Big Sandy Power Plant Fly Ash Pond Alternative Source Demonstration

The Big Sandy Fly Ash Pond initiated an assessment monitoring program in accordance with 40 CFR 257.95 on April 13, 2018. Groundwater protection standards (GWPS) were set in accordance with 257.95(d)(2) and a statistical evaluation of the assessment monitoring data was conducted. This statistical evaluation revealed an exceedance of the GWPS for beryllium, cobalt, and lithium at Monitoring Well MW-1603 on February 10, 2022. A successful alternative source demonstration (ASD) was completed per 257.95(g)(3), therefore, the Big Sandy Fly Ash Pond will remain in assessment monitoring. An alternative source demonstration is documentation that shows a source other than the CCR unit was responsible for causing the statistics to exceed the GWPS. The ASD document will explain the alternate cause of the GWPS exceedances. The successful ASD is attached.

Alternative Source Demonstration Addendum Report for the October 2021 Monitoring Data Big Sandy Fly Ash Pond Louisa, Kentucky

Prepared for: American Electric Power

Prepared by: EHS 5 Support

March 2022



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Acronyms

μg/L	micrograms per liter
AEP	American Electric Power
ASD	alternative source demonstration
bgs	below ground surface
BSFAP	Big Sandy Fly Ash Pond
CCR	coal combustion residual
CFR	Code of Federal Regulations
EPRI	Electric Power Research Institute
ft	foot/feet
GWPS	Groundwater Protection Standards
KGS	Kentucky Geological Survey
LCL	lower confidence level
MDL	method detection limit
mg/L	milligrams per liter
msl	mean sea level
NORM	naturally occurring radioactive materials
ORP	oxidation-reduction potential
pCi/L	picocuries per liter
ppm	parts per million
S.U.	standard units (pH)
SSL	statistically significant level
TDS	total dissolved solids
UCL	upper confidence level
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey

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Alternative Source Demonstration Addendum Report for the October 2021 Monitoring Data Big Sandy Fly Ash Pond Certification by Qualified Professional Engineer

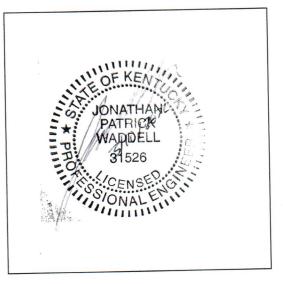
Certification by Qualified Professional Engineer

I certify that the alternative source demonstration (ASD) conducted and presented within this report is accurate and appropriate for evaluating the groundwater monitoring data for the Big Sandy Fly Ash Pond Coal Combustion Residual (CCR) management area associated with the Big Sandy Power Plant located in Louisa, Kentucky. This ASD meets the requirements of the United States Environmental Protection Agency CCR Rule defined at 40 Code of Federal Regulations 257.95(g)(3)(ii).

Jonathan Patrick Waddell

Printed Name of Licensed Professional Engineer

Mall Signature



31526

License Number

Licensing State

3/10/2022

Date



1 Introduction

EHS Support LLC ("EHS Support") was retained by the American Electric Power (AEP) – Kentucky Power Company in December 2018 to conduct an alternative source demonstration (ASD) investigation for coal combustion residual (CCR) constituents in groundwater near the Big Sandy Fly Ash Pond (BSFAP or "Site"). The BSFAP is associated with the Big Sandy Power Plant located in Louisa, Kentucky (EHS Support, 2019a). The ASD determined that groundwater in the vicinity of the Site was not being impacted by CCR constituents from the BSFAP. The statistically significant levels (SSLs) of beryllium, cobalt, and lithium concentrations present in excess of the Groundwater Protection Standards (GWPS), which triggered the ASD investigation, were determined to be a result of the oxidation of coal seams that were intersected by the borehole and well screen for well MW-1603.

Since the initial ASD investigation was completed (incorporating data from September 2016 to October 2018), the following ASD investigations have been conducted:

- The second ASD investigation was conducted after the March 2019 groundwater monitoring data indicated continued SSLs of beryllium, cobalt, and lithium exceeding the GWPS at MW-1603 (EHS Support, 2019b).
- The third ASD investigation was conducted following continued detections of beryllium, cobalt, and lithium at SSLs above the GWPS in MW-1603 during the August 2019 sampling event (EHS Support, 2020). In addition, an SSL of radium 226 combined with radium 228 (hereafter radium 226/228) was measured above its GWPS for the first time in MW-1603 groundwater during the August 2019 sampling event (EHS Support, 2020).
- The fourth ASD investigation was conducted following continued detections of four constituents (beryllium, cobalt, lithium, and radium 226/228) at SSLs above the GWPS in MW-1603 in March and June 2020 (EHS Support, 2021a).
- The fifth ASD investigation was conducted following continued detections of three constituents (beryllium, cobalt, and lithium) at SSLs above the GWPS in MW-1603 in October 2020 (EHS Support, 2021b).
- The sixth ASD investigation was conducted following continued detections of three constituents (beryllium, cobalt, and lithium) at SSLs above the GWPS in MW-1603 in March and June 2021 (EHS Support, 2021c).

In October 2021, four constituents (beryllium, cobalt, lithium, and radium 226/228) were detected at SSLs above the GWPS in MW-1603, thus requiring the ASD addendum investigation presented in this report. This ASD addendum investigation has been prepared per the requirements of the United States Environmental Protection Agency (USEPA) CCR Rule (40 Code of Federal Regulations [CFR] §257.95). The concentrations of beryllium, cobalt, lithium, and radium 226/228 in MW-1603 groundwater were determined herein to result from Type IV natural variations in groundwater (ASD types are discussed in **Section 3.1**). This conclusion was reached by examining analytical results for compounds detected at SSLs in the context of the broader list of CCR constituents analyzed at the Site.

1.1 Objective

The objective of this ASD investigation is to assess groundwater monitoring data collected in compliance with the CCR Rule, as allowed under paragraph 40 CFR §257.95(g)(3)(ii). This part of the CCR Rule allows



AEP to determine whether the source(s) for SSLs of beryllium, cobalt, lithium, and radium 226/228 exceeding the GWPSs, as reported in groundwater monitoring well MW-1603, are associated with the CCR unit; or alternatively if the SSL resulted from an error in sampling, analysis, statistical evaluation, or natural variation in groundwater quality.

1.2 Lines of Evidence

This ASD investigation for the BSFAP has been conducted to further evaluate potential alternate sources or reasons for the continued detection of SSLs of beryllium, cobalt, lithium, and radium 226/228 in groundwater samples from monitoring well MW-1603.

A potential alternate source was previously identified in prior ASD investigations (EHS Support, 2019a, 2019b, 2020, 2021a, 2021b, and 2021c), based on the following lines of evidence:

- A lack of exceedances and increasing trends of primary indicators of CCR.
- Constituent concentrations in BSFAP water are lower than those of the corresponding constituent observed in groundwater from MW-1603.
- Major ion chemistry was not indicative of mixing between BSFAP water and groundwater.
- Acidic groundwater in MW-1603 (pH 3 to 5.5 standard units [S.U.]) is not indicative of BSFAP water (pH 7.97).

For the purposes of this ASD addendum investigation, constituents were identified that would serve as a primary indicator for CCR. A primary indicator must meet **both** of the following criteria:

- 1. The constituent typically has a high concentration in CCR leachate, relative to background, such that it is expected to have an elevated concentration in the event of a release.
- 2. The constituent is unreactive and has high mobility in groundwater, such that it is expected to be at the leading edge of the plume. Consequently, the constituent will have elevated concentrations relative to background across the entire area of the plume.

As boron and sulfate are primary indicators for CCR (Electric Power Research Institute [EPRI], 2012) and have previously been evaluated, they have been re-evaluated herein as primary indicators for this ASD investigation. In addition, chloride is used as a primary indicator for this ASD. Other potential indicators that were evaluated in this ASD investigation include bromide, fluoride, molybdenum, potassium, and sodium.



2 Project Background

A detailed description of Site location, history, and geology was provided in the *Alternative Source Demonstration Report for Beryllium, Cobalt and Lithium, Big Sandy Fly Ash Pond, Louisa, Kentucky* (EHS Support, 2019a). Attached **Figure 1** and **Figure 2** show the Site layout and groundwater monitoring network, respectively.

To support and provide context to this ASD addendum investigation, **Section 2.1** and **Section 2.2** describe the groundwater monitoring network and groundwater monitoring activities.

2.1 Groundwater Monitoring Network Evaluation

On behalf of AEP, Geosyntec Consultants, Inc. ("Geosyntec") conducted an assessment of the groundwater monitoring network in the uppermost aquifer associated with the BSFAP (Geosyntec, 2016). Geosyntec determined that the hydrostratigraphy in the vicinity of the BSFAP is characterized by an interconnected water-bearing system comprised of Pennsylvanian-aged bedrock (of the Breathitt Group, Conemaugh Formation) and Quaternary alluvium. The Conemaugh Formation and Breathitt Group consist of sandstones, siltstones, shale, and coal that may grade laterally and vertically into one another. The overlying Quaternary alluvial deposits include sandy lean clay to silty sand and gravel at the bottom of the Horseford Creek valley and the floodplain of Blaine Creek. Based on these hydrogeologic conditions, Geosyntec defined the interconnected water-bearing system of the fractured bedrock and alluvium as the uppermost aquifer for the BSFAP CCR unit. This determination was based on the presence of groundwater in numerous monitoring wells screened in the water-bearing unit (fractured bedrock and alluvium), the recovery of these wells during pumping and development, and a potentiometric surface generally consistent with Site topography and surface water elevations.

Geosyntec defined the groundwater detection monitoring network as consisting of ten monitoring wells to assess the upper water-bearing aquifer (fractured bedrock and alluvium) (Geosyntec, 2016). Of these monitoring wells, six locations (MW-1011, MW-1012, MW-1203, MW-1601, MW-1602, and MW-1603) are screened in fractured sandstone and shale layers of the Breathitt formation. The remaining four monitoring wells (MW-1604 through MW-1607) are screened in the alluvium. The location of each groundwater monitoring well within the uppermost aquifer is shown in **Figure 2**.

Three of the monitoring wells (MW-1011, MW-1012, and MW-1203) screened in bedrock were installed on the hillside slopes upgradient of the BSFAP to support background monitoring. Three monitoring wells (MW-1601, MW-1602, and MW-1603) were installed in bedrock located downgradient of the BSFAP and used for compliance monitoring. Two monitoring wells (MW-1604 and MW-1605) side gradient of the BSFAP are screened in alluvium and are used for background monitoring. The remaining two monitoring wells (MW-1606 and MW-1607) are located south of the Main Dam (**Figure 1**). These locations are screened in the alluvium downgradient of the BSFAP and used for compliance monitoring.

Geosyntec determined that the groundwater monitoring well network described above meets the requirements of 40 CFR §257.91, as it consists of a sufficient number of wells installed at the appropriate locations and depths to yield groundwater samples from the uppermost aquifer. Thus, the current groundwater monitoring network accurately represents the quality of background groundwater and groundwater passing the waste boundary of the BSFAP.



As bedrock monitoring well MW-1603 is the focus of this ASD, the boring log was reviewed to assess the lithology that could impact groundwater chemistry (EHS Support, 2019a). The boring log descriptions show alternating sequences of yellowish-brown sandstones and bluish-gray to black shales beginning at 13 feet below ground surface (ft bgs) and extending to the total depth of the boring at 39.5 ft bgs. This lithologic description is indicative of the upper portion of the Princess Formation (uppermost formation in the Breathitt Group [Rice and Hiett, 1994]). Within the MW-1603 screened interval (22 to 32 ft bgs), the shale at a depth of 24 to 25 ft bgs was described as "intensely fractured, black, wet, nearly all organic matter; slight coaly texture." This depth (24 to 25 ft bgs) corresponds with the measurements by the Kentucky Geological Survey (KGS) of the elevation of the Princess Number 8 coal, which is present within the Princess Formation of the Breathitt Group (EHS Support, 2019a).

Coal or "organic material" was also visually identified on the MW-1608, MW-1609, and MW-1610 boring logs at the same approximate elevation, between 630 and 650 feet, that aligns with the KGS measurements (**Table 2-1**). No coal was documented in this section in three monitoring wells (MW-1601, MW-1602, and MW-1611). Four monitoring wells (MW-1604, MW-1605, MW-1606, and MW-1607) were installed stratigraphically below this coal layer.

Well/Boring	Surface Elevation (ft msl)	Screened Interval (ft msl)	Coal or "Organics" Description at ~632-650 ft
MW-1601	713.8	646.8-636.8	No coal logged
MW-1602	711.6	632.1-622.1	No coal logged
MW-1603	673.2	651.2-641.2	Yes, at a depth of ~25 ft (Elevation of 648 ft)
MW-1604	553.1	513.1-503.1	
MW-1605	554.4	538.9-528.9	
MW-1606	551	513.1-503.1	
MW-1607	542.2	518.7-508.7	
MW-1608	716.2	606.6-596.6	Yes, at depths of ~74 ft (Elevation of 642 ft), ~ 75.3 to 76.6 ft (Elevation of 641 to 640 ft), and ~ 83.5 to 84 ft (Elevation of 633 to 632 ft)
MW-1609	~728		Yes, at a depth of ~79 ft (Elevation of 649 ft)
MW-1610	~716		Yes, at a depth of ~81 ft (Elevation of 635 ft)
MW-1611	~711	606-596	No coal logged

Table 2-1	Screened Interval	of Monitoring Wells
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--- = Boring advanced below the coal interval

~ = Approximate

ft = feet

msl = mean sea level

2.2 Groundwater Monitoring

AEP has conducted groundwater monitoring of the uppermost aquifer to meet the requirements of the CCR Rules. Groundwater monitoring generally included the following activities:

Alternative Source Demonstration Addendum Report for the October 2021 Monitoring Data Big Sandy Fly Ash Pond Project Background



- Collection of groundwater samples and analysis for Appendix III and Appendix IV constituents, as specified in 40 CFR §257.94 et seq. and AEP's Groundwater Sampling and Analysis Plan (AEP and EHS Support, 2016).
- Completion of validation tests for groundwater data, including tests for completeness, valid values, transcription errors, and consistent units.
- Establishment of background data for each Appendix III and Appendix IV constituent.
- Initiation of detection monitoring sampling and analysis.
- Evaluation of the groundwater data using a statistical process per 40 CFR §257.93, which was
 prepared, certified, and originally posted to AEP's CCR website in April 2017 in AEP's Statistical
 Analysis Plan (Geosyntec, 2017) and updated as Revision 1 in January 2021 (Geosyntec, 2021);
 the statistical process was guided by USEPA's Statistical Analysis of Groundwater Monitoring
 Data at RCRA Facilities, Unified Guidance (USEPA, 2009).
- Initiation of assessment monitoring sampling and analysis.
- Completion of statistical data evaluation and determination of GWPS.

Assessment monitoring for the BSFAP has been conducted on a semi-annual basis since April 2018. The groundwater data collected through the October 2021 monitoring event have been used for this ASD addendum investigation. Historical groundwater monitoring data for MW-1603 is provided in **Table 1** (attached). The October 2021 groundwater data was evaluated, and no data usability issues were found (Geosyntec, 2021b). Assessment monitoring data for well MW-1603 in October 2021 is provided in **Table 2-2**.

Analyte	Unit	October 2021 Value
Antimony	μg/L	< 0.02
Arsenic	μg/L	1.01
Barium	μg/L	17.1
Beryllium	μg/L	17.4
Boron	mg/L	0.054
Bromide	mg/L	0.03
Cadmium	μg/L	0.0931
Calcium	mg/L	93.1
Chloride	mg/L	3.93
Chromium	μg/L	0.59
Cobalt	μg/L	95.1
Fluoride	mg/L	0.96
Lead	μg/L	6.10
Lithium	mg/L	0.186
Mercury	μg/L	0.003

Table 2-2	MW-1603 October 2021 Groundwater Quality
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Analyte	Unit	October 2021 Value
Molybdenum	μg/L	< 0.1
рН	S.U.	3.23
Potassium	mg/L	4.6
Radium 226/228	pCi/L	10.51
Residue, Filterable, TDS	mg/L	1,040
Selenium	μg/L	4.26
Sodium	mg/L	24
Sulfate	mg/L	735
Thallium	μg/L	2.2

< = non detect at method detection limit (MDL)

µg/L = micrograms per liter

mg/L = milligrams per liter

NA = constituent not analyzed

pCi/L = picocuries per liter

S.U. = standard units

TDS = total dissolved solids

AEP submitted the October 2021 monitoring data to Groundwater Stats Consulting, LLC for statistical analysis. A GWPS was established for each of the Appendix IV parameters. Confidence intervals, including lower confidence levels (LCLs) and upper confidence levels (UCLs), were calculated for Appendix IV parameters at the compliance wells to assess whether Appendix IV parameters were present at an SSL above the GWPS. Based on this statistical analysis of the October 2021 data, the following SSLs were identified at the BSFAP in MW-1603 (no other monitoring well had constituents exceeding a GWPS):

- The LCL for beryllium exceeded the GWPS of 0.004 milligrams per liter (mg/L) at MW-1603 (0.0166 mg/L).
- The LCL for cobalt exceeded the GWPS of 0.006 mg/L at MW-1603 (0.0855 mg/L).
- The LCL for lithium exceeded the GWPS of 0.04 mg/L at MW-1603 (0.181 mg/L).
- The LCL for radium 226/228 exceeded the GWPS of 5.00 picocuries per liter (pCi/L) at MW-1603 (5.11 pCi/L).

Alternative Source Demonstration Addendum Report for the October 2021 Monitoring Data Big Sandy Fly Ash Pond Alternative Source Demonstration Requirements



3 Alternative Source Demonstration Requirements

Potential causes that may support an ASD include, but are not limited to, sampling causes (ASD Type I), laboratory causes (ASD Type II), statistical evaluation causes (ASD Type III), and/or natural variation causes (ASD Type IV).

3.1 Alternative Source Demonstration

This ASD for the BSFAP is focused on assessing whether Type IV natural variations in groundwater could be the cause of the SSLs of beryllium, cobalt, lithium, and radium 226/228 reported for groundwater collected from monitoring well MW-1603 during the October 2021 sampling.

Historical groundwater monitoring data for MW-1603 is provided in **Table 1** (attached).

3.2 Assessment of Groundwater Monitoring Results

The following constituents will typically provide the information required for a complete ASD:

- Primary indicators (boron and sulfate) are evaluated for potential BSFAP leachate.
- Major ion concentrations (alkalinity, chloride, sulfate, calcium, magnesium, potassium, and sodium) in leachate and groundwater are used to evaluate whether downgradient groundwater chemistry remains representative of background groundwater chemistry. Major ion chemistry can also be used to evaluate natural variability due to seasonal changes or other causes.
- Field turbidity of groundwater is used as an indicator of the presence of suspended solids that may contribute to elevated concentrations of constituents monitored in unfiltered samples under the CCR Rule.
- The pH of leachate and groundwater provides information on chemical reactions and potential mobility of constituents in groundwater.
- Dissolved oxygen, oxidation-reduction potential (ORP), iron, and manganese in groundwater are
 used as indicators of redox conditions. Redox changes can affect the chemical state and
 solubility of sulfate, in addition to trace elements including arsenic and selenium. For example,
 under strongly reduced conditions (ORP less than -200 millivolts at pH 7), sulfate can be reduced
 to form hydrogen sulfide, or it can precipitate as iron sulfide, arsenic reduces to more mobile
 arsenite species, and selenium reduces to the low-mobility selenite species.

Groundwater monitored at a CCR unit for compliance with the CCR Rule is a compilation of the history of all sources of water comingling at that particular monitoring well. Different sources may contribute to the presence and detection of the same constituents, making source identification challenging. The identification and use of water quality "signatures" can be used as a tool for deciphering the similarity between potential sources and the water quality at a specific monitoring point.



4 Alternative Source Demonstration Assessment

As stated within **Section 1.2**, the primary indicators for CCR leachate impacts to groundwater are boron and sulfate. In addition to these two constituents, chloride is also used as a primary indicator for this ASD. Other potential indicators that have been evaluated include bromide, fluoride, molybdenum, potassium, and sodium.

As identified in **Section 1.1**, SSLs of beryllium, cobalt, and lithium have been reported in groundwater samples above the GWPS from monitoring well MW-1603 in October 2021. The water quality signatures for well MW-1603 are discussed in **Section 4.3** and compared to the water quality of the BSFAP.

EPRI (2012) defines three tiers of investigation for evaluation of water quality signatures to determine if elevated concentrations represent a release from a CCR facility:

- Tier I: Trend Analysis and Statistics
- Tier II: Advanced Geochemical Evaluation Methods
- Tier III: Isotopic Analyses

Conversely, these tools can also be used to evaluate whether or not sources other than CCR are contributing to groundwater quality degradation.

The CCR Rule requires statistical analysis under assessment monitoring for the determination of SSLs above the GWPS. Many of the primary and potential indicator constituents listed for CCR (EPRI, 2017) are included in AEP's constituent list for the BSFAP groundwater monitoring programs, including primary constituents boron and sulfate. If there is an SSL without a corresponding increase in a primary indicator constituent (boron and usually sulfate for CCR), then this is a key line of evidence for an ASD.

4.1 Groundwater Data Analysis

Temporal plots are provided in **Section 4.1.1** through **Section 4.1.3** for monitoring well MW-1603 (**Figure 4-1** through **Figure 4-13**). Each of the plots uses the following color-coding system:

- Red indicates a concentration reported above the reporting limit.
- Orange indicates a concentration reported below the reporting limit but greater than the method detection limit (MDL) (denoted as estimated "J" values).
- Green indicates a concentration not detected at or above the MDL (denoted as "U"); results were conservatively plotted as the MDL.

The BSFAP water signature from October 2017 is plotted as a constant concentration in **Figure 4-1** through **Figure 4-13** for comparison. It is probable that BSFAP water quality historically varied over time since the BSFAP accepted fly ash before 1970. However, the BSFAP ceased accepting fly ash in November 2015 and the surface water quality is anticipated to be more stable following this termination of relatively constant fly ash addition. Therefore, the October 19, 2017 data provides a reasonable representation of BSFAP surface water conditions. Shortly after the October 2017 sample collection, BSFAP closure work, including contouring of CCR in preparation for geomembrane cover installation, began near the surface water collection area and samples were no longer representative. Geomembrane installation was completed over the entire BSFAP in November 2020 and the BSFAP is now closed.



Groundwater constituents for well MW-1603 are plotted on the primary y-axis and BSFAP water constituents are plotted on the secondary y-axis due to the differences in concentration (**Figure 4-1** through **Figure 4-13**).

4.1.1 Primary Indicators

Temporal plots for primary indicators boron, sulfate, and chloride reported in groundwater monitoring well MW-1603 are provided in **Figure 4-1** to **Figure 4-3**, respectively (note the y-axis scales associated with the BSFAP data).

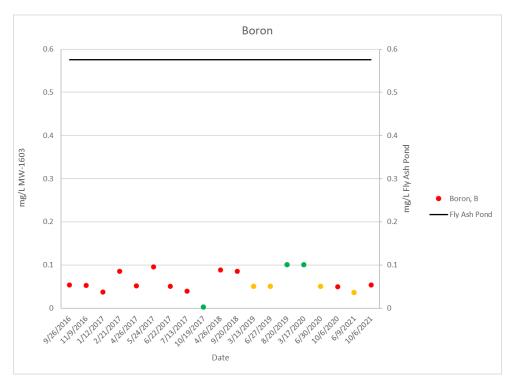
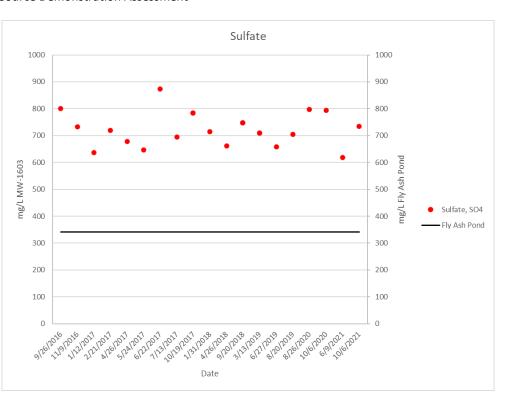


Figure 4-1 MW-1603 Boron Concentrations

Alternative Source Demonstration Addendum Report for the October 2021 Monitoring Data Big Sandy Fly Ash Pond Alternative Source Demonstration Assessment





MW-1603 Sulfate Concentrations

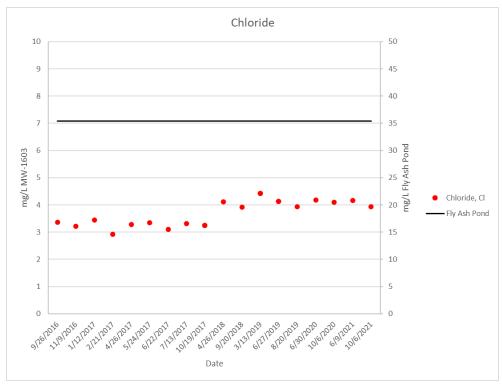


Figure 4-3 MW-1603 Chloride Concentrations



Boron and sulfate concentrations in MW-1603 have remained relatively stable, within the same order of magnitude, with minor variability over the monitoring period (September 2016 through October 2021). Chloride concentrations in MW-1603 remained relatively stable until April 2018, after which a slight increase is observed and is followed by stable concentrations. Given the overall very low chloride concentrations at MW-1603 (an order of magnitude lower than in the BSFAP), this slight apparent increase in chloride of approximately 1 mg/L is minimal and most likely reflects a change in sampling or analytical procedure. Boron and chloride in water from the BSFAP are present at higher concentrations than in groundwater at MW-1603, whereas sulfate is present at higher concentrations in groundwater at MW-1603 than in water from the BSFAP.

In summary, there were negligible changes in primary indicator concentrations since the last review in November 2021 (EHS Support, 2021c).

4.1.2 Potential Indicators

Temporal plots for potential indicators (bromide, fluoride, molybdenum, potassium, and sodium) reported in groundwater monitoring well MW-1603 are provided in **Figure 4-4** to **Figure 4-8**, respectively.

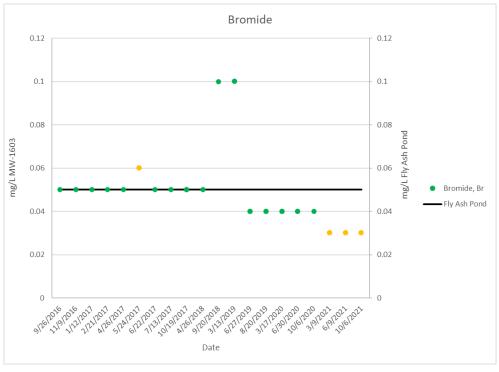


Figure 4-4

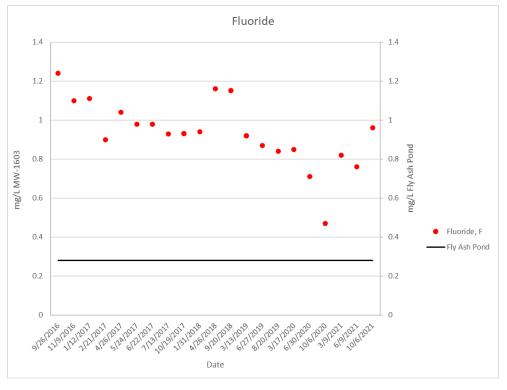
MW-1603 Bromide Concentrations¹

 $^{^1}$ Bromide is below the reporting limit for BSFAP water; therefore, it is plotted at the MDL of 0.05 mg/L.

Alternative Source Demonstration Addendum Report for the October 2021 Monitoring Data Big Sandy Fly Ash Pond



Alternative Source Demonstration Assessment





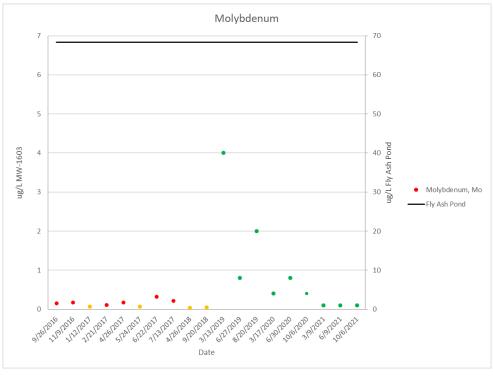
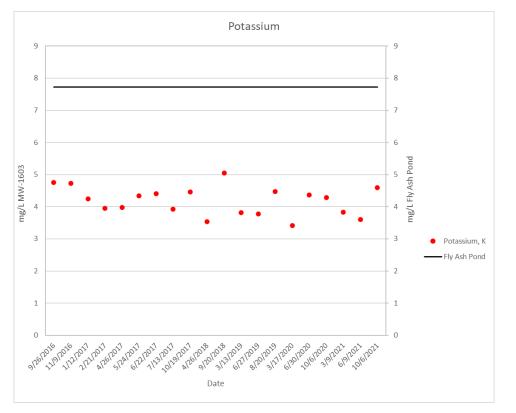


Figure 4-6 **MW-1603 Molybdenum Concentrations**

Alternative Source Demonstration Addendum Report for the October 2021 Monitoring Data Big Sandy Fly Ash Pond Alternative Source Demonstration Assessment





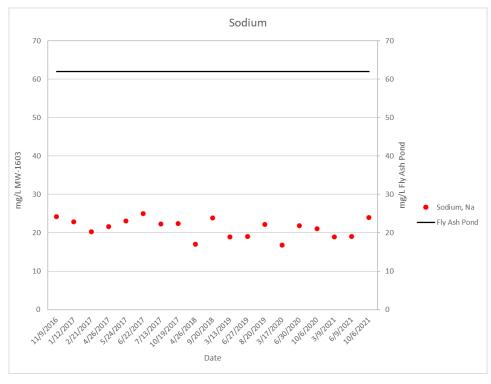


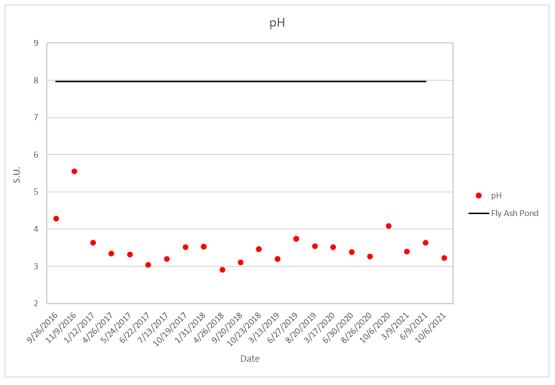
Figure 4-8 MW-1603 Sodium Concentrations



The following summarizes the data presented in **Figure 4-4** through **Figure 4-8**.

- Molybdenum, potassium, and sodium concentrations in groundwater from MW-1603 have consistently been lower than water from the BSFAP (Figure 4-6, Figure 4-7, Figure 4-8 respectively).
- Molybdenum was last detected above the MDL in MW-1603 in September 2018 (Figure 4-6). • The recent variation in molybdenum concentrations, as shown in green, is due to variable MDLs achieved in the laboratory analyses.
- Fluoride concentrations in groundwater from MW-1603 have consistently been higher than water from the BSFAP but have exhibited an overall declining concentration trend with time (Figure 4-5).
- Bromide concentrations in groundwater from MW-1603 have historically been below the MDL of 0.5 mg/L, except an estimated "J" value detection of 0.06 mg/L in May 2017. Estimated "J" value detections of 0.03 mg/L have been reported for bromide during the last three sampling events (March, June, and October 2021) due to lowering of the MDL (Figure 4-4).

A comparison of the pH of BSFAP water and groundwater from MW-1603 is provided in Figure 4-9. The figure illustrates the substantial difference in pH between the BSFAP water and groundwater of approximately three to five S.U. This is using the standard (logarithmic) pH scale which converts to a factor of 1,000 to 100,000 difference in the hydrogen ion concentration. The pH in MW-1603 is acidic with values generally between 3 and 4 standard pH units, whereas the BSFAP water is alkaline at a pH of approximately 8 S.U.







In summary, there were negligible changes in potential indicator concentrations since the last review in November 2021 (EHS Support, 2021c).

4.1.3 ASD Constituent Trends

Temporal plots for the ASD constituents, beryllium, cobalt, lithium, and radium 226/228 reported in groundwater monitoring well MW-1603 are provided in **Figure 4-10** to **Figure 4-13**, respectively.

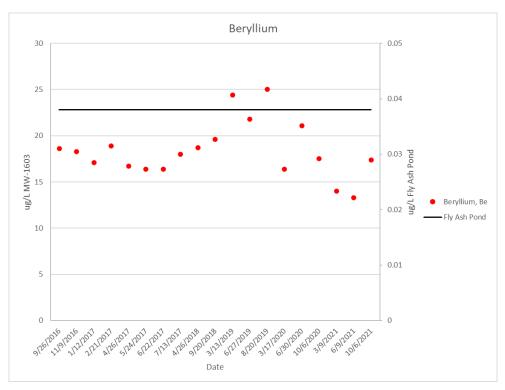
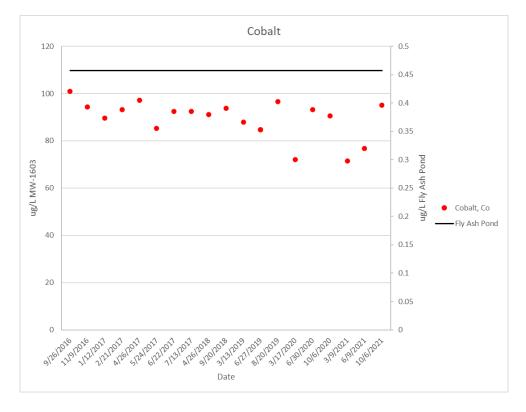


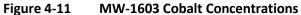
Figure 4-10 MW-1603 Beryllium Concentrations

Alternative Source Demonstration Addendum Report for the October 2021 Monitoring Data Big Sandy Fly Ash Pond



Alternative Source Demonstration Assessment





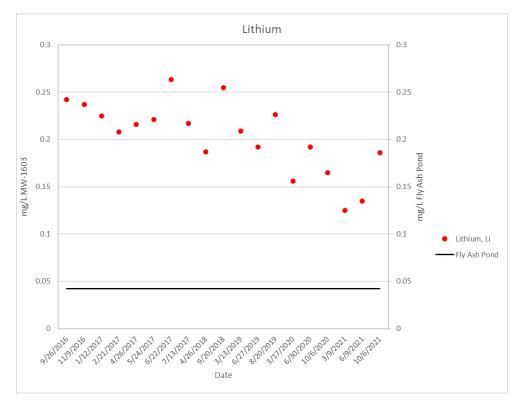


Figure 4-12 **MW-1603 Lithium Concentrations**

Alternative Source Demonstration Addendum Report for the October 2021 Monitoring Data Big Sandy Fly Ash Pond Alternative Source Demonstration Assessment



Radium combined 12 10 8 pCi/L MW-1603 Radium combined 4 2 0 2121/2017 613012025 612112012 A12612019 81201201 3/17/20 A1261201 51241201 612220 1/13/20 91201201 3/13/20 Date

Figure 4-13 MW-1603 Radium 226/228 Concentrations

Beryllium, cobalt, and lithium concentrations are higher in groundwater from MW-1603 compared to BSFAP water (note the y-axis scales associated with **Figure 4-10** and **Figure 4-11**). This data indicates that the source of beryllium, cobalt, and lithium in groundwater at MW-1603 is not associated with the BSFAP.

Radium 226/228 concentrations in the BSFAP water are unknown, therefore, a comparison between the BSFAP water and MW-1603 groundwater cannot be made. However, radium 226/228 concentrations in MW-1603 are stable across most of the dataset, except for the result from August 2019 and the current result from October 2021. Both concentrations are considered anomalies which is supported by the outliers on the box and whisker plot of radium 226/228 on Figure A-12 of **Appendix A**.

4.1.4 Indicator Analysis Findings

Based on the temporal plots for primary indicators, potential indicators, and ASD constituents, it is considered unlikely that CCR constituents from the BSFAP are influencing the chemistry of surrounding groundwater. This is based on the primary indicator sulfate, potential indicators fluoride and bromide, and the ASD constituent's beryllium, cobalt, and lithium all being present at higher concentrations in surrounding groundwater in comparison to the BSFAP water (EHS Support, 2019a). As the concentrations of these constituents in surrounding groundwater are higher, it is unlikely that there is a concentration gradient extending from the BSFAP into groundwater. A key line of evidence that CCR constituents are not affecting groundwater at MW-1603 is the vastly different pH values between the locations. It is more likely that an alternate source is contributing to the higher concentrations observed in groundwater.



In summary, based on the analyses presented above, no trends in the MW-1603 groundwater dataset suggest that CCR constituents are migrating from the BSFAP into groundwater.

4.2 Tier I Evaluation - Statistical Evaluation

Statistical evaluations of analytes have been conducted previously (EHS Support, 2019a, 2019b, 2020, 2021a, 2021b, 2021c). The evaluations concluded that groundwater in the vicinity of MW-1603 is statistically the same as that which the United States Geological Survey (USGS) reported for regional background (Ruppert et al., 2000) for arsenic, boron, calcium, chloride, chromium, fluoride, molybdenum, potassium, sodium, and strontium.

The box plots from the earlier ASD investigation (EHS Support, 2019a) also show a difference between monitoring well MW-1603, BSFAP water, and/or the regional background for pH, alkalinity, barium, cobalt, lead, lithium, magnesium, selenium, and sulfate. No background values were provided by the USGS for beryllium, chromium, lead, lithium, molybdenum, and selenium.

Updated box and whisker plots for constituents reported in MW-1603 groundwater are provided in **Appendix A**. Plots for fluoride, pH, beryllium, cobalt, lithium, and radium 226/228 exhibit outliers which are calculated to be outside the range of distribution (Figure A-4, Figure A-8, Figure A-9, Figure A-10, Figure A-11, and Figure A-12 of **Appendix A**, respectively).

It is likely that the acidic groundwater conditions identified at MW-1603, relative to regional background, are driving the observed SSLs. The geochemical conditions within well MW-1603, including a strongly acidic pH, low alkalinity, and high sulfate, are indicative of conditions similar to those observed at acid mine drainage sites. At MW-1603, the geochemical conditions have developed due to the presence of the sulfide-bearing Princess coal seams being intersected by the screened interval of the monitoring well (discussed in EHS Support, 2019a). The combination of the well installation and effects of well sampling has resulted in the development of aerobic and water-saturated conditions within the coal seams. These conditions have led to a lowering of the pH through oxidation of sulfides present in the coal which has subsequently enhanced rock dissolution. Enhanced host rock dissolution at MW-1603 is evident from the much higher total dissolved solids (TDS) values at this location in comparison to groundwater samples from the other Site wells, including water from the BSFAP.

In addition to an abundance of sulfides, rock and coal samples from the Princess Formation in Kentucky have been shown to contain parts per million (ppm) levels of beryllium, cobalt, and lithium (Hood et al., 2020), thereby, providing a viable source for the observed SSLs. Part per million concentrations of the radioactive elements thorium and uranium are also reported for the Princess coal (Gabbard, 1993; Hood et al., 2020), and radium is a typical decay product of thorium and uranium that is often detected at elevated levels in coal deposits (Zielinski and Finkelman, 1997).

Conditions that are associated with the highest radium concentrations in groundwater include (1) oxygen poor water, (2) acidic conditions (low pH), and high concentrations of dissolved solids (Szabo et al, 2012). Radium is removed from groundwater under shifts to oxidizing conditions by co-precipitation with barite and adsorption onto iron/manganese oxide precipitates. Radium is mobilized into groundwater following shifts to more reducing conditions where it is desorbed following reduction of iron and manganese (McMahon et al., 2019).



For context, studies have demonstrated that the pH of groundwater in contact with fly ash is maintained alkaline (pH 7 to 10) for decades due to buffering by reactions with carbonates and amorphous aluminum silicates in the fly ash (Twardowska et al., 2003). The BSFAP water is consistent with this range, with a pH of 7.97 S.U. Therefore, the acidic pH of groundwater identified at MW-1603 is compelling evidence that groundwater at this location has not mixed with, and is not representative of, water from the BSFAP.

4.3 Tier II Evaluation - Geochemical Evaluation

A simple analysis of primary and potential indicator constituents (as performed in **Section 4.1**) may not provide the lines of evidence required for a robust ASD investigation. It is recognized that naturally occurring indicator constituents and upgradient sources may have an additional influence on groundwater quality. Spatially across a site, groundwater quality may be observed to change due to chemical interactions with the aquifer matrix. EPRI (2012) recommended the use of more sophisticated methods for multiple parameters over multiple locations, such as ion ratios and ternary plots.

4.3.1 Ion Ratios

The development of ion ratios involves first selecting two non-competing, non-sorbing constituents (boron and chloride). The ratios of these constituents are then compared spatially across the Site and a judgment is made as to whether the hydraulically downgradient groundwater is similar to the background groundwater quality.

The calculation of ion ratios was conducted using median concentrations of the indicator species. The median concentrations of boron, chloride, and sulfate over the monitoring period (September 2016 through October 2021) are provided in **Table 4-1**. These three constituents were selected based on the EPRI (2017) recommended indicator species. Whereas bromide is also a recommended indicator species, it was not included in the assessment as it was non-detect in the BSFAP water, indicating its presence in groundwater was either naturally derived or from an off-site source. The median concentrations for sulfate, boron, and chloride show minimal change since January 2019.

Location	Location ID	Median Concentrations September 2016 to October 2021								
Location		Boron (mg/L)	Chloride (mg/L)	Sulfate (mg/L)						
Source	Fly Ash Pond	0.58	35.4	342						
Downgradient	MW-1603	0.052 ± 0.025	3.685 ± 0.463	714 ± 67						

Table 4-1	Median Concentrations of Boron, Chloride, and Sulfate
	inculari concentrations of borony emorracy and surface

mg/L = milligrams per liter

Ion ratios have been calculated using boron, chloride, and sulfate as recommended in EPRI (2017) and are provided in **Table 4-2**. The ion ratios show little change since the last evaluation in November 2021.



		Median Concer	trations September 201	6 to October 2021		
Location	Location ID	Boron/Sulfate (x1000)	Boron/Chloride	Chloride/Sulfate		
Source	Fly Ash Pond	1.68	0.002	0.10		
Downgradient	MW-1603	0.07 ± 0.03	0.01 ± 0.01	0.005 ± 0.001		

Based on the previous and current ion ratio analysis, the conclusion that MW-1603 is not impacted by CCR constituents from the BSFAP is unchanged.

4.3.2 Ternary Plots

Ternary plots are used to identify changes in major or minor ion distributions over time. A ternary plot using calcium, chloride, and sulfate measured in the vicinity of MW-1603 is provided in **Figure 4-14**. The close grouping of ratios from all events on the ternary plot shows that the major ion groundwater ratios have not changed during the five-year period of groundwater quality monitoring at well MW-1603 and that the ratios are distinct from the BSFAP.

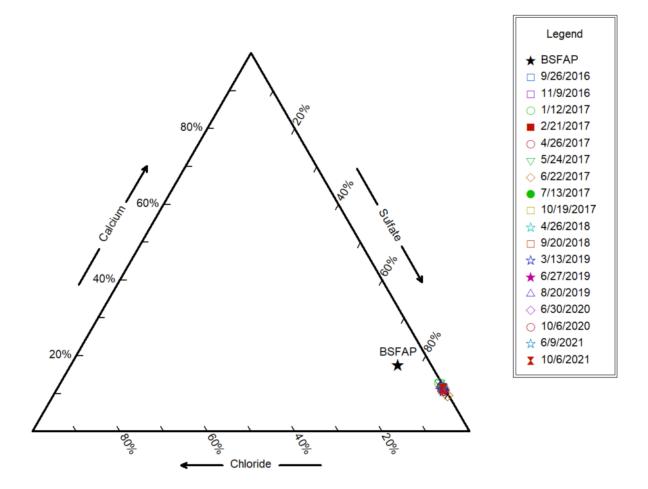


Figure 4-14 Ternary Plot MW-1603

4.3.3 Summary

In summary, based on the previous geochemical evaluations (EHS Support, 2021a, 2021b, 2021c) and the updated review presented in this ASD investigation, there is insufficient evidence to support the presence of CCR constituents (beryllium, cobalt, lithium, and radium 226/228), derived from the BSFAP, in groundwater sampled at MW-1603. The ternary plot does not support temporal changes of MW-1603 groundwater quality. The boron, chloride, and sulfate ion ratios remain relatively unchanged since September 2019. Therefore, it is unlikely that beryllium, cobalt, lithium, and radium 226/228 detected within MW-1603 groundwater are sourced from the BSFAP. It is likely that beryllium, cobalt, lithium, and radium 226/228 are sourced from the lithologies in which MW-1603 is screened across, primarily the Princess coal.



5 Summary and Conclusions

Using the EPRI (2017) guidance for ASD investigations, the conclusions based on the lines of evidence presented and discussed within **Section 3** and **Section 4** indicate that groundwater in the vicinity of the Site is not being impacted by CCR constituents from the BSFAP. The elevated beryllium, cobalt, lithium, and radium concentrations that triggered the ASD investigation are due to the oxidation of sulfide minerals present in coal seams that have been intersected by well MW-1603, including organic material within the screened interval that is identified as having "a slight coaly texture." This is supported by the visual evidence recorded during the logging of the core from this location (EHS Support, 2019a), the low pH reported in groundwater, and the subsequent mobilization and leaching of trace metals (beryllium, cobalt, and lithium) into groundwater by the elevated acidity.

Consistent with the August 2019, March 2020, and June 2020 sampling events, radium 226/228 detections have been reported for MW-1603 as an SSL in the October 2021 groundwater monitoring statistics. Radium is sourced from radioactive decay of naturally occurring radioactive materials (NORM), including uranium and thorium, which are present in the Princess coal at ppm levels. Therefore, the presence of radium 226/228 is likely due to elevated uranium and thorium in the coal seams that have been intersected at well location MW-1603. Natural variations in redox conditions likely cause sorption and desorption of radium to iron/manganese oxides that leads to fluctuation in the detections in groundwater. As a result of the installation, screening, and extraction of groundwater from MW-1603, radium 226/228 may now be considered a technologically enhanced NORM.

The higher pH in the BSFAP water and the corresponding lower concentrations of minor ions in the BSFAP also support the unlikely influence of the BSFAP on groundwater. Therefore, it is concluded that the elevated signatures of beryllium, cobalt, lithium, and radium 226/228 in MW-1603, as noted in the October 2021 groundwater monitoring data, are related to the dissolution of naturally occurring, coal seam-derived constituents within the shale layers of the Breathitt Group, as supported by the discussion of local and regional geology in **Section 2.1** and EHS Support (2019a).

In conclusion, this ASD addendum for the BSFAP has determined that Type IV natural variations in groundwater resulted in the SSLs of beryllium, cobalt, lithium, and radium 226/228 detected at MW-1603.



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Tables

Table 1 MW-1603 Historical Groundwater Data September 2016 to October 2021 Big Sandy Fly Ash Pond Groundwater Monitoring, American Electric Power, Kentucky Power Company, Louisa, Kentucky

Analytes	Units	9/26/2016	11/9/2016	1/12/2017	2/21/2017	4/26/2017	5/24/2017	6/22/2017	7/13/2017	10/19/2017	1/31/2018	4/26/2018	9/20/2018	10/23/2018	3/13/2019	6/27/2019	8/20/2019	3/17/2020	6/30/2020	8/26/2020	10/6/2020	3/9/2021	6/9/2021	10/6/2021
Antimony, Sb	μg/L	0.01 J	< 0.01	< 0.01	< 0.01	0.01 J	< 0.01	< 0.01	< 0.01	NA	NA	0.04 J	0.02 J	NA	< 0.2	< 0.04	< 0.1	< 0.02	< 0.04	NA	< 0.02	< 0.02	0.04 J	< 0.02
Arsenic, As	μg/L	1.51	1.19	1.4	1.26	1.3	1.34	1.29	0.89	NA	NA	1.6	1.4	NA	1.26	1.36	1.39	0.83	1.12	NA	1.12	0.84	0.69	1.01
Barium, Ba	μg/L	13.4	15.4	11.4	10.3	12.4	11.5	11.4	11.3	NA	NA	10.5	11.4	NA	12	11	13.6	9.92	12.2	NA	14.6	10.1	13.1	17.1
Beryllium, Be	μg/L	18.6	18.3	17.1	18.9	16.7	16.4	16.4	18	NA	NA	18.7	19.6	NA	24.4	21.8	25	16.4	21.1	NA	17.5	14	13.3	17.4 M
Boron, B	mg/L	0.054	0.053	0.037	0.085	0.052	0.096	0.051	0.039	< 0.002	NA	0.088	0.085	NA	0.05 J	0.05 J	< 0.1	< 0.1	0.05 J	NA	0.05	NA	0.036 J	0.054
Bromide	mg/L	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	0.06 J	< 0.05	< 0.05	< 0.05	NA	< 0.05	< 0.1	NA	< 0.1	< 0.04	< 0.04	< 0.04	< 0.04	NA	< 0.04	0.03 J	0.03 J	0.03 J
Cadmium, Cd	μg/L	0.84	0.93	0.79	0.75	0.87	0.77	0.86	0.8	NA	NA	0.74	0.83	NA	0.78	0.7	0.89	0.64	0.85	NA	0.87	0.62	0.709	0.0931
Calcium, Ca	mg/L	105	94.7	92.7	91.9	90.5	93.9	90.6	90.2	91	82.2	83.6	97.5	NA	84.6	83.3	95.8		96.6	NA	94.5	NA	79	93.1
Chloride, Cl	mg/L	3.37	3.22	3.45	2.93	3.28	3.34	3.1	3.32	3.24	NA	4.12	3.92	NA	4.42	4.13	3.93	NA	4.18	NA	4.1	NA	4.16	3.93
Chromium, Cr	μg/L	1.1	1.12	0.731	0.771	0.829	0.62	0.821	0.485	NA	NA	0.771	0.713	NA	1 J	0.618	0.8	0.56	0.694	NA	0.743	0.659	0.51	0.59
Cobalt, Co	μg/L	101	94.4	89.6	93.2	97.1	85.3	92.4	92.5	NA	NA	91.1	93.8	NA	87.9	84.7	96.6	72	93.2	NA	90.5	71.4	76.8	95.1 M
Comb. Radium 226/228	pCi/L	6.04	6.6	5.86	4.03	5.72	6.4	6	6.36	NA	NA	5.09	6.75	NA	4.8	7.149	10.92	7.19	6.22	NA	2.681	3.73	7.18	10.51 B
Fluoride, F	mg/L	1.24	1.1	1.11	0.9	1.04	0.98	0.98	0.93	0.93	0.94	1.16	1.15	NA	0.92	0.87	0.84	0.85	0.71	NA	0.47	0.82	0.76	0.96
Lead, Pb	μg/L	9.75	8.18	6.11	6.3	6.41	4.96	6.47	3.72	NA	NA	5.27	4.39	NA	4.28	3.68	4.17	3.95	4.67	NA	4.85	3.37	3.39	6.1
Lithium, Li	mg/L	0.242	0.237	0.225	0.208	0.216	0.221	0.263	0.217	NA	NA	0.187	0.255	NA	0.209	0.192	0.226	0.156	0.192	NA	0.165	0.125	0.135	0.186 M
Mercury, Hg	μg/L	< 0.002	< 0.002	< 0.002	< 0.002	0.002 J	< 0.002	< 0.002	< 0.002	NA	NA	< 0.002	NA	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	NA	< 0.002	0.002 J	0.002 J	0.003 J
Molybdenum, Mo	μg/L	0.15	0.17	0.06 J	0.11	0.18	0.07 J	0.32	0.22	NA	NA	0.03 J	0.04 J	NA	< 4	< 0.8	< 2	< 0.4	< 0.8	NA	< 0.4	< 0.1	< 0.1	<0.1
рН	S.U.	4.29	5.56	3.64	4.51	3.34	3.32	3.04	3.20	3.52	3.52	2.91	3.10	3.46	3.19	3.73	3.54	3.52	3.38	3.27	4.09	3.4	3.64	3.23
Potassium, K	mg/L	4.76	4.73	4.25	3.95	3.98	4.34	4.41	3.92	4.46	NA	3.53	5.05	NA	3.81	3.78	4.48	3.42	4.36	NA	4.29	3.83	3.6	4.6
Residue, Filterable, TDS	mg/L	1,060	1,010	948	1,020	994	936	1,040	1,000	962	915	926	974	NA	896	954	1,010	NA	NA	1,040	1,020	NA	880	1040
Selenium, Se	μg/L	5.4	4.8	5.6	4.9	6.1	6.3	6.1	2.7	NA	NA	8.1	6.3	NA	4	4.9	5.6	4	6.2	NA	5.8	3.9	3.3	4.26
Sodium, Na	mg/L	NA	24.2	22.9	20.3	21.6	23.1	25	22.3	22.4	NA	17	23.9	NA	18.9	19.1	22.2	16.8	21.9	NA	21.1	18.9	19	24
Sulfate, SO ₄	mg/L	801	733	636	720	678	646	873	694	784	714	661	747	NA	709	658	704	NA	NA	798	794	NA	618	735
Thallium, Tl	μg/L	1.29	1.55	1.39	1.2	1.41	1.35	1.43	1.43	NA	NA	1.39	1.7	NA	1 J	1.4	2 J	1.34	1.57	NA	1.82	1.39	1.62	2.2

Notes:

< = not detected at or above the method detection limit

µg/L = Micrograms per liter

B = Analyte detected in a blank sample

J = Estimated value. Analyte detected at a level less than the reporting limit but greater than the method detection limit.

M = the associated MS or MSD recovery was outside acceptance limits.

mg/L = Milligrams per liter

MS = Matrix spike

MSD = Matrix spike duplicate

NA = Not analyzed

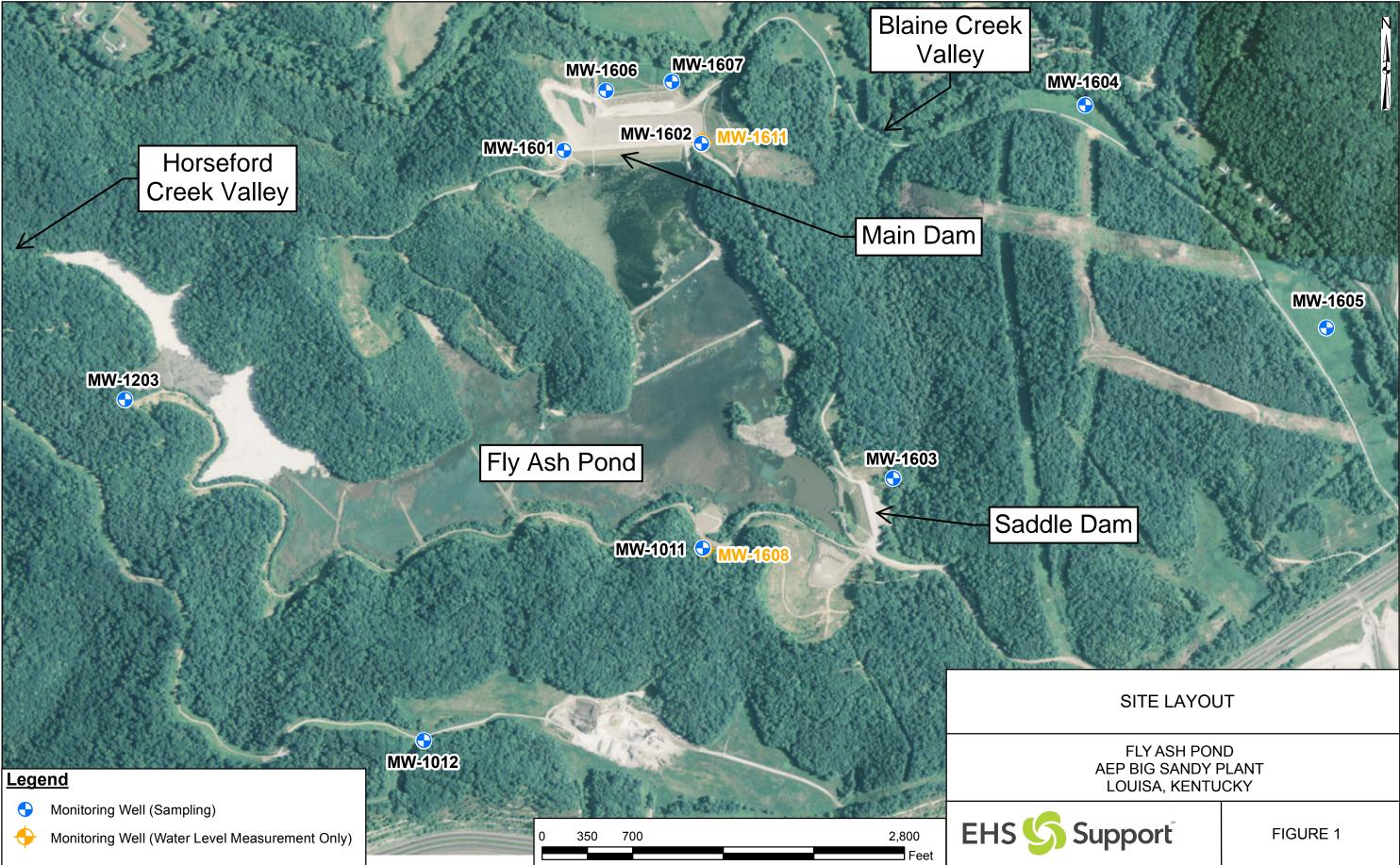
pCi/L = Picocuries per liter S.U. = Standard Units

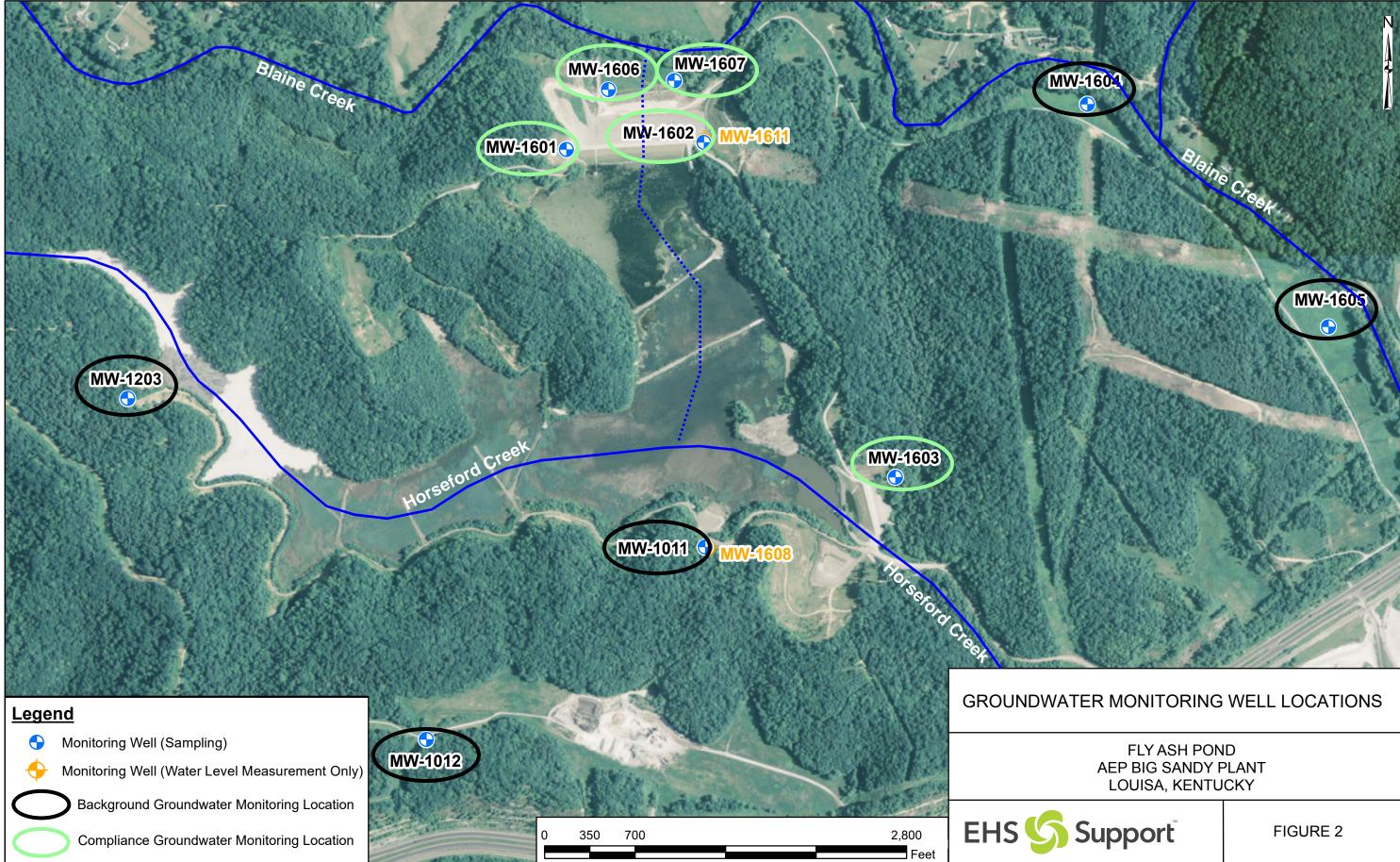
TDS = Total Dissolved Solids











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Figure A-1 Boron Box Plot

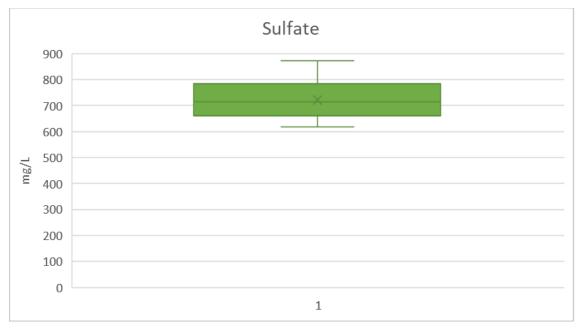


Figure A-2 Sulfate Box Plot

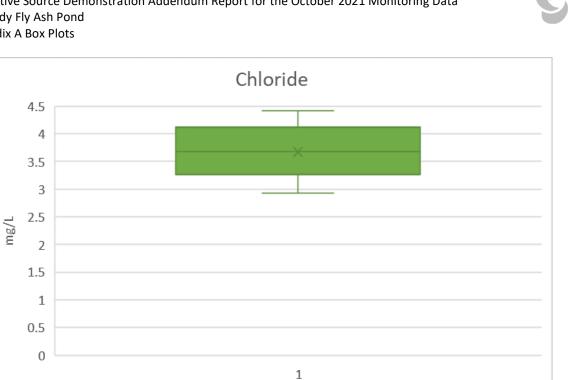


Figure A-3

Chloride Box Plot

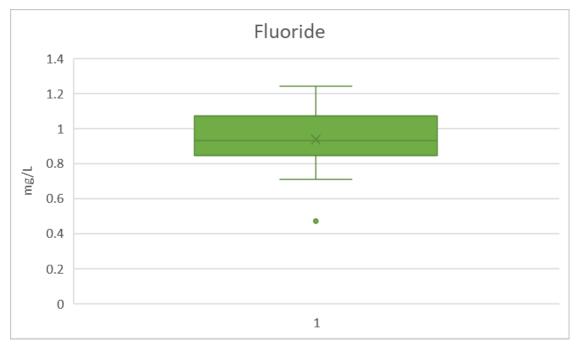


Figure A-4 **Fluoride Box Plot**



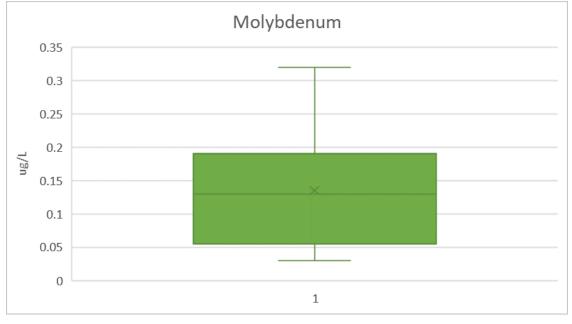


Figure A-5

Molybdenum Box Plot

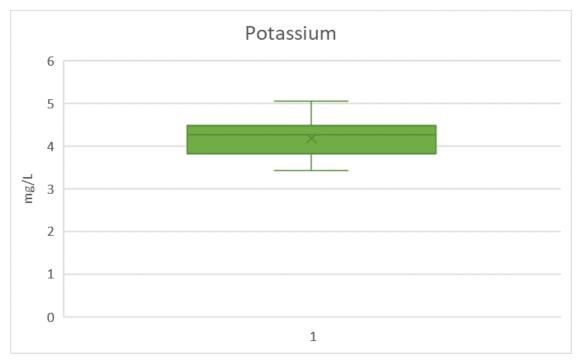


Figure A-6 Potassium Box Plot



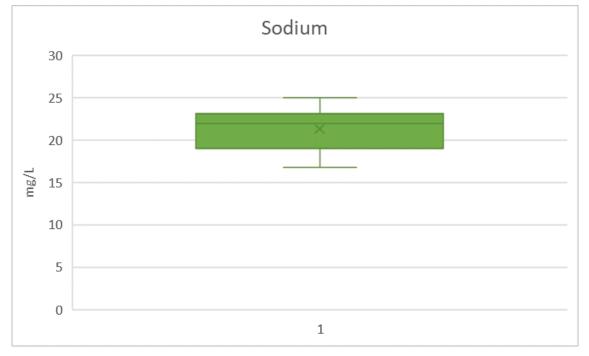


Figure A-7 Sodium Box Plot

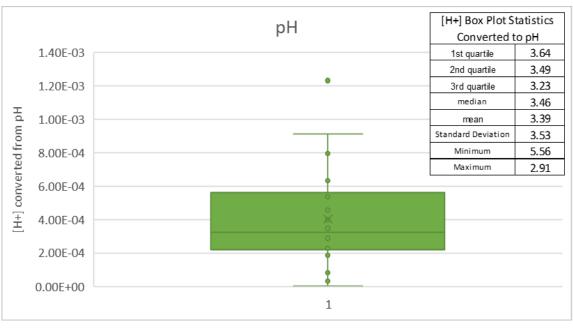
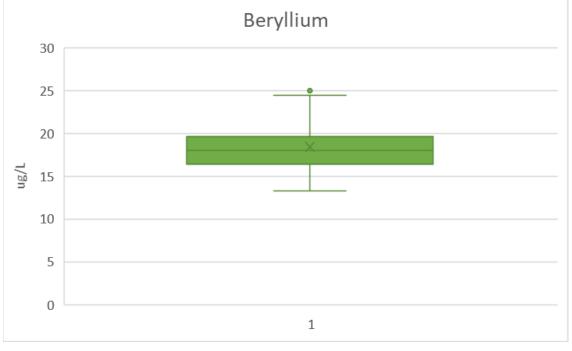
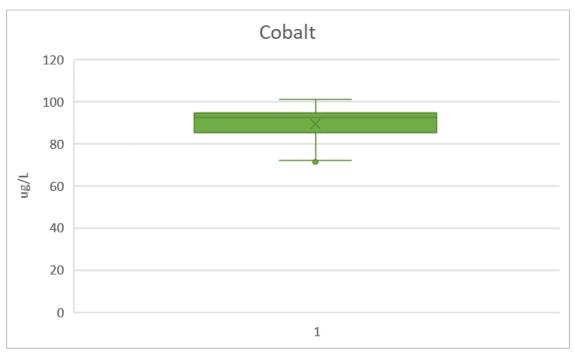


Figure A-8 pH Box Plot

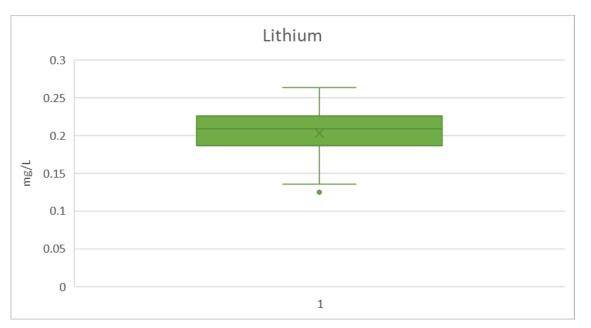














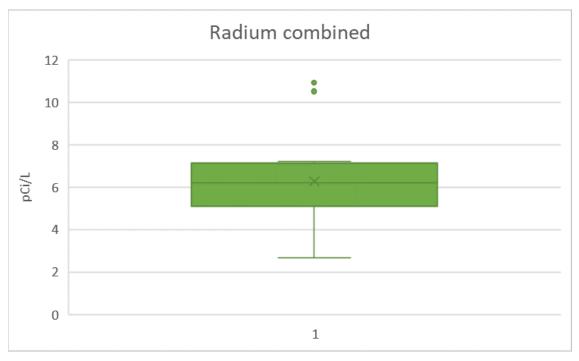


Figure A-12 Radium 226/228 Box Plot