REGIONAL AND LOCAL HYDROGEOLOGY AND GEOCHEMISTRY VERMILION POWER PLANT, ILLINOIS

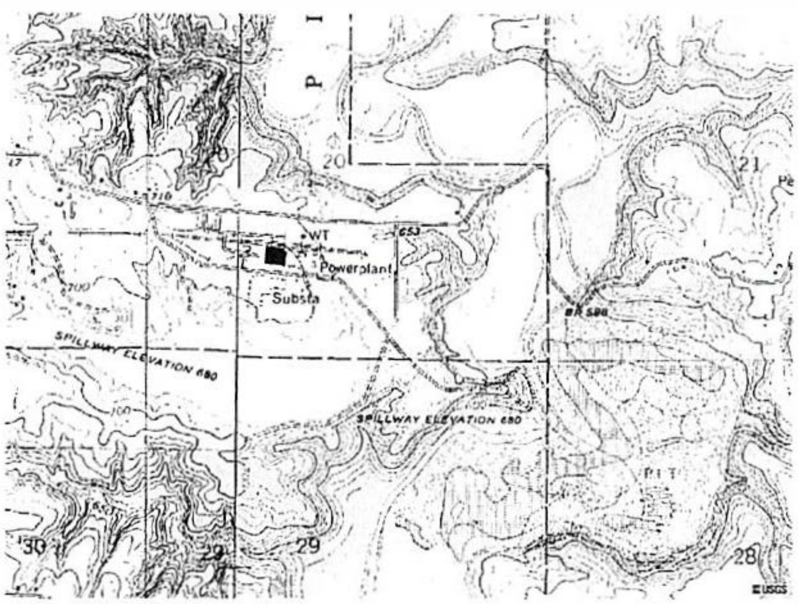
VOLUME 1 OF 2

November 30, 2003

Prepared for:

Dynegy Midwest Generation, Inc.

Decatur, Illinois



KELRON ENVIRONMENTAL
CHAMPAIGN, ILLINOIS

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RELEASABLE

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EXECUTIVE SUMMARY

Background and Objectives

The East Ash Pond System (East Ash Pond) of the Vermilion Power Plant is owned and operated by Dynegy Midwest Generation, Inc. (DMG). The Vermilion Power Plant is located in Vermilion County, Illinois. Following a hydrogeologic investigation by Mathes Geotechnical Services, Inc. in 1987, the primary and secondary cells of the East Ash Pond were constructed in 1989. A planned expansion of the primary cell of the East Ash Pond beginning in 2002 prompted DMG to authorize in October 2001 a comprehensive regional and local hydrogeologic and geochemical investigation. Secondary objectives of the study were:

- To determine if the East Ash Pond was causing any changes to groundwater quality in the alluvial deposits or underlying bedrock;
- To assess the impacts of nearby coal mines on the hydrology and groundwater quality; and,
- To determine the appropriate groundwater classification for the East Ash Pond.

Due to the large scope of work involved and the need to establish the background geochemistry both in the vicinity of the study site (see Figures 1, 2, 3) and within the larger region, the Illinois State Geological Survey (ISGS) was contracted by Kelron Environmental (Kelron) to provide technical assistance in determining the background geochemistry of the bedrock deposits in the vicinity of the study site. The results of the ISGS investigation have been incorporated into this report.

Investigation Methods

In order to characterize both the geology and groundwater quality in the vicinity of the study site, a total of 40 borings and 16 monitoring wells were utilized. Groundwater and surface-water quality data were collected monthly over a six-month period for 19 inorganic parameters and four field parameters. In addition, as part of their separate study the ISGS collected groundwater samples from both DMG wells and private wells for inorganic and isotopic (tritium and Carbon-14) chemical analysis.

Other data collection activities employed during the study included:

- field permeability testing and analysis of the geologic materials by Kelron;
- seismic investigation of bedrock and coal mines near the East Ash Pond by URS Corp.;
- downhole geophysical logging of borings by the ISGS; and,
- laboratory analysis of rock-core samples by the ISGS.

The field and laboratory data collected during 2001 and 2002 were used to create a variety of products, including topographic maps, geologic maps, potentiometric surface maps, geologic cross-sections, hydrographs, and geochemical tables and figures.

Results

Geology

The deposits covering the bedrock in the study site are derived from recent river deposition (alluvial sediments) in the river valleys and glacial drift deposits occurring below the alluvial sediments and in the upland areas. Thickness of these deposits in the region range from zero thickness along portions of the Middle Fork of the Vermilion River (Middle Fork) where bedrock is exposed, to over 200 feet in the upland areas. The unlithified alluvial and glacial deposits in the vicinity of the East Ash Pond and within the floodplain generally range in thickness from 10 to 25 feet.

Rocks of Pennsylvanian age form the bedrock surface in the region surrounding the site. The Danville area is located on the northeast flank of the Illinois basin. Regionally, the Pennsylvanian bedrock consists of mainly shale with thin limestone, sandstone, and coal beds. The upper 75 feet of bedrock at the study site typically consists of the Shelburn Formation, which is composed of non-marine and marine, silty and micaceous shales. The Shelburn Formation contains a major coal seam mined in the region, the Danville Coal, also called the No. 7 Coal.

The top of the Danville Coal, or the void remaining where the coal was removed through mining, was intercepted at depths of 80 to 102.5 feet on the floodplain adjacent to the East Ash Pond. The thickness of the coal seam ranged from four to seven feet with an average thickness of 5.4 feet.

Hydrogeology

Groundwater within the alluvial and, where present, the glacial (till) deposits within the floodplain generally conforms to the ground surface topography. Groundwater elevations in the glacial and alluvial deposits demonstrate that groundwater elevations in the unlithified materials are higher than those in the adjacent Middle Fork through much of the year. The groundwater surface in the alluvial deposits fluctuates in response to changes in river stage and variations in precipitation. The groundwater surface is not affected by water levels in the East Ash Pond, which has been hydraulically isolated from both the shale and alluvial deposits by soil/bentonite slurry walls and a compacted clay core. Changes in pond elevation do not result in any corresponding changes in the shallow groundwater levels.

Groundwater elevations in the bedrock shale are highest in the topographically highest areas to the west and east of the Middle Fork of the Vermilion River. The lowest groundwater elevations occur at wells located adjacent to the Middle Fork. **Flow lines derived from the potentiometric surface maps indicate that the Middle Fork of the Vermilion in this area is a zone of discharge for the shale. The occurrence of the Middle Fork in this area as a regional discharge zone for the shallow bedrock is supported by the upward vertical hydraulic gradients measured within the shale. The shale outcrops along the banks of the Middle Fork and groundwater moving**

upward through the shale discharges into both the alluvium and directly into the Middle Fork.

The coal mines in the vicinity of the East Ash Pond System have been shown to have significant collapse features where the overlying shale has collapsed or partially collapsed downward into the void or mined coal seam. The collapse of the shale into the void translates upward through the shale, resulting in fracturing and in some cases surface subsidence.

Groundwater Chemistry

Based on the groundwater and surface water quality data collected in 2002, the affects of the East Ash Pond on groundwater quality are either negligible or not present. Groundwater quality data for most major ions and trace constituents is similar to background groundwater quality. In cases where elevated concentrations of a parameter were found to occur in groundwater near the East Ash Pond there were also elevated concentrations in background wells screened within coal deposits or in the proximity of abandoned coal mines.

Trace metal concentrations in groundwater were compared to East Ash Pond water samples and there was no commonality between the two water types. The deficiency of trace metals such as molybdenum, selenium, and vanadium in groundwater within both the alluvial deposits and the Pennsylvanian age bedrock at both background and East Ash Pond wells, as compared to their ubiquitous presence within waters of the East Ash Pond, suggests that **based on trace water quality data there is no impact to unlithified or bedrock groundwater quality by the East Ash Pond.**

The results of the isotopic analyses of groundwater samples from the background bedrock wells by the ISGS resulted in Carbon-14 ages ranging from 13,000 to 35,000 RYBP (radiocarbon years before present). In support of the Carbon-14 results, tritium concentrations for the same set of bedrock groundwater samples were all below detection limits ranging from 0.43 to 0.52 TU (tritium units). Water with non-detectable tritium concentrations is considered to be greater than 50 years old (Mehnert and Dreher, 2002).

The isotopic and other geochemical data from background monitoring wells supports the hydrogeologic conceptualization that **the Middle Fork of the Vermilion River is a regional discharge area for the bedrock.** Groundwater within the bedrock is at the end of its flow path and has upward hydraulic gradients, high dissolved mineral content, and is thousands of years older than recent groundwater in the overlying unlithified deposits.

Groundwater Classification

No groundwater parameters measured in the unlithified (i.e., alluvium and till) deposits of the study site exceeded Class I or II groundwater standards during March through August 2002. However, background well MW28 (see Figures 7, 8) exceeded the sulfate and TDS standards of 400 and 1,200 mg/L, respectively, during January and February 2002. Three bedrock monitoring wells at the East Ash Pond and four background wells regularly exceeded standards for at least one of the parameters of chloride, sulfate, and TDS.

The occurrence of parameters within the bedrock at sufficiently high concentrations to exceed groundwater standards can be attributed to three sources: natural geochemistry; natural geochemistry associated with coal deposits; and, anthropogenic (man-made) affects on geochemistry associated with former coal mines and mine spoil. Similarly, high concentrations of inorganic parameters within the unlithified deposits can be attributed to natural geochemistry and the impacts of former coal mines and mine spoil.

Based on the hydrogeology and geochemistry established for the vicinity of the East Ash Pond and surrounding region, and given the influence of former coal mines documented at the study site on the geochemistry of groundwater, it appears that the groundwater designation is Class IV – Other Groundwater, in accordance with Section 620.201 of Part 620 (IAC Title 35, Subtitle F, Chapter I). Class IV groundwater is defined as groundwater within a previously mined area that cannot meet the standards of Class I or II groundwater.

1.0 INTRODUCTION

1.1 PURPOSE

The East Ash Pond System (East Ash Pond) of the Vermilion Power Plant, which is owned and operated by Dynegy Midwest Generation, Inc. (DMG), is located in Vermilion County, Illinois (Figures 1, 2, 3). Following a hydrogeologic investigation by Mathes Geotechnical Services, Inc. (Mathes) in 1987, the primary and secondary cells of the East Ash Pond were constructed in 1989. A planned expansion of the primary cell of the East Ash Pond beginning in 2002 prompted DMG to authorize in October 2001 a comprehensive regional and local hydrogeologic and geochemical investigation by Kelron Environmental (Kelron). The secondary purpose of the investigation was to determine if the East Ash Pond was impacting groundwater quality in the surficial and underlying bedrock deposits.

1.2 APPROACH

In order to characterize both the regional and local groundwater quality, the existing groundwater data collected from five monitoring wells from the earlier Mathes investigation had to be supplemented with new data from an expanded network of downgradient and background wells. Eleven new monitoring wells were installed to expand the existing network from 5 to 16 wells (Figures 7, 8). The larger network of wells and new boring data were used to re-define and expand upon the earlier hydrogeologic conceptualization by Mathes. In addition, the new groundwater quality data were combined with surface-water quality data collected from the East Ash Pond and the Middle Fork of the Vermilion River to determine potential interactions between natural and man-made surface water bodies with the shallow and deeper groundwater systems.

Due to the large scope of work involved and the need to establish the background geochemistry both in the vicinity of the study site and within the larger region, the Illinois State Geological Survey (ISGS) was contracted by Kelron to conduct an independent research investigation. The ISGS research and approach is discussed in the following section.

1.2.1 Illinois State Geological Survey Research

Kelron Environmental contracted with the ISGS to provide technical assistance in determining the background geochemistry of the bedrock deposits in the vicinity of the study site. As part of their independent study of background geochemistry, the ISGS performed the following tasks.

- Literature search, including unpublished data sources, for information pertaining to groundwater geochemistry of shale and coal. The search focused on the groundwater quality of Pennsylvanian-age shale and coal in Illinois and the Midwest. Unpublished data sources included the ISGS and Illinois State Water Survey (ISWS) databases.

- Reviewed geologic data from bedrock cores obtained during drilling of monitoring wells by Kelron and also reviewed geophysical logs recorded by the ISGS scientists.
- Reviewed and incorporated groundwater chemistry data for samples collected from background monitoring wells by Kelron and Dynegy.
- Provided advice on the list of analytes for groundwater sampling of monitoring wells by Kelron.
- Analyzed rock samples from bedrock cores for mineralogy.
- Collected groundwater samples from four private wells, two in the vicinity of the study site, and analyzed samples for anions, cations, pH, and alkalinity.
- Collected groundwater samples from two private wells and analyzed for the isotopes tritium [^{3}H] and Carbon-14 [^{14}C].
- Collected groundwater samples from six background monitoring wells installed by Kelron and analyzed for anions, cations, pH, alkalinity, and selected isotopes (^{3}H and ^{14}C).
- Prepared a final report that included pertinent literature and data on the geochemistry of shale and coal, discussion of the geochemistry of shallow bedrock groundwater in background wells based on the data collected as part of the study, and conclusions on the geochemistry of shallow bedrock groundwater in background wells in the region surrounding Dynegy's Vermilion Power Plant.

The results of the ISGS study have been incorporated into this report. The full ISGS study report is included as Appendix A.

1.3 SITE DESCRIPTION

The East Ash Pond is located in Vermilion County, primarily in the east half of the northeast quarter of the southeast quarter of Section 20, Township 20 North, Range 12 West (Figure 1). The entire study site, encompassing both the East Ash Pond and background wells, is located in the east half of Section 20 and the west half of Section 21. The Middle Fork of the Vermilion River (Middle Fork) borders the East Ash Pond along its north and east edges. The East Ash Pond lies in the flood plain of the Middle Fork and is bordered by bluffs to the west.

A topographic map (Figure 2) and aerial photograph (Figure 3) show the topographic and natural features in the vicinity of the East Ash Pond. The V-shaped lake in the lower right hand corner of the aerial photograph is a remnant of strip mining activity southeast of the East Ash Pond on the east side of the Middle Fork.

1.4 SITE HISTORY

1.4.1 Previous Investigations

A hydrogeological investigation was performed by Mathes in 1987 in the vicinity of the current East Ash Pond. The purpose of the 1987 study was to obtain sufficient information concerning subsurface conditions at the site to make recommendations concerning location and construction of a new ash pond system for the Vermilion Power Plant.

Information from the 1987 Mathes investigation was incorporated into the current study. In addition, several monitoring wells from the Mathes study, which were not destroyed during construction of the East Ash Pond in 1989, were incorporated into the current investigation.

1.4.2 East Ash Pond Construction and Expansion

The East Ash Pond consists of two cells: an 11-acre primary (main) pond and a 0.8-acre secondary (polishing) pond. Ash in the main pond settles out of the sluice water, is decanted to the secondary pond, and then discharged to the Middle Fork in accordance with the effluent limits and monitoring requirements of an NPDES permit.

The original primary and secondary cells of the East Ash Pond System were constructed in 1989. The entire East Ash Pond was built directly overtop a thick shale formation which is greater than 80 feet thick in the vicinity of the ash ponds. The alluvial deposits overlying the shale formation were excavated so that the shale surface was exposed. The earthen berms on the north, east, and south sides of the primary cell are "keyed" into the underlying shale formation with two four-foot thick soil/bentonite slurry walls. Bentonite is an absorbent aluminum silicate clay formed from volcanic ash. These walls extend approximately 8 feet down into the shale and approximately 12 feet above the shale surface into the clay-core center of the earthen berms (see Figure 4). A natural earthen bluff composed of low permeability native clays forms the west side of the primary cell. The maximum permeability of the soil/bentonite slurry wall was specified not to exceed 1×10^{-8} cm/s.

The earthen berms built on top of the soil/bentonite slurry walls are approximately 18 feet tall, 80 to 120 feet wide at the base, and 15 feet wide at the top. The outside portion of the berms is constructed of locally excavated sand and clay. The center of these berms is constructed with a compacted clay core ranging in thickness from 15 feet at the top to 30 feet near the base. The permeability of the clay core is approximately 10^{-7} cm/s.

The new berms constructed to expand the capacity of the primary cell of the East Ash Pond System in 2002 raised the height of the original berms by approximately 20 feet. The new berms are constructed with 8-foot clay liners keyed into the underlying clay core. The 8-foot clay liners are on the wetted-side of the berm surrounding the expanded ash pond. The clay liners are placed within berms constructed of local clay and silty clay materials. The permeabilities of these materials are within the same specification range as for the original ash pond. A natural earthen bluff wall forms the west side of the enlarged primary cell.

The secondary pond is not being expanded or modified as part of the East Ash Pond System expansion.

1.4.3 Coal Mines

The vicinity of the Vermilion Power Plant has seen extensive coal-mining activity from 1893 to 1970. Two coal mines, called the Crawford Mine (ISGS Mine Index No. 3889) and Fletcher's Middlefork Mine (ISGS Mine Index No. 3888), are located beneath the East Ash Pond and vicinity (Figure 5). Based on data and maps obtained from the ISGS, the former entrances to the two coal mines beneath the site are located just north of the secondary cell of the East Ash Pond (Mine 3889) and 600 hundred feet southwest of the primary cell (Mine 3888) (ISGS, 1996). Information pertaining to both these mines and other mines in the vicinity of the Site are provided in Appendix B.

The entrance to the Crawford Mine was field located. It is a slope shaft mine with the main coal seam (the Danville, or No. 7 Coal) located between the depths of 80 and 92 feet below land surface (BLS). The average thickness of the main coal seam is approximately 5 ½ feet. Several borings were advanced in order to locate both this mine and the Middlefork Mine. The procedures and data gathered during the coal-mine investigation, in addition to the subsequent geophysical investigation, are discussed later in the report. The Middlefork Mine operated between 1939 and 1949 using the room-and-pillar method, whereby the coal is removed in 'rooms' with 'pillars' of coal left in place to support the roof. During the course of the investigation of this mine both mined and un-mined areas were intercepted during exploratory borings. Mined areas were identified based on the drill bit dropping through voids where the coal had been removed. In addition to locating the mined interval, the slope shaft descending to the coal seam was intercepted near the mine entrance at a depth of 28 to 37 feet BLS.

The exact entrance to Middlefork Mine was not located, although based on mine tailings, topography, and historic records it is somewhere between the north end of the secondary cell and the Middle Fork of the Vermilion River. This mine is a vertical shaft mine with the main seam of the Danville Coal located between the depths of 102 and 115 feet BLS. The average thickness of the seam in this area is estimated at five to six feet. This mine operated between 1905 and 1919 using the room-and-pillar method. Three borings were advanced to locate this mine and two of them intercepted mined-out coal seams, one of which had collapsed. The coal mine collapse and subsidence at the Middlefork Mine caused some fracturing of the overlying shale and also changed the groundwater hydraulics in the vicinity of the mine. The potential effect of the coal mine on the groundwater hydrology is discussed in Section 5.

Other mines, both shaft and strip, are located south and southeast of the Crawford and Middlefork mines discussed above (Appendix B). Some of these mines are located within or adjoining the property of the Vermilion Power Plant. The Danville Coal has been extensively mined using both subsurface and strip methods in the vicinity of the Site. To varying degrees, these mining activities have altered the natural topography, hydrology, surface water chemistry, and groundwater chemistry that existed in the area before mining began.

A geophysical study was conducted by URS Corp. in early 2002 to further investigate and locate the coal mines in the vicinity of the East Ash Pond. The results of this investigation are presented in Section 4.2.1.2.

2.0 STUDY METHODS AND PROCEDURES

The objective of the investigation was to conduct a full hydrogeologic and groundwater geochemical characterization in the vicinity of the East Ash Pond of the Vermilion Power Plant and compare the investigation results to the regional background hydrogeology and geochemistry. Secondary objectives of the study were:

- To determine if the East Ash Pond was causing any changes to groundwater quality in the alluvial deposits or underlying bedrock;
- To assess the impacts of nearby coal mines on the hydrology and groundwater quality; and,
- To determine the appropriate groundwater classification for the site.

Data collected from the previous investigation at the site (Mathes, 1987) and quarterly groundwater quality data collected since 1994 were incorporated into the study. The methods used to conduct the study and procedures used for obtaining the necessary geologic, hydrologic, and chemical data are presented in this section.

2.1 METHODS

2.1.1 Previous Data

As mentioned earlier, the prior investigation by Mathes (1987) was incorporated into the study, both as background data for developing an initial conceptual understanding of the hydrogeology and for inclusion of pertinent hydrogeologic data directly into the current investigation. Five wells installed by Mathes in 1987 that were not destroyed by the subsequent construction of the East Ash Pond were incorporated into the study. These five wells include the alluvial wells MW13B and MW16B, which were nested with the shale bedrock wells MW13A and MW16A, respectively, and the till well MW10 (Figures 6, 7, 8). In addition to the existing wells, the Mathes study provided borehole geologic data and hydraulic conductivity data.

Supplementing the geologic data available for the site, inorganic groundwater quality data and water-level data were available for the five monitoring wells for the period of 1994 to the present. Quarterly groundwater monitoring for selected inorganic parameters was instituted beginning in 1994.

Site topographic maps, as-built diagrams of the East Ash Pond, and aerial photographs were used to develop base maps, locate wells, and develop geologic cross-sections.

2.1.2 Geologic Data

The geology presented in this report is primarily based on the geotechnical and monitoring well borings listed in Table 1 and summarized below.

- Nine borings drilled by Mathes (1987) as part of a hydrogeologic investigation for construction of the East Ash Pond.

- Eleven borings drilled in 2001 as part of the current investigation. Four borings were drilled at locations near the East Ash Pond and seven were placed at locations to the south, east, and north.
- Twelve borings drilled in 2001 for geotechnical characterization for expansion of the East Ash Pond; and,
- Eight exploratory borings drilled in 2002 for locating and characterizing the coal mines in the vicinity of the East Ash Pond.

Detailed geologic logs are provided for all of the borings in Appendix C.

Other information incorporated into the study for characterizing the geology was provided by the ISGS. The ISGS performed downhole geophysical logging of three of the deepest borings, logged three bedrock cores, and provided geologic logs and well construction data for a one-mile radius around the study site. The ISGS also provided information for coal mines and coal seams in the vicinity of the site.

In addition to the above geologic information, the results of the geophysical investigation into coal mine locations at the East Ash Pond, conducted in early 2002 by URS Corp., have also been incorporated into this report.

The assembled geologic data were used to develop the following:

- thickness maps of the unlithified deposits;
- bedrock elevation map;
- coal seam elevation map; and,
- coal mine location maps.

2.1.3 Hydrologic Data

The hydrology of the unlithified deposits and underlying bedrock presented in this report was based on the data obtained from a network of 16 monitoring wells installed at the site: five from the 1987 Mathes study and 11 installed in 2001 (Table 2 and Figure 6). Six monitoring wells are installed in the unlithified deposits, with four located near the East Ash Pond and two background wells located north of the Middle Fork (Figure 7). Ten monitoring wells are installed in the bedrock, with five installed near the East Ash Pond, four background wells located to the north and east of the Middle Fork, and one background well located south near the river pump station. Water-level measurements were made monthly for the eight months from January through August 2002 (Table 3 and Figure 8).

In addition to the hydrologic data collected from the monitoring wells, surface water measurements were obtained from the Middle Fork upriver from the East Ash Pond near nested wells MW26/MW27, downriver at MW25, and from the primary and secondary cells of the East Ash Pond. Surface water measurements of the East Ash Pond were not conducted after May 22 because the primary and secondary ponds were drained during construction activities. The last discharge from the East Ash Pond outfall to the Middle

Fork during 2002 was on May 26. Discharging from the East Ash Pond System resumed in January 2003 after construction of the enlarged primary cell was completed.

The groundwater and surface water measurements were used to develop the following:

- potentiometric surface maps;
- groundwater and surface water hydrographs showing temporal variations in water levels;
- horizontal groundwater flow directions and velocities;
- vertical hydraulic gradients between the alluvial deposits and underlying bedrock;
- hydraulic connection between groundwater in the alluvium and bedrock with surface water in the Middle Fork; and,
- impact assessment of the East Ash Pond on alluvium and bedrock groundwater levels.

2.1.4 Groundwater and Surface Water Chemical Data

The groundwater chemistry data presented in this report is based on six months (March through August 2002) of field and laboratory data collected from 16 monitoring wells. Three of the wells (MW13B, MW16B, and MW22) were typically dry or had insufficient water for groundwater sampling. In addition to the above samples, inorganic and isotopic chemistry data analyzed by the ISGS for the five background bedrock wells (MW25, MW27, MW29, MW30 and MW31) sampled in June 2002 were also incorporated into this report. The surface water chemistry data are based on five months of data collected from the East Ash Pond primary cell (January through May 2002) and six months (March through August 2002) of data collected upriver on the Middle Fork at the Higginsville Bridge. No East Ash Pond samples were collected after May 2002 because the pond was drained and no further effluents were being discharged into the impoundment during construction activities.

The chemical data presented in this report for the monitoring wells includes the field parameters temperature, pH, and conductivity and the following laboratory analytical parameters:

Alkalinity	Aluminum	Barium	Boron	Calcium
Chloride	Iron	Lithium	Magnesium	Manganese
Molybdenum	Phosphorus	Potassium	Selenium	Sodium
Strontium	Sulfate	TDS	Vanadium	

The above parameters, with the exception of the field parameters, were also analyzed in the surface water samples. However, all of the inorganic parameters in groundwater were analyzed as dissolved while those in surface water were analyzed as totals.

In addition to the samples collected and analyzed monthly from March through August 2002, the background monitoring wells MW25 through MW31 and the East Ash Pond primary cell were sampled in February 2002 for the same inorganic constituents listed above plus cadmium, chromium, and zinc. Based on this first round of sampling in February, the analytes cadmium, chromium, and zinc were dropped from the study because they were below their respective method detection limits (1, 1, and 5 micrograms per liter [ug/L], respectively) in almost all of the samples analyzed.

2.2 TECHNICAL PROCEDURES

2.2.1 Borehole Drilling

Eleven boreholes drilled for the installation of monitoring wells were numbered sequentially from MW22 to MW32. Borehole logs are provided in Appendix C for both the current and prior studies at the Site. The eight boreholes drilled for the coal mine investigation were numbered sequentially from B201 through B208. Boreholes were drilled using a Diedrich D-120 rig equipped with hollow-stem augers and rock coring equipment. Drilling through the unlithified deposits was performed utilizing hollow-stem augers. Samples were obtained using a 24-inch long by two-inch outside diameter (O.D.) split-spoon sampler. The sampler was mechanically driven using a 140-pound hammer with a 30-inch drop. Soil samples were collected continuously in unlithified deposits less than 25 feet thick and at intervals of five to ten feet in deposits greater than 100 feet thick.

All soil samples were logged in the field for sample interval and soil recovery, stratum thickness and depth, visual soil classification by the Unified Soil Classification System [(USCS); ASTM D 2487 and 2488], moisture content and presence of water, soil stiffness, and horizontal compressive strength using a pocket penetrometer.

For those boreholes cored into the underlying bedrock, 4.5-inch O.D. steel surface casing was installed to the top of the bedrock. The outer casing was left permanently in place for all of the bedrock holes with the exception of MW25, MW30, MW31, and the coal mine boreholes. Following installation of the outer casing, continuous sampling of the bedrock was performed using an HQ-core (2.25-inch I.D.) for the monitoring well locations and NQ-core (1.88-inch I.D.) for coal mine borings. Wireline coring, which is a type of rotary drilling, was used to obtain continuous samples of consolidated (i.e., bedrock) formations. A hollow coring bit was used to cut the rock and the samples of rock were removed at designated intervals, in the case of this study every 10 feet. Clean water was used as the drilling fluid.

All core samples were logged in the field for sample interval and soil recovery, stratum thickness and depth, and visual soil classification by the USCS System. In addition, the cores obtained from boreholes MW25, MW30, and MW31 were delivered to the ISGS for more detailed classification and analysis (Appendix A).

2.2.2 Monitoring Well Installation and Development

Groundwater monitoring wells were constructed of two-inch diameter, flush-threaded (Schedule 40) polyvinyl chloride (PVC) screens and risers. Well screens were 0.010-inch slot size machine cut. Screen lengths (Table 2) were 20 feet for all of the bedrock wells except MW32, which had a 10-foot screen. Screen lengths for new wells installed in the unlithified deposits were five feet for MW26 and MW28 and 10 feet for MW23.

Following placement of the screen and riser, the annular space between the well screen and borehole wall was backfilled with well-sorted quartz sand. The sand filter was placed from the bottom of the borehole to approximately 2-feet above the top of the well screen. A minimum two-foot thick bentonite seal (bentonite chips, pellets, or grout) was placed above the sand pack. The remainder of the borehole annulus was filled to the surface with bentonite grout using a 1.25-inch ID PVC tremie pipe which was placed down the inside of the augers as they were removed from the ground. Monitoring wells were completed with steel well protectors extending approximately 2 ½ to 3 feet above ground surface and set in a cement pad. Monitoring well construction forms and diagrams are provided in Appendix C. In addition, the Well Completion Reports and Well Construction Reports required by the Illinois Environmental Protection Agency and the Illinois Department of Public Health, respectively, are provided in Appendix D.

At least 48-hours following well completion, all monitoring wells were developed to attempt to restore the natural hydraulic conductivity of the monitored formation and remove all drilling-induced sediment to provide turbidity-free groundwater samples. Development was performed using air-lift displacement and submersible pumps. The wells were developed until a minimum three to five well volumes were removed from each well. However, some of the wells installed into the shale did not produce sufficient groundwater before being pumped dry (i.e., MW25, MW31 and MW32); in those cases the wells were developed on more than one occasion in order to remove at least two to three well volumes. Water samples collected during well development were monitored for the field parameters pH, temperature, and conductivity. Development was considered complete when the field parameters had stabilized. Well development data sheets are provided in Appendix E.

2.2.3 Site Surveying

Monitoring well locations were surveyed by an Illinois Professional Land Surveyor to an accuracy of 0.1-foot horizontal and 0.01-foot vertical relative to the state planar horizontal datum NAD83 and vertical datum NAVD88 Geoid 96, respectively. Borehole locations were surveyed to a minimum accuracy of 1-foot horizontal and 0.1-foot vertical. Boring and monitoring well locations are shown in Figure 7 and elevations are provided in Table 1.

2.2.4 Water-Level Measurement Collection

Prior to collecting groundwater samples, static water depth was measured to an accuracy of 0.01 foot in each monitoring well using a Solinst-101 electronic water-level indicator. The groundwater depths were measured relative to the top of the PVC riser and subsequently subtracted from the measuring point elevation to determine the groundwater elevation within the well. In addition to groundwater elevation at all of the monitoring wells, surface water elevation measurements were obtained from the following locations:

- Middle Fork of Vermilion River adjacent to wells MW26/MW27;
- Middle Fork of Vermilion River adjacent to well MW25 at the downriver pump station;

- Primary cell of the East Ash Pond; and,
- Secondary cell (i.e., Polishing Pond) of the East Ash Pond.

Groundwater and surface water level measurements were conducted on a monthly basis from January through August 2002. The measurements were used to develop hydrographs, potentiometric surface maps, vertical gradients between formations, and evaluate hydrologic interactions between the unlithified deposits, bedrock, Middle Fork, and East Ash Pond. Water levels and elevations for the period of investigation are provided in Table 3.

2.2.5 Groundwater and Surface Water Sampling and Chemical Analyses

Water samples were collected from the background wells MW25 through MW31 and the primary cell of the East Ash Pond on a monthly basis by the DMG Environmental Laboratory beginning in January 2002. The remaining monitoring wells in the vicinity of the East Ash Pond, and upriver samples from the Middle Fork at the Higginsville Bridge, were sampled monthly beginning in March 2002. Samples from all wells and surface-water collection points were obtained within a period of one to two days each month with the exception of the March sampling event, when poor weather and equipment problems extended the sampling period to three days.

Groundwater samples were collected using a low-flow sampling technique with Well Wizard® bladder pumps and MicroPurge® equipment. The bladder pumps prevent contact between the pump drive air and the sample, and the downhole equipment is permanently dedicated to each well, preventing cross-contamination caused by transporting pumps between wells. The specification sheets for each of the bladder pumps placed in monitoring wells at the Site are provided in Appendix F. The bladder pumps were placed within the screened interval of each well so that groundwater being pumped would come from the formation pore water and minimize pumping of the overlying static water within the well casing. The only wells that did not have bladder pumps installed were MW10, MW13B, and MW16B. These three wells are typically dry or have insufficient groundwater for sampling. In those cases where there was sufficient groundwater to be sampled from these wells it was removed using dedicated bailers or a peristaltic pump.

The low-flow ground water sampling procedures followed for this study are based on the sampling protocol provided by the United States Environmental Protection Agency (USEPA) in a document authored by Puls and Barcelona (1995). This document has been incorporated into the report as Appendix G. Due to the extremely low permeability of the shale formation from which many of the groundwater samples were obtained, passive sample collection techniques were utilized. Passive sample collection was conducted at the bedrock wells by setting the pump rate at less than 0.2 Liters per minute (L/m), pumping sufficient water to clear the tubing and bladder pump of stagnant water, and collection of samples for laboratory analysis. Three sets of measurements for the field parameters of temperature, pH, and conductivity were collected and documented as follows: at the start of pumping, prior to sample collection, and at the conclusion of sample collection. Sampling of the higher permeability wells installed within the unlithified deposits was conducted at higher flow rates of 0.2 to 0.5 L/m.

Analysis of field parameters (pH, specific conductivity, and temperature) were conducted using either a Hydrolab® Minisonde Model 4a or a Hydrolab Surveyor Model 4a water quality analyzer connected directly to the discharge tubing from the bladder pump. Samples for laboratory chemical analysis were collected using in-line filtration (0.45 micron filter size) that prevented contract with air prior to collection. Water samples were collected in new or acid-washed polypropylene bottles and subsequently stored at 4° C for transport back to the laboratory.

Surface water samples were collected from the East Ash Pond primary cell and the Middle Fork upriver by submerging the sample bottles directly into the water and, where possible, capping under water to minimize air contact. Surface water samples were collected for analysis of total inorganic parameters and were not field filtered. No field parameters were analyzed for the surface water samples.

Chemical analyses were performed by the DMG laboratory. Inorganic analyses were performed in accordance with U.S. EPA SW-846 and Standard Methods for the Examination of Water and Wastewater, 19th Edition. The following parameters and analytical methods were analyzed by DMG for the groundwater and surface water samples:

- Total Alkalinity: EPA Method 310.1 (Titremetric Method);
- Total Dissolved Solids (TDS): EPA Method 160.1 (Gravimetric Method);
- Chloride: Standard Methods, Method 4500-Cl (Potentiomeric Method);
- Sulfate: EPA Method 375.4 (Turbidimetric Method);
- Phosphorus: EPA SW-846 Method 365.2 (ascorbic-acid Colorometric Method); and,
- Boron, Manganese, Magnesium, Calcium, Potassium, Iron, Aluminum, Lithium, Molybdenum, Selenium, Strontium, Vanadium, Barium: EPA Method 200.7 (ICP).

2.2.6 Illinois State Geological Survey Sampling and Chemical Analyses

The ISGS accompanied DMG laboratory personnel on June 18, 2002 in order to obtain split samples for analysis. The ISGS returned to the study site on June 25 and 26 along with Kelron to obtain groundwater for isotope analyses. The methods by which samples were collected and analyzed by the ISGS for their background water quality study are presented in detail in the ISGS report (Appendix A).

2.2.7 Field Permeability Tests

In-situ hydraulic conductivity tests were performed on seven of the newly installed shale monitoring wells (MW24, MW25, MW27, MW29, MW30, MW 31, and MW32) and two of the newly installed alluvial monitoring wells (MW26 and MW28) during September 2002. The monitoring wells were tested by the variable head ("slug") test method.

Most of the slug tests were conducted using three and four foot long by 1-1/4 inch diameter PVC slugs with rope and recorded using In-Situ® Troll 8000 datalogger with 15 pounds per square inch (psi) transducer. The Troll 8000 is a combination downhole transducer and datalogger. Due to the slow recharge of some of the shale monitoring wells, a few tests were conducted without the Troll 8000 by measuring water levels using the Solinst 101 electronic water-level meter and recording the measurements by hand. In some cases only rising head tests were performed and in others both rising and falling head tests were performed.

A laptop computer was used to download the data from the datalogger and analyze the data with the use of AQTESOLV™ for Windows (Version 2.5), an aquifer test analysis software package by HYDROSOLVE. All of the analytical solutions used the Bouwer-Rice method (1980). The AQTESOLV™ for Windows output is included in Appendix H.

2.2.8 Data Management

Field data were recorded on pre-printed forms including:

- Daily field reports;
- Boring logs;
- Monitoring well completion reports;
- Well development reports; and,
- Water sampling forms.

Groundwater and surface water sample data, including water levels, field parameter analyses, and laboratory chemical analyses, were entered and stored on a proprietary groundwater data management software package (MANAGES™ Version 2.7, Electric Power Research Institute). Data collected from wells MW10, MW13A/13B, and MW16A/16B beginning in 1994 were already incorporated into the database prior to the beginning of the current study.

3.0 REGIONAL GEOLOGY AND HYDROLOGY

3.1 TOPOGRAPHY

The uplands are fairly uniform in elevation. They generally occur between the elevations of 650 and 700 feet National Geodetic Vertical Datum (NGVD) in the vicinity of the study site. The lowland areas (floodplains) along the Middle Fork lie between elevations of 550 and 600 feet NGVD. The natural surface topography within the floodplain is relatively flat with drainage toward the river.

3.2 BEDROCK GEOLOGY

The Danville area is located on the northeast flank of the Illinois basin. The bedrock strata are of Pennsylvanian age and in general dip gently southwestward toward the center of the basin.

The study site lies approximately 3 miles west of the central axis of the Danville Bedrock Valley, which is oriented northwest to southeast and midway between the Middle Fork and North Fork of the Vermilion River (Selkregg and Kempton, 1958).

Regionally, the Pennsylvanian bedrock consists of mainly shale with thin limestone, sandstone, and coal beds (Selkregg and Kempton, 1958). The bedrock surface elevation in the vicinity of the study site is between 500 and 600 feet NGVD (Willman et al., 1967). The rocks were originally deposited as unlithified sediments in coastal marshes or in shallow seas that repeatedly formed in the area. The shale was originally deposited as clay, while coal was formed from plants buried in the coastal swamps. Sandstone was deposited as sand and the limestone was formed by precipitation of carbonates and by accumulation of seashells on the sea floor (Selkregg and Kempton, 1958).

After the Pennsylvanian sediments were deposited, the seas retreated and the upper part of the bedrock was deeply eroded. During the Pleistocene epoch, continental glaciers advanced from the north and overrode the eroded bedrock surface (Selkregg and Kempton, 1958), leaving the glacial deposits that mantle the area today.

The principal formations within the Pennsylvanian bedrock in the region are, from upper to lower, the Bond, Shelburn, and Carbondale Formations. In the vicinity of the Site the principal formation is the Shelburn, which contains a major coal seam mined in the region, the Danville (No. 7). The Danville coal has been mined extensively in the region both as surface (strip) mines and underground mines. The northernmost mines identified by the ISGS (ISGS, 1996) are located in the immediate vicinity of the Site (Figure 5) within Township 20 North and Range 12 West. Additional information pertaining to coal seams and mines in the vicinity of the Site is provided in Section 4.2.1.1.

Several geologic logs obtained from the ISGS files (ISGS, 2001) were for exploratory borings for coal seams in 1910 and 1911 (Appendix I). In the vicinity of the site (Sections 20 and 21), the deepest borings were to depths of 166 and 131 feet BLS with bedrock intercepted at depths of 105 and 26 feet BLS, respectively. The formations intercepted by the two borings consisted of shale containing the following two coal seams:

- Danville (No. 7) coal at depths of 113 to 120 feet BLS and 79 to 83 feet BLS; and,
- Herrin (No. 6) coal at depths of 144 to 148 feet BLS and 110 to 114 feet BLS.

No limestone or sand layers were identified on these borings. However, further to the south in Section 28, a 1910 boring for the Big Four Railroad was progressed to 312 feet BLS. The Danville and Herrin coal seams were intercepted at depths of 72 and 96 feet BLS, respectively. Several other layers of coal, less than two feet in thickness, were intercepted. Five limestone layers ranging in thickness from one to eight feet were intercepted between 99 and 257 feet BLS. One sandstone layer was intercepted at 211 to 213 feet BLS. The entire bedrock interval cored was 247 feet, of which 220 feet was shale, 11 feet coal, 14 feet limestone, and 2 feet sandstone.

3.3 UNLITHIFIED DEPOSITS GEOLOGY

The deposits covering the bedrock in the region surrounding the study site are derived from recent river deposition (alluvial sediments) in the river valleys and glacial drift deposits occurring below the alluvial sediments and in the upland areas. The glacial and interglacial geologic events that shaped the topography seen today occurred during the Pleistocene Epoch, about two million to 12,000 years ago (ISWPTF, 1997). Thickness of these deposits in the region range from zero thickness along portions of the Middle Fork where bedrock is exposed to over 200 feet in the upland areas (Piskin and Bergstrom, 1975).

Although there were several major glaciations – pre-Illinoisan, Illinoisan, and Wisconsin – glaciers of only the last three are known to have entered the east-central Illinois region (Selkregg and Kempton, 1958). Each glaciation was followed by an interglacial period in which the climate warmed and the ice front moved back. The surficial features seen in the upland areas are part of the Gifford Moraine, which was formed during the Woodfordian Substage of the Wisconsinan Stage of glaciation (Willman and Frye, 1970).

Based on stack-unit maps of geologic materials to a depth of 15 meters (49.3 feet) prepared by Berg and Kempton (1988), the lowlands (floodplains) adjacent to the Middle Fork are characterized by the following downward sequence of unlithified deposits:

- Less than six meters (19.7 feet) of Cahokia Alluvium (i.e., alluvial sediments deposited by streams and rivers);
- Less than six meters of Henry Formation deposits of Wisconsinan age, which consist of glacial outwash dominated by sand and gravel; and,
- Less than six meters of Glasford Formation deposits of Illinoian age, which consist of silty and clayey diamictons.

Diamicton is unsorted, nonstratified sediment with a wide range of particle sizes (i.e., clay, silt, sand, gravel, cobbles, and boulders). When diamicton is due to glacial deposition it is known as till. The diamictons in the vicinity of the study site are till deposits characterized by a clay matrix containing variable percentages of silt, sand, gravel, cobbles, and boulders.

The unlithified deposits of the upland areas bordering the Middle Fork are characterized by the following downward sequence:

- Greater than six meters (19.7 feet) of Wedron Formation deposits of Wisconsinan age, which consist of silty and clayey diamictons; and
- Less than six meters of Glasford Formation silty and clayey diamictons (Berg and Kempton, 1988).

Unlithified deposits below 15 meters (49.3 feet) are not identified in the stack-unit maps, but based on published literature the Glasford Formation deposits either extend to the top of bedrock or are underlain by the Banner Formation of pre-Illinoisan age (i.e., greater than 500,000 years of age). The Banner Formation, which consists of till and intercalcated outwash where present, is draped over the bedrock surface and is generally deepest where the bedrock is deepest.

3.4 BEDROCK HYDROLOGY

The Pennsylvanian rocks generally have low porosities and permeabilities. The porosity of shale typically ranges from 1 to 20 percent (Walton, 1988). Representative horizontal field hydraulic conductivity (permeability) for shale typically ranges from $5x10^{-6}$ to $5x10^{-10}$ centimeters per second (cm/s). Representative aquitard field permeability ranges for shale, which is defined as the rate of vertical flow of water through a unit horizontal cross-sectional area of the aquitard, are $5x10^{-8}$ to $5x10^{-12}$ cm/s. In contrast to the low permeability of shale, coal deposits have horizontal permeability ranging from $5x10^{-2}$ to $5x10^{-5}$ cm/s (Walton, 1988).

The Pennsylvanian rocks in the region yield small amounts of water to wells from interconnected pores, cracks, fractures, crevices, joints, and bedding planes. Water-bearing openings are variable from place to place and are best developed near the surface in thin limestones and sandstones, when present, within the predominantly shale formation. Shallow sandstone and creviced limestone may yield small supplies in some areas, but water quality becomes poorer with increasing depth. The Pennsylvanian bedrock is not a reliable source of groundwater and the quality varies considerably. Small domestic supplies have been obtained from creviced limestone, permeable sandstone, or cracked shale and coal in the upper part of the bedrock (Selkregg and Kempton, 1958).

Water in the Pennsylvanian rocks becomes highly mineralized with increasing depth. Recharge to the Pennsylvanian rocks is derived locally from vertical leakage through the glacial drift and other unlithified materials that are in turn recharged from precipitation.

Water occurs in these rocks mainly under artesian and leaky-artesian conditions (Csallany, 1966).

3.5 UNLITHIFIED DEPOSITS HYDROLOGY

Alluvial deposits along the Middle Fork valley contain a wide variety of sediments ranging from clay to sand, gravel, and cobbles. The effective porosities for the types of sediments found in the vicinity of the study site range from 20 to 35 percent for poorly sorted sand and gravel alluvial deposits to 10 to 20 percent for the diamictons found in the upland areas (Fetter, 1980). Effective porosity, which is a measure of the pore space thorough which saturated flow can occur, typically ranges from 10 to 30 percent for poorly sorted sand and gravel deposits to 5 to 20 percent for diamictons (Walton, 1988).

Horizontal hydraulic conductivity for the alluvial deposits as measured by field tests can vary greatly depending on the percentage of fine-grained materials within those deposits. Deposits with materials ranging from sand to gravel typically have horizontal permeability ranging from 10^{-1} to 10^{-4} cm/s. Silt, clay, and mixtures of sand, silt, and clay typically have horizontal permeability ranging from 10^{-4} to 10^{-7} cm/s (USDI, 1981; Fetter, 1980).

Groundwater in the alluvial deposits discharges into the Middle Fork during most of the year with the exception of flood events, when localized flow-reversals may occur. No published information is available concerning the hydrology of the shallow deposits in the vicinity of the study site.

Permeable deposits capable of supplying sufficient groundwater for domestic use are scattered and discontinuous, with aquifers varying in permeability (Selkregg and Kempton, 1958). Water-well logs and a well location map were obtained from the ISGS during October 2001 (Appendix I; ISGS, 2001) for a four square mile area surrounding the study site. Ten water wells installed between 1967 and 1999 in upland areas were screened across permeable formations ranging in depth from 40 to 160 feet BLS. Eight of the ten wells were screened at depths greater than 100 feet BLS and had an average depth of 132 feet BLS. Groundwater was obtained primarily from sand and gravel deposits within the drift. The sand and gravel layers ranged from 3 to 13 feet in thickness. However, one well obtained groundwater from gravelly clay at 135 to 160 feet BLS and another well, drilled in 1999, was a dry hole.

4.0 STUDY SITE GEOLOGY AND HYDROLOGY

Characterization of the geology and hydrogeology at the study site is based on previous investigations conducted prior to construction of the East Ash Pond in 1989 and on new boring and monitoring well data from the current 2001-2002 investigation. Mathes Geotechnical Services, Inc. conducted a hydrogeologic investigation in a portion of the current study site (Mathes, 1987) prior to construction of the original East Ash Pond. The information used to describe the study site geology and hydrogeology is based on the borings and monitoring wells summarized in Table 1 and provided in Appendix C in addition to all of the field data collected during the course of the study in 2001 and 2002.

The two types of materials present at the study site consist of unlithified deposits (alluvium and glacial deposits) and bedrock. Each of these materials will be discussed in detail in order to establish a framework with which to understand the hydrogeology, and in later sections the geochemistry, of the site. Figure 7 shows the locations of all of the borings used in describing the geology of the site. Figure 9 shows the locations of the east-west (Figure 10) and north-south (Figure 11) geologic cross-sections through the study site.

4.1 UNLITHIFIED DEPOSITS

4.1.1 Alluvial and Glacial Geology

The cross-sections across the Site (Figures 9, 10, and 11) best demonstrate the correlation between topography and stratigraphy of the unlithified deposits. The other variable that affects the thickness and composition of the unlithified deposits is the bedrock surface topography. Glacial deposits are thickest (greater than 100 feet) where the shale bedrock decreases in elevation. The glacial materials consist primarily of low plasticity silty to sandy clays with occasional layers of silt, sand, and gravel.

The unlithified alluvial and glacial deposits in the vicinity of the East Ash Pond and within the floodplain generally range in thickness from 10 to 25 feet (Figure 12). Thickness of the alluvial deposits immediately adjacent to the Middle Fork is generally 10 to 15 feet. The unlithified deposits increase in thickness towards the uplands as the alluvial deposits pinch out and are supplanted by glacial deposits at higher topographic elevations.

Along the western portion of the study site, to the west of the East Ash Pond, the thickest glacial deposits range from 71 feet at Well MW22 to the north to 103 feet at Boring B208 to the south. North and east of the Middle Fork the thickness of the glacial deposits are 116 feet at Well MW30 and 155 feet at Well MW31, respectively.

The uppermost unlithified deposits in the floodplain consist of alluvium composed primarily of sand with occasional layers of silty clay. The sand is generally a fine to medium sand that contains silts, clays, and gravels in varying amounts. The sand in some areas may be overlain by silty to sandy clay. In places where the unlithified deposits in the floodplain become thicker, the alluvium may be underlain by glacial deposits consisting of outwash sand and gravel or diamictons. The shallow geology at Boring MW23, located within 25 feet of the south bank of the Middle Fork, has approximately 14 feet of alluvial deposits ranging from silt to gravel overlying eight feet of glacial deposits consisting of sandy clay with gravel.

4.1.2 Alluvial and Glacial Hydrology

Groundwater elevation within the alluvial and, where present, the glacial deposits within the floodplain generally conform to the ground surface topography. Prior to construction of the East Ash Pond, groundwater elevations documented by Mathes (1987) in the alluvial deposits generally ranged from five to six feet below ground surface in most of the alluvial wells where the East Ash Pond was constructed.

The only alluvial wells remaining from the 1987 study are MW13B and MW16B, located between the East Ash Pond and the Middle Fork. Hydrographs of groundwater levels in these two wells for 2002 are provided in Figures 13 and 14. Groundwater elevations measured in Well MW13B in 2002 have ranged from dry (no groundwater) in January and July to 573.44 feet NGVD in May, which is approximately 1.9 feet above the bottom of the screen and two feet above the bedrock surface. Groundwater elevations in Well MW16B were dry (no groundwater) in January, February, May, July, and August and were approximately 570 feet NGVD in March, April and June. The bottom of the well screen and the bedrock surface are at elevations of 566.5 and 566 feet NGVD, respectively.

Figure 15 shows the relationship of groundwater-levels in the alluvial wells MW26 and MW28 versus the Middle Fork of the Vermilion River elevations during 2002. During the period of measurement in 2002 groundwater levels in both these wells were above river elevation, demonstrating the potential for shallow groundwater discharge to the Middle Fork.

Groundwater elevations in the till and alluvial deposits in January 2002 (Figure 16) and hydrographs (Figure 15) demonstrate that groundwater elevations in the unlithified materials are higher than those in the adjacent Middle Fork through much of the year. The groundwater surface in the alluvial deposits fluctuates in response to changes in river stage and variations in precipitation. Based on the groundwater levels measured in wells MW13B and MW16B during 2002 and earlier years, groundwater elevations within the alluvial deposits in the vicinity of the East Ash Pond have not been elevated since the East Ash Pond was constructed. Groundwater levels are frequently measured at or near the base of the well screens of MW13B and MW16B, suggesting that the East Ash Pond has been hydraulically isolated from both the shale and alluvial deposits by soil/bentonite slurry walls and a compacted clay core.

Groundwater-level contour maps of the unlithified deposits could not be prepared due to the limited number and distribution of shallow wells. All of the shallow wells with the exception of Well MW10, which is installed in till, are adjacent to the Middle Fork. The presence of the East Ash Pond prevented the installation of upgradient wells within the alluvial deposits.

Groundwater gradients in the alluvial deposits prior to pond construction were determined by Mathes (1987). During the period of April to July 1987, horizontal gradients between downgradient wells MW13B and MW16B and upgradient alluvial wells ranged from 0.014 to 0.028 ft/ft and flow direction was towards the Middle Fork.

The hydraulic conductivity of the alluvium was estimated by Mathes (1987) by conducting field permeability (slug) tests. The horizontal hydraulic conductivity ranged from $1x10^{-3}$ to $7x10^{-3}$ cm/s. Field hydraulic conductivities determined during September 2002 for the alluvial deposits at monitoring wells MW26 and MW28, located on the north side of the Middle Fork across from the East Ash Pond, resulted in a computed geometric mean hydraulic conductivity of $1.5x10^{-2}$ cm/s (Table 4). The higher permeabilities calculated at wells MW26 and MW28 during 2002 relative to the lower values calculated by Mathes (1987) could be either from actual permeability differences of the alluvial deposits (i.e., coarser-grained or better sorted alluvium at MW26 and MW28 relative to the Mathes well locations) or systematic differences due to differences in analysis methods.

4.2 BEDROCK

The bedrock at the study site has been investigated using the following sources of data:

- Six borings from the 1987 Mathes hydrogeologic investigation;
- Two monitoring wells (MW13A and MW16A) remaining from the 1987 Mathes investigation;
- Eight borings and monitoring wells installed in 2001 as part of the current hydrogeologic investigation;
- Eight borings from the 2001 geotechnical investigation for expansion of the East Ash Pond;
- Eight borings from the 2002 coal mine investigation at the East Ash Pond;
- Geophysical logging of three boreholes by the Illinois State Geological Survey in 2001 (Appendix A);
- Geophysical investigation for location of coal mines by URS Corp in 2002;
- Bedrock core logs prepared by the ISGS (Appendix A); and,
- Mineralogical analyses of 19 rock samples (from three bedrock cores) by the ISGS in addition to geochemical modeling (Appendix A).

Based on the above sources of information a comprehensive evaluation of the bedrock geology and hydrology is presented below.

4.2.1 Bedrock Geology

The upper 75 feet of bedrock was cored at the study site and consists of non-marine and marine, silty and micaceous shales of the Pennsylvanian Age Shelburn Formation. The Shelburn Formation contains a major coal seam mined in the region, the Danville Coal, also called the No. 7 Coal. Geologic logs of selected cores (from borings for Wells MW25, MW30, and MW31) were prepared by the ISGS (Appendix A). Based on these logs, the shale has been described as medium to dark gray, massive, and with blocky fracture. Some intervals have thin interbeds of light gray shale.

The shale cores at Well MW25, located to the south of the East Ash Pond, are non-marine and contain abundant carbonized plant material. The shale cores at Well MW30, a background well located at the north end of the study area, have been identified as non-marine from 116 to 135 feet BLS and marine from 135 to 144 feet BLS, with abundant fossils, including brachiopods, gastropods, and bivalves. The Danville Coal was intercepted at 145 feet BLS before the coring was discontinued at 148 feet BLS. The coal contained abundant pyrite along cleats. The shale cores at Well MW31, located at the east end of the study site, also consist of a non-marine shale overlying a fossiliferous marine shale.

The upper zone of the shale is often weathered so that it appears as a greenish-gray to bluish-gray silty clay. Determination of the interval at which weathered shale turns into an unlithified silty clay is often based on the presence of fissility.

Based on the mineralogical analyses of 19 samples from three cores (from the borings for MW29, MW30, and MW31) conducted by the ISGS (Appendix A), the shale is composed principally of clay minerals and quartz with minor amounts of potassium feldspar, plagioclase feldspar, siderite, and marcasite or pyrite. The most abundant clay minerals in the cores were illite, kaolinite, and chlorite, with minor amounts of illite/smectite mixed-layer clay.

The depth to the top of the bedrock (i.e., shale), bedrock surface elevation, and depth/elevation of the Danville Coal are provided in Table 5. Figure 12, which shows the thickness of the unlithified deposits, also provides the depth to bedrock. Generally, the top of the shale occurs within 10 to 25 feet of ground surface in the vicinity of the East Ash Pond and rapidly increases in depth toward the western upland bordering the Site. The depth to bedrock is greatest towards the east, where it exceeds 150 feet.

Another way to view the shale bedrock is by looking at a bedrock elevation map, which can also be called a bedrock topography map. Figure 17 shows that the bedrock high within the study area occurs directly west of the East Ash Pond and the higher elevations trend toward the northeast. The lowest bedrock elevations occur to the north (530 feet NGVD at Well MW30) and the east (544 feet NGVD at Well MW31). The slope of the bedrock surface between the bedrock high and the eastern low at MW31 is approximately 0.018 foot per foot (95 feet per mile), which is a relatively mild slope when compared to the greater relief of the glacially-carved Middle Fork valley.

4.2.1.1 Danville (No. 7) Coal

The Danville (No. 7) Coal is found within the Shelburn Formation (ISGS, 1996) and was intercepted at eight locations (Table 5) in the vicinity of the East Ash Pond (Borings B201 to B208) and one location to the north of the Middle Fork (Boring MW30). Most of the borings advanced during both this and prior studies did not penetrate deep enough into the bedrock to intercept the coal seam. The top of the Danville Coal was intercepted at depths of 80 to 102.5 feet BLS on the floodplain adjacent to the East Ash Pond. Greater boring depths were required to intercept the coal seam in the upland areas. Borings B203, B208, and MW30 intercepted the coal seam at depths of 127, 152, and 144 feet BLS, respectively.

The top of the Danville Coal, or the void remaining where the coal was removed through mining, was intercepted at elevations between 496 and 509 feet NGVD. The thickness of the coal seam ranged from four to seven feet with an average thickness of 5.4 feet. Thin layers of coal interlayered with shale occurred above or below the main coal seam; these were not included in calculating the main seam thickness. The elevation of the top of the Danville Coal has been mapped on Figure 18. The Danville Coal generally decreases in elevation northward under the East Ash Pond at a gradient of 0.004 ft/ft (22 feet per mile). The coal increases in elevation from north of the East Ash Pond (493 to 496.6 feet NGVD at B201 and B202) to 501.5 feet NGVD at Well MW30 at a gradient of 0.0024 ft/ft (12.8 feet per mile).

Further information about the occurrence and mining of the Danville Coal in the vicinity of the East Ash Pond and other portions of the Vermilion Power Plant is provided in Section 1.4.3. Coal mine maps prepared by the ISGS, and other historical information pertaining to coal mining at the site is discussed. The potential effects of coal mines on subsurface geology, groundwater hydraulics, and water quality are discussed in greater detail in Sections 4.2.1.2, 4.2.2.5, and 5.2, respectively.

4.2.1.2 Geophysical Investigation of East Ash Pond

A geophysical investigation was conducted by URS Corp. in April 2002 (URS, 2002) to determine if mining occurred below the East Ash Pond, and if so to determine its lateral extent. The investigation was conducted by running five separate high-resolution seismic lines (Figure 19): three along the south, east, and north dikes (Lines A, B, and C, respectively), one calibration line (Line D) over an area of known mine voids based on test borings, and a final Line E over an area of suspected mine collapse features north of the secondary pond.

Based on the data obtained from the geophysics investigation, the findings are summarized below.

- The survey confirmed that mining occurred in the vicinity of the East Ash Pond; however, the mining appeared to be sporadic and of limited extent along the lines of seismic investigation.
- The surface depressions north of the secondary (polishing) pond (along Line E of Figure 19) are most likely mine collapse features. The largest of these features is about 100 feet across and shows 4 to 5 feet of vertical displacement. These features are pit-type collapses consistent with mining depths less than about 150 feet below grade.

- The survey detected 12 anomalies judged to be mine-related voids, collapse features, or partial collapse features along the five lines A through E. The mine-related voids are locations where the coal has been mined, leaving a void in the bedrock. The voids may eventually work to the surface resulting in settlement (surface depressions) similar to the collapse features north of the secondary pond.

4.2.2 Bedrock Hydrology

Hydrologic data have been incorporated from data collected from both the current investigation and from the previous hydrogeologic study completed in 1987 (Mathes, 1987). Both observed and predicted effects of coal mines on the hydrology of the bedrock are discussed at the conclusion of this section.

4.2.2.1 Hydraulic Conductivity

The upper zone of the shale is moderately weathered at the surface at most of the boring locations. Generally, the shale is massive with very few horizontal joints or partings. Some near vertical joints were observed near the surface, but these were typically irregular and closed.

The horizontal hydraulic conductivity of the shale was determined by Mathes (1987) from field permeability tests. Seven wells screened in the shale were tested and the computed hydraulic conductivity ranged from $4x10^{-10}$ to $1x10^{-8}$ cm/s. The geometric mean hydraulic conductivity of the shale based on the seven wells tested was $4.3x10^{-9}$ cm/s. The vertical hydraulic conductivity calculated from tests performed in the laboratory on one shale core ranged from $1x10^{-8}$ to $5x10^{-8}$ cm/s. The field and laboratory values for hydraulic conductivity of the shale all fall within the range of $5x10^{-6}$ to $5x10^{-10}$ cm/s reported by Walton (1988).

Field hydraulic conductivity tests conducted by Kelron in 2002 (Table 4) on seven monitoring wells screened within the Pennsylvanian Shale at the Site resulted in a higher estimate of permeability than Mathes (1987). The geometric mean hydraulic conductivity for all seven shale wells was $3x10^{-6}$ cm/s and the range was $1.04x10^{-4}$ to $1.45x10^{-7}$ cm/s.

The higher permeabilities calculated by Kelron during 2002 relative to the lower values calculated by Mathes (1987) could be either from actual permeability differences of the bedrock deposits or systematic differences due to differences in analysis methods.

4.2.2.2 Potentiometric Surface Maps

Potentiometric surface maps of the upper shale were prepared using groundwater-elevation data from January and May 2002 for the nine shale monitoring wells located at the study site (Figures 20 and 21). Groundwater elevations in the shale are highest in the topographically highest areas to the west and east of the Middle Fork. The lowest groundwater elevations occur at wells located adjacent to the Middle Fork. Flow lines derived from the potentiometric surface maps indicate that the Middle Fork of the Vermilion River in this area is a zone of discharge for the shale.

Horizontal hydraulic gradients in the shallow shale range from 0.026 to 0.038 ft/ft and are towards the Middle Fork. However, the upland wells are screened at shallower (MW22) or deeper (MW30 and MW31) elevations then most of the shale wells along the Middle Fork, possibly resulting in lower or higher gradient calculations then actually exist.

The occurrence of the Middle Fork in this area as a regional discharge zone for the shallow bedrock is supported by the upward vertical hydraulic gradients measured within the shale and the upward vertical hydraulic gradients observed during various periods and at multiple locations between the shale and the alluvium. The shale outcrops along the banks of the Middle Fork in this area and groundwater moving upward through the shale discharges into both the alluvium and directly into the Middle Fork.

The east-west and north-south cross sections shown on Figures 22 and 23, respectively, show the groundwater elevations at the monitoring wells relative to the geology

4.2.2.3 Vertical Hydraulic Gradients

Vertical hydraulic gradients are a measure of the change in total head with a change in vertical distance. The vertical hydraulic gradient measures the potential for groundwater to move upward or downward. Vertical gradients were calculated using the monthly groundwater data for the five paired (nested) well sets within the shale and alluvium and at one nested set within the shale. Gradients were computed by dividing the difference in the potentiometric head in the nested wells (i.e., dh) by the difference in the midpoint of the screened elevations (i.e., dl). A positive vertical gradient indicates a downward potential for groundwater movement and a negative gradient indicates an upward potential for groundwater movement.

All of the nested wells within the floodplain of the Middle Fork, with the exception of MW23/MW24, had an upward gradient from the shale to the overlying unlithified deposits during part of the eight months of monitoring (Table 6). Two sets of nested wells, MW13A/MW13B/MW32 and MW28/MW29, had large upward gradients during the entire study period with only one exception during May.

Nested wells MW13A/MW13B/MW32, located between the East Ash Pond and the Middle Fork, had an average upward gradient of 0.043 ft/ft between the shale well MW13B and alluvial well MW13A. The average upward gradient within the shale, between wells MW32 and MW13A, was even greater at 0.585 ft/ft. The only time that the gradient was measured as downward instead of upward between the alluvium and shale (MW13A and MW13B) was during May, when a slight downward gradient of 0.003 ft/ft was measured. However, during this same time the gradient within the shale was upward at 0.588 ft/ft. Figure 24 shows the relationship between water levels in the shale and alluvial wells relative to the land surface. The upward gradient within the shale is so great that groundwater at the deepest shale well (MW32) was under flowing artesian conditions during the study.

Nested wells MW16B and MW16A, also located between the East Ash Pond and Middle Fork, had an upward gradient during one of the three months during which the alluvial well (MW16B) was not dry (Figure 25). The vertical gradient at this location was downward during the March and April measurements and upward in June.

Nested wells MW28 and MW29, located northeast of the East Ash Pond on the north side of the Middle Fork, had an average upward gradient of 0.228 ft/ft between the shale and alluvium (Figure 26). The upward gradient over the eight months study period was very consistent, ranging from 0.204 to 0.251. Similarly, nested wells MW26 and MW27, located west of MW28/MW29, had an upward gradient of 0.01 to 0.053 ft/ft during five of the eight months (Figure 26). During March, April, and May the gradient at this location was downward from the alluvium to the shale at 0.001 to 0.032 ft/ft.

The only location within the floodplain where the gradient between the unlithified deposits and the shale was downward throughout the study was at nested wells MW23 and MW24, located north of the East Ash Pond. The unlithified deposits are thicker at this location and consist of finer grained alluvial deposits overlying glacial sediments. The 8-month average downward gradient at this location was 0.018 ft/ft. This is most likely a very localized flow cell where groundwater moves downward from the unlithified deposits to the shale. However, groundwater elevations in the shale during the study were still higher then river elevations, meaning that groundwater was discharging from the shale into the river.

Unlike the lowlands along the Middle Fork where groundwater within the shale is typically discharging upward into the unlithified deposits and the river, vertical groundwater movement in the uplands to the east, west, and north is downward. Figure 27 shows groundwater levels within the diamicton and shale wells MW10 and MW22, respectively. Groundwater levels in the glacial deposits are consistently higher than those in the underlying shale.

4.2.2.4 Groundwater-Flow Direction and Velocity

In upland areas bordering the Middle Fork valley the groundwater within the glacial deposits flows downward into the shale bedrock and along the top of the shale. Groundwater within the shale moves from upland areas and discharges into the regional discharge area of the Middle Fork (Figure 28). Groundwater generally moves upward from the shale deposits into the overlying alluvial (and glacial) sediments within the Middle Fork valley. Groundwater from the shale also discharges into the Middle Fork either through the overlying alluvium or, where bedrock is exposed, directly into the river. The groundwater elevations measured in the shale monitoring wells and shown on Figure 28 support this conceptualization of groundwater movement within the Pennsylvanian bedrock.

Groundwater flow velocity within the shale bedrock, computed based on a horizontal gradient of 0.027 ft/ft, hydraulic conductivity of 3×10^{-6} cm/s, and an effective porosity of 0.10, was 0.26 meters per year (0.85 feet per year), or 10.2 inches per year. The calculated velocity is based on the geometric mean hydraulic conductivity determined by Kelron in 2002.

4.2.2.5 Coal Mine Effects on Hydrology

The presence of a coal mine beneath portions of the East Ash Pond and study area has been documented based on exploratory borings, geophysics, and historic data acquired from the ISGS. The coal mine has been shown to have significant collapse features where the overlying bedrock (shale) has collapsed or partially collapsed downward into the void or mined coal seam. The collapse of the shale into the void translates upward through the shale, resulting in fracturing and in some cases surface subsidence. Both surface depressions from subsidence and fractured shale within bedrock cores were observed during coal mine investigation activities.

A hydrologic feature noted during the exploratory boring phase of the coal mine investigation was the presence of substantial hydraulic head within the coal and overlying fractured shale in proximity to mined areas. Borings B201 and B202 (Figure 18 and Appendix C), located northwest of the East Ash Pond and secondary pond, both intercepted groundwater under high hydraulic head that resulted in temporary suspension of drilling. Upon intercepting fractured shale above the coal mines during coring, the groundwater, which had accumulated within the fractured shale and underlying coal seam and voids, rose to over 30 feet above ground surface at an estimated flow volume of greater than 100 gallons per minute. The flow rate slowly subsided, but groundwater continued to flow above the ground surface for several hours following penetration of the fractured (collapsed) shale.

The high hydraulic head that developed in the coal mine and overlying shale would be expected based on the strong upward gradient measured within the shale in monitoring wells located along the Middle Fork of the Vermilion River (see Section 4.2.2.3). Since groundwater within the shallow Pennsylvanian bedrock at the study site discharges upward into the Middle Fork, the buildup of groundwater with high hydraulic head within a more permeable confined unit of coal and fractured shale would be expected.

In addition to the high hydraulic head associated with the mined area at borings B201 and B202, hydrogen sulfide gas (developed within the reducing environment of the sulfur-rich coal beds) vented at a high rate and continued to vent until the borings were sealed over 12 hours later.

A major concern at the study site is the affects of abandoned mines on the water quality of the overlying shale, alluvial deposits and the Middle Fork. Groundwater quality issues related to coal mines are discussed further in Sections 5.2.1.3 and 6.4.

5.0 WATER QUALITY

Water quality of the groundwater and surface water at the East Ash Pond and in the surrounding region has been extensively assessed during 2002. Kelron has assessed groundwater quality at background and site wells for 22 parameters. The ISGS has evaluated background groundwater quality for 40 parameters, including the carbon and hydrogen (tritium) isotopes. In addition, the ISGS evaluated the background bedrock groundwater quality for 31 samples acquired from databases from the ISGS, ISWS, IEPA, and Indiana Geological Survey.

DMG collected groundwater samples from all of the site and background wells, both in the unlithified and bedrock deposits, monthly from March through August of 2002. Various wells were also sampled during January and February 2002, but that data was not used in statistical analyses because it was only a subset of all wells used in the study, the wells were still being developed and uniform sampling equipment had not been put into all the wells.

During June 2002 the ISGS split samples with DMG at background wells MW25 through MW 30 (ISGS designation KELRON 25 to KELRON 30) for separate analysis by the ISGS laboratory. In addition to groundwater samples, surface water samples were collected by DMG from the East Ash Pond monthly from January through May of 2002 and from upriver on the Middle Fork from March through August 2002. No East Ash Pond water samples were collected after May 2002 because of construction activities associated with expansion of the East Ash Pond. All effluent discharges to the East Ash Pond were halted and the remaining water was pumped to the secondary pond for discharge to the Middle Fork, resulting in almost no standing water within the East Ash Pond. The last discharge from the East Ash Pond outfall into the Middle Fork of the Vermilion River during the study period was May 26, 2002. Discharging from the East Ash Pond System did not resume until January 2003.

Water quality analytical results for both groundwater and surface water are provided in Appendix J for analyses conducted by DMG. All analytical results for ISGS samples are included with their report in Appendix A.

5.1 GROUNDWATER QUALITY OF THE UNLITHIFIED DEPOSITS

Water quality in the unlithified deposits at the East Ash Pond was evaluated by looking at groundwater in background wells MW26 and MW28 and comparing to East Ash Pond well MW23, located north of the secondary (polishing) pond. Groundwater quality was also compared to surface water quality upgradient on the Middle Fork and in the East Ash Pond. In addition, isotopic data collected and evaluated by the ISGS are included for the background wells MW26 and MW28 (ISGS designation's KELRON 26 and KELRON 28). No water quality data were available for East Ash Pond wells MW10, MW13B, and MW16B due to the lack of water in the wells. Wells MW13B and MW16B are typically dry or have insufficient water-column depth to obtain groundwater samples.

5.1.1 Summary of Groundwater and Surface Water Quality

5.1.1.1 Major Anions and Cations

Groundwater compositions can be grouped into identifiable categories to assist in interpreting the distribution of principal types of groundwater. A hydrochemical facies diagram, also called a Piper diagram, displays the position of water samples with respect to their major cation and anions so that composition categories can be defined (Walton, 1998). Figure 29 shows the position of groundwater samples obtained in June 2002 from East Ash Pond well MW23 and background wells MW26 and MW28. Also shown on the diagram are the surface water samples from the East Ash Pond and from the Middle Fork (labeled as "Upstream River" on the diagram).

The principal anion in background wells MW26 and MW28 and in the Middle Fork sample is bicarbonate. Well MW23 has no dominant type of anion, but is dominated by both bicarbonate and sulfate. In contrast is the East Ash Pond water sample, which has sulfate as the dominant anion. The cation portion of the diagram is much more definitive in grouping the data. All three of the wells and the Middle Fork sample cluster together between calcium and magnesium while the East Ash Pond sample is clearly dominated by calcium. Based on the observed cations and anions, and looking at the upper portion of the diagram, the hydrochemical facies of the water samples can be defined as follows: wells MW26, and MW28 and the Middle Fork of the Vermilion River are calcium-magnesium and bicarbonate type waters; the East Ash Pond is a calcium-sulfate dominated water; and, MW23 falls in-between.

The above categorizations of water types based on principal anions and cations are further demonstrated by the Stiff diagrams shown on Figure 30. The Stiff diagram for the June 2002 water samples shows the similarity between all three of the wells. The higher sulfate in well MW23 relative to bicarbonate is again demonstrated, but all other cations and anions in MW23 are similar to the background wells. The East Ash Pond water is clearly dominated by the cation calcium and the anion sulfate.

The correlation between parameters in groundwater within the unlithified materials is displayed on Table 7. The cations calcium and magnesium have a high correlation of 0.84, which indicates that these parameters vary proportionately within groundwater adjacent to the Middle Fork. The bicarbonate anion has a very high correlation of 0.94 with magnesium and the sulfate anion has a very high correlation of 0.92 with calcium. TDS concentrations in the shallow groundwater are principally controlled by the cations calcium and magnesium (correlation coefficients with TDS of 0.97 and 0.89, respectively) and the anions bicarbonate and sulfate (correlation coefficients with TDS of 0.72 and 0.89, respectively).

5.1.1.2 Statistical Analyses

In order to summarize all of the water quality data generated during 2002 so that some clear observations can be made about both the major and minor ions, including trace elements, several types of tables and figures were prepared. Each of the forms of analysis is discussed below with a summary of all the inorganic data and statistical analyses provided in Section 5.1.1.3.

Detailed Statistical Tables

A summary of groundwater quality data for the unlithified wells, East Ash Pond, and Middle Fork of the Vermilion River (Table 8) lists the mean, median, minimum, and maximum concentration for each chemical parameter. The comments under each parameter include the results of a non-parametric test called the Wilcoxon Rank-Sum Test for Comparison of Means. This statistical test, which has no distributional assumptions, was used to compare the data collected for each parameter at East Ash Pond well MW23 versus the pooled background data from wells MW26 and MW28 to determine if there was any significant difference between their means at a 95 percent confidence level. The detailed test results (Appendix K) were used to make one of three statements for each individual parameter: (1) groundwater from the East Ash Pond well MW23 comes from the same population as the background wells; (2) groundwater from the East Ash Pond well has a statistically significant lower concentration than the background wells; or, (3) groundwater from the East Ash Pond well has a statistically significant higher concentration than the background wells.

Box-and-Whisker Plots

The box-and-whisker plots in Figure 31 provide a visual representation of some of the statistical data presented on Table 8. The rectangular part of the plot extends from the lower quartile to the upper quartile, covering the center half of each sample. The center lines within each box show the sample medians and the plus signs the sample means. The whiskers extend from the box to the minimum and maximum values in each sample, except for any outside or far outside points, which are plotted separately. Outside points are points that lie more than 1.5 times the interquartile range above or below the box and are shown as small squares. Far outside points, more than 3 times the interquartile range above or below the box, are shown as small squares with plus signs through them. Far outside points may indicate outliers or a highly skewed distribution.

Cluster Analysis

Cluster analysis is a descriptive statistical method used to identify groupings (i.e., clusters) of samples or variables. Cluster analysis is used to reveal the latent structure within a data set and is an exploratory tool only. The data from the East Ash Pond study were analyzed using cluster analysis to demonstrate the following:

- grouping of samples from wells and the Middle Fork into clusters based on water quality as defined by absolute concentrations of the major cations and anions (alkalinity, calcium, chloride, potassium, magnesium, sodium, and sulfate);
- grouping of samples from wells and the Middle Fork into clusters based on water quality as defined by absolute concentrations of minor and trace metals (aluminum, boron, barium, iron, lithium, manganese, selenium, and strontium);
- grouping of major cations and anions into clusters with common characteristics; and,
- grouping of minor and trace metals into clusters with common characteristics.

The cluster analysis results can be presented in several ways. In order to visually interpret how the data have been categorized, a graphical depiction of the clusters is shown with a dendrogram. The dendrogram is a linkage tree which first links those samples or parameters that have the greatest similarity (i.e., highest correlation). Each subsequent linkage (or cluster) is less similar than earlier linkages. The greater the distance on the y-axis between linkages, the lower the significance between the linked samples or variables.

The dendrograms of major and minor/trace ions (Figure 32) both show that the first sets of clusters are within each sample location (i.e., samples from each monitoring point cluster together first since they are most similar). The next set of clusters occurs between some of the samples from background well MW26 and samples from the Middle Fork. Although the major ions do not result in any significant linkages after well MW26 and the Middle Fork are grouped together, the minor/trace metals in the water samples result in clustering of East Ash Pond well MW23 with MW26 and the Middle Fork. The final cluster, based on minor/trace metals, is the samples from background well MW28. Based on these dendrograms, the samples from well MW28 are the least similar to samples from the other locations.

The dendrograms formed by looking only at the parameters irrespective of the specific sample locations (Figure 33) used the same data as for Figure 32. The most similar major ions (i.e., the first linkages) were calcium and sulfate followed by: magnesium, alkalinity, sodium, chloride, and finally potassium. The relationship between the parameters clustered together in the dendrograms is partially quantified by the correlation coefficients listed in Table 7. The correlation coefficient between calcium and sulfate was very high at 0.92. The correlation between calcium and magnesium was 0.84 and between sulfate and magnesium was 0.97. Alkalinity had a correlation with magnesium of 0.94. The least similar parameter to the other major ions was potassium, which had a negative (i.e., inverse) correlation with magnesium of −0.69.

The dendrogram for the minor/trace metal parameters (Figure 33) has the first clusters between iron and manganese (correlation coefficient {R} = 0.82 [Table 7]) and lithium and strontium (R = 0.89). These two clusters are then clustered with selenium. Later linkages with boron, barium, and aluminum are much less significant as the similarities between parameters in all of the groundwater and Middle Fork river samples markedly decrease.

5.1.1.2 Summary of Data

All of the statistical analyses and observations listed on Table 8 and graphically presented in Figures 29 to 33 are summarized and consolidated onto Table 9 so that all of the parameters can be assessed together. Based on the Wilcoxon Rank-Sum tests presented in Table 8, the only parameters that have statistically significant greater concentrations in East Ash Pond well MW23 relative to background groundwater concentrations are boron, chloride, potassium, sodium, and sulfate. Each of these parameters will be discussed in detail below along with other trace parameters.

Boron
The box-and-whisker diagram for boron on Figure 31 shows the relative concentrations of boron in the East Ash Pond versus the background wells, well MW23, and the Middle Fork of the Vermilion River. The median boron concentration of 0.27 milligrams per liter (mg/L) in MW23 is 0.15 mg/L above background concentrations, but is 38 times lower than the 10 mg/L median concentration in the East Ash Pond samples. Figure 34a shows the trend in boron concentrations in shallow groundwater versus the river during 2002. Boron concentrations in groundwater at MW23 trend independently from wells MW26 and MW28 and the river. Boron in wells MW26 and MW28 has a parallel trend. Boron concentrations in the river generally lay between those observed in MW26 and MW28.

Boron concentrations in MW23 are due to either natural variation as a result of geologic and hydrologic differences at MW23 relative to the background wells or may be partly affected by the presence of the former coal mine, mine spoil, or the presence of the East Ash Pond. Any impact by the East Ash Pond on shallow groundwater quality is uncertain due to the similarity between groundwater quality impacts from coal ash disposal, coal mine spoil, and coal mine drainage.

Chloride
Chloride concentrations on the box-and-whisker diagram (Figure 31) are similar between the East Ash Pond well MW23 and the Middle Fork of the Vermilion River. Well MW23 has a median chloride concentration of 38.5 mg/L, which is only 9 mg/L above the median Middle Fork concentration. Chloride in MW23 is 5.2 times lower than the median East Ash Pond concentration of 200 mg/L. Chloride has a high correlation of 0.89 (Table 7) with boron based on data from both background wells and MW23. The natural correlation between boron and chloride makes it difficult to distinguish the co-variance of these parameters in groundwater versus potential impacts from the East Ash Pond water, which also has a high correlation between boron and chloride.

The trend in chloride concentrations (Figure 34b) are very different between groundwater sampled from well MW23 versus wells 26, 28, and the river. Wells 26 and 28 have similar chloride trends but are markedly different from chloride concentration changes in the Middle Fork.

The chloride concentrations observed in MW23 are most likely due to either natural variation as a result of geologic and hydrologic differences at MW23 relative to the background wells or may be partly affected by the presence of the former coal mine and mine spoil. Impact by the East Ash Pond on shallow groundwater quality is uncertain due to the similarity between groundwater quality impacts from coal ash disposal, coal mine spoil, and coal mine drainage.

Potassium
Potassium concentrations are similar between East Ash Pond wells MW23, background wells, and the Middle Fork. Median concentrations of 3.25 mg/L in MW23 are 0.9 mg/L above background. Potassium in MW23 is 7.7 times lower than the median East Ash

Pond concentration of 25 mg/L. The trend in potassium concentrations (Figure 34c) demonstrate the similarity between background wells MW26 and MW28, although concentrations in MW23 and the river also have similar trends to the background wells.

The potassium concentrations observed in MW23 are most likely due to either natural variation as a result of geologic and hydrologic differences at MW23 relative to the background wells or may be partly affected by the presence of the former coal mine or associated mine spoils. Impact by the East Ash Pond on potassium concentrations is uncertain due to the similarity between groundwater quality impacts from coal ash disposal, coal mine spoil, and coal mine drainage. However, the similarity between potassium concentration trends in well MW23 and background wells suggests that the East Ash Pond has negligible impact on shallow groundwater concentrations of potassium.

Sodium

Median sodium concentration of 19.5 mg/L in well MW23 is 2.5 mg/l above the median in the background well MW28 and 10.3 mg/L above the median concentration in the Middle Fork of the Vermilion River. Sodium in MW23 is 7.2 times lower than the median East Ash Pond concentration of 140 mg/L. Maximum observed sodium concentrations in 2002 at MW23 and the East Ash Pond were 26 and 240 mg/L, respectively. Similar to chloride trends, the trend in sodium concentrations (Figure 34d) are very different between groundwater sampled from well MW23 versus wells 26, 28, and the river.

The sodium concentrations observed in MW23 are most likely due to either natural variation as a result of geologic and hydrologic differences at MW23 relative to the background wells or may be partly affected by the presence of the former coal mine and mine spoil. Impact by the East Ash Pond on shallow groundwater quality is uncertain due to the similarity between groundwater quality impacts from coal ash disposal, coal mine spoil, and coal mine drainage.

Sulfate

Sulfate concentrations in East Ash Pond well MW23 in 2002 ranged from 280 to 380 mg/L with a median concentration of 320 mg/L. Concentrations in surface water at the East Ash Pond ranged from 440 to 1,500 mg/L with a median concentration of 780 mg/L, or approximately 2.4 times higher than observed in groundwater at MW23. Sulfate concentrations in the shallow unlithified deposits at MW23 and MW28 have a high variability, as seen by the box-and-whisker diagram for sulfate (Figure 31). Sulfate also has a very high correlation of 0.92 with calcium (Table 7) and these two parameters are within the first (most similar) cluster in the dendrogram discussed earlier (Figure 33).

Trends in sulfate concentration (Figure 34e) at well MW23 and background well MW28 are very similar. Sulfate concentrations at wells MW23 and MW28 are above those observed in background well MW26 and the river, which also trend closely together.

The concentrations observed for sulfate in well MW23 can partly be attributed to natural groundwater variations in conjunction with changes observed for calcium. Calcium in groundwater at MW23 is statistically from the same population as background groundwater concentrations and the high correlation between calcium and sulfate in groundwater suggests that the sulfate concentrations at MW23 are also partly natural. Impacts by the East Ash Pond, coal mine, or mine spoils on sulfate concentrations are uncertain.

Aluminum, Barium, Lithium, Molybdenum, Selenium, Strontium, and Vanadium
Concentrations of the trace metals aluminum, barium, lithium, molybdenum, selenium, strontium, and vanadium in the East Ash Pond during 2002 were all significantly higher than those in groundwater within the unlithified deposits (background and on-site). Lithium, molybdenum, selenium, and vanadium concentrations in all shallow groundwater samples were typically below or near their detection limits compared to significantly higher concentrations in the East Ash Pond surface water samples.

Statistically, the trace metal groundwater parameters sampled at well MW23 near the East Ash Pond are from the same population as the background groundwater (exception is barium, which has lower concentrations than background). The deficiency of all the trace metals in shallow groundwater near the East Ash Pond, as compared to their ubiquity in the surface water of the pond itself, suggests there is no impact on shallow groundwater by the East Ash Pond.

5.1.2 Exceedances of Groundwater Quality Standards

During March through August 2002 no groundwater samples collected from the unlithified deposits at the East Ash Pond or from the background monitoring wells exceeded any of the Class I or II groundwater standards (Illinois Administrative Code [IAC] Title 35, Part 620, Section 620.410 and 620.420) for inorganic parameters. However, background well MW28 did exceed the sulfate and TDS standards of 400 and 1,200 mg/L, respectively, during January and February 2002.

5.2 GROUNDWATER QUALITY OF THE BEDROCK DEPOSITS

Water quality in the bedrock was evaluated by comparing background wells to the East Ash Pond wells. Both the ISGS and Kelron investigated background groundwater quality through independent investigations. The ISGS investigated background groundwater quality of the Pennsylvanian age bedrock in two ways: literature and database search, including unpublished data sources, for information pertaining to groundwater geochemistry of shale and coal in Illinois and the Midwest; and, groundwater sampling and analysis during June 2002 using four private wells in Vermilion County and four of the site background wells (MW25, MW27, MW29, and MW30). Kelron investigated the background groundwater quality of the bedrock by utilizing the same four Site wells as the ISGS in addition to well MW31 and had the wells sampled by DMG for 6 consecutive months from March through August 2002.

Utilizing the data collected and analyzed by both the ISGS and DMG, the groundwater quality data from the background wells was grouped according to the source of the data and compared to the East Ash Pond bedrock wells (MW13A, MW16A, MW22, MW24, and MW32) using a variety of statistical and graphical methods.

5.2.1 Summary of Groundwater Quality

5.2.1.1 Major Anions and Cations

The major anions and cations of background and East Ash Pond wells are graphically displayed on the hydrochemical facies (Piper) diagram of Figure 35 and the Stiff diagrams of Figure 36. The principal cations in groundwater from the background wells are typically sodium and potassium, although a few wells have groundwater with higher concentrations of calcium and magnesium. The median value derived from the ISGS literature and database search, which is weighted heavily by groundwater samples from coal-bearing deposits, is dominated by calcium. A ternary plot of the cation data for background bedrock wells (Figure 37; modified from ISGS Figure 13, Appendix A) displays the linear nature of the data points. The ISGS (Mehnert and Dreher, 2002) hypothesized that "groundwater with greater concentrations of sodium plus potassium (Na+K, e.g., KELRON 27 or KELRON 29) migrated over a longer distance from the recharge area to the respective well than samples with lower concentrations of Na+K (e.g., well 23343). During migration, the groundwater dissolved increasingly greater amounts of sodium from the aquifer rocks and increasing amounts of calcium and magnesium were removed from the water, probably by adsorption of clay minerals in the aquifer rocks."

Cation data for groundwater sampled from the East Ash Pond wells plots along the same line as the background wells. Most of the East Ash Pond wells are dominated by sodium and potassium relative to calcium and magnesium. Conversely, surface water sampled from the East Ash Pond is dominated by calcium.

The principal anion in groundwater from background wells and East Ash Pond wells in the vicinity of the Site is chloride. The median value from the ISGS database is dominated by bicarbonate. Surface water from the East Ash Pond is also dominated by sulfate.

The correlation between parameters in groundwater sampled from background and East Ash Pond bedrock wells at the Site is displayed on Table 10. The cations calcium and magnesium have a very high correlation of 0.98, which reflects the data shown on the Piper and Stiff diagrams that calcium and magnesium have been removed from the groundwater by clay minerals in the shale during migration. Sodium and chloride, the principal cations and anions in bedrock groundwater at the Site, are also highly correlated with a coefficient of 0.94. These two parameters, as will be discussed later, account for much of the variability observed in groundwater from the bedrock. In addition, sodium and chloride have correlation coefficients of 0.88 and 0.93, respectively, with TDS. A large amount of the TDS observed in groundwater from the bedrock wells, both background and at the East Ash Pond, is directly correlated to changes in sodium and chloride concentrations.

As observed by the ISGS (Mehnert and Dreher, 2002) for samples from bedrock wells, "sodium and chloride concentrations apparently increase at the expense of calcium, magnesium, and other high valence cations due to adsorption as groundwater moves away from recharge areas."

5.2.1.2 Statistical Analyses

Several types of tables and figures were prepared to summarize the groundwater quality data for the bedrock. Each of the forms of analysis is discussed in the following sections. A summary of all the anlyses for each of the major ions and minor ions, including trace metals, is provided in Section 5.2.1.3

Detailed Statistical Tables

A summary of groundwater quality data is presented in Table 11 for the following groupings of data:

- Background bedrock wells at the Site using all results from the 6 monthly samplings from March through August 2002: wells MW25, MW27, MW29, MW30, and MW30;
- ISGS background data for 27 wells derived from the scientific literature and state databases (see Appendix A);
- ISGS background data for 4 wells sampled and analyzed by the ISGS in Vermilion County: wells 1349, 21903, 23343, and 25531;
- East Ash Pond bedrock wells using all results from the 6 monthly samplings in 2002: MW13A, MW16A, MW22, MW24, and MW32; and,
- East Ash Pond surface water samples from the 5 monthly samplings from January to May 2002.

The statistical summary lists the mean, median, minimum, and maximum concentration for each parameter. The comments under each parameter include the results of a non-parametric test called the Wilcoxon Rank-Sum Test for Comparison of Means. This statistical test, which has no distributional assumptions, was used to compare the data collected for each parameter at each individual East Ash Pond bedrock well (MW13A, MW16A, MW22, MW24, and MW32) versus the pooled background data from the Site background wells (MW25, MW27, MW29, MW30, and MW31) to determine if there was any significant difference between their means at a 95 percent confidence level. The detailed test results (Appendix K) were used to make one of three statements for each individual parameter: (1) groundwater from the East Ash Pond well(s) comes from the same population as the background wells; (2) groundwater from the East Ash Pond well(s) has a statistically significant lower concentration than the background wells; or, (3) groundwater from the East Ash Pond well(s) has a statistically significant higher concentration than the background wells.

Box-and-Whisker Plots

The box-and-whisker plots in Figure 38 provide a visual representation of some of the statistical data presented in Table 11. The rectangular part of the plot extends from the lower quartile to the upper quartile, covering the center half of each sample. The center-lines within each box show the sample medians and the plus signs the sample means. The whiskers extend from the box to the minimum and maximum values in each sample, except for any outside or far outside points, which are plotted separately. Outside points are points that lie more than 1.5 times the interquartile range above or below the box and are shown as small squares. Far outside points, more than 3 times the interquartile range above or below the box, are shown as small squares with plus signs through them. Far outside points may indicate outliers or a highly skewed distribution.

Cluster Analysis

Cluster analysis is a descriptive statistical method used to identify groupings (i.e., clusters) of samples or variables. Cluster analysis is used to reveal the latent structure within a data set and is an exploratory tool only. The data from the East Ash Pond study was analyzed using cluster analysis to demonstrate the following:

- grouping of samples from background wells and East Ash Pond wells at the Site into clusters based on water quality as defined by the major cations and anions (alkalinity, calcium, chloride, potassium, magnesium, sodium, and sulfate);
- grouping of samples from background wells and East Ash Pond wells at the Site into clusters based on water quality as defined by minor and trace metals (aluminum, boron, barium, iron, lithium, manganese, and strontium);
- grouping of major cations and anions into clusters with common characteristics; and,
- grouping of minor and trace metals into clusters with common characteristics.

The cluster analysis results can be presented in several ways. In order to visually interpret how the data have been categorized, a graphical depiction of the clusters is shown with a dendrogram. The dendrogram is a linkage tree which first links those samples or parameters that have the greatest similarity. Each subsequent linkage (or cluster) is less similar than earlier linkages. The greater the distance on the y-axis between linkages, the lower the significance between the linked samples or variables.

The dendrogram of major ions (Figure 39 top) shows that the first sets of clusters are typically within each sample location (i.e., groundwater sample data from each monitoring point cluster together first since they are most similar). The next set of clusters occur between East Ash Pond well MW32 and background well MW30, followed by a cluster with East Ash Pond well MW13A. Wells MW13A and MW32, located immediately east of the East Ash Pond, are nested within the bedrock; well MW32 is the screened at a lower elevation than well MW13A. Another separate clustering occurs between East Ash Pond wells MW22 and MW24 with background wells MW27 and MW29, located on the other side of the Middle Fork of the Vermilion River. The clusterings of background wells with East Ash Pond wells based on major ion composition is indicative of strong similarities between the overall groundwater composition at these locations and depths within the Pennsylvanian bedrock.

The dendrogram of minor ions and trace metals (Figure 39 bottom) has a slightly different set of clusters than that of the major ions above. The first sets of clusters following those within each sample location are between wells MW13A - MW32, MW27 - MW29, and MW22 - MW24. Wells MW13A and MW32 are the nested wells that clustered together for the major ions, but well MW30 no long clusters with these wells due to the differences in the trace element composition of the groundwater. This may be due to the presence of coal within the screened interval of well MW30. The next level of clusters occurs between all of the wells listed above: MW13A, MW32, MW27, MW29, MW22, and MW24; four of these wells are at the East Ash Pond and two (MW27 and MW29) are background wells. The next set of clusters in order of distance along the dendrogram incorporates background wells MW25 and MW31 followed by East Ash Pond well MW16A. The trace metal data from MW30 is very dissimilar from all other wells and is clustered last.

The dendrograms formed by looking only at the parameters irrespective of the specific sample locations (Figure 40 used the same data as for Figure 39. The most similar major ions (i.e., the first linkages) were calcium-magnesium and sodium-chloride followed by: calcium-magnesium and sulfate, sodium-chloride and alkalinity, and sodium-chloride-alkalinity and potassium. The relationship between the parameters clustered together in the dendrograms is partially quantified by the correlation coefficients listed in Table 10. The correlation coefficients between calcium-magnesium and sodium-chloride were very high at 0.98 and 0.94, respectively. The correlations between calcium and magnesium with sulfate were both 0.86. The correlations between sodium and chloride with alkalinity were 0.70 and 0.46, respectively.

The dendrogram for the minor/trace metal parameters (Figure 40, bottom) has the first clusters between barium and iron (correlation coefficient {R} = 0.87 [Table 10]) and aluminum and lithium (R = 0.63). Next, barium-iron is clustered with strontium (R = 0.54 and 0.56, respectively) and aluminum-lithium is clustered with boron (R= -0.02 and 0.47, respectively). Manganese concentrations in groundwater at the study site are very poorly correlated with all the other minor/trace metals and there is no cluster formed with any other parameters.

5.2.1.3 Summary of Data

All of the statistical analyses and observations listed on Table 11 and graphically presented in figures 35 to 40 are summarized on Table 12 so that all of the parameters can be assessed together. Based on the Wilcoxon Rank-Sum tests presented in Table 11, the only parameters that have statistically significant greater concentrations in any of the East Ash Pond wells relative to background groundwater quality in the bedrock are the following:

- Boron at wells MW13A and MW32;
- Calcium at well MW16A;

- Lithium at wells MW13A and MW16A;
- Magnesium at well MW16A;
- Manganese at wells MW13A and MW16A;
- Phosphorus at well MW24;
- Sodium at wells MW13A and MW32;
- Sulfate at wells MW16A, MW22, and MW24; and,
- TDS at wells MW13A and MW32.

Each of these parameters and wells listed above will be discussed in detail below. Other parameters measured in groundwater samples from the bedrock and East Ash Pond will also be discussed.

Boron

The box-and-whisker diagram for boron on Figure 38 shows the relative concentrations of boron in the East Ash Pond wells relative to background wells and the East Ash Pond. The range of boron concentrations in the Site background wells during 2002 was between 0.20 and 1.30 mg/L versus a range for the East Ash Pond wells of 0.30 to 1.60 mg/L. Median boron concentrations at East Ash Pond wells MW13A and MW32 were 1.40 and 1.50 mg/L, respectively. These median boron concentrations are approximately 7 times lower than those observed in the East Ash Pond sluice water.

Wells MW13A and MW32 are both at a location where groundwater has a large upward vertical gradient as it discharges into the alluvial deposits and the Middle Fork of the Vermilion River. The similarity of boron concentrations at this nested well location, along with the upward gradient, indicates that the occurrence of boron is either naturally occurring or may be influenced by the occurrence of past coal mining activities as discussed earlier in Section 4.2.2.5.

Calcium

Calcium concentrations in all of the East Ash Pond wells with the exception of MW16A are either equal to or below background concentrations based on the Wilcoxon Rank-Sum Test. Well MW16A has a median calcium concentration of 135 mg/L, which is above the range of values observed at the Site background wells (median values of 29.5 to 85.5 mg/L). However, the concentrations measured for calcium at well MW16A in 2002 are well above the historical median of 33 mg/L for the period of 1993 through 2001. Calcium concentrations at well MW16A have historically been similar to those at well MW13A and the Site background wells. East Ash Pond surface water samples had calcium concentrations ranging from 150 to 450 mg/L and a median concentration of 350 mg/L.

It is uncertain what factors may have resulted in higher calcium concentrations at well MW16A during 2002. However, well MW16A also had historically high concentrations of magnesium, sulfate, and TDS during 2002. Calcium and magnesium are very highly correlated ($R = 0.98$, Table 10) in groundwater at the Site and the higher observed concentrations of both these parameters at only one location may be due to the affects of the former coal mine on groundwater geochemistry.

Chloride

Chloride concentrations at the East Ash Pond wells are generally below those observed at Site background wells (Figure 38). The highest chloride concentrations at the East Ash Pond are found in groundwater at nested wells MW13A and MW32, with median concentrations of 570 and 845 mg/L, respectively. These concentrations are below the median chloride concentrations of 840 and 1,200 mg/L measured in groundwater at Site background wells MW25 and MW30, respectively. It is of interest that the highest chloride concentrations occur at well MW30, which is partially screened across coal deposits, and at wells MW25, MW13A, and MW32, all of which occur near (and may be impacted by) former coal mines.

The median chloride concentration in surface water at the East Ash Pond ranged from 100 to 240 mg/L with a median value of 200 mg/L during the study period, or approximately 3 to 4 times lower than the median chloride concentrations observed at wells MW13A and MW32. Chloride in groundwater at the Site is naturally occurring at most bedrock well locations, including the elevated concentrations observed at well MW30 due to coal deposits. However, elevated concentrations observed in some bedrock wells may occur due to former coal mines located nearby.

Lithium

Although lithium concentrations in groundwater at East Ash Pond wells MW13A and MW32 were identified by the Wilcoxon Rank-Sum Test as being above site background, a closer look at the data on the box-and-whisker diagrams (Figure 38) and on Table11 show that the relative concentrations of lithium in wells MW13A and MW32 are within the range of data at Site background wells MW25 and MW30. Lithium concentrations in all of the East Ash Pond wells range from non-detect at 0.005 mg/L to 0.19 mg/L versus a range of non-detect to 0.40 mg/L in the Site background wells.

Similar to observed chloride concentrations, the lithium concentrations in groundwater at wells MW13A and MW32 are higher than other East Ash Pond wells but within the range of values observed in background wells MW25 and MW30. As discussed for chloride, the higher lithium concentration at well MW30 may be caused by the presence of coal in the screened interval. Similarly, higher lithium concentrations in wells MW13A, MW32, and MW25 may be related to the presence of former coal mines.

Lithium concentrations in the East Ash Pond ranged from non-detect to 0.30 mg/L with a median concentration of 0.27 mg/L, or approximately 3 to 14 times greater than the median concentrations observed in the East Ash Pond wells.

Magnesium

Magnesium concentrations in all of the East Ash Pond wells with the exception of MW16A are either equal to or below background concentrations based on the Wilcoxon Rank-Sum Test. Well MW16A has a median manganese concentration of 72.5 mg/L, which is above the range of values observed at the Site background wells. However, the concentrations measured for magnesium at well MW16A in 2002 are well above the historical median of 20 mg/L for the period of 1993 through 2001. Magnesium concentrations at well MW16A have historically been similar to those at well MW13A and the Site background wells. East Ash Pond surface water samples had magnesium concentrations ranging from 8.4 to 42 mg/L and a median concentration of 30 mg/L.

It is uncertain what factors may have resulted in higher magnesium concentrations at well MW16A during 2002. However, well MW16A also had historically high concentrations of calcium, sulfate, and TDS during 2002. Magnesium and calcium are very highly correlated ($R = 0.98$, Table 10) in groundwater at the Site and the higher observed concentrations of both these parameters at only one location may be attributed to impacts from the former coal mine.

Manganese

As with magnesium, manganese concentrations in well MW16A are statistically above Site background concentrations. The highest manganese concentrations observed in any of the East Ash Pond or background wells occurs in groundwater at well MW16A. The median manganese concentration at well MW16A during the study was 14 times greater than the median in surface water from the East Ash Pond. Since manganese is highly correlated with magnesium concentrations in groundwater at the Site ($R = 0.86$, Table 10), the higher manganese concentrations observed at well MW16A would be expected based on the high magnesium concentrations also observed in groundwater at this location.

Manganese concentrations at Well MW13A were also above Site background, but were similar to the concentrations observed at background well MW31. The concentrations at MW13A were also within the range documented by the ISGS from the scientific literature and state databases (Table 11).

The degree to which manganese concentrations at MW13A and MW16A might be impacted by the presence of former coal mines is unknown, although any decrease in pH values or presence of reducing conditions associated with former mines would result in increased manganese concentrations in groundwater.

Phosphorus

Phosphorus concentrations in all of the East Ash Pond wells with the exception of MW24 are either equal to or below background concentrations based on the Wilcoxon Rank-Sum Test. Well MW24 has a median phosphorus concentration of 0.047 mg/L, which is within the range observed in groundwater at wells MW16A and MW31. Phosphorus concentrations at well MW24 are most likely naturally occurring based on concentrations observed in the East Ash Pond, other East Ash Pond wells, and Site background wells.

Sodium

Sodium concentrations at the East Ash Pond wells are generally within the same range as those observed at Site background wells (Figure 38). The highest sodium concentrations at the East Ash Pond are found in groundwater at nested wells MW13A and MW32, with median concentrations of 505 and 735 mg/L, respectively. These concentrations are well below the median sodium concentration of 890 mg/L measured in groundwater at Site background well MW30.

Sodium concentrations in the bedrock wells have a high correlation coefficient of 0.94 with chloride (Table 10). As with chloride, it is on interest that the highest chloride concentrations occur at well MW30, which is partially screened across coal deposits, and at wells MW13A, MW32, and MW25, all of which occur near (and may be impacted by) former coal mines.

The median sodium concentration in surface water at the East Ash Pond ranged from 100 to 240 mg/L with a median value of 140 mg/L during the study period, or approximately 3.6 to 5.3 times lower than the median sodium concentrations observed at wells MW13A and MW32. Similarly, median sodium concentration in the East Ash Pond was 1.4 to 6.4 times lower than median observed in the Site background bedrock wells.

Given the higher concentrations of sodium in groundwater within both background wells and East Ash Pond wells relative to the East Ash Pond sluice water, it can be stated that sodium in groundwater occurs at naturally high concentrations in the bedrock. Elevated concentrations of sodium in groundwater, as observed at some of the background and East Ash Pond wells, can be attributed to either natural variation or the affects of natural coal deposits or former coal mines.

Sulfate

Well MW16A has a median sulfate concentration of 510 mg/L, which is significantly greater than the range of values observed at the Site background wells or other East Ash Pond wells. The concentrations measured for sulfate at well MW16A in 2002 are significantly above the historical median of 30 mg/L for the period of 1993 through 2001. East Ash Pond bedrock wells MW22 and MW24 also had sulfate concentrations statistically greater than background concentrations; median concentrations in MW22 and MW24 were 31 and 34 mg/L, respectively, and similar to historical concentrations at MW16A. East Ash Pond surface water samples had sulfate concentrations ranging from 440 to 1,500 mg/L and a median concentration of 780 mg/L.

The correlation coefficient between sulfate and magnesium in groundwater at all Site bedrock wells was high at 0.86. The low concentrations of the coal-ash indicator parameters boron and chloride in groundwater at well MW16A, combined with high magnesium and sulfate concentrations, would suggest that the higher concentrations of sulfate observed at well MW16A are strongly influenced by the anthropogenic affects of the former coal mine on groundwater geochemistry.

TDS

Total Dissolved Solids in groundwater sampled from the bedrock is highest at background wells MW25 and MW30 (median values of 1400 and 2400 mg/L) and East Ash Pond wells MW13A, MW16A, and MW32 (median values of 1450, 1400, and 1900 mg/L). The highest TDS concentrations observed in groundwater in 2002, ranging from 2,400 to 2,500 mg/L, occurred at background well MW30. Well MW30 is partially screened across a coal seam. The median TDS concentration of 1,400 mg/L in groundwater at well MW16A is statistically from the same population as the background bedrock wells using the Wilcoxon Rank-Sum Test and 1,000 mg/L below the median TDS concentration in groundwater at background well MW30.

The high TDS concentrations observed at wells MW13A and MW32 can be attributed to the high sodium and chloride concentrations in groundwater at this nested well location. TDS is most highly correlated with sodium ($R = 0.93$) and chloride ($R = 0.88$). As discussed earlier, high sodium and chloride concentrations in groundwater at the Site are a function of naturally occurring conditions at most bedrock wells. Naturally elevated concentrations of these major ions are reflected by similarly high TDS concentrations. However, the highest elevated concentrations of TDS (as with sodium and chloride) may occur in some bedrock wells due to coal deposits (i.e., at well MW30) or former coal mines located nearby (MW25, MW13A, and MW16A).

The median TDS concentration of 1,400 mg/L in groundwater at well MW16A in 2002 is significantly higher than the historical median of 760 mg/L for the period 1993 through 2001. The high TDS concentrations observed at well MW16A in 2002 are attributed primarily to calcium, magnesium, and sulfate, all of which were elevated in groundwater at well MW16A relative to other bedrock wells.

Factors contributing to the higher concentrations of these parameters at well MW16A are difficult to determine since this is the only well with elevated calcium, magnesium, and sulfate concentrations relative to background. However, based on an upward hydraulic gradient within the bedrock and the presence of former coal mines in the vicinity of the well, it is surmised that the occurrence of high TDS in groundwater in this area may be impacted by the former coal mines.

Barium

Barium concentrations in the East Ash Pond wells are at statistically significant lower concentrations than observed in the background bedrock wells based on the Wilcoxon Rank-Sum Test. The lowest mean and median concentrations of barium are found in surface water of the East Ash Pond. The highest barium concentrations are found in the background bedrock wells and the nested East Ash Pond bedrock wells MW13A and MW32.

The nested bedrock wells MW13A and MW32 may have higher barium concentrations than other East Ash Pond wells due to either naturally higher concentrations or may be affected by the former coal mines. The influence of former coal mines on groundwater quality of the bedrock at MW13A and MW32 is hypothesized based on the higher barium concentrations observed in background bedrock wells MW25 and MW30. Wells MW25 and MW30 have elevated barium concentrations relative to the other background wells. Well MW25 is located near a former coal mine and well MW30 is partially screened across a coal seam.

Strontium

Strontium concentrations in the East Ash Pond bedrock wells are at statistically significant lower concentrations or from the same population as the background bedrock wells based on the Wilcoxon Rank-Sum Test. Concentrations of strontium in the East Ash Pond water samples are within the range of both background wells and East Ash Pond wells. Based on the data collected, strontium is not a useful parameter for distinguishing groundwater types or the potential influence of anthropogenic sources.

Aluminum, Molybdenum, Selenium, and Vanadium

Concentrations of the trace metals aluminum, molybdenum, selenium, and vanadium in the East Ash Pond during 2002 were all significantly higher than observed in groundwater within the bedrock deposits (background and on-site). Concentrations of aluminum, molybdenum, selenium, and vanadium in groundwater samples from all bedrock wells were typically below or near their detection limits compared to significantly higher concentrations in the East Ash Pond surface water samples. All of the East Ash Pond bedrock well samples for these four trace metals are statistically from the same population as the background samples using the Wilcoxon Rank-Sum Test for comparison of means.

The deficiency of these four trace metals in groundwater within the Pennsylvanian age bedrock at both background and East Ash Pond wells, as compared to their presence within waters of the East Ash Pond, suggests there is no impact to bedrock groundwater quality by the East Ash Pond.

5.2.2 Exceedances of Groundwater Quality Standards

Groundwater samples collected from bedrock wells at the East Ash Pond and background locations in 2002 (Appendix J) exceeded several Class II groundwater standards (IAC Title 35, Part 620.420) for inorganic parameters. The parameters exceeded by one or more groundwater samples from the bedrock wells at the Site include chloride, sulfate, and TDS. As discussed in Section 5.2.1.3 and displayed on Table 11, many parameters detected at elevated concentrations in groundwater were elevated in both background wells and the East Ash Pond wells.

As seen on the following table, the chloride standard was exceeded at four background wells and two East Ash Pond wells, the sulfate standard at one East Ash Pond well, and the TDS standard at two background wells and three East Ash Pond wells.

Parameter	Class II Groundwater Standard (mg/L)	Background Bedrock Wells Exceeding Class II Standard in 2002	East Ash Pond Bedrock Wells Exceeding Class II Standard in 2002
Chloride	200	MW25, MW27, MW29, MW30	MW13A, MW32
Sulfate	400	none	MW16A
TDS	1,200	MW25, MW30	MW13A, MW16A, MW32

The occurrence of parameters in groundwater at sufficiently high concentrations to exceed groundwater standards can be attributed to three sources: natural geochemistry of the shale bedrock; natural geochemistry associated with coal deposits, particularly at MW30; and, anthropogenic affects on geochemistry associated with former coal mines in the vicinity of background well MW25 and the East Ash Pond wells, particularly wells MW13A, MW16A, and MW32.

5.3 ISOTOPE RESEARCH RESULTS

The carbon and hydrogen (tritium) isotopic data analyzed by the ISGS for groundwater "reveal that some wells produce recent water, while others yield much older water" (Mehnert and Dreher, 2002; Appendix A). Groundwater sampled from the alluvial deposits at wells MW26 and MW28 is indicative of recent water. Tritium values in Illinois precipitation as reported by the ISGS (Appendix A, Table 11) typically range from 3 to 10 tritium units (TU). In the subsurface, tritium has a half-life of 12.3 years and water with tritium concentrations greater than 5 TU is considered recent water. Tritium concentrations in groundwater from the unlithified deposits at wells MW26 and MW28 were 5.3 and 5.8 TU, respectively. Conversely, tritium concentrations in groundwater from the bedrock deposits at wells MW25, MW27, MW29, and MW30 were all below detection limits ranging from 0.43 to 0.52 TU. Water with non-detectable tritium concentrations is considered to be greater than 50 years old.

The Carbon-14 (^{14}C) data for groundwater from the alluvial deposits was consistent with the tritium data. ^{14}C, which has a much longer half-life than tritium, is presented by the ISGS (Appendix A, Table 11) as radiocarbon years before present (RYBP) and as percent (%) modern carbon, both of which provide relative ages. Groundwater from the shallow alluvial wells (MW26 and MW28) had % modern carbon values of 97 and 102 and RYBP values of 210 and "modern", respectively. Based on the tritium and ^{14}C data for groundwater from MW26 and MW28, it is apparent that wells completed in Quaternary geologic materials (i.e., alluvial deposits) "appear to draw water from the local groundwater flow system" (Mehnert and Dreher, 2002).

In contrast to water sampled from the alluvial wells, ^{14}C data from the bedrock wells indicates that the groundwater is significantly older. The ^{14}C data for the background wells installed in the Pennsylvanian bedrock is listed below.

Well Number	Radiocarbon Years Before Present (RYBP)	% Modern Carbon
MW25 (Kelron 25)	13,920	18
MW27 (Kelron 27)	19,400	8.9
MW29 (Kelron 29)	34,610	1.4
MW30 (Kelron 30)	20,850	7.5

The conclusions of the ISGS concerning the four bedrock wells sampled for ^{14}C analysis were that they "apparently draw water from the bedrock and are either only slightly connected to or completely isolated from the local groundwater flow system".

The results of the isotopic analyses of groundwater samples from the background bedrock wells support the hydrogeologic data and conceptualization established earlier. Namely, the Middle Fork of the Vermilion River is a regional discharge area for the bedrock and groundwater within the bedrock is at the end of its flow path, with upward hydraulic gradients, high dissolved mineral content, and significantly older by 13,000 to 35,000 RYBP than groundwater in the overlying unlithified deposits.

6.0 CONCLUSIONS

A comprehensive hydrogeologic and geochemical study of the East Ash Pond System and surrounding region at DMG's Vermilion Power Plant was conducted during 2001-2002. Background geochemical data on the bedrock and groundwater was collected and evaluated by the ISGS for comparison to site-specific data. The collected body of data has been summarized below for the geology, hydrogeology and groundwater chemistry. Utilizing all the available data from the study site and surrounding region, a final section provides the proposed groundwater classification for groundwater at the Vermilion Power Plant and East Ash Pond System.

6.1 GEOLOGY

The deposits covering the bedrock in the region surrounding the study site are derived from recent river deposition (alluvial sediments) in the river valleys and glacial drift deposits occurring below the alluvial sediments and in the upland areas. The glacial and interglacial geologic events that shaped the topography seen today occurred during the Pleistocene Epoch, about 2 million to 12,000 years ago. Thickness of these deposits in the region range from zero thickness along portions of the Middle Fork where bedrock is exposed to over 200 feet in the upland areas.

The unlithified alluvial and glacial deposits in the vicinity of the East Ash Pond and within the floodplain generally range in thickness from 10 to 25 feet. The unlithified deposits increase in thickness as the alluvial deposits pinch out and are supplanted by glacial deposits at higher topographic elevations. Along the western portion of the study site, to the west of the East Ash Pond, the thickest glacial deposits range from 71 feet to the north to 103 feet in the south.

Rocks of Pennsylvanian age form the bedrock surface in the region surrounding the study site. The Danville area is located on the northeast flank of the Illinois basin. Regionally, the Pennsylvanian bedrock consists of mainly shale with thin limestone, sandstone, and coal beds. The upper 75 feet of bedrock at the Site consists of non-marine and marine, silty and micaceous shales of the Pennsylvanian Age Shelburn Formation. The Shelburn Formation contains a major coal seam mined in the region, the Danville Coal, also called the No. 7 Coal.

The top of the Danville Coal, or the void remaining where the coal was removed through mining, was intercepted at depths of 80 to 102.5 feet BLS on the floodplain adjacent to the East Ash Pond. The thickness of the coal seam ranged from 4 to 7 feet with an average thickness of 5.4 feet. A geophysical survey by URS Corp. along 5 lines in 2002 detected 12 anomalies judged to be mine-related voids, collapse features, or partial collapse features in the vicinity of the East Ash Pond System.

The region surrounding the Vermilion Power Plant, including portions of the plant property, has seen extensive coal-mining activity from 1893 to 1970. Two coal mines are located within the vicinity of the East Ash Pond System. Based on data and maps obtained from the ISGS, the former entrances to the two coal mines beneath the site are located just north of the secondary cell of the East Ash Pond and 600 feet southwest of the primary cell.

6.2 HYDROGEOLOGY

Groundwater within the alluvial and, where present, the glacial (till) deposits within the floodplain generally conforms to the ground surface topography. Groundwater elevations in the till and alluvial deposits demonstrate that groundwater elevations in the unlithified materials are higher than those in the adjacent Middle Fork through much of the year. The groundwater surface in the alluvial deposits fluctuates in response to changes in river stage and variations in precipitation. The groundwater surface is not affected by water levels in the East Ash Pond, which has been hydraulically isolated from both the shale and alluvial deposits by soil/bentonite slurry walls and a compacted clay core. Changes in pond elevation do not result in any corresponding changes in the shallow groundwater levels.

Groundwater elevations in the shale are highest in the topographically highest areas to the west and east of the Middle Fork of the Vermilion River. The lowest groundwater elevations occur at wells located adjacent to the Middle Fork. Flow lines derived from the potentiometric surface maps indicate that the Middle Fork in this area is a zone of discharge for the shale. The occurrence of the Middle Fork in this area as a regional discharge zone for the shallow bedrock is supported by the upward vertical hydraulic gradients measured within the shale and the upward vertical hydraulic gradients observed during various periods and at multiple locations between the shale and the alluvium. The shale outcrops along the banks of the Middle Fork and groundwater moving upward through the shale discharges into both the alluvium and directly into the Middle Fork.

The coal mines in the vicinity of the East Ash Pond System have been shown to have significant collapse features where the overlying shale has collapsed or partially collapsed downward into the void or mined coal seam. The collapse of the shale into the void translates upward through the shale, resulting in fracturing and in some cases surface subsidence. A hydrologic feature noted during the exploratory boring phase of the coal mine investigation was the presence of substantial hydraulic head within the coal and overlying fractured shale in proximity to mined areas. Borings located northwest of the East Ash Pond intercepted groundwater under flowing artesian conditions that resulted in temporary suspension of drilling.

6.3 GROUNDWATER CHEMISTRY

Based on all of the groundwater and surface water quality data collected in 2002, the affects of the East Ash Pond on groundwater quality are either negligible or not present. Groundwater quality data for most major ions and trace constituents is similar to background groundwater quality. In cases where elevated concentrations of a parameter were found to occur in groundwater near the East Ash Pond there were also elevated concentrations in background wells screened within coal deposits or in the proximity of abandoned coal mines.

Trace metal concentrations in groundwater were compared to East Ash Pond water samples and there was no commonality between the two water types. The deficiency of trace metals such as molybdenum, selenium, and vanadium in groundwater within both the alluvial deposits and the Pennsylvanian age bedrock at both background and East Ash Pond wells, as compared to their ubiquitous presence within waters of the East Ash Pond, suggests that based on trace water quality data there is no impact to unlithified or bedrock groundwater quality by the East Ash Pond.

Finally, the results of the isotopic analyses of groundwater samples from the background bedrock wells by the ISGS resulted in Carbon-14 ages ranging from 13,000 to 35,000 RYBP (radiocarbon years before present). In support of the Carbon-14 results, tritium concentrations for the same set of bedrock groundwater samples were all below detection limits ranging from 0.43 to 0.52 TU (tritium units). Water with non-detectable tritium concentrations is considered to be greater than 50 years old (Mehnert and Dreher, 2002).

The isotopic and other geochemical data supports the hydrogeologic conceptualization established earlier. Namely, the Middle Fork of the Vermilion River is a regional discharge area for the bedrock and groundwater within the bedrock is at the end of its flow path, with upward hydraulic gradients, high dissolved mineral content, and significantly older by 13,000 to 35,000 RYBP than recent groundwater in the overlying unlithified deposits.

6.4 GROUNDWATER CLASSIFICATION

During March through August 2002, no groundwater parameters measured in shallow monitoring wells in the unlithified deposits exceeded Class I or II groundwater standards. However, background well MW28 exceeded the sulfate and TDS standards of 400 and 1,200 mg/L, respectively, during January and February 2002.

Three bedrock monitoring wells at the East Ash Pond and four background wells regularly exceeded standards for at least one of the parameters of chloride, sulfate, and TDS. The occurrence of parameters within the bedrock at sufficiently high concentrations to exceed groundwater standards can be attributed to three sources: natural geochemistry of the shale bedrock; natural geochemistry associated with coal deposits; and, anthropogenic (man-made) affects on geochemistry associated with former coal mines.

Based on the hydrogeology and geochemistry established for the vicinity of the East Ash Pond and surrounding region, and given the influence of former coal mines documented at the Site on the geochemistry of groundwater within the unlithified and bedrock deposits, it is proposed that the groundwater designation in accordance with Section 620.201 of Part 620 (IAC Title 35, Subtitle F, Chapter I) be Class IV – Other Groundwater, as documented by the following excerpt from Section 620.240:

"g) Groundwater within a previously mined area, unless monitoring demonstrates that the groundwater is capable of consistently meeting the standards of Sections 620.410 or 620.420. If such capability is determined, groundwater within the previously mined area shall not be Class IV."

The groundwater quality established at the East Ash Pond is within a previously mined area and has been documented to be influenced by both natural geochemistry and the influences of abandoned coal mines and mine spoils. Groundwater quality at the Vermilion Power Plant and in background wells have consistently <u>not met</u> the Class I and II standards for chloride, sulfate, and TDS as documented in Sections 620.410 and 620.420, respectively, of the IAC. Therefore, groundwater in the unlithified deposits and bedrock at the East Ash Pond and surrounding area of the DMG property at the Vermilion Power Plant should be designated Class IV.

7.0 REFERENCES

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