Memorandum

To: Jane Witheridge (Pawnee Waste, LLC) **Date:** October 3, 2017

From: Matthew Tymchak, M.S., and Samuel Flewelling, Ph.D. (Gradient)

Subject: Radioactivity and BTEX in Shale-oil and Shale-gas Exploration and Production Wastes

1 Introduction and Methods

Gradient was retained by Pawnee Waste, LLC to compile and review publicly available information on the levels of radioactivity and benzene, toluene, ethylbenzene, and total xylenes (BTEX) concentrations found in exploration and production (E&P) wastes from oil and gas from shale formations in Colorado and other states. This review included data from the vertical, transitional, and horizontal[1] components of wells completed in shale formations. It is our understanding that the Colorado Department of Public Health and Environment (CDPHE) is reviewing the disposal requirements for E&P wastes that have radioactivity levels above background levels. We also understand that CDPHE has requested information on the radioactivity of E&P wastes to assess appropriate options for the disposal of these materials. This memorandum summarizes publicly available information on the radioactivity and BTEX content of E&P wastes to date. Specifically, we summarize this information in the context of CDPHE's administration levels for Technologically Enhanced Naturally Occurring Radioactive Material (TENORM) waste (hereafter "CDPHE administrative levels") for radium-226 + radium-228, natural thorium, natural uranium (CDPHE, 2017), and the Colorado Oil and Gas Conservation Commission's (COGCC) BTEX standards (CDNR, 2015, Table 910-1). As part of this research, we reviewed publicly available reports from government agencies and trade associations, government databases, operator assays, and the peer-reviewed literature for relevant information. Although the amount of data for E&P waste streams are limited, they cover multiple basins in Europe and the US, thereby providing a basis for comparing levels of radioactivity and BTEX from different areas. We found that E&P wastes have detectable levels of radioactivity and BTEX and that data from Colorado are in the range of concentrations found in other areas of oil- and gas-shale development. The data from Colorado also indicate that multiple types of E&P wastes can have levels of radioactivity and BTEX that exceed CDPHE administrative levels and COGCC standards, respectively.

2 Results and Discussion

2.1 Radioactivity of E&P Wastes

We identified radionuclide data for various wastes, including drill cuttings, proppant, drilling mud, sludge, flowback solids, pipe and tank scale, filter cake, sludge, and other solid wastes associated with E&P activities. Publicly available data for radioactivity in these waste streams is summarized in Table 1

[1] Wells completed in oil and gas shales are commonly drilled vertically from the surface, but the drill bit may deviate in a horizontal direction as the borehole approaches and enters the targeted shale. Once in the targeted shale, the drill bit continues drilling horizontally (or at an angle) to follow the bedding direction of the shale.

(attached). We grouped these wastes into the following categories for discussion purposes due to similarities in their levels of radioactivity and the character of the waste: (1) drill cuttings, proppant, and drilling mud; (2) pipe and tank scale; and (3) filtration wastes, sludge, and sump solids. Samples from each of these waste materials had detectable levels of radioactivity. Furthermore, analytical data indicate that E&P wastes can exceed CDPHE administrative levels, particularly for radium-226 + radium-228. A large portion of the compiled data was for drill cuttings. While both vertical and horizontal drill cuttings have the potential to exceed CDPHE administrative levels, cuttings from horizontal sections of the borehole tend to have higher radioactivity, and hence a higher likelihood of exceeding CDPHE administrative levels. Other production wastes that are exposed to produced fluids continuously (*e.g.*, pipe and tank scale, filtration wastes) have the potential to exhibit radium-226 + radium-228 activity substantially above levels found in drill cuttings and other types of E&P waste due to the accumulation of radium in precipitates.

Drill Cuttings, Proppant, and Drilling Mud

We identified measured levels of radioactivity in drill cuttings from Colorado, New York, Pennsylvania, West Virginia, and Poland. The concentrations of radioactivity found in the cuttings from these different areas were generally consistent, suggesting that the radioactivity of oil- and gas-shale formation cuttings can be expected to vary within the same general range. For example, the radium-226 + radium-228 activity in horizontal cuttings from Colorado was 7.42 pCi/g, which is within the range of 0.107-13.6 pCi/g reported for horizontal cuttings from other areas (Table 1). The activities of natural thorium and uranium in cuttings from Colorado were also within the ranges of those found in other areas of oil- and gas-shale development (Table 1).

Apart from the overlapping ranges of radioactivity in drill cuttings from Colorado and other areas, the data indicate that horizontal cuttings tend to have higher radioactivity than vertical cuttings. For example, drill cuttings from a Denver-Julesburg Basin well had radium-226 + radium-228 activity of 4.47 pCi/g in a sample collected from the transitional (*i.e.*, in the course of changing from vertical to horizontal) leg of the well, whereas a sample from the horizontal leg had radium-226 + radium-228 activity of 7.42 pCi/g. Studies in the Marcellus Shale have also found that horizontal drill cuttings tend to have higher radioactivity than vertical cuttings (Carr, 2017; Perma-Fix Environmental Services, Inc., 2016; Marshall University, 2015), which is consistent with the data from Colorado. In one study, the Pennsylvania Department of Environmental Protection (PADEP) (Perma-Fix Environmental Services, Inc., 2016) found that radium and uranium concentrations were significantly higher in horizontal than in vertical cuttings, even though the highest radium-226 + radium-228 activity was found in a single vertical cutting sample. Thus, while PADEP found, to a high degree of statistical confidence, that horizontal cuttings had higher radioactivity than vertical cuttings on average (Perma-Fix Environmental Services, Inc., 2016), the individual sample results also indicate that the radioactivity of vertical cuttings can sometimes exceed the CDPHE administrative levels.

Levels of radioactivity in proppant samples were variable across the three basins with available data, with some samples exceeding CDPHE administrative levels (Table 1). Samples from drilling muds had radioactivity that was comparable to, or lower than, drill cuttings.

Pipe and Tank Scale

The oil and gas industry has known for decades that pipe and tank scale ("scale") can accumulate high levels of radioactivity, mainly due to radium (Wilson and Scott, 1992). Scale has been found to exhibit activities as high as 410,000 pCi/g (White and Rood, 2001, and references therein). High radioactivity in scale results from radium associating with other alkaline earth metals (*e.g.*, calcium, barium, strontium) in sulfate- and carbonate-based mineral deposits that precipitate from production fluids onto pipe and tank walls (White and Rood, 2001). Soils impacted by scale cleaning operations may also exhibit elevated

radioactivity. For example, one study found that such soils had radium-226 + radium-228 activities ranging from 6.75-1,681 pCi/g (Wilson and Scott, 1992). Thus, there is a high likelihood that pipe and tank scale, as well as soil impacted by scale cleaning operations, would exceed CDPHE administrative levels for radioactivity.

Filtration Wastes, Sludge, and Sump Solids

Filtration wastes, sludge, and sump solids have varying levels of radioactivity, with some of the higher observed values falling between drill cuttings and scale (Table 1). This result is not surprising, considering that the solids from filtration or settling will be derived from the formation (*e.g.*, containing cuttings, proppant, or mud), but are also subject to formation fluids that allow for mineral precipitates to accumulate, similar to the process that creates pipe and tank scale. Thus, based on the data, and the possibility of precipitate accumulation, we expect filtration wastes and sump solids to have a high likelihood of exceeding CDPHE administrative levels for radioactivity.

2.2 BTEX Content of E&P Wastes

BTEX data were compiled for the same E&P waste streams as radioactivity, with the exception of scale (Table 2). Oil and gas source rocks targeted for production contain BTEX, which is a natural component of crude oil and natural gas. Using BTEX data for crude oil produced from shales in North Dakota and Texas (which have similar BTEX levels compared to other crude oils from the US and abroad), a rock with 1% porosity filled with crude oil or a waste material composed of 1% crude oil would exceed the COGCC standard for benzene by a factor of approximately 86-212. The available data for drill cuttings and a variety of other E&P wastes indicate that these materials are likely to exceed the COGCC standards for BTEX (Table 2).

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Table 1 Summary of Radioactivity in Background Soil and Wastes from Oil- and Gas-shale Exploration and Production

Shale Formation or Basin	State or Country	Material Sampled	Activity (pCi/g)						Data Source
			Combined Ra-226+228		Thorium (Natural)		Uranium (Natural)		
			Min.	Max.	Min.	Max.	Min.	Max.	
Colorado Department of Public Health and Environment Administrative Levels			**3**		**3**		**30**		**CDPHE (2017)**
Denver-Julesburg	**CO**	**Background Soil Samples**	**1.38**	**4.2**	**2.42**	**5.93**	**0.82**	**2.80**	**Colorado Oil & Gas Conservation Commission (2014)**
Denver-Julesburg	CO	Drill Cuttings and Drill Cuttings Mixed with Soil	1.36	4.15	2.61	5.06	0.906	4.15	Colorado Oil & Gas Conservation Commission (2014)
Denver-Julesburg	CO	Drill Cuttings (Vertical/Horizontal Transition)	4.47						ALS Environmental (2017)
Marcellus[a,b]	NY	Drill Cuttings	0.872	1.84	0.567	1.02	0.079	0.185	NYSDEC (2015)
Marcellus[a,c]	PA	Drill Cuttings	0.84	6.30	1.27	8.05	2.22	15.57	Eitrheim *et al.* (2016)
Lublin Trough	Poland	Drill Cuttings	3.27	4.41	0.95	1.16	1.89	2.68	Jodlowski *et al.* (2017)
Baltic Basin[d,e]	Poland	Drill Cuttings	1.38	3.30	0.51	1.27	0.95	2.35	Jodlowski *et al.* (2017)
Marcellus	PA	Vertical Drill Cuttings	0.805	20.0	0.110	2.74	0.18	2.14	Perma-Fix Environmental Services, Inc. (2016)
Marcellus	WV	Vertical Drill Cuttings	3.40	4.11					Marshall University (2015)
Marcellus	WV	Vertical Drill Cuttings	3.0	3.3					Carr (2017)
Denver-Julesburg	CO	Horizontal Drill Cuttings	7.42						ALS Environmental (2017)
Marcellus	PA	Horizontal Drill Cuttings	0.107	13.6	0.016	1.14	0.272	5.75	Perma-Fix Environmental Services, Inc. (2016)
Marcellus	WV	Horizontal Drill Cuttings	5.67	8.98					Marshall University (2015)
Marcellus[a]	PA	Horizontal Drills Cuttings	0.6	4.3	0.5	1.2			NYSDEC (2015)
Marcellus	WV	Horizontal Drills Cuttings	4.7	10.8					Carr (2017)
Not Specified	ND	Proppant	4.86	20.3	8.1	10.2			Argonne National Laboratory (2014)
Marcellus	PA	Proppant Sand	0.196	0.396	0.007	0.115	0.012	0.332	Perma-Fix Environmental Services, Inc. (2016)
Lublin Trough	Poland	Proppant, Waste	0.62	12.49	0.14	6.62	0.38	5.03	Jodlowski *et al.* (2017)
Baltic Basin	Poland	Proppant, Waste	20.3	25.16	11.3	13.92	9.84	10.62	Jodlowski *et al.* (2017)
Marcellus	PA	Flowback Solids, Sand	0.957	8.35	0.191	0.609	0.397	1.03	Perma-Fix Environmental Services, Inc. (2016)
Lublin Trough	Poland	Solid Waste	1.03	1.89	0.43	0.65	0.95	1.03	Jodlowski *et al.* (2017)
Baltic Basin	Poland	Solid Waste	0.86	1.62	0.35	0.70	0.95	1.24	Jodlowski *et al.* (2017)
Marcellus	PA	Drilling Solids, Mud	0.857	4.05	0.120	0.435	0.215	1.75	Perma-Fix Environmental Services, Inc. (2016)
Barnett Shale	TX	Reserve Pit (Drilling Fluid) Sludge	ND	3.11	0.64	0.72	ND		Rich and Crosby (2013)
Not Specified	ND	Scale	16.9	8,290	6.5	460			Argonne National Laboratory (2014)
Not Specified[a]	N/A	Soil from Pipe Scale Cleaning Field	6.75	1,681					Wilson and Scott (1992)
Denver-Julesburg	CO	Sump Pump Grit and Filter Cake	2.91	32.6	0.045	3.98	0.426	2.92	Tetra Tech, Inc. (2016)
Not Specified	ND	Sludge (from tanks, flare pit, treatment)	3	1,293	2.1	97.5			Argonne National Laboratory (2014)
Not Specified	ND	Filter Sock	3.51	504	6.5	18.9			Argonne National Laboratory (2014)
Denver-Julesburg	CO	Filter Cake (Oil Recycling Operations)	12.42		2.12		2.08		Pace Analytical Services, Inc. (2014)
Denver-Julesburg	CO	Filter Cake (Water)	15.05		0.778		1.45		Pace Analytical Services, Inc. (2014)
Denver-Julesburg	CO	Filter Press Solids (Oil Recycling Operation)	32.56		2.93		2.15		Pace Analytical Services, Inc. (2015)
Denver-Julesburg	CO	Sump Pit Solids (Oil Recycling Operation)	2.91		3.98		1.58		Pace Analytical Services, Inc. (2015)

Notes:

N/A = Not Available; ND = Not Detected; Ra = Radium; Th = Thorium; U = Uranium.

(a) Only Ra-226 was reported.

(b) Only U-235 was reported.

(c) Only Th-230 was reported.

(d) Only Th-228 was reported.

(e) Only U-238 was reported.

Table 2 Summary of BTEX in Crude Oil and Wastes from Oil- and Gas-shale Exploration and Production

Shale Formation, Basin, or Location	State or Country	Material Sampled	Concentration (mg/kg)								Data Source
			Benzene		Toluene		Ethylbenzene		Xylenes		
			Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	
Colorado Oil and Gas Conservation Commission Standards			**0.17**		**85**		**100**		**175**		**CDNR (2015, Table 910-1)**
Denver-Julesburg	CO	Drill Cuttings (Vertical/Horizontal Transition)	0.45		7.8		5.2		42		ALS Environmental (2017)
Marcellus	WV	Drill Cuttings (Vertical)	19.5	115	N/A		N/A		N/A		Marshall University (2015)
Marcellus	WV	Drill Cuttings (Vertical)	0.1262		0.8924		0.2035		2.249		Ziemkiewicz *et al.* (2014)
Denver-Julesburg	CO	Drill Cuttings (Horizontal)	0.65		9.2		6.7		52		ALS Environmental (2017)
Marcellus	WV	Drill Cuttings (Horizontal)	773	2,010	N/A		N/A		N/A		Marshall University (2015)
Kern County & LA County	CA	Drilling Waste (Cuttings, Muds)	ND		ND		ND		ND	0.37	CalEPA and CalDTSC (2002)
Not Specified	US (except CA)	Oil-based Cuttings	9		25.25		10.35		90.25		Green (c. 2013)
Denver-Julesburg[a]	CO	Pit Solids	0.026	11	0.14	33	0.038	8.3	0.43	44	URS (2008)
Piceance[a,b]	CO	Pit Solids	<0.000035	7.3	<0.000115	280	<0.0000613	47	<0.000124	730	URS (2008)
Raton[a,b]	CO	Pit Solids	<0.000035	0.48	<0.000115	1.8	<0.0000613	0.25	<0.000124	3.1	URS (2008)
San Juan[a,b]	CO	Pit Solids	<0.000035	0.016	<0.000115	0.02	<0.0000613	0.0047	<0.000124	0.075	URS (2008)
Denver-Julesburg	CO	Sump Pit Solids	22.8		126		20.9		159		Pace Analytical Services, Inc. (2015)
Not Specified	US (except CA)	Pit and Sump Waste	607		2,254		710		4,092		Green (c. 2013)
Not Specified	US (except CA)	Produced Sand	20		93		17		130		Green (c. 2013)
Denver-Julesburg	CO	Filter Cake Waste (Oil Recycling Operations)	121		757		111		1,070		Pace Analytical Services, Inc. (2014)
Denver-Julesburg	CO	Filter Cake Waste (Water)	77.3		407		56.4		543		Pace Analytical Services, Inc. (2015)
Denver-Julesburg	CO	Filter Press Solids (Oil Recycling Operations)	242		805		206		814		Pace Analytical Services, Inc. (2015)
Bakken	ND	Crude Oil	1,800		6,600		N/A		N/A		Statoil ASA (2017)
Bakken	ND	Crude Oil	1,470	1,850	2,770	3,170	768	852	4,390	5,160	TSB (2014)
Eagle Ford	TX	Crude Oil (Chem Grade)	2,200		16,900		N/A		N/A		Statoil ASA (2017)
Eagle Ford	TX	Crude Oil (General Grade)	3,600		11,400		N/A		N/A		Statoil ASA (2017)

Notes:

BTEX = Benzene, Toluene, Ethylbenzene, Xylenes; N/A = Not Available; ND = Not Detected.

(a) Only m+p xylenes were reported.

(b) Method detection limits were reported as the lower range when the analyte was not detected.