Comparison of Hydraulic Fracturing Fluids Composition with Produced Formation Water following Fracturing – Implications for Fate and Transport

Chesapeake ENERGY

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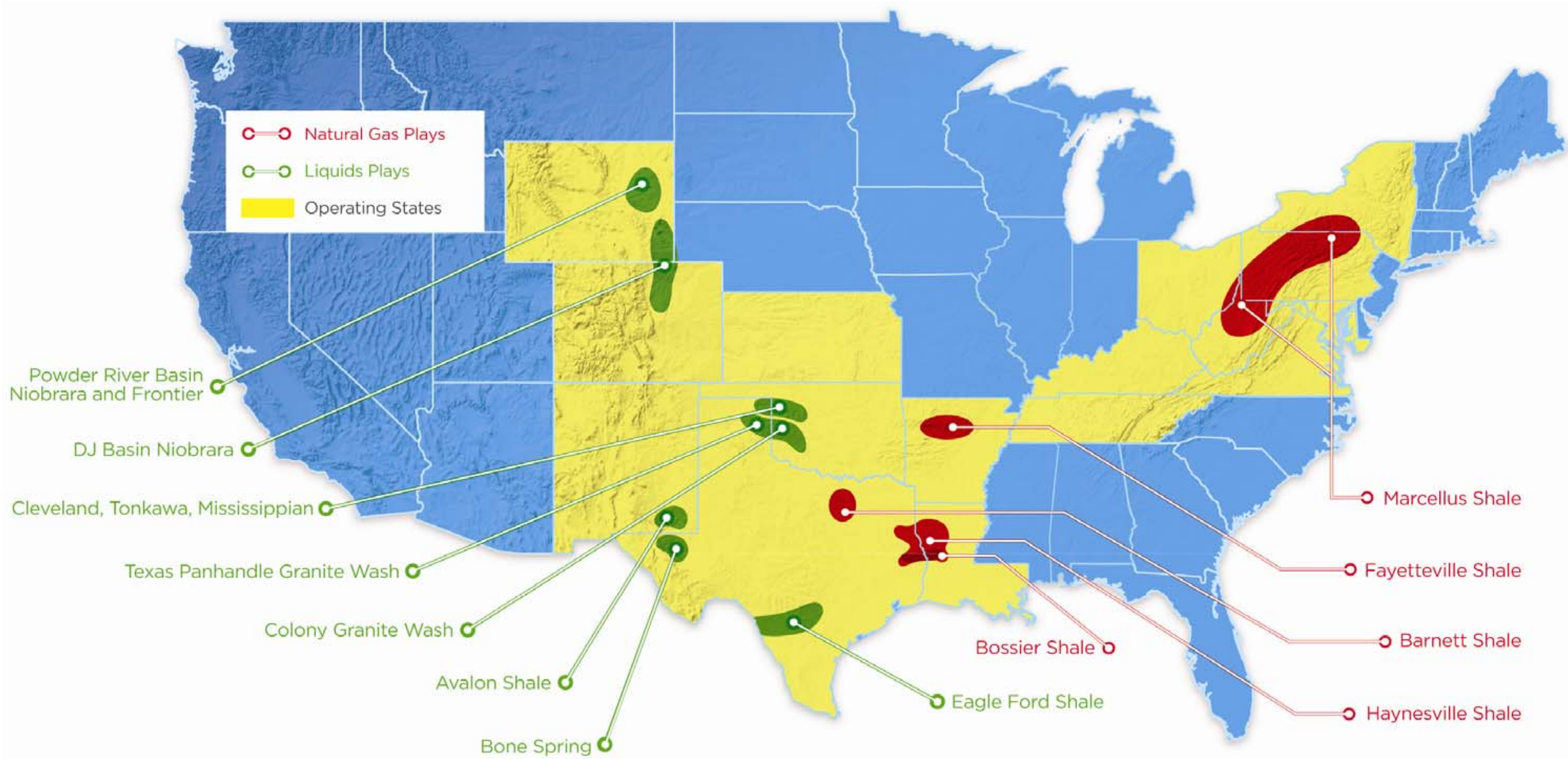
NATURAL GAS: FUELING AMERICA'S FUTURE

Presentation Outline

- Introduction
- Predicted Fate and Transport of Hydraulic Fracture Chemicals
- Fate Evaluation - Comparisons of Predicted Concentrations with Measured Concentrations of Indicator Parameters
- Transport Evaluation – Selected Radionuclides
- Conclusions

Chesapeake Energy Operating Areas



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Predicted Downhole Fate for Hydraulic Fracturing Fluid Components

HF Fluid Component	Predicted Downhole Fate
Acid	Reacts with minerals to create salts, water and CO_2
Corrosion Inhibitor	Bonds with pipe surfaces, broken down by micro-organisms or returned in produced formation water
Iron Control	Reacts with minerals to create salts, water and CO_2
Anti-Bacterial Agent	Broken down by micro-organisms or small amount returned in formation produced water
Scale Inhibitor	Attaches to the formation; majority returns with produced formation water
Friction Reducer	Remains in formation; broken down by micro-organisms or small amount returned in formation produced water
Surfactant	Returned with produced formation water or produced natural gas
Gelling Agent	Broken down by breaker and returns with produced formation water
Breaker	Reacts with “gel” and “crosslinker” to form ammonia and sulfate salts which are returned in produced formation water
Crosslinker	Combines with the “breaker” in the formation to create salts that are returned in produced formation water

Fate and Transport of Components in Fracturing Fluids

- **Elevated temperatures and pressure as well as the interactions within the fluid itself changes the form of most components**
- **Reactions between hydraulic fracturing fluid components and/or the formation produce constituents which can be measured as surrogates, e.g. salts, sulfates, nitrogen compounds, etc., using accepted analytical methods**
  - Salts can be measured as Total Dissolved Solids
  - Sulfates
  - Nitrogenous compounds – Total Kjeldahl Nitrogen and Ammonia used as surrogate
- **Often can not measure for the chemical itself, can only measure the individual pieces**
  - KCl – can not easily measure KCl but instead measure Potassium and Chloride
  - Sodium Hydroxide – measure Sodium as an indicator
- **The matrix of fracturing fluids are products rather than typical environmental samples, therefore holding times, etc. are not valid**

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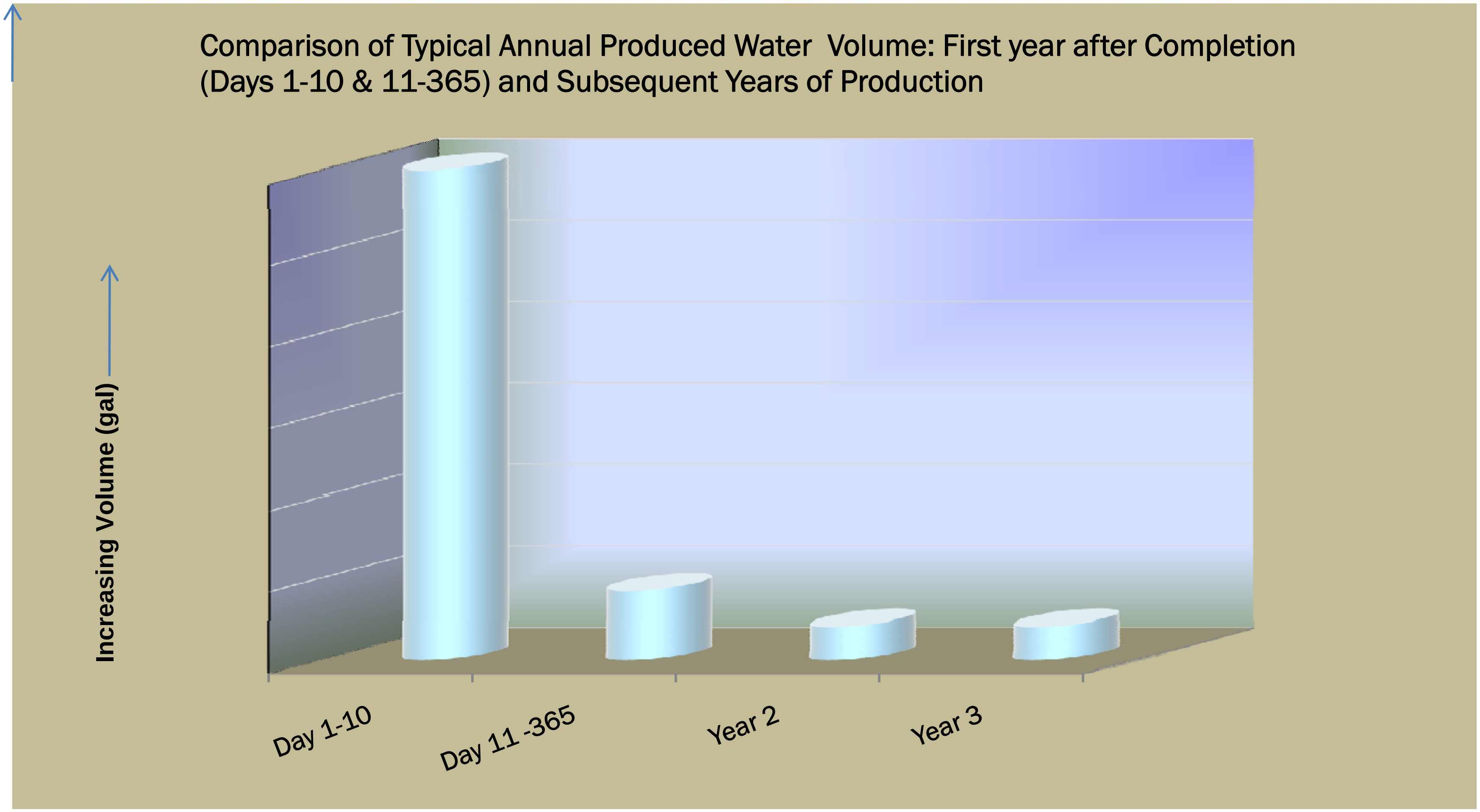
Data Evaluated

- **Vendor supplied information regarding quantity of hydraulic fracture fluids used**
- **Mixed hydraulic fracturing fluids**
- **Produced formation water after hydraulic fracturing activities**
  - Iterative samples over time
- **Analytical results available for the following parameters:**
  - Volatile organics, including glycols
  - Semi-volatile organics
  - Metals, total and dissolved
  - General chemistry
  - Radiochemistry (gross alpha/beta, Radium 226/228, and some additional isotopic nuclides by gamma spectroscopy)

Produced Formation Water Production Volumes – Location 1 (Western U.S.)



Hydraulic Fracture Fluid Components used in Location 1 – Western U.S.

- Acid – hydrochloric acid
- Corrosion and Scale Inhibitors – alcohols, organic acid and polymer, sodium salt
- Iron Control – sodium compound
- Biocide – gluteraldehyde and an alcohol
- Friction Reducer - polymer and hydrocarbon
- Breaker – ammonium persulfate
- Crosslinker – polyol and borax

Summary of Analytical Results

Selected Indicator Compounds
Produced Formation Water after Hydraulic Fracture (First 30 Days)
Location 1 - Western U.S.

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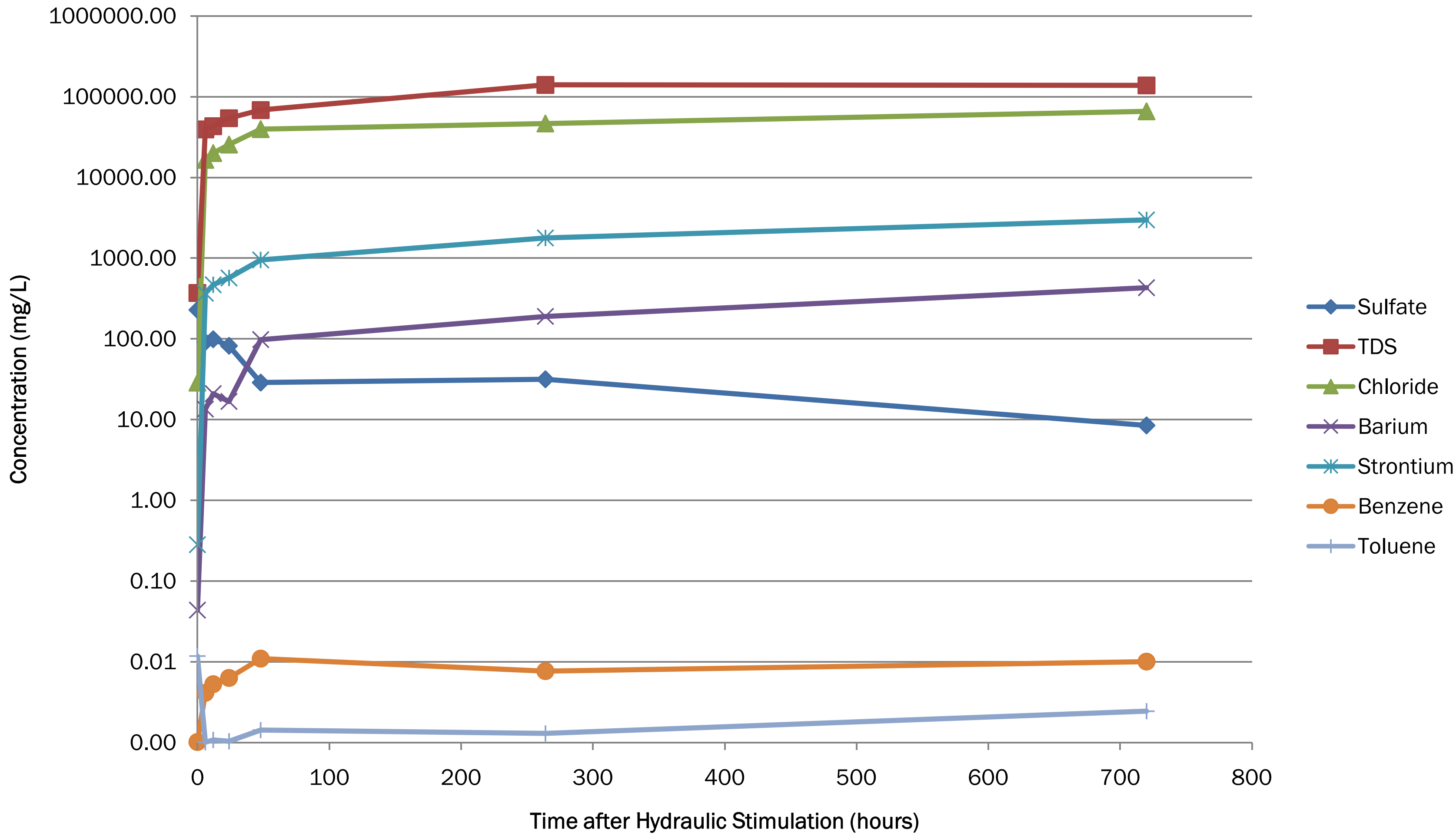
Parameter	Hydraulic Fracture Fluid	Concentrations in Produced Formation Water following Hydraulic Fracturing with Time (mg/L)				
		6 Hours	Day 1 (24 Hours)	Day 2	Day 9	Day 30
Total Kjeldahl Nitrogen	41.3	523	3,770	5,200	315	257
Ammonia	38.5	110	140	201	273	352
Chloride	126	16,500	25,500	39,600	46,500	65,800
Sulfate	162	91.6	82.1	28.8	31.6	8.47
Total Dissolved Solids	1,500	39,300	54,100	68,300	140,000	138,000
Sodium	94.9	7,260	10,800	14,700	27,100	38,100
Boron	0.0785	0.075	17.5	20.6	28.8	<50
Benzene	<1	4.15	6.34	11	7.69	10.1
Toluene	1.44	1.01	1.04	1.43	1.30	2.45

Summary of Analytical Results

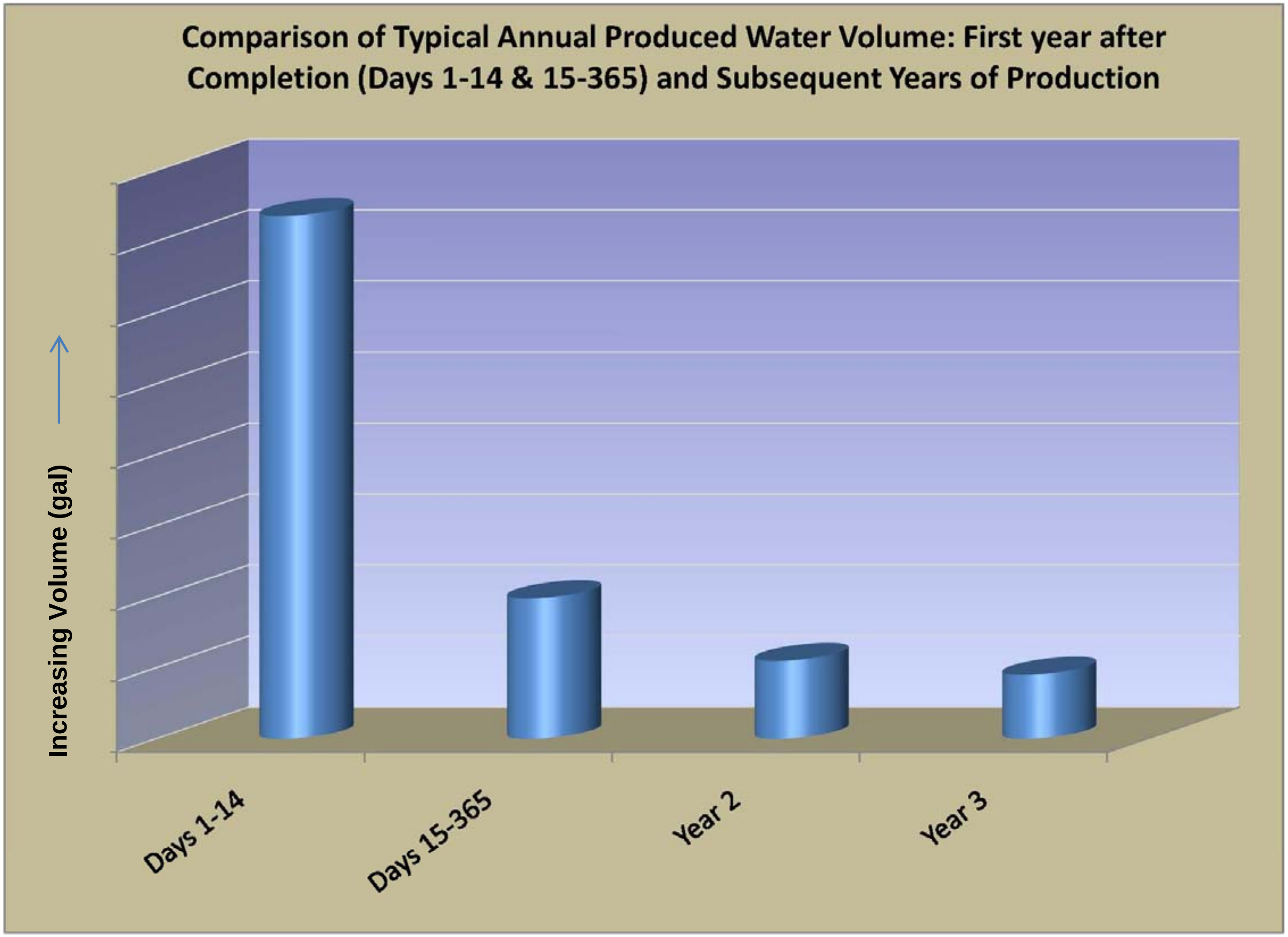
Selected Indicator Compounds
Produced Formation Water after Hydraulic Fracture (First 30 Days)
Location 1 - Western U.S.

Parameter	Calculated Concentration In Hydraulic Fracture Fluid (µg/L)	Hydraulic Fracture Fluid	Concentrations in Produced Formation Water following Hydraulic Fracturing with Time (µg/L)	
			12 Hour	**Day 2**
Glycols	55,000	35,800	<10,000	<10,000

Concentration of Indicator Parameters and Time after Hydraulic Stimulation Location 1 – Western U.S.



Produced Formation Water Production Volumes
Location 2 - Eastern U.S.



Hydraulic Fracture Fluid Components used in Location 2 - Eastern U.S.

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- Acid – hydrochloric acid
- Corrosion and Scale Inhibitors – alcohol, glycol, and amide
- Iron Control – citric acid
- Biocide – sodium salt, sodium hydroxide, and a bromide salt
- Friction Reducer – water soluble polymer (nitrogenous)
- Breaker – sodium and potassium salts
- Gel – guar gum, hydrocarbon, and polymer
- Surfactant – alcohol, glycol and hydrocarbon

Summary of Analytical Results

Selected Indicator Compounds
Produced Formation Water after Hydraulic Fracture (First 30 Days)
Location 2 – Eastern U.S.

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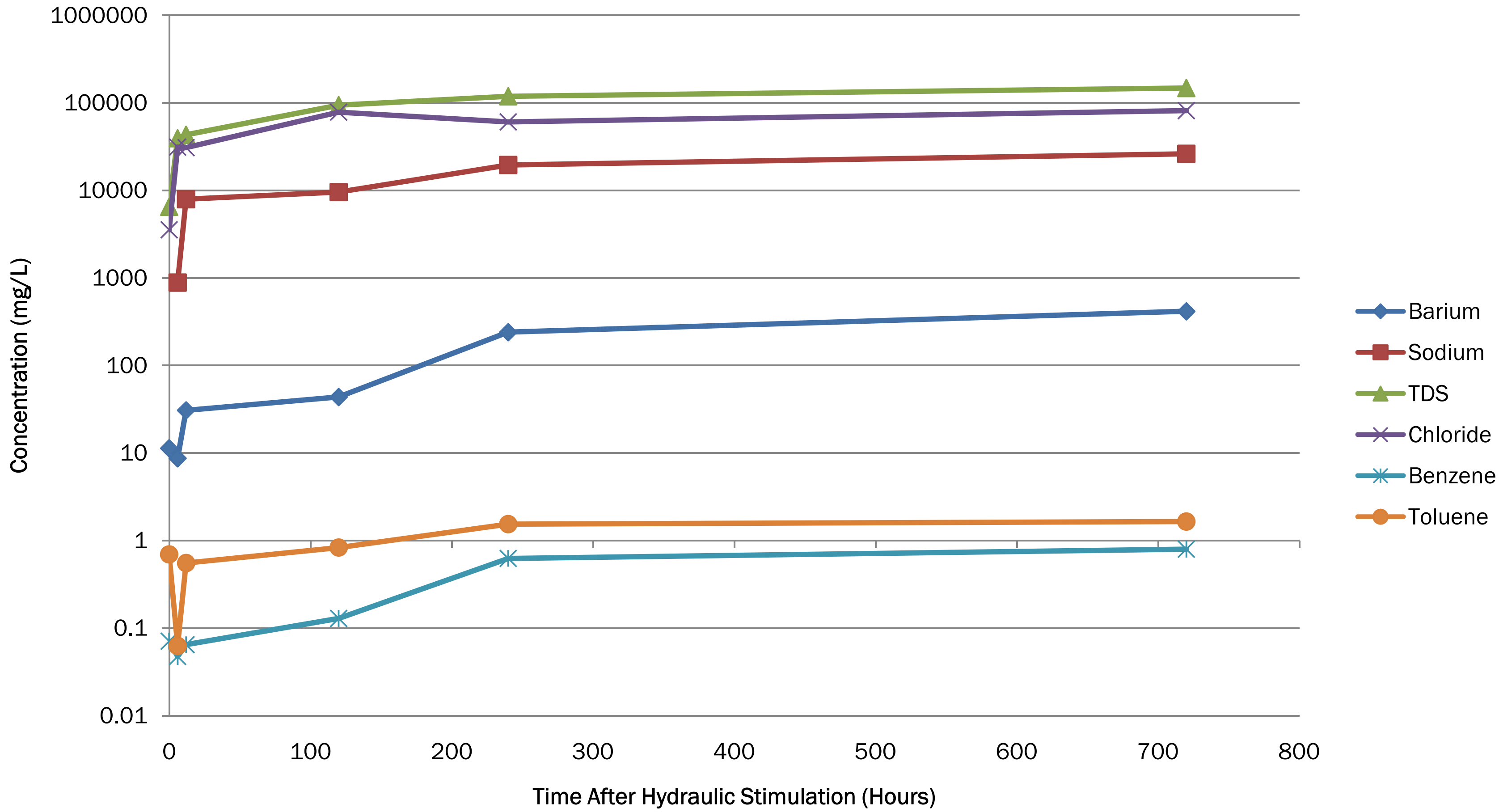
Parameter	Hydraulic Fracture Fluid	Concentrations in Produced Formation Water following Hydraulic Fracturing with Time (mg/L)				
		6 Hours	12 Hours	Day 5	Day 10	Day 30
Sulfate	35.3	86	<50	27.2	8.9	1.56
Total Kjeldahl Nitrogen	97.2	112	104	224	150	139
Ammonia	9.62	39.3	42.5	70.2	60.9	160
Chloride	2,790	31,200	30,800	78,300	6,0600	81,500
Total Dissolved Solids	7,700	39,400	43,200	94,300	119,000	148,000
Sodium	793	7940	9570	19,500	26,200	29,100
Benzene	77	64.7	129	625	797	740
Toluene	198	62.6	554	833	1,540	1,650

Summary of Analytical Results

Selected Indicator Compounds
Produced Formation Water after Hydraulic Fracture (First 5 Days)
Location 2 - Eastern U.S.

Parameter	Calculated Concentration in Hydraulic Fracture Fluid (μg/L)	Hydraulic Fracture Fluid	Concentrations in Produced Formation Water following Hydraulic Fracturing with Time (μg/L)	
			12 Hours	Day 5
Glycols	6,000	1,080,000	17,100	29,700
2-Butoxyethanol	117,000	<10,000	<10,000	<10,000

Concentration of Indicator Parameters and Time after Hydraulic Stimulation Location 2 – Eastern U.S.



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Transport of Radionuclides in Produced Formation Water

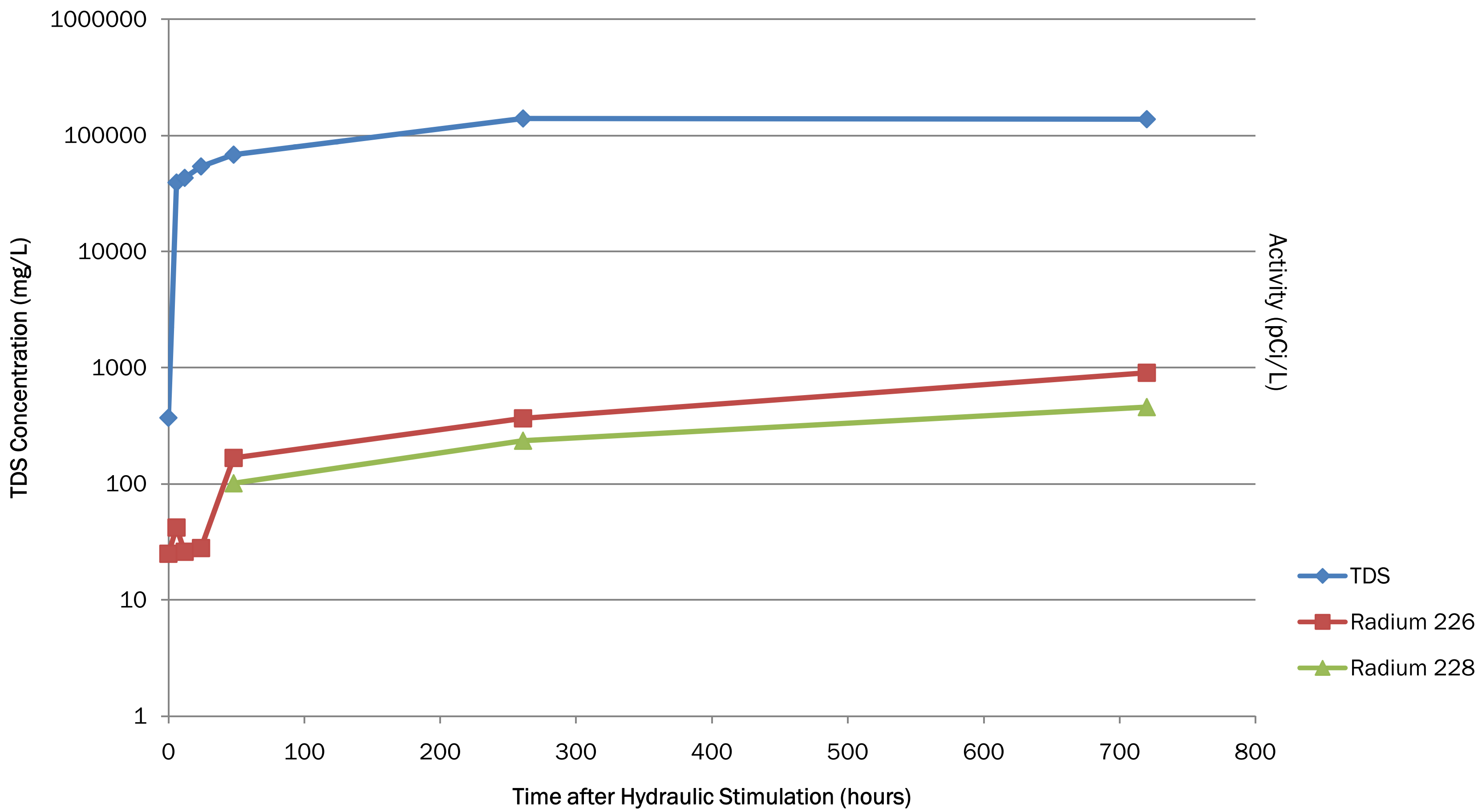
- **Presence of radionuclides in shale formation water is well documented**
- **Analytical method of choice: EPA Method 901.1 modified (Gamma Spectroscopy)**
  - Less influenced by matrix interferences
- **Data must be reported with activity, accompanied by standard deviation and minimum detectable concentration ("MDC")**
  - Example: 970 ± 130 pCi/L (MDC 30 pCi/L) Radium-226
- **Focus should be on Radium-226 and Radium-228**
  - Radium 226 and radium 228 represent more than 80% of the potential radiation dose in ingested water

Selected Total Radionuclide Data for Produced Formation Water Western U.S.

Parameter	Methods	Units	Minimum	Maximum	Mean	Error (±1 SD)	MDC
RadioChemistry							
Gross Alpha	*SW 9310 MOD; EPA 900.0*	pCi/L	620	4,000	1,750	±1,261	2,000
Gross Beta	*SW 9310 MOD; EPA 900.0*	pCi/L	250	1,200	760	±392	310
Radium 226	*EPA 901.1 Mod.*	pCi/L	167	904	616	±285	79
Radium 228	*EPA 901.1 Mod.*	pCi/L	101	459	329	±139	39
Uranium 238	*EPA 901.1 Mod.*	pCi/L	Not Detected				580
Total Dissolved Solids		mg/L	125,000	140,000	132,500	±10,600	NA

MDC – Minimum Detectable Concentration

Selected Radionuclides and Time After Hydraulic Stimulation Location 1 – Western U.S.

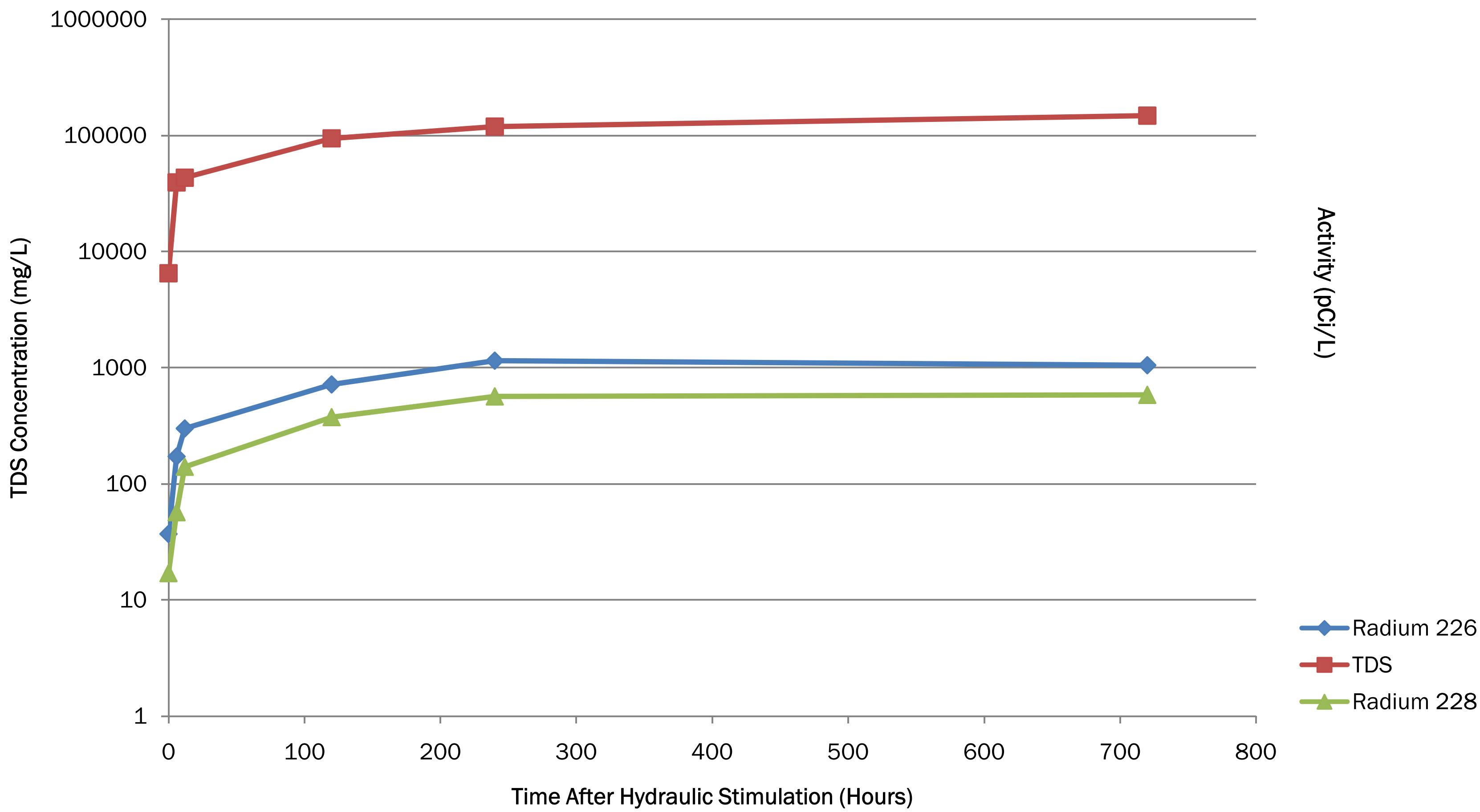


Selected Total Radionuclide Data for Produced Formation Water Eastern U.S.

Parameter	Methods	Units	Minimum	Maximum	Mean	Error (± 1 SD)	MDC
RadioChemistry							
Gross Alpha	*SW 9310 MOD; EPA 900.0*	pCi/L	4,100	6,600	5,350	±1,767	2,700
Gross Beta	*SW 9310 MOD; EPA 900.0*	pCi/L	ND	2,400	---	±1,131	2,100
Lead 210	*EPA 901.1 Mod.*	pCi/L	Not Detected				310
Radium 226	*EPA 901.1 Mod.*	pCi/L	867	1,050	959	±129	38
Radium 228	*EPA 901.1 Mod.*	pCi/L	584	620	602	±25	52
Uranium 238	*EPA 901.1 Mod.*	pCi/L	Not Detected				400
Total Dissolved Solids		Mg/L	148,000	153,000	150,500	±3,536	NA

MDC – Minimum Detectable Concentration

Selected Radionuclides and Time After Hydraulic Stimulation Location 2 – Eastern U.S.



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Conclusions

- Produced formation waters are highly variable within and between shale formations
- The elevated temperature and pressure effects the fate and transport of hydraulic fracturing fluid components
- The concentration of components in produced formation water is related to produced water volumes

Conclusions

- Most reliable sentinel compounds are TDS, chloride and divalent cations because they are in the highest concentrations in produced formation water
- The concentration of TDS is predictive of the concentration of the other species
- The concentrations of potential indicator parameters in produced formation water are overshadowed by the naturally-occurring concentrations of these parameters in formation waters
- The presence of NORM is delayed and associated with higher percentages of produced formation water with time

Comparison of Hydraulic Fracturing Fluid Composition with Produced Formation Water following Fracturing – Implications for Fate and Transport

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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.

Chesapeake Energy Corporation (Chesapeake) as a part of an evaluation of produced formation water had examined the composition of hydraulic fracturing chemicals used in natural gas production wells. Samples of the hydraulic fracturing fluid prior to the addition of proppant had been analyzed as well as time series samples of produced formation water for a natural gas well located in a shale formation west of the Mississippi River (Location 1) and another well in the eastern U.S. (Location 2). Some of the data evaluated is subject to attorney-client privilege (hereinafter "privileged data"). The major conclusions from Chesapeake's evaluation of produced formation water data are:

- Produced formation water is highly variable within and between shale plays.
- The elevated temperature and pressure affect the fate and transport of hydraulic fracturing fluid components and can create safety issues for sampling.
- Analytical techniques used for chemical and radiochemical characterization of the produced formation water must be robust to the matrix interferences presented by total dissolved solids.
- The most reliable sentinel compounds appear to be total dissolved solids, chloride and divalent cations. The concentrations of these components are related to each other and are also related to the formation water volume.
- The concentration of total dissolved solids is predictive of the concentration of other species.
- The concentration of indicator parameters for hydraulic fracturing mixtures, such as chloride, sulfate, and boron, are overshadowed by the naturally-occurring concentrations of these parameters in formation water.
- The presence of NORM is delayed and associated with higher percentages of formation water in the produced water with increasing time.

Based on the predicted downhole behavior of the hydraulic fracturing fluid, Chesapeake designed a sampling program for hydraulic fracturing fluid and produced formation water in order to understand the fate of hydraulic fracture chemicals in the produced formation water. The sampling design incorporated a review of chemicals used in two Chesapeake wells during hydraulic fracturing. Produced formation water samples were taken in a time series, hours to days, following hydraulic fracturing. The analyte list Chesapeake utilized was the complete list found at 40 CFR Part 264, Appendix IX, and commonly associated with groundwater monitoring supplemented with three glycols. All of the analyses were conducted using EPA analytical methods and were performed by a single NELAC-certified laboratory.

Table 1. Predicted Downhole Fate for Hydraulic Fracturing Fluid Components

HF Fluid Component	Predicted Downhole Fate
Acid	Reacts with minerals to create salts, water and CO_2
Corrosion Inhibitor	Bonds with pipe surfaces, broken down by micro-organisms or returned in produced formation water
Iron Control	Reacts with minerals to create salts, water and CO_2
Anti-Bacterial Agent	Broken down by micro-organisms or small amount returned in formation produced water
Scale Inhibitor	Attaches to the formation; majority returns with produced formation water
Friction Reducer	Remains in formation; broken down by micro-organisms or small amount returned in formation produced water
Surfactant	Returned with produced formation water or produced natural gas
Gelling Agent	Broken down by breaker and returns with produced formation water
Breaker	Reacts with "gel" and "crosslinker" to form ammonia and sulfate salts which are returned in produced formation water
Crosslinker	Combines with the "breaker" in the formation to create salts that are returned in produced formation water

Source: Chesapeake, 2010. Marcellus Shale Hydraulic Fracturing Fact Sheet, July.

Since it was predicted that many of the hydraulic fracture fluid chemicals would undergo transformation, the focus of this paper is indicator parameters, such as total Kjeldahl nitrogen, ammonia, sulfate, and sodium, which are used as surrogates for the presence of breakdown products of the hydraulic fracturing chemicals. In many cases, analytical methods are not available to analyze a compound but instead the analysis is conducted on a compound's predicted components since these results can be combined to provide an estimate of the compound's concentration. Focusing on indicator or sentinel parameters is also cost effective and does not require use of exotic or yet-to-be developed methodology.

There are significant issues regarding sampling of produced formation water. Natural gas is contained under high pressure in specialized equipment that is not designed for producing high quality environmental samples. The sample matrix itself presents challenges such as foaming and changes in surface tension. Analytical techniques are also impacted by the presence of elevated concentrations of total dissolved solids and chloride. The inorganic and wet chemistry methods were most affected by the presence of high total dissolved solids. EPA Method 8015 has been found to be insufficiently robust to overcome the matrix issues which are attendant to the analysis of produced formation water. The range of detection limits seen in the available data sets ranged from 10,000 to 50,000 µg/L. It does not appear that the glycol methods can provide meaningful results for samples with these matrix issues. EPA Method 8270 has some utility for larger glycols, such as glycol ethers; however for the smaller, more soluble, ethylene and diethylene glycols, the extraction methods are not useful. Radiochemistry methods are particularly affected by the elevated concentrations of barium and total dissolved solids. Since hydraulic fracture fluid is a product rather than an environmental sample, certain standard requirements for environmental samples, such as holding time, are not applicable.

Hydraulic fracturing service vendor-supplied data was available to compile the water volume, proppant volume, and specific hydraulic fracturing products and related volumes used for fracturing of the individual well. Component information for each of the hydraulic fracturing products was drawn from the Material Safety Data Sheets. These data were utilized to calculate the concentrations of the individual chemicals used in the hydraulic fracture fluid for each of the two subject wells. For some, surrogate chemical species, e.g. sodium or chloride, were calculated for comparative purposes.

Produced formation water volumes have been estimated for the Location 1 well. Typically, produced water volumes decrease markedly with time once a natural gas well is in production. In the first ten days of production, about 600,000 gallons or 60,000 gallons per day are produced; between days 11 and 365, the volume drops to approximately 8,400 gallons per day. In subsequent years of production, the well would be expected to produce about 4,200 gallons per million standard feet of gas (MMCF) of gas produced average for the life of the well. Chesapeake used approximately 4 million gallons of water for drilling and fracture stimulation.

For the Location 1 well, a hydraulic fracture fluid containing the following compounds was utilized: biocide (gluteraldehyde and an alcohol); beaker (ammonium persulfate); iron control (sodium compound); friction reducer (polymer and a hydrocarbon); crosslinker (polyol and borax); corrosion and scale inhibitors (alcohols, organic acids, and sodium salt of a polymer); and acid (hydrochloric acid). Therefore, boron, sodium, sulfate, and total Kjeldahl nitrogen were expected to be useful as surrogate analytes.

Analytical results were available for the hydraulic fracture fluid (pre-injection) and produced formation water samples in time series for 6 hours, 1 day, 2 days, 9 days, and 30 days following fracturing. The results for several surrogate/indicator species, total Kjeldahl nitrogen, ammonia, chloride, total dissolved solids, sodium, boron and glycols, were summarized. Data were also available for two radium isotopes (Ra-226 and Ra-228). Since the hydraulic fracture fluid did contain a hydrocarbon carrier, benzene and toluene were also evaluated (most other volatile organic compounds and semi-volatile organics were below detection limits).

In general, the concentrations for the analytes of interest increased, especially the total dissolved solids, chloride and sodium, with time following hydraulic stimulation. These increases reflect increasing percentages of formation water entering the produced water volume. It should be noted that the sodium, chloride and boron concentrations in hydraulic fracture fluids were rapidly overshadowed by the naturally-occurring concentrations of these compounds on formation water. The increasing concentrations of the nitrogenous compounds probably reflect degradation of the nitrogen compounds in the hydraulic fracture fluid and microbial activity.

The results for the divalent cations, barium and strontium concentrations were examined for relationship with total dissolved solids concentrations. The correlation coefficient for barium and total dissolved solids was 0.998 and that for strontium and total dissolved solids was 0.935. The correlation between chloride and total dissolved solids was 0.943. The relationship between total dissolved solids and radium-226 and radium-228 appear to be similar to that of the other divalent cations. It is evident that the presence of total dissolved solids can be used as a sentinel parameter.

The calculated concentration of glycols was 55,000 µg/L; however, the analytical result for the hydraulic fracture fluid was 35,800 µg/L. As the total dissolved solids increased in the 12 hour and day 2 samples, the detection limit for EPA Method 8015 increased to <10,000 µg/L. These results point to the limitations of Method 8015 for glycol analyses in produced formation water.

Produced formation water volumes have been estimated for the Location 2 well located in the eastern U.S. Typical produced water volumes decrease markedly with time a natural gas well is in production. In the first ten days of production, about 600,000 gallons or 60,000 gallons per day are produced; between days 11 and 365, the volume dropped to approximately 8,400 gallons per day. In subsequent years of production, the well would be expected to produce less than 200 gallons per MMCF average for the life of the well. Chesapeake used approximately 3.4 million gallons for fracture stimulation.

For the Location 2 well, the hydraulic fracture fluid contained the following: biocide (sodium salt, sodium hydroxide, and a bromide salt); breaker (sodium and potassium salts); iron control (citric acid); friction reducer (water soluble nitrogenous-based polymer); gel (guar gum, a hydrocarbon, and polymer); corrosion and scale inhibitors (alcohol, glycol and an amide); surfactant (alcohol, glycol and a hydrocarbon); and acid (hydrochloric acid). Sodium, chloride, total Kjeldahl nitrogen, and sulfate were expected to serve as surrogates for the components of the fracture fluid.

Analytical results were available for the hydraulic fracture fluid (pre-injection) as well as for the subsequent produced formation waters at 6 hours, 12 hours, 5 days, 10 days and 30 days following fracture stimulation. The results for surrogate and indicator parameters were evaluated. These included sulfate, total Kjeldahl nitrogen, ammonia, total dissolved solids, sodium, glycol and 2-butoxyethanol. Examination of the glycol and 2-butyoxyethanol results reveals the difficulty in accurately quantitating glycol using the available EPA approved method. Benzene and toluene results were found to increase within 12 hours to concentrations well above that in the original hydraulic fracture fluid. The occurrence of these compounds is attributed to natural occurrence within the natural gas production zone.

The results for the divalent cations, barium and strontium concentrations were examined for relationship with total dissolved solids concentrations. The correlation coefficient for barium and total dissolved solids was 0.966 and that for strontium and total dissolved solids was 0.988. The correlation between chloride and total dissolved solids was 0.933. There appears to be a similar relationship between total dissolved solids and radium-226 and radium-228 as well. It is evident that the presence of total dissolved solids can be used as a sentinel parameter.

The appearance of gross alpha, gross beta, two radium isotopes and uranium-238 in produced formation water following hydraulic fracturing represents an example of transport of naturally-occurring materials from the shale formation into these waters and the time at which concentrations appear to stabilize varies considerably from shale play to shale play. For locations in the western U.S., the measured activity for these radiochemistry parameters varies considerably. The range of gross alpha and gross beta is from 620 to 4,000 pCi/L (mean value 1,750 pCi/L) and 250 to 1,200 pCi/L (mean value 760 pCi/L), respectively. Radium 226 and 228 appear together with the radium 228 being the lesser in terms of activity. No uranium-238 was detected. The activities encountered in the well samples from the eastern U.S. covered a wider range of activity levels and exhibited higher maximum values. When results for a single location are examined, there does appear to be a relationship with increasing total dissolved solids. This appears to be true for results for both Location 1 and Location 2.

The major conclusions from the review of produced formation water data are:

- Produced formation water is highly variable within and between shale plays.
- The elevated temperature and pressure affect the fate and transport of hydraulic fracturing fluid components and can create safety issues for sampling.
- Analytical techniques used for chemical and radiochemical characterization of the produced formation water must be robust to the matrix interferences presented by total dissolved solids.
- The most reliable sentinel compounds appear to be total dissolved solids, chloride and divalent cations. The concentrations of these components are related to each other and are also related to the formation water volume.

- The concentration of total dissolved solids is predictive of the concentration of other species.
- The concentration of indicator parameters for hydraulic fracturing mixtures, such as chloride, sulfate, and boron, are overshadowed by the naturally-occurring concentrations of these parameters in formation water.
- The presence of NORM is delayed and associated with higher percentages of formation water in the produced water with increasing time