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June 3, 2019

John Sager
Wisconsin Department of Natural Resources
Superior Service Center
1701 N 4th Street
Superior, WI 54880

Dear Mr. Sager:

RE: Clarification on Site Investigation Report for Former Manufactured Gas Plant, WDNR BRRTS #02-16-275446 owned by Superior Water, Light & Power, Superior, Wisconsin

The intent of this letter is to clarify some of the information and conclusions included in the Site Investigation Report (SIR) for the Former Manufactured Gas Plant (Site), dated March 2019, associated with WDNR BRRTS #02-16-275446, owned by Superior Water, Light & Power, Superior, Wisconsin. In a meeting on May 9, 2019, Wisconsin Department of Natural Resources (WDNR), Superior Water, Light & Power (SWL&P), and Foth Infrastructure & Environment (Foth) discussed your questions about the SIR, which are addressed in the sections below.

DNR Comment 1:

Elevated concentrations of benzene were reported in soil at boring B-31 (13,000 mg/kg), which is east of the former MGP source area and currently occupied by Lakehead Concrete. The WDNR discussed an interest to further clarify the SIR reporting of this benzene as not being associated with historic MGP operations and as potentially related to an aboveground storage tank (AST) in use by Lakehead Concrete.

SWL&Ps Response 1:

The conceptual site model has concluded that the benzene noted in a soil sample from boring B-31 is not related to any MGP source area associated with historic MGP operations. This is based primarily on our review of historic MGP operations (SIR Figure 2-2, referenced SIR figures are provided in Attachment 1), aerial imagery (SIR Figures 2-4 to 2-6), and other distribution of contaminants sampling data.



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However, we discussed that the benzene detected at boring B-31 may be indirectly associated with one of the MGP source areas through a preferential migration pathway discussed in the SIR and explained below: migration along utility pipe sand and gravel bedding or through higher permeability fill materials such as wood/wood chips and fill with gravel.

This subsurface geology and potential preferential migration pathways are illustrated on the SIR Figures 2-3 and 2-10 through 2-14. SIR Figure 2-3 best illustrates the locations of the utility piping and shows a 48-inch storm sewer, a sanitary sewer, and water distribution mains (all generally laid in gravel or sand bedding at depths greater than 5 to 6 feet below ground surface to prevent freezing). With ground surface near 615 ft amsl, the pipe bedding would generally extend to an elevation of about 608 to 610 ft amsl or deeper near the MGP source area as on SIR Figures 2-11, 2-13, and 2-14. The benzene at B-31 was detected in woody fill material at an elevation of approximately 598 to 600 ft amsl. This boring may be downgradient of the source area associated with the Hortonsphere when the alignments of the utility pipe bedding are considered either:

- Migrating towards the boat slip along cross-section A-A' (from monitoring well (MW) -4 to the sanitary sewer near boring B-12 on SIR Figure 2-11) and then towards MW-09 along cross-section B-B' as shown on SIR Figure 2-12 (from B-11 to MW-09 which is near B-31 as shown on SIR Figure 2-13); or
- Migrating towards B-31 more or less along cross-section C-C', but following the storm sewer, sanitary sewer, and/or water main pipe bedding towards B-31 where the geologic profile also shows evidence of some woody material along the former shoreline atop the red clay that can create a preferential flow surface as well when the pipe bedding in the trench fills with stormwater during storm events. This is consistent with the high water elevations noted at MW-14 on SIR Figure 2-13.

Once perched groundwater containing dissolved benzene from a source area migrates to the area near B-31, the woody material (which is high in organic carbon; ~40 to 50%, Agronomy Research, 2007, Attachment 3) can then preferentially adsorb and absorb the benzene (and other dissolved organic compounds) which are hydrophobic. This can theoretically then increase the benzene concentration at those locations relative to the surrounding soils that are lower in organic carbon content (typically less than 1 percent by weight).

It is still possible that a release from an AST or other localized petroleum product spill could cause contributions to the detected benzene impacts at B-31. SWL&P has found no record of a fuel release from Lakehead Concrete's AST or operation, and therefore cannot confirm a localized source of benzene and that fate and transport pathway, as the information is incomplete.



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The site investigations summarized in the SIR have created a conceptual model of the presence of benzene, naphthalene, and Benzo(a)pyrene (BaP) in soil and groundwater (as illustrated on SIR Figure 5-2 for benzene for example) that illustrates the location and migration pathways of chemicals of interest in the subsurface. These data will allow SWL&P to address on-site benzene, naphthalene, and BaP and the nearby off-site areas such as at B-31, as needed, regardless of source.

As noted in the discussion of fate and transport in the SIR, it is the opinion of SWL&P that source area remedies that target the key on-site source areas will result in rapid natural attenuation of off-site impacts resulting from migration of dissolved organics along utility pipe bedding. Evaluation of remedial alternatives in the Remedial Action Options Report (RAOR) will consider the soil with benzene impacts near B-31. Data gaps will be filled during the pre-design investigation to inform the remedial design (RD), by advancing additional soil borings in the area of B-31 to evaluate sources and remedial effectiveness.

DNR Comment 2:

The SIR uses the term “false positives¹” when describing potential anomalies in the soil laser induced florescence (LIF) data. The WDNR discussed further explanation of the term “false positive,” particularly in the area to the southeast along the railroad tracks, and clarification as to how the LIF data is being interpreted and used for remedial alternatives..

SWL&Ps Response 2:

The term “false positive” was not intended to discount the LIF data set in the SIR data evaluation but rather to evaluate multiple factors of analysis. The LIF data set was evaluated alongside other investigation data to arrive at conclusions about the extent of impacts at the Site. The section below provides clarification to the use and interpretation of the LIF data in the SIR.

The initial LIF data was collected in 2006 as part of the Phase II, Part IV Site Investigation in order to help delineate the extent of impacted materials in the subsurface. The data was collected using the Tar-specific Green Optical Screening Tool (TarGOST™) and the results were mapped by Dakota Technologies to show the approximate extent of potential impacted material in the subsurface (see Figure 4-3 of Phase II, Part IV SIR). Typically, TarGOST™ fluorescence responses of greater than 100% were used to identify the potential presence of impacted materials. Based upon this criteria for LIF response data, a continuous area of elevated response was mapped

¹ See reference to “false positives” on Page 17, 21, 34, and 35 of the SIR.



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along the former Superior Bay shoreline; however, there are several lines of evidence (LOEs) that suggest that the LIF results when viewed alone may overestimate the presence and extent of impacted material in the subsurface.

- To fully interpret the LIF response, it is beneficial to look at 1) the corresponding physical boring logs to see if evidence of visual contamination and/or other substrate (such as wood and peat) that could elicit a LIF response is documented; and 2) available analytical soil data:
 - In some areas the LIF responses are clearly linked to visual contamination. For example, the impacted and odorous layer described at a depth of 12 feet below ground surface (bgs) in B-11 log correlates with the LIF responses observed in SLIF-07 (Figure 1, additional Figures 1 through 7 have been prepared and are included in Attachment 2). While the peat material observed just above the impacted layer may also have affected the LIF readings, the visual staining observed in the boring combined with the elevated soil sample results (tPAHs = 61 mg/kg) confirms that this is an area where impacted material is present in the discharge area and consistent with the MGP site boundaries.
 - In areas outside of the discharge area, LIF responses were present that also corresponded with observations of sheen and odor. For example, the depth of the LIF response (at 5 to 8 ft bgs) in SLIF-34 corresponds to a layer of wood chips, odor, and sheen noted in the associated boring log for MW-10 (Figure 2). It should be noted that “odor” was mentioned without additional description in the log and can result from many organic sources other than Site chemicals of interest. Corresponding soil sampling results at 5 to 6 feet bgs report tPAH of 2,565 mg/kg. Despite these observations, low groundwater concentrations of naphthalene and BaP of 5.6 ug/L and 0.27 ug/L, respectively, were measured in MW-10 in 2017. This additional information beyond the LIF response suggests that soil concentrations of PAH detected at MW-10 have either attenuated over time or do not pose a risk to groundwater. Lines of evidence related to groundwater are discussed further below.
 - In the area further to the southeast of the discharge area, LIF responses were present but no staining was observed in the log. For example, the depth of the LIF response (at 4 to 7 ft bgs) in LIF-55 corresponds to a layer of wood chips noted in the associated boring log (Figure 3). Because no visual staining was observed in the LIF-55 boring log and the soil sample results were low (tPAHs = 3.9 ug/kg), the TarGOST™ response is likely due to the presence of wood chips or other organic materials in the soil matrix rather than impacted material. Similar observations can be



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made for LIF-48 which is shown on Figure 4. This is a possible “false positive” example.

- To illustrate a broader compilation of soil data available for the Site Investigation, the maximum BaP concentration observed in any soil boring is shown on Figure 5. Concentrations that exceed WDNR criteria are colored red to illustrate areas with BaP impacts. By superimposing the soil boring data on top of the LIF interpretation from the Phase II, Part IV SIR, it shows the historical extent of PAH impacts in soil analytical data are more constrained to near the discharge area than those interpolated using only the LIF responses. Also shown on Figure 5 is the area where excavation and off-site disposal of impacted soil occurred in 2008. The excavation targeted removal of a clay pipe and nearby soil contamination that contained material associated with the historical MGP process.
- If mobile quantities of free product were present in the subsurface, then one would expect to find layers of dense non-aqueous phase liquids (DNAPLs) in groundwater. Interface probes were utilized during groundwater sampling to look for NAPL in groundwater, but no NAPL has been reported in any of the monitoring wells during any of the monitoring events. This suggests that any residual impacted material present in the subsurface is likely bound to soil (e.g., immobilized), rather than present as mobile product.

Although understanding where residual impacted materials may be present in soil is helpful in understanding the conceptual site model and potential land-use restrictions, the mobility of contamination is often a more important driver when evaluating current risk and weighing potential cleanup options. The soil to groundwater pathway is the primary indicator of potential risk from subsurface soils. The primary PAH influencing the potential need for remediation of groundwater at this Site is BaP. BaP concentrations in groundwater over time are shown in Figure 6. As illustrated, concentrations in groundwater have decreased substantially since November 2004, likely due in part to removal of contaminated soil from the former MGP source area (Figure 5). As with soil, the observed impacts of PAHs in groundwater are more limited in extent than the extent of the potential area of impacted material that was interpolated using the LIF responses.

In conclusion, the LIF data were collected as a qualitative screening tool and those results were helpful in defining the areas that were evaluated as part of the site investigation. The LIF responses were further evaluated based on other potential sources of fluorescence such as wood chips or peat and visual observations of the presence or absence of odor, mobile oil, and oily soil. The quantitative soil and groundwater data collected throughout the entire site investigation then created a better understanding of the true nature and extent of impacts in the subsurface. The decreasing trends in groundwater concentrations and area are especially important in illustrating that PAH sources have been adequately identified and primarily exist in the vicinity of the historic



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MGP operations area. Data also demonstrate that they can be controlled (e.g. through the 2008 soil removal) or are being attenuated and have become immobilized over time due to sorption and weathering.

Evaluation of remedial alternatives in the RAOR can focus largely on the quantitative groundwater and soil data to facilitate selection of a preferred remedial action option. Data gaps may need to be filled during the pre-design investigation to refine the design extents, obtain information related to monitored natural attenuation (MNA), and provide information on potential land-use restrictions (institutional controls) for the property.

DNR Comment 3:

As a follow-up to the discussion of the LIF data, WDNR also discussed the elevated LIF response observed at TG-07, located at the berm next to the wastewater treatment plant (WWTP).

SWL&Ps Response 3:

Thirty (30) additional LIF borings were advanced along the perimeter of the boat slip during the Supplemental Site Investigation (Summit Envirosolutions, 2017). The majority of these TarGOST™ borings showed low values of reflectance which indicates a lack of subsurface impacted materials. A few individual TarGOST™ borings produced higher responses that may suggest remnants of impacted materials. These higher values were found at isolated locations and do not suggest a significant, nor contiguous, impacted layer at depth. The associated berm was constructed between 1976 and 1983, which was many decades later than MGP operations at the site. Given the shoreline filling and disturbances that created the existing shoreline features, the original lake bed materials may not be found in their original positions near the boat slip.

Boring TG-07 showed three layers of higher fluorescence materials between a depth of approximately 16 to 25 feet, as shown on Figure 7. The nearby boring log SB09 notes the presence of wood in the boring from 12 to 20 ft bgs (the total depth explored). No evidence of visual contamination is noted on the SB09 log. Although the PAHs are slightly elevated in the soil sample collected from 13.5 to 15.5 ft bgs in SB09, the BaP result of 0.297 mg/kg is less than the 0.39 mg/kg WDNR soil standard for direct contact. The LIF response at TG-07 is likely due to wood or other borrow material used to construct the berm and the results at SB-09 do not indicate that this location is an area of remedial interest.

DNR Comment 4:



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The WDNR discussed the groundwater-surface water interaction and the impact of the Waste Water Treatment Plant (WWTP) on groundwater flow, specifically what SWL&P's conclusions are regarding this interaction.

SWL&Ps Response 4:

Shallow groundwater at the Site flows northeast to Superior Bay. However, the groundwater elevations in the immediate vicinity of the WWTP appear to be influenced by the WWTP pond. In SIR Figures 2-7 and 2-8, the water level elevations measured in monitoring wells MW-12, MW-15, and MW-20 are very similar to the water elevation in the WWTP pond, rather than the boat slip. Cross-section E-E', shown in SIR Figure 2-15, indicates that the WWTP pond is hydraulically separated from the Bay, but is in hydraulic connection with the upgradient shallow groundwater. The water level in the WWTP pond fluctuates frequently in response to storm events, which in turn causes frequent fluctuations in groundwater levels near the pond. This interaction may have caused smearing of contaminants exacerbating impacts within the groundwater column. Due to the resulting variations in gradients and discharge, the influence of the WWTP pond also poses a challenge for groundwater remediation.

Evaluation of groundwater remedial alternatives in the RAOR will consider the influence that the WWTP pond has on groundwater levels for remedial technologies such as groundwater extraction and injection of amendments. Data gaps such as more frequent groundwater elevation data may need to be evaluated during Remedial Design (RD).

DNR Comment 5:

WDNR discussed the underground sewer lines affect regarding contaminant transport at the Site and how SWL&P will considered this in the RAOR.

SWL&Ps Response 5:

Utility lines are typically installed in excavated trenches that are bedded with sand or gravel, as illustrated in the attached revised SIR Figure 2-15. The storm sewer and sanitary sewer lines crossing the Site were installed by the City of Superior in the mid-1970s, a period of time when the City's standard operating procedure was to use sand as the bedding material. Bedding material is placed in the bottom of the trench and the pipes are laid on top. The bedding material protects the pipes from damage when the trench is backfilled and compacted. The result, in the context of groundwater contaminant flow and transport, is a linear conduit of higher permeability and transmissivity material that can create a preferential pathway for flow of groundwater. Groundwater flows relatively slowly in the sandy clay and clayey sand material generally prevalent at the Site, but when groundwater (or surface water infiltrating through source area soils) encounters the trench and the backfill, it moves more rapidly through the permeable material. The



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dissolved contaminants also generally follow the path of least resistance which may be along these preferential pathways. Many underground utilities cross through the Site, as shown in SIR Figure 2-3, that may affect the transport of contaminants in groundwater. In the area of the Site near the WWTP pond, the flow of groundwater may even reverse direction at times due to fluctuations in the WWTP pond level, as discussed above in Response 5.

Evaluation of groundwater remedial alternatives in the RAOR will consider the different types of underground utility trenches crossing the Site as potential groundwater contaminant pathways to be addressed by specific remedial technologies considered for groundwater in the remedial alternatives.

Conclusions:

SWL&P appreciates the opportunity to provide you with these clarifications to the SIR. The SIR serves as the basis for the development of the remedial action objectives and remedial alternatives in the RAOR. SWL&P requests that WDNR consider these clarifications and approve the SIR so that preparation of the RAOR can continue to move forward. If you have any additional questions, please contact Rachael Snyder the MGP Project Manager at (715) 395-6224.

Sincerely,

A handwritten signature in black ink, appearing to read 'R. Sandstrom', written over a horizontal line.

Robert Sandstrom
Manager-Customer Excellence & Electric Operations

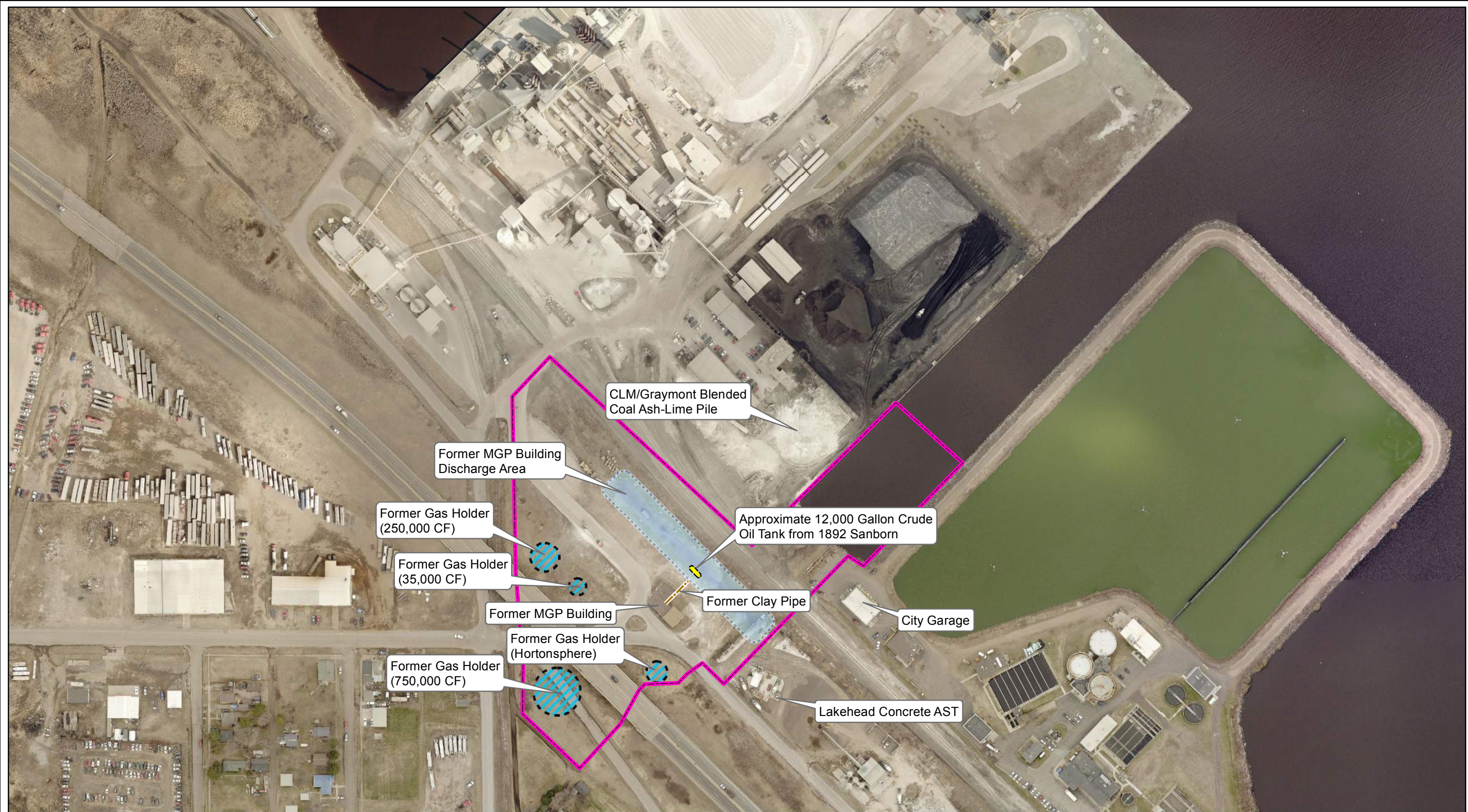
Attachments:

- Attachment 1: Referenced SIR Figures
- Attachment 2: Clarification Letter Figures
- Attachment 3: Soil Organic Content Reference






cc:

Rachael Snyder, SWL&P
Gregory Prom, ALLETE
Steve Garbaciak, Foth
Brian Hanks, Foth

Attachment 1
Referenced SIR Figures



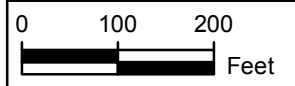
- NOTES:**
1. 2016 - 3" resolution air photo from Douglas County.
 2. Horizontal coordinate system: NAD 1983 Douglas County, units in feet.
 3. Pond from Chart of Harbor at Duluth, Minn. and Superior, Wis. / Prepared Under the Direction of Major W.L. Fisk, USACE
 4. Former 12,000 Gallon Crude Oil Tank from 1892 Sanborn.

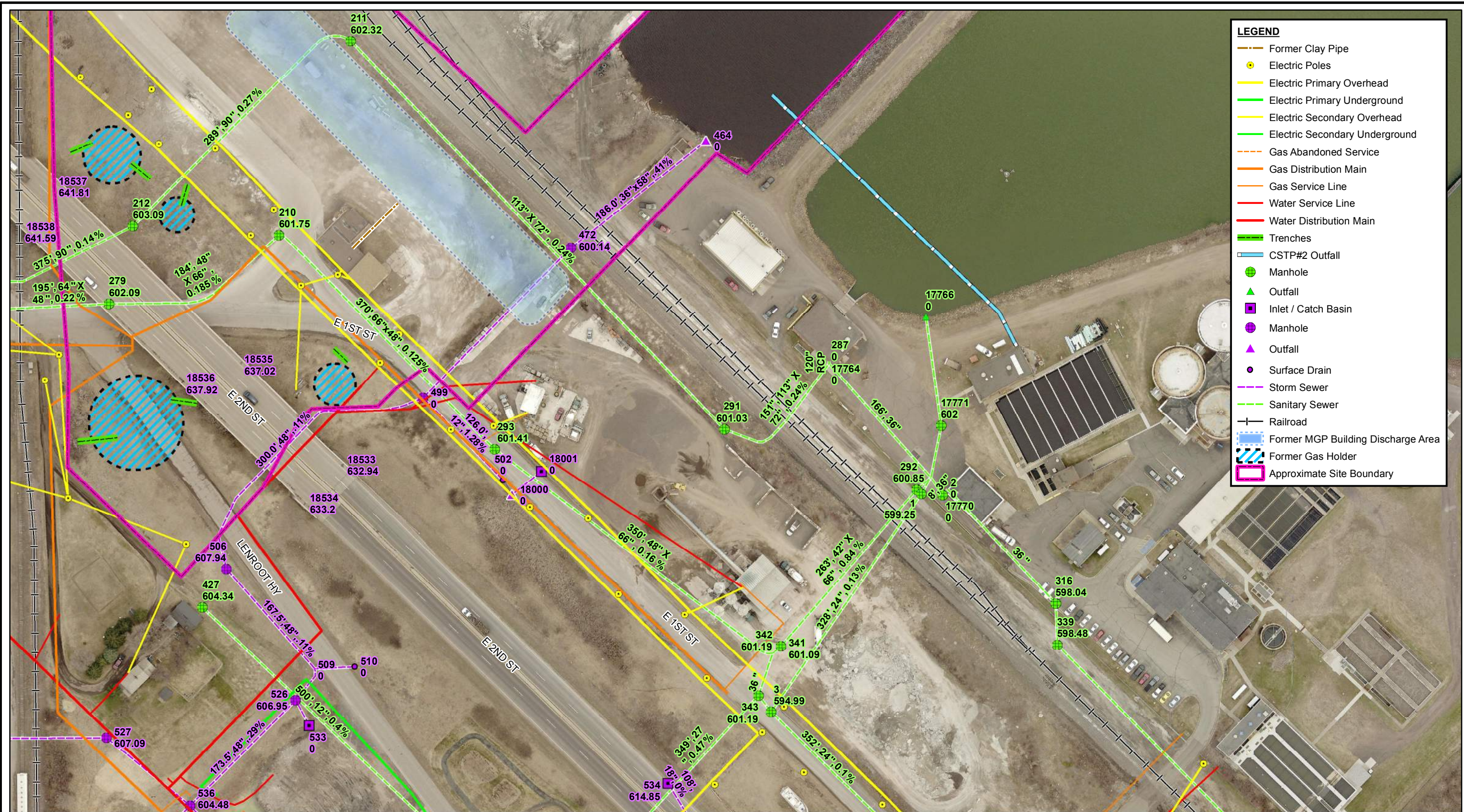
- LEGEND**
-  Former 12,000 Gallon Crude Oil Tank
 -  Approximate Site Boundary
 -  Former Clay Pipe
 -  Former MGP Building Discharge Area
 -  Former Gas Holders



SUPERIOR WATER, LIGHT & POWER	
FIGURE 2-2 HISTORICAL PLANT LAYOUT SITE INVESTIGATION REPORT SUPERIOR, WISCONSIN	
Date: MARCH 2019	Revision Date:
Drawn By: DAT	Checked By: MJD2 Project: 18S024

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LEGEND

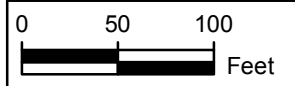
- Former Clay Pipe
- Electric Poles
- Electric Primary Overhead
- Electric Primary Underground
- Electric Secondary Overhead
- Electric Secondary Underground
- Gas Abandoned Service
- Gas Distribution Main
- Gas Service Line
- Water Service Line
- Water Distribution Main
- Trenches
- CSTP#2 Outfall
- Manhole
- ▲ Outfall
- Inlet / Catch Basin
- Manhole
- ▲ Outfall
- Surface Drain
- Storm Sewer
- Sanitary Sewer
- Railroad
- Former MGP Building Discharge Area
- Former Gas Holder
- Approximate Site Boundary

- NOTES:**
1. 2016 - 3" resolution air photo from Douglas County.
 2. Horizontal coordinate system: NAD 1983 Douglas County, units in feet.
 3. Storm and Sanitary Sewer data supplied by Douglas County GIS.
 4. Electric, Gas and Water datasets supplied by Superior Water, Light and Power.



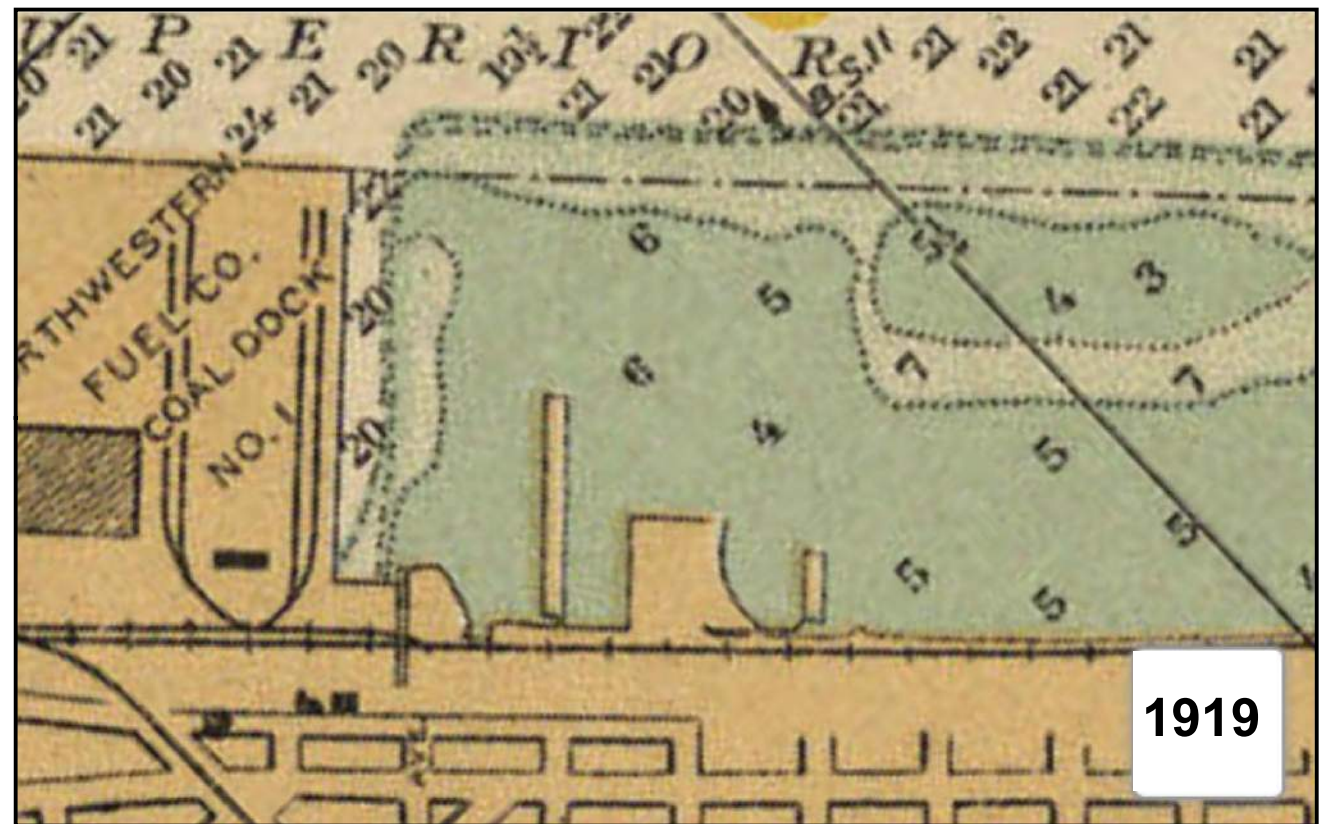
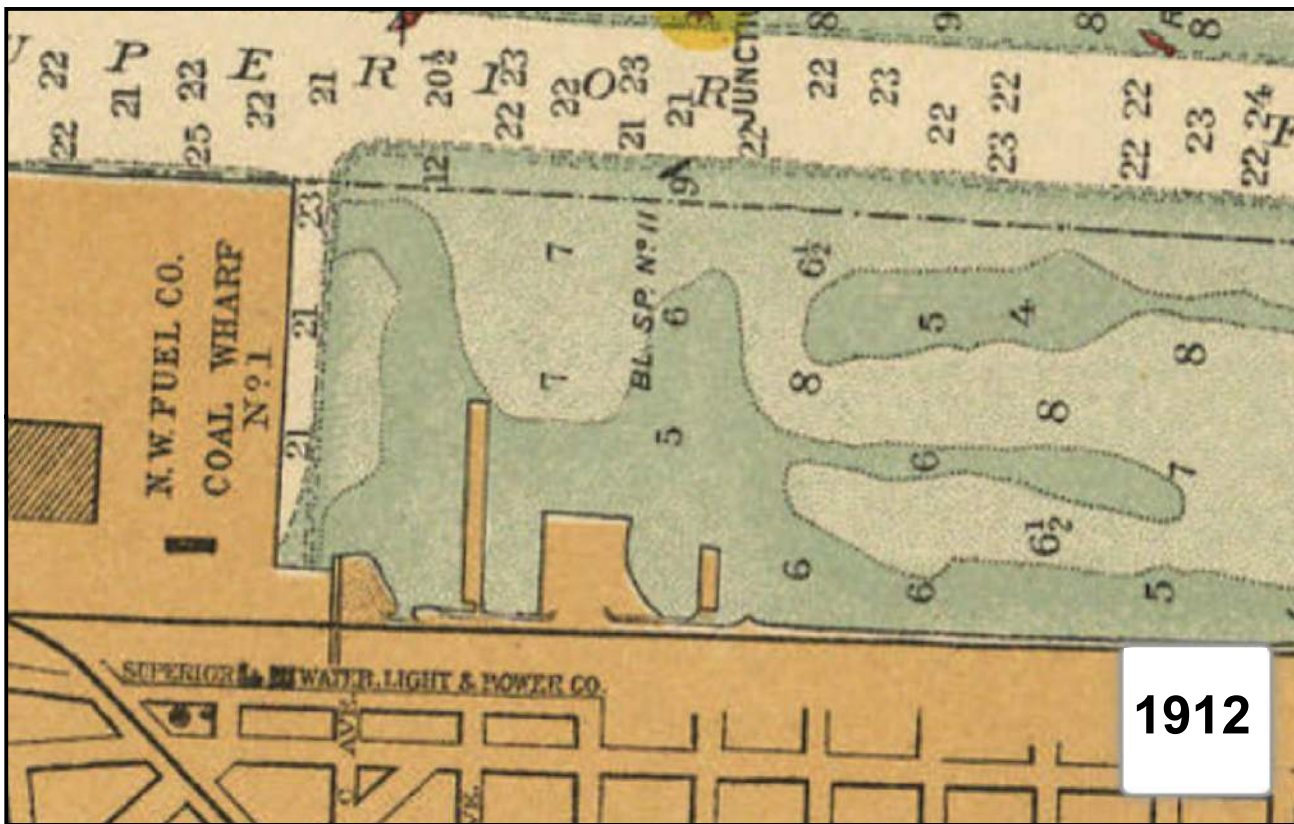
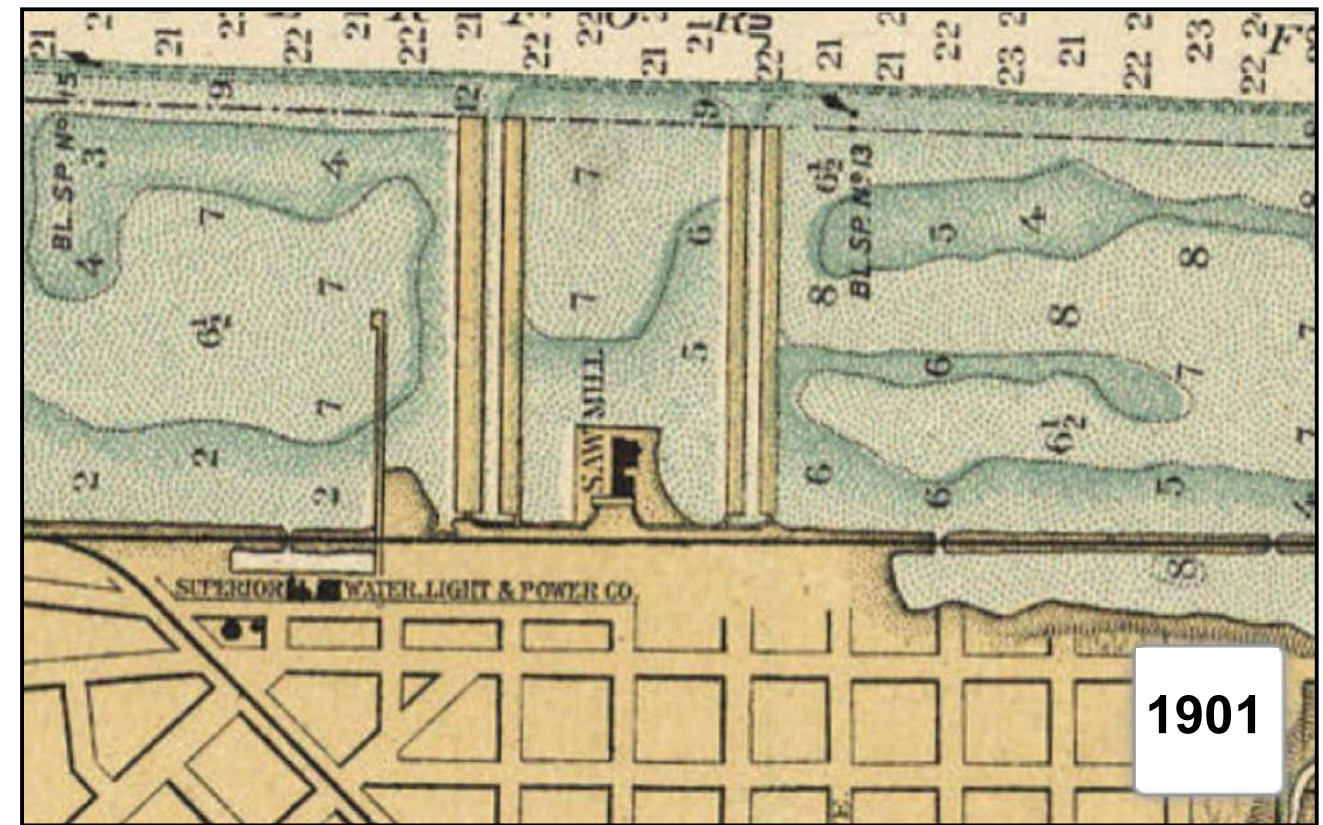
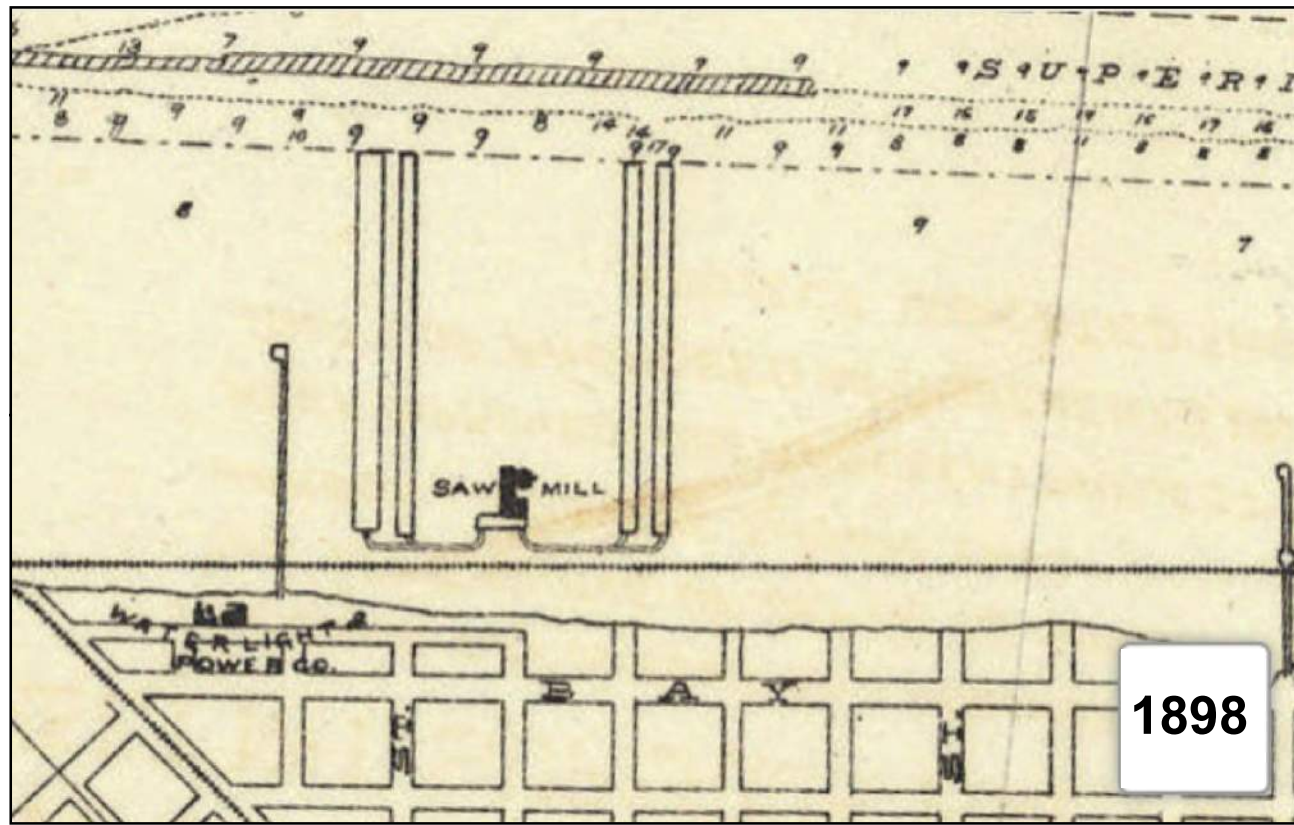
SUPERIOR WATER, LIGHT & POWER

FIGURE 2-3
VICINITY SEWER AND UTILITY MAP
SITE INVESTIGATION REPORT
SUPERIOR, WISCONSIN



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NOTES:
 1. Images from USACE Harbor Maps
 downloaded from Wisconsin Historical Society.



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FIGURE 2-4
 HISTORICAL SHORELINE CHANGES
 SITE INVESTIGATION REPORT
 SUPERIOR, WISCONSIN

NOT TO SCALE

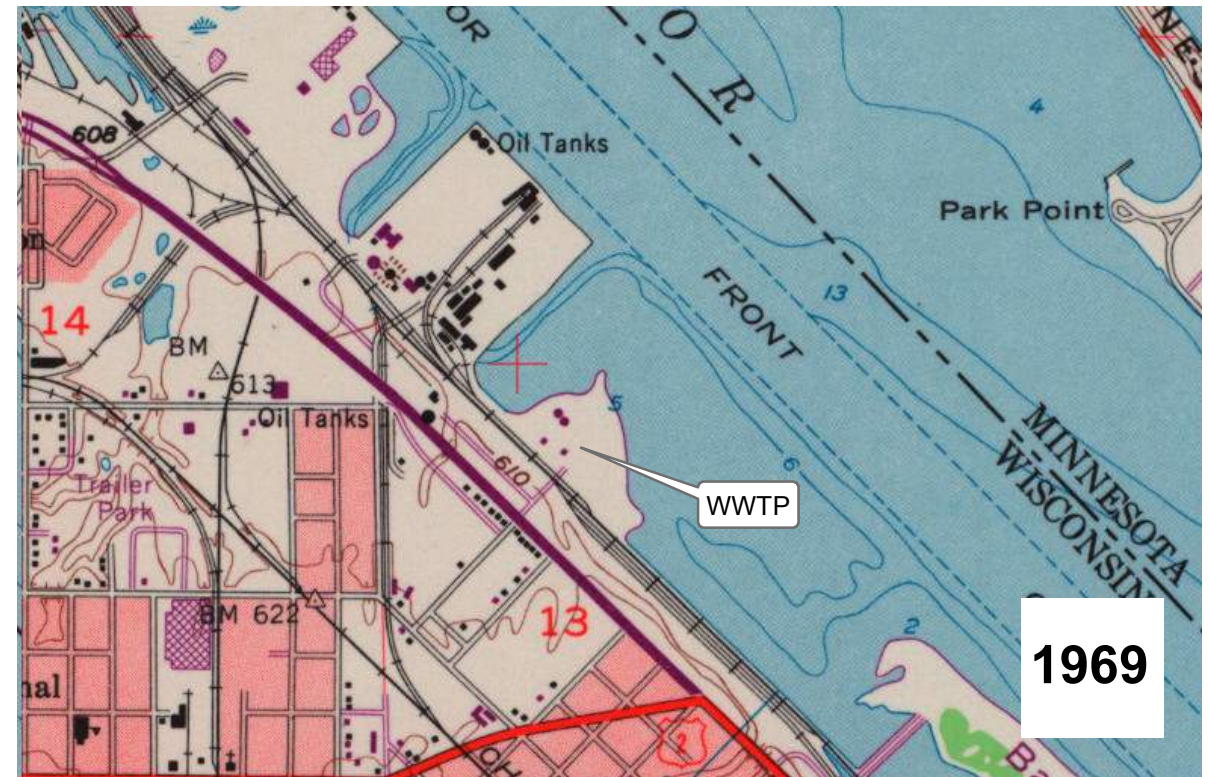
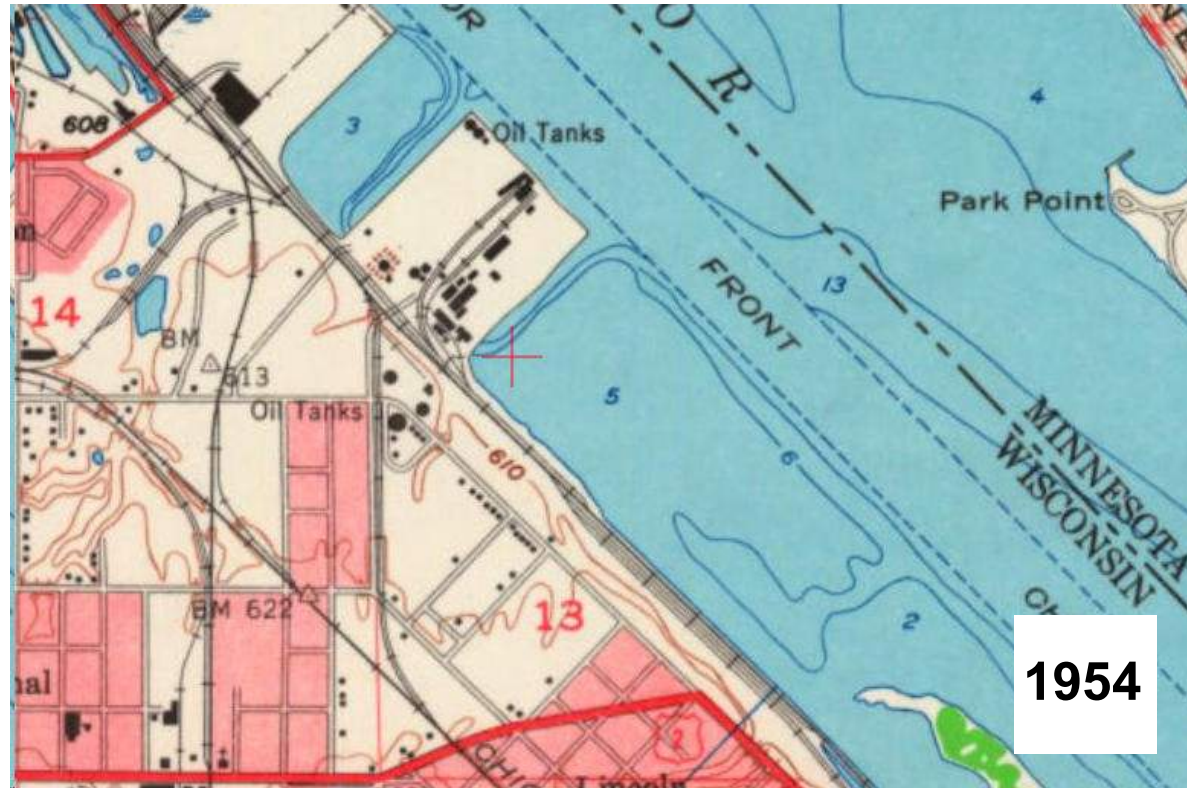
Date: MARCH 2019

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Project: 18S024



NOTES:
 1. Images downloaded from USGS Historical Topographic Map Explorer. <http://historicalmaps.arcgis.com/usgs/>



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FIGURE 2-5
 HISTORIC USGS MAPS
 SITE INVESTIGATION REPORT
 SUPERIOR, WISCONSIN

NOT TO SCALE

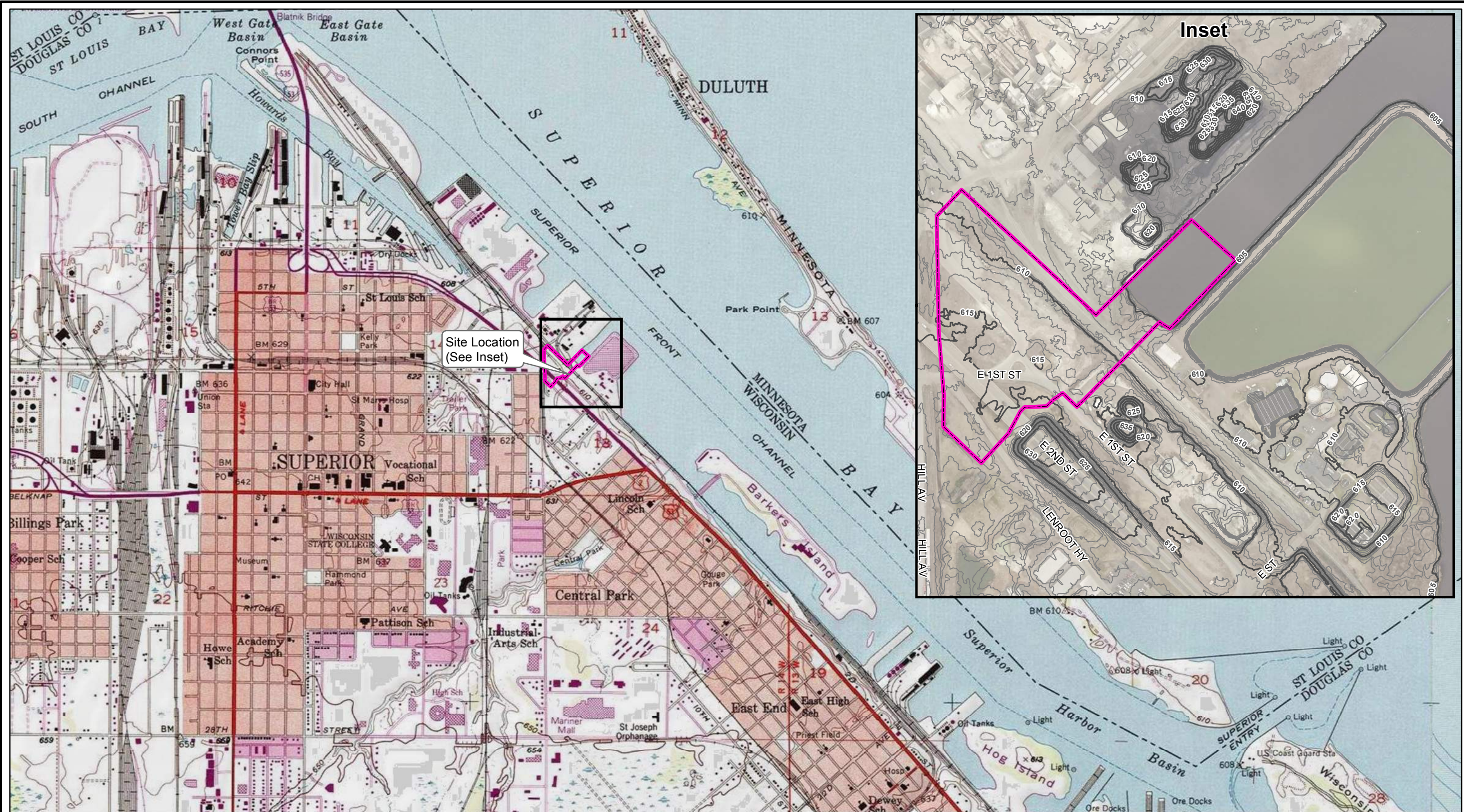
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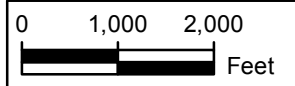
- NOTES:**
1. Topographic basemap supplied by Esri and its suppliers.
 2. Horizontal coordinate system: NAD 1983 Douglas County, units in feet.
 3. 2016 - 3" resolution air photo from Douglas County.
 4. Contours supplied by Douglas County GIS.



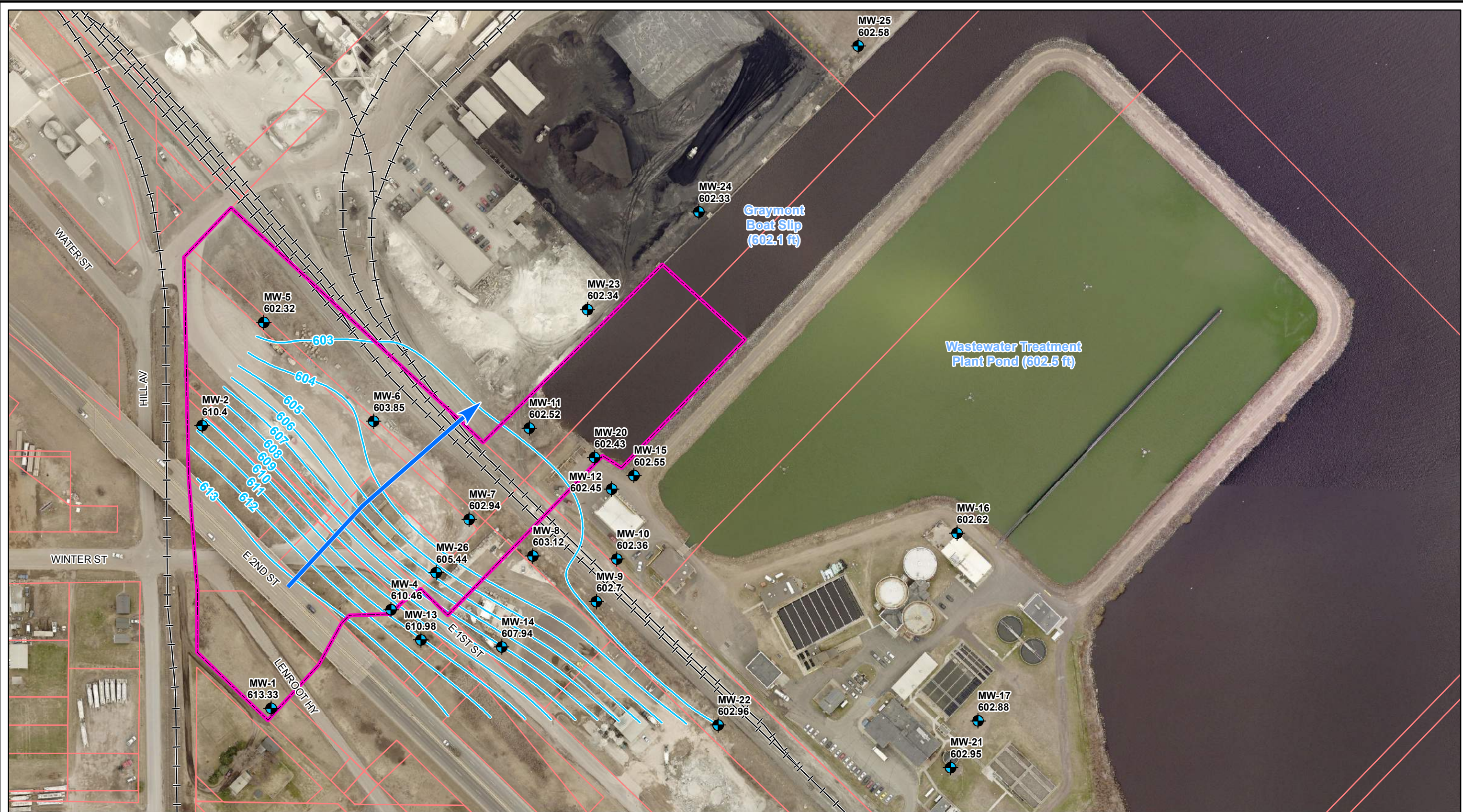
SUPERIOR WATER, LIGHT & POWER

FIGURE 2-6
 TOPOGRAPHIC SITE MAP
 SITE INVESTIGATION REPORT
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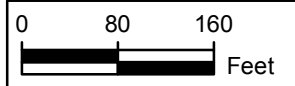


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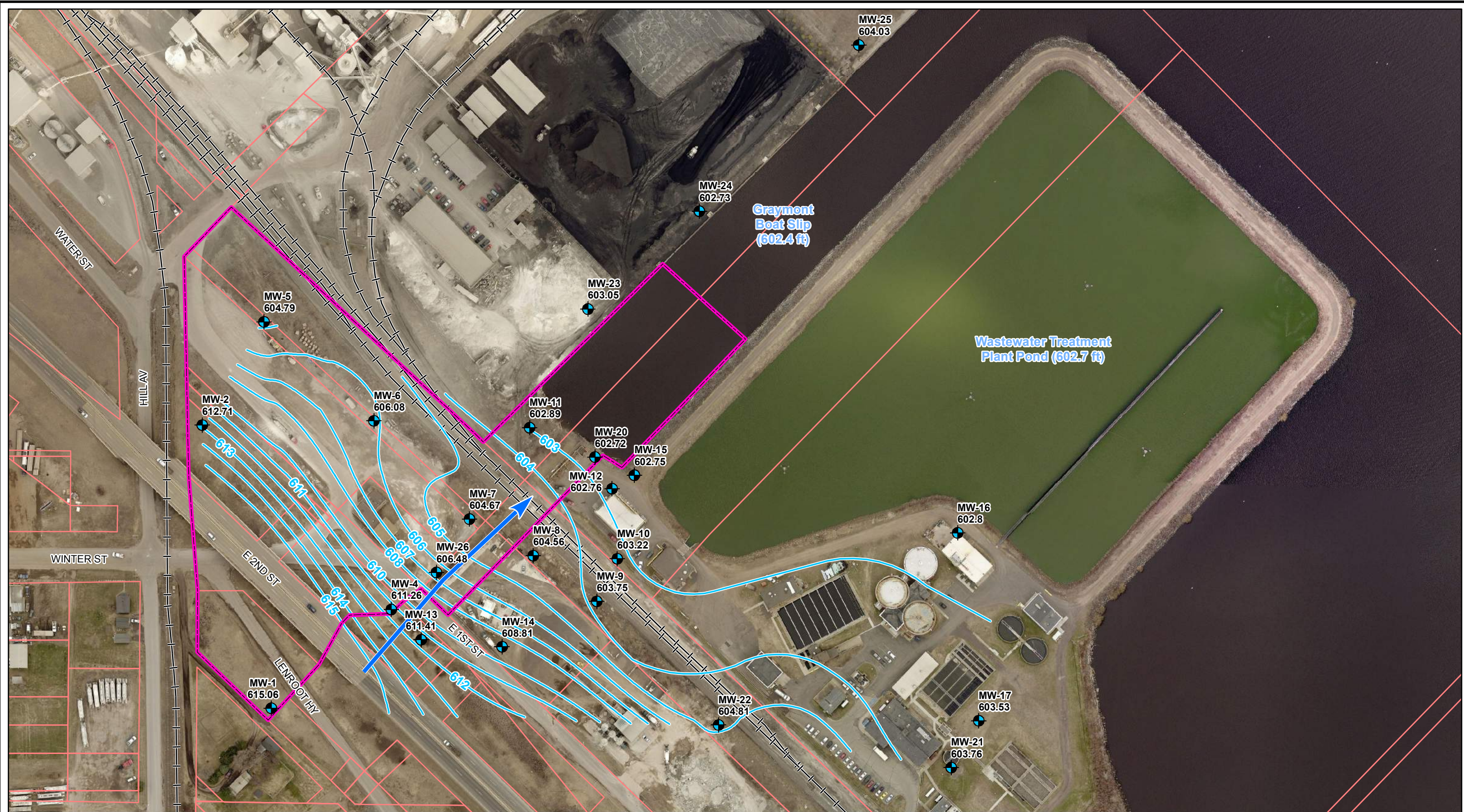
- NOTES:**
- 2016 - 3" resolution air photo from Douglas County.
 - Horizontal coordinate system: NAD 1983 Douglas County, units in feet.
 - Elevation is given in feet above mean sea level.

- LEGEND**
- Groundwater Monitoring Well with January 2017 Groundwater Elevation
 - Groundwater Elevation Contour (1' Contour Interval)
 - Railroad
 - Approximate Site Boundary
 - Tax Parcel
 - GW Flow Direction



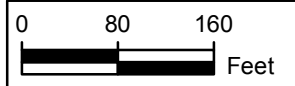
SUPERIOR WATER, LIGHT & POWER	
FIGURE 2-7	
GROUNDWATER CONTOUR PLOT - JANUARY 2017 SITE INVESTIGATION REPORT SUPERIOR, WISCONSIN	
Date: MARCH 2019	Revision Date:
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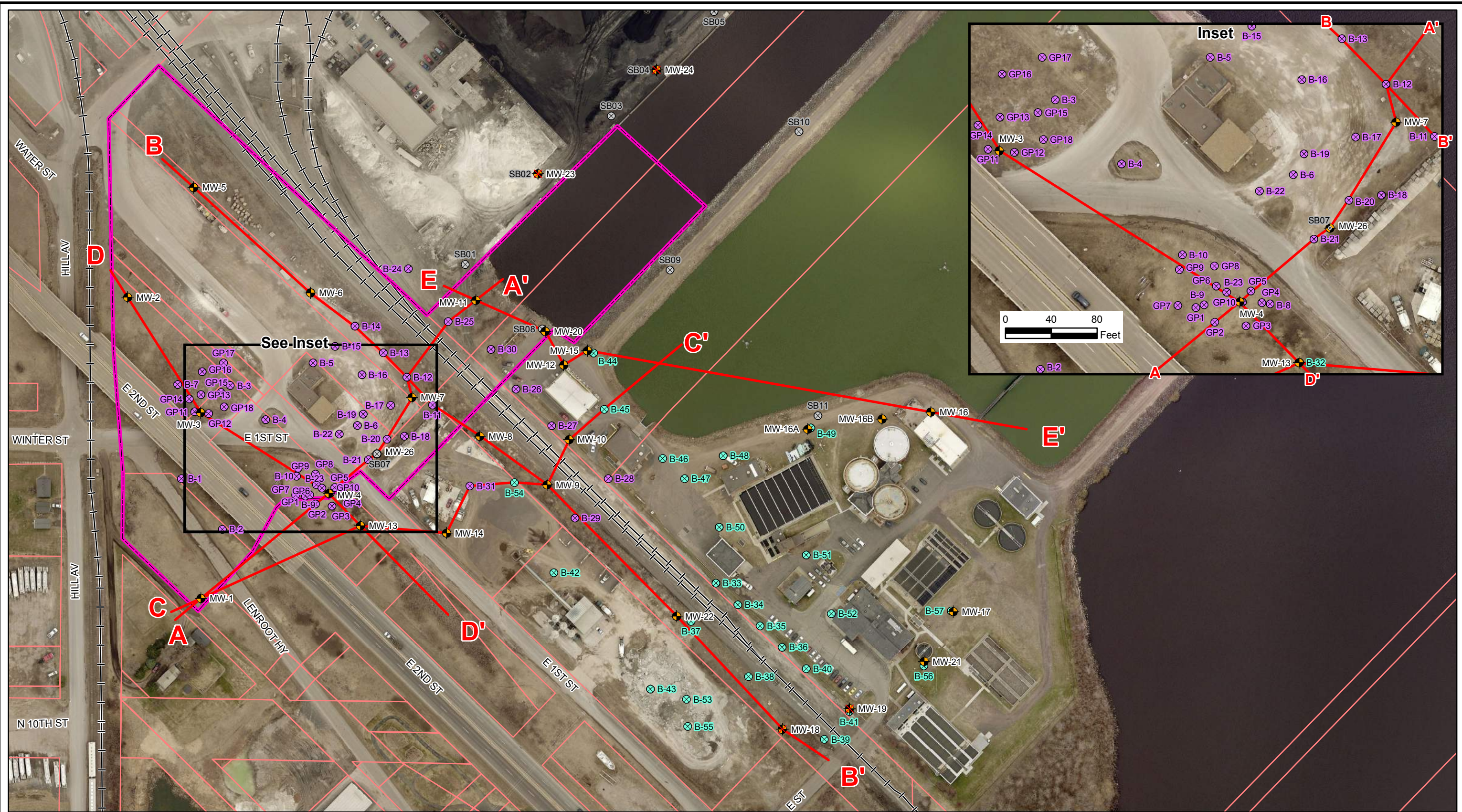
- NOTES:**
1. 2016 - 3" resolution air photo from Douglas County.
 2. Horizontal coordinate system: NAD 1983 Douglas County, units in feet.
 3. Elevation is given in feet above mean sea level.

- LEGEND**
- Groundwater Monitoring Well with April 2017 Groundwater Elevation
 - Groundwater Elevation Contour (1' Contour Interval)
 - Railroad
 - Approximate Site Boundary
 - Tax Parcel
 - GW Flow Direction



SUPERIOR WATER, LIGHT & POWER		
FIGURE 2-8		
GROUNDWATER CONTOUR PLOT - APRIL 2017 SITE INVESTIGATION REPORT SUPERIOR, WISCONSIN		
Date: MARCH 2019	Revision Date:	
Drawn By: DAT	Checked By: MJD2	Project: 18S024

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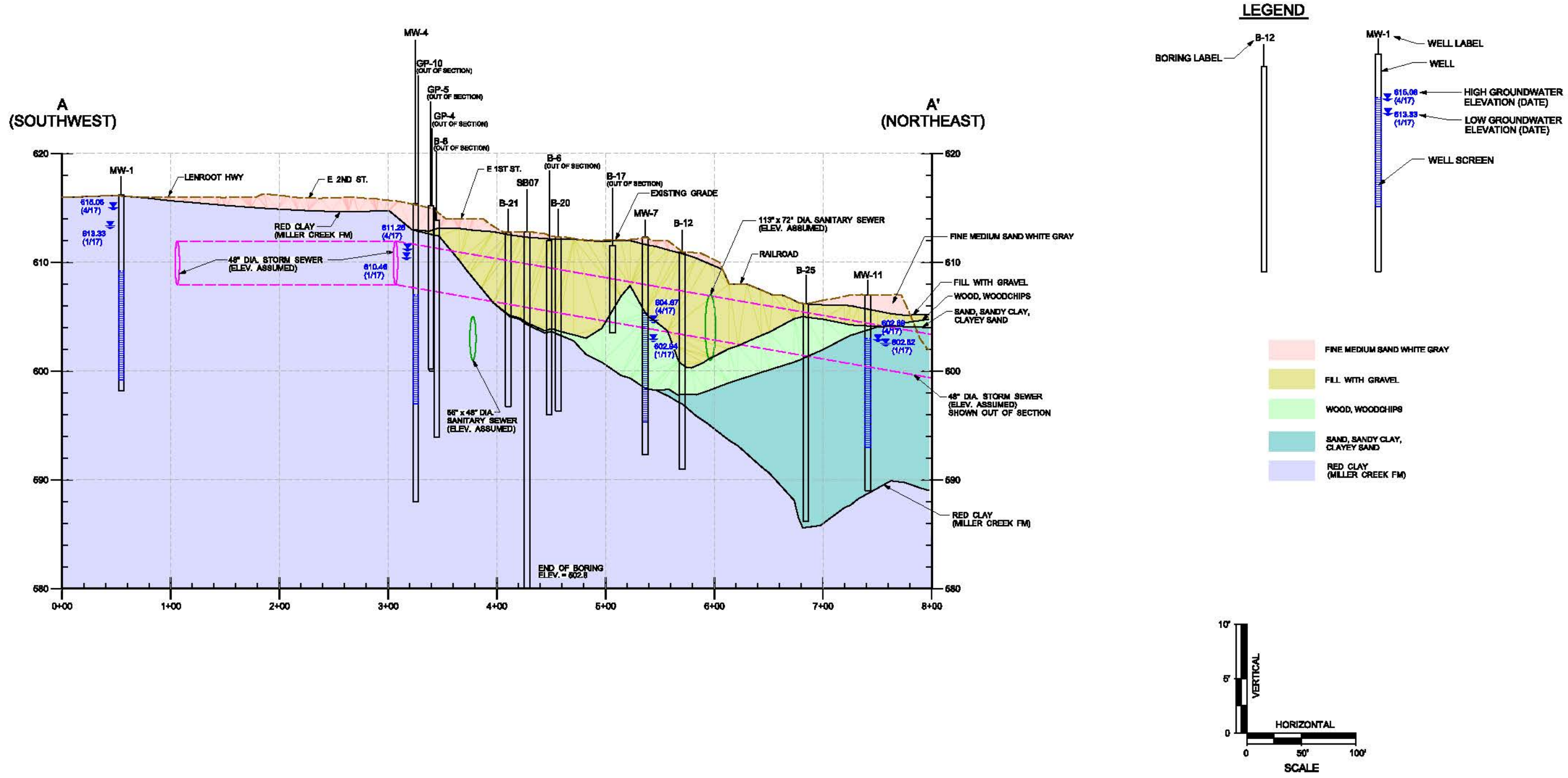
NOTES:
 1. 2016 - 3" resolution air photo from Douglas County.
 2. Horizontal coordinate system: NAD 1983 Douglas County, units in feet.

LEGEND	
	Abandoned Monitoring Well
	Geoprobe Boring
	Mobile Laboratory Boring
	Monitoring Well
	Rotosonic Boring
	Railroad
	Tax Parcel
	Upland Cross Section Locations
	Approximate Site Boundary



SUPERIOR WATER, LIGHT & POWER		
FIGURE 2-10		
ON-SHORE CROSS SECTION LOCATION MAP SITE INVESTIGATION REPORT SUPERIOR, WISCONSIN		
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FIGURE 2-11

ON-SHORE CROSS SECTION A - A'

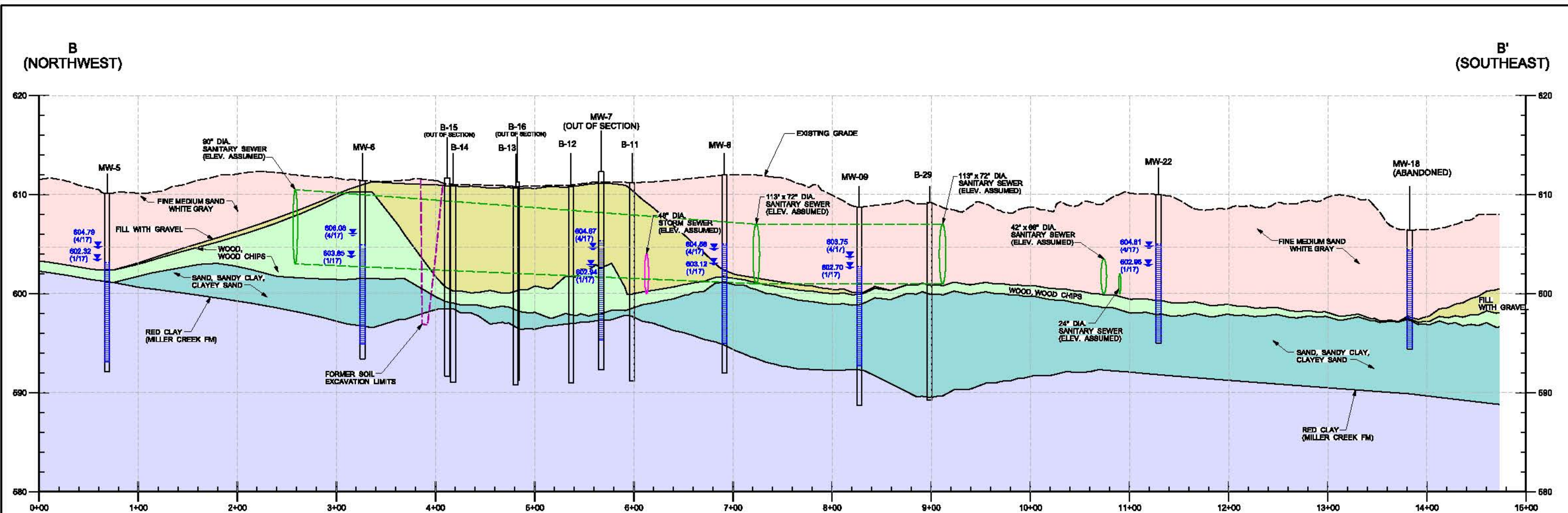
SITE INVESTIGATION REPORT

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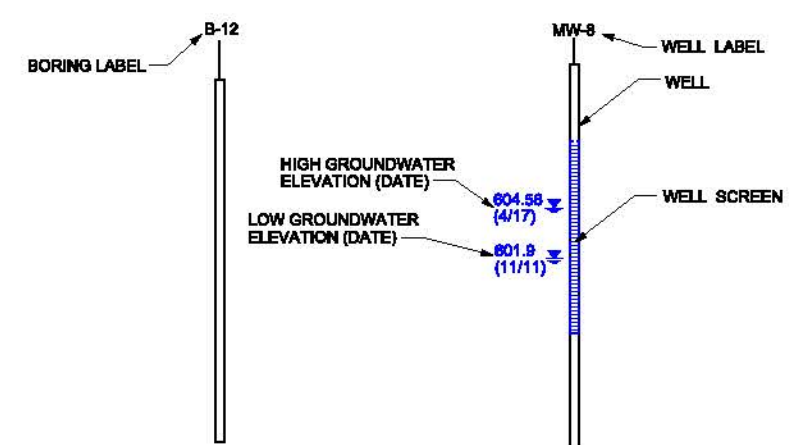
Date: MARCH 2019	Revision Date:
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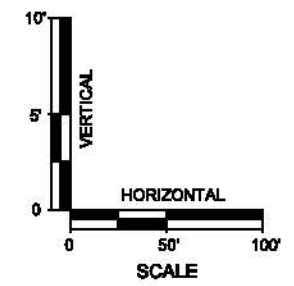
SCALE AS SHOWN



LEGEND



- FINE MEDIUM SAND WHITE GRAY
- FILL WITH GRAVEL
- WOOD, WOODCHIPS
- SAND, SANDY CLAY, CLAYEY SAND
- RED CLAY (MILLER CREEK FM)

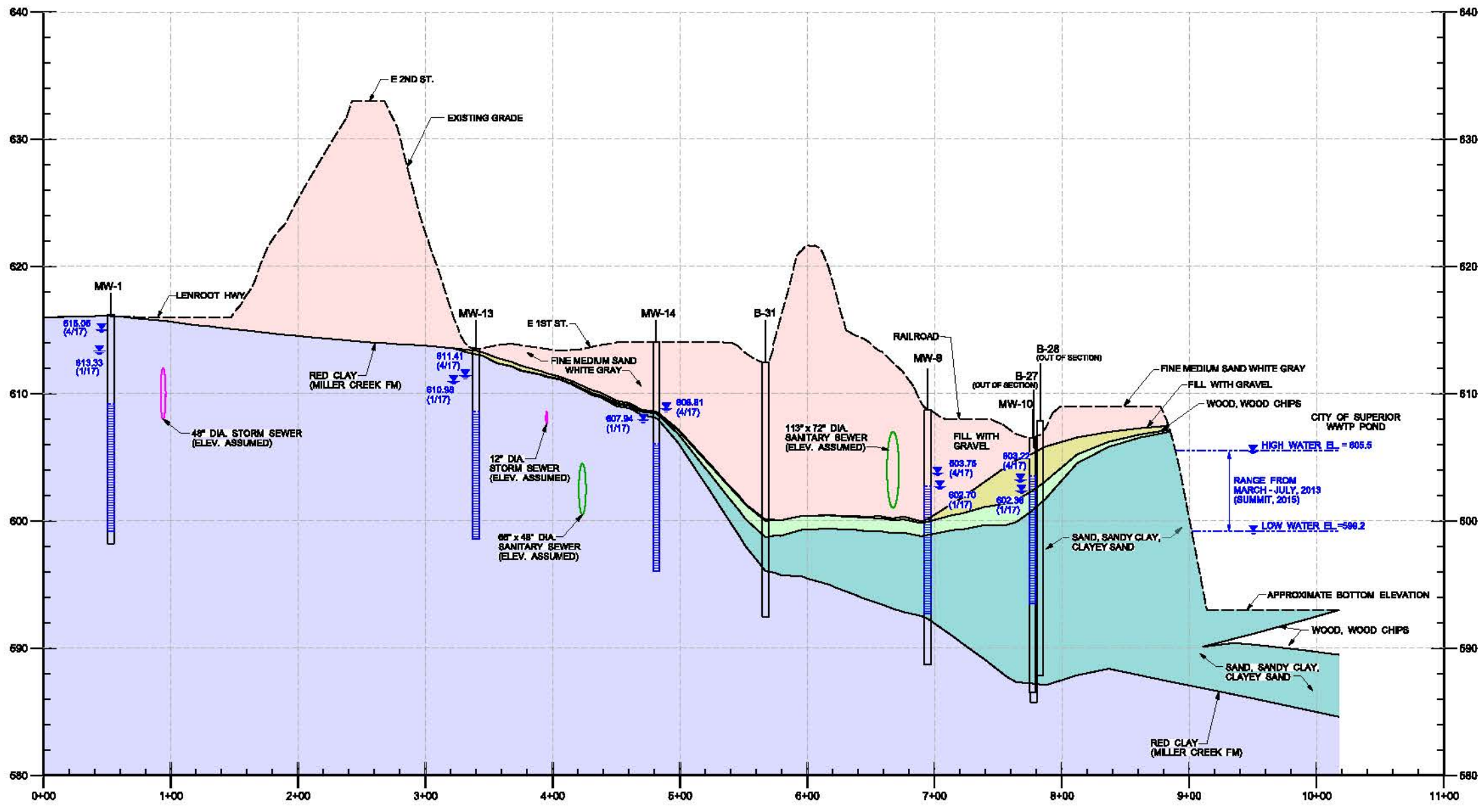


SUPERIOR WATER, LIGHT & POWER		
FIGURE 2-12		
ON-SHORE CROSS SECTION B - B' SITE INVESTIGATION REPORT SUPERIOR, WISCONSIN		
Date: MARCH 2019	Revision Date:	
Drawn By: JOW	Checked By: MJD2	Project: 18S024

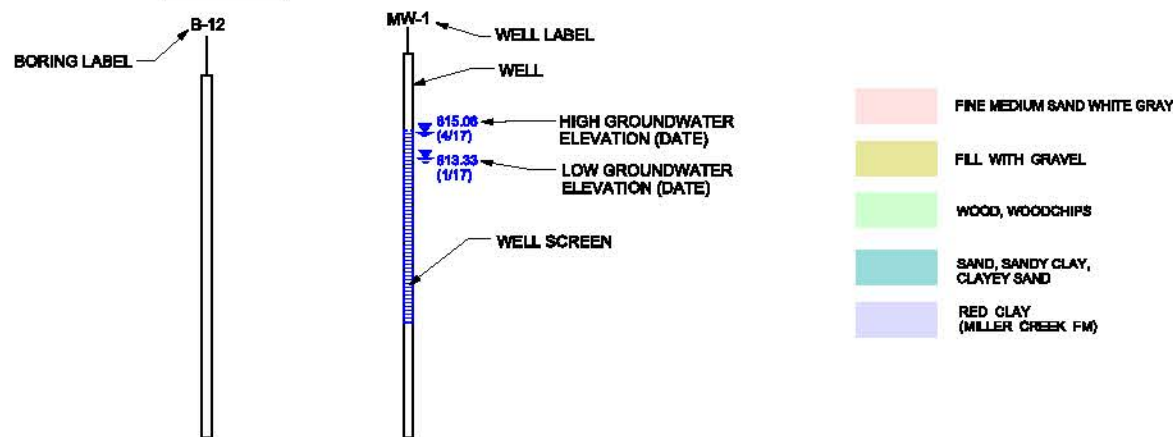
SCALE AS SHOWN

C
(SOUTHWEST)

C'
(NORTHEAST)



LEGEND

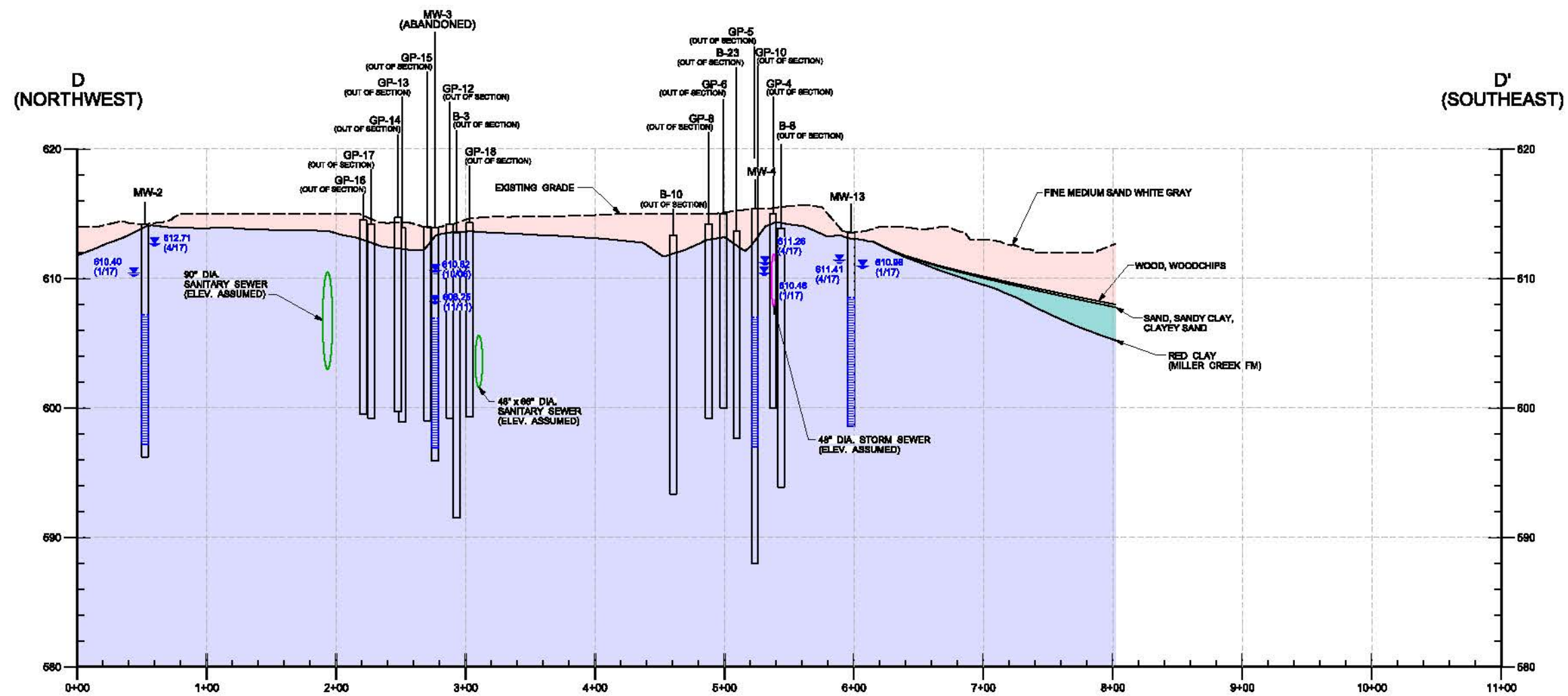


SCALE AS SHOWN

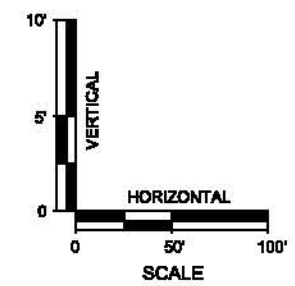
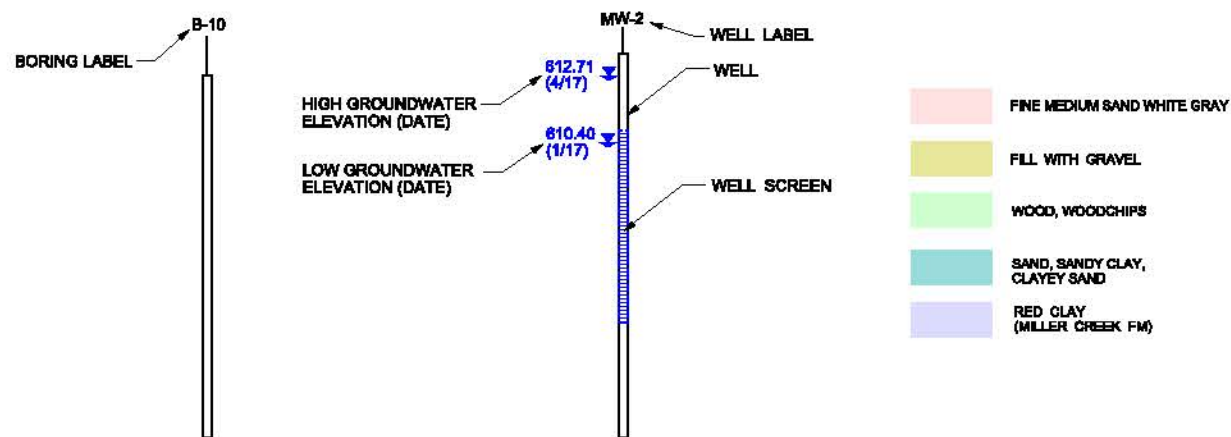
SUPERIOR WATER, LIGHT & POWER

FIGURE 2-13
ON-SHORE CROSS SECTION C - C'
SITE INVESTIGATION REPORT
SUPERIOR, WISCONSIN

Date: MARCH 2019	Revision Date:
Drawn By: JOW	Checked By: MJD2
Project: 18S024	



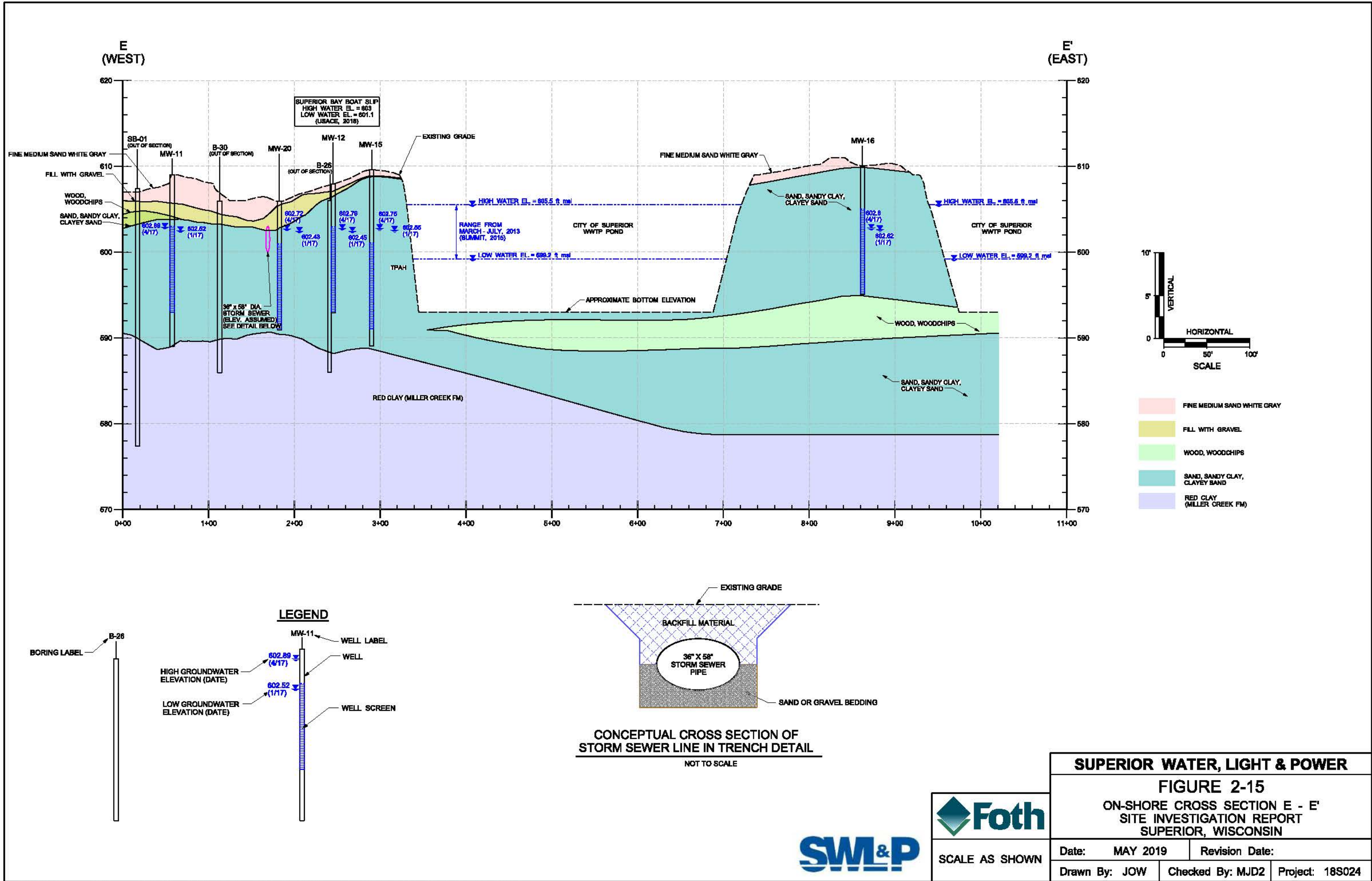
LEGEND



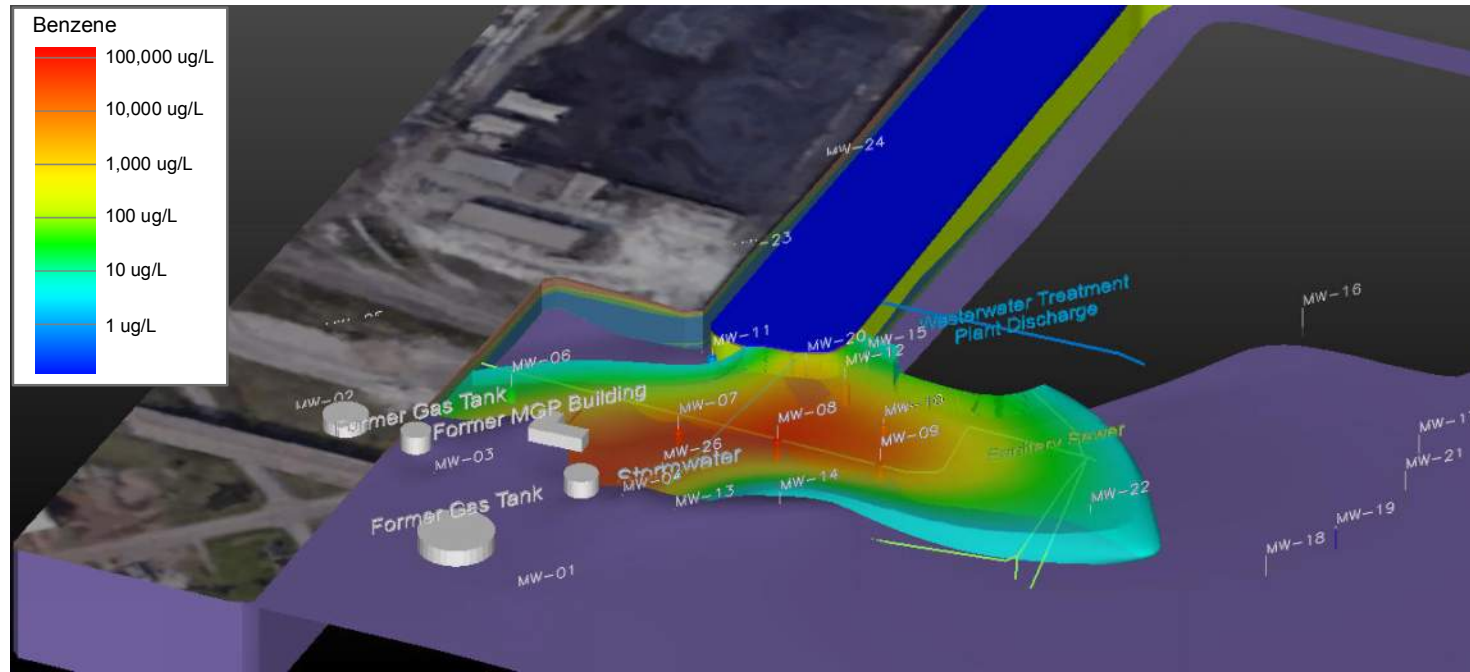
SUPERIOR WATER, LIGHT & POWER		
FIGURE 2-14		
ON-SHORE CROSS SECTION D - D' SITE INVESTIGATION REPORT SUPERIOR, WISCONSIN		
Date: MARCH 2019	Revision Date:	
Drawn By: JOW	Checked By: MJD2	Project: 18S024



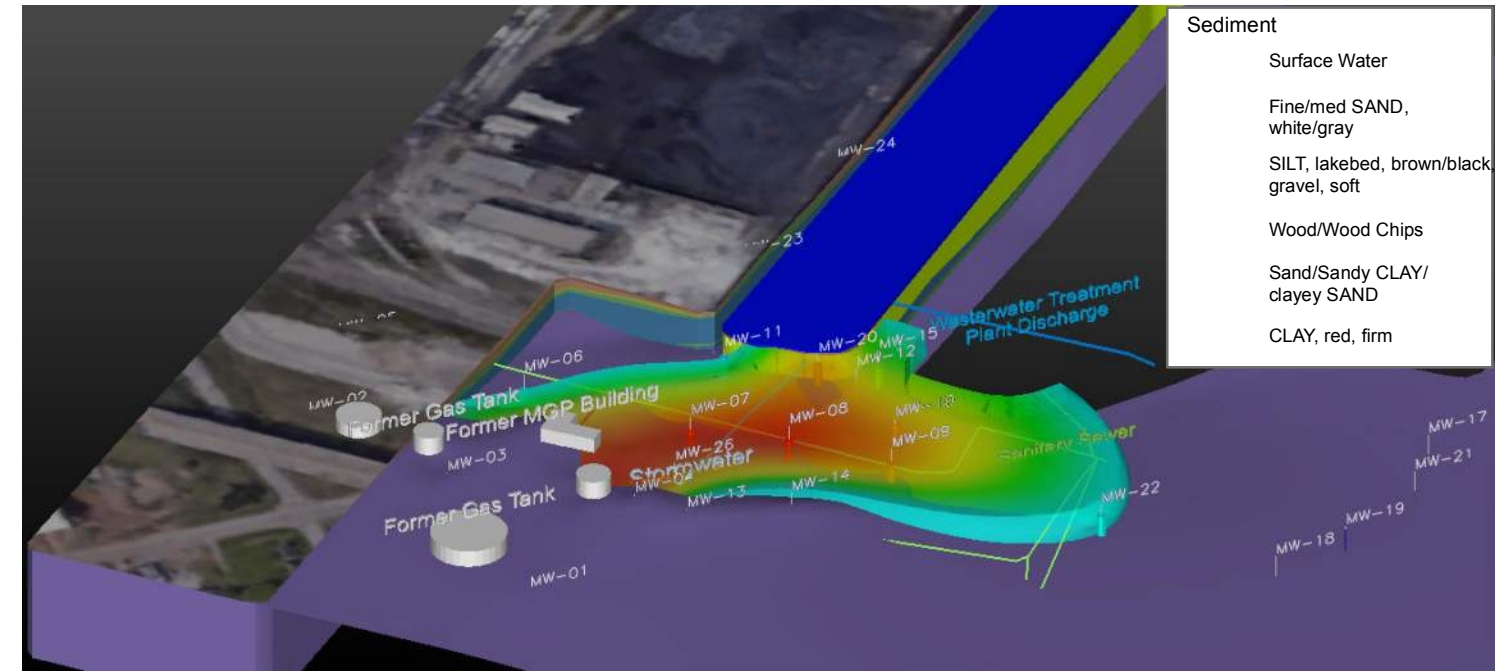
SCALE AS SHOWN



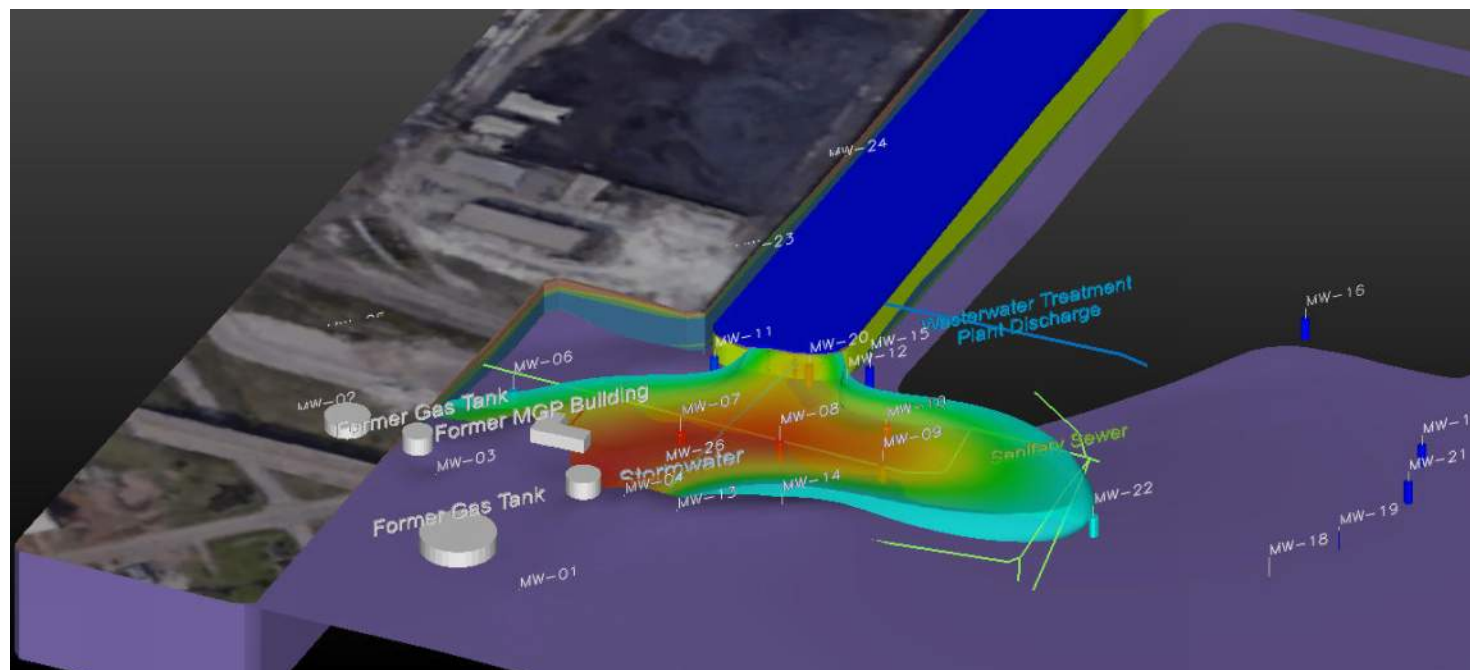
November, 2004



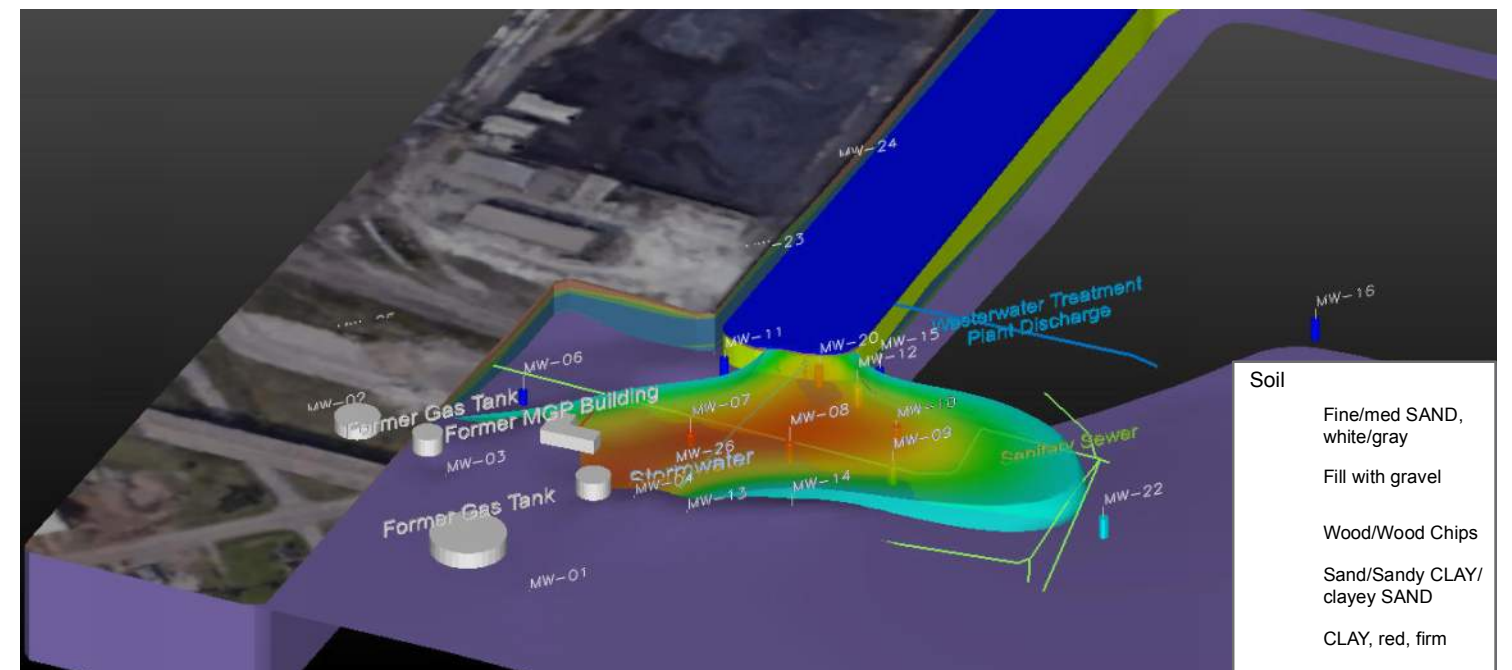
August, 2012



December, 2014



April, 2017



Groundwater Benzene Plume >5 ug/L (NR140 ES)

NOTES:

1. Groundwater interpolation based on the November 2004, August 2012 and December 2014 monitoring events (Groundwater Monitoring Report; Summit, 2015) and the April, 2017 monitoring event (SSI Report; Summit, 2017).
2. Kriging was performed through Earth Volumetric Studio v2017.6 by C Tech Development Corporation.



NOT TO SCALE

SUPERIOR WATER, LIGHT & POWER

FIGURE 5-2
SPATIAL-TEMPORAL DISTRIBUTION OF
BENZENE IMPACTS IN GROUNDWATER
SITE INVESTIGATION REPORT
SUPERIOR, WISCONSIN

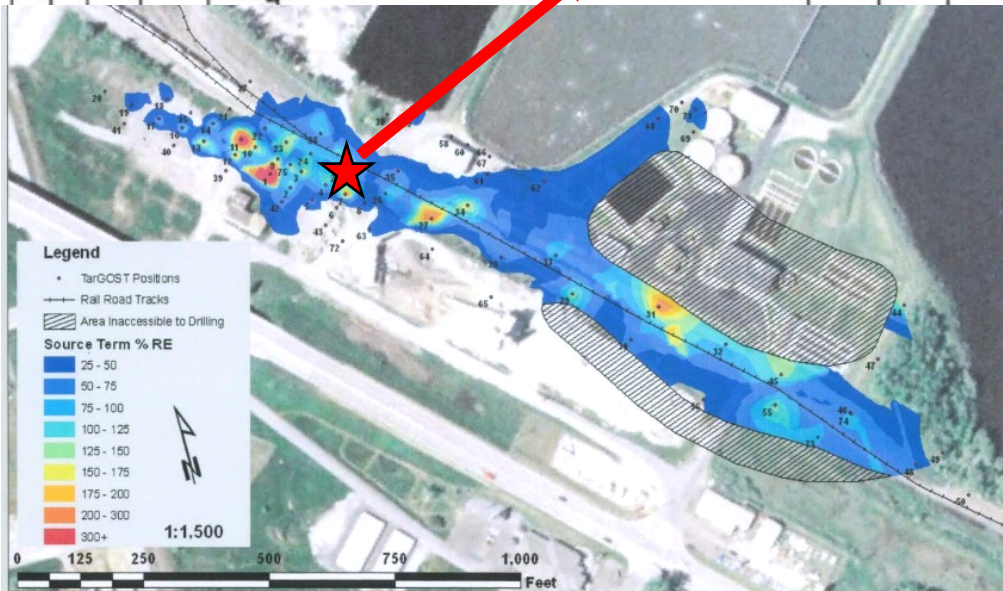
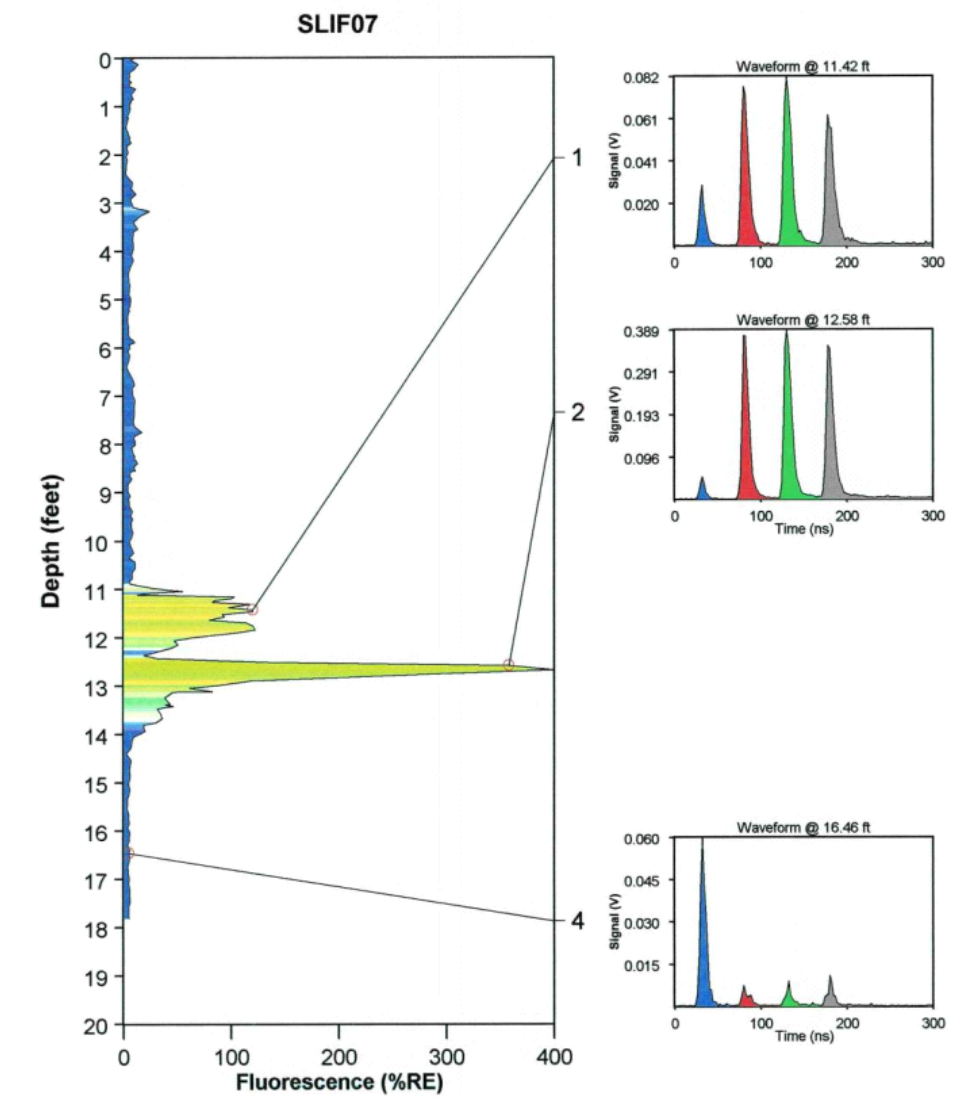
Date: MARCH 2019	Revision Date:
Drawn By: DAT	Checked By: SLG
Project: 18S024	

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Attachment 2
Clarification Letter Figures

B-11

Numb	Type	Length Recov	Blow f	Depth In Feet	Soil/ Rock Description And Geologic Origin For Each Major Unit	U.S.C.S.	Graphic	Well	PID/FID	Soil Properties					RQD/ Comments
										Compressive Strength	Moisture Content	Liquid Limit	Plasticity Index	P 200	
1	GP	45.6	NA	1	2 inches gravel, then lime-like material, hard, gray, no odor				6.6						EnChem B-11-1-3
2	GP	48	NA	2-10	Same as above except dark gray and slight odor				11						
3	GP	48	NA	11	1" dark brown peat layer, odor				220						
4	GP	38.4	NA	12-13	Cinder-like material with sand, loose, wet and tarry, strong odor	CH			1261						EnChem B-11-10-12 GTI B-11-12-13
5	GP	36	NA	14-18	Clay, red-brown, stiff, moist, slight odor				3300						
				17-18	Same as above, except coated with sand and tar sluff from 12-13 foot layer				NA						
				20	END OF BORING - 20 FEET				NA						



NOTES:

In source area there is great correspondence between LIF reactions and contamination observed from 11 to 13 ft bgs. B-11 total PAH = 61 ppm at 10 to 12 ft bgs



NOT TO SCALE

SUPERIOR WATER, LIGHT & POWER

FIGURE 1

Source Area SLIF-07
LETTER OF CLARIFICATION
SUPERIOR, WISCONSIN

Date: MAY 2019

Revision Date:

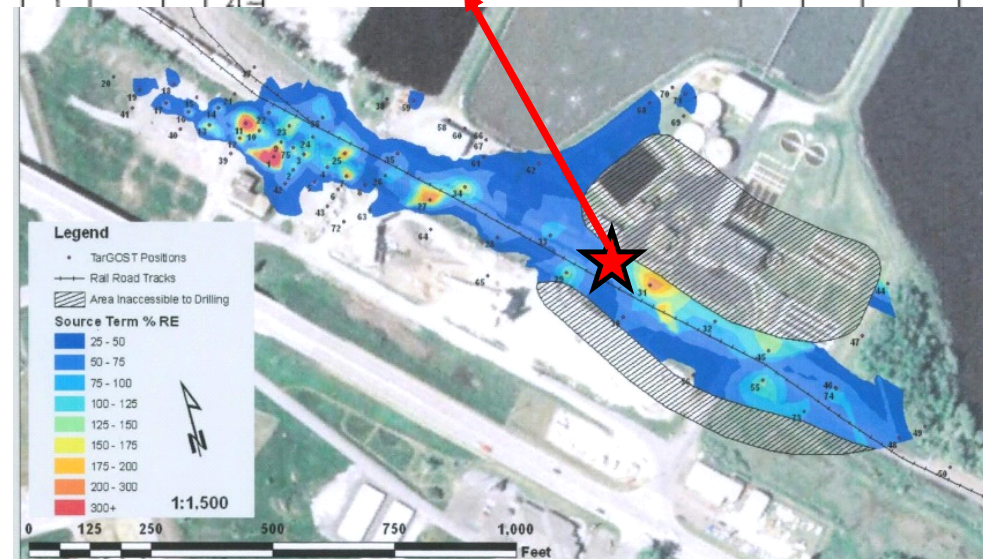
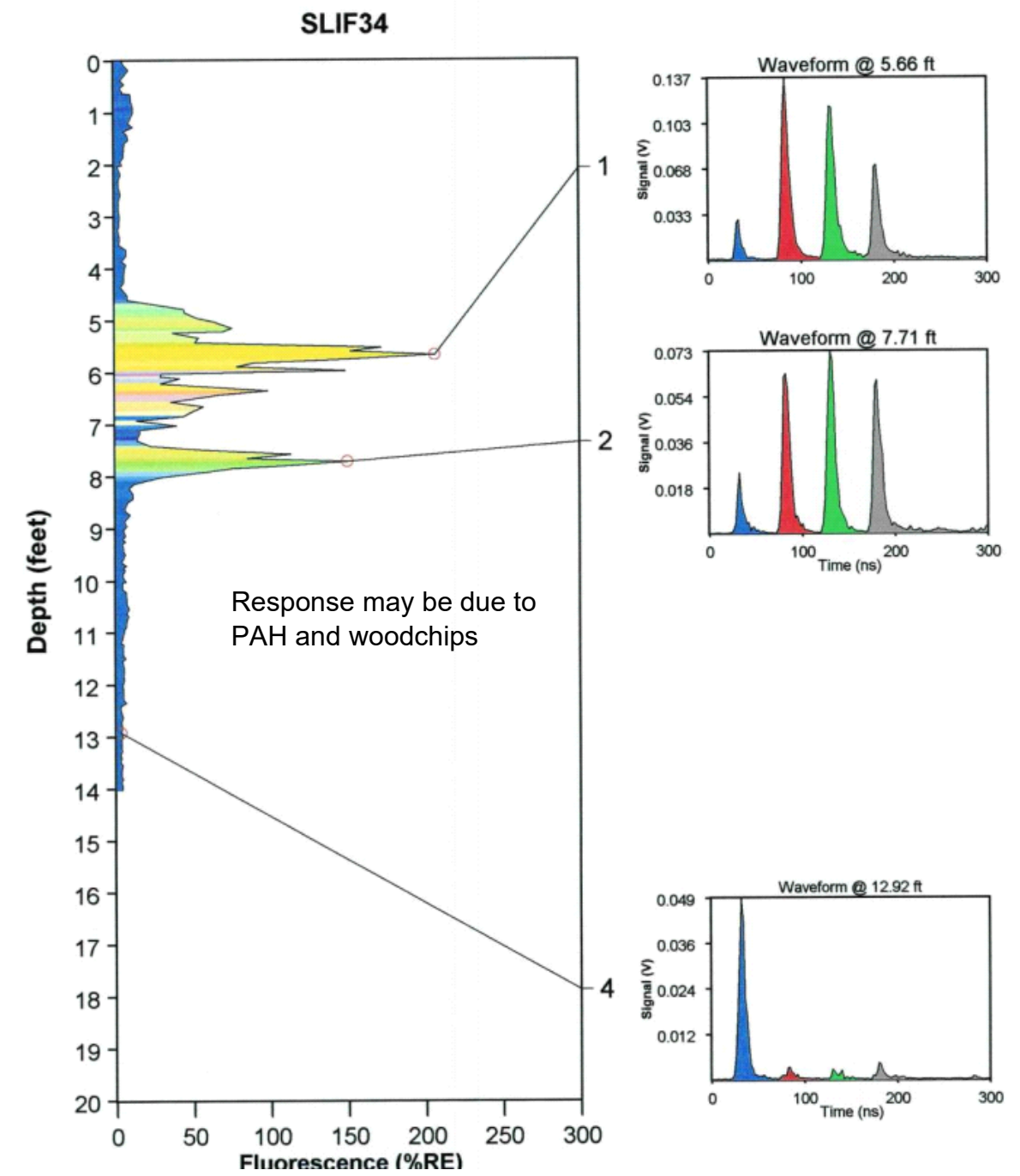
Drawn By: DAT

Checked By: SLG

Project: 18S024

MW-10

Sample				Depth In Feet	Soil/ Rock Description	U.S.C.S.	Graphic	Well	PID/FID	Soil Properties					RQD/	
Number	Type	Length Att. & Recovered (ft)	Blow Counts							Compressive	Moisture	Liquid	Plasticity	P 200		
1	GP	2.0		1-4	Lime-like material, gray, moist, no odor. Mixed sand and gravel, black slag and coal, crumbly, moist, no odor.	Fill		6								
2	GP	2.1		5-7	Fine sand with silt, brown, wet, slight sheen and odor, woodchip layer at five feet with sheen.			128							5-6 ft Soil Sample	
3	GP	4.1		8-12	Same as above, but no woodchips, slight sheen and strong odor.	SP		435								
4	GP	3.2		13-16				941								
					END OF BORING-20 FEET											



PAH = 2,565 ppm at 5 to 6 ft bgs
 GW Naph 5.6 ppb, BaP 0.27 ppb - 2017



SUPERIOR WATER, LIGHT & POWER

FIGURE 2

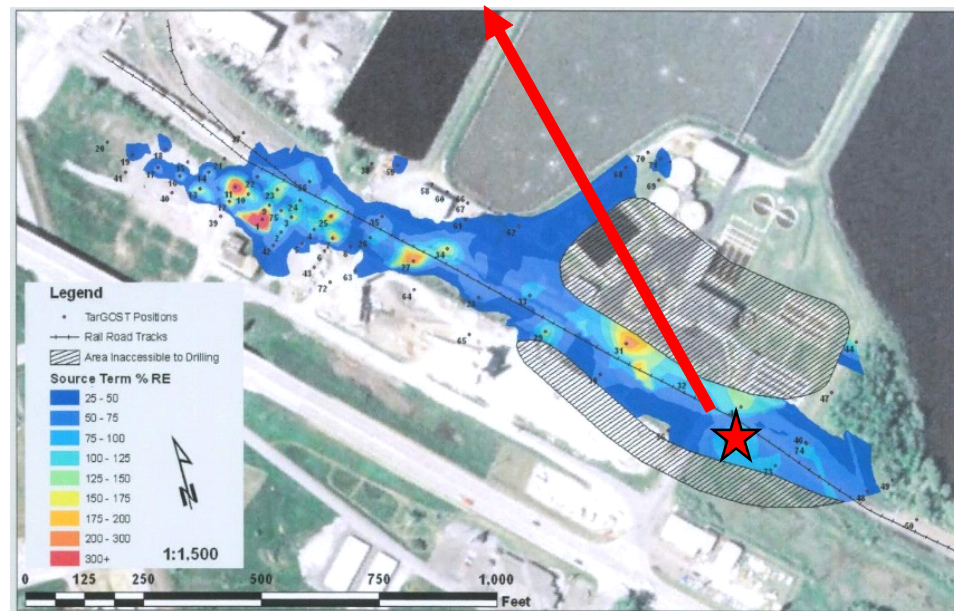
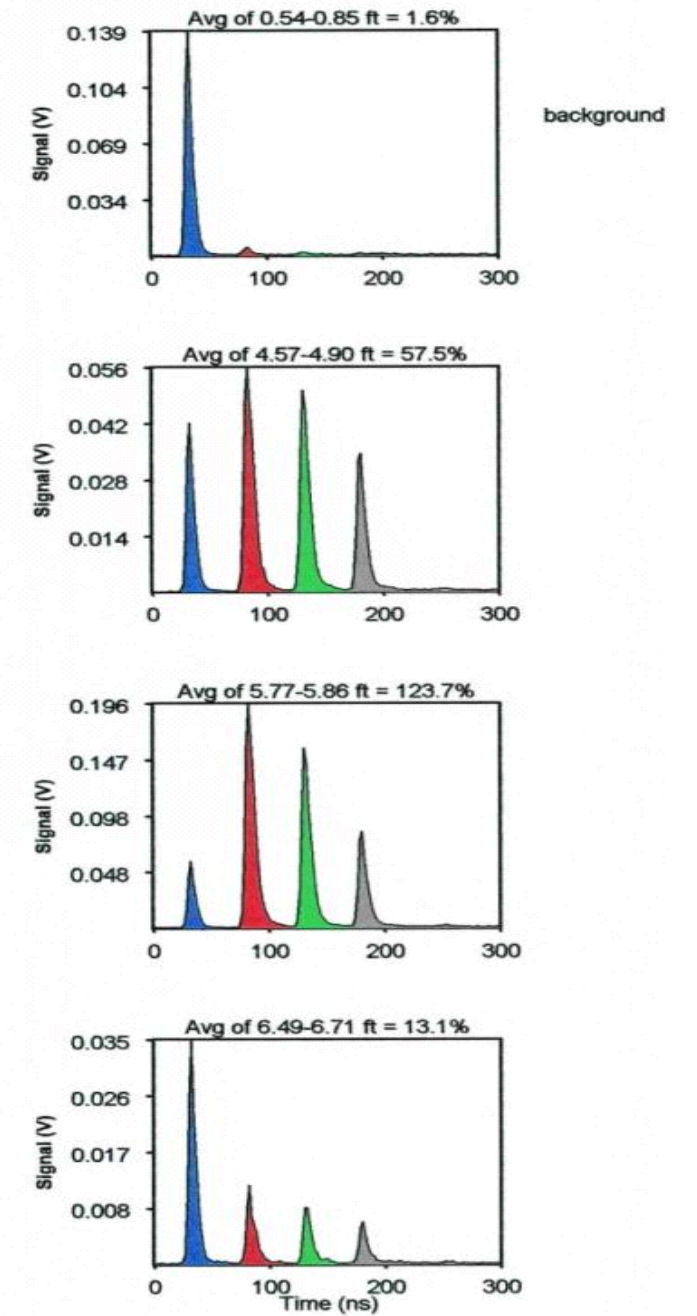
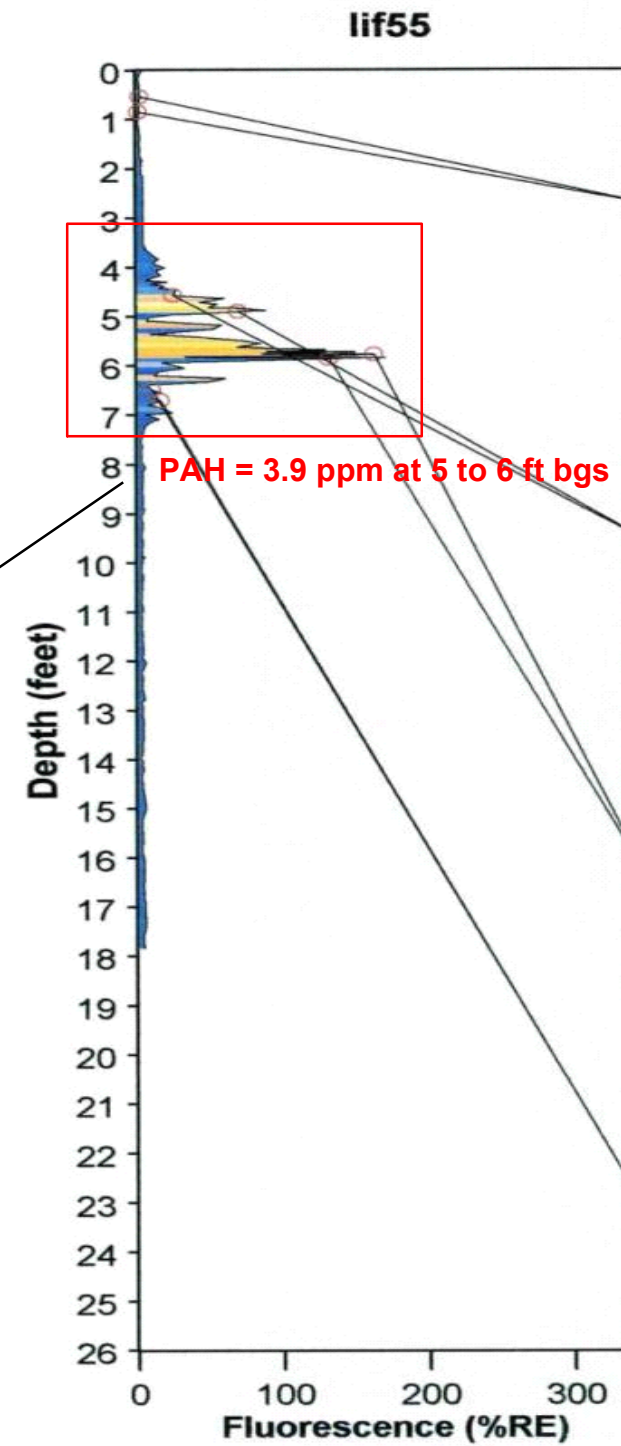
Central Area SLIF-34
 LETTER OF CLARIFICATION
 SUPERIOR, WISCONSIN

Date: MAY 2019	Revision Date:
Drawn By: DAT	Checked By: SLG
Project: 18S024	

NOT TO SCALE

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LIF-55				(ppm)	Recovery (ft)	USCS	Lithological Description
0						NA	Brown topsoil. Moist, crumbly.
-1						NA	Black cinders. Crumbly, moist, no odor
-2	0-4 ft	NA	2.8			SP	Brown fine sand with fines. Moist to wet at 2ft, well sorted, no odor
-3						SP	
-4						NA	Dark brown wood chips with a little sand and fines. Wet, rotten wood odor.
-5	4-8 ft	NA	4			NA	
-6						NA	
-7						NA	
-8						NA	



No visual evidence of contamination and LIF reported as due to wood by ENSR



SUPERIOR WATER, LIGHT & POWER

FIGURE 3

SE Area LIF-55
LETTER OF CLARIFICATION
SUPERIOR, WISCONSIN

Date: MAY 2019	Revision Date:
Drawn By: DAT	Checked By: SLG
Project: 18S024	

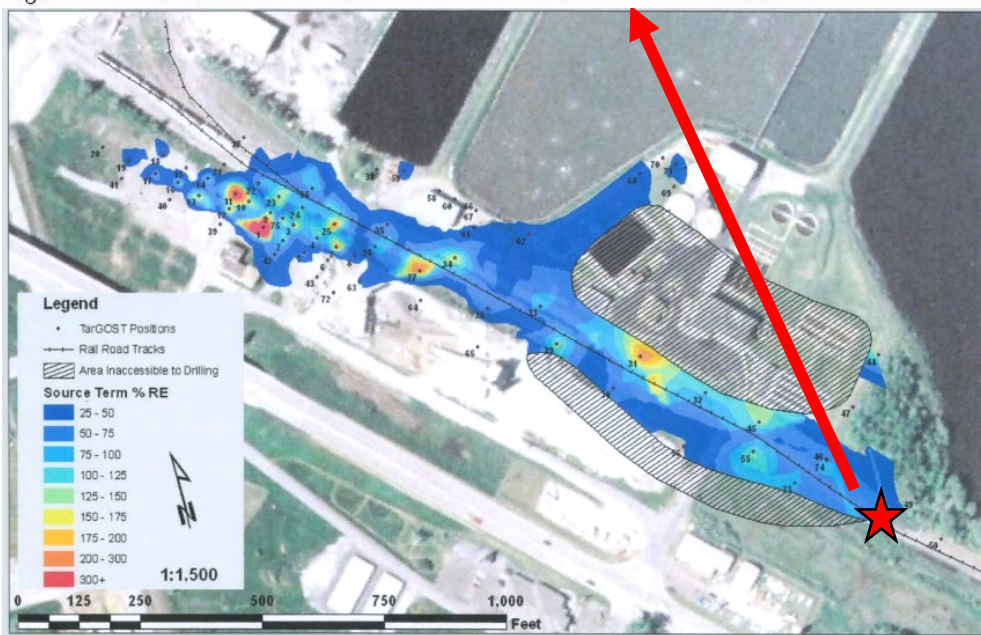
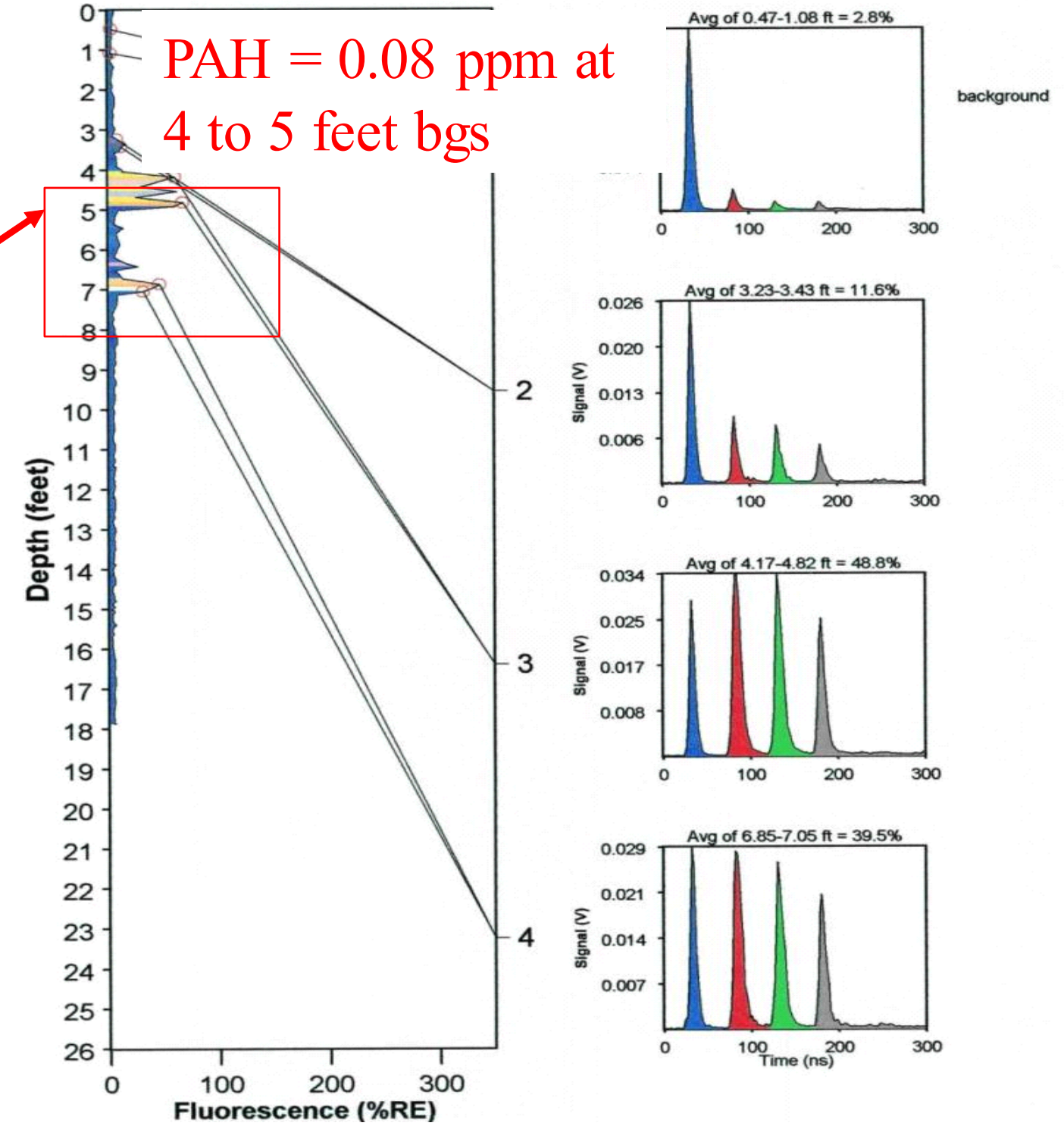
NOT TO SCALE

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LIF-48

Recovery (ft)	USCS	Lithological Description
0		Topsoil, brown, moist, no odor.
0 to 2	NA	Sand with fines, brown to dark brown, moist to wet at 3ft, no odor.
2-6 ft	NA	4.0 Wood chips w/fines and sand, brown and dark brown, wet, fuel oil odor.

PAH = 0.08 ppm at 4 to 5 feet bgs



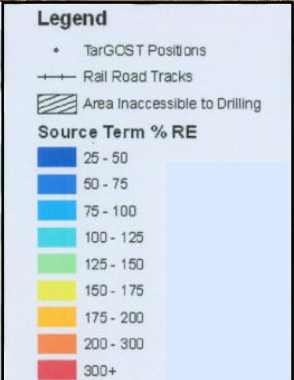
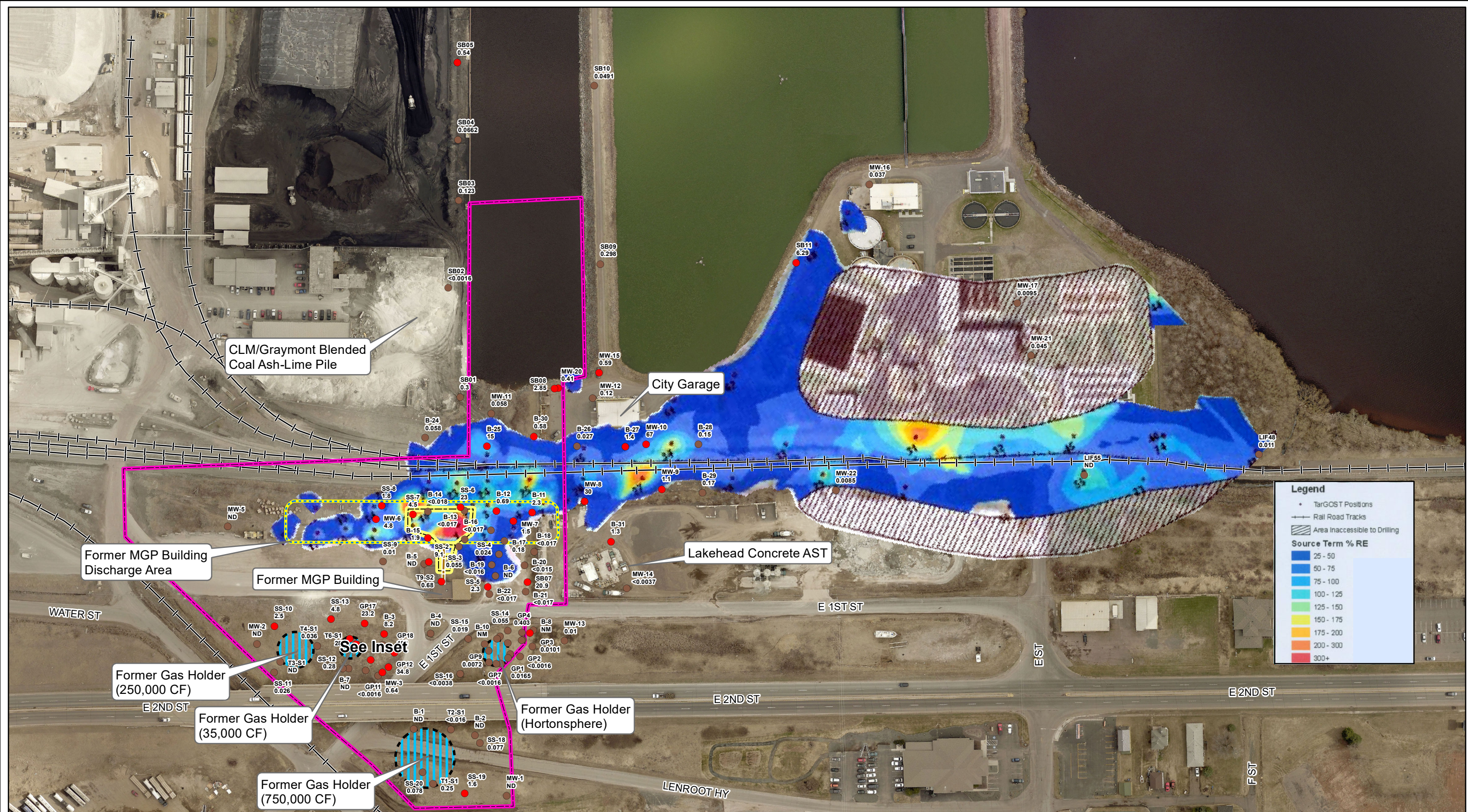
NOTES:
No visual evidence of contamination and LIF reported as due to wood by ENSR



SUPERIOR WATER, LIGHT & POWER		
FIGURE 4		
SE Area LIF-48 LETTER OF CLARIFICATION SUPERIOR, WISCONSIN		
Date: MAY 2019	Revision Date:	
Drawn By: DAT	Checked By: SLG	Project: 18S024

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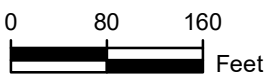


- NOTES:**
- 2016 - 3" resolution air photo from Douglas County.
 - Horizontal coordinate system: NAD 1983 Douglas County, units in feet.
 - ND = No Detect
 - Image from TarGOST figure 4-3 from the Phase II, Part IV SIR (ENSR/AECOM report).

- LEGEND**
- SS-19 1.6 • Soil Sample Location with Maximum Benzo(a)pyrene Concentration (mg/kg) that exceeds the WDNR Direct Contact Soil Cleanup Standard of 0.39 mg/kg
 - SS-18 0.077 • Soil Sample Location with Maximum Benzo(a)pyrene Concentration (mg/kg) less than the WDNR Direct Contact Soil Cleanup Standard of 0.39 mg/kg
 - Former Clay Pipe

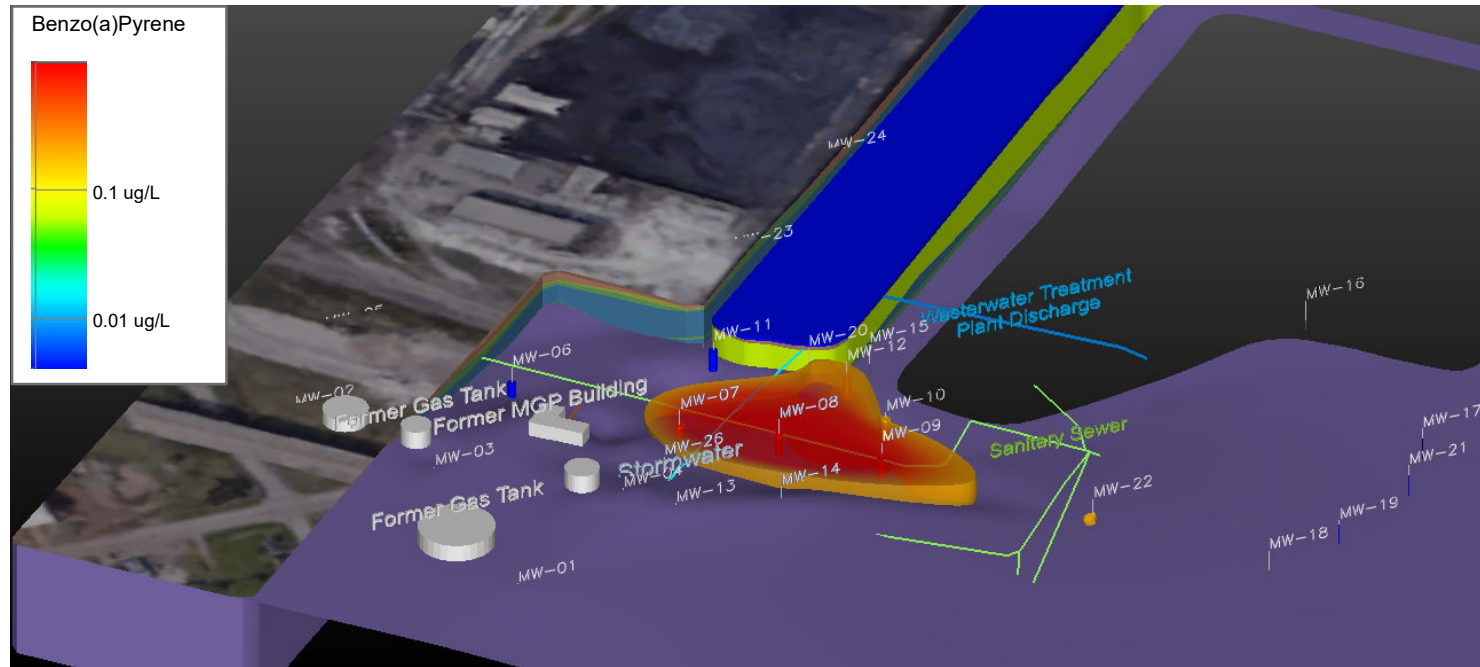
- ▭ Approximate 2008 Remedial Excavation
- ▭ Former MGP Building Discharge Area
- ▨ Former Gas Holders
- ▭ Approximate Site Boundary
- Railroad

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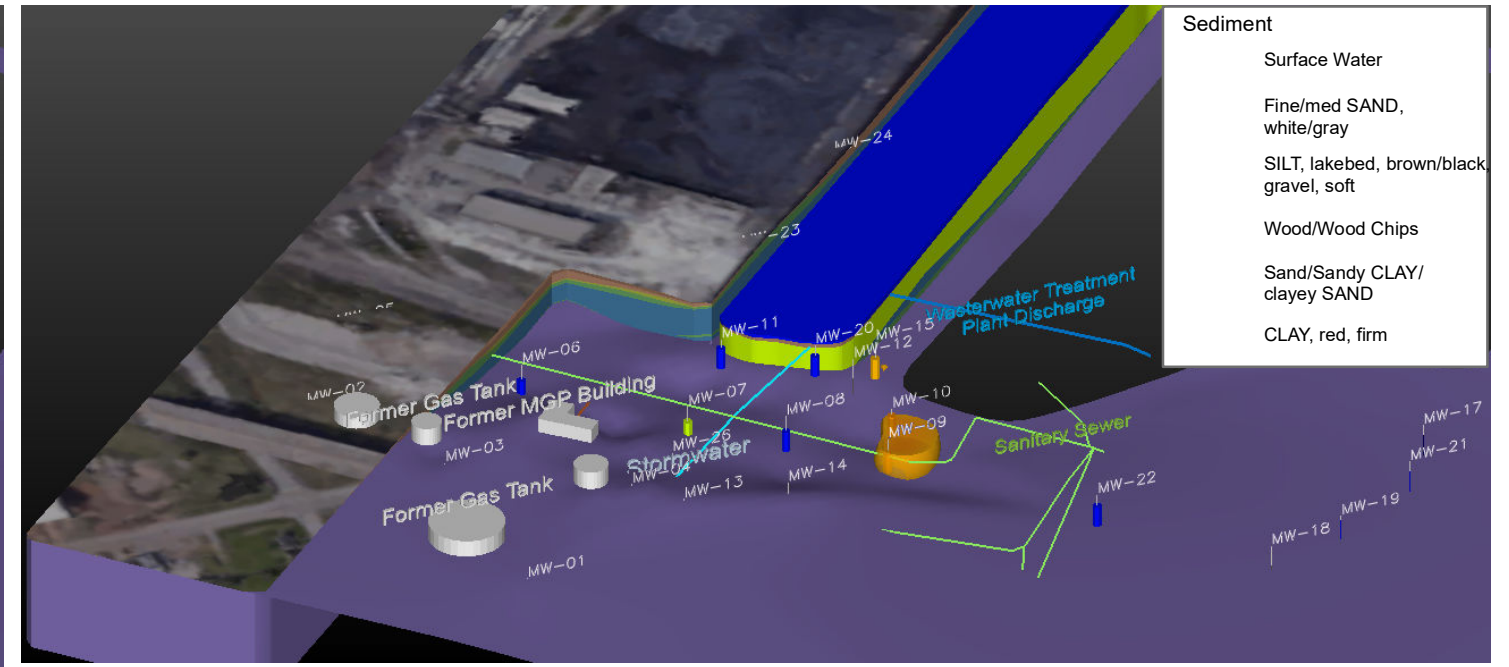


SUPERIOR WATER, LIGHT & POWER		
FIGURE 5		
Comparison of Benzo(a)pyrene in Soil to TarGOST Results LETTER OF CLARIFICATION SUPERIOR, WISCONSIN		
Date: MAY 2019	Revision Date:	
Drawn By: DAT	Checked By: MJD2	Project: 18S024

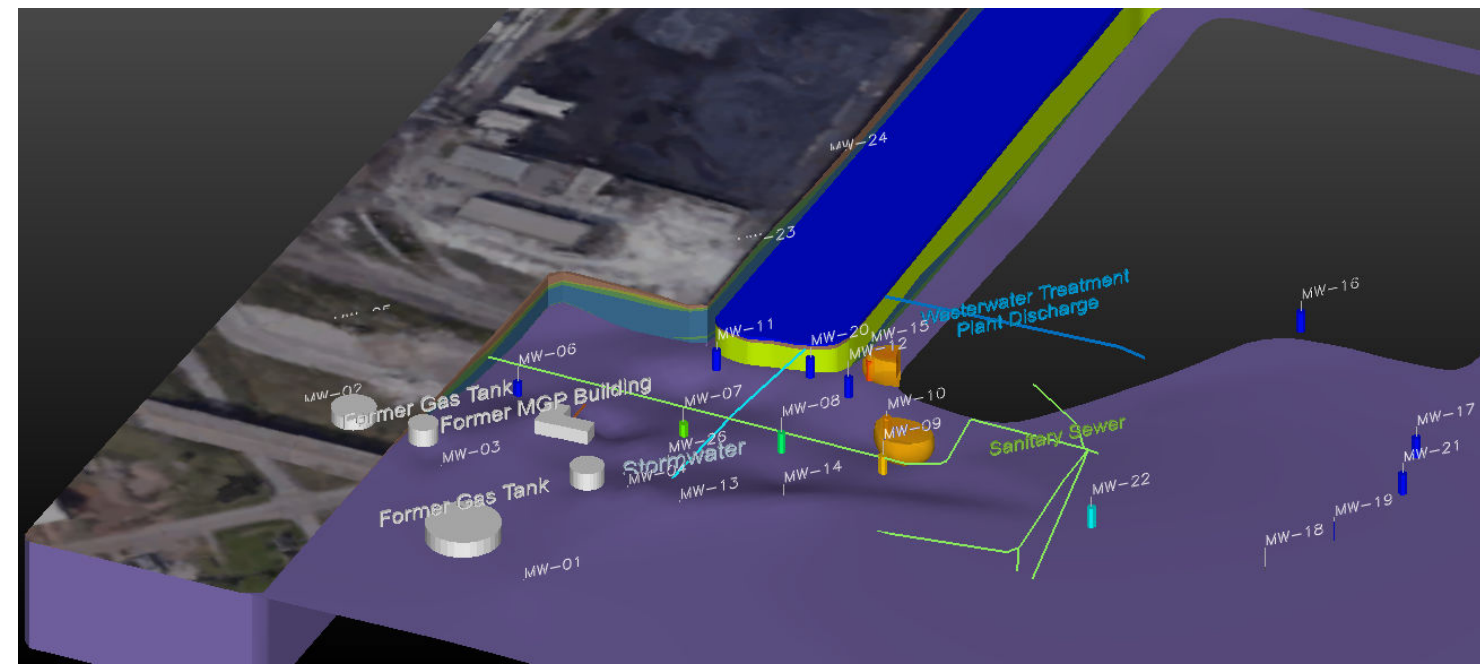
November, 2004



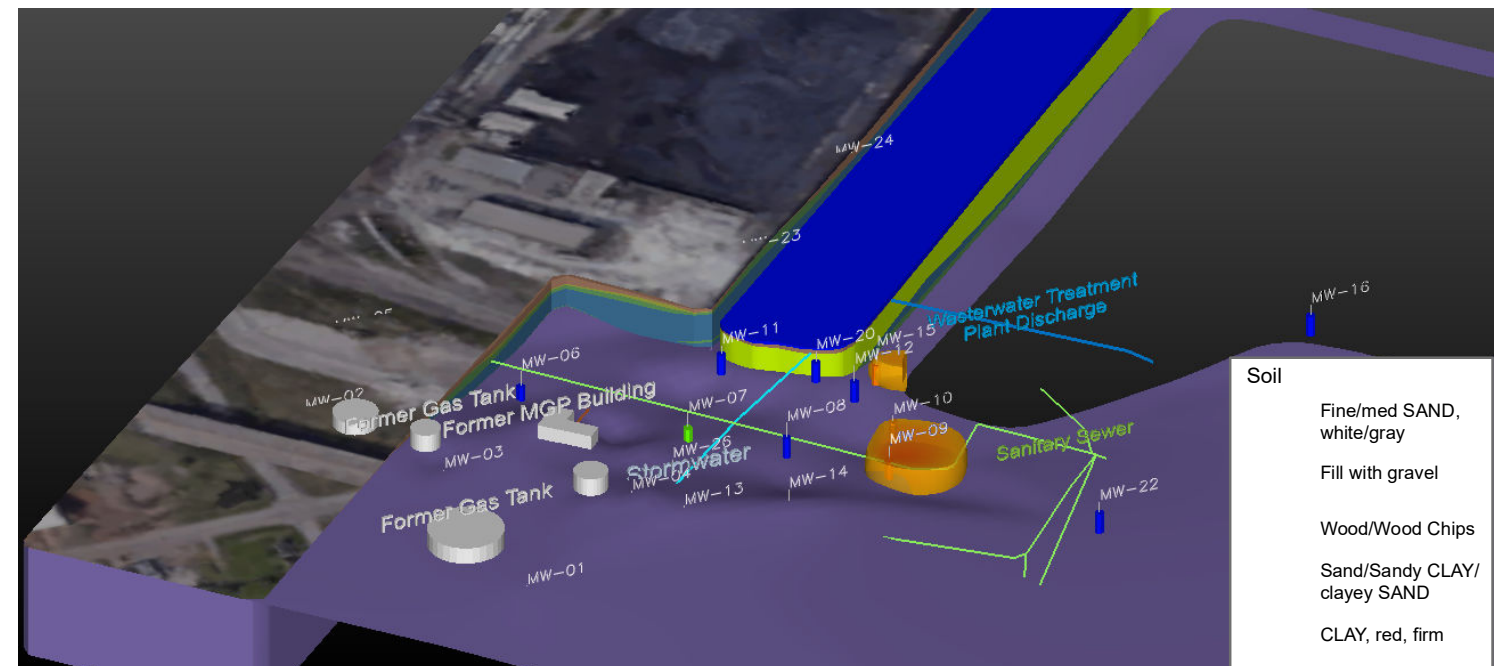
August, 2012



December, 2014



April, 2017



Groundwater Benzo(a)Pyrene Plume >0.2 ug/L (NR140 ES)

NOTES:

1. Groundwater interpolation based on the November 2004, August 2012 and December 2014 monitoring events (Groundwater Monitoring Report; Summit, 2015) and the April, 2017 monitoring event (SSI Report; Summit, 2017).
2. Kriging was performed through Earth Volumetric Studio v2017.6 by C Tech Development Corporation.



NOT TO SCALE







SUPERIOR WATER, LIGHT & POWER

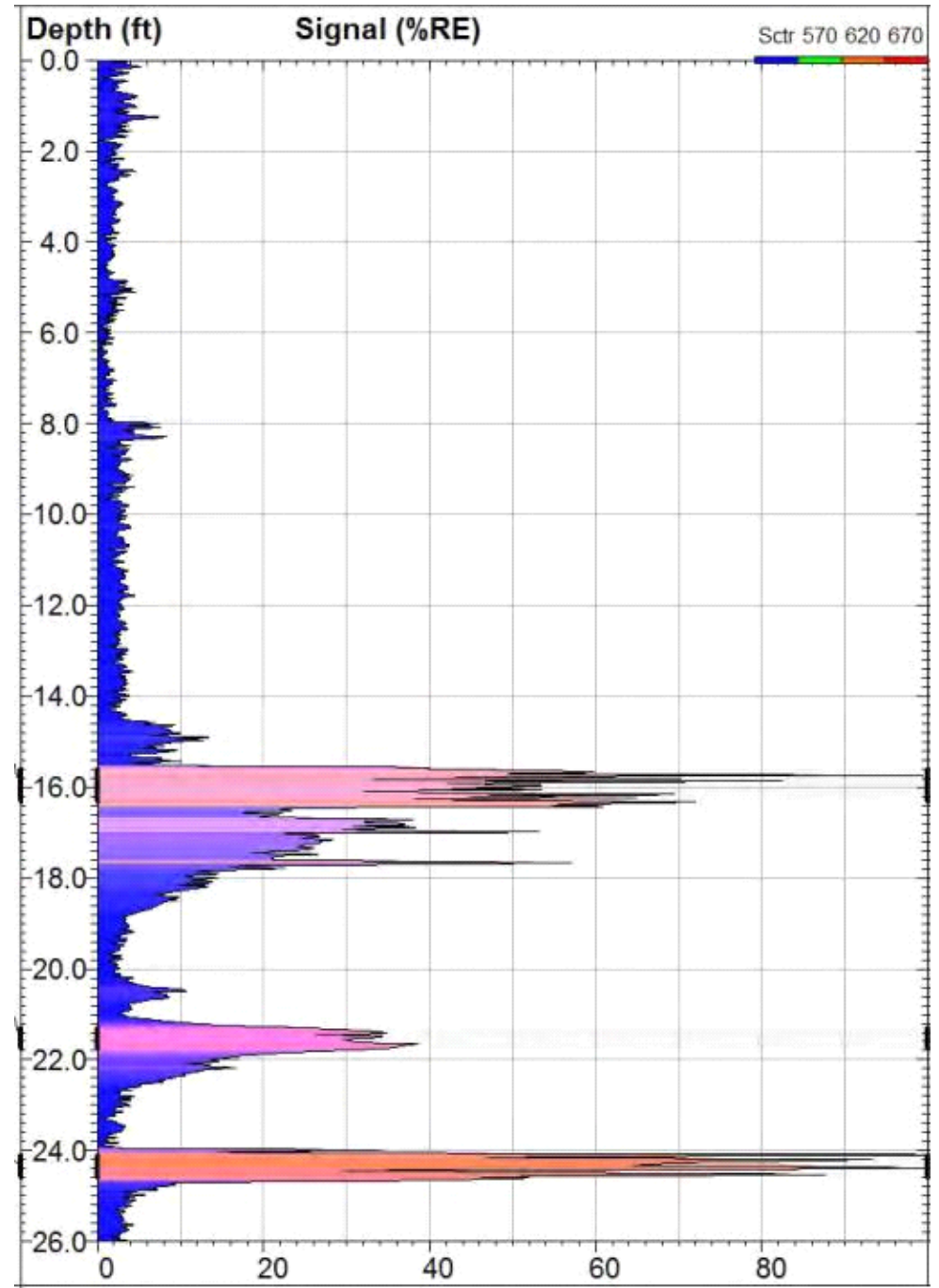
FIGURE 6
SPATIAL-TEMPORAL DISTRIBUTION OF
BENZO(A)PYRENE IMPACTS IN GROUNDWATER
LETTER OF CLARIFICATION
SUPERIOR, WISCONSIN

Date: MAY 2019	Revision Date:
Drawn By: DAT	Checked By: SLG
Project: 18S024	

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SB09

Depth in Feet Below Grade	Sample ID	PID (ppm)	Recovery %	GRAPHIC LOG	Description
0			100		Topsoil, brown, sandy silt, trace gravel, moist.
			100		Sand, brown, firm, moist.
	SB09_5-10	3.6	75		
			100		
	SB09_13.5-15	9.1			Silty sand, dark grey, some wood, wet, odor.
					Sand, dark grey, some wood, wet, odor.



No visual evidence of contamination and wood is present in boring log below 13 ft. Soil sample from 13 to 15.5 ft had 0.298 mg/kg BaP (less than EPA criterion)

TG-07



SUPERIOR WATER, LIGHT & POWER		
FIGURE 7		
WWTP Berm Area TG-07 LETTER OF CLARIFICATION SUPERIOR, WISCONSIN		
Date: MAY 2019	Revision Date:	
Drawn By: DAT	Checked By: SLG	Project: 18S024

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Attachment 3
Soil Organic Content Reference

Chemical properties of different peat-moorsh soils from the Biebrza River Valley

L. Szajdak¹, T. Brandyk² and J. Szatyłowicz²

¹Research Centre for Agricultural and Forest Environment, Polish Academy of Sciences, ul. Bukowska 19, 60-809 Poznan, Poland, szajlech@man.poznan.pl

²Department of Environmental Improvement, Warsaw Agricultural University, ul. Nowoursynowska 159, 02-776 Warsaw, Poland

Abstract. The relationship between soil structure and the ability of soil to stabilize soils organic matter is a key element in soil C dynamics. In this investigation the chemical properties were determined for three different peat-moorsh soils – Czarna Wieś, Otoczne and Kwaterna 17 located in the Biebrza River Valley in Poland. Each considered soil, utilised as meadow, was sampled at two depths. The measured concentrations of total organic carbon in the considered soils ranged from 37.19% to 45.58%. Generally, a decrease of total organic carbon concentration with the depth of profiles was observed. The contents of dissolved organic carbon in the soils ranged from 5.34 to 19.39%. The quantities of dissolved organic carbon decreased simultaneously with E_4/E_6 values with the increasing depth of the soil profiles.

Key words: peat-moorsh soils, TOC, DOC, E_4/E_6

INTRODUCTION

Peat represents a mixture of organic compounds characterised by high molecular weight – humic and fulvic acids and their salts as well as cellulose, lignite, bitumines, peptides, enzymes and fats. Additionally, peat includes low molecular organic compounds like amino acids, alkaloids, purine and pyrimidine bases, carbohydrates, vitamins, sugars, phenols, antibiotics, steroids, triterpenoids, β -sitosterol etc. (Kondo, 1976; Bambalov et al., 2000; Szajdak, 2002). These substances establish colloidal behavior of peat and lead to loss of wetability caused by drying (Kwak et al., 1986). The structure, origin and fate of such molecular configurations are thus clearly linked to the water-retention properties of peat (Sokołowska et al., 2005).

The transformation of peat organic matter by chemical, biochemical and biological decay leads to the formation of a number of chemical substances. During the peat transformation the principal changes of the organic matter are the following: decrease of the total water content, increase of specific gravity, increase of compaction, decrease of pore space, increase of the degree of decomposition, colour changes towards dark brown and black and increase of the calorific value (Gotkiewicz & Kowalczyk, 1977; Lüttig, 1986; Lishtvan et al., 1989). The variations in peat organic matter arise from the variety of plants whose residues impact the peat formation and from the environmental conditions in which humification takes place (MacCarthy et al., 1990).

The long-term cultivation and agricultural use of peatland has an impact on the environment leading to decrease of ground water level, changes of aerobic conditions, changes in plant communities, and root exudates of cultivated plants as well as degradation and mineralization of peat (Grootjans et al., 1985, 1986; Lishtvan et al., 1989; Borys, 2002). Due to these factors peat may undergo a process of secondary transformation. In general, this process led to an increase of the total variable surface charge, which is manifested by the decrease of water holding capacity. Also, the progressive hydrophobic properties of moorsh are observed (Szajdak, 2002). Kalbitz et al., (1999) showed that the land use of peatlands has effects on fulvic acid (FAs) properties, which account for the major fraction of dissolved organic matter. The above mentioned authors suggested that long-term intensive land use (from 50 to above 200 years) resulted in a larger proportion of the aromatic structures and a larger degree of polycondensation of FAs. However it is unknown what changes in the units of the structure of FAs they cause. Leinweber et al., (2001) reported that in water-soluble FAs, which are the main component (about 60%) of dissolved organic matter, the proportion of carbohydrates and phenols together with lignin monomers increased with increasing intensity of soil tillage, aeration and peat degradation.

A great number of biochemical, chemical, and biological processes in peat require aqueous conditions. The drainage and agricultural use of peatlands result in intensive changes of biotic and abiotic properties, which lead to the degradation of the peat organic matter. Peat organic matter regulates long-term C storage and the availability of nutrients to plants and microbes. The content of water, dissolved organic matter (DOM), is closely associated with microbial activity, because this fraction of the organic carbon can be vulnerable to microbial degradation. The quantities of dissolved organic matter are sensitive to land management, especially agricultural use which reduces inputs to the soil's organic matter evolution through removal of plant biomass (Marscher & Noble, 2000; Marscher & Bredov, 2002). The mechanism of the DOM degradation depends on the aromaticity and complexity of dissolved organic matter molecules whereas carbohydrates and amino acids increase this process. DOM degradation results also in a relative enrichment of the lignin-derived parts, which affects the thermal behaviour of individual compounds classes and increases thermal stability of residual dissolved organic matter. Analysis of soil profile under a wide range of conditions is necessary to fully understand the nature and extent of processes and mechanisms in the agricultural use of organic soils. In spite of extensive studies of the organic matter of peat soils (Dragunov & Kartatstsi, 1960; Efrimov & Tsaresenko, 1992; Bambalov & Belenkaya, 1993, 1997) the transformation of organic matter upon drainage is not yet fully understood.

The object of this study was to characterize the chemical properties of the three different peat-moorsh soils from the Biebrza River Valley used as meadows.

MATERIALS AND METHODS

Peat-moorsh soils were sampled from Czarna Wieś, Otoczne and Kwaterna 17 sites located in the Middle Biebrza Basin (Poland). The sites can be characterised as follows:

- Czarna Wieś – peat-moorsh soil profile with a low degree of decomposition (sedge-moss peat) with a minor influence of a drainage system, and with significant surface level changes, used as an extensive meadow;

- Otoczne – peat-moorsh soil profile with medium degree of decomposition (sedge-reed peat) with only the influence of a drainage system, used as an extensive meadow;
- Kwatera 17 – peat-moorsh soil profile with medium degree of decomposition (alder peat) located in a drainage sub-irrigation system with managed groundwater level, used as an intensive meadow.

Samples were collected at two different depths: the first, 5–10 cm and the second in the range of 45–80 cm (Table 1). Soils were sampled in 10 replications for each layer at each site. Samples were air-dried and crushed to pass through a 1 mm-mesh sieve. These 10 replications collected for each layer were mixed in order to prepare a “mean sample”, which then was used for the potentiometric determination of pH (in H₂O and in 1M KCl) and for the measurements of dissolved organic carbon (DOC) as well as total organic carbon (TOC).

Twice-distilled water from silica glass equipment was used for the laboratory analysis. For the investigation of DOC, soil samples were heated in redistilled water at a temperature of 100°C for two hours under a reflux condenser. Extracts were separated by using the mean filter paper and analysed on TOC 5050A equipment produced by Shimadzu, Japan (Smolander & Kitunen, 2002).

Table 1. The depth of sampling and basic characteristics of peat-moorsh soils.

Place of sampling	Sampling depth [cm]	Soil type	Degree of decomposition [von Post scale]
Czarna Wieś	5–10	moorsh	–
	50–70	sedge-moss peat	H ₁
Otoczne	5–10	moorsh	–
	45–50	sedge-reed peat	H ₅
Kwatera 17	5–10	moorsh	–
	70–80	alder peat	H ₆

Isolation of HA was achieved using standard IHSS procedure (Swift, 1996). A BECKMAN DU[®]-68 spectrophotometer with 1 cm thickness of layer was used for spectrophotometric measurements and according to Chen et al. (1977), 3 mg of HA was dissolved in 10 ml of 0.05 M NaHCO₃. Absorbances at 445 nm (E₄) and at 665 nm (E₆) of HA in this solution were measured and E₄/E₆ ratios calculated from spectrums in the visible region.

All the measurements were run in triplicate, and the results were averaged. All the chemicals used in this study were of analytical grade.

RESULTS AND DISCUSSION

The chemical, biochemical, physical and biological processes in peat represent its catalytic character. Thus, these processes and their mechanisms occurring in peat-forming plants are significantly dependent on the properties of the environment. The examined peat-moorsh soils with pH (in H₂O) ranging from 5.05 to 6.02 belong to middle acidic range. However, the samples taken from the upper layer (5–10 cm) of the Kwatera 17 soil profile represent highly acidic properties, the most acidic among investigated soil layers (Table 2).

Table 2. The values of pH and the concentrations of total (TOC) and dissolved organic carbon (DOC) of investigated soils.

Place of sampling	Sampling depth [cm]	pH		TOC	Δ TOC*	DOC	Δ DOC*
		H ₂ O	1 N KCl				
Czarna Wieś	5–10	5.54	5.19	37.19 ±1.7 [#]	6.83	12.81 ±0.4	7.01
	50–70	5.66	5.16	44.02 ±1.9		5.80 ±0.2	
Otoczne	5–10	6.02	5.46	38.10 ±1.7	7.48	10.80 ±0.4	3.25
	45–50	6.10	5.63	45.58 ±1.7		7.55 ±0.3	
Kwaterna 17	5–10	5.05	4.70	38.20 ±1.3	2.03	19.39 ±0.7	14.05
	70–80	5.88	5.39	40.23 ±1.4		5.34 ±0.2	

* – Δ TOC and Δ DOC are the differences between concentrations in upper and lower soil layers of the soil profiles, [#] – mean concentration and \pm 95% confidence interval of TOC or DOC

The chemical composition of peat-forming plants is evidently decisive for the peat composition. Thus, soil organic matter refers to a critical component of the soil – plant ecosystem: it constitutes the major part of organic carbon. There are different classes of biogenic, heterogeneous, dynamic and refractory organic compounds, characterising various contents of C and N having molecular structure. A principal feature of organic matter is its ability to absorb and retain water molecules. Depletion of organic matter cause a loss of water-holding capacity, poor aggregation, acceleration of soil erosion, poor retention of applied nutrients as well as reduced biological and enzymatic activities in the soil. Changes in land use or agricultural management lead to changes in the organic matter content (Ghani et al., 2003) of soils. Among the factors accelerating the decomposition of organic matter are the high content of cellulose and the total concentrations of hexoses, nitrogen compounds, and active mineral elements (P₂O₅, and CaO). However the following factors restrict the decomposition: the content of antiseptics (phenols and phenolcarbonic acids) and biochemically stable components (lignin, wax, cork tissues, etc.) (Inisheva & Dementeva, 2000). The drying of peat as a result of agricultural use leads to considerable shrinkage, activation of erosion, decrease of the nutrient content as well as a decrease of the biological and enzymatic activities. Shrinkage of peat increases with the increase of the degree of peat decomposition and humification. Thus, shrinkage of peat is related to its humic components (Van Dijk, 1971).

The biodegradation of organic carbon drives biogeochemical cycles. The data presented in Table 2 indicate that no significant concentrations of TOC were detected in the investigated moorsh soil samples collected from the 5–10 cm layer. These concentrations ranged from 37.19% to 38.20%. The highest amount of TOC equal to 38.20% was measured for the sample from Kwaterna 17; the lowest content, 37.17%, was determined for soil from Czarna Wieś. The results showed that all samples collected from the peat layers located at 45 to 80 cm depth were characterised by higher contents of TOC in comparison with moorsh samples taken from the 5 to 10 cm layer. The concentration of TOC for the depth 45–60 cm ranged from 40.23% to

45.58%. The highest amount of TOC, 45.58%, was determined for the sample collected from Otoczne and the lowest value, 40.23%, from Kwaterna 17. Generally, the sample collected from Kwaterna 17 from the moorsh layer (5–10 cm) manifested the highest content and the peat sample collected from 70–80 cm for the same profile represented the lowest concentration of TOC from all investigated samples.

Several products of the hydrolysis of peat humic substances were studied for their relevance to molecular structure and to changes occurring during humification. Primary polysaccharides, representing un-decomposed plant carbohydrates, can be converted to levulinic acid on prolonged hydrolysis. However, humic substances yield higher levels of levulinic acid than those obtainable by conventional methods of carbohydrate hydrolysis. This excess is attributed to altered carbohydrates, presumably attached to the central core of humic acid molecular structure. The primary polysaccharides in pyrolysis studies are associated with dianhydromonosaccharide fragments, whereas secondary polysaccharides yield furan fragments. The fen peat showed a steady increase of nonpolypeptide nitrogen with increasing depth. The loss of some phenolic compounds and fulvic acid components by natural drainage of the bog waters may account for the apparent changes in organic matter content with advanced humification (Anderson & Hepburn, 1986). Dissolved organic matter can contribute significantly to the cycling of soil nutrients. It can be a substrate for microbial growth, but its production is also partly mediated by microbes. This fraction is responsible for the microbiological activity (Puget et al., 1999). Fischer (1993) showed the relationship between the content of dissolved organic carbon and the amount of CO₂ evolution from soils to the atmosphere. This fraction of organic carbon is also connected with the movement of xenobiotics in soils. Therefore it seems to be most important to know the actual quantity of this fraction in soils.

It was shown for all investigated peat–moorsh soil samples that the concentrations of DOC, in contrast to TOC contents, decreased with the increase of the depth of the soil profiles (Table 2). The amounts of DOC measured for 0–10 cm depths ranged from 10.80% to 19.39%. The highest content of DOC, equal to 19.39%, was determined for the moorsh sample collected from Kwaterna 17, and the lowest, equal to 10.8% , for the sample collected from Otoczne. The samples collected from peat layers located at depths from 45 to 80 cm revealed lower contents of DOC than in moorsh layers, which ranged from 5.34% to 7.55%. Contrary to TOC measurements the moorsh sample from Kwaterna 17 representing depth 0–10 cm was characterised by the highest concentration of DOC; the peat sample collected from depth 70–80 cm showed the lowest content.

Spectrophotometry UV–VIS is a well known and commonly used method for the investigation of the structure of humic substances of soils. The light absorption of humic substances appears to increase with an increase in the degree of condensation of the aromatic rings that these substances contain, and in the ratio of C in aromatic ring to C in aliphatic side chains and total C content as well as molecular weight.

Measured values of HA for moorsh layers (5–10 cm), with the exception of samples collected from Kwaterna 17, are characterised by significantly higher optical density at 465 nm and higher E₄/E₆ ratios than the HA from lower depths representing peat (Table 3). The results of this study suggest a lower degree of condensation and polyconjugation in the molecules of HA from the upper depth (moorsh) compared to those from deeper layers (peat).

Table 3. The values of E_4/E_6 ratios for HA of investigated peat-moorsh soils.

Place of sampling	Sampling depth [cm]	Absorbance at		E_4/E_6	$\Delta E_4/E_6^*$
		$\lambda = 465 \text{ nm} (E_4)$	$\lambda = 665 \text{ nm} (E_6)$		
Czarna Wieś	5–10	0.892	0.128	6.968 $\pm 0.25^{\#}$	0.724
	50–70	0.868	0.139	6.244 ± 0.21	
Otoczne	5–10	1.350	0.196	6.887 ± 0.23	1.210
	45–50	1.215	0.214	5.677 ± 0.19	
Kwatera 17	5–10	1.152	0.165	6.981 ± 0.25	1.290
	70–80	1.753	0.308	5.691 ± 0.21	

* – $\Delta E_4/E_6$ are the differences between the ratios in upper and lower layers of the soil profiles, $\#$ – mean concentration and $\pm 95\%$ confidence interval of E_4/E_6

The measured values for HA of the investigated samples showed a decrease of E_4/E_6 ratio with the increase of the soil depth, indicating the increase in the degree of polyconjugation in their molecules (Chen et al., 1977). Lower E_4/E_6 ratios for measured HA values for peat samples collected from higher depths are due to an increase in the absorption at 625–665 nm, which can be explained by the presence of Pg-fraction (green fraction of HA) in these samples (Kumada, 1967; Orlov, 1985).

In addition, some trends for chemical properties of humic acids and the contents of the forms of organic carbon have been observed. The humic acids isolated in this study support the previous suggestions that these compounds collected from deeper peat layers of the soil profiles represent less secondary transformed structure than those collected from the upper layers, representing moorsh (Maryganova & Szajdak, 2000).

Natural, un-decomposed peat deposits are characterised by a relatively low degree of humification (Malterer et al., 1992). Consequently much of the humin fraction forming the peat organic matter may consist of unchanged substances originally present in the living plants. In some cases a decrease in humic acid content appears despite an apparent increase in humification, as indicated by the actual humin content. The decrease of humic acids may be attributed to loss of the humic acid fragments by selective oxidation and solution as well as by water removal during the natural bog drainage (Hatcher et al., 1986).

The phenomenon of increasing absorbance as result of an increase of total organic carbon in the structure of humic substances is known (Schnitzer & Khan, 1978). The performed investigations allowed the formulation of the linear relationship between the values of E_4/E_6 ratio and total and dissolved organic carbon concentrations. The correlation coefficients calculated for these linear relationships are equal to $r = -0.777$ and $r = 0.793$ (Fig. 1 and 2). The evaluation of the regression line shows proportional and inversely proportional correlation between these two forms of organic carbon and E_4/E_6 ratios. Hence, we expect that changes in the contents of organic carbon forms are reflected in temporal changes of HA properties.

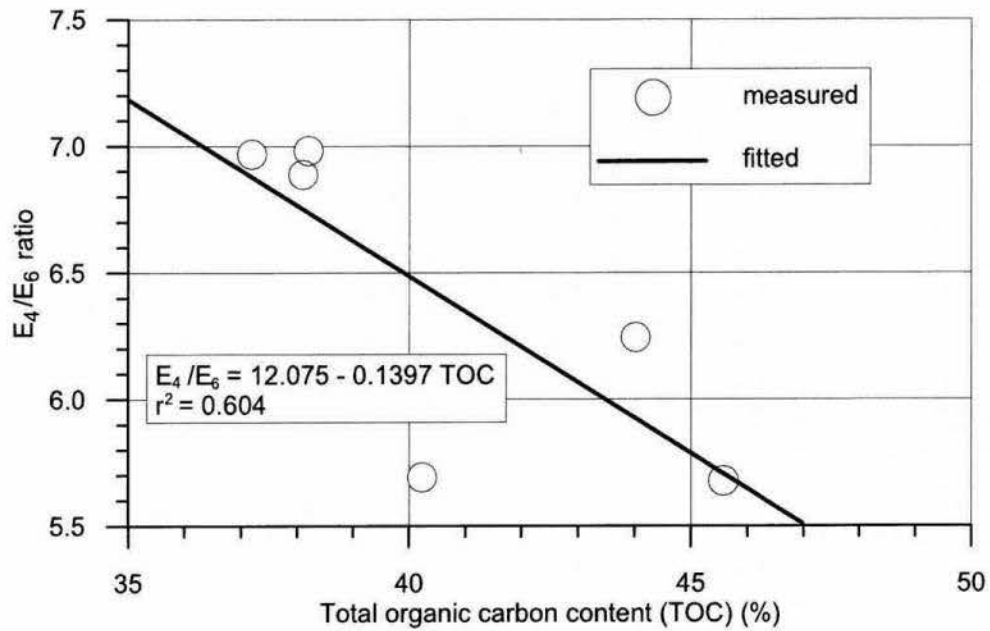


Fig. 1. The relationship between E_4/E_6 ratio and total organic carbon content for investigated peat-moorsh soils.

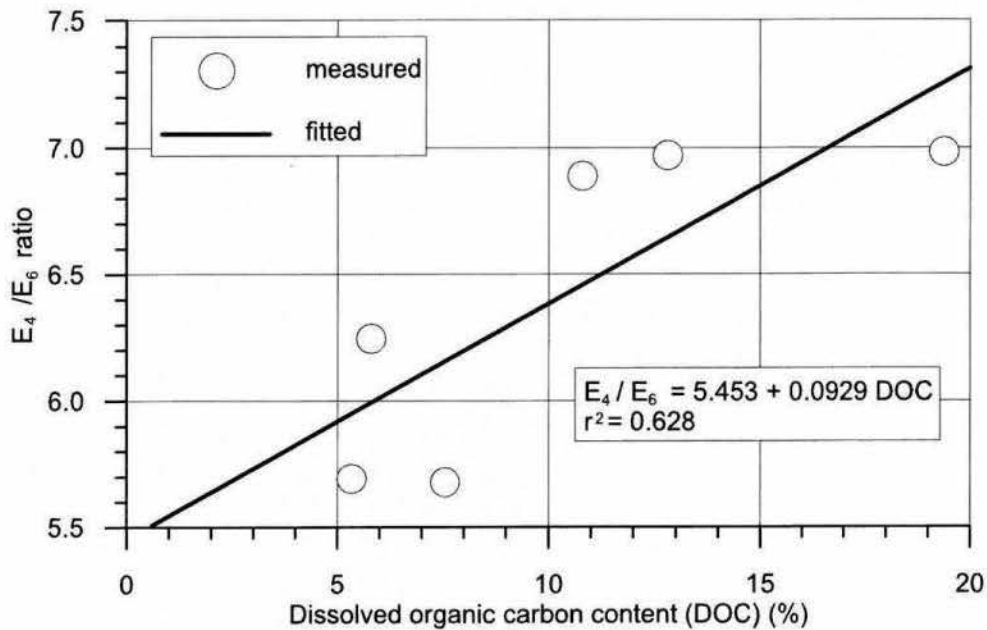


Fig. 2. The relationship between E_4/E_6 ratio and dissolved organic carbon content for investigated peat-moorsh soils.

The investigations revealed that organic matter of the investigated peat-moorsh soils ranged from 64.2% to 78.7% of the total amount (Table 2). These results suggest significant participation of humus in total amounts of peat organic matter in which

humic and fulvic acids predominate (Maryganova & Szajdak, 1999; Maryganova, 2000).

These results have shown that the measured values of HA from peat-moorsh soil from both depths of Kwaterna 17 characterised the lowest difference of TOC, measured value equal to 2.03%, and the highest difference of the measured DOC values equal to 14.5% (Table 2) as well as the lowest differences in of E_4/E_6 ratio values equal to 1.29 (Table 3). Our results suggest the impact of environmental factors on the content of the forms of organic carbon in peat-moorsh soils as well as revealing the relationships between the chemical properties of organic matter of peat-moorsh soils and the maturity of isolated humic and fulvic acids. The chemical and physical conditions in the soil profile suggest that the development of the structures of humic acid was driven by anaerobic conditions, which caused (a) continued reduction of pH, (b) accumulation of TOC, (c) decrease of DOC. These three factors would be expected to accumulate and to limit degradation of HA.

Moreover, it is useful to view the water retention by peat from another vantage point: It can be seen as an important factor in geological transformation. The alteration of peat's affinity for water by chemical treatment has been extensively studied. Considerable attention has been paid to the chemical composition and molecular structure of peat, identifying the molecular properties of substances and aggregates most likely to hold water strongly. Knowledge of these structures can provide a rationale for treatments intended to remove, or render less water-retentive, the most hydrophilic fraction. The substances of greatest immediate interest are humic acids, peptides and carbohydrates (Fuchsman, 1986).

CONCLUSIONS

The study showed the significant influence of agricultural use of peatlands on the content of different forms of carbon and chemical properties of humic acids:

1. The investigation has shown the impact of the peat type and the decomposition degree on the chemical properties of organic matter and the chemical structure of HA.
2. The highest content of TOC characterised reed-sedge moorsh with the decomposition degree of H₅.
3. Investigated peats are characterised by the increase of TOC values and by the decrease of DOC values with the increasing depths in the soil profile.
4. For the investigated peat range it was found that the increase of depth of sampling in the soil profile is connected with an increase of the degree of condensation, aromatic polyconjugation, with the decrease of TOC and with an increase of DOC values.
5. For the investigated range of peat soils, the decrease of the depth is accompanied by the decrease in chemical maturity of HA.

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