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## The Marcellus Shale Energy and Environmental Laboratory (MSEEL): Water and Solid Waste Findings—Year One

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### **Summary**

The Marcellus Shale Energy and Environment Laboratory (MSEEL) is centered on four producing, horizontal wells located across the Monongahela River from Morgantown WV. The wells are within 600m of the River and 950m from the Morgantown Utility Board (MUB) water intake. Two horizontal wells were completed in the Marcellus Formation in 2011. In 2015 WVU was awarded a contract by the USDOE/National Energy Technology Laboratory to implement a long-term field study around two new wells on the site to develop and validate new knowledge and technology to improve recovery efficiency and minimize environmental implications of shale gas development.

Prior to MSEEL, there had been no comprehensive field study coupling same site environmental baseline, completion and production monitoring with environmental outcomes. The water and solid waste component of the MSEEL project include monitoring the Monongahela River upstream of the MSEEL site, at the MUB water intake and downstream of MUB. Solid waste characterization includes drilling mud and drill cuttings through the vertical and horizontal well legs. Liquids analysis includes completion fluid, and time-series flowback and produced water sampling and analysis. Analytical parameters include organic, inorganic and radionuclides. MSEEL is generating an unprecedented body of data which will be available to researchers at NETL and researchers from other agencies and institutions for advancement of the science around shale gas development and evaluation of procedures needed to protect the public and the environment.

This presentation summarizes results of the first year: drilling, completion, flowback and produced water sampling as well as River monitoring. Important findings include the role of drilling fluids in determining the toxicity of drill cuttings, radioactivity levels in drill cuttings and time series trends in aqueous phase organic compounds (BTEX), radium, alpha and beta emitters and twenty inorganic ions. River monitoring indicated no effects attributable to well development and production. Risk reduction practices at the MSEEL well site will also be discussed.

### Approach

The Marcellus Shale Energy and Environment Laboratory (MSEEL) is the first comprehensive field study coupling same site environmental baseline, completion and production monitoring with environmental outcomes. One year into the post completion part of the program, the water and solid waste component of MSEEL has systematically sampled flowback and produced water volumes, hydraulic fracturing fluid, flowback, produced water, drilling muds, drill cuttings and characterized their inorganic, organic and radio chemistries. In addition, surface water in the nearby Monongahela River was monitored upstream and downstream of the MSEEL drill pad. Toxicity testing per EPA method 1311 (TCLP) was conducted on drill cuttings in both the vertical and horizontal (Marcellus) sections to evaluate their toxicity potential.

The MSEEL production wells 3H and 5H were developed by Northeast Natural Energy, LLC (NNE) on the MIP well pad and completed in December 2015. The MIP pad contained two previous production wells: 4H and 6H.

The older wells were completed in 2011. The MIP pad is at an elevation 75 m above and a linear distance of 580 m from the Monongahela River, at a point 700 m upstream of the Morgantown Utility Board's primary drinking water intake. Prior to construction of the MIP pad NNE adopted a secondary containment strategy to minimize the risk of offsite contamination. This included a double HDPE liner and berms sufficient to contain any accidental leakage within the pad. Makeup water was taken from the Monongahela River and stored in a lined pond adjacent to the MIP pad. To ensure integrity of the water supply, the river was sampled at three stations: upstream, downstream and at the Morgantown Utility Board's water intake. Sampling began prior to installation of the 3H and 5H wells and continued for one year post completion.

### Background

Hydraulic fracturing stimulates wells by injecting high volumes of water, sand and chemical additives into an otherwise non-producing, hydrocarbon rich formation at high pressures to induce porosity by developing and supporting fractures (US EPA 2010). Combined with horizontal drilling and development of extended, lateral well bores, hydraulic fracturing technology is critical to the viability of unconventional hydrocarbon plays.

Hydraulic fracturing requires significant quantities of water: Requirements commonly range from 11,000 to 19,000 m<sup>3</sup> for a horizontal well, but volumes as high as 34,000 m<sup>3</sup> have been reported (Xu et al., 2011; Lewis, 2012; Bai et al., 2013). Fracturing fluid typically consists of between 80 to 90 percent water; 8 to 15 percent proppant while the remaining 0.5- 1 percent consists of chemical additives. Commonly used additives include about 11 chemicals with different functions such as friction reducers, biocides, scale inhibitors, clay stabilizers, and surfactants (URS, 2011; McCurdy, 2011). Exposure pathways (Ziemkiewicz et al., 2014a) and protective measures (Ziemkiewicz et al., 2014b) have stressed the potential toxicity of produced water.

#### Methods

**Produced water sampling.** During well completion, hydraulic fracturing fluids are injected into the target formation and the injected fluids return to surface via the well bore as flowback. Figure 1 shows the general processes of fluid flow during hydraulic fracturing and gas production. Produced water is returned via the well bore along with gas during production phase. The distinction between flowback and produced water is not well defined and these two terms are sometimes used interchangeably in the vernacular.



Figure 1. Flow of fluids during the well completion (hydraulic fracturing) and production phases of well operations (from Ziemkiewicz, 2014c)

Samples of frac makeup water, the hydrofrac fluid, flowback and produced water were sampled monthly over an interval of 392 days at the 3H and 5H wells. In addition, the 4H and 6H wells which were shut in when the newer wells came on line were re-activated and sampled starting in late 2016. Makeup water was pumped from the Monongahela River and mixed with the hydraulic fracturing fluids. Produced water samples were taken at the upstream end of each well's separator. Table 1 summarizes the analytical parameters: inorganic, organic and radiochemical.

**Solid waste sampling and testing**. Solid waste consisted of drill cuttings collected during the vertical and horizontal legs of the 3H and 5H wells. They were characterized according to the parameters listed in table 2. In addition both vertical and horizontal (Marcellus) samples were subjected to USEPA method 1311, the Toxic Characteristic Leaching Procedure (TCLP) to determine whether the drill cuttings constituted hazardous waste under the USEPA's Resource Conservation and Recovery Act (RCRA).

Aqueous chemistry parameters - HF fluids and PW									
	nic		Organics		Radionuclides				
	Anions		Cations*						
рН	Br		Ag	Mg		Benzene		α	
TDS	Cl		Al	Mn		Toluene		β	
TSS	SO <sub>4</sub>		As	Na		Ethylbenzene		<sup>40</sup> K	
Conductance	sulfides		Ва	Ni		Total xylene		<sup>226</sup> Ra	
Alkalinity	nitrate		Ca	Pb		m,p-xylene		<sup>228</sup> Ra	
Bicarbonate	nitrite		Cr	Se		o-xylene			
Carbonate			Fe	Sr		MBAS			
ТР			К	Zn		O&G			

### Table 1. Aqueous analytical parameters.

\* total and dissolved

### Table 2 Analytical parameters drill cuttings and mud.

Solids chemistry parameters - Cuttings & Muds											
Inorganics				Organics		Radionuclides	5	TCLPs			
	Anions		Cations*		Propane						
alkalinity**	Br		Ag	Mg	DRO		α		Arsenic	1,4-Dichlorobenzene	Methly ethyl ketone
conductance	CI		Al	Mn	ORO		β		Barium	1,2-Dichloroethane	Nitrobenzene
рН	SO <sub>4</sub>		As	Na	GRO		<sup>40</sup> K		Benzene	1,1-Dichloroethylene	Pentrachlorophenol
bicarbonate**	sulfide		Ва	Ni	Ethylbenze	ne	<sup>226</sup> Ra		Cadmium	2,4-Dinitrotoluene	Pyridine
carbonate**	nitrate		Ca	Pb	m,p-xylen	2	<sup>228</sup> Ra		Carbon tetrachloride	Endrin	Selenium
TP	nitrite		Cr	Se	o-xylene				Chlordane	Heptachlor	Silver
			Fe	Sr	Styrene				Chlorobenzene	Heptachlor epoxide	Tetrachloroethene
			К	Zn	Toluene			0	Chloroform	Hexachlorobenzene	Toxaphene
					Total xylen	es			Chromium	Hexachlorobutadiene	Trichloroethylene
		тос				o-Cresol	Hexachlororethane	2,4,5-Trichlorophenol			
					COD				m-Cresol	Lead	2,4,6-Trichlorophenol
					O&G				p-Cresol	Lindane	2,4,5-TP (Silvex)
						Cresol	Mercury	Vinyl chloride			
									2,4-D	Methoxychlor	

### **Results and Discussion**

The MSEEL wells used green completion strategy including a synthetic based drilling fluid (Bio-Base 365). All drill cutting samples fell below TCLP thresholds for organic and inorganic components indicating that they are non-hazardous per the Resource Conservation and Recovery Act. Maximum specific isotopic activity in drill cuttings was recorded for  $^{40}$  K which was 28.32 pCi/g. Gross alpha accounted for the highest reading at 60 pCi/g. The

maximum combined radium isotope values ( $^{226+228}$  Ra) was 10.85 pCi/g. These radioactivity levels are within the West Virginia standard of 5 pCi/g above regional background levels.

The composition of the hydraulic fracturing (HF) fluids in both wells was similar to the makeup water which was drawn from the Monongahela River. Its chemistry was typical of Monongahela River water. This is true of inorganics, organics and radioisotopes. Organic surrogate recoveries were in the range of 90 to 104% indicating good quality control at the analytical laboratory. There was no evidence that Monongahela River quality was influenced by well development, completion or production at the MSEEL site.

Produced water is severely contaminated indicating care in handling. Concentrations of all parameters increased through the flowback/produced water cycle. <sup>226+228</sup> Ra reached 20,000 pCi/L at post completion day 251 indicating an important trend that will be carefully assessed in ongoing monitoring.

**Produced water volume trends in wells MIP 3,5H and MIP 4,6H.** NNE's water production logs were used to estimate produced water volumes. While water production rates were similar in the first two months post completion, cumulative rates soon diverged yielding very different curves for each well (figure 2). It is noted that the older wells (4H, 6H) were shut in between 12 Dec 15 and 17 Oct 16, an interval of 315 days.

The proportion of injected hydraulic fracturing fluid returned as produced water, even after 1844 days (5 years) was only 12% at MIP 4H and 7.5% at MIP 6H (table 3). The reason for the variation among wells both with respect to cumulative and proportional produced water returns remains unclear.



Figure 2. Cumulative water production at the four MSEEL wells. The estimated proportion of produced water to HF fluids are shown in the callouts.

Table 3. Produced water volumes relative to injected HF fluid for each MSEEL well.

	days post	cumulative	e produced water	HF injected	
	completion	gal	% injected	gal	
MIP 3H	392	274,102	2.6%	10,404,198	
MIP 5H	392	192,134	2.0%	9,687,888	
MIP 4H	1844	501,396	12.0%	4,160,982	
MIP 6H	1844	229,183	7.5%	3,042,396	

#### Trends in produced water chemistry

**Major ions.** While makeup water was characterized by low total dissolved solids (TDS) and a dominance of calcium and sulfate ions, produced water from initial flowback is essentially a sodium/calcium chloride water (figure 3). Other than slight increases in the proportion of barium and strontium, the ionic composition of produced changed very little through 314 days post completion.



# Figure 3 Changes in major ion concentrations in produced water from well MIP 3H. From left to right the charts represent makeup water from the Monongahela River, produced water on the first day of flowback and produced water on the 314th day post completion.

In fact, after 1858 days ionic composition in the older 4H and 6H wells remained nearly identical to the initial produced water from the 3H and 5H wells (figure 4).



### Figure 4 Major ion composition of wells MIP 4H and 6H 1858 days after completion.

While TDS increased rapidly over the initial 90 days post completion, it appears to have levelled off between 100,000 and 150,000 mg/L (figure 5). The older 4H and 6H wells offer insight into the longer term TDS trend.

Those wells only came back on line in October 2016 after a shut in period of 315 days and while those results vary they are much lower than the recent values for wells MIP 3H and 5H. Thus far, results are only available for two sampling dates: 16 Nov 16 and 14 Dec 16. TDS varied between 62,176 mg/L at well MIP 4H and 16,099 mg/L at MIP 6H. If these trends continue, it would suggest that available formation salt is being exhausted.



### Figure 5 Changes in produced water $TDS_{sdc}$ (sum of dissolved constituents) through the first 340 days post completion.

Water soluble organics. The water soluble aromatic compounds in produced water: benzene, toluene, ethylbenzene and xylene were never high. With one exception at post completion day 321, benzene has remained below  $30 \ \mu g/L$  (figure 6). This may be a characteristic of dry gas geologic units and is consistent with Hayes (2009). After five years, benzene has declined below the drinking water standard of 5  $\mu g/L$ .



### Figure 6 Changes in benzene concentration. The figure shows data from well 5H through the first 342 days post completion, followed by results from well 6H.

**Radium isotopes.** Radium concentrations generally increased over the 314 days post completion at wells MIP 3H and 5H. Maximum levels of the radium isotopes reached about 20,000 pCi/L at the unchoked 3H well and about half that amount at 5H (figure 7).



### Figure 7 The radium isotopes are plotted against days post well completion. Well 5H was choked periodically. It produced less water and lower concentrations of radium.

At the older wells (MIP 4H and 6H), all isotope concentrations declined to low levels, often below the MDC (minimum detectable concentration) (table 4). This, like the apparent decline in TDS at the older wells is an interesting result and, if sustained by future sampling, would suggest exhaustion of contaminant reserves within the fracture field.

		1	16-Nov-16		16-Nov-16				
			MIP 4H		MIP 6H				
		days post	completio	n: 1828	days post completion: 1828				
		$\operatorname{act}^1$	unc <sup>2</sup>	mdc <sup>3</sup>	act1	unc <sup>2</sup>	mdc <sup>3</sup>		
α	pCi/L	228.0	53.6	27.2	57.7	10.9	1.6		
β	pCi/L	48.7	20.1	29.2	7.4	1.6	0.8		
<sup>226</sup> Ra	pCi/L	353.3	260.6	309.2	199.3	333.5	390.3		
<sup>228</sup> Ra	pCi/L	31.1	31.9	48.6	0.0	20.9	54.6		
<sup>40</sup> K	pCi/L	49.7	95.5	102.7	0.0	21.9	151.4		
	1	activity							

### Table 4 Radiochemistry of the older wells 4H and 6H at 1828 (5 years) days post completion.

<sup>2</sup> +/- uncertainty

<sup>3</sup> minimum detectable concentration

**Solid waste.** The TCLP (toxicity characteristics leaching procedure) or USEPA method 1311is prescribed under the Resources Conservation and Recovery Act (RCRA) to identify hazardous solid waste. Both organic and inorganic TCLP was applied to thirteen drill cutting samples, twelve from MIP 3H and 5H and one from another well in western Monongalia County. All three wells had been developed using green, synthetic drilling fluid. All samples fell below the TCLP criteria for hazardous waste (RCRA subtitle C) and would be classified under RCRA subtitle D (industrial solid waste). Bio-Base 365 drilling fluid (Shrieve Chemical Products, Inc.) had been used at the MSEEL wells and ABS 40 (AES Drilling Fluids Inc.) was used at the other well.

### Conclusions

This paper summarizes the results of the first year of a planned four year study and should be regarded as preliminary. Nonetheless, important trends have developed. They are summarized below.

#### **Risk Reduction**

The study was centered on Northeast Natural Energy's MIP well pad near Morgantown WV. Several important risk reduction measures were taken in its construction, development and completion to protect offsite risk to water resources. These included secondary containment on the well pad consisting of HDPE lining within a berm that enclosed the entire 1.1 ha pad. The makeup water impoundment also included an HDPE liner with adequate freeboard. Condensate tanks were continuously monitored using a SCADA system with results accessible from multiple locations allowing real time access to remaining capacity and changes in stored volume. Finally, use of the green drilling fluid BioBase 360 rendered the cuttings and muds non-hazardous according to both organic and inorganic TCLP testing.

The nearest receiving stream, the Monongahela River serves as Morgantown's primary drinking water supply, river water quality was monitored at stations upstream of the MIP pad, at the city's water intake and also downstream of the MIP pad. No evidence of contamination with drilling fluids or produced water was detected.

### **Drill Cuttings**

- Drill cutting radioactivity levels were within West Virginia DEP standards of 5 pCi/g above background. This was true of both vertical and horizontal (Marcellus) sections.
- Using the green drilling fluid Bio-Base 365, all drill cutting samples, vertical and horizontal, passed the USEPA's method 1311 (Toxicity Characteristics Leaching Procedure or TCLP) for inorganic and organic contaminants. This indicates that under Federal and West Virginia solid waste rules, these solid wastes would not be considered hazardous.
- The absence of hazardous TCLP findings suggest that drilling fluids, not the inherent properties of the Marcellus formation, play the dominant role in determining drill cutting toxicity.

### **Produced Water Quality**

- Hydraulic fracturing fluid was nearly identical to makeup (Monongahela River) water. Initial produced water was radically changed in ionic composition and underwent a two order of magnitude increase in total dissolved solids (TDS).
- Produced water is highly saline and total dissolved solids (TDS) rapidly increased to a maximum between 100 and 150 g/L. However, there was negligible change in ionic composition between the initially produced water and that sampled five years post completion.
- Concentrations of both <sup>226</sup> Ra and <sup>228</sup> Ra increased rapidly through the produced water cycle to combined maximum concentrations of 20,000 pCi/L in the first year post completion. These radium isotopes are critical regulatory determinants.

### **Produced Water Quantity**

- The volume of produced water decreased rapidly from nearly 500 bbl/day to less than 1 bbl/day after one year. Over this cycle produced water averaged about 6 bbl/day.
- After five years cumulative flowback and produced water represented only 7.5 and 12% of injected fluids at wells 6H and 4H respectively. After 392 days only 2% and 2.6% reported to the wellhead at the 5H and 3H wells respectively.

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