



Geochemical evaluation of flowback brine from Marcellus gas wells in Pennsylvania, USA

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ABSTRACT

Large quantities of highly saline brine flow from gas wells in the Marcellus Formation after hydraulic stimulation (“fracking”). This study assesses the composition of these flowback waters from the Marcellus shale in Pennsylvania, USA. Concentrations of most inorganic components of flowback water (Cl, Br, Na, K, Ca, Mg, Sr, Ba, Ra, Fe, Mn, total dissolved solids, and others) increase with time from a well after hydraulic stimulation. Based on results in several datasets reported here, the greatest concentration of Cl⁻ in flowback water is 151,000 mg/L. For total Ra (combined ²²⁶Ra and ²²⁸Ra) in flowback, the highest level reported is 6540 pCi/L. Flowback waters from hydraulic fracturing of Marcellus wells resemble brines produced from conventional gas wells that tap into other Paleozoic formations in the region. The Br/Cl ratio and other parameters indicate that both types of brine formed by the evaporation of seawater followed by dolomitization, sulfate reduction and subsurface mixing with seawater and/or freshwater. Trends and relationships in brine composition indicate that (1) increased salt concentration in flowback is not mainly caused by dissolution of salt or other minerals in rock units, (2) the flowback waters represent a mixture of injection waters with highly concentrated *in situ* brines similar to those in the other formations, and (3) these waters contain concentrations of Ra and Ba that are commonly hundreds of times the US drinking water standards.

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1. Introduction

With accelerated production of natural gas from shales using hydraulic fracturing of wells diverted along the bedding, there is a growing concern over the composition and fate of water that flows back up the wells (Soeder and Kappel, 2009; Gregory et al., 2011; Howarth et al., 2011). Typically, many million litres of normal surface or ground water plus sand and chemical additives are injected and pressurized into an individual well to accomplish fracturing (“fracking”) and release of gas from shales. Typically about 25% of this volume flows back to the surface on release of pressure. These waters commonly have very high concentrations of some inorganic solutes, and the potential for return of the organic additives. Safe disposal and handling of these waters can be improved by understanding their origin and characteristics.

Flowback waters are commonly considered to be fluids that flow out of a well within the first 2 weeks after stimulation by fracturing, whereas production waters are the remaining fluid that flows from the well after the initial 2-week period. Flowback is driven by release of the pressure and rock deformation induced by the

fracturing process. In this paper, flowback waters are extended to include any aqueous fluid that flows from a well up to 90 days after hydraulic fracturing in order to encompass a series of samples over 90 days.

Strictly speaking, a “brine” is water with more than 35,000 mg/L total dissolved solids (Kharaka and Hanor, 2004). The term “Marcellus brine” will be used for brines emerging from wells penetrating the Marcellus Formation, but does not necessarily indicate that the waters had been hosted mainly in the low-porosity Marcellus, as discussed later.

After hydraulic fracturing in the Marcellus and some other gas-producing shales, the concentration of dissolved salts in flowback and production waters increases dramatically with time (Blauch et al., 2009; Rowan et al., 2011; Haluszczak, 2011; Pritz and Kirby, 2010; Fig. 1; Table 1).

The purpose of this paper is to document the increase in solute concentrations, and to provide evidence for the origin of these highly saline flowback waters. The main existing hypothesis is that the increased concentration of salts in flowback waters is due to dissolution of constituents from the shale by the water injected during hydraulic fracturing (Blauch et al., 2009). However, an alternative origin of the high salinity is release of *in situ* brines (formation water) similar to those that Poth (1962), Dresel (1985) and Dresel and Rose (2010) found were produced from most oil and natural gas wells in Pennsylvania.

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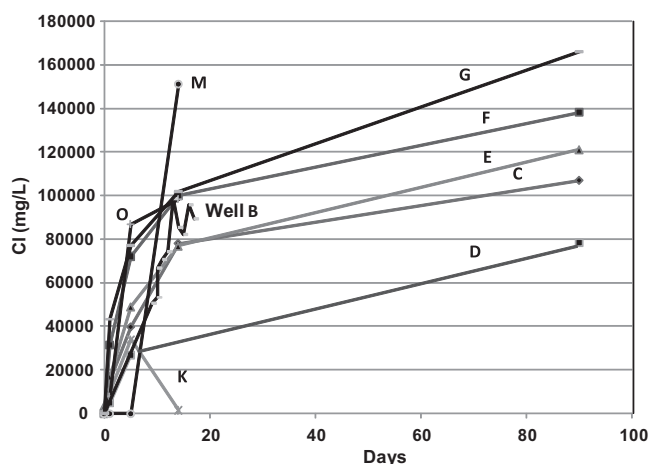


Fig. 1. Chloride concentration in flowback water vs. days after hydrofracturing. Data from Hayes (2009) and Blauch et al. (2009).

Table 1

Median concentrations in injected water and day 14 flowback water. Data from seven horizontal wells (C, E, F, G, K, M and O) reported by Hayes (2009).

	Concentrations in mg/L		
	Injected fluid median, day 0	Flowback median, day 14	Flowback range, day 14
pH	7.0	6.2	5.8–6.6
Alkalinity as CaCO ₃	126	71	26–95
Total dissolved solids	735	157000	3010–228,000
Total organic carbon	205	14	1.2–509
Chemical oxygen demand	734	8370	228–128,000
Cl	82	98300	1070–151,000
Br	<10 (<0.2–19)	872	16–1190
SO ₄	59	<50*	0.8–89
NH ₃ –N	16	193	4–359
P	0.36	0.55*	0.04–2.2
Al	0.3*	0.5	0.15–0.91
Ba	0.6	1990	76–13,600
B	0.5	20	2.7–3880
Ca	32	11200	204–14,800
Fe	0.68	47	14–59
K	<50 (3–57)	281	8–1010
Li	0.04	95	4–202
Mg	3.7	875	22–1800
Mn	0.074	5.6	1.2–8.4
Na	80	36400	1100–44,100
Sr	0.82	2330	46–5350
Zn	0.08	0.09	0.07–0.14

* Approximated because some < values. For an even number of samples, the two middle values are averaged to obtain the median.

Several workers have shown that the origin of saline waters can be inferred from their chemical fingerprint relative to seawater (Collins, 1975; Carpenter, 1978; Stoessel and Moore, 1983; Steuber et al., 1998; Kim et al., 2003; Kharaka and Hanor, 2004). Poth (1962) and Dresel (1985) have suggested that oilfield brines in Pennsylvania originate by evaporation of seawater, followed by migration and mixing with other waters.

In this study, the chemical composition of the brines and the flowback fluids are evaluated using plots of the various dissolved constituents. By using plots of relatively conservative constituents such as Cl and Br, the flowback waters can be compared with the oilfield brines sampled by Dresel and Rose (2010) and brines formed by other processes. A secondary focus of this study is to determine if the fluids mobilized from impermeable rocks (shales)

by hydraulic fracturing differ from the brines produced from permeable units in the region.

2. Background

Recently, environmental indicators of elevated TDS have been noted in the Monongahela River, including elevated Cl⁻ and golden algal blooms that produce toxins that can suffocate aquatic organisms (Water and Wastes Digest, 2008). The PA DEP determined that one possible contributor could be the introduction of Cl⁻ into the water system. It became evident that the increasing use of hydraulic fracturing processes for extraction of natural gas could be contributing Cl⁻, and thereby the TDS, in the water system.

Waters produced from oil and gas wells can contain TDS and Cl⁻ exceeding 100,000 mg/L (Dresel and Rose, 2010), compared to values of a few tens of mg/L in normal fresh water. As a result, if oil or gas well brine were entering the waterways, TDS and Cl⁻ levels would rise, along with other constituents of the brine.

Prior to 2008, before the Marcellus Shale boom began, Pennsylvania's gas industry historically had drilled vertical wells into permeable sandstone reservoirs. However, with recent advances in drilling technology and, up until recently, very favorable natural gas prices, the use of hydraulic fracturing combined with directional drilling allows economic production of gas from shales like the Marcellus, a previously untapped formation (Soeder and Kappel, 2009). Residents in towns like Montrose and Dimock, PA, have become concerned about the impacts that hydraulic fracturing and drilling can have on their water, air and forests (McGowan, 2011). Many claims of contaminated ground and surface water have recently been made, and the origin and processes leading to contamination are, therefore, of interest. A recent study (Warner et al., 2012) concluded that saline Marcellus Formation brines are affecting the water quality of shallow drinking-water aquifers, although the lack of a geographical relationship to shale-gas wells indicates that brine migration is occurring along natural pathways.

Dresel and Rose (2010) provide insight into the possible sources of Cl⁻. They investigated the chemistry of brines from oil and gas wells in order to determine the origin of the solutions. The samples were collected from the Silurian Medina and Tuscarora formations, Lower Devonian Oriskany group, and several Upper Devonian horizons within the Canadaway and Conneaut formations. The Medina, Tuscarora and Oriskany are sandstones that allow for permeation of the units by fluids. Therefore, the brine compositions that Dresel (1985) explored are susceptible to mixing with subsurface waters that could affect their chemical composition. In relation to this study, the brines that Dresel (1985) sampled might be expected to differ from the Marcellus flowback waters because the latter are tapping into shale units in which flow and mixing are greatly inhibited. However, if the Marcellus brines have TDS, Cl and other chemistry similar to the brines from conventional oil and gas wells, they may have similarities in origin.

3. Data and methods

Data on flowback and production waters from wells in central and western Pennsylvania were collected from four main sources: (1) brines from 40 conventional oil and gas wells in Pennsylvania (Dresel, 1985; Dresel and Rose, 2010); (2) A set of 22 flowback waters from Marcellus gas wells collected by the Pennsylvania Department of Environmental Protection (PA DEP), Bureau of Oil and Gas Management (BOGM series), (3) flowback waters from two Marcellus gas wells in Pennsylvania (Blauch et al., 2009), and (4) a set of flowback samples from 8 hydrofractured horizontal wells in the Marcellus reported in an industry study by the Marcellus Shale Coalition and reported in a Gas Technology Institute (GTI)

report (Hayes, 2009). Fig. 2 shows the location of these wells. Refer to Table 2 for location information for some of the wells.

In the following discussion, the gas and oil wells sampled by Dresel (1985) are called conventional wells, and the samples are called conventional brines in view of the simple vertical orientation of wells and production from sandstones. Dresel (1985) and Dresel and Rose (2010) describe the sampling and analytical methods for this set of samples, including both field and laboratory determinations.

The Marcellus flowback data obtained from the PA Department of Environmental Protection Bureau of Oil and Gas Management (BOGM) were collected to establish base line data for chemical characterization of the flowback waters, and to obtain radioactivity

data (Table 3). The data were obtained from James Fuller of PA DEP Bureau of Oil and Gas Management in Harrisburg.

The BOGM samples were collected and analyzed in DEP laboratories under a DEP sampling and analytical protocol (PA Department of Environmental Protection, 2011), that includes Field Tests/Calibration Procedures, and Sampling Procedures. Samples were collected by James Fuller and other DEP personnel. Sites were selected randomly based on a grid and site accessibility. Samples were from active flowback or the most recent flowback impoundment. Analyses were by the PA DEP Laboratory, using DEP method SAC 996 for most inorganic constituents. For dissolved metals, water was filtered through 0.45 μm membranes. The analytical methods were mostly those of EPA method 200.7, and for radioac-

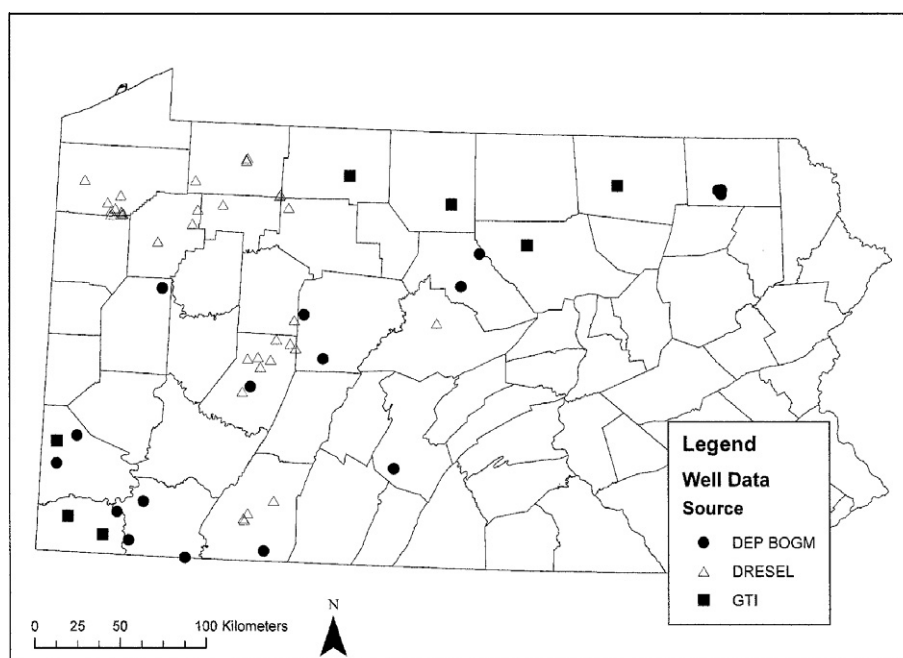


Fig. 2. Map of sites in Pennsylvania.

Table 2
Location data for BOGM wells.

Number	Spl. Date	Days after fracturing	County	Permit no.	Well name	Latitude	Longitude
4	6/3/2008	10	Washington	125-23023	Cowden Unit 1	40.3295	-80.2811
7	6/5/2008		Butler	019-21476	R Blaser Trust 1	41.1221	-79.7526
10	6/10/2008	7	Washington	125-23048	Zappi Constance 2H	40.1783	-80.41
11	6/25/2008	37	Butler	019-21476	R. Blauser Trust 1	41.1222	-79.7529
12	7/1/2008	12	Huntington	061-20004	Hess 2073	40.2341	-78.1054
16	10/9/2008	1	Susquehanna	115-20036	Costello # 1	41.7274	-75.8785
17	10/9/2008		Susquehanna	115-20045	Teel 7	41.7031	-75.8809
20	10/23/2008	1	Clearfield	033-26585	Bosnall 7	41.0189	-78.761
21	10/27/2008	5	Clearfield	033-26585	Bosnall 7	41.0189	-78.761
22	11/5/2008	13	Clearfield	033-26585	Bosnall 7	41.0189	-78.761
23	5/29/2009	2	Somerset	111-20268	Yoder	39.7759	-78.9709
25	7/1/2009		Clearfield	033-26803	Hutton #1H	40.7917	-78.6198
26	7/8/2009	1	Greene	059-25137	Consol USX #66	39.9448	-79.9801
27	7/14/2009		Clearfield	033-26803	Hutton #1H	40.7917	-78.6198
28	7/22/2009	1	Fayette	051-24206	LEE #11	40.0059	-79.8048
30	8/5/2009		Fayette	051-24209	Bezjak #26	39.7994	-79.8913
31	8/19/2009		Fayette	051-24098	W. Smith #1	39.7228	-79.5057
32	9/2/2009	19	Clinton	035-21162	COP Tract 653 1001H	41.1961	-77.6824
35	9/25/2009		Indiana	063-36435	Ind. Co. Airport 8391H	40.6301	-79.1102
39	11/18/2009		Clinton	035-21155	COP Tract 285 2H	41.3689	-77.5588
40	11/19/2009		Susquehanna	115-20171	J. Grimsley H2	41.7258	-75.9027
41	11/19/2009		Susquehanna	115-20095	J. Grimsley 1	41.7259	-75.9028

Note: Latitude and longitude in decimal degrees.

Table 3
Chemical data, BOGM samples.

Site no.	SpC (umhos/cm)	TDS (mg/L)	pH (pH units)	ALKAL. (mg/L CaCO ₃)	SO ₄ (mg/L)	Br (mg/L)	Cl (mg/L)	Ca (mg/L)
4	71,200	69,700	6.6	143	226	349	30,200	4540
7	–	–	–	–	59	572	51,800	–
10	120,600	136,000	6.4	130	49	528	60,200	3730
11	39,200	28,900	7.6	273	25	154	14,700	1040
12	46,200	33,700	5.9	309	51	148	18,000	1350
16	–	47,800	7.4	223	<5	174	25,600	100
17	–	50,700	7.7	241	<5	142	24,900	112
20	10,990	7520	7.5	238	30	45	3700	230
21	137,000	181,000	6.3	112	7	548	70,600	10,800
22	178,200	197,000	6.1	106	<5	8	105,000	17,900
23	57,100	42,200	7.0	298	15	150	23,500	2120
25	26,700	15,100	11.6	607	384	300	8010	–
26	19,240	13,900	5.1	29	296	62	6900	730
27	21,900	13,700	10.8	939	420	<2.2	390	675
28	17,650	11,600	7.8	172	279	–	6200	949
30	60,500	45,600	7.2	199	394	233	25,000	2680
31	43,700	29,700	6.9	165	16	133	–	1300
32	>111,900	170,000	6.3	235	<5	613	83,500	12,500
35	101,700	128,000	6.9	152	11	283	46,400	5750
39	72,200	91,800	7.6	247	<5	217	47,000	2240
40	28,900	18,800	7.7	212	<5	69	10,300	291
41	43,600	31,000	–	–	<5	112	16,800	523
	Ba (mg/L)	Mn (µg/L)	K (mg/L)	Na (mg/L)	Sr (mg/L)	Ra-226 (pCi/L)	Ra-228 (pCi/L)	U (pCi/L)
4	10	1620	161	13,400	–	–	–	–
7	7	3000	4	24,500	–	–	–	–
10	4	3450	337	24,200	–	–	–	–
11	161	553	68	7910	–	–	–	–
12	15	29,400	40	9530	–	–	–	–
16	1870	970	57	1280	–	–	–	–
17	1430	1110	54	1210	–	–	–	–
20	40	670	20	2350	–	–	–	–
21	1010	3030	616	25,200	–	–	–	–
22	1430	3260	890	37,800	–	–	–	–
23	314	2420	79	10,600	–	40	69	0*
25	3380	2200	5240	2110	–	77	0	0
26	4	2330	95	3090	–	352	0	0
27	2490	3130	3560	2280	6	159	0	–
28	9	535	161	4090	217	78	0	0
30	9	497	421	11,000	527	63	10	93
31	75	1670	67	9730	187	348	60	0
32	6270	4990	224	34,300	3570	5830	710	0
35	1320	7400	215	17,500	1650	605	304	0
39	1200	800	66	13,500	687	1310	115	0
40	340	280	25	4100	99	262	30	0
41	861	780	50	7540	213	617	54	0

* Detection limit for U is less than 38 pCi/L based on other reported values.

tivity, EPA methods 900.0 and 903.0. For 12 sites at which the fracturing date is available, the samples ranged from 1 day to 37 days after fracturing.

Data for 2 wells studied by [Blauch et al. \(2009\)](#) are utilized in this study. In their study, at Well B in northern West Virginia, 17 samples were collected over a 45-day period. Methods are described by [Blauch et al. \(2009\)](#).

Data on multiple samples from eight horizontal Marcellus wells were obtained from a report by [Hayes \(2009\)](#) of the Gas Technology Institute (GTI) in a comprehensive study by the Marcellus Shale Coalition, an industry group. The eight horizontal wells are designated C, D, E, F, G, K, M and O in [Hayes \(2009\)](#). Samples were collected of the injected water (day 0) and of flowback at days 1, 5, 14 and 90 after hydrofracturing. Samples were collected by an independent contractor according to a protocol developed by the Coalition, with input from state regulators, and analyzed by a single laboratory for 45 inorganic constituents and about 200 organic constituents. Sampling and analytical methods are described in [Hayes \(2009\)](#). Data for Cl and Ca are plotted in [Figs. 1 and 3](#). Eleven additional samples from vertical Marcellus wells are reported in the study but are not discussed here because of their vertical rather than horizontal geometry.

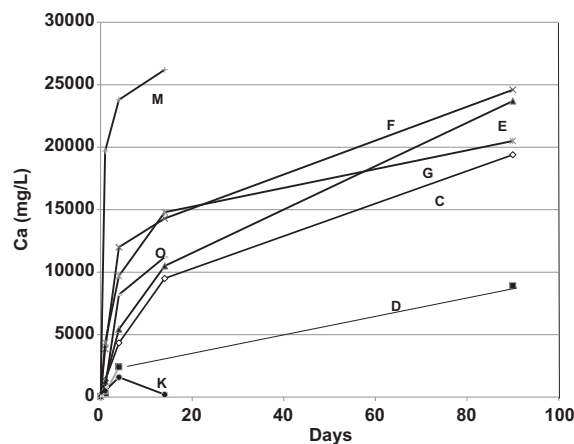


Fig. 3. Calcium in flowback water vs. days after hydrofracturing. Data from [Hayes \(2009\)](#).

Most wells are located in western and central Pennsylvania ([Fig. 2](#)); however, a few are in northeastern Pennsylvania and 2 in northern West Virginia. In the Dresel set, there are 14 samples

of brine from oil wells; the remaining 26 of the Dresel samples are from gas wells. There are 17 hydrofractured Marcellus wells from the DEP BOGM well data.

4. Results

Fig. 1 illustrates the Cl content of flowback water from eight horizontal Marcellus wells from Hayes (2009), plus Well B of Blanch et al. (2009). Flowback waters from these wells of the GTI series show a major increase in Cl⁻ as later flowback waters are returned from the well over the 14 days of the flowback period (Fig. 1), though one sample drops to lower values at 14 days. The later concentrations in others are many times the seawater concentration of 19,000 mg/L. The median Cl content in the eight samples increases from 82 mg/L in the injected water to 98,000 mg/L in the 14-day flowback. A further increase is observed for the four wells sampled at 90 days. Other significant constituents showing increased concentration in later flowback water are Na, Ca, Mg, Br, Ba, Sr, Fe, Mn, K and total dissolved solids (TDS) (Table 1), as well as Ra (Rowan et al., 2011). Many minor elements, including B and Li are also enriched. The pH remains near neutrality in the flowback.

Sulfate decreases in the flowback, probably because SO₄ is very low in the *in situ* brine. The low SO₄ allows high contents of alkaline earth elements (Ca, Sr, Ba, Ra). Alkali elements (Na, K, Li) and halides (Cl, Br) are generally greatly enriched.

The data from Blanch et al. (2009) also show greatly increased concentrations of Cl⁻ and other constituents as flowback progresses after hydraulic fracturing. Blanch et al. (2009) show a strong correlation of increased Ca with Cl for well A.

Hayes (2009) reports low concentrations of Cl, TDS and other constituents in the injected water at most of the wells, in the range of local surface and shallow ground waters. For a few, the injected water evidently consisted partly of flowback water from previous wells, based on elevated Cl, Ca, Ba and other elements. Both the injected waters and the flowback have pH in the range 6–8, indicating that dissolution of rock minerals by an acidic solution does not explain the increased cation concentrations. Low contents of Cl and SO₄ as well as near-neutral pH in the injected water indicate that HCl and H₂SO₄ were not components of the injection fluid, and that acid attack by the injected water does not explain the high concentrations of cations in the flowback water.

A map of the Cl content of flowback was examined. Based mainly on the Dresel data, an area of low Cl in water from oil wells appears to exist in part of NW PA, but other regions seem to have generally high Cl and TDS in both conventional gas well and Marcellus flowback brines.

Carpenter (1978) and others (Stoessel and Moore, 1983; Dresel, 1985; Steuber et al., 1998; Kharaka et al., 1987; Connelly et al., 1990; Gupta et al., 2011) used a plot of Br vs. Cl to examine the relationship of brines to evaporated seawater (Fig. 4). Evaporation of seawater leads to enrichment in both Cl and Br during initial evaporation and precipitation of calcite and gypsum, but when halite precipitates, the halite contains much lower Br than the associated brine, leading to a nearly horizontal trend for the residual brine on the graph. Because of this effect, brines with high Br/Cl result from evaporation of seawater past the point of halite precipitation. These highly evaporated brines may then be diluted by fresh water, sea water, other brines or injected water to produce brines plotting at Br values greater than the seawater evaporation curve. In contrast, later dissolution of the low-Br halite would lead to lower Br/Cl in the brine.

The Cl–Br plot was used by Dresel (1985) and Dresel and Rose (2010) to show that the conventional brines in Pennsylvania were derived from highly evaporated seawater that had been diluted

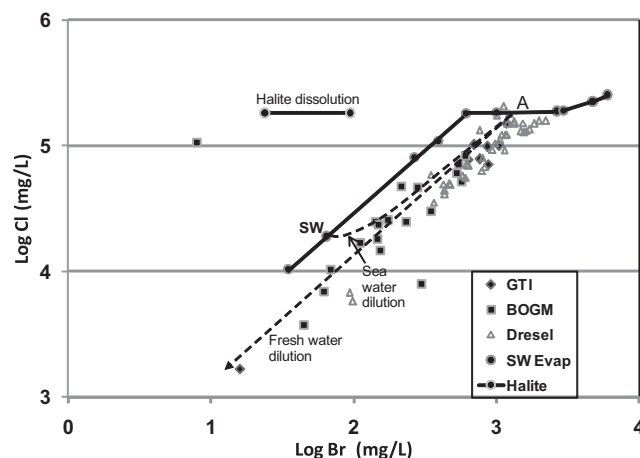


Fig. 4. Plot of Log Cl vs. Log Br, showing seawater (SW) evaporation path and composition of flowback brines and production water from oil and gas wells. Dashed lines indicate dilution paths. Seawater evaporation line from McCaffrey et al. (1987).

with fresh water or seawater (Fig. 4). A contribution from halite dissolution is possible, though probably minor.

Plotting the Marcellus flowback waters on this graph indicates that they also can be explained as mixtures of highly evaporated brine with more dilute water (Fig. 4). Using the seawater and fresh-water mixing lines Dresel (1985) presented in the original figure, both the conventional brine and the flowback waters plot in positions that indicate dilution of an original brine with freshwater, seawater or injected fracturing fluid.

The Marcellus waters plot to the high-Br side (low Cl/Br) of the seawater evaporation path, indicating that halite dissolution is not the major source of Cl⁻, as was proposed by Blanch et al. (2009). The halite observed in Marcellus cores by these workers may have precipitated by evaporation from pore fluid on removal of the core from the well, but except for one sample, halite dissolution cannot have been a major process in the formation of the Marcellus brines.

Gupta et al. (2011) show that highly evaporated seawater can be diluted and then dissolve appreciable halite but still remain below the seawater evaporation curve. They show that in the Alberta basin, brines plotting below the curve are mixtures of four processes: seawater evaporation, dilution by fresh water, dilution by seawater and halite dissolution. Thus, halite dissolution can be a contributing process for waters plotting below the seawater evaporation curve, but must be subordinate to the evaporation effects. Based on the results of the Cl–Br plot, the Marcellus flowback water is considered to have developed analogously to the conventional brines, by evaporation of seawater into the halite stage, and then dilution to the present composition. Most of the samples fall near dilution curves for the Composition A postulated by Dresel and Rose (2010) to have been the parent evaporated seawater brine, as shown in Fig. 4. Some scatter to lower Br could be interpreted as halite dissolution.

Graphs of both Ca and Mg vs. Br show clear similarities between the conventional brines and the flowback waters (Fig. 5). Calcium and Mg show a positive linear relation with Br, which is relatively conservative during evaporation and dilution. The flowback waters contain markedly higher Ca than any evaporated seawater, and markedly lower Mg. This pattern was also found for the conventional brines (Dresel, 1985), indicating a common process of origin for the conventional and Marcellus brines. Dresel (1985) showed that this pattern could be explained by conversion of calcite to dolomite during the early history of the evaporated brine, and that the evaporated seawater contained sufficient Mg to account for the excess Ca by dolomitization of calcite.

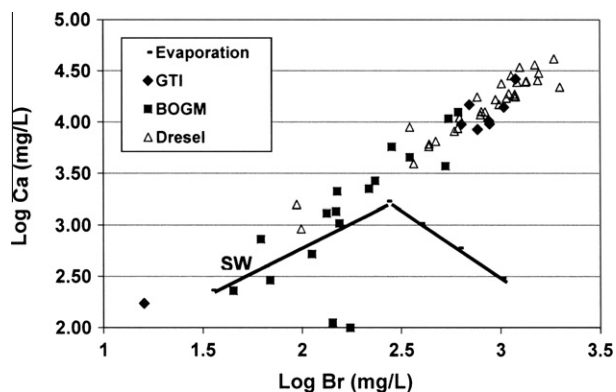


Fig. 5a. Log Ca vs. Log Br of brines, showing similarity of Marcellus flowback to brines from conventional oil and gas wells, and markedly higher Ca than seawater evaporation path.

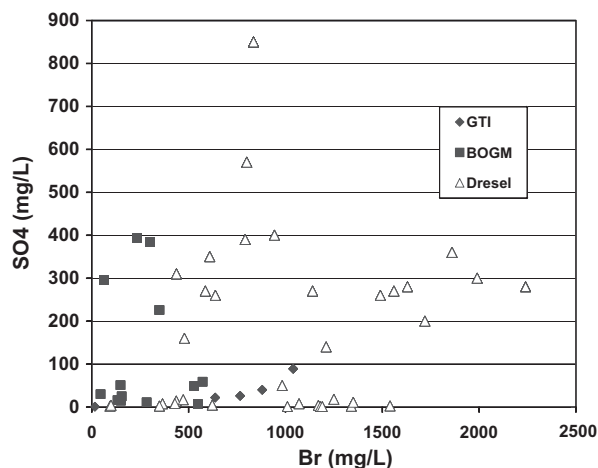


Fig. 6. SO_4 vs. Br, showing lack of any relationship and low concentrations of SO_4 . Seawater composition and seawater evaporation path lie above 1900 mg/L.

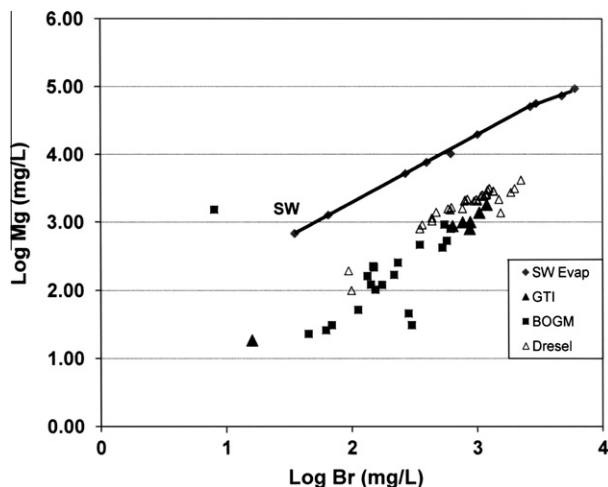


Fig. 5b. Log Mg vs. Log Br of brines, showing similarity of Marcellus flowback to brines from conventional oil and gas wells, and markedly lower Mg compared to seawater evaporation path.

Sulfate concentrations in the Marcellus brines are low; many less than 100 mg/L and nearly all less than 500 mg/L (Fig. 6), as observed for the conventional brines (Dresel, 1985). The low SO_4 could be caused by sulfidation of Fe to form pyrite and perhaps by reactions involving Ca and other alkaline earths, as discussed by Dresel (1985). Sulfur isotope data indicate later dissolution of pyrite as a source of some S (Dresel, 1985).

Finally, analyses of ^{226}Ra and ^{228}Ra concentrations in flowback waters show very high concentrations (Table 3). The total ^{226}Ra and ^{228}Ra concentrations range from 73 to 6540 pCi/L in the flowback water samples from the DEP BOGM dataset. Relative to the US EPA maximum contaminant level (MCL) for total ^{226}Ra and ^{228}Ra in drinking water, which is 5 pCi/L, the concentrations in flowback exceed the MCL by 13–1300 times (US Environmental Protection Agency, 2011a). Rowan et al. (2011) show similarly high Ra concentrations and an increase in later flowback.

Both Ra and Ba are enriched in the flowback waters. Fig. 7 illustrates a correlation of ^{226}Ra with Ba, though it is most evident for two high-Ra samples. A poorer relationship is found for ^{226}Ra vs. Cl (Fig. 8). The high Ra evidently arises by the same process generating high Ba and other alkaline earths. Apparently the low SO_4 has allowed leaching of alkaline earths from the rock.

The levels of total Ra, 13–1300 times the maximum contaminant level for drinking water standards, show that the potential

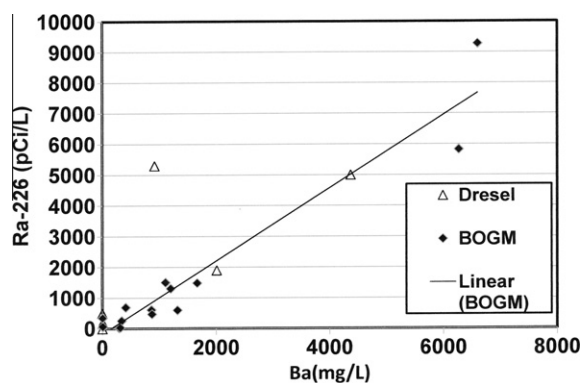


Fig. 7. Ra-226 vs. Ba, showing correlation of these alkaline earths.

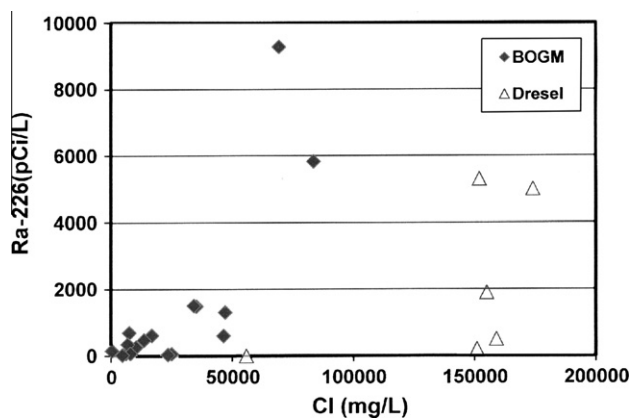


Fig. 8. Ra-226 vs. Cl, showing little relationship.

radiation hazard must be considered for these brines from hydraulic fracturing. High Ra concentrations were also present in the conventional brines of Dresel and Rose (2010). This similarity suggests that *in situ* brines are the source of the high Ra, not dissolution during the fracturing process. High Ra in production waters is also predicted. The fate of Ra after deep injection, or disposal into waterways, drinking water sources, and highways needs to be investigated.

The U concentrations in the brines are low (Table 3). The low concentrations, despite relatively high U in the Marcellus black shale, are evidently due to the reducing nature of the pore water, and the resulting very low solubility of U. However, Ra and its daughters diffuse out of their host and into the SO₄-poor brine.

The drinking water limit for Ba is 2 mg/L (US EPA, 2011b). Concentrations of Ba in the late stage flowback are commonly thousands of mg/L. Barium is another potentially toxic constituent in the Marcellus brines, along with Br and other solutes.

Because of the low porosity of the Marcellus shale, the source of the brine deserves consideration. Logs of Marcellus holes indicate low porosity and low conductance of any water phase (Engelder, pers. comm., 2012). However, conductance of pore water inferred from drill logs may not be reliable (Kharaka, pers. comm., 2012). The brine clearly is derived from the zone of completion and fracturing in and adjacent to the Marcellus. It seems possible that brine is derived from a combination of pore space in the Marcellus plus fractures in the Marcellus and fractures and porosity in the adjacent formations.

5. Conclusions

1. Flowback water from later stage flowback from Marcellus wells contains very high concentrations of TDS, Cl, Br, Na, Ca, Sr, Ba, Ra and other elements. The levels of TDS, Cl and some other constituents can be 5–10 times the concentration in seawater.
2. Late stage flowback did not originate by dissolution of rock minerals by acidified injected water, because the injected water for the GTI wells has near-neutral pH and low levels of Cl and SO₄.
3. The chemistry of the later flowback water is similar to brines produced from conventional oil and gas wells tapping permeable host formations ranging in age from Ordovician to Devonian.
4. The Cl–Br relations indicate that the late flowback waters developed from a highly saline brine evaporated from seawater into the stage of halite precipitation, and then diluted and mixed with seawater, fresh water and injected fluids.
5. The late stage flowback contains concentrations of Ra²²⁶, Ra²²⁸, Ba and other constituents far higher than drinking water limits. Improper disposal of the flowback can lead to unsafe levels of these and other constituents in water, biota and sediment from wells and streams.
6. The high salinity and toxicity of these waters must be a key criterion in the technology for disposal of both the flowback waters and the continuing outflow of production waters.

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