ore and is widely found in soils and plants. Chromium found in waters usually enters a water supply through industrial wastes from metal plating baths and from industrial cooling towers where chromate is used to inhibit metal corrosion.

Conductivity/TDS – Conductivity will measure the amount of salt and Total Dissolved Solids in the water. Flow back water often has high amounts of salts and material that causes increased levels of TDS. Excess salinity in the water is harmful to both livestock and irrigation. TDS levels are also impacted by drainage from abandoned coal mines, storm-water runoff, and discharges from water treatment plants.

Dissolved Oxygen - Adequate dissolved oxygen is necessary for good water quality. Oxygen scavengers are sometimes used in hydraulic fluid to prevent degradation of steel well casing. Dissolved oxygen levels may be low due to agriculture run off or due to other chemicals in the water.

Hardness – Monitor for changes in the water's hardness

Iron – Iron is not a characteristic of fracturing or flow back fluids. Iron found in the water may be due to rocks and soils containing iron.

Nitrate - Presence of Nitrate may also indicate water contamination due to agricultural activity indicate biological wastes in the final stages of stabilization, or run-off from fertilized fields.

Nitrite - Nitrites are often used as corrosion inhibitors in industrial process water and cooling towers and is also used as preservatives in the food industry. Nitrites readily oxidize to nitrates and not often found in surface waters. The presence of large quantities of nitrites indicates partially decomposed organic wastes in the water being tested.

pH – Low pH levels indicates possible unsafe water

Phosphorus – Levels of phosphorus are sometimes found in flow back fluid. Other sources of phosphorus include industry and water treatment plants, fertilizer runoff, and septic tanks.

Sulfate –A by product of the some of the reactions taking place in the wellbore while hydraulically fracturing. Sulfate is sometimes found in low concentrations in flow back fluids. Some soils and rocks contain sulfate minerals and as groundwater moves through these, some of the sulfate is dissolved into the water.

Turbidity – Turbidity measures the water's cloudiness which may be caused by a variety of factors such as amount of bacteria, clay, silt, and other sediments in the water as well as by nearby industry or storm water pollution.

Based on an investigation into commercially available water test kits, and a comparison in terms of functionality, ease of use, acceptance by other organizations and groups as well as cost, it is recommended that the Hach CEL/850 aquaculture Laboratory kit, with the addition of reagents for the analysis of sulfate and chromium, be used by the county agents to test for groundwater quality. Utilizing this kit will greatly assist county extension agents and landowners to efficiently and affordably test the agricultural water for the presence of hydraulic fracturing contamination. If a set number of the parameters indicate high presence of chemicals, then it is suggested that a full laboratory test is conducted. If most of the parameters indicate low to no presence of chemicals in the water, then presence of hydraulic fracturing contamination is unlikely. The results of this kit have the potential to save landowners significant resources from unnecessary analytical testing from commercial laboratories. Additionally, land owners may be be more willing to test the water on their land using this kit rather than going to a laboratory because tests using the kit are a fraction of the cost of conducting a full laboratory cost.

Conclusion

The parameter list suggested in this report, are the most practical constituents to test for in terms of convenience and cost for a plausible connection between groundwater contamination and hydraulic fracturing. The modified Hach CEL/850 aquaculture Laboratory kit is meant to serve as a screening tool to determine whether further investigation, by an accredited laboratory, is warranted. Using the suggested scoring rubric below, Agrilife extension agents can use the data generated from the analysis to make the determination of what action to take. . The suggested scoring rubric uses a point system to assign values of correlation of a contaminant to hydraulic fracturing activity. For example, chromium, an element commonly found in hydraulic fracturing but not usually found naturally in the environment and would receive a higher point value than nitrate, which is often found in fertilizers applied to the soil. Finding high amounts of chromium does not necessarily indicate that nearby hydraulic fracturing activities are the direct causes of a contamination because industrial waste from a nearby hypothetical steel coating factory may be a possible source. By the same token, finding high amounts of nitrate also does necessarily correlate with applied fertilizer being the source of the contaminant either. The point value given is based on the concentration of the contaminant in the sample and its association with hydraulic fracturing fluids. Factors taken into account are that the contaminated water would probably be

diluted when mixing with existing ground water. Most parameters will be given up to three points, while some will be given only one or two points depending on the probability of correlation. When summing the points derived from the rubric, the final number of points will determine whether or not further testing is suggested. The maximum points a sample of water can get is thirty eight. The closer to thirty eight the water is, the higher probability that the water will need to be tested by a certified laboratory for a full range of tests. It is important to note however that the numbers of the scoring rubric are nominal and that further research is needed to more accurately determine the values assigned to the individual parameters.

The cost per test using the water testing kit is relatively inexpensive and accurate and should yield values with sufficient precision to make a determination as to the need of further investigations. A certified laboratory would be able to test for many more contaminants with better accuracy, but may have a significant cost for a full range of tests. Using the modified Hach CEL/850 aquaculture Laboratory kit water testing kit, Agrilife extension agents will be able to alleviate constituents concerns that their water is contaminated with hydraulic fracturing fluid. Since this kit is affordable, an extension agent would be able to test many more groundwater samples than was previously able to while saving time and money. If a low score is given on the worksheet sample, then the landowner may not have to purchase a full laboratory test. If a high score is given, it is suggested that the landowner proceed to the next level of testing in the county. If a landowner is concerned about their water being “different than normal” the kit will help identify, if any, what contaminant is present in high amounts in the water and what factors contribute to that contamination that way the landowner may identify causes of water contamination.

Test Results

In order to test the validity of the kit, a simulated contaminated water sample was analyzed using modified Hach CEL/850 aquaculture Laboratory kit with the parameters described earlier. A 5 ml sample of produced water obtained from Advanced Hydrocarbons was diluted 20:1 with 100 ml of deionized water was tested. Tap water from the School of Rural Public Health laboratory at Texas A&M University and surface water from the golf course at Texas A&M were also tested. The full suite of parameters with the exception of barium and chromium due to unavailability of

reagents in the lab was conducted on the sample. The testing of the water took approximately 90 minutes for each water sample which did not include setting up or cleaning. The following table summarizes the results of the tests kit.

Parameter	*5/100 dilution Pr. Water*	*Surface Water*	*Tap water*
Acidity	57 mg/L	207 mg/L	110 mg/L
Alkalinity	71 mg/L	830 mg/L	380 mg/L
Ammonia	1.25 mg/L	0 mg/L	0 mg/L
Barium			
Chlorides	1170 mg/L	254 mg/L	105 mg/L
Chromium			
Conductivity	12.16uc		
TDS	6.1 mg/L	12.7 mg/L	3.7 mg/L
Dissolved Oxygen	8.8 mg/L	8.4 mg/L	8 mg/L
Hardness	222 mg/L	132 mg/L	355 mg/L
Iron	0.53 mg/L	0 mg/L	0.03 mg/L
Nitrate	3.5 mg/L	2.1 mg/L	1.2 mg/L
Nitrite	0 mg/L	.010 mg/L	.002 mg/L
pH	7.3	7	8.25
Phosphorus	0.19 mg/L	2.29 mg/L	.76 mg/L
Sulfate	1 mg/L	164 mg/L	7 mg/L
Turbidity	18 FAU	2 FAU	

Table 1

The data generated was input into the chart below to derive a rubric that indicates a positive correlation in a sample that is known to be contaminated with produced water. It is important to note that results of the rubric may vary depending on water source and contaminants. For this reason, the scoring rubric's numbers are nominal but may serve as a starting point for extension agents in making a determination if further investigation is warranted. The initial test resulted in

a score of 17 out of 32 (due to chromium and barium being taken out) for the diluted produced water, 9 out of 32 for the surface water, and 8 out of 32 for the tap water. The 17 for the diluted produced water would be suggestive of contamination due to drilling activity according to the rubric and the tap and surface water received relatively low scores which would not be suggestive of drilling contamination. Depending on how close to the source the contamination is, a higher or lower score would have been achieved. Agrilife extension agents are advised to make decisions on each test independently and to take into account local external factors such as other contamination sources nearby, that may affect the score.

Water Testing Paramter Rubric						
Parameter Tested	**Parameter Ranger**	Give **1 point**	**Parameter Ranger**	Give **2 points**	**Parameter Ranger**	Give **3 points**
Acidity	15-30 mg/L		Greater than 30 mg/L			
Alkalinity	50-70 mg/L		Greater than 70 mg/L			
Ammonia	.25-0.5 mg/L		.5-1.0 mg/L		Greater than 1 mg/L	
Barium	0.5 - 1.5 mg/L		1.5 - 3.5 mg/L		Greater than 3.5 mg/L	
Chlorides	300- 500 mg/L		500- 700 mg/L		Greater than 700 mg/L	
Chromium	.05 - .15 mg/L		.15 - .35 mg/L		Greater than .35 mg/L	
Conductivity/ TDS	300-500 mg/L		500-1000 mg/L		Greater than 1000 mg/L	
Dissolved Oxygen	Less than 15 mg/L		Less than 10 mg/L		Less than 5 mg/L	
Hardness	100-200 mg/L		Greater than 200 mg/L			
Iron	.25 - .5 mg/L		.5 - 1 mg/L		Greater than 1 mg/L	
Nitrate	Greater than 25 mg/L					
Nitrite	Greater than 3 mg/L					
pH	5.0 - 6.5		Below 5			
Phosphorus	2-3 mg/L		3-4 mg/L		Greater than 4 mg/L	
Sulfate	100-200 mg/L		200-300 mg/L		Greater than 300 mg/L	
Turbidity	Greater than 15 FAU					
Add Column Totals						
					Total Points =	

Water Kit Paramters				
Parameter	Maximum recommended amounts for drinking water	Maximum amounts for Agricultural use	Human affects	Livestock affects
Acidity	Not Established			
Alkalinity	Not Established			
Ammonia	1.5 mg/L		Health based guidelines not derived	
Barium	2 mg/L		Increased blood pressure	
Chlorides	250 mg/L		Health based guidelines not derived	
Chromium	0.1 mg/L or 100ppb	1mg/L	severe acute affects may occur if the ingestion of greater than 1-5g of chromate	Causes skin and soft tissue problems.
Conductivity	0.4 - 0.85 micromoles/cm		-	
TDS	500 mg/L			
Dissolved Oxygen	-			
Hardness	500 mg/L is extremely Hard			
Iron	0.3 mg/L			
Nitrate	10 mg/L	25 mg/L	Infants below 6 months could become ill	
Nitrite	1 mg/L	3 mg/L	Infants below 6 months could become ill	
pH	6.5-8.5			
Phosphorus	5 mg/L			
Sulfate	250 mg/L	300 mg/L		
Turbidity	1 NTU		Short term symptoms such as nausea, cramps, diarrhea, and headaches	

Works Cited

Abdallah, Charles, comp. "Water's Journey Through the Shale Gas Drilling and Production Processes in the Mid-Atlantic Region." *Penn State Cooperative Extension* (n.d.): n. pag. Web.

Alkire, Deke. "Livestock Water Guidelines." *The Samuel Roberts Noble Foundation* (n.d.): n. pag. Print.

Burnett, David, and Zachary Bateman. *Hydraulic Fracturing and Brackish Groundwater Desalination*. N.p.: Texas A&M - GPRI, n.d. Print.

"Chemical Hazards in Drinking-water." *WHO*. N.p., n.d. Web. 2 Aug. 2012. <http://www.who.int/water_sanitation_health/dwq/chemicals/en/>.

Faries, Floron, John M. Sweeten, and John C. Reagor. "Water Quality: Its Relationship to Livestock." *Texas Agricultural Extension Service* (2011): n. pag. Print.

Gibbons, Dayna. "The Potential Impacts of Hydraulic Fracturing on Drinking Water Resources." *EPA Science in Action* (n.d.): n. pag. Print.

Guy Fipps. *Irrigation Water Quality Standards and Salinity Management Strategies*. N.p.: Texas Cooperative Extension, n.d. Print.

"Home | FracFocus Chemical Disclosure Registry." *Home | FracFocus Chemical Disclosure Registry*. N.p., n.d. Web. 2 Aug. 2012. <http://fracfocus.org/>.

Johnson, Roxanne, and Tom Scherer. *Drinking Water Quality: Testing and Interpreting Your Results*. N.p.: NDSU Extension Service, n.d. Print.

Molofsky, Lisa, and Albert Wylie, Jr. "Methane in Pennsylvania Water Wells Unrelated to Marcellus Shale Fracturing." *Exploration & Development* (2011): 54-67. Print.

Mukhtar, Saqib. "Water Quality Guide for Livestock and Poultry." *Texas Agricultural Extension Service* (n.d.): n. pag. Print.

Office of Research and Development. "EPA's Study of Potential Impacts of Hydraulic Fracturing on Drinking Water." *EPA Science in Action* (n.d.): n. pag. Print.

Palacios, Virginia. *BASELINE GROUNDWATER QUALITY TESTING NEEDS IN THE EAGLE FORD SHALE REGION*. Thesis. Duke University, 2012. N.p.: n.p., n.d. Print.

"Pavillion." *EPA*. Environmental Protection Agency, n.d. Web. 2 Aug. 2012. <http://www.epa.gov/region8/superfund/wy/pavillion/>.

"Preventing Mother-to-child Transmission of HIV in Swaziland." *WHO*. World Health Organization, n.d. Web. 2 Aug. 2012. <http://www.who.int/en/>.

Twort, A. C., D. D. Ratnayaka, and M. J. Brandt. *Water Supply. 5th Ed.* London: Arnold and IWA Pub., 2000. Print.

"US Environmental Protection Agency." *EPA*. Environmental Protection Agency, n.d. Web. 2 Aug. 2012. <http://www.epa.gov/>.

"Water Testing." *Water Testing*. N.p., n.d. Web. 10 Aug. 2012. <http://www.testthewater.com/pages/farms.html>.

Waxman, Henry A. United States. Energy and Commerce. *Chemicals Used in Hydraulic Fracturing*. 112th Cong. Cong. Rept. N.p.: U.S. Congress, 2011. Print.