Chesapeake ENERGY

KEY INDICATOR PARAMETERS AND EVALUATION APPROACH

January 28, 2013

PRESENTATION OUTLINE

- Predicted Fate and Transport of Hydraulic Fracture Chemicals
- Key Indicator Parameters
- Fate Evaluation – Comparison of Predicted Concentrations with Measured Concentrations of Indicator Parameters
- Tracers

DOWNHOLE CONDITIONS IN SHALE FORMATIONS

Shale Play	Barnett	Haynesville	Marcellus	Utica	Eagle Ford	Niobrara
Average Depth From Surface (ft)	7,400	11,500	6,750	6, 250	7,000	10,250
Bottom Hole Temperature (F)	190	320	140	140	220	225
Bottom Hole Pressure (psi)	3,400	10,000	4,200	4,000	4,200	6,200

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**
  - Potassium chloride – cannot easily measure potassium chloride but instead measure potassium and chloride
  - Sodium hydroxide – measure sodium as an indicator

INDICATOR PARAMETER SELECTION

- **Criteria for selection of indicator parameters :**
  - Relative abundance in produced water
  - Potential mobility in groundwater systems
  - Toxicity
  - Ability to accurately quantitate the parameter in produced formation water
- **Identification of appropriate indicator parameters**
  - Chloride is the most abundance anion; divalent cations are most prevalent
  - Indicators for breakdown/reaction products or metabolites
    - Nitrogen series -- amide-based polymers
    - Chloride -- hydrochloric acid or potassium chloride
  - Use of key indicator compounds
    - Cost-effective
    - No new methods or modifications to existing methods needed

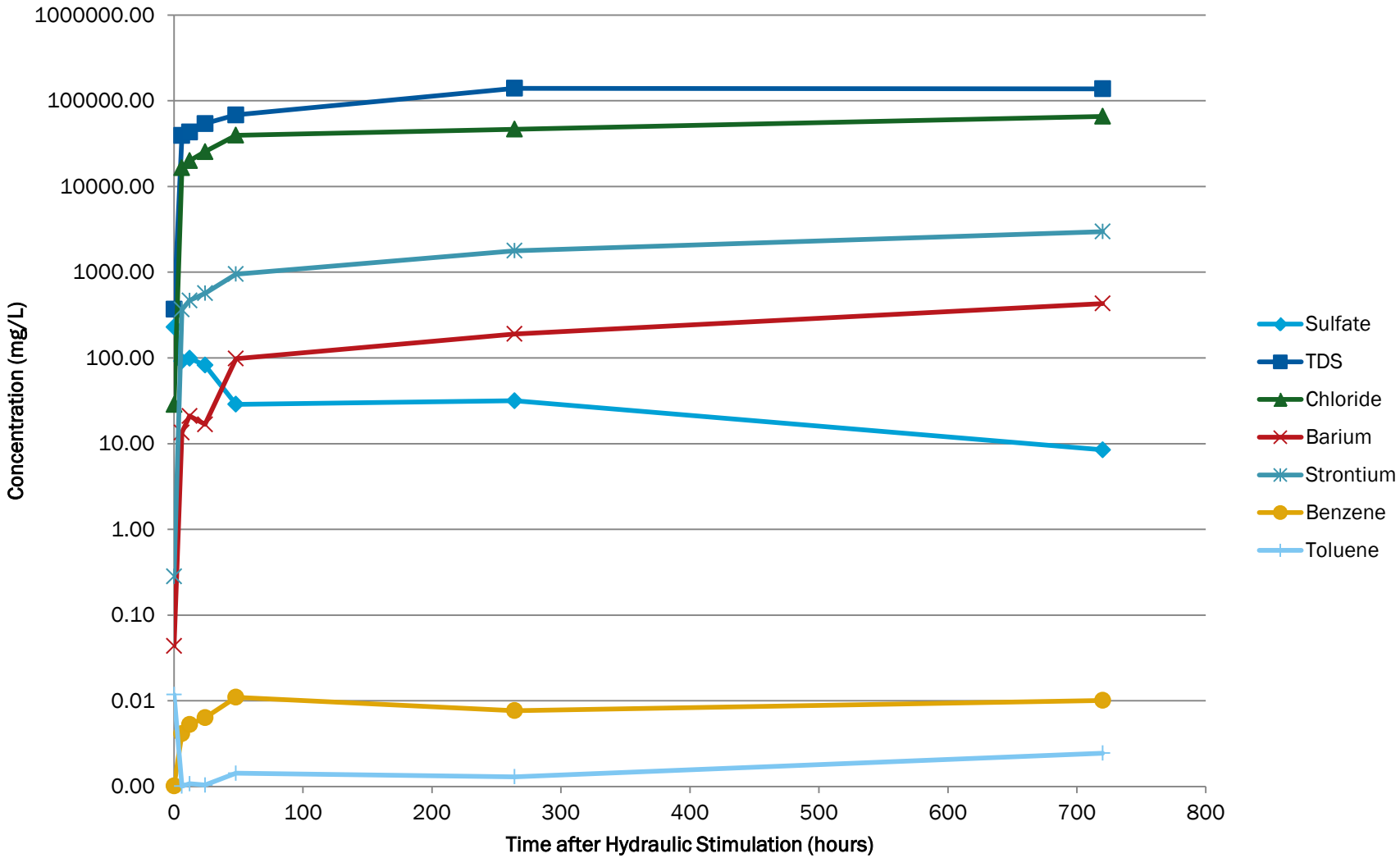
HYDRAULIC FRACTURE FLUID COMPONENTS USED IN LOCATION 1 – WESTERN U.S.

- 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.

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 (μg/L)	<1	4.15	6.34	11	7.69	10.1
Toluene (μg/L)	1.44	1.01	1.04	1.43	1.30	2.45

CONCENTRATION OF INDICATOR PARAMETERS AND TIME AFTER HYDRAULIC STIMULATION LOCATION 1 – WESTERN U.S.



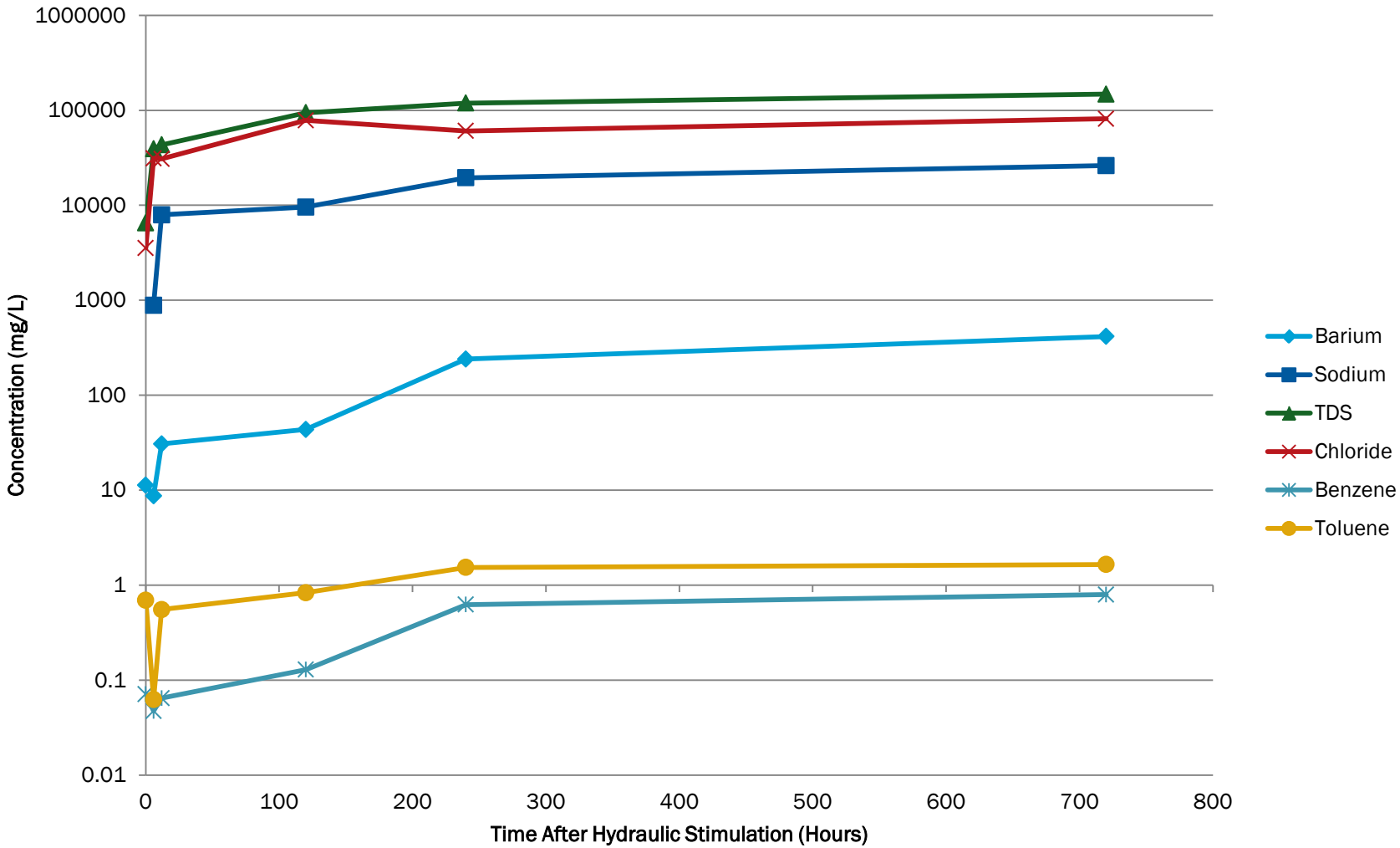
HYDRAULIC FRACTURE FLUID COMPONENTS USED IN LOCATION 2 - EASTERN U.S.

- 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.

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 (μg/L)	77	64.7	129	625	797	740
Toluene (μg/L)	198	62.6	554	833	1,540	1,650

CONCENTRATION OF INDICATOR PARAMETERS AND TIME AFTER HYDRAULIC STIMULATION LOCATION 2 – EASTERN U.S.



EVALUATION OF USE OF GLYCOLS AS INDICATOR COMPOUNDS IN PRODUCED FORMATION WATER AFTER HYDRAULIC STIMULATION

Parameter	Calculated Concentration in Hydraulic Fracture Fluid (µg/L)	Hydraulic Fracture Fluid	Concentrations in Eastern U.S. 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

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

Breakdown and analytical interferences with glycol analyses make them unsuitable for use as a key indicator for movement of produced water.

TRANSPORT OF RADIONUCLIDES IN PRODUCED FORMATION WATER

- **Presence of radionuclides in shale formation water is well documented**

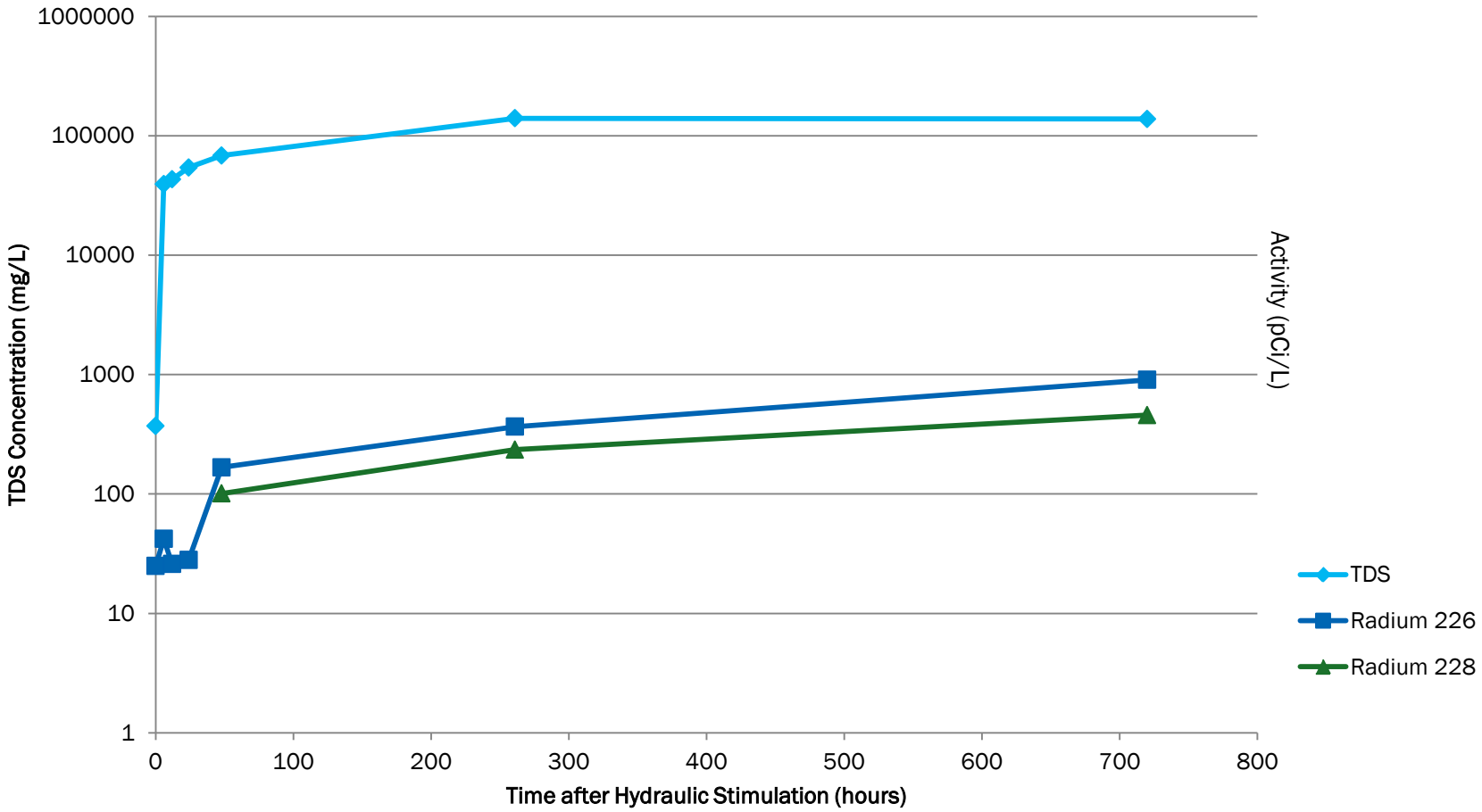
- **Data must be reported with activity, accompanied by standard deviation and minimum detectable concentration ("MDC")**
  - Example: 970 ± 130 pCi/L (MDC 30 pCi/L) Radium-226

- **Indicator parameters should be on Radium-226 and Radium-228**
  - Radium-226 and Radium-228 represent more than 80% of the potential radiation dose
  - Mobility of Radium-226 and Radium-228 is similar to the other divalent cations

SELECTED TOTAL RADIONUCLIDE DATA FOR PRODUCED FORMATION WATER – WESTERN U.S.

Parameter	Methods	Units	Minimum	Maximum	Mean	Error (±1 SD)	MDC
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

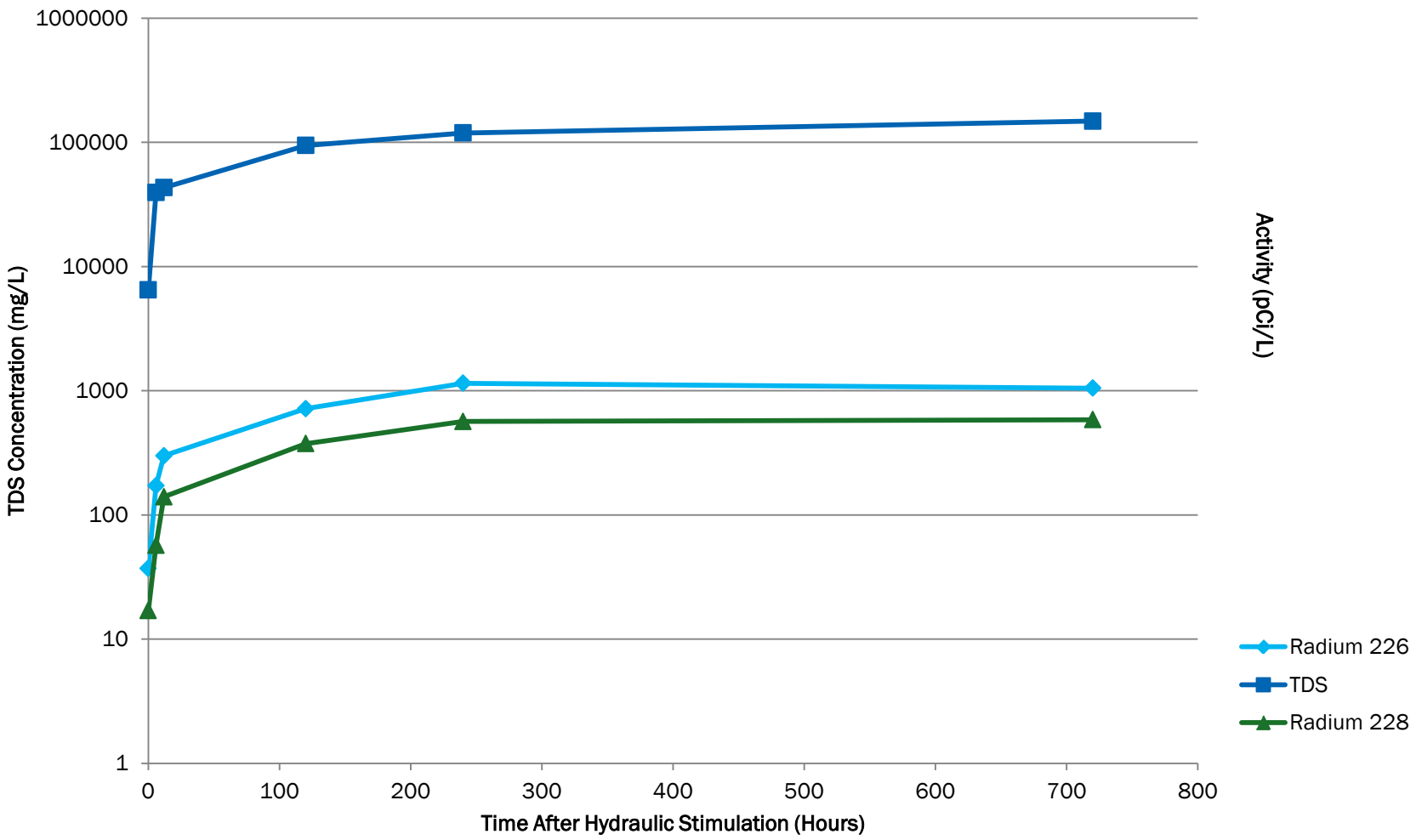
SELECTED RADIONUCLIDES AND TIME AFTER HYDRAULIC STIMULATION – LOCATION 1 (WESTERN U.S.)



SELECTED TOTAL RADIONUCLIDE DATA FOR PRODUCED FORMATION WATER – EASTERN U.S.

Parameter	Methods	Units	Minimum	Maximum	Mean	Error (± 1 SD)	MDC
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
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

SELECTED RADIONUCLIDES AND TIME AFTER HYDRAULIC STIMULATION LOCATION 2 – EASTERN U.S.



TRACERS

- **Possible tracers evaluated**
  - Biological -- enzymes
  - Chemical – dyes, chemical tracer
  - Metals -- tagged sand
  - Radiochemical
- **Fate under extreme temperature and pressures**
  - Commercially available chemical tracer alternatives were not guaranteed to perform in the downhole environment
  - All vendors contacted indicated that dyes and chemical tracers would disassociate at the temperatures encountered downhole
  - Biological tracers would be destroyed at the downhole temperatures
- **Concentrations necessary to achieve meaningful results**
  - For the tracer metals on tagged sand, such as indium, antimony, or scandium, would have to be added in extremely high concentrations to have the possibility of being seen in groundwater
    - Lack of mobility is an issue
    - Expensive
- **Public perceptions regarding the use of radiochemical tracers**
- **Timing of sampling and lack of specific attribution to cause**

CONCLUSIONS

- The elevated temperature and pressure effects the fate and transport of hydraulic fracturing fluid components
- Most reliable indicator 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
- Tracers are either unstable in the downhole environment, too expensive, non-specific, or inappropriate from a public perception standpoint
- Chloride and divalent cations are the best key indicator parameters for evaluation of potential migration of both produced water and hydraulic stimulation fluids