

REPORT ON
GROUNDWATER FLOW MODELING
ADDENDUM TO CORRECTIVE MEASURES ASSESSMENT
A.B. BROWN GENERATING STATION
ASH POND
MOUNT VERNON, INDIANA

by Haley & Aldrich, Inc. Cleveland, Ohio

for Southern Indiana Gas and Electric Company Evansville, Indiana

File No. 129420-021 September 2019 Issued as CMA Addendum November 24, 2020

Table of Contents

			Page
	of Table		ii ii
1.		Indwater Flow Modeling	1
	1.1	MODEL DOMAIN	1
	1.2	BOUNDARY CONDITIONS	2
		1.2.1 Specified Head Boundaries	2
		1.2.2 Recharge Boundaries	2
	1.3	HYDRAULIC MODEL PROPERTIES	3
		1.3.1 Calibrated Horizontal and Vertical Hydraulic Conductivity	3
		1.3.2 Porosity, Storage, and Yield	3
	1.4	METHODS OF EVALUATING MODEL CALIBRATION QUALITY	3
2.	Fate	and Transport Modeling	6
	2.1	TRANSPORT MODELING APPROACH	6
	2.2	KEY PARAMETERS FOR TRANSPORT MODELING	6
		2.2.1 Effective Porosity	7
		2.2.2 Dispersivity	7
		2.2.3 First-Order Degradation Rate Constant – Lambda (λ)	7
		2.2.4 Retardation Effects	7
		2.2.6 Source Initial Concentration Data	9
	2.3	TRANSPORT MODEL RESULTS - MOLYBDENUM	
Ref	erences		11

Tables Figures



List of Tables

Table No.	Title
I	June 2019 Groundwater Elevations

List of Figures

Figure No.	Title
1	Site Plan with Model Domain
2	Site Plan with Model Grid
3	Model Layers 1 through 4 with Hydraulic Conductivities and Layer Thicknesses
4	Site Plan with Constant Head Boundary Conditions Layers 2 Through 4
5	Calibration Scatter Plot (in text)
6	Initial Molybdenum Concentration
7	Molybdenum Eh-Ph Diagram (in text)
8	Modeled Molybdenum Concentrations for CMA Options Over Time



1. Groundwater Flow Modeling

A groundwater flow and solute transport model was constructed to evaluate and compare potential corrective measures in support of the Corrective Measures Assessment (CMA) for the A.B. Brown Generating Facility (Site) near Mount Vernon, Indianapolis. The Appendix IV constituents above the Groundwater Protection Standard (GWPS) at the Site include lithium and molybdenum. Molybdenum was chosen for the solute transport portion of the model since it was the most conservative constituent which would require the most amount of time to attenuate for each remedial option. The following text describes the model construction, calibration and subsequent simulations of remedy alternatives for Appendix IV constituents above the GWPS.

The numerical model MODFLOW-2005 (Harbaugh, 2005) was selected for the modeling effort and is a three-dimensional, finite difference groundwater flow model capable of simulating the groundwater conditions under various scenarios including pumping and changes to infiltration over time. Models were built using available information and for the purpose of aiding decision making in the CMA process. The level of accuracy is directly dependent on the data available to construct the model and should not be construed by the user as a definitive predictor of the future. Instead the CMA alternatives model simulations should be viewed relative to one another to enable the user to determine (when appropriate) favorable, less favorable and least favorable CMA alternatives.

1.1 MODEL DOMAIN

The model domain was established to encompass the Site and surrounding areas that represented model boundaries including the nearby Ohio River located south of the ash pond and landfill.

MODFLOW uses a rectangular grid within the domain and allows for establishing irregular groundwater flow boundary conditions that represent actual and Site-specific features in the study area. The setup is facilitated by assigning boundary types and values to specific grid cells. **Figure 1** depicts the model domain boundary overlain on an aerial photograph of the Site.

Figure 2 depicts the model domain with the grid spacing selected for the model. The three-dimensional finite difference groundwater flow model domain covers a length of 13,000 feet (ft) in the x-direction (west to east), 13,000 ft in the y-direction (north to south), and approximately 45 ft in the z-direction (vertical). The model consists of 474 rows, 384 columns, and 4 layers for a total of 728,064 cells covering an approximate area of 3306 acres. In MODFLOW, the groundwater-flow system is subdivided laterally and vertically into rectilinear blocks called cells. The hydraulic properties of the material in each cell are assigned and assumed to be uniform within each cell. The row and column dimension of each cell is variable based on proximity to the Site. This variability was created to allow for finer resolution within the vicinity of the primary flow pathway for the Site.

A Digital Elevation Model was obtained from the United States Geological Survey website to create the surface of the model for the Site. Lithologic descriptions contained in the boring logs generated during various phases of geo-environmental investigations as well as cross-sections were used to develop formation geometry and hydraulic properties. The Site was divided into two vertical lithologic units to represent geologic conditions underlying the Site and to account for vertical heterogeneities within the model. A summary of each geologic unit is as follows:



- Unconsolidated alluvial deposits which consist primarily of silty clay containing discontinuous layers of sand (Haley & Aldrich, Inc., 2017).
- Weathered sandstone, shale, or siltstone.

Elevations used in the model were determined from digital elevation models for the area. The topography of the ground surface is mimicked in the subsequent lower layers; however, the elevation has been reduced by the layer thickness. Layer thicknesses were determined through the review of the above-mentioned Site geology.

Figure 3 depicts the two-dimensional views of the model layer elevations. The surfaces shown in **Figure 3** represent the model top (i.e., land surface), the flat model bottom, and all the lithologic interfaces between.

1.2 BOUNDARY CONDITIONS

Boundary conditions define the locations and manner in which water enters and exits the active model domain. The conceptual model for the groundwater system that forms the basis for the model boundaries are as follows:

- 1. A specified head boundary condition is used to control groundwater flow across the western side of the model.
- 2. Recharge at the Site creates radial flow away from the Site toward lower elevations to the west,
- 3. There is a topographic divide at approximately 470 ft along the eastern boundary.

The specified boundaries of the model coincide with predicted natural hydrologic boundaries. To recreate observed groundwater a specified head boundary was used. The location of this boundary condition in the model is illustrated in **Figure 4**.

1.2.1 Specified Head Boundaries

The MODFLOW Time Variant Specified Head Package (Harbaugh, 2005) also known as the Constant Head Package, was used to simulate boundaries presented in **Figure 4**. The package is used to fix the head values in selected grid cells regardless of the conditions in the surrounding grid cells. The cell with the assigned constant head acts either as a source of water entering or a sink of water leaving the system. The value for this boundary is referenced to datum NAVD 88 and is set to 371.0 ft to the north and decreases to 355.07 ft to the south and is active in Layer 2 through Layer 4. These values were estimated based on topography, the depths to water in wells at the Site, the pattern of groundwater flow, elevations of nearby water bodies, and through calibration of the groundwater flow model as described in **Section 1.3** below.

1.2.2 Recharge Boundaries

The magnitude of recharge varies between 4.7×10^{-5} ft per day (ft/day) and 2.6×10^{-3} ft/day. The lowend value represents model area surrounding the site and the high-end value represents conditions for the pond area.



1.3 HYDRAULIC MODEL PROPERTIES

Hydraulic properties were initially assigned consistent with observations presented in the 2017 Groundwater Monitoring Program (Haley & Aldrich, Inc., 2017). Values were assigned for horizontal hydraulic conductivity and vertical hydraulic conductivity. These parameters were iteratively varied during model calibration to achieve the best fit to observed hydraulic patterns including head elevations, hydraulic gradients, and flow directions.

For calibration, uniform hydraulic properties were applied within discrete model layers. Results of the initial calibration indicated that hydraulic conductivities in the range of those values associated with material described in boring logs were representative with regard to groundwater flow observed at the Site. The hydraulic conductivity values used in the model are presented below for the five hydrogeologic units underlying at the Site:

- Silty sand 30 ft/day or 1.1 x 10-2 centimeters per second (cm/s)
- Silty clay 4.1 ft/day or 1.4 x 10-3 cm/s
- Weathered sandstone, shale, or siltstone 0.5 ft/day or 1.8 x 10-4 cm/s

1.3.1 Calibrated Horizontal and Vertical Hydraulic Conductivity

The calibrated horizontal (K_X and K_Y) and vertical (K_Z) hydraulic conductivity values in Model Layer 1 through Layer 4 were distributed uniformly across the model domain. Vertical hydraulic conductivity values were estimated at $1/10^{th}$ of the horizontal hydraulic conductivity values. This ratio between horizontal and vertical conductivities was selected to represent resultant hydraulic conductivity when stratification typical of alluvial sediments is evident.

1.3.2 Porosity, Storage, and Yield

Effective porosity values are needed for particle tracking and solute transport simulations. The effective porosity values were conservatively estimated based on the soil type through the examination of boring logs. For areas that are generally silty clay, a porosity of 0.35, specific storage of 0.33 ft⁻¹ and specific yield of 0.02 were utilized.

1.4 METHODS OF EVALUATING MODEL CALIBRATION QUALITY

Model calibration is the process of refining the model representation of the hydrogeologic framework, hydraulic properties, and boundary conditions to minimize the difference between the simulated heads and fluxes to the measured data. Construction of a complex model with more parameters than the data support may reduce the residuals (difference between measured and simulated values) but does not ensure a more accurate model. Therefore, calibrated model parameters also need to be checked for their validity. Throughout the calibration process, no adjustments were made that conflicted with the general understanding of the groundwater system and previously documented information.

The iterative calibration process of "trial and error" was used for model calibration. It involves making changes to the input values, running MODFLOW, and assessing the impact of the changes. Beside the trial and error approach, a model independent parameter optimization software tool – PEST was used to adjust selected input values to further improve model calibration (Doherty, 2016).



The quality of model fit can be assessed from many statistical and graphical methods. One method is based on the difference between simulated and observed heads and flows, or residuals. The overall magnitude of the residuals is considered, but the distribution of those residuals, both statistically and spatially, can be equally important. The magnitude of residuals can initially point to gross errors in the model, the data (measured quantity), or how the measured quantity is simulated (Hill, 2000). A useful graphical analysis is a simple scatter plot of all simulated values as a function of all observed values.

For the flow calibration, the statistics of the mean error (ME), mean absolute error (MAE), and the root mean square (RMS) error were used to assess the calibration quality. They are defined as follows:

$$ME = \frac{\sum_{i=1}^{n} (O_i - C_i)}{n}$$

$$MAE = \frac{\sum_{i=1}^{n} |O_i - C_i|}{n}$$

$$RMS = \frac{\sum_{i=1}^{n} (O_i - C_i)^2}{n}$$

Where:

Oi = Observed head at observation point i

Ci = Calculated head at observation point i

n = Number of observation points

The mean error is the average of the differences between the observed and calculated heads (or residuals) and can indicate the overall comparison between computed and observed data. Negative and positive residuals can cancel each other out, resulting in a mean error close to zero even when the calibration is not good. The sign of the mean error is an indication of the overall comparison of the model to the data (e.g. a positive mean error indicates the model is generally computing heads that are too high).

The mean absolute error is the average of the absolute values of the residuals. The absolute value prevents positive and negative residuals from canceling each other, providing a clearer picture of the magnitude of errors across the model, without an indication of the direction (high or low) of the errors. The RMS error is the square root of the average of the squares of the residuals. The RMS adds additional weight to points where the residual is greatest. If the residuals at all points are very similar, the RMS will be close to the mean absolute error. Alternatively, a few points with high errors can add significantly to the RMS for an otherwise well calibrated model. For all three of these criteria the optimal value is zero.

The numerical goals for the groundwater flow model calibration are to (1) minimize the ME and MAE errors and (2) achieve the ratio of the RMS error of the head residuals to the range of observed heads (i.e., normalized RMS error) to be at least less than 10 percent (%) (Anderson, M.P., Woessner, WW., 1992).

Groundwater flow field calibration for the Site has been conducted to provide a reasonable representation of the groundwater flow field in the vicinity of the Site, which forms the basis of assessing cobalt migration potential through the fate and transport process. To accomplish this objective, a MODFLOW numerical model was developed to simulate observed groundwater conditions



at the Site through calibrating a representative steady-state flow field. The decision of using a steady-state flow field for the flow model calibration was made through an evaluation of the available groundwater elevation data for the Site. Most importantly is that historical flow patterns have been relatively consistent at the Site; therefore, a steady-state flow model was deemed reasonable to represent average flow conditions.

The evaluation of collected groundwater elevation data resulted in the selection of 31 May 2019 as the observed heads for the flow model calibration for representing Site conditions (**Table 1**).

Based on the outcome of this quality of model fit evaluation, it is concluded that the numerical calibration goals have been achieved for the Site. The mean error in head was 5.55 ft or 7.7 percent (%) of the head observation range, 72.15 ft. The absolute residual is +4.33 ft. The RMS error for the calibrated model was +5.59 ft and the normalized RMS error was 6.0 percent (%). Presented below is the scatter plot of the observed versus simulated heads, which generally fall along the theoretical slope of 1 to 1. **Table 1** provides the observed heads on 4 June 2019, as discussed above, used to generate the plot below. The quality of the flow model calibration meets the calibration goals as described herein. Observed versus computed target values is shown in **Figure 5.**

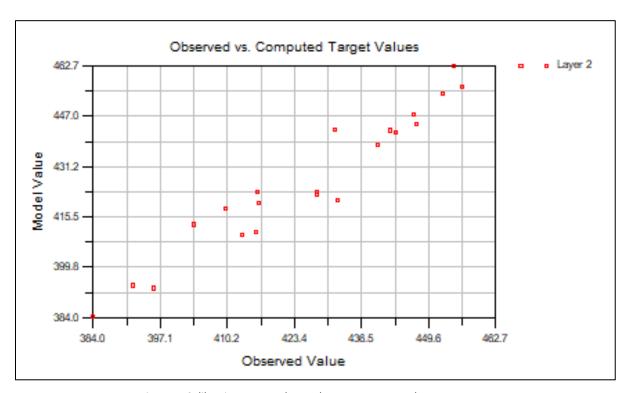


Figure 5: Calibration scatter plot. Values represent steady-state targets.

Furthermore, the calibration assessment has met the acceptable calibration goals, and therefore, the groundwater flow model is considered to be usable for the development of the molybdenum fate and transport models described in **Section 2**.



2. Fate and Transport Modeling

Contaminant fate and transport modeling was conducted utilizing the three-dimensional, numerical model MT3DMS (Version 5 of MT3D) (Zheng, C. and Wang, P.P., 1999). MT3DMS simulates advection, dispersion, adsorption and decay of dissolved constituents in groundwater using a modular structure similar to MODFLOW to permit simulation of transport components independently or jointly. MT3D interfaces directly with MODFLOW for the head solution and supports all the hydrologic and discretization features of MODFLOW. The MT3D code has a comprehensive set of solution options, including the method of characteristics, the modified method of characteristics, a hybrid of these two methods, and the standard finite-difference method. MT3D was originally released in 1990 as a public domain code from the United States Environmental Protection Agency and has been widely used and accepted by federal and state regulatory agencies.

For this modeling effort, the MT3DMS model utilized the flow regime from the steady-state, calibrated Site groundwater flow model presented in **Section 1** to simulate transport of molybdenum. The steady state model was transformed into a transient model so various CMA options could be evaluated with respect to time. The strength and locations of the potential molybdenum sources specified in the transport models were based on surface water concentrations from the Site.

In addition to the MODFLOW groundwater flow field discussed in **Section 1**, the fate and transport models require inputs of effective porosity values, dispersivity coefficients, and adsorption rate constants for molybdenum. In the modeling effort, input parameter values were defined from Site data, whenever possible, or through the use of conservative literature values.

2.1 TRANSPORT MODELING APPROACH

The solute transport portion of the modeling effort focused mainly on the future flow pathway for molybdenum at the Site. As such, the initial concentration including the current plume extent and the estimated leachable mass near the ash pond were utilized in place as a constant source. The location and initial concentrations for molybdenum within the model (layer 4) is presented in **Figure 6**.

The calibrated flow model was allowed to run for 300 years following implementation of the groundwater remedy. Calibration of the concentrations through time was not performed on the predictive model as the starting conditions were the current conditions at the Site and thus represent a conservative estimate of transport through the Site.

2.2 KEY PARAMETERS FOR TRANSPORT MODELING

The following sections describe the key input parameters of the transport model, and how they were derived. Note that these parameters were selected for the purpose of comparative evaluation of relative benefits of various corrective measures. The parameters and conditions used for the modeling are selected based on the data available to date. Therefore, simulated remedial timeframes using the parameters described in this section should not be construed as absolute predictions of remedial time frames for various corrective measures.



2.2.1 Effective Porosity

The effective porosities used in the model were presented in previous Section 1.3.2.

2.2.2 Dispersivity

Dispersion incorporates the effects of fluid mixing that result from heterogeneities within the groundwater system and molecular diffusion, which is the random movement of ions or molecules. If the molecules of water and dissolved constituents traveled at the average seepage velocity, there would be an abrupt interface and dispersion would be negligible. However, in natural systems water molecules and dissolved contaminants do not all travel at the same rate; some travel faster and some slower. Dispersion in the model accounts for the spreading of the dissolved plume. Diffusion is time dependent and is significant at low velocities. In general, dispersion acts to decrease the contaminant concentration on the leading edge of the plume, while increasing the size and rate of transport of the dissolved plume. Longitudinal dispersion occurs in the direction of advective groundwater flow, while transverse dispersion occurs perpendicular to groundwater flow.

The groundwater modeling generally accepted longitudinal dispersity value (α_L) estimate is 1 to 100. The horizontal transverse dispersivity (α_T) can be estimated as approximately one-tenth of the α_L , and vertical transverse (α_v) dispersivity can be estimated as one-hundredth of the α_L . The values utilized for dispersivity values are as follows:

- α_L 100 ft,
- α_T 10 ft, and
- α_V 1 ft

2.2.3 First-Order Degradation Rate Constant – Lambda (λ)

Another input parameter for the fate and transport model is the first order degradation rate constant (λ) for molybdenum. This rate constant only takes into account degradation of the dissolved constituent during transport, as it leaves the source. This rate constant does not factor in effects of advection, sorption or dispersivity (dispersion). The field-scale degradation rate constant usually can be expressed as a first order decay process. Due to the general lack of decay for metals within the groundwater system, a first-order decay rate was not specified for model simulations.

2.2.4 Retardation Effects

Chemical retardation occurs when a solute (contaminant) reacts with the porous media and its rate of movement is retarded relative the advective groundwater velocity. Retardation can occur by a variety of processes including adsorption and mass transfer in porous media. The effects of retardation are often related to site-specific adsorption isotherms. For this modeling purpose, a liner adsorption isotherm is used to account for the effects of transport retardation that may occur for Site-related contaminants. The effects of retardation on contaminant mobility is usually expressed in terms of a retardation factor (R), which is the ratio of the groundwater velocity to contaminant transport velocity (Bedient, P.B., Rifai, H.S. and Newell, C.J., 1994). When a linear adsorption isotherm is used to characterize contaminant mobility, the linear adsorption coefficient (K_d) can be linked to the retardation factor with the mathematical relationship below:



$$R = \frac{v_{gw}}{v_c} = 1 + \frac{\rho_b}{n} \times K_d$$

Where:

R = Retardation factor

 v_{gw} = Groundwater velocity

 v_c = Contaminant transport

 ρ_b = Aquifer solid bulk density

n = Effective transport porosity of the medium

K_d = Linear adsorption coefficient

The following describe the adsorption effects on solute transport based on the geochemical properties and published empirical data, as well as the choice of the linear adsorption coefficient for each contaminant used for transport modeling.

2.2.5 Adsorption of Molybdenum on Aquifer Solids

Molybdenum (atomic number 42) is a transition metal in Group VI of the periodic classification of the elements. The affinity for molybdenum to adsorb to the geologic matrix can be affected by factors such as pH, redox conditions, mineral contents of aquifer solids, organic matter abundance, and the presence of organic ligands in the groundwater system.

The aqueous speciation of molybdenum and potential formation of molybdenum-related minerals under a spectrum of the electro-potential (Eh) and pH conditions are shown below (**Figure 7**). Based on Site groundwater monitoring results, the range of pH is within the neutral pH range (between 6.5 and 7.5) and the range of oxidation-reduction potential is generally near or higher than 100 millivolts. The Site geochemical conditions are likely between microaerobic and iron-reducing conditions and not sulfidegenic; therefore, the main molybdenum species in groundwater is expected to be molybdenum species of a valence state of +6. Due to high concentrations of molybdenum and calcium in Site groundwater at some locations, it is likely that the mineral, powellite (CaMoO₄), may form and precipitate in the aquifer matrix where molybdenum concentrations are high (e.g., > 1 milligrams per liter (mg/L)). This precipitation reaction may reduce molybdenum concentrations in groundwater during its transport.

2.2.5.1 Empirical data on adsorption

The adsorption of molybdenum has been studied on a variety of minerals, sediments, soils, and crushed rock materials. The extent of adsorption is greatly influenced by pH; generally, the degree of adsorption decreases with an increase in pH (Sheppard, S., Long, J., Sanipelli, B. and Sohlenius, G., 2009). Metal oxides (iron, manganese, and aluminum oxides) in aquifer solids are shown to play a major role in molybdenum adsorption; the K_d values reported by Goldberg et al. (1996) for oxide minerals range from 10 to 10^3 liter per kilogram (L/Kg). Adsorption on a weight basis of iron oxide minerals increased in the order: hematite< goethite < amorphous Fe oxide < poorly crystalline goethite; adsorption on a weight basis for clay minerals increases in the order: well crystallized kaolinite < poorly crystallized kaolinite < illlite < montmorillonite.

2.2.5.2 K_d value used for molybdenum transport modeling

There is no site-specific iron concentration data for aquifer solids. Based on the total iron concentrations found at the nearby FB Culley Generating Station, a total iron concentration of 24,000



mg/Kg is considered representative. Site aquifer zones that are permeable for flow exhibit redox conditions between microaerobic and iron-reducing. The source of the weather material at both Sites have a similar provenance in terms of parent rock. The geometric mean of the published Kd values for iron oxide minerals for more weathered iron oxides (e.g., hematite and goethite) are approximately 100 L/Kg at pH = 7. Assuming that only 10,000 mg/Kg of iron oxide minerals in aquifer solids is available for adsorption, a nominal K_d value of 1 L/Kg for bulk aquifer solids is estimated (= 10,000 mg/Kg x 10^{-6} Kg/mg x 100 L/Kg). This value is considered a representative, yet conservative value for evaluation of molybdenum transport in the saturated zone.

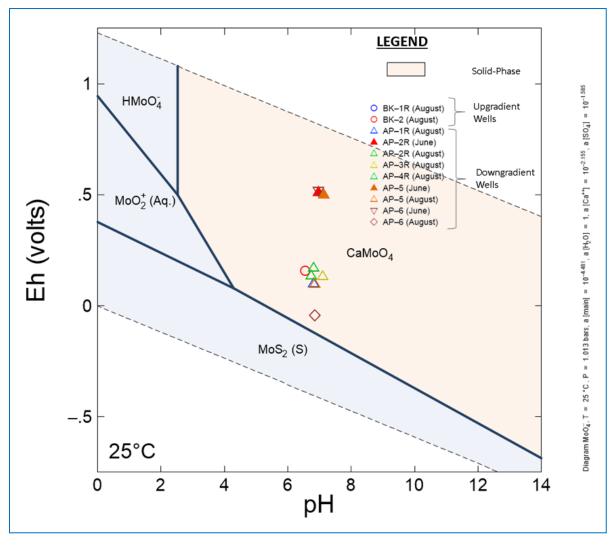


Figure 7: Molybdenum Eh-pH Diagram for a molybdenum-sulfur-oxygen-hydrogen-calcium system; groundwater monitoring data collected in June and August 2018 used; field ORP measurements converted to the Standard Hydrogen Electrode (SHE); field pH measurements plotted; assumptions: solute activities = measured concentrations in mols/L; analytical concentrations results for AP-2R used to generate stability diagram. Thermodynamic database used: thermo.com.V8.R6+, fully modified with molybdenum solubility data from Vlek and Lindsay (1977).

2.2.6 Source Initial Concentration Data

To conservatively predict the transport of molybdenum and preserve the mass transported through the Site, the source area was defined utilizing initial concentration and constant sources in the form of



recharge. The current extent of the groundwater plume for molybdenum was generated based on groundwater concentrations in the monitoring well network.

Four discrete areas with concentrations of molybdenum above detection are present at the Site within the vicinity of the ash pond. Initial concentrations were created near the following wells at concentrations observed from groundwater sampling events conducted in May and June 2019.

- CCR-AP-2R 1.9 milligrams per liter (mg/L)
- CCR-AP-3R 0.89 mg/L
- CCR-AP-5 0.059 mg/L
- CCR-AP-9 0.021 mg/L

With the exception of scenarios where the source material was removed from the Site, ash was modeled as a continuous source.

2.3 TRANSPORT MODEL RESULTS - MOLYBDENUM

Model results for Molybdenum concentrations for each CMA option is shown in **Figure 8**. A detailed discussion of each option is presented in the CMA report (Haley & Aldrich, Inc., 2019).



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TABLES

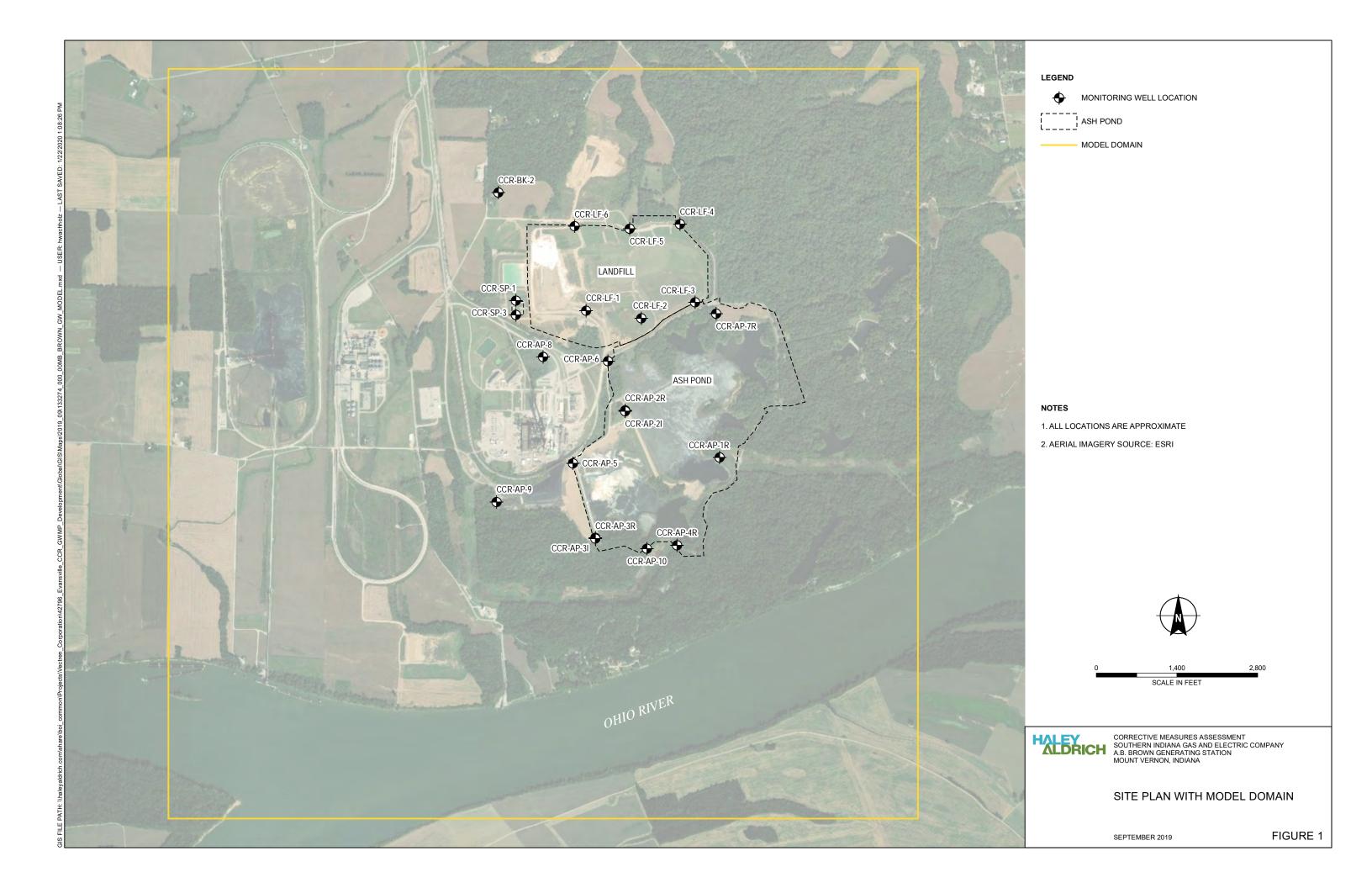


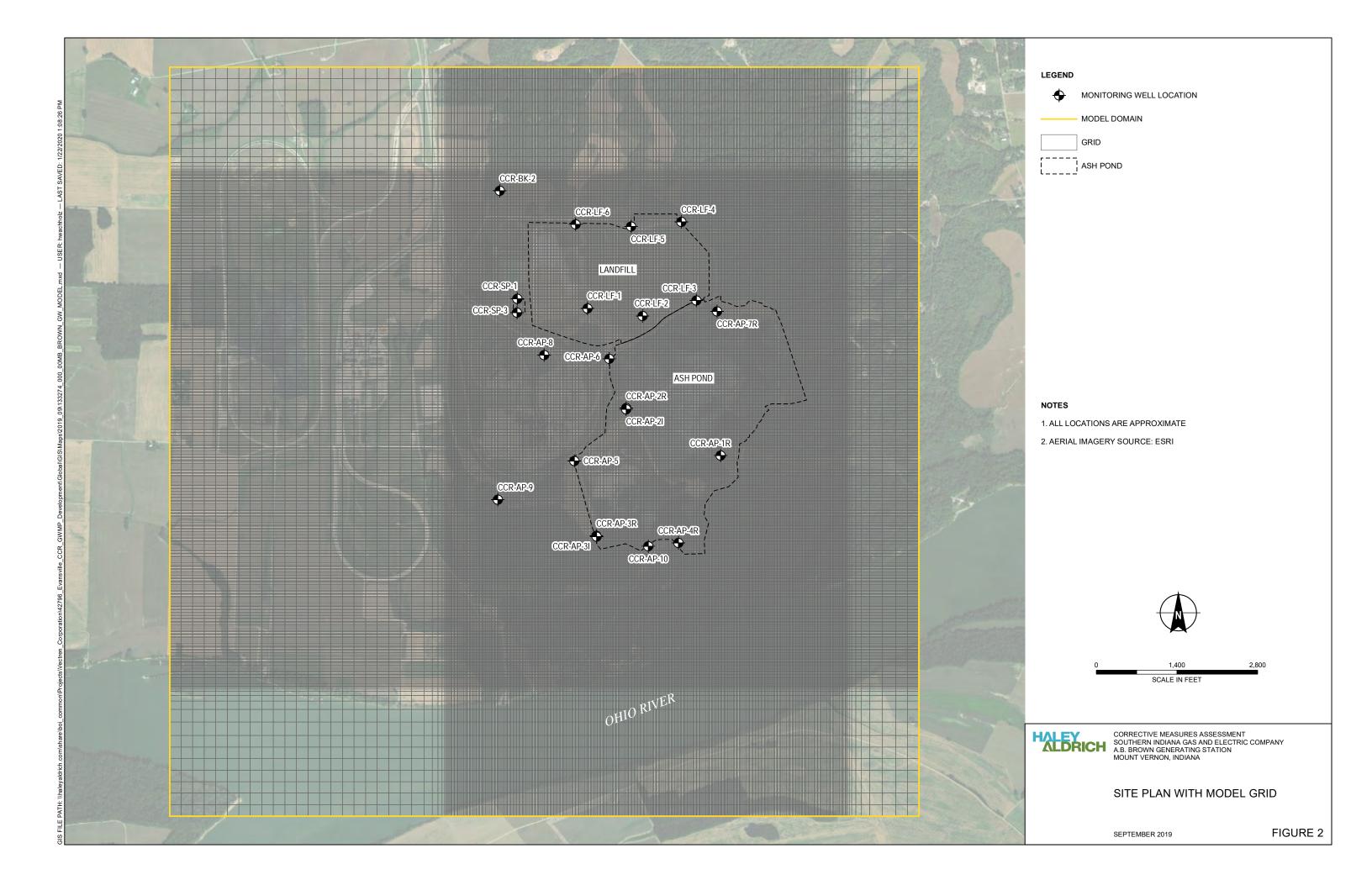
Table 1
June 2019 Groundwater Elevations
A.B. Brown Generating Station
Mount Vernon, Indiana

Well	Easting	Northing	Depth To Water	Groundwater Elevation
Location	Feet	Feet	Feet	Feet (NAVD88)
CCR-AP-1R	2773560.00	968260.82	15.28	452.29
CCR-AP-2R	2771920.00	969079.16	37.90	431.23
CCR-AP-2I	2771920.00	969063.77	26.69	442.19
CCR-AP-3R	2771404.27	966865.12	33.11	416.02
CCR-AP-3I	2771408.31	966855.06	22.68	427.67
CCR-AP-4R	2772827.01	966741.47	32.29	443.09
CCR-AP-5	2772827.01	968166.03	37.40	416.37
CCR-AP-6	2771626.75	969932.76	14.39	447.18
CCR-AP-7R	2773501.63	970758.70	33.94	454.63
CCR-AP-8	2770500.58	970005.00	4.05	413.12
CCR-AP-9	2769695.14	967494.17	8.50	384.01
CCR-AP-10	2772304.46	966679.13	34.74	439.60
CCR-LF-1	2771247.76	970812.18	7.80	427.83
CCR-LF-2	2772205.05	970681.32	26.21	446.79
CCR-LF-3	2773138.97	970949.70	28.59	456.16
CCR-LF-4	2772876.83	972312.24	46.98	431.87
CCR-LF-5	2772003.91	972228.16	20.60	409.81
CCR-LF-6	2771046.15	972269.53	8.38	403.67
CCR-SP-1	2770030.26	970981.89	11.83	391.68
CCR-SP-3	2770027.64	970735.02	7.77	395.80
CCR-BK-2	2769728.14	972854.33	14.68	415.92

FIGURES







Layer 1 - Approximately 10 Feet Thick Hydraulic Conductivity - 1.1 x 10⁻² cm/s

Layer 2 - Approximately 5 Feet Thick Hydraulic Conductivity - 1.1 x 10⁻² cm/s

Layer 3 - Approximately 10 Feet Thick Hydraulic Conductivity - 1.1 x 10⁻² cm/s

Layer 4 - Approximately 20 Feet Thick Hydraulic Conductivity - 1.8 x 10⁻⁴ cm/s

NOTES:

Layer Thicknesses Approximate Due To Variability In Model
 Layers 1 , 2, and 3 represent silty clay ; Layers 4 represents weathered sandstone, shale, or siltstone



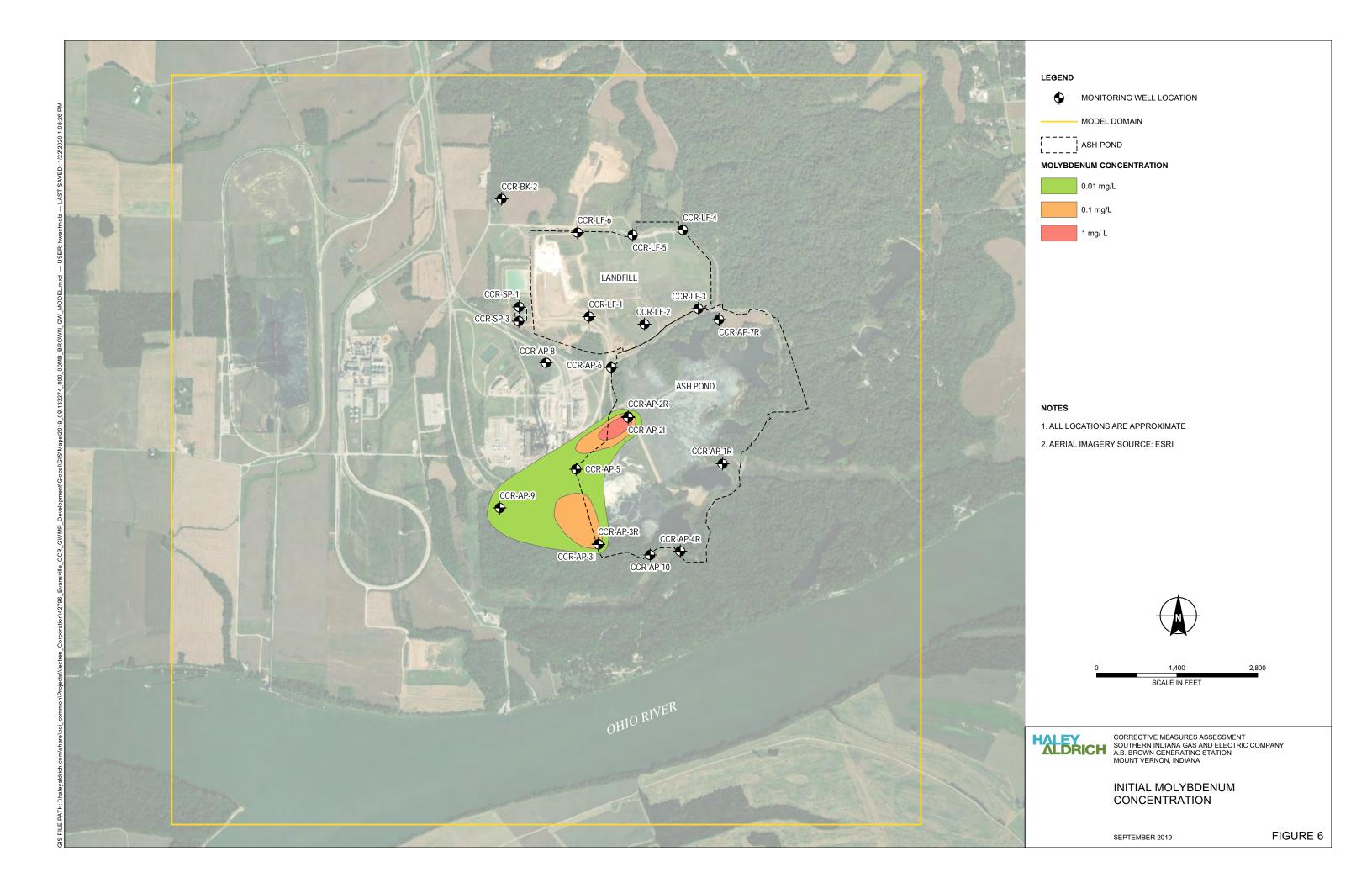
VECTREN CORPORATION A.B BROWN GENERATING STATION MOUNT VERNON, IN 47620

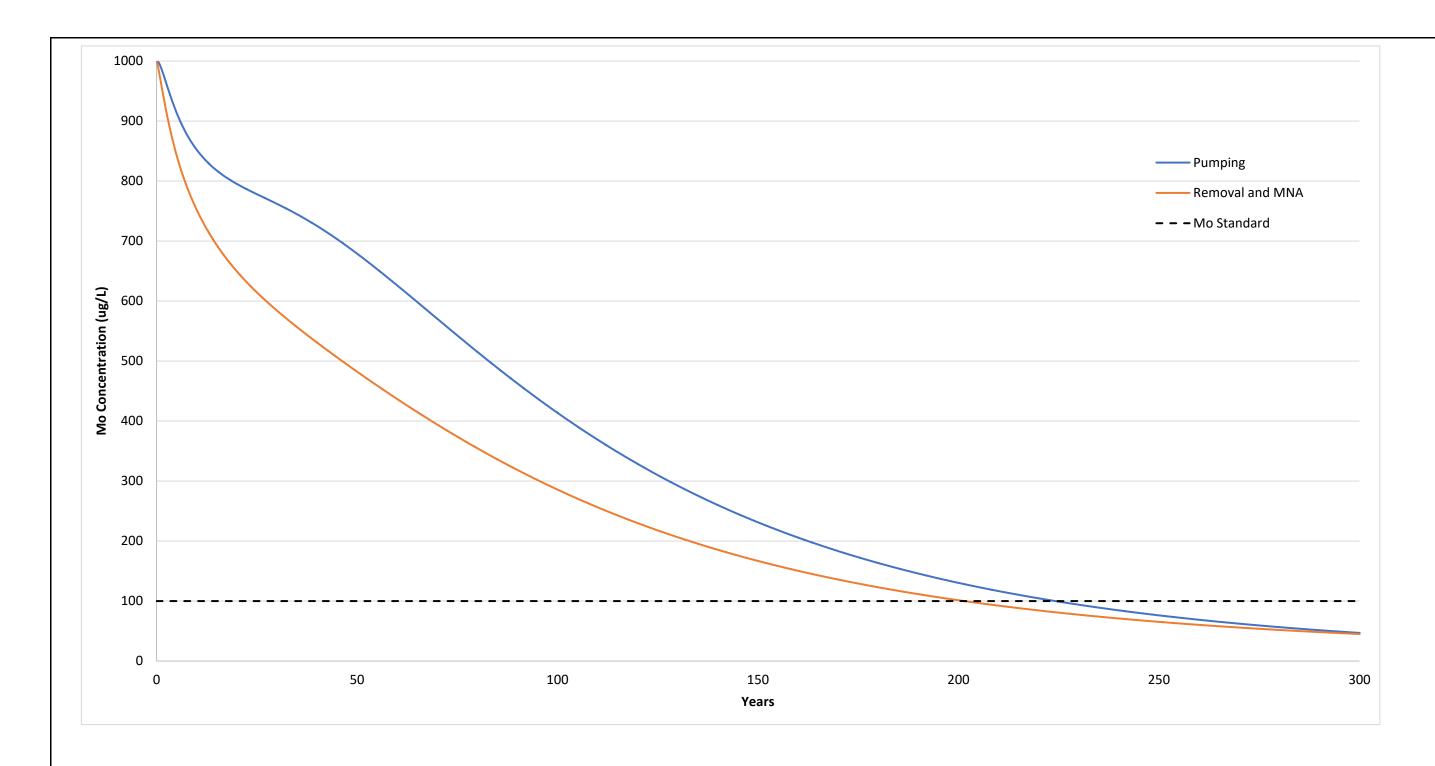
MODEL LAYERS 1 THROUGH 4 WITH HYDRAULIC CONDUCTIVITIES AND LAYER THICKNESSES

SEPTEMBER 2019

FIGURE 3







NOTES:

1. Modeled Monitoring Well Located Approximately 600 Feet Downgradient from Pond Toward The West.



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MOUNT VERNON, INDIANA 47620

MODELED MOLYBDENUM CONCENTRATIONS FOR CMA OPTIONS OVER TIME

SEPTEMBER 2019

FIGURE 8