

TECHNICAL MEMORANDUM

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Re: Assessment of Groundwater Sampling Results Completed by the U.S. Geological Survey

Summary

The organic chemistry at MW01 has not changed substantially since the EPA sampled the well; some constituents have increased and some have decreased, as would be expected with organic contaminants discharging from a series of event, the hydraulic fracturing of natural gas wells. Because the water chemistry data at MW01 has essentially been replicated, the evidence supporting the hypothesis that natural gas drilling activities, including fracking, have contaminated the Wind River aquifer near Pavillion WY has been strengthened. The conclusions based on that analysis should be more widely accepted now that the water quality has been replicated.

The concentrations of gas, including methane and ethane, have increased and that of propane has remained relatively constant. The ratio of ethane and propane to methane and the isotopic signature of methane all indicate that the gas source is thermogenic, meaning a deep formation. An increasing concentration indicates the formation is likely the source because the concentration will increase as more of the formation contributes to gas at the monitoring well.

EPA monitoring well 2 was not sampled because it did not yield sufficient water. The EPA had been able to purge over a borehole's volume of water, therefore they were clearly sampling formation water. There is no reason to consider that the current condition of MW02 negates the results of the EPA in 2011.

The problems with MW02 however indicate other problems with the sampling of these wells. The USGS used standard purge techniques, not techniques designed to minimize losses of volatile organics to the atmosphere. Purging too fast or drawing the water level too low could cause the measurement to be biased too low.

Introduction

The U.S. Environmental Protection Agency (EPA) published in late 2011 a study assessing the association of various organic compounds, which could be associated with the presence of

natural gas development, or hydraulic fracturing (fracking), in water wells and monitoring wells near Pavillion WY. This study was one of the first to document fracking fluid chemicals in water wells and monitor wells away from the actual natural gas wells. The U.S. Geological Survey (USGS) recently published a data-series report (Wright et al 2012) that reports groundwater quality sampling completed in one of EPA's monitoring wells that had been constructed and sampled for the EPA study.

Wright et al (2012) do not make any conclusions regarding the data presented nor do they compare it to the original EPA report (EPA 2011). They present sampling and quality control data in detail. This memorandum takes the USGS study an additional step by comparing the results released in the new study with the original EPA report (EPA 2011). It considers whether the new data refutes the original EPA study, either with the actual chemistry data collected or by showing problems with EPA monitoring well 2.

Sampling and Chemistry of EPA Monitoring Well 1

USGS sampled EPA monitoring well # 1 (MW01) in late April 2012. The USGS collected four types of blank samples and two replicates from the well after purging more than a borehole's volume of water. Spike samples were also created to assess the accuracy of the testing equipment at the labs. EPA monitoring well # 2 (MW02) was not similarly sampled for reasons discussed in a following section.

Sampling commenced by purging groundwater from the well to remove the static water from the borehole. Their goal had been to remove at least one borehole volume, or 429 gallons, or to the point where several parameters including pH and EC stabilized. The USGS began pumping about 6 gpm which lowered the water level about 135 feet within the time that 300 gallons were removed from the well bore. At that point, the pumping rate dropped to about 2.5 gpm and the water level quickly recovered about 60 feet. Sampling commenced at about 670 cumulative gallons. Purging continued, and the second environmental sample commenced after about 1300 cumulative gallons. Thus the samples were taken after about one and half and three bore holes volume, respectively. The purge rate was commensurate with that used by the EPA for MW01 in that they started at 7.3 gpm and reduced it to about 6 gpm as the water level quickly dropped (EPA 2011).

The USGS did not sample exactly the same constituents as did the EPA. The USGS sampled many constituents and their Table 7 lists many that had below detect (ND) levels, as did the EPA. Table 1 compares constituents found by either the EPA (2011) or the USGS (Wright et al 2012), or by both.

Table 1: Comparison of water chemistry for EPA Monitoring Well # 1 for EPA phase 3 and 4 sampling (EPA 2011) with environmental samples 1 and 2 as reported by Wright et al (2012). The table includes only constituents for which there were detectable values at least once. Nd means no detect. Blank table cells under Phase 3 or 4 mean no sample. P means preservative added.

Name	Units	Phase 3	Phase 4	Env Sample 1	Env Sample 2
pH		11.9	11.2	11.4	10.7
K	mg/l	54.9	24.7	15	13
Cl	mg/l	23.3	23.1	26	27
Diesel-range organics [C10–C28]	µg/L	634	924	180	85
Gasoline-range organics [C6–C10]	µg/L	389	592	700	730
Gasoline-range organics [C6–C10]	µg/L			1100p	700p
3 & 4 Methylphenol	µg/L	included in phenol		0.95	0.47
Benzoic acid	µg/L	212	457	340	190
Benzyl alcohol	µg/L			0.59	nd
Phenol	µg/L	11.1	20.9	10	6.1
1-Methylnaphthalene	µg/L			0.0096	nd
2-Methylnaphthalene	µg/L			0.0110	0.0072
Benzo[<i>a</i>]anthracene	µg/L			nd	0.0042
Benzo[<i>a</i>]pyrene	µg/L			nd	0.0410
Benzo[<i>b</i>]fluoranthene	µg/L			nd	0.0310
Benzo[<i>g,h,i</i>]perylene	µg/L			0.0410	0.0740
Benzo[<i>k</i>]fluoranthene	µg/L			nd	0.0290
Chrysene	µg/L			nd	0.0037
Dibenz[<i>a,h</i>]anthracene	µg/L			nd	0.0510
Fluoranthene	µg/L			nd	0.0063
Indeno[1,2,3- <i>cd</i>]pyrene	µg/L			0.0160	0.0570
Pyrene	µg/L			0.0089	0.0130
Methylene blue active substances	mg/L			0.14	0.15
Methane	µg/L	15950	17930	27,500	25,500
Methane	µg/L			27,000p	20,000p
Ethane	µg/L	2230	2950	3,600	3,200
Ethane	µg/L			3,800p	2,600p
Ethylene	µg/L			7.2	7.2
Ethylene	µg/L			7.2p	7.2p

Propane	µg/L	790	1250	1,400	1,100
Propane	µg/L			1,300p	1,000p
Toluene	µg/L	0.75	0.56	nd	nd
xylene (total)	µg/L		0.89	nd	nd
isopropanol	µg/L		212	nd	nd
diethylene glycol	µg/L		226	nd	nd
triethylene glycol	µg/L		46	nd	nd
tetraethylene glycol	µg/L		7.3	nd	nd
2-butoxyethanol	µg/L		12.7	not tested	
acetate	µg/L		8050	not tested	
formate	µg/L		112	not tested	
lactate	µg/L		69	not tested	
propionate	µg/L		309	not tested	

The concentrations of potassium (K) and the pH level are still much higher than the background levels in the formation, although K has decreased since the EPA sampling. EPA linked the presence of potassium to its use as a crosslinker and solvent during fracking, according to the Material Data Safety Sheets provided by the industry. Most of the fracking occurred several years ago, therefore the source is not a continuous release. A relatively conservative element such as potassium could move through the aquifer much more quickly than some of the organics.

Gasoline range organics and the various carbon-chain gases were found at concentrations that have increased significantly since the EPA study. Benzoic acid was found at concentrations similar to the EPA (2011). Diesel range organics and phenol remained present but at lower concentrations. The USGS found at least nine organic constituents that the EPA had either not found or not tested for. USGS found acrylonitrile at 21 ug/l in one of the replicate samples, not presented in Table 1¹. At least six constituents that had been detected by the EPA (2011) were not detected by the USGS. At least six constituents that EPA has found at various concentrations were not tested for by the USGS.

The concentration of organics at Pavillion should vary for several reasons. Changes from one sampling event to the next do not represent a trend. A non-detect does not prove the constituent does not exist.

Organics are measured at very low concentrations, parts per billion, so a relatively small change proportionally seems much larger. An acceptable spike sample is one for which the measured

¹ According to Dr. Glenn Miller, acrylonitrile is “perhaps the single best indicator of fracking, and should be considered presumptive evidence that fracking fluids have contaminated the groundwater”, although he also acknowledged that one observation, in a replicated sample, is not proof. Email communication, 9/27/2012.

concentration varies from 70 t 130% of the known concentration which indicates just how variable the test methods are. Even 70% recovery could cause a sample which otherwise should have had a detectable concentration to be missed; a 130% recovery means however that a concentration can be overestimated, although it will not find a constituent in a sample in which it does not exist.

Organics attenuate by interactions with clay and silt sized particles so seasonal changes could be expected. This sampling occurred during late April, a time period during which recharge should be highest, since there is a mound in the shallow groundwater suggesting downward movement of water. Such vertical flow could dilute the formation water and cause seasonal changes not accounted for in spot samples as collected by the USGS.

The concentration of methane and ethane increased substantially and that of propane remained relatively constant. The stable isotope ratios of carbon vs. hydrogen in methane are also almost exactly as found by the EPA. The gas in MW01 is thermogenic, and its concentration is increasing. An increasing concentration of thermogenic gas suggests its source is the formation rather than a leaky gas well. The continued increase in concentration reflects that gas flow from more of the formation has reached the monitoring well, a process which will continue until it reaches equilibrium; in other words, the flow of gas through the formations, released by fracking, could reach equilibrium at the current or a higher concentration. If the formation is the source, the gas contamination will continue as long as the source releases gas.

In summary, the organic chemistry at MW01 has not changed substantially since the EPA sampled the well. The chemistry of MW01 found by the USGS is similar to that found by the EPA (2011). The new data does not disprove the hypothesis made by the EPA that natural gas drilling activities, including fracking, have contaminated the Wind River aquifer near Pavillion WY. The conclusions based on that analysis should be more widely accepted because the water quality has been replicated.

Monitoring Well 2

The USGS did not sample MW02 because the well reportedly yielded only about 1 gallon per hour (Wright et al 2012). This differs from the EPA's purging which for Phase IV reportedly removed 1249 liters (330 gallons) of water prior to sampling; EPA did find that the water level lowered more quickly than they could measure it. The USGS redeveloped the well but this did not improve the yield sufficiently for sampling, therefore they did not obtain a sample.

MW02 had been completed in a layer of sandstone approximately 20 feet thick with a shale confining layer both above and below. The resistivity logs also suggest this should be a productive zone. There is no good explanation for the well's failure to produce sufficient water for sampling, but its failure does not obviate the results found by the EPA for that well. The fact

that the well produced substantial water from the sandstone twice indicates that the formation contained the constituents.

Bias Due to Volatilization

Most of the organic chemicals sampled for at the EPA monitoring wells will volatilize, meaning be lost to the air from the sample, under the correct conditions. In general those conditions are due to exposure to air which can be enhanced due to turbulence (Nielsen and Nielsen 2006). Sampling a well just after purging without allowing the well to recover without pumping can cause more volatilization and decrease the amount of constituent recovered in the sample (Herzog et al 1988). Too much purging or purging that causes too much drawdown can also increase volatilization because of the speed with which groundwater flows back into the well (McAlary and Barker 1987). Purging too rapidly or not sampling at the correct time after recovery can cause a bias in the resulting sample concentration. This could have occurred at both the USGS sampling of MW01 and in the EPA's sampling of MW01 and MW02. Concentrations of organics, particularly VOCs, should be considered as potentially low compared to the background groundwater.

References

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