Produced Formation Water Sample Results from Shale Plays

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Produced Formation Water Review

- **Conducted a review of the analytical results of non-potable produced formation water from four shale plays**
  - Marcellus
  - Barnett
  - Fayetteville
  - Haynesville
- **Utilized several available data sources**
  - Gas Technology Institute Study for the Marcellus
  - USGS database
  - Additional privately generated data sources

Purpose of the Data Review

- **Identify sentinel parameters to be included in baseline potable water sampling program**
  - Criteria for selection of sentinel parameters was based on potential mobility in groundwater systems, toxicity, and the ability to accurately quantitate the parameters in produced formation water
- **Identify parameters which could be released from host rock**
- **Support decision making on disposal and treatment and reuse/recycling related to produced water**

Shale Play Data Evaluated

- **Source water for hydraulic fracturing fluids**
- **Mixed hydraulic fracturing fluids**
- **Produced formation water from operating wells**
- **Produced formation water after hydraulic fracturing activities**
  - Iterative samples over time
  - Varying sampling times utilized by different data sources
    - GTI Study in Marcellus – samples up to 90 days after hydraulic fracturing
    - Additional Data – samples up to 30 days after hydraulic fracturing
- **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)

Shale Information

Shale Play	Barnett	Fayetteville	Haynesville	Marcellus
Average Depth From Surface (ft)	7,400	4,500	11,500	6,750
Bottom Hole Temperature (F)	190	130	320	140
Bottom Hole Pressure (psi)	2,900	2,000	10,000	4,000

- Natural gas producing shale zones are thousands of feet below the formations which produce potable water

Sampling and Analytical Challenges for Produced Formation Water

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- **Analytical data has limitations due to sampling challenges**
  - Natural gas is contained under high pressure in specialized equipment not designed for producing a high quality environmental sample
  - Sample matrix causes collection problems
  - Initial produced water pressures are thousands of psi
  - Temperature of produced water 30-70 degrees Celsius
  - Safety issues for sampling personnel
- **Analytical data has limitations due to analytical challenges**
  - Organic chemistry analyses has fewer issues
  - Inorganic and Wet Chemistry tests were affected by very high solids content and other matrix complexities
  - Radiochemistry affected by solids and barium

Glycols in Produced Formation Water

- **Data available for ethylene glycol and 1,2-propylene glycol**
- **Data is inconclusive with regards for use as a sentinel compound**
  - Detected values ranged from 12,000 to 87,400 µg/L
  - Detected in 14 of 34 samples
- **Results for all formation produced water samples were inconsistent in all shale plays due to issues with the analytical method**
- **Analytical method: EPA Method No. 8015**
  - Insufficiently robust to achieve meaningful detection limits due to sample matrix
  - Detection limits ranged from 10,000 to 50,000 µg/L

Volatile and Semi-Volatile Organics in Produced Formation Water

- Data was available for produced formation water from operating wells and iterative (time series) samples for produced water following hydraulic fracturing activities
- The majority of the VOC and SVOC results were below detection limits for both sets of samples
- Benzene, Ethyl benzene, Toluene and Xylenes most consistently detected VOCs - produced in formation
- Phenol and Pyridine most consistently detected SVOCs
- No consistent trends in VOC or SVOC concentrations with time in the iterative samples

Summary of Analytical Results

Selected Volatile Organic Compounds
Produced Formation Water after Hydraulic Fracture (First 30 Days)

Parameter	Concentrations in Produced Formation Water by Shale Play (µg/L)			
	Barnett	Fayetteville	Haynesville	Marcellus
Benzene	< 1 – 97	<1 – 140	<1 -3,460	<1 – 1,950
Ethyl benzene	<1 - 249	<1 – 11	<1 – 1,470	<1 - 164
Toluene	1 – 578	<1 – 117	2.6 – 11,400	<1 – 3,190
Xylenes, total	<3 – 2,480	<3 – 60.1	12 – 10,700	<2 – 1,970
No. of Wells Sampled	3	2	3	4

Summary of Analytical Results

Selected Volatile Organic Compounds
Produced Formation Water from Operating Wells

Parameter	Concentrations in Produced Formation Water by Shale Play (µg/L)			
	Barnett	Fayetteville	Haynesville	Marcellus
Benzene	4.37 – 1,600	<1 – 1.05	76 – 3,140	<1 - 513
Ethyl benzene	<1 – 102	ND	2.5 – 839	<1 – 51.6
Toluene	8.8 – 3,250	ND	84 – 11, 300	<1 - 918
Xylenes, total	<3 – 2,630	<3 – 4.86	31 – 14,500	<3 - 439
No. of Wells Sampled	15	9	5	15

Summary of Analytical Results

Selected Semi-Volatile Organic Compounds
Produced Formation Water after Hydraulic Fracture (First 30 days)

Parameter	Concentrations in Produced Water by Shale Play (µg/L)			
	Barnett	**Fayetteville**	**Haynesville**	**Marcellus**
Phenol	ND – 1,160	ND	ND - 971	ND - 459
Pyridine	ND – 264	ND – 534	ND	ND
No. of Wells Sampled	3	2	3	4

Summary of Analytical Results

Selected Semi-Volatile Organic Compounds Produced Formation Water from Operating Wells

Parameter	Concentrations in Produced Water by Shale Play (µg/L)			
	Barnett	**Fayetteville**	**Haynesville**	**Marcellus**
Phenol	12 - 31	ND - 32	250 – 3,720	ND - 34
Pyridine	12 - 758	ND – 92	ND – 15.5	ND - 56
No. of Wells Sampled	15	9	5	15

General Chemistry Analytical Results from Produced Formation Water

- Total Dissolved Solids, Divalent Cations, and Chloride were elevated in produced formation water samples for all Shale plays
- Concentrations of Barium and Strontium tended to correlate with Total Dissolved Solids results
- Chloride represents the most abundant anion
- The data are generally consistent between the data sources
- The data are generally consistent with the reported ranges of Total Dissolved Solids in produced formation water from all types of wells available in the literature

Arsenic Analytical Results for Produced Formation Water

- Initial concern due to known potential for interactions between refined hydrocarbon products in groundwater and naturally-occurring arsenic
- Arsenic concentrations were rarely found to be above method detection limits in the produced formation waters sampled
  - GTI results for Marcellus
    - Influent water – ND – 9.1 μg/L
    - 5-Day produced water – ND – 124 μg/L
    - 90-day produced water - ND - 114 μg/L
  - Other data sources reviewed for the Barnett, Fayetteville and Haynesville – all concentrations below the analytical detection limit

Radionuclides in Produced Formation Water

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- **Presence of radionuclides in produced 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 detected concentration**
  - Example: 970 ± 130 pCi/L (MDC 30 pCi/L) Radium-226
  - Necessary to put data result into context, particularly for non-detected values. Unless data is presented in this format, it is meaningless.
- **Focus should be on Radium-226, Radium-228, and Uranium-238**
  - Radium 226 and radium 228 represent more than 80% of the potential radiation dose in ingested water

Conclusions

- Produced formation waters are highly variable within and between shale formations
- Analytical techniques must be robust to the matrix interferences from TDS
- Most reliable sentinel compounds are TDS, chloride and divalent cations
- Few VOCs and SVOCs are consistently found in produced formation water.
- Benzene, ethyl benzene, toluene and xylenes are the most frequently detected VOCs and are naturally occurring
- The concentrations of VOCs and SVOCs in produced formation water are generally too low for use as sentinel compounds