From: Glenn C Miller
Sent: Monday, April 15, 2013 6:41 PM
To: Hanlon, Edward
Subject: Comments on Hydraulic Fracturing

Dear Mr. Hanlon,

Dave Dzombak indicated that the proper method for offering contributions to the EPA Hydraulic Fracturing Research Advisory Panel is to submit them to you. Attached is a cover letter and an extended abstract that Ann Maest and I presented at an EPA workshop on hydraulic fracturing at RTP in February of 2013. I included a PDF of the extended abstract and a WORD version.

Let me know if you have any questions.

Sincerely,

Glenn

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April 15, 2013

Mr. Edward Hanlon
Designated Federal Officer
USEPA Science Advisory Board (1400R)
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Washington, D.C. 20460

Dear Mr. Hanlon,

I have learned from Professor Dave Dzombak that you are the appropriate person at EPA to submit comments on Hydraulic Fracturing to be included in the formal comments on the EPA Hydraulic Fracturing Research Advisory Panel. As you are aware, Dr. Dzombak is the chair of this Panel.

I have been working with the Natural Resources Defense Council (NRDC) for the past three years on the New York SDEIS on Hydraulic Fracturing, as well as on a specific water quality problem associated with hydraulic fracturing in Dimock, Pennsylvania. It appears that the water quality in at least two Dimock wells has substantially deteriorated, and is associated with hydraulic fractured gas wells near these drinking water wells. The well drilling and hydraulic fracturing were done by Cabot Oil and Gas Corporation. The EPA has also taken a series of water samples from these wells, and after I examined the EPA data, I initially concluded that there was not much of a problem with the water, except for slightly elevated iron and manganese- but, no elevated chloride, no medium weight organics, no fracturing additives (e.g. ethylene glycol).

However, when NRDC attorneys pressed me and sent a large series of analytical reports, it became clear that one of the wells had a serious problem with iron, manganese and aluminum. The pH was over 9 (highest 9.8) and contained sulfide intermittently. It also contained saturation concentrations of methane of 28 mg/L (+/-). But, the chloride concentrations were relatively constant- at least there was not a consistent rise in chloride concentrations, which would necessarily be required if the wells were contaminated with produced or flowback water.

Since we have long been working on using SRB systems for acid mine remediation at the Leviathan Mine in Alpine County, California, it occurred to me that perhaps the methane leak in the Ely well (established as a Marcellus source using isotope data) may be stimulating SRB activity in the groundwater, and a brief look into the literature indicated that indeed, natural gas can be used by an SRB consortium. After going back to the data set, I became convinced that SRB activity could explain the substantial degradation of

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water quality in the Ely's (the affected family) drinking water well. Although only one pre-frac sample was available, it indicated very good quality water- neutral pH, and low iron, manganese and aluminum. Within six months, the pH had gone up to over 9, iron in the 1-15 mg/L range, elevated manganese, intermittent sulfide and saturated methane. The ORP was at times negative, which could have resulted in reduction of iron and manganese oxides to soluble forms. The aluminum is likely related to the high pH. I have included an extended abstract that Ann Maest and I presented for a recent EPA workshop on hydraulic fracturing at RTP that discusses this issue a bit more and presents the data (condensed) obtained by Cabot.

I have heard many concerns from the public on mixing of the very poor flowback and produced water with drinking water aquifers, but have yet to see this as a common problem. However, from anecdotal accounts (and the Dimock data in the extended abstract) I have frequently heard of water becoming "sulfury" and turbid (iron and aluminum precipitation on contact with air) and even a black (FeS) coloration to the water. The accounts of methane migration to aquifers are common, although I do not have much data on the extent of gas leaks in each state. But, they are apparently much more common than extensive mixing of produced or flowback water with drinking water aquifers. Thus, I am suggesting that a currently unrecognized groundwater impact from fracking is leakage of natural gas to an aquifer, followed by stimulation of SRB activity. It is not unreasonable to assume that SRB's are present nearly everywhere, and the literature (see the extended abstract) does indicate that SRB's can utilize natural gas. While methane really does not have many toxicological implications directly, the SRB activity will make the water undrinkable, and the aquifer will be impacted, until the leak is stopped and the aquifer re-aerated.

I suggest that this issue deserves additional focus, since gas leaks during fracturing are common. If it is a general problem, then it also makes an additional compelling argument to obtain pre-fracturing water quality in a wider area of a well field, and also provides an additional compelling argument that careful well construction is even more important to ensure that the well casing is sealed properly. Also of interest would be the consortium of bacteria that would be needed to utilize methane (or other components of natural gas), and the time lags for stimulation of a sufficient population to affect groundwater.

I thought this might be of interest in the panel discussions. Let me know if any additional information might be helpful.

Sincerely,

Glenn C. Miller, Ph.D.

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

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

Introduction

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

Potential Sources and Baseline Sampling

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

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

Distinguishing Sources

Exclusive reliance on the constituents in produced water is insufficient, because those compounds are naturally occurring and contamination of drinking water can not be

proven to be associated with hydraulic fracturing, particularly when samples from the same well prior to fracturing were not collected and analyzed. The surface expression of the area of fracturing (sometimes several hundred acres) renders the likelihood of sampling each drinking water well to be small, and if constituents in produced water are present in drinking water, there is no proof that fracturing caused the groundwater contamination. Many constituents from hydrofracking additives (see EPA, 2012 and NYSDEC, 2009) and the produced water, however, will necessarily be found in the same sample, especially in flowback water. If the water sample lacks elevated salts or some of the other mobile constituents found in produced water, it is unlikely that the measured constituents are associated with hydraulic fracturing, except potentially from a surface spill of the specific hydraulic additive.

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

Anthropogenic Hydrofracking Chemicals

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

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

detection of alcohols and glycols but are severely compromised by the lack of specificity of gas chromatography/flame ionization detection.

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

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

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

Sulfate Reduction as a Potential Indicator of Methane Release

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

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

In this process, where methane is the carbon source, sulfate is converted to sulfide and bicarbonate is produced. Thus, the pH is expected to rise as alkalinity is increased, and soluble aluminum concentrations are expected to increase at the elevated pH produced. The oxidation-reduction potential (ORP) of the medium is shifted negative, insoluble iron

oxides (various forms of ferric hydroxide) are reduced and ferrous iron (Fe^{2+}) is produced, and manganese oxide (MnO_2) is reduced and dissolved manganese (Mn^{2+}) is released.

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

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

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

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

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

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

Table 1. A series of water quality results from a Pennsylvania domestic well located within 1,000 feet of a hydraulically fractured well. The 7/8/2008 results are a pre-fracturing sample. These data and supplied to the authors by NRDC. Units are mg/L, except for ORP (mV) and pH (standard units).

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

5/27/2010	-101.4	9.03	--	--	--	--	--	--	0.018
6/7/2010	-78.3	9.81	--	<1	--	--	--	--	25
1/2/2013	-23.9	9.73	8.7	0.27	303	0.438	0.381	0.0073	34

-- analyte not determined

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

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

Boron's concentrations in hydrofracturing fluids and flowback water are less well known, although McElreach (Date Unknown) reports a value of 0.07 mg/L in hydraulic fracturing fluids. Boron occurs naturally in produced waters and derives from borosilicate minerals and hydrated borate minerals. Concentrations of boron in produced water can be in the low to moderate mg/L range (Carty et al., 1999).

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

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

Summary

Distinguishing the sources of groundwater contamination at sites with hydrofracturing operations can be accomplished by using multiple approaches that rely on knowledge of baseline groundwater quality and the composition of hydrofracturing fluids and produced waters. In addition to the identification of anthropogenic hydraulic fracturing chemicals

in groundwater, the examination of changes incurred by sulfate-reducing bacteria and the potential use of boron isotopes should be examined further as part of a program to investigate the potential effects of hydraulic fracturing on drinking water resources.

References

Ainley, B.R., K.H. Nimerick, and R.J. Card, 1993. High-Temperature, Borate-Crosslinked Fracturing Fluids: A Comparison of Delay Methodology. Society of Petroleum Engineers, SPE Production Operations Symposium, 21-23 March 1993, Oklahoma City, Oklahoma. Available: http://www.onepetro.org/mslib/servlet/onepetropreview?id=00025463

Alperin. M.J., and T.M. Hoehler, 2009. Anaerobic methane oxidation by archaea/sulfate-reducing bacteria aggregates: 2. Isotopic constraints. American Journal of Science, **309:**958-984

Barton, L. L. and G. D. Fauque, 2009. Biochemistry, Physiology and Biotechnology of Sulfate-Reducing Bacteria. *Advances in Applied Microbiology* **68**: 41–9.

Carty, D.J., D.O. Whittemore, and R.L. Bassett, 1999. Identifying environmentally detrimental saltwater in oilfields using boron isotopes and anion ratios, in Sublette, K.L, 1999, Proceedings of the 6th International Petroleum Environmental Conference, November 16-18, 1999, Houston, Texas, p. 1241-1274. Available online at http://ipec.utulsa.edu/Conf/6thIPEC.pdf

Girguis, P.R. A. E. Cozen, and E.F. F. DeLong, 2005. Growth and Population Dynamics of Anaerobic Methane-Oxidizing Archaea and Sulfate-Reducing Bacteria in a Continuous-Flow Bioreactor. Appl Environ Microbiol. **71**: 3725–3733..

McElreath, D. Date Unknown. Comparison of hydraulic fracturing fluids composition with produced formation water following fracturing – Implications for fate and transport. Chesapeake Energy. Presentation for EPA.
Available:
http://www.epa.gov/hfstudy/comparisonofhffluidscompositionwithproducedformationwater.pdf

Otton, J.K., 2006. Environmental aspects of produced-water salt releases in onshore and coastal petroleum-producing areas of the conterminous U.S. – A bibliography. U.S. Geological Survey Open-File Report 2006-1154.

Orem, W.H., C.A. Tatu, H. E. Lerch, C.A. Rice, T.T. Bartos, A.L. Bates, S.Tewalt, and M.D. Corum, 2007. Organic compounds in produced waters from coalbed natural gas wells in the Powder River Basin, Wyoming, USA. Applied Geochemistry **22**: 2240–2256.

NYSDEC, 2009. Draft Supplemental Generic Environmental Impact Statement on the Oil, Gas and Solution Mining Regulatory Program. New York Dept. of Environmental Conservation, Division of Mineral Resources.

Tsukamoto, T., H. Killian, and G. C. Miller, 2004. Column Experiments for Microbiological Treatment of Acid Mine Drainage; Low Temperature, Low pH, and Matrix Investigations. Water Research **38**:1405-1418.

US EPA, 2012. Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources. EPA 601/R-12/011, December. Available: www.epa.gov/hfstudy

US House of Representatives, 2011. Chemicals Used in Hydraulic Fracturing. Committee on Energy and Commerce, Minority Staff. April. Available: http://democrats.energycommerce.house.gov/sites/default/files/documents/Hydraulic-Fracturing-Chemicals-2011-4-18.pdf

Welton, T.D. and P.D. Nguyen, 2010. Polymer Coated Particulates. US Patent 7799744, Haliburton Co. Available: http://www.docstoc.com/docs/58860687/Polymer-Coated-Particulates---Patent-7799744