Tenmile Creek Sampling Summary

December 15, 2015

Background

In 2014, DEP's California District Mining Office collected surface water samples from three locations on Tenmile Creek (TMC) in the vicinity of the Clyde Mine Treatment Facility (CMTF), near Clarksville, Greene County. The samples were analyzed using the basic laboratory methodology of gamma spectroscopy that provides a limited sensitivity for most naturally occurring radioactive materials. All three samples indicated levels of naturally occurring radioactive materials above normal background levels.

As a follow up to the 2014 sampling, DEP's Bureau of Radiation Protection (BRP) and District Mining Office conducted a more comprehensive sampling in June of 2015 that included the 2014 locations and was expanded to include additional areas and media both upstream and downstream of the CMTF. During the 2015 sampling stream flow, recorded at the nearest United States Geological Service (USGS) stream gauge on South Fork Tenmile Creek located approximately 5 miles upstream of the sampling points, averaged 155 cubic feet per second. This flow rate was lower than the average stream flow of 251 cubic feet per second recorded at the same gauge during the April 10, 2014, sampling event and within 3.1 percent of the historical daily average of 160 cubic feet per second for that day. Based on those stream gauge readings and historical flows DEP believes the 2015 sampling effort occurred during near normal stream flow conditions within the Tenmile Creek watershed.

The 2015 samples were analyzed using radiochemistry methodologies that are more precise for these naturally occurring radioisotopes than gamma spectroscopy. Water samples were also analyzed for non-radiological parameters to evaluate water quality.

Sample Locations and Types

Sampling was conducted at 12 locations on the North and South Forks of TMC, the Monongahela River, the CMTF, and the Tri-County Joint Municipal Water Authority (TCJMWA). Samples included the following: water, sediment, sludge, soil, aquatic vegetation, and fish. Materials sampled were dependent on availability at each location. Water and sediment were taken at all 10 of the creek locations. Sludge was obtained at the CMTF and at the TCJMWA which consisted of water and the material precipitated out of solution during the treatment processes. Soil was collected at a location near the CMTF where untreated mine pool water occasionally seeps to the surface. Aquatic vegetation was taken where available, and fish samples were obtained near the CMTF outfall and also at a background reference area 24 miles upstream in an area the Pennsylvania Fish and Boat Commission designated as Approved Trout Waters. Attachment 1 includes two maps of all sampling locations.

Laboratory Analysis

DEP's Bureau of Laboratories conducted the analyses using several analytical methods. All of these methods are approved by EPA for the determination of radium-226 and radium-228 in various media. These analytical methods are approved under the Code of Federal Regulations in Title 40, Chapter 1, Subchapter D, parts 141.25 and 141.27[1]. Water samples were analyzed using radiochemistry extraction methods. For radium-226 EPA method 903.1 was used, and for radium-228 the Brooks and Blanchard method was used. In addition, all water samples were analyzed for non-radiological parameters used by DEP to assess water quality associated with mining and hydraulic fracturing. Soil and sediment samples also used radiochemistry extraction methods. For radium-226 DOE Ra-04 was used, and for radium-228 the same Brooks and Blanchard method was used after chemical digestion. The radiochemistry methods selected provide the ability to detect much lower levels of radium-226 and radium-228 in water and sediment than what was used for the initial sampling in 2014. These radiochemical analyses were not available from the laboratory for plant or fish; gamma spectroscopy with a 21-day ingrowth was used for those samples to obtain as low of a detection sensitivity as possible.

Results

Radiological: All environmental samples collected in June of 2015 had radiological results typical to naturally occurring background levels normally found in the environment. All water samples were below EPA's drinking water limit of 5 picocuries per liter (pCi/L) combined for radium-226 and radium-228. Water results ranged from 0.065 pCi/L to 0.222 pCi/L for radium-226, and only one result was above the Minimum Detectable Activity (MDA) for radium-228 (0.215 pCi/L). There is no indication of radiological accumulation occurring in the sediment, plants, or fish. All sample results were within the expected normal backgrounds for those media. Sediment ranged from 0.123 picocuries per gram (pCi/g) to 0.323 pCi/g of radium-226 and from 0.483 pCi/g to 1.492 pCi/g of radium-228. Vegetation ranged from 0.116 pCi/g to 0.613 pCi/g of radium-226 and from 0.032 pCi/g to 0.213 pCi/g of radium-228. All results are summarized in Attachment 2.

Only one sample, the sludge from the CMTF, had radiological parameters noticeably above the laboratory detection limits (radium-226 at 1.312 pCi/L and radium-228 at 19.539 pCi/L). A possible explanation for this elevated sample result is provided in a memo from DEP's Bureau of Mining Programs to BRP, stating "The elevated radium found in the treatment sludge may be explained by the radium adsorbing to the ferric iron which is precipitated out of solution during the treatment process. The Clyde Mine Treatment Facility uses a high density sludge which recirculates sludge over and over, thus concentrating radium values." (Greenfield 2015.) By comparison, the sludge sample at TCJMWA

[1] U.S. Government Publishing Office, Electronic Code of Federal Regulations, http://www.ecfr.gov/cgi-bin/text-idx?SID=adc28002836a6c9b208da4bc63206116&mc=true&tpl=/ecfrbrowse/Title40/40cfr141_main_02.tpl (December 8, 2015)

was 0.41 pCi/L for radium-226, and the radium-228 value was less than the detection limit. (Refer to Attachment 2.)

Non-Radiological: The results of the non-radiological water sampling are provided in Attachment 3. After reviewing the non-radiological parameters of the raw and treated mine discharge samples, DEP's Bureau of Mining Programs concluded that sample results of the raw and treated mine water are consistent with typical mine drainage originating from a flooded Pittsburgh seam underground coal mine in southwestern Pennsylvania. Please see Attachment 4.

Conclusions

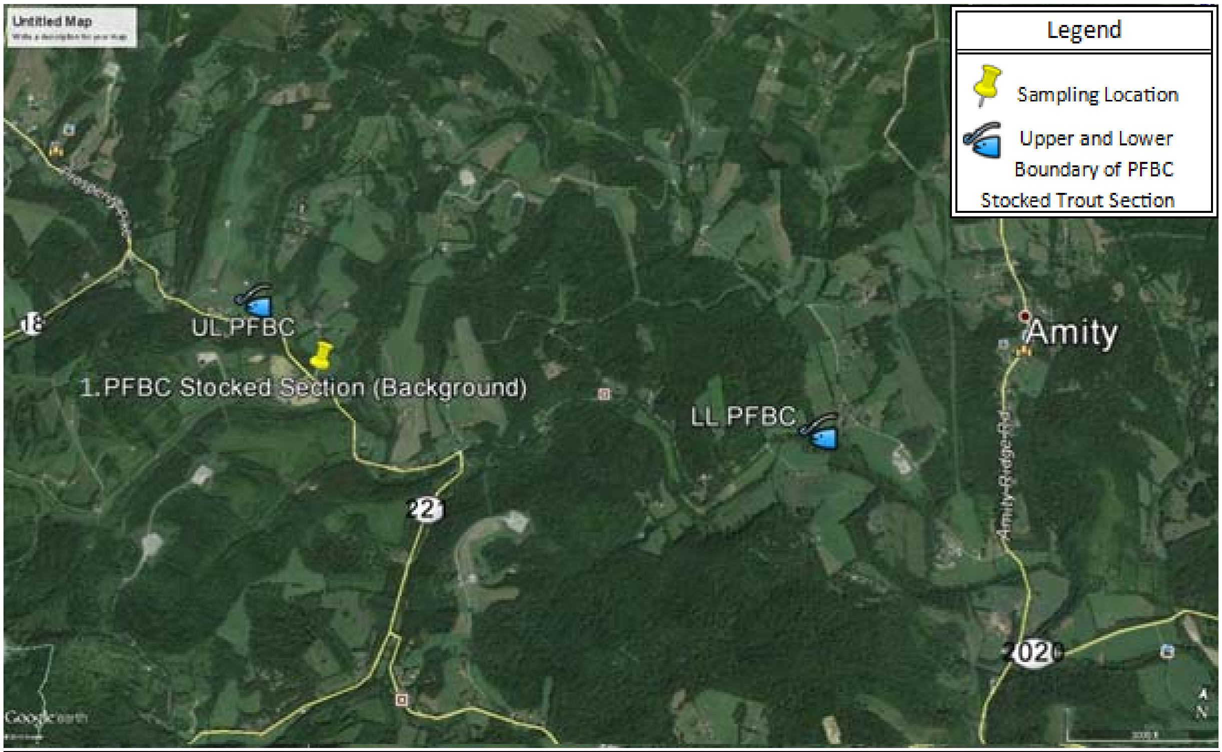
The laboratory analysis did not indicate elevated radiological levels within any of the sampled environmental media. They appear to be consistent with expected naturally occurring background values for similar media. The non-radiological results are also consistent with similar conditions associated with a flooded mine in this area of Pennsylvania. The single radium-228 finding in the CMTF sludge is not at a level that causes any concerns for the public's health and safety or the environment. The Department will as a matter of public interest collect and analyze additional samples of the CMTF sludge to establish a more robust dataset to verify these findings.

References

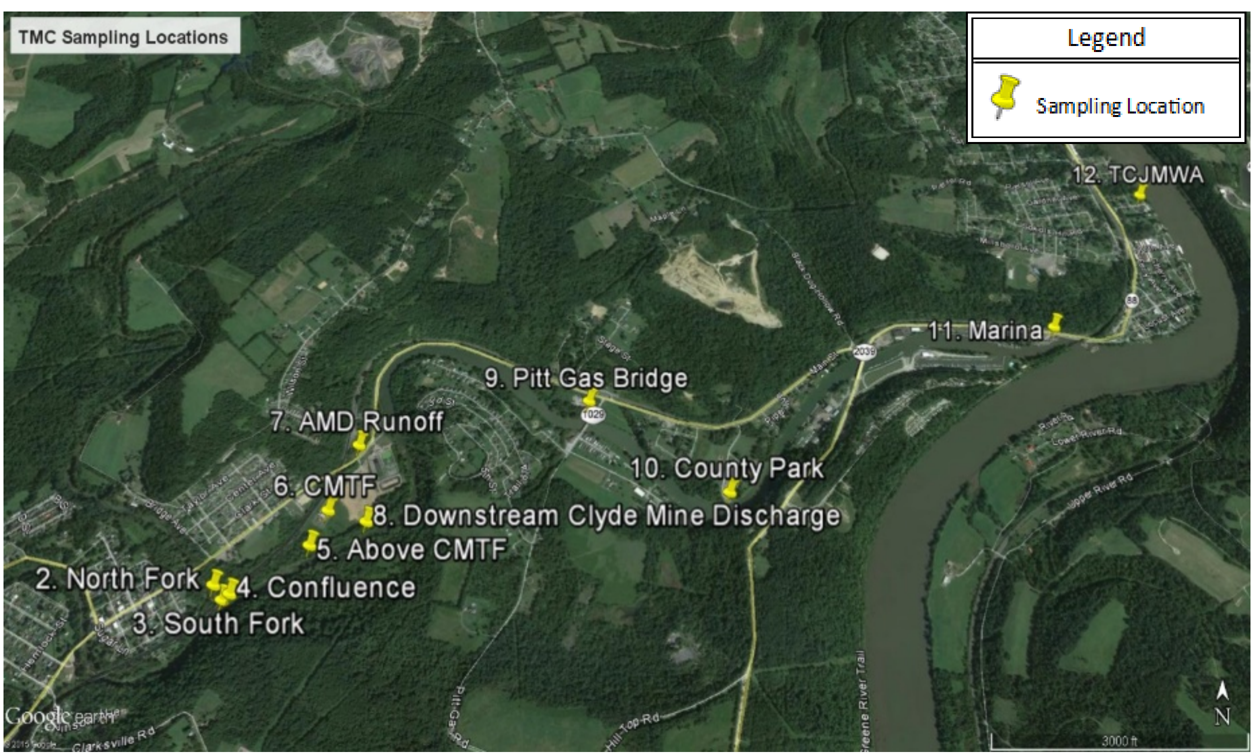
Greenfield, G., 2015. Non-Radiological Parameter Analysis of the Tenmile Creek Sampling, Memo from Bureau of Mining Programs to Bureau of Radiation Protection, p. 2.

Attachment 1:

Sampling Map of Background Location



Sampling Map near the Clyde Mine Treatment Facility



Attachment 2:

Radiological Results from June 22-23, 2015, Sampling Effort at Tenmile Creek by Location

Sample Location ID	Sampling Location	Type	Analysis*	Unit	**Ra-226**	**Ra-228**
1	Background	Water	R	pCi/L	0.222	<MDA**
		Sediment	R	pCi/g	0.217	1.492
		Vegetation	G	pCi/g	0.488	0.032
		Fish	G	pCi/g	0.242	<MDA
2	North Fork	Water	R	pCi/L	<MDA	<MDA
		Sediment	R	pCi/g	0.22	0.892
		Vegetation	G	pCi/g	0.116	0.044
3	South Fork	Water	R	pCi/L	0.124	<MDA
		Sediment	R	pCi/g	0.255	0.672
		Vegetation	G	pCi/g	0.138	0.037
4	Confluence	Water	R	pCi/L	<MDA	0.215
		Sediment	R	pCi/g	0.323	0.483
		Vegetation	G	pCi/g	0.364	0.213
5	Above CMTF	Water	R	pCi/L	0.082	<MDA
		Sediment	R	pCi/g	0.215	0.803
		Vegetation	G	pCi/g	0.142	<MDA
6	Clyde Mine Treatment Facility	Raw	R	pCi/L	0.169	<MDA
		Treated	R	pCi/L	0.155	<MDA
		Sludge	R	pCi/L	1.312	19.539
7	AMD Runoff	Soil	R	pCi/g	0.099	0.710
8	Downstream Clyde Mine Discharge	Water	R	pCi/L	0.112	<MDA
		Sediment	R	pCi/g	0.123	0.677
		Vegetation	G	pCi/g	<MDA	0.042
		Fish	G	pCi/g	0.052	0.012
9	Pitt Gas Bridge	Water	R	pCi/L	0.089	<MDA
		Sediment	R	pCi/g	<MDA	1.435
		Vegetation	G	pCi/g	0.186	0.107
10	County Park	Water	R	pCi/L	0.083	<MDA
		Sediment	R	pCi/g	0.161	1.467
		Vegetation	G	pCi/g	0.134	0.071
11	Marina	Water	R	pCi/L	<MDA	<MDA
12	Tri-County Joint Municipal Authority	Raw	R	pCi/L	0.065	<MDA
		Treated	R	pCi/L	<MDA	<MDA
		Sludge	R	pCi/L	0.41	<MDA
		Sediment	R	pCi/g	0.128	1.100
		Vegetation	G	pCi/g	0.613	0.097

Note: Sample Location ID #7 is soil only and not included in non-radiological sampling.
* R: Radiochemistry G: Gamma Spectroscopy
** <MDA indicates activity values were below the minimum detection capabilities of the laboratory equipment.

Attachment 3:

Non-Radiological Results from June 22-23, 2015, Sampling Effort at Tenmile Creek by Location

Sample Location ID	1	2	3	4	5	6		8	9	10	11	12	
	Background	**North Fork**	**South Fork**	**Confluence**	**Above CMTF**	**CMTF-Raw**	**CMTF-Treated**	**Downstream CMTF**	**Pitt Gas Bridge**	**County Park**	**Marina**	**TCJMWA-Raw**	**TCJMWA-Treated**
Alkalinity	146.2	133.6	99.8	113.2	129.4	548	290	133.2	121.8	117.2	114.8	52.2	51.4
Aluminum	0.43	0.513	0.794	0.944	0.53	<0.200	<0.200	0.526	0.616	0.822	0.621	0.425	<0.200
Ammonia, Tot. as N	0.02	<0.02	<0.02	0.03	<0.02	2.24	2.12	0.13	0.04	0.06	0.05	0.04	<0.02
Barium	0.079	0.068	0.054	0.065	0.063	0.012	<0.01	0.059	0.063	0.068	0.066	0.039	0.033
B O D - 5 DAY	0.4	0.6	0.8	0.8	0.8	9.6	0.8	0.9	0.7	0.9	0.9	0.9	0.6
Boron	<0.200	<0.200	<0.200	<0.200	<0.200	0.288	0.304	<0.200	<0.200	<0.200	<0.200	<0.200	<0.200
Calcium	49.1	49.7	39.7	44.3	51.2	279	275	60.8	48.1	47.8	42.5	25.6	23.9
Hardness	151	154	126	140	156	1107	1096	203	153	155	141	86	81
Iron	0.907	0.971	1.481	1.802	1.043	164	2.397	1.143	1.063	1.61	1.148	0.835	0.02
Lithium	<0.025	<0.025	<0.025	<0.025	<0.025	0.147	0.14	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025
Bromide	<0.025	<0.025	0.028	<.025	4.457	0.037	4.482	0.235	0.0399	0.0329	0.042	<0.025	<0.025
Magnesium	6.751	7.289	6.607	7.117	6.744	99.3	99.1	12.5	7.85	8.64	8.324	5.259	5.122
Manganese	0.068	0.066	0.098	0.116	0.07	2.689	2.444	0.195	0.099	0.19	0.108	0.091	<0.010
Molybdenum	<0.070	<0.070	<0.070	<0.070	<0.070	<0.070	<0.070	<0.070	<0.070	<0.070	<0.070	<0.070	<0.070
Osmotic Pressure*	5	4	4	6	3	133	126	11	6	7	7	<1	2
ph (lab) in S.U.	8.4	8.4	8.3	8.3	8.3	6.6	6.6	7.9	8.3	8.1	8.2	7.7	8.3
Sodium	16.8	14.4	17.5	16.5	15.7	1760	1760	107	27.5	27.3	23.6	13.6	21.1
Specific Conductivity**	361	375	331	348	375	8570	8420	841	424	428	397	250	273
Strontium	0.209	0.193	0.173	0.188	0.181	6.656	5.991	0.485	0.234	0.262	0.246	0.134	0.127
Chloride	9.65	14.77	17.27	16.21	15.18	656	698	48.35	20.3	19.54	18.36	8.93	17.19
T D S	232	236	206	228	240	6992	6850	734	274	264	250	166	166
Total nitrate & nitrite	0.28	0.5	0.49	0.49	0.5	<0.05	<0.05	0.48	0.5	0.48	0.49	0.42	0.39
Sulfate	30.15	38.27	40.68	39.77	38.84	3672	3714	220	64.92	68.87	59.06	53.28	51.82
Tot Susp Solids	22	34	40	68	36	72	<5	26	14	88	18	22	<5
Zinc	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
Uranium	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002

Note: Units in parts per million (ppm) unless otherwise noted.

*Osmotic Pressure (MOS/KG)

**Specific Conductivity (umhos/cm)

Attachment 4:

Memo from Bureau of Mining Programs to the Bureau of Radiation Protection regarding the Non-Radiological Parameter Analysis of the Tenmile Creek Sampling

pennsylvania
DEPARTMENT OF ENVIRONMENTAL PROTECTION

MEMO

TO	Bryan Werner Radiation Protection Program Manager
FROM	Gregory Greenfield, P.G. Permits Section Bureau of Mining Programs
THROUGH	Sharon Hill, P.G. Bureau of Mining Programs
DATE	December 3, 2015
RE	Non-Radiological Parameter Analysis of the Ten Mile Creek Sampling

The provided sample of the raw water entering the Clyde Mine Treatment Facility is characteristic of mine drainage from a flooded underground mine in southwestern Pennsylvania - pH 6 to 7, high alkalinity, and high sulfate.

The treatment system was installed to treat water originating from the flooded Pittsburgh coal seam underground mine, known as the Clyde Mine. The Pittsburgh coal seam is the base member of the Monongahela Group, which is a sedimentary sequence dominated by limestone, calcareous mudstones, shales, and thin-bedded siltstones and laminites, all of which were deposited in a relatively low energy environment. The section is entirely non-marine and several coal beds are present, one being the Pittsburgh coal which is generally 4 to 10 feet thick and unique in its areal continuity (Edmunds 1998).

The water quality from flooded underground coal mines is different from typical mine drainage found elsewhere in Pennsylvania. Infiltration of alkaline groundwater from overlying units and subsequent flooding of the mine slowed pyrite oxidation, therefore, the water quality within the Clyde mine pool became net-alkaline over time. The current raw water that is sent to the treatment plant is net alkaline with elevated concentrations of ferrous iron (164 mg/L) which remains in solution at a pH between ~6 and 7.

The chemistry of the sampled treated mine water is typical of treated mine water - reduction in iron (from 164 mg/L to 2.4 mg/L) and barium (2.24 mg/L to <0.01 mg/L), while manganese and sulfate remain unchanged (the pH isn't high enough to precipitate manganese out of solution and sulfate is a conservative parameter that is extremely difficult to treat). This likely explains why the sample taken in Ten Mile Creek, downstream of the treatment plant, had a sulfate concentration of 220 mg/L and a manganese concentration of 0.195 mg/L compared to the upstream sample with 38.84 mg/L and 0.07 mg/L of sulfate and manganese, respectively. The elevated radium found in the treatment sludge may be explained by the radium adsorbing to ferric iron which is precipitated out of solution during the treatment process. The Clyde Treatment Facility uses a high density sludge which recirculates sludge over and over, thus concentrating radium values.

The samples taken from the raw and treated mine water contain bromide, chloride, and sodium which are several orders of magnitude larger than all the other samples. The location of a mine within the groundwater flow system influences the chemistry of water associated with that mine. The coal-bearing rocks of the Appalachian Plateau were once deeply buried (Reed, et al., 2005; Blackmer, et al., 1994) and saturated with brine waters. The degree to which these brines have left remnants behind depends on the degree of flushing by meteoric water. Shallow rocks are more fractured and thus allow for greater flushing by meteoric water than deeper portions of the flow system. The primary residues of brine within the rocks encountered by mining are sodium, chloride and bromide. These ions are largely flushed from the shallow flow system and thus the water has a Ca-Mg-HCO_3 signature. The intermediate and regional flow systems have sodium attached to cation exchange sites and release of this sodium contributes to Ca-Na-HCO_3 type water. The regional flow system, in addition to sodium, can have measureable concentrations of chloride and bromide.

Some of Pennsylvania's deepest underground mines have penetrated the regional flow system. The deepest coal mines in Pennsylvania, at ~800 to 1000 feet, occur at about the same depth as the shallowest oil wells in a study conducted by Dressel and Rose in 2010 which looked at the chemistry and origin of oil and gas well brines in western Pennsylvania. The results from that study were combined with the results from a study published by Cravotta in 2015, which sampled raw and treated mine water from a variety of coal mine settings (shallow, deep, and refuse) throughout Pennsylvania. The figure below is a plot of the ratio of chloride to bromide. Since chloride and bromide are conservative parameters, and if the source of these ions is brine, the ratio will remain, regardless of meteoric water dilution. The linear distribution of data indicates that the ratio in the deep and intermediate flow systems, represented by deep mine and coal refuse waters, is similar to that of the brine waters. The ratio is least evident in the surface mine waters because shallow flow systems are subject to meteoric and anthropogenic inputs for chloride and bromide. The plot indicates that these shallow system waters frequently have a lower bromide to chloride ratio than found in brines.

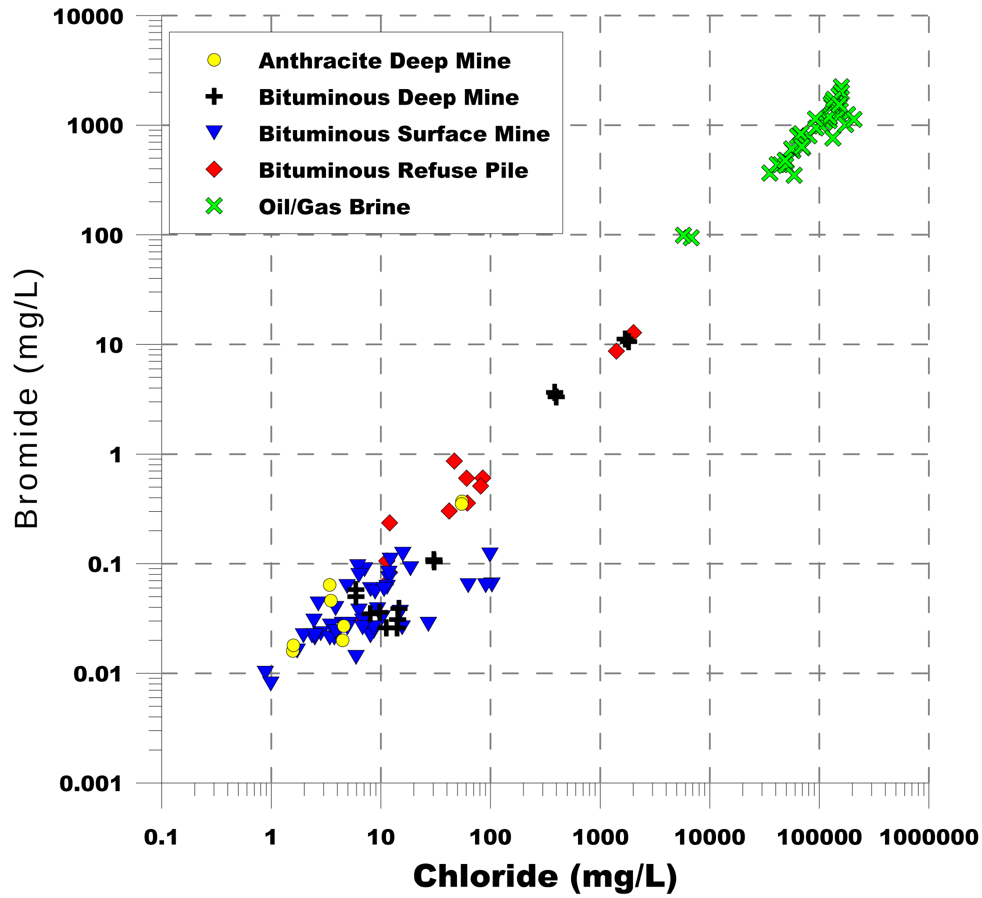


Figure 1 Plot showing chloride and bromide concentrations for surface mines, deep mines, coal refuse and oil/gas well brine waters. Mining data are from Cravotta (2015). Oil and gas data are from Dresel and Rose (2010).

Conclusion

It is my professional opinion that the sample results of the raw and treated mine water are consistent with typical mine drainage originating from a flooded Pittsburgh seam underground coal mine in southwestern Pennsylvania.

References

Blackmer, G.C., G.I. Omar, and D.P. Gould, 1994. Post-Alleghanian unroofing history of the Appalachian Basin, Pennsylvania, from apatite fission track analysis &and thermal models. Tectonics, v. 13, p. 1259-1276.

Cravotta, C.A. III, and K. B.C. Brady, 2015. Priority pollutants and associated constituents in untreated and treated discharges from coal mining or processing facilities in Pennsylvania, USA: Applied Geochemistry, v. 62, p. 108-130.

Dresel, P.E. and A.W. Rose, 2010. Chemistry and Origin of Oil and Gas Well Brines in Western Pennsylvania. Pennsylvania Geological Survey, Open-File Report OFOG 10-01.0, 48 p.

Edmunds, W.E., V.W. Skema, and N.K. Flint, 1998. Pennsylvanian. Part II. Stratigraphy and Sedimentary Tectonics. Geology of Pennsylvania, pp. 156-157.

Reed, J.S., J.A. Spotila, K.A. Eriksson and R.J. Bodnar, 2005. Burial and exhumation history of Pennsylvanian strata, central Appalachian basin: an integrated study. Basin Research, v. 17, p. 259-268.