Pirkey Power Plant East Bottom Ash Pond Alternate Source Demonstration

The Pirkey East Bottom Ash Pond initiated an assessment monitoring program in accordance with 40 CFR 257.95 on April 3, 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. The statistical evaluation revealed an exceedance of the cobalt and lithium GWPS on July 12, 2019. A successful alternate source demonstration (ASD) was completed per 257.95(g)(3), therefore, the Pirkey East Bottom Ash Pond will remain in assessment monitoring. An alternate 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 exceedance. The successful ASD is attached.

ALTERNATIVE SOURCE DEMONSTRATION REPORT FEDERAL CCR RULE

H.W. Pirkey Power Plant East Bottom Ash Pond Hallsville, Texas

Submitted to



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Submitted by



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September 23, 2019

CHA8462

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LIST OF ACRONYMS

AEP American Electric Power

ASD Alternative Source Demonstration

CCR Coal Combustion Residuals

CFR Code of Federal Regulations

EBAP East Bottom Ash Pond

EDS Energy Dispersive Spectroscopic Analyzer

EPRI Electric Power Research Institute

GSC Groundwater Stats Consulting, LLC

GWPS Groundwater Protection Standard

LCL Lower Confidence Limit

MCL Maximum Contaminant Level

QA Quality Assurance

QC Quality Control

SEM Scanning Electron Microscopy

SPLP Synthetic Precipitation Leaching Procedure

SSL Statistically Significant Level

UTL Upper Tolerance Limit

USEPA United States Environmental Protection Agency

VAP Vertical Aquifer Profiling

XRD X-Ray Diffraction

SECTION 1

INTRODUCTION AND SUMMARY

The H.W. Pirkey Plant, located in Hallsville, Texas, has four regulated coal combustion residuals (CCR) storage units, including the East Bottom Ash Pond (EBAP, Figure 1). In February 2019, a semi-annual assessment monitoring event was conducted at the EBAP in accordance with 40 CFR 257.95(d)(1). The monitoring data were submitted to Groundwater Stats Consulting, LLC (GSC) for statistical analysis. Groundwater protection standards (GWPSs) were established for each Appendix IV parameter in accordance with the statistical analysis plan developed for the facility (AEP, 2017) and United States Environmental Protection Agency's (USEPA) Statistical Analysis of Groundwater Monitoring Data at RCRA Facilities – Unified Guidance (Unified Guidance; USEPA, 2009). The GWPS for each parameter was established as the greater of the background concentration and the maximum contaminant level (MCL) or risk-based level specified in 40 CFR 257.95(h)(2). To determine background concentrations, an upper tolerance limit (UTL) was calculated using pooled data from the background wells collected during the background monitoring and assessment monitoring events.

Confidence intervals were calculated for Appendix IV parameters at the compliance wells to assess whether Appendix IV parameters were present at a statistically significant level (SSL) above the GWPSs. An SSL was concluded if the lower confidence limit (LCL) of a parameter exceeded the GWPS (i.e., if the entire confidence interval exceeded the GWPS). The following SSLs were identified at the Pirkey EBAP:

- LCLs for cobalt exceeded the GWPS of 0.0094 mg/L at AD-2 (0.0100 mg/L), AD-31 (0.00943 mg/L), and AD-32 (0.0333 mg/L).
- LCLs for lithium exceeded the GWPS of 0.052 mg/L at AD-31 (0.077 mg/L) and AD-32 (0.075 mg/L).

No other SSLs were identified (Geosyntec, 2019a).

1.1 CCR Rule Requirements

United States Environmental Protection Agency (USEPA) regulations regarding assessment monitoring programs for coal combustion residuals (CCR) landfills and surface impoundments provide owners and operators with the option to make an alternative source demonstration when an SSL is identified (40 CFR 257.95(g)(3)(ii)). An owner or operator may:

Demonstrate that a source other than the CCR unit caused the contamination, or that the statistically significant increase resulted from error in sampling, analysis, statistical evaluation, or natural variation in groundwater quality. Any such demonstration must be supported by a report that includes the factual or evidentiary basis for any conclusions and must be certified to be accurate by a

qualified professional engineer or approval from the Participating State Director or approval from EPA where EPA is the permitting authority. If a successful demonstration is made, the owner or operator must continue monitoring in accordance with the assessment monitoring program pursuant to this section....

Pursuant to 40 CFR 257.95(g)(3)(ii), Geosyntec Consultants, Inc. (Geosyntec) has prepared this Alternative Source Demonstration (ASD) report to document that the SSLs identified for cobalt and lithium should not be attributed to the EBAP.

1.2 <u>Demonstration of Alternative Sources</u>

An evaluation was completed to assess possible alternative sources to which the identified SSL could be attributed. Alternative sources were identified amongst five types, based on methodology provided by EPRI (2017):

- ASD Type I: Sampling Causes;
- ASD Type II: Laboratory Causes;
- ASD Type III: Statistical Evaluation Causes;
- ASD Type IV: Natural Variation; and
- ASD Type V: Alternative Sources.

A demonstration was conducted to show that the SSLs identified for cobalt and lithium were based on a Type IV cause and not by a release from the Pirkey EBAP.

SECTION 2

ALTERNATIVE SOURCE DEMONSTRATION

The Federal CCR Rule allows the owner or operator 90 days from the determination of an SSL to demonstrate that a source other than the CCR unit caused the SSL. The methodology used to evaluate the SSLs identified for cobalt and lithium and the proposed alternative source are described below.

2.1 **Proposed Alternative Sources**

Initial review of site geochemistry, site historical data, and laboratory quality assurance/quality control (QA/QC) data did not identify alternative sources due to Type I (sampling), Type II (laboratory), or Type III (statistical evaluation) issues. As described below, the SSLs for cobalt and lithium have been attributed to natural variation associated with the underlying geology, which is a Type IV issue.

2.1.1 Cobalt

In a previous ASD for cobalt at the EBAP, evidence was provided to show that the observed cobalt concentrations were due to natural variation (Geosyntec, 2019b). The previous ASD discussed that the EBAP itself did not appear to be a source for cobalt in downgradient groundwater, based on observed concentrations of cobalt both in the ash material and in leachate from Synthetic Precipitation Leaching Procedure (SPLP) analysis (SW-864 Test Method 1312, [USEPA, 1994]) of the ash material. Cobalt was not detected in the SPLP leachate above the reporting limit of 0.01 mg/L. Because cobalt mobility is affected by pH, the SPLP test results are likely even more conservative than actual pond conditions. SPLP is run at a pH of 5 SU, whereas the operational pH of the pond varies between approximately 5.8 and 7.0 SU. Cobalt mobility increases under more acidic conditions, although even at a pH of approximately 5, only 2% of cobalt in fly ash is mobile (Izquierdo and Ouerol, 2012).

Cobalt was detected at an estimated concentration of 0.0024 mg/L in a grab sample of the pond water. However, the reported concentration of cobalt in the pond water sample is significantly lower than the average concentration of cobalt observed at all three wells where SSLs were identified (Table 1). Since the previous ASD was prepared, there have been no notable changes in coal handling or sourcing at the plant that would have affected the composition of the ash or pond water.

Since completion of the prior ASD, four additional permanent wells (B-2, B-3, AD-40, and AD-41) have been installed upgradient of the EBAP. The most recent data available for select wells in the vicinity of the EBAP, including the new upgradient locations, are shown in Figure 2. Groundwater cobalt concentrations at upgradient locations vary from 0.0008 mg/L to 0.0345 mg/L at AD-40 and B-3, respectively. This wide range in cobalt concentrations provides further

evidence for the natural variation of cobalt at the Site, particularly as the concentrations at B-3 exceed both the GWPS for the EBAP and the LCLs calculated for cobalt at the wells of interest.

As noted in the prior ASD, soil samples collected across the site, including from locations near the EBAP, identified cobalt in the aquifer solids at varying concentrations. Since completion of the prior ASD, additional soil samples have been collected from locations upgradient of the EBAP. Select soil sample data from the previous ASD and recently collected data are summarized in Table 2. Cobalt was identified in the aquifer solids at varying concentrations, with the highest value of 23.5 milligrams per kilogram (mg/kg) reported at AD-41, which is upgradient of the EBAP (Figure 3). Other testing included collection of aquifer solids to evaluate for the presence of cobalt-containing minerals. X-ray diffraction evidence identified pyrite and marcasite (both iron sulfides) at select locations at concentrations up to 3% by weight (Table 2). Cobalt is known to substitute for iron in crystalline iron minerals such as pyrite and marcasite due to their similar ionic radii (Krupka and Serne, 2002; Hitzman et al., 2019).

Groundwater samples were collected from upgradient location B-3 via vertical aquifer profiling (VAP), as described in an ASD previously generated for lithium exceedances at the EBAP (Geosyntec, 2019c). The VAP groundwater samples were centrifuged to separate solid and liquid phases, and the solid material was submitted for analysis of total metals and mineralogy by X-ray diffraction (XRD). The samples were also submitted for analysis of chemical composition and mineralogy by scanning electron microscopy (SEM) using an energy dispersive spectroscopic analyzer (EDS). Following installation of permanent monitoring wells at B-2 and B-3, groundwater samples were collected by purging groundwater through the filter pack using a submersible pump. An additional groundwater sample was collected at AD-32. These permanent well groundwater samples were filtered through a 1.5-micron filter and the solid material retained on the filter was submitted for analysis of total metals and by SEM/EDS.

Based on total metals analysis, cobalt was identified both in the centrifuged solid material collected from upgradient location B-3 [VAP-B3-(40-45)] and in the material retained on the filter after processing groundwater from B-2 and B-3 (Table 2). Cobalt was detected in the AD-32 solid material at 5.4 mg/kg, which is comparable to the concentration observed in bulk soil collected at the same location at the screened interval (9.1 mg/kg). These results provide further evidence that cobalt concentrations reported during groundwater sampling are naturally occurring and associated with the solid phase in the aquifer.

According to XRD results of the centrifuged solid sample [VAP-B3-(40-45)], pyrite was present as approximately 3% of the solid phase, with hematite (an iron(III) oxide) present at 2% (Table 3). Logging completed while the VAP boring was advanced identified lignite at several intervals, including 45 and 48 ft bgs (Figure 4). Furthermore, SEM/EDS of both centrifuged solid samples [VAP-B3-(40-45) and VAP-B3-(50-55)] identified pyrite in backscattered electron micrographs by the distinctive framboid pattern (Harris, 1981; Sawlowicz, 2000). Major peaks involving iron and sulfur were identified in the EDS spectrum, which further support the identification of pyrite (Attachment A). While cobalt was not identified in the EDS spectrum, it would likely be present

at concentrations below the detection limit. Pyrite was also identified during SEM/EDS analysis of lignite which is mined immediately adjacent to the site.

The wide distribution of pyrite across the site provides evidence that naturally occurring cobalt, which may substitute for iron in pyrite, may also be present in the aquifer solids near the EBAP. The presence of lignite in the area is well-documented, including at upgradient and downgradient locations relative to the EBAP (Broom and Myers, 1966; ETTL, 2010). Additionally, the pond was not identified as the source of cobalt at wells downgradient of the EBAP in the previous ASD based on the documented low mobility of cobalt under the pond conditions and lack of detectable cobalt in the pond itself.

2.1.2 Lithium

An ASD was previously generated for lithium exceedances at the EBAP which attributed the observed concentrations to natural variation in the aquifer, and more specifically to variations in naturally suspended matter that likely originates from lignite and is ubiquitous in the aquifer (Geosyntec, 2019c). New data gathered since completion of the prior ASD provides additional evidence that the observed lithium concentrations at AD-31 and AD-32 are due to natural variation in the aquifer.

Groundwater samples were collected in August 2019 at B-2, B-3, and AD-32 using low-flow sampling techniques. Total lithium concentrations in permanent upgradient wells B-2 and B-3 were measured at 0.055 mg/l and 0.090 mg/l, respectively, both of which are above the GWPS of 0.052 mg/L (Figure 5). Lithium was detected at AD-32 at 0.103 mg/L, which is comparable to the observed concentration at B-3. Because B-2 and B-3 were installed at upgradient locations Site activities, they suggest that lithium concentrations above the GWPS are naturally present in the vicinity of the EBAP.

The previous ASD generated for lithium at the EBAP developed a proposed mechanism for lithium mobility in groundwater which pointed to desorption from clay minerals associated with naturally occurring lignite material as the source of lithium in both up and downgradient wells at the EBAP (Geosyntec, 2019c).

As described in Section 2.1.1, groundwater samples were collected from B-2, B-3, and AD-32 and filtered to separate captured solid material. Both the solid material and the filtered groundwater were submitted for total metals analysis. Lithium was detected in the solid material at concentrations comparable to bulk soil at all locations, providing evidence that the particulates captured during groundwater sampling contain lithium (Table 4).

The total metal concentrations in the solid materials separated from the groundwater samples during filtration and the filtered groundwater concentrations were used to calculated partition coefficients values (K_d) for lithium, potassium, and sodium. These constituents were selected as they are all monovalent cations, and so have similar geochemical behavior. Partition coefficients are used to express the tendency of a chemical (e.g. lithium) to become adsorbed onto soil (or

sediment). K_d is a ratio of the amount of chemical adsorbed per unit weight of the soil to the concentration of the chemical in solution (i.e., groundwater), as shown in the following equation:

$$K_d = \frac{mg \ adsorbed/kg \ soil}{mg/L \ solution}$$

 K_d is characteristic of the soil, so its value varies with soil type. While K_d values were previously calculated using results from the VAP samples, the K_d values presented in this ASD are more likely to represent turbid groundwater which would be captured during regular sampling events, as they were calculated using material collected from permanent wells with conventional filter packs.

K_d values for groundwater and particulate collected from wells B-2, B-3, and AD-32 are comparable to literature K_d values reported for organic-rich media such as bogs and peat beds (Table 5) (Sheppard et al., 2009; 2011). These calculations provide further evidence that lithium mobility in Site groundwater is similar to other sites with organic-rich soils. Additionally, the calculated K_d values for Pirkey soils are consistent with the literature, with potassium being the largest (most sorbable) and sodium the smallest (least sorbable). Furthermore, the values are similar for groundwater from all three wells, suggesting a universal mechanism is controlling the mobilities of lithium, sodium, and potassium in groundwater.

Previously completed XRD analysis of the centrifuged solid material samples [VAP-B3-(40-45) and VAP-B3-50-55] found that clay minerals made up at least 60% of the aquifer solid (Table 3). Clay minerals include kaolinite, smectite, and illite/mica. SEM/EDS analysis identified the presence of silicon, aluminum and oxygen, all of which are indicative of clay minerals (Attachment A). The backscattered electron micrographs of these samples also identified clay particles by morphology. The largest clay particles (> 5 μm) are likely kaolinite, while smectite and illite dominate the smaller size fraction. These results are comparable to preliminary investigation of the VAP material completed by SEM/EDS described in the previous ASD, all of which presented evidence for clay fractions (Geosyntec, 2019c).

These multiple lines of evidence show that elevated lithium concentrations at AD-31 and AD-32 are not due to a release from the EBAP, and instead can be attributed to natural variation. This variation appears related to the distribution of clay fractions associated with lignite materials in the soil aquifer material.

2.2 **Sampling Requirements**

As the ASD presented above supports the position that the identified SSLs are not due to a release from the Pirkey EBAP, the unit will remain in the assessment monitoring program. Groundwater at the unit will continue to be sampled for Appendix IV parameters on a semi-annual basis.

SECTION 3

CONCLUSIONS AND RECOMMENDATIONS

The preceding information serves as the ASD prepared in accordance with 40 CFR 257.95(g)(3)(ii) and provides evidence that the SSLs for cobalt at AD-2, AD-31, and AD-32 and for lithium at AD-31 and AD-32 identified during assessment monitoring in February 2019 were not due to a release from the EBAP. The identified SSLs were, instead, attributed to natural variation in the underlying geology. Therefore, no further action for cobalt or lithium is warranted, and the EBAP will remain in the assessment monitoring program. Certification of this ASD by a qualified professional engineer is provided in Attachment B.

SECTION 4

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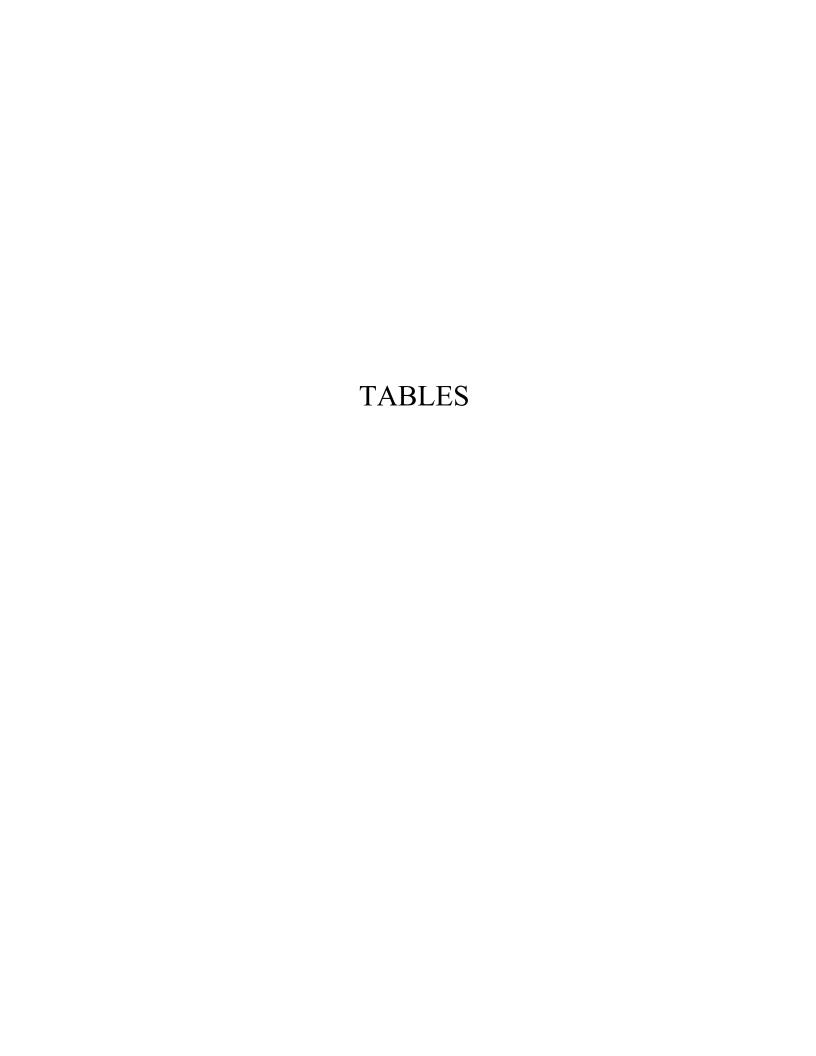


Table 1: Summary of Key Cobalt Analytical Data East Bottom Ash Pond - H.W. Pirkey Plant

Sample	Unit	Cobalt Concentration
Bottom Ash (Solid Material)	mg/kg	6.1
SPLP Leachate of Bottom Ash	mg/L	<0.01
EBAP Pond Water	mg/L	0.0024 J
AD-2 - Average	mg/L	0.0111
AD-31 - Average	mg/L	0.0107
AD-32 - Average	mg/L	0.0504

Notes:

mg/kg - milligram per kilogram

mg/L - milligram per liter

J - Estimated value. Result is less than the reporting limit but greater than or equal to the method detection limit.

Average values were calculated using all cobalt data collected under 40 CFR 257 Subpart D, excluding any identified outliers.

Table 2: Soil Cobalt and Mineralogy Data East Bottom Ash Pond - H.W. Pirkey Plant

Location ID	Sample Depth (ft bgs)	Cobalt (mg/kg)	Pyrite/Marcasite (%)	
		Soil Samples	, ,	
AD-17	7	3.10	2	
AD-17	15	1.50	0	
AD-18	8	3.60	1	
AD-10	22	2.90	0	
AD-30	7	1.00	3	
AD-30	23	15.0	1	
AD-31	12	1.90	2	
AD-31	26	0.83	0	
AD-32	11	1.70		
AD-32	20-25	9.10		
	15	< 1.0		
AD-41	35	23.5		
	95	1.90		
	10	2.36		
	16	3.62		
B-2	71	10.30		
	82	7.21		
	87	3.11		
	10	1.30		
B-3	20	0.59		
	97	1.11		
Solid Material Retained After Filtration				
AD-32	13-33	5.4		
B-2	38-48	4.3		
B-3	29-34	12.0		
D-3	VAP 40-45	18.0	3	

Notes:

'--' - analysis not completed

mg/kg- milligram per kilogram

ft bgs - feet below ground surface

For AD-XX locations, samples were collected from additional boreholes advanced in the immediate area of the location identified by the well ID. Samples were not collected from the cuttings of the borings advanced for well installation. Samples for B-X locations were collected from cores removed from the borehole during well lithology logging.

Depths for samples collected after filtration represent the screened interval for the permanent well where the sample was collected.

Table 3: X-Ray Diffraction Results East Bottom Ash Pond - H. W. Pirkey Plant

Constituent	VAP-B3-(40-45)
Quartz	15
Plagioclase Feldspar	0.5
Orthoclase	ND
Calcite	ND
Dolomite	ND
Siderite	0.5
Goethite	ND
Hematite	2
Pyrite	3
Kaolinte	42
Chlorite	4
Illite/Mica	6
Smectite	12
Amorphous	15

Notes:

ND: Not detected

VAP-B3-(40-45) is the centrifuged solid material from the groundwater sample collected at that interval.

Table 4: Soil Lithium Data East Bottom Ash Pond - H.W. Pirkey Plant

Location ID	Sample Depth (ft bgs)	Lithium (mg/kg)		
	Bulk Soil Samples			
AD-32	11	0.53		
AD-32	20-25	1.60		
	10	5.30		
B-2	16	3.97		
D-2	71	7.42		
	87	13.10		
	10	3.64		
B-3	20	2.59		
	97	11.10		
Lignite	N/A	2.9 Ј		
Solid Material Retained After Filtration				
AD-32	13-33	9.8 J		
B-2	38-48	6.5 J		
B-3	29-34	7.8 J		
D-3	VAP 40-45	13.0		

Notes:

J - estimated value

mg/kg- milligram per kilogram

ft bgs - feet below ground surface

For AD-32, samples were collected from additional boreholes advanced in the immediate area of the location identified by the well ID. Samples were not collected from the cuttings of the borings advanced for well installation. Samples for B-X locations were collected from cores removed from the borehole during well lithology logging.

Depths for samples collected after filtration represent the screened interval for the permanent well where the sample was collected.

VAP - vertical aquifer profiling

Table 5: Calculated Site-Specific Partition Coefficients East Bottom Ash Pond - H. W. Pirkey Plant

Source		B-2		Literature Value
Unit	mg/L	mg/kg	L/kg	L/kg
Element	Aqueous Phase	Adsorbed	Kd	Kd
Li	0.081	6.5	80	43-370
K	2.6	1100	423	42-1200
Na	14	130	9	5.2-82

Source		B-3		Literature Value
Unit	mg/L	mg/kg	L/kg	L/kg
Element	Aqueous Phase	Adsorbed	Kd	Kd
Li	0.097	7.8	80	43-370
K	2.9	1100	379	42-1200
Na	32	240	8	5.2-82

Source		AD-32		Literature Value
Unit	mg/L	mg/kg	L/kg	L/kg
Element	Aqueous Phase	Adsorbed	Kd	Kd
Li	0.11	9.8	89	43-370
K	3.9	1800	462	42-1200
Na	57	220	4	5.2-82

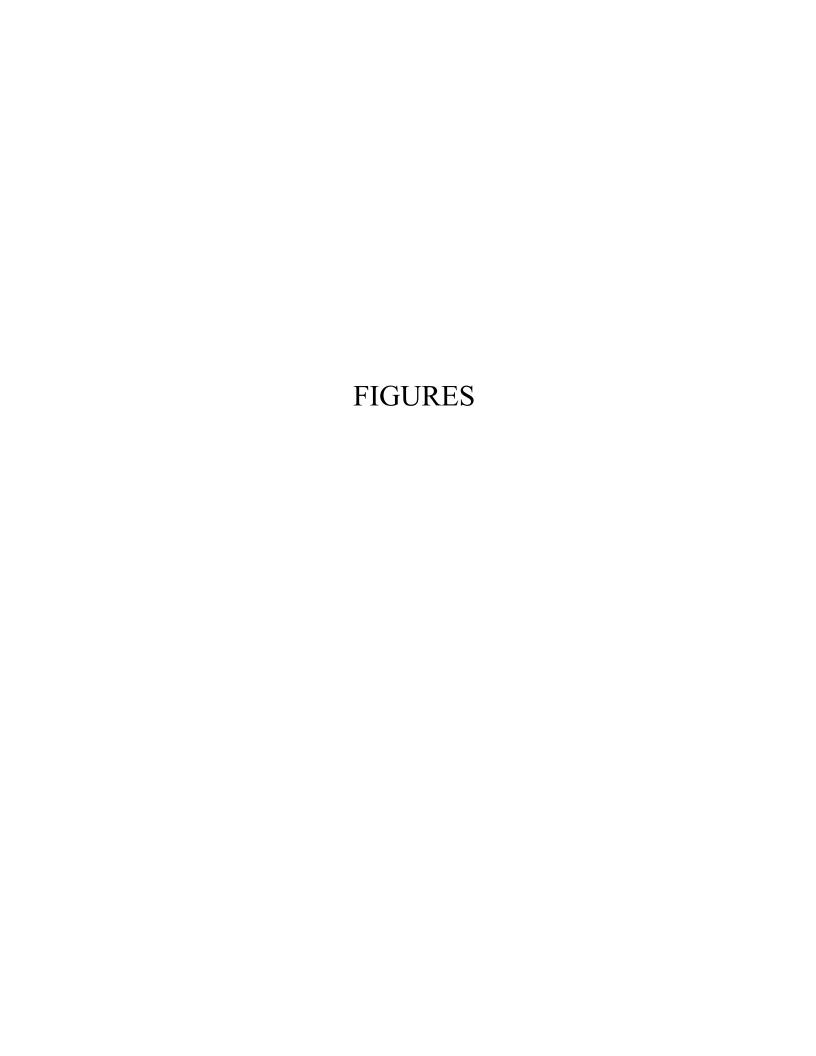
Notes:

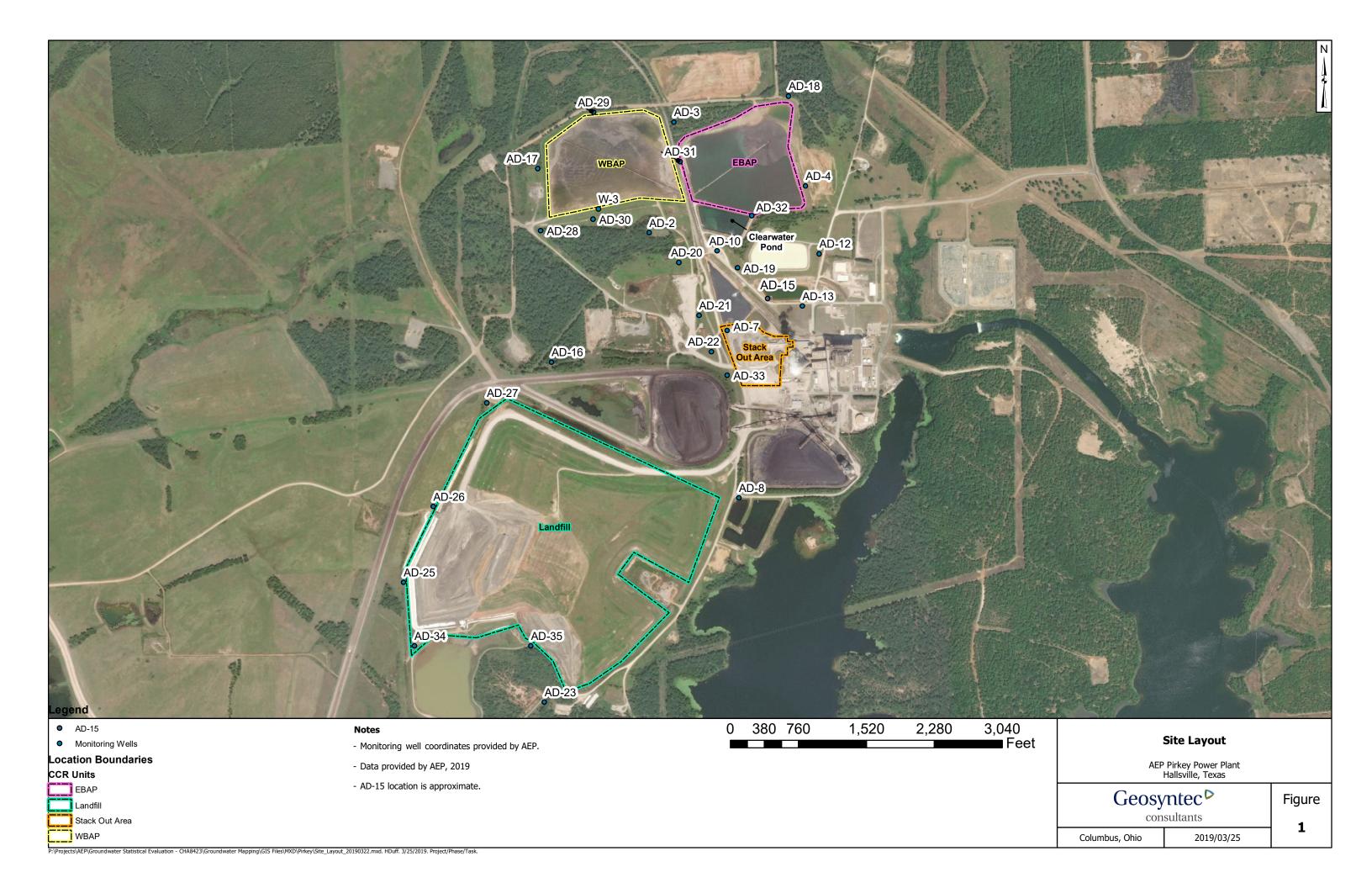
mg/L: milligrams per liter mg/kg: milligrams per kilogram

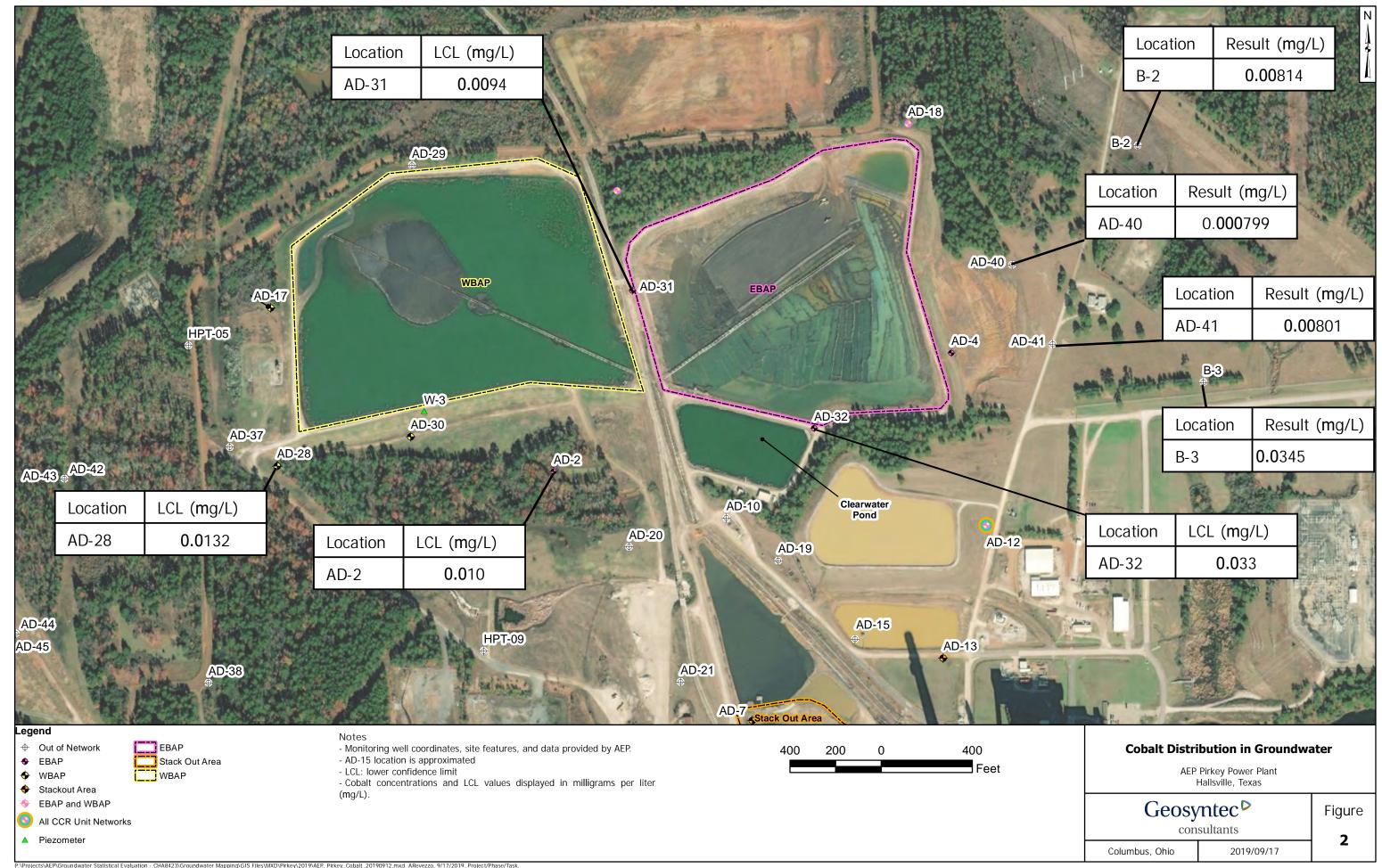
L/kg: liters per kilogram Kd: partition coefficient

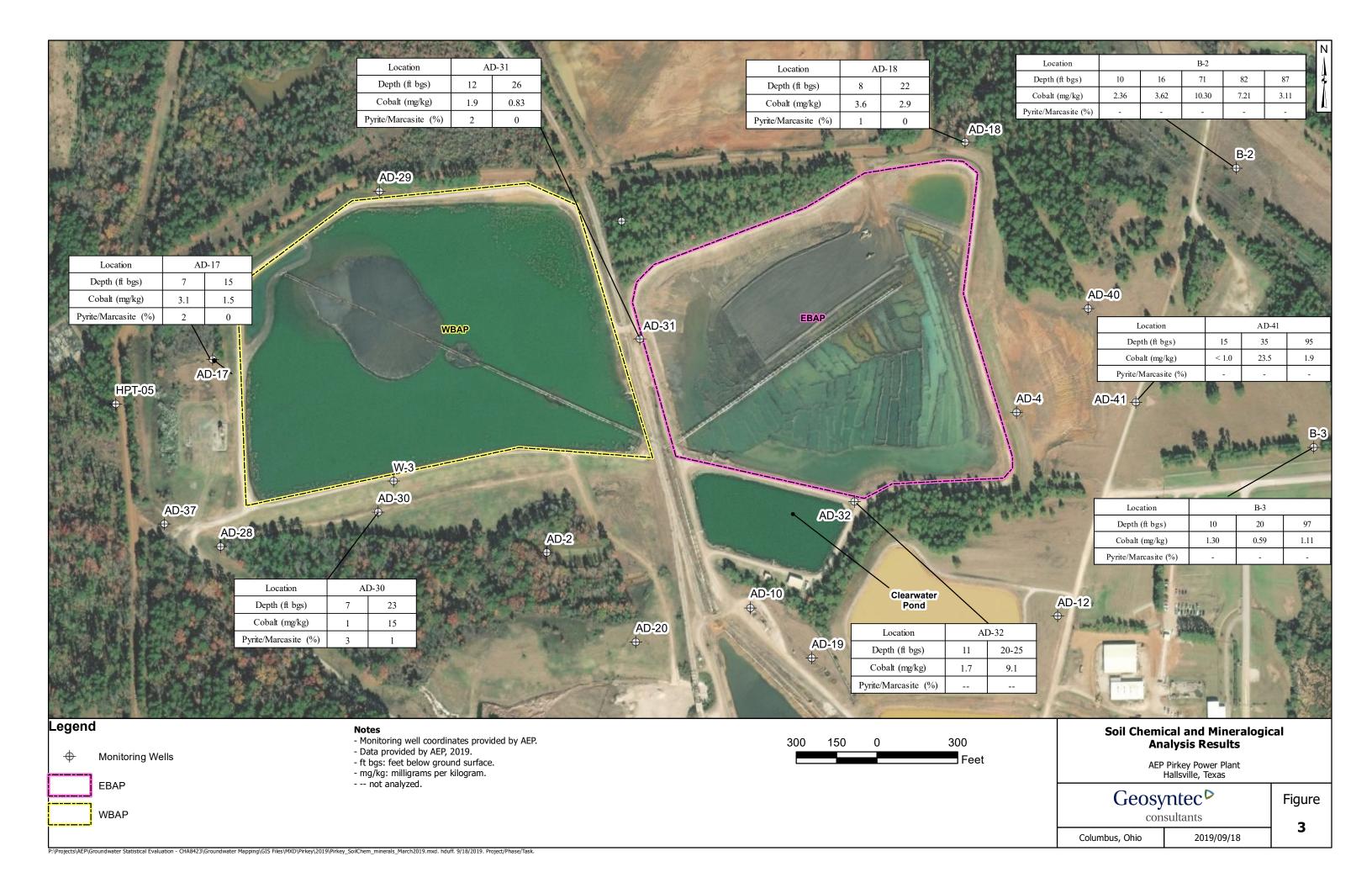
Adsorbed values are total metals concentrations reported by USEPA Method 6010B.

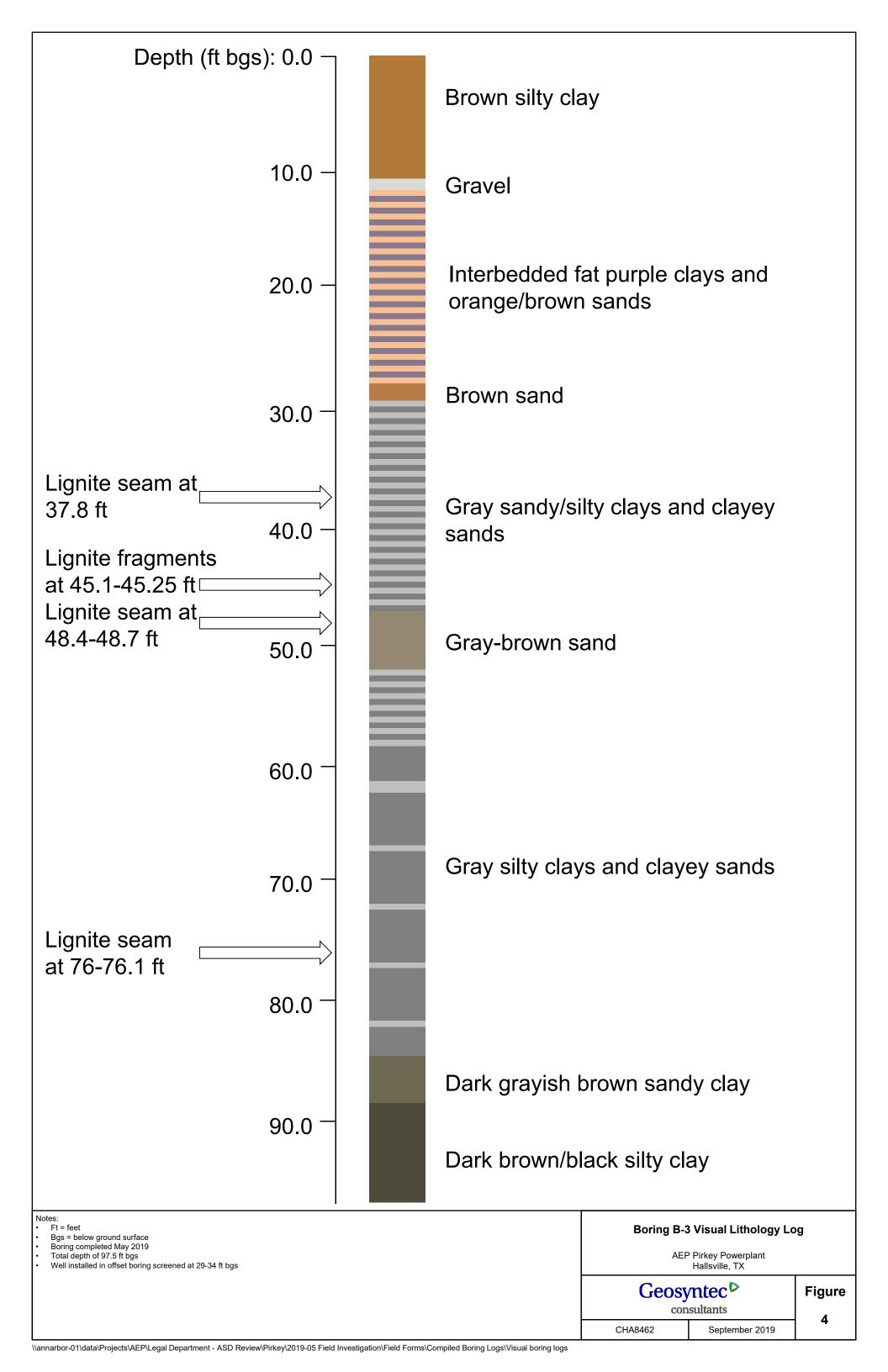
Literature values represent maximum and minimum values for the parameter as reported in Sheppard et al, 2009 (Table 4-1, all sites) and Sheppard et al, 2011 (Table 3-3 cultivated peat and wetland peat only).

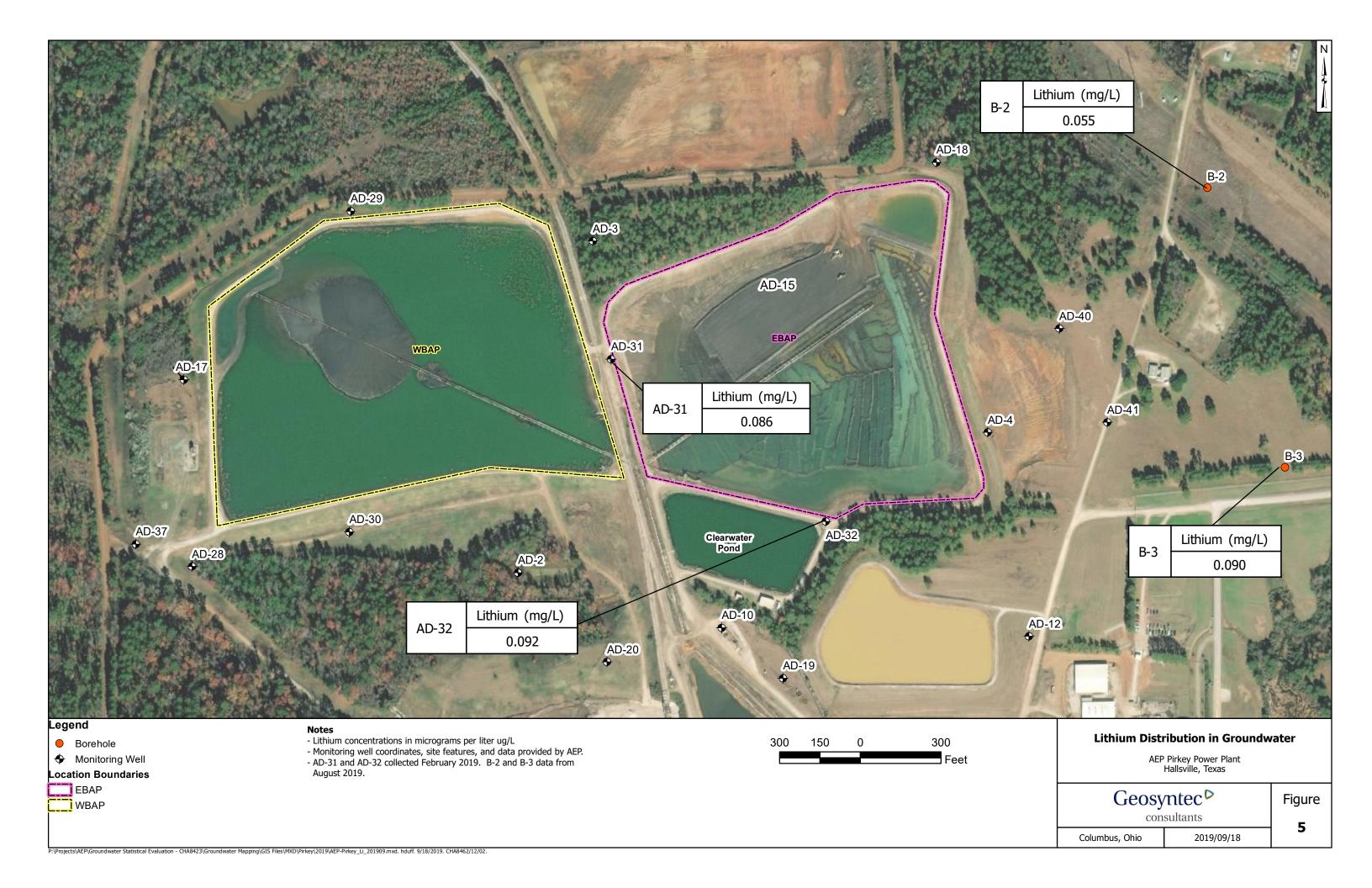




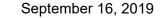








ATTACHMENT A SEM/EDS Analysis



via Email: BSass@geosyntec.com

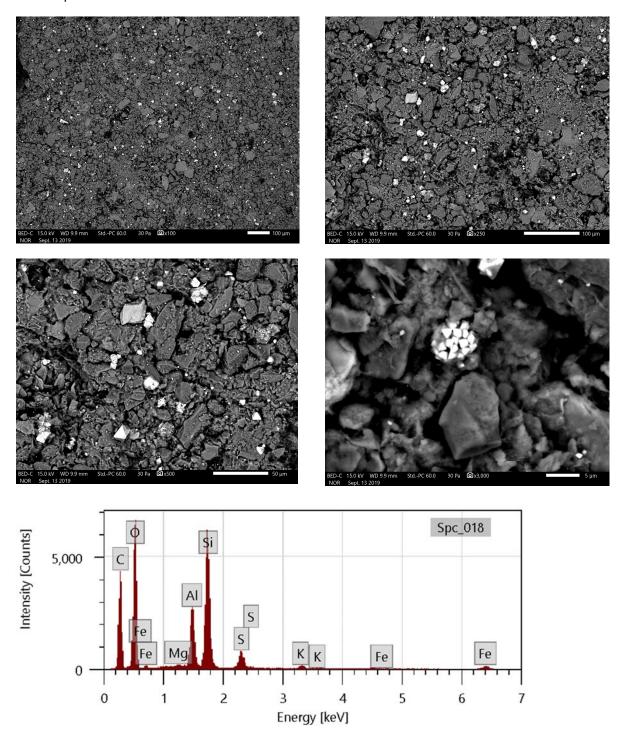


Dr. Bruce Sass 941 Chatham Lane, Suite 103, Columbus, OH 43221

Spc_004 Intensity [Counts] 1,500 Αl 1,000 500 Fe

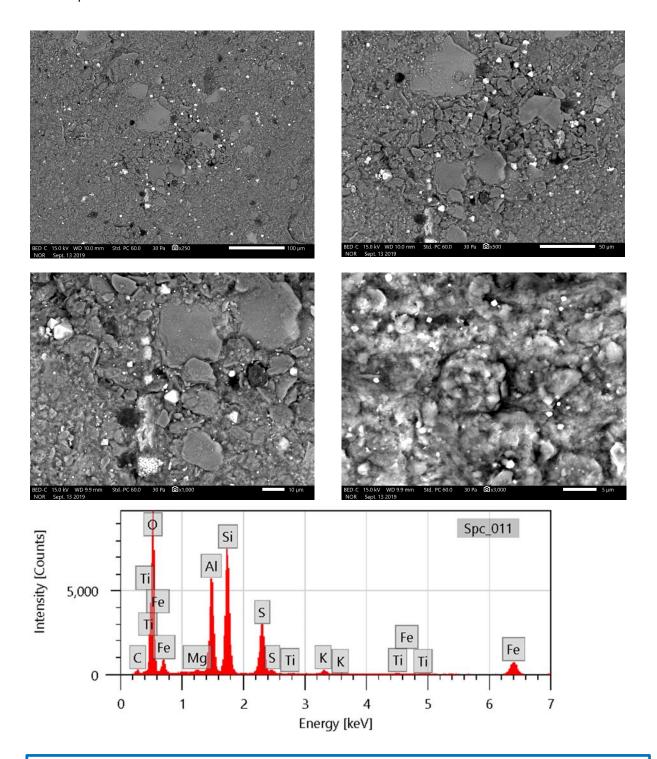
Lignite. Backscattered electron micrographs show the sample at 100X, 1,100X, and 1,500X. EDS spectrum at bottom is an area scan of the region shown in top right micrograph. Bright particles are mostly quartz and feldspar. Major peaks for carbon, oxygen, silicon, and aluminum suggest coal and clay.

Energy [keV]



Sample VAP B3 40-45. Backscattered electron micrographs show the sample at 100X, 250X, 500X, and 3000X. EDS spectrum at bottom is an area scan of the region shown at 500X. Bright particles are pyrite (framboid in bottom right micrograph). Major peaks for carbon, oxygen, silicon, and aluminum suggest coal and clay.





Sample VAP B3 50-55. Backscattered electron micrographs show the sample at 250X, 500X, 1000X, and 3000X. EDS spectrum at bottom is an area scan of the region shown at 3000X. Bright particles are mostly pyrite (framboid in bottom left micrograph); occasional particles of Fe-Ti oxide are detected. Major peaks for oxygen, silicon, and aluminum suggest clay. Large blocky particles are mostly quartz, feldspar, and clay.



ATTACHMENT B Certification by Qualified Professional Engineer

CERTIFICATION BY A QUALIFIED PROFESSIONAL ENGINEER

I certify that the selected and above described alternative source demonstration is appropriate for evaluating the groundwater monitoring data for the Pirkey East Bottom Ash Pond CCR management area and that the requirements of 40 CFR 257.95(g)(3)(ii) have been met.

Beth Ann Gross Printed Name of	Licensed Professional Engineer	BETH ANN GROSS
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Date

Licensing State

License Number