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April 22, 2015

Mr. Tauren Beggs  
Wisconsin Department of Natural Resources  
2984 Shawano Avenue  
Green Bay, WI 54313-6727

Subject: Kewaunee Marsh  
Kewaunee, Wisconsin  
Treatability Study Report

Dear Tauren:

Enclosed is one hard copy and one electronic copy the treatability study report on remediating the moderately contaminated area of the Kewanee Marsh. Treatment using biological reduction of arsenic and removal on ferrous sulfide was successful at bringing arsenic concentrations down to low mg/L levels using sodium lactate and ferrous sulfate. The report includes a ball-park cost for remediating the moderately contaminated area using the lactate-ferrous sulfate approach.

I recommend that field trials be conducted prior to a full-scale remediation. As far as I know, this is the first time that arsenic remediation using ferrous sulfate and sodium lactate has been done. Scale-up from bench-scale tests to full-scale application is not always seamless, and it would be helpful to have the added confidence of a pilot test prior to implementing the remediation on a larger scale. Since the remediation utilizes a Geoprobe® with a fairly low mobilization cost, the added cost of performing the pilot scale test is not that high.

Please let me know if you have questions.

Sincerely,

TRC Environmental Corporation

Robert Stanforth, Ph.D.  
Senior Applied Chemist

Attachment



# Moderately Contaminated Groundwater Remediation Treatability Testing and Conceptual Remediation Analysis Report

**Kewaunee Marsh  
Kewaunee, Wisconsin**

**April 2015**

*Prepared For  
Wisconsin Department of Natural Resources  
Green Bay, Wisconsin*

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Theodore O'Connell  
Project Geologist

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Robert Stanforth, Ph.D.  
Senior Applied Chemist

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# Section 1

## Background

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An area of the Kewaunee Marsh CD Besadny Fish and Wildlife area in Kewaunee, Wisconsin is contaminated with arsenic (Figure 1). The contaminated area is adjacent to the Ahnapee State Trail near the Kewaunee River approximately one mile upstream of the Kewaunee River mouth from Lake Michigan and slightly north of the City of Kewaunee. Access to the site is via vehicular access along the trail. A historic arsenic spill caused contamination in the marsh sediment/soil, surface water, and groundwater. The Wisconsin Department of Natural Resources (WDNR) is conducting the monitoring and remediation of the contaminated area. The cleanup standard for arsenic at the site was determined by discussions between the Department of Natural Resources' (Department) Bureaus of Watershed Management and Remediation & Redevelopment. The cleanup goal for sediment/soil is 19 mg/kg and 0.148 mg/L for groundwater/surface water.

The most heavily contaminated area of the marsh was remediated in 2011, as discussed in the report to WDNR titled "Arsenic Source Area In-Situ Remediation Documentation Report and Baseline Performance Monitoring", TRC Corporation, March 2012. WDNR is interested in treating the moderately contaminated sediment lying just outside the area of highly contaminated sediment remediated in 2011. "Sediment" is used here to refer both to the solids and to the associated pore water. DNR would like the treatment to be done by injecting a treatment reagent into the subsurface, rather than by disturbing the sediment during the remediation. The sediment pore water has arsenic concentrations of around 300 mg/L, as represented by the water in MW11-03, which is just downgradient of the remediated zone.

### 1.1 Area to be Treated

The area to be treated is outlined in Figure 2, from the March 2012 report "Arsenic Source Area In-Situ Remediation Documentation Report and Baseline Performance Monitoring" from TRC. The area to be treated is an area that has over 1000 mg/kg but less than 2000 mg/kg arsenic in the sediment. The delineation was based on laboratory leaching studies that showed that arsenic concentrations of over 1000 mg/kg in the sediment would leach arsenic concentrations of over 5 mg/L in either a DI water test or a TCLP test (Attachment 1). Since the groundwater arsenic concentrations in the area of the impacted marsh outside the areas being remediated are in the 1 – 5 mg/L range, this seemed like a reasonable target value for the initial remediation.

Arsenic concentrations in the sediment in the target area are shown in two cross-sections from the "Bioreductant Test Plots Pilot Study: Kewaunee Marsh" report from RMT dated January

2011 (Figures 2.10 and 2.12) shown as Figure 3 and 4. Of key interest are the arsenic concentration with depth profiles from borings M5A, M5B, M5C, M5D, M5F, M6E, M7E, and M8E. The arsenic concentrations at different depths are given in Table 1. Groundwater levels fluctuate throughout the year, with high levels in the spring and sometimes fall. Since the treatment selected involves generating and maintaining anaerobic conditions (to prevent oxidation of the ferrous sulfide), we need to inject the reagents below the stable groundwater elevation of about 4 feet bgs. The lowest elevated arsenic concentrations are at levels down to 8 feet bgs in the area to be already remediated (M5F, M6E, and M7E) and in areas just upgradient of the moderately contaminated zone (M5A, M5B, M5C, and M5D). The only boring with arsenic above 1,000 mg/kg at below 8 feet is M5C. Contamination at this depth will need to be confirmed to remediate the extra 2 feet. For estimating purposes it is assumed that the contamination extends only to 8 feet bgs in the moderately contaminated area. The depth to be remediated is thus 4 feet to 8 feet bgs.

A large portion of the area outlined in Figure 2 as requiring remediation has not been thoroughly investigated, both north and south of the A transect in Figure 2. It would be worthwhile to delineate arsenic concentrations in these areas prior to remediating them, such that the remediation targets the contaminated areas. Pictures of the area from the early 1990's show a plume of contamination extending from the original source area at and near the railroad tracks down towards the river (see pictures in the January 2011 test plot pilot study report). The plume was covered by the cap that was installed in the mid 1990's. The A transect was attempting to locate this plume. There is reason to think, therefore, that the areas to the north and south of the A transect, especially the areas to the north, may not have arsenic levels requiring remediation.

# Section 2

## Treatment Testing

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### 2.1 Adsorption Testing

The initial approach was to evaluate injection of adsorbents that could remove arsenic from the pore water into the solid phase, and hence immobilize it. Testing with two adsorbents (aluminum oxide and titanium dioxide) showed that the amount of adsorbent required to bring arsenic down to the desired range was fairly high (Table 2), and was likely to be both cost-prohibitive and technically difficult. Also tested was the concept of injecting reagents that would immobilize arsenic as an arsenic sulfide or as part of a ferrous sulfide solid, including sodium bisulfide (NaHS), preformed ferrous sulfide solid, and a combination of ferrous sulfate and dissolved sulfide which will form ferrous sulfide in-situ (Table 2). The combination of ferrous iron and sulfide lowered arsenic concentrations, albeit not to the desired low levels and resulted in elevated concentrations of both iron and sulfur

### 2.2 In-situ Reduction

Due to the results of the adsorption testing, a second approach was evaluated, namely injecting reagents that will generate very reducing conditions in the sediment such that arsenic is converted to the elemental form and immobilized as an arsenic-sulfur compound (either realgar (AsS) or arsenopyrite (Fe<sub>2</sub>AsS)). The reduction is predominantly done by bacteria, and hence the reagents need to enhance the bacterial populations responsible for reducing the arsenic. The reagents evaluated included the following:

1. Ferrous sulfate – sodium lactate: Lactate provides a carbon source for the bacteria while ferrous sulfate provides a quick reductant for any oxygen present, sulfate for the formation of sulfide ion and, iron for the formation of arsenopyrite.
2. Fe(0): Metallic iron (or ZVI) provides a strong reductant for the naturally occurring sulfur as well as arsenic.
3. Fe(0) + ferrous sulfate + sodium lactate: A combination of approaches 1 and 2, using metallic iron to provide a strong reducing environment, lactate as a food source for the bugs and sulfate to precipitate arsenopyrite, and to keep iron concentrations at low levels (less than a few mg/L).

### 2.3 Methods

The Kewaunee Marsh groundwater from the area of current concern contains around 300 mg/L As, or 4 mM As. For testing, the majority of the arsenic in the system comes from the water

(since we are using relatively clean solids for the testing), however in the actual samples, roughly half the arsenic is tied up in the solids. This should not impact the results of the testing, since the aim of the testing is to reduce groundwater concentrations. Very likely, arsenic in the solids in the treated area will be converted to the sulfur forms, since over time the arsenic will be solubilized and then be treated. However, this assumption needs to be tested in the field.

Molar ratios of 2.5:1, 12.5:1 and 25:1 iron to arsenic (or 10, 25, and 50 mM iron) were used with excess lactate added. A solution was prepared of a 60% sodium lactate and ferrous sulfate monohydrate solution containing a 2:1 lactate to ferrous iron ratio, consisting of 29 g of 60% sodium lactate and 12.1 g ferrous sulfate monohydrate in 100 mL total volume.

Most analysis were done using an inductively coupled plasma optical emission spectrometer (ICP). The instrument measures elemental concentrations, including sulfur. Sulfur concentrations have been presented in terms of sulfur (S) although the sulfur is mostly present as sulfate (SO<sub>4</sub>). pH was measured using a pH probe and meter.

## 2.4 Sample Preparation

First, the solids were homogenized by blending them in a mechanical blender until they formed a uniform slurry. The water and solids were mixed at a ratio of 1 L slurry and 3 L groundwater. This provided a sufficiently dilute slurry to be able to easily centrifuge the sample while at the same time having sufficient solids for the bacterial population to get started.

The following samples were prepared

1. Blank samples (6)
2. Ferrous sulfate plus sodium lactate (FeL). Sufficient lactate-ferrous sulfate slurry was added to form samples that had 10, 25, and 50 mM iron (5.64 mL ferrous lactate slurry/400 mL sediment slurry for 10 mM; 14.1 mL Fe lactate /400 mL for 25 mM, 28.2 mL Fe lactate/400 mL or 50 mM). The samples were mixed thoroughly, then placed in six 60 mL glass jars filled to the top.
3. Fe(0). Metallic iron filings were added at rates of 0.227 g, 0.56 g, and 1.12 g/400 mL to give 10 mM, 25 mM, and 40 mM Fe samples respectively.
4. Fe(0) + ferrous sulfate-sodium lactate (FeFe). Half of each of the above amounts was added to the samples, namely
  - a. 2.82 mL Fe Lactate + 0.114 g Fe(0) / 400 mL
  - b. 7.05 mL Fe lactate + 0.27 g Fe(0) / 400 mL
  - c. 14.1 mL Fe Lactate + 0.56 g Fe(0) / 400 mL



The samples were placed in a dark area and allowed to sit for sufficient time for the bacteria to utilize the lactate and sulfate and generate reducing conditions. The samples were visually inspected to determine when reducing conditions had been generated. A strongly reducing situation generates black ferrous sulfide, especially for the samples with lactate present. Samples were analyzed when the samples started to turn black (after approximately one month) and then again after a second month.

# Section 3

## Results

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The results of the reductive immobilization of arsenic are given in Tables 2 through 5. Table 2 gives an overview of the results, presenting dissolved arsenic, iron and sulfur concentrations, while Table 3, 4, and 5 give more detailed results for the ferrous sulfate – lactate (FeL), Metallic iron (Fe(O)), and combined approaches (FeFe) samples, respectively.

Both the FeL and FeFe treatments had significant reductions in arsenic concentrations, down to the concentrations of a few mg/L levels and below (i.e. <3.0 mg/L). This indicates that the approach can successfully reduce arsenic concentrations to the target range. Metallic iron (Fe(0)) by itself did not have much impact on arsenic concentrations. The optimal concentration for the ferrous sulfate – sodium lactate combination is the 25 mM dose. The 10 mM dose reduced arsenic concentration to a few mg/L, but both the iron and sulfur concentrations are low and suggest that there is little capacity left for reducing arsenic concentrations still further. The 50 mM dose left high concentrations of both iron and sulfur in the water.

Therefore, the target concentration of ferrous sulfate-sodium lactate for cost-estimating purposes is 25 mM. It should be noted that these concentrations are for the laboratory prepared samples, in which the reagents are added to a measured volume of contaminated groundwater and the concentration could be carefully controlled.

### 3.1 Units Conversion

Each liter of treated groundwater at the 25 mM dose used 10 g of a 60% sodium lactate solution and 4.24 g ferrous sulfate monohydrate ( $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ ). The conversion to gallons and pounds is given below:

- Grams per gallon
  - 37.8 g 60% solution of sodium lactate
  - 16.0 g ferrous sulfate monohydrate
- Pounds per 1,000 gallons
  - 83 lbs 60% sodium lactate solution
  - 35.2 pounds ferrous sulfate monohydrate

Ferrous sulfate is available with several different waters of hydration, including none (anhydrous), one – monohydrate, seven – heptahydrate, or moist which is a wet form of the heptahydrate. The monohydrate is stable in air (i.e. it does not oxidize over time) and so was used in the testing. The cost per unit iron for all but the moist is about the same.

# Section 4

## Conceptual Design – In-situ Treatment – Chemical Injection

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The conceptual approach for field implementation of this remedy is to inject the reagents into the contaminated groundwater using temporary wells installed by a Geoprobe.

The proposed area of treatment is approximately 150,000 ft<sup>2</sup>. With the lack of appreciable groundwater gradient, and nature of the underlying peat, it will be necessary to treat the entire area with the sodium lactate and ferrous sulfate solution. A pilot test is proposed to evaluate the performance of this conceptual approach and to define critical design parameters for full scale application (e.g. radius of influence and optimal injectate concentration).

### 4.1 Pilot Injection

The pilot scale test will be performed in the area immediately upgradient of monitoring well MW 11-3, at 15 injection locations spaced 10 feet apart. One additional monitoring well will be installed within the pilot scale test area to provide adequate data to assess the effectiveness of the injection results. Contractor will inject approximately 50 gallons of a solution of sodium lactate and ferrous sulfate heptahydrate at multiple depths (between 4' and 8' bgs) through Geoprobe rods. Approximately 50 lbs of sodium lactate and 35 lbs of ferrous sulfate will be used at each location, for a total of approximately 750 lbs of sodium lactate and 525 lbs of ferrous sulfate heptahydrate in approximately 750 gallons for all 15 wells. The injections will take approximately 2 days to complete

Estimated costs for this task include:

■ WDNR permitting/HASP preparation	\$ 2,000
■ Injection equipment, chemicals, and labor	\$11,000
■ Installation of performance monitoring wells (1 well)	\$ 1,400
■ Contractor oversight, documentation, and reporting	<u>\$ 7,000</u>
<b>Total (Pilot Scale)</b>	<b>\$21,400</b>

It is assumed that WDNR will perform the groundwater monitoring for the pilot study, as such no additional costs for groundwater sample collection or analysis have been included.

## 4.2 Full Scale Injection

It is assumed that the 1,500 ft<sup>2</sup> from the pilot scale test will have been successfully treated, and that the remainder of the 150,000 ft<sup>2</sup> treatment area will require 135 injection locations to complete the remediation. For purposes of costing, the well spacing and injectate volume and concentration per well used in the pilot test are assumed for full scale; however, these are subject to change based on the results of the pilot test. Based on this, a total of approximately 6750 lbs of sodium lactate and 4725 lbs of ferrous sulfate heptahydrate in approximately 6750 gallons of injectate will be used in the full scale injection. It will take approximately 4 days to complete this task.

Four shallow (8 ft bgs) and one intermediate (12 ft bgs) NR 141 groundwater monitoring wells will be installed to monitor the performance of the injections. The wells will be installed within the area of injections (Figure 5). It will take approximately 1 day to complete this task.

Estimated costs for this task include:

■ Injection equipment, chemicals, and labor	\$30,000
■ Installation of performance monitoring wells (5 wells)	\$ 6,000
■ Waste disposal	\$ 1,500
■ Contractor oversight, documentation, and reporting	<u>\$12,500</u>
<b>Total (Full Scale)</b>	<b>\$50,000</b>

It is assumed that WDNR will perform the groundwater monitoring at the site, as such no additional costs for groundwater sample collection or analysis have been included in this scenario. Injection boreholes will be abandoned using bentonite, which will constitute the cap repair.

## 4.3 Option: Further Site Characterization Prior to Injection

Further soil and groundwater sampling prior to in-situ treatment could be completed to increase the certainty of the size of treatment area. Further site characterization could potentially decrease or increase the treatment area depending on results. The additional characterization would consist of two additional transects of 4 boring each for a total of 8 geoprobe borings. The proposed transects would run parallel with the M5 transect that was performed to define the hot spot area. Soil samples would be collected for laboratory analysis on 2-foot intervals, and each boring would be converted to a temporary groundwater monitoring well in order to collect a groundwater sample for laboratory analysis of arsenic. It will take approximately 1 day to complete this task.

Estimated costs for this task include:

■ Geoprobe soil borings/temporary well installation	\$2,000
■ Contractor oversight and Soil and GW sampling	\$2,500
■ Documentation and reporting	\$2,000
■ Lab analysis (soil and groundwater) for As	<u>\$ 500</u>
<b>Option Total (Further Site Characterization)</b>	<b>\$7,000</b>

#### 4.4 Option 2: In-situ Treatment – Chemical Injection with Phytoremediation TreeWell System

The effectiveness of in situ remediation at this site may be limited because of a low hydraulic gradient and very slow movement of groundwater. An option to improve performance of the in situ chemical injections is to attempt to induce a stronger gradient across the site with phytoremediation. For this option, TRC is proposing to install 12 patented TreeWell® systems. The TreeWell® systems will be located downgradient from the proposed treatment area and from the proposed performance monitoring wells (Figure 5). Implementing a TreeWell® system blocks shallow root growth and forces tree roots to grow down to the zone directly above the water table, thereby using groundwater exclusively rather than infiltrating rainwater which increases the effectiveness of the phytoremediation system. The TreeWell® installation method is also less invasive, as a skid steer with large diameter auger is used for planting vs. a trencher for traditional methods. In addition to creating a hydraulic gradient, the phytoremediation system will also remove the arsenic impacted groundwater and act as a long term treatment system.

Estimated costs for this task include:

■ TreeWell® installation (materials, equipment, and labor)	\$30,000
■ Waste Disposal	\$ 2,500
■ Documentation and Reporting	<u>\$ 1,500</u>
<b>Option Total (Phytoremediation)</b>	<b>\$34,000</b>

It is assumed that WDNR will maintain the trees, as such no additional costs for long-term care of the trees have been included.

Table 1  
 Arsenic Concentration for Different Depth Intervals for Borings In or Near the Moderately Contaminated Area

Note: Depth intervals other than the 2 foot intervals in the left hand column are noted in brackets (e.g. 0-2.5). Arsenic concentrations above the criterion of 1,000 mg/kg in the area to be treated are noted in bold.

DEPTH INTERVAL	BORING								
	AREA	IN REMEDIATED "HOT-SPOT" AREA				IN MODERATELY CONTAMINATED AREA			OUTSIDE
	BORING	M5A	M5B	M5C	M5D	M5F	M6E	M7E	M8E
0-2	20.8	1,460	3,070 (0-2.5)			98.2 (0-2.5)	895 (0-4)	15.1	311 (0-4)
2-4	1,090	400	5,060 (2.5-5)	4,960 (0-5)	<b>1,300</b> (2.5-5)			277	
4-6	3,000	4,350					<b>1,910</b>	<b>1,260</b>	24.4
6-8	590	4,300	4,080 (5-7.5)	7,300 (5-7)	<b>1,260</b> (5-7.5)		<b>2,020</b>	470	12.8
8-10	3.9	91.6	1,760 (7.5-10)	500 (7-10)	111 (7.5-10)				

Table 2  
Treatment Using Adsorption on Aluminum or Titanium Oxides and Ferrous Sulfide Injection Results

SAMPLE		RESULTS		
REAGENT	DOSE (g/L)	pH	As (mg/L)	OTHER PARAMETERS (mg/L)
Untreated		6.95	280	1.1 Al
		7.06	290	0.96 Al
Al <sub>2</sub> O <sub>3</sub>	0.10	6.99	280	
	0.25	7.01	280	
	0.50	7.01	270	
	1.0	6.99	260	
	2.0	7.04	240	
	2.5	7.08	250	
	5.0	7.11	210	
	10	7.11	150	0.73 Al
	20	7.00	64	0.82 Al
	50	7.17	7.7	0.72 Al
	100	-	7.9	0.59 Al
TiO <sub>2</sub>	0.10	7.08	290	
	0.25	7.08	280	
	0.50	7.05	280	
	1.00	7.09	280	
	2.00	7.04	250	
	2.5	7.15	260	
	5.0	7.09	230	
Preformed FeS	2.5	7.12	170	0.58 Fe, 33 S
	5.0	7.25	110	2.0 Fe, 54 S
	10	7.43	98	1.9 Fe, 110 S
	25	7.76	100	0.57 Fe, 400 S
NaHS (10% solution, mL/40mL)	0.25	8.11	140	1700 S
	0.50	8.26	130	9400 S
	1.0	8.37	120	28000 S
	2.0	8.47	120	57000 S
1 mL 10% FeSO <sub>4</sub> + 10% NaHS	0.25	6.56	70	740 Fe, 1400 S
	0.50	6.44	45	560 Fe, 960 S
	1.0	6.25	51	140 Fe, 830 S
	2.0	6.34	51	140 Fe, 760 S
2 mL 10% FeSO <sub>4</sub> + 10% NaHS	0.25	6.31	82	2000 Fe, 1400 S
	0.50	6.31	61	1700 Fe, 1300 S
	1.0	5.89	24	1300 Fe, 1300 S
	2.0	5.89	23	1300 Fe, 1300 S

**Table 3**  
**Summary of Treatment Testing Using In-Situ Reduction Results**

Note: The dates given are the sampling dates. The experiment started November 10, 2014.

SAMPLE		CONCENTRATIONS			
REAGENT	DOSE	pH	As (mg/L)	Fe (mg/L)	S (mg/L)
<b>Nov 10, 2014 (Start)</b>					
Untreated		7.20	190	1.3	<10
Ferrous Lactate	10 mM	6.90	140	99	320
	25 mM	6.67	130	510	710
	50 mM	6.48	140	1500	1400
Fe(0)	10 mM	7.27	180	5.9	<10
	25 mM	7.28	180	1.2	<10
	50 mM	7.35	170	0.80	<10
Ferrous lactate + Fe(0)	10 mM	7.07	140	25	160
	25 mM	6.86	110	150	380
	50 mM	6.67	110	530	740
<b>Dec 18, 2014 (One Month)</b>					
Untreated		7.33	200	5.2	<10
Ferrous Lactate	10 mM	7.06	2.2	35	<10
	25 mM	6.45	0.28	220	200
	50 mM	6.40	30	1500	1300
Fe(0)	10 mM	7.31	180	10	<10
	25 mM	7.34	180	5.5	<10
	50 mM	7.47	130	1.4	<10
Ferrous lactate + Fe(0)	10 mM	7.20	2.6	26	<10
	25 mM	6.80	1.0	63	<10
	50 mM	6.50	9.4	590	590
<b>January 12, 2015 (Two Months)</b>					
Ferrous Lactate	10 mM	7.41	2.2	21	15
	25 mM	6.65	0.56	95	<10
	50 mM	6.22	<0.13	1,100	975
Fe(0)	10 mM	7.35	180	4.6	<10
	25 mM	7.37	120	1.4	<10
	50 mM	7.42	180	8.5	<10
Ferrous lactate + Fe(0)	10 mM	7.58	0.92	10.3	<10
	25 mM	7.67	3.1	6.6	22
	50 mM	6.59	0.35	100	<10



Table 4  
Treatment Testing Results Using Ferrous Sulfate-Sodium Lactate

PARAMETER	RESULTS AT DIFFERENT REACTION TIMES (mg/L, except for pH)					
	UNTREATED	INITIAL <sup>(1)</sup>	START	ONE MONTH	TWO MONTHS <sup>(2)</sup>	
<b>10 mM Ferrous Lactate</b>						
pH	7.20	7.33	-	6.90	7.06	7.41
As	190	200	200	140	2.2	2.9/1.5
Ca	240	270	260	390	350	280
Fe	1.3	5.2	560	99	35	24/18
Mg	96	110	105	130	120	110
Na	22	22	460	450	440	420
S	<10	<10	320	320	<10	15/14
<b>25 mM Ferrous Lactate</b>						
pH	7.20	7.33	-	6.67	6.45	6.65
As	190	200	200	130	0.28	0.56
Ca	240	270	260	490	470	380
Fe	1.3	5.2	1420	510	220	97/94
Mg	96	110	105	140	140	130
Na	22	22	1150	1,000	1,000	970/980
S	<10	<10	800	710	200	<10
<b>50 mM Ferrous Lactate</b>						
pH	7.20	7.33	-	6.48	6.40	6.22
As	190	200	200	140	30	<0.13
Ca	240	270	260	610	720	630/640
Fe	1.3	5.2	2800	1,500	1,500	1,100
Mg	96	110	105	150	170	160
Na	22	22	2300	2100	2,200	2,100
S	<10	<10	1600	1400	1,300	970/980

Note:

- (1) Calculated concentrations of iron, sodium and sulfur based on reagents added.
- (2) Duplicate samples were analyzed. The results for both duplicates are presented. A single number indicates the duplicates had the same concentration.

Table 5  
Treatment Testing Results Using Metallic Iron (Fe(0))

PARAMETER	RESULTS AT DIFFERENT REACTION TIMES (mg/L, except for pH)				
	UNTREATED	START	ONE MONTH	TWO MONTHS <sup>(1)</sup>	
<b>10 mM Fe(0)</b>					
pH	7.20	7.33	7.27	7.31	7.35
As	190	200	180	180	180
Ca	240	270	230	280	270
Fe	1.3	5.2	5.9	10	4.5/4.7
Mg	96	110	91	110	110/100
Na	22	22	27	28	12/11
S	<10	<10	<10	<10	<10
<b>25 mM Fe(0)</b>					
pH	7.20	7.33	7.28	7.34	7.37
As	190	200	180	180	120
Ca	240	270	230	260	230
Fe	1.3	5.2	1.2	5.5	1.4
Mg	96	110	93	100	91
Na	22	22	21	21	10/8.3
S	<10	<10	<10	<10	<10
<b>50 mM Fe(0)</b>					
pH	7.20	7.33	7.35	7.47	7.42
As	190	200	170	130	180
Ca	240	270	220	210	280
Fe	1.3	5.2	0.80	1.4	7.7/9.2
Mg	96	110	92	90	110
Na	22	22	21	21	8.7/7.4
S	<10	<10	<10	<10	<10

Note:

<sup>(1)</sup> Duplicate samples were analyzed. The results for both duplicates are presented. A single number indicates the duplicates had the same concentration.

Table 6  
Treatment Testing Results Using Ferrous Sulfate-Sodium Lactate and Metallic Iron

PARAMETER	RESULTS AT DIFFERENT REACTION TIMES (mg/L, except for pH)					
	UNTREATED	INITIAL <sup>(1)</sup>	START	ONE MONTH	TWO MONTHS <sup>(2)</sup>	
<b>10 mM Ferrous Lactate – Fe(0)</b>						
pH	7.20	7.33	-	7.07	7.20	7.58
As	190	200	200	140	2.6	0.92
Ca	240	270	260	310	320	230/220
Fe	1.3	5.2	560	25	26	12/8.6
Mg	96	110	105	120	120	100/97
Na	22	22	230	250	240	240/230
S	<10	<10	160	160	<10	<10
<b>25 mM Ferrous Lactate– Fe(0)</b>						
pH	7.20	7.33	-	6.86	6.80	7.67
As	190	200	200	110	1.0	3.2/3.0
Ca	240	270	260	410	380	160
Fe	1.3	5.2	1420	150	63	6.7/6.5
Mg	96	110	105	140	120	81/80
Na	22	22	675	570	540	510
S	<10	<10	400	380	<10	22
<b>50 mM Ferrous Lactate– Fe(0)</b>						
pH	7.20	7.33	-	6.67	6.50	6.59
As	190	200	200	110	9.4	0.31/0.39
Ca	240	270	260	510	580	410
Fe	1.3	5.2	2800	530	590	100
Mg	96	110	105	150	150	130
Na	22	22	1150	1,100	1,100	1,100
S	<10	<10	800	740	590	<10

Notes:

- (1) Calculated concentrations of iron, sodium and sulfur based on reagents added.
- (2) Duplicate samples were analyzed. The results for both duplicates are presented. A single number indicates the duplicates had the same concentration.



BASE MAP FROM USGS 7.5 MINUTE TOPOGRAPHIC QUADRANGLE SERIES.



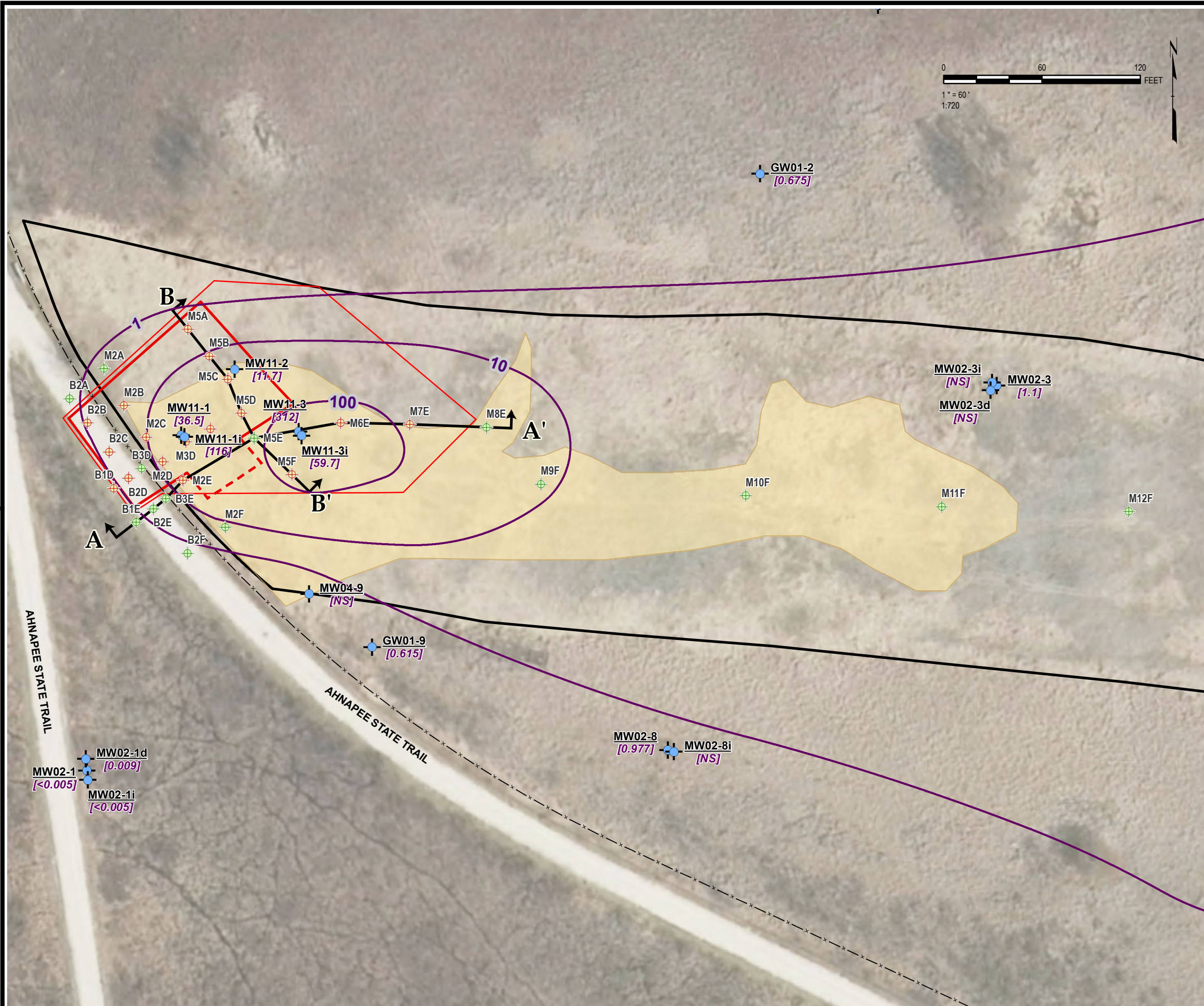
708 Heartland Trail  
 Suite 3000  
 Madison, WI 53717  
 Phone: 608.826.3600

**WISCONSIN DEPARTMENT OF  
 NATURAL RESOURCES  
 KEWAUNEE MARSH**

**SITE LOCATION MAP**

DRAWN BY:	PAPEZ J
APPROVED BY:	O'CONNELL T
PROJECT NO:	226345
FILE NO:	226345-007slm.mxd
DATE:	APRIL 2015

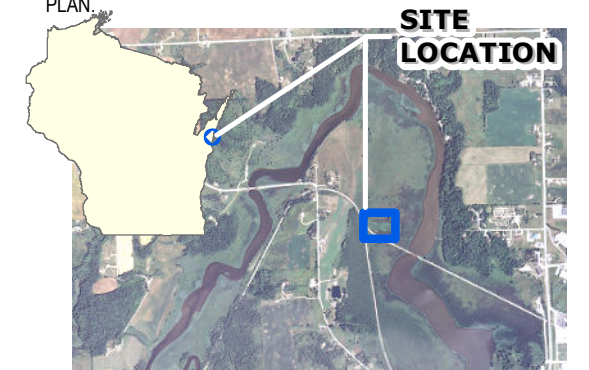
FIGURE 1



### LEGEND

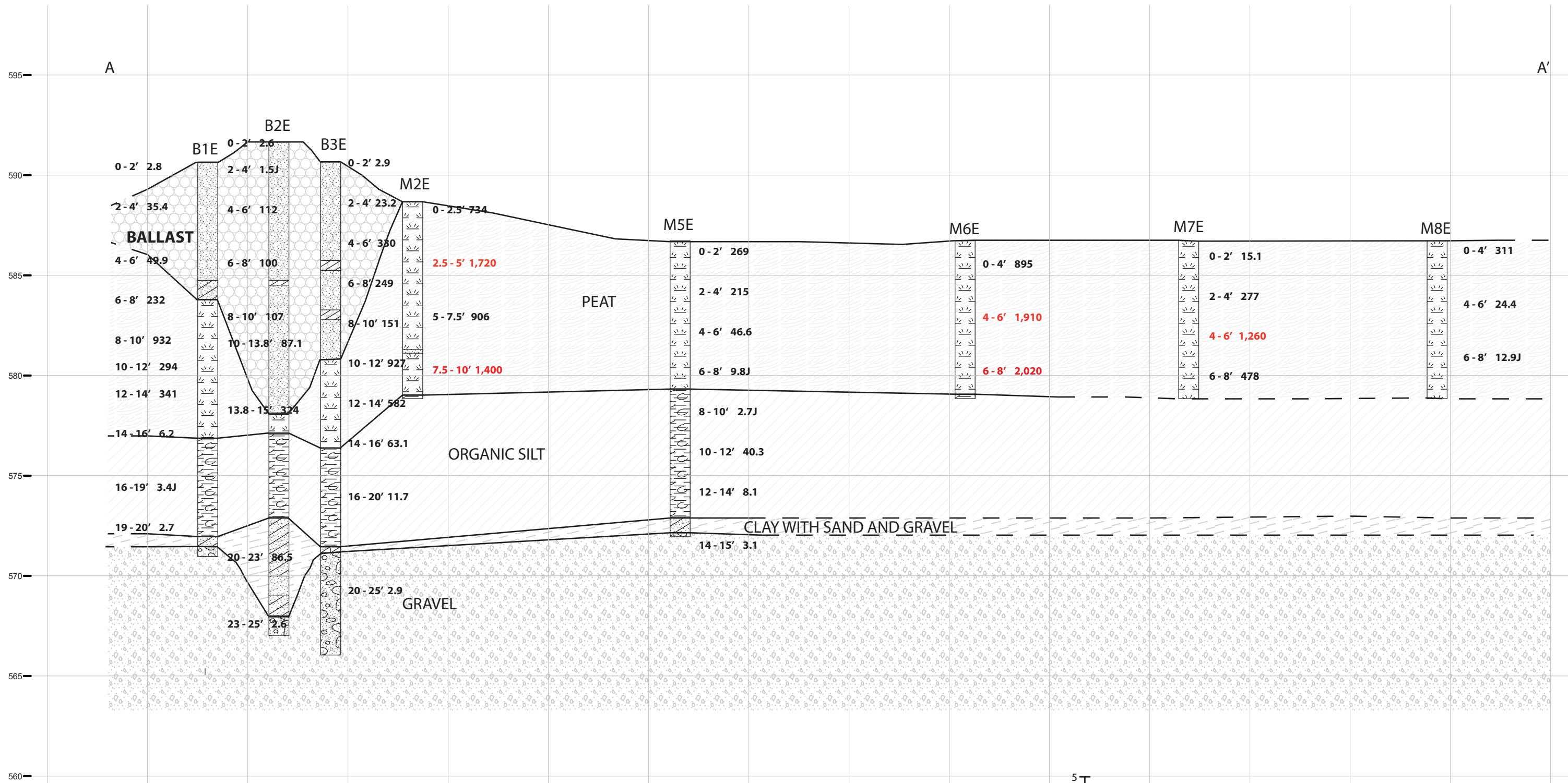
- CAPPED AREA
- FENCE
- APPROXIMATE AREA OF PREVIOUSLY DISTRESSED VEGETATION
- EXTENT OF TOTAL ARSENIC CONCENTRATION > 1,000 mg/kg (SEE NOTE 2)
- EXTENT OF SOURCE AREA TARGETED FOR REMEDIATION (>2,000 mg/kg) (SEE NOTES 3 AND 4)
- CROSS-SECTION TRANSECT
- GROUNDWATER MONITORING WELL LOCATION
- ARSENIC ISOCONCENTRATION LINE (mg/L)
- SOIL BORINGS**
  - ARSENIC > 1,000 mg/kg
  - ARSENIC < 1,000 mg/kg

- ### NOTES:
1. ALL GEOPROBE BORINGS WERE LOCATED USING A TRIMBLE GEOXH GPS UNIT.
  2. COMPOSITIONAL ARSENIC CONCENTRATIONS GREATER THAN 1,000 mg/kg CORRELATES TO POTENTIALLY HAZARDOUS MATERIAL (TCLP > 5 mg/kg).
  3. THE SOURCE AREA TARGETED FOR REMEDIATION COVERS THE AREA THAT WILL LIKELY HAVE ARSENIC > 1,000 mg/kg IN 2015 BASED ON THE OBSERVED RATE OF DECREASE IN CONCENTRATION OVER THE LAST 15 YEARS IN THE MARSH.
  4. DASHED LINE SHOWS ADDITIONAL TREATMENT AREA INCLUDED IN THE FINAL REMEDY BUT NOT TARGETED FOR TREATMENT IN THE ORIGINAL PLAN.



PROJECT:		<b>WISCONSIN DEPARTMENT OF NATURAL RESOURCES KEWAUNEE MARSH</b>	
SHEET TITLE:			
<b>MAP OF CONTAMINATED AREA</b>			
DRAWN BY:	PAPEZ J	SCALE:	PROJ. NO. 226345
CHECKED BY:	O'CONNELL T	1: 720	FILE NO. 226345-005.mxd
APPROVED BY:	STANFORTH B	DATE PRINTED:	<b>FIGURE 2</b>
DATE:	APRIL 2015		

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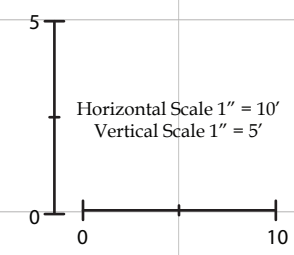


**LEGEND**

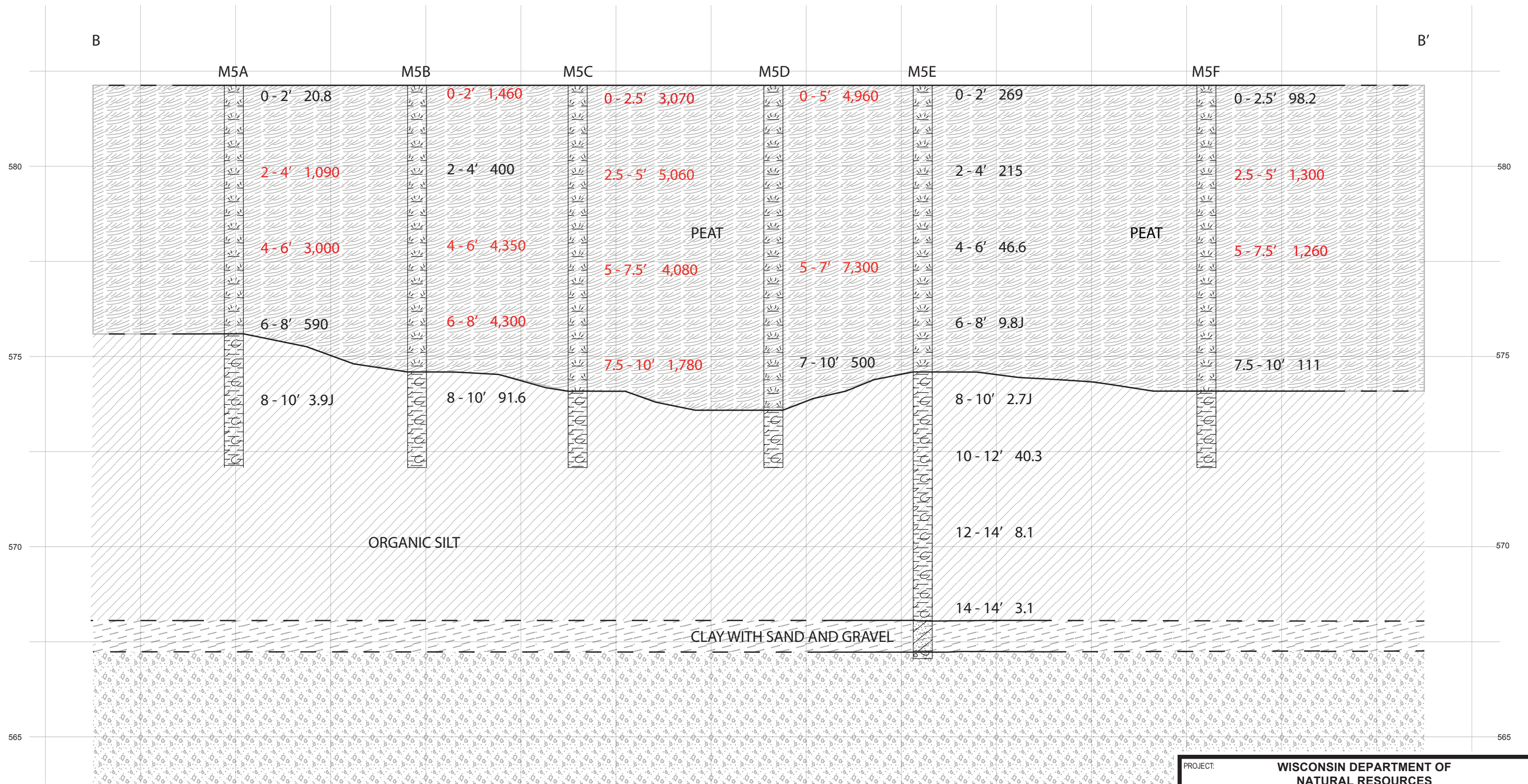
- Stratigraphic Boundary (Dashed Where Inferred)
- 0-2' 654 Sample depth and Arsenic Concentration (mg/Kg).

**NOTES**

1. Boring elevations are approximate.



PROJECT: <b>WISCONSIN DEPARTMENT OF NATURAL RESOURCES KEWAUNEE MARSH</b>			
SHEET TITLE: <b>GEOLOGIC CROSS SECTION A-A' Arsenic Concentrations</b>			
DRAWN BY: O'CONNELL T	SCALE:	PROJ. NO. 226345.0000	
CHECKED BY: O'CONNELL T		FILE NO. 226345-001.ai	
APPROVED BY: STANFORTH R	DATE PRINTED:	<b>FIGURE 3</b>	
DATE: APRIL 2015			
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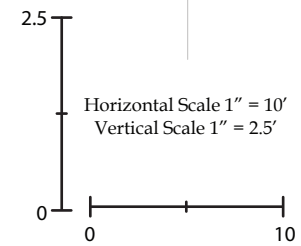


**LEGEND**

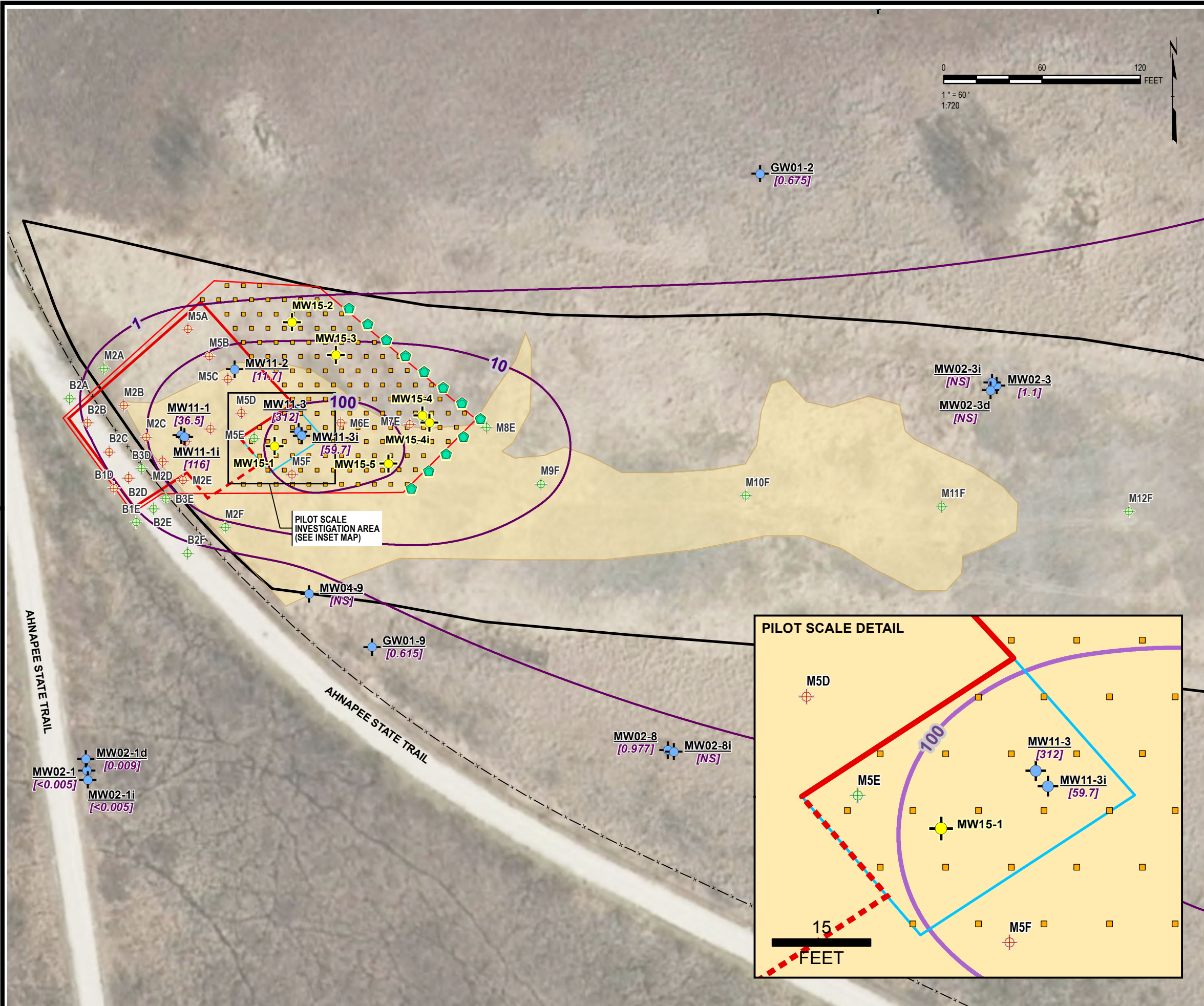
- Stratigraphic Boundary (Dashed Where Inferred)
- 0-2' 654** Sample depth and Arsenic Concentration (mg/Kg).

**NOTES**

- Boring elevations are approximate.



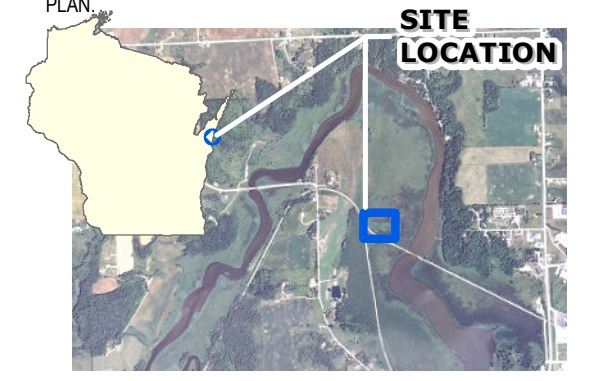
PROJECT: <b>WISCONSIN DEPARTMENT OF NATURAL RESOURCES KEWAUNEE MARSH</b>		
SHEET TITLE: <b>GEOLOGIC CROSS SECTION B-B' Arsenic Concentrations</b>		
DRAWN BY: O'CONNELL T	SCALE:	PROJ. NO. 226345.0000
CHECKED BY: O'CONNELL T		FILE NO. 226345-002.ai
APPROVED BY: STANFORTH R	DATE PRINTED:	<b>FIGURE 4</b>
DATE: APRIL 2015		
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### LEGEND

- CAPPED AREA
- FENCE
- APPROXIMATE AREA OF PREVIOUSLY DISTRESSED VEGETATION
- EXTENT OF TOTAL ARSENIC CONCENTRATION > 1,000 mg/kg (SEE NOTE 2)
- EXTENT OF SOURCE AREA TARGETED FOR REMEDIATION (>2,000 mg/kg) (SEE NOTES 3 AND 4)
- GROUNDWATER MONITORING WELL LOCATION
- PROPOSED INJECTION GRID (145 POINTS)
- ARSENIC ISOCONCENTRATION LINE (mg/L)
- SOIL BORINGS**
- ARSENIC > 1,000 mg/kg
- ARSENIC < 1,000 mg/kg
- PROPOSED PERFORMANCE MONITORING WELL
- PROPOSED TREETWELL LOCATION
- PILOT SCALE INVESTIGATION AREA (SEE INSET)

- ### NOTES:
1. ALL GEOPROBE BORINGS WERE LOCATED USING A TRIMBLE GEOXH GPS UNIT.
  2. COMPOSITIONAL ARSENIC CONCENTRATIONS GREATER THAN 1,000 mg/kg CORRELATES TO POTENTIALLY HAZARDOUS MATERIAL (TCLP > 5 mg/kg).
  3. THE SOURCE AREA TARGETED FOR REMEDIATION COVERS THE AREA THAT WILL LIKELY HAVE ARSENIC > 1,000 mg/kg IN 2015 BASED ON THE OBSERVED RATE OF DECREASE IN CONCENTRATION OVER THE LAST 15 YEARS IN THE MARSH.
  4. DASHED LINE SHOWS ADDITIONAL TREATMENT AREA INCLUDED IN THE FINAL REMEDY BUT NOT TARGETED FOR TREATMENT IN THE ORIGINAL PLAN.



PROJECT:		<b>WISCONSIN DEPARTMENT OF NATURAL RESOURCES KEWAUNEE MARSH</b>	
SHEET TITLE:		<b>PROPOSED IN-SITU TREATMENT AREA AND PHYTOREMEDIATION SYSTEM</b>	
DRAWN BY:	PAPEZ J	SCALE:	PROJ. NO. 226345
CHECKED BY:	O'CONNELL T	1:720	FILE NO. 226345-006.mxd
APPROVED BY:	STANFORTH B	DATE PRINTED:	<b>FIGURE 5</b>
DATE:	APRIL 2015		

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Attachment 1  
Comparison of DI Water and TCLP  
Leaching Test Results for Kewaunee Sediments

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## Comparison of DI Water and TCLP Leaching Test Results for Kewaunee Sediments

### Introduction

The focus of leaching studies for the Kewaunee soils has been predominantly using distilled water leaching tests (using the SPLP procedure but with DI water), or modifications thereof with different solids concentrations. Less work has been done using screening TCLP tests, since the focus has not been on whether the sediments are hazardous, but rather on the potential for contributing dissolved arsenic to the marsh. However, one approach to delineating the “hot-spot” area requiring treatment would be to determine the areas of the marsh that leach arsenic at over 5 mg/L in a TCLP test, and would be considered hazardous were they to be removed.

Compositional analysis and screening TCLP and DI Water tests have been run on a number of composite sediments from the two recent Geoprobe investigations on the site (in December 2009, and March 2010). These results can be used for two purposes: first to compare DI Water and TCLP results and see if the DI Water test (at 2 g/40 mL) can be used as a surrogate for the TCLP test, and second, to compare leaching test concentrations (TCLP or DI Water) with the compositional values.

### Results

Compositional and leaching test results for the different composites are given in Table 1.

SAMPLE	ARSENIC CONCENTRATION		
	COMPOSITIONAL (mg/kg)	TCLP (mg/L)	DI WATER (mg/L) <sup>(1)</sup>
<b>December 2009 Composites</b>			
Ballast	1,400	8.4	13
Peat Under ballast	1,500	11	11
Peat in Marsh	2,600	24	18
Organic Silt in marsh	550	3.1	2.5
<b>March 2010 Composites</b>			
>10,000 mg/kg	8,900	94	99
~5,000 mg/kg	4,550	38	42
2,000 – 4,000 mg/kg	2,950	22	16
1,000 – 2,000 mg/kg	1,200	3.0	2.8
500 – 1,000 mg/kg	920	3.6	1.7
250 – 500 mg/kg	440	0.26	0.18

Note:

<sup>(1)</sup> 2 g/40 mL sample

## Comparison of TCLP and DI Water leaching test results

A comparison of the two leaching test results, using the same solid/solution ratio (2 g/40 mL) is given in Figure 1.

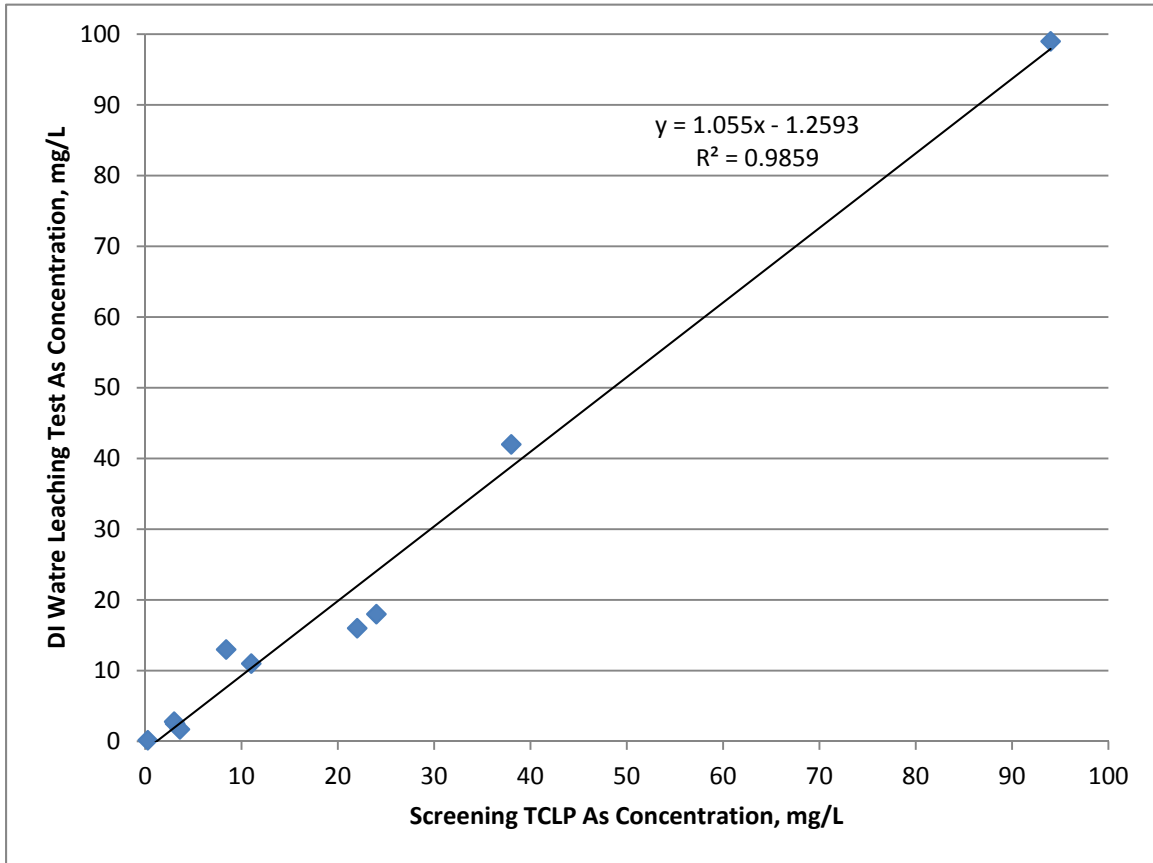


Figure 1  
Comparison of DI Water Leaching Test Arsenic Concentrations  
With TCLP Arsenic Concentrations for Composite Kewaunee Samples

The two leaching tests give very similar arsenic concentrations, indicating that the DI water leaching test (at the correct solids concentration) gives a good indication of the expected TCLP test arsenic concentration.

A second comparison can be made between the compositional arsenic concentration and the leaching test concentration, as shown in Figure 2.

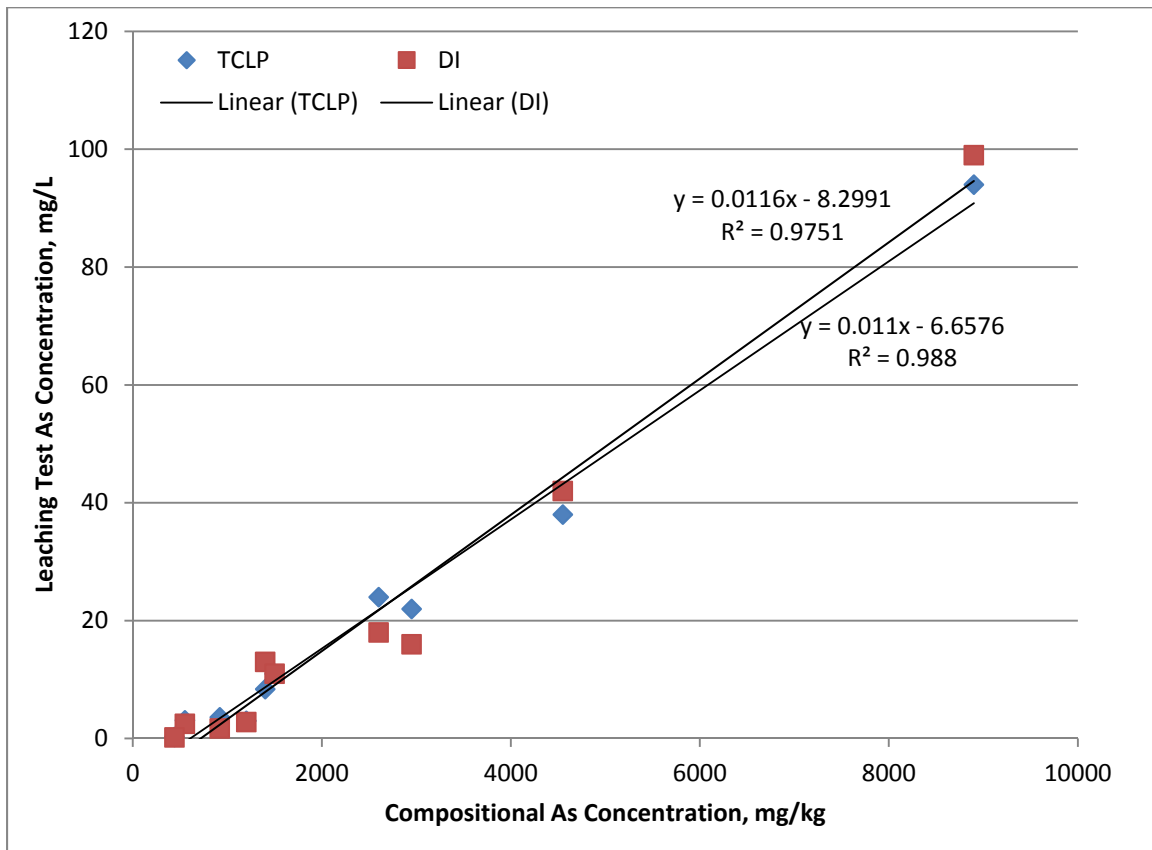


Figure 2  
Comparison Between Compositional and TCLP and DI Water Test Leachable Arsenic Concentrations

There is a good correlation between the compositional levels of arsenic in the samples and the leachable concentrations, in either the TCLP or DI water tests. Increasing compositional levels of arsenic increase the amount leached in the TCLP or DI Water tests. However, for both tests, the lines do not go through the origin, but rather there is a compositional threshold below which arsenic is not very leachable, and above which leaching concentrations increases linearly with compositional arsenic. The threshold value for the TCLP test is 605 mg/kg, while for the DI Water test it is 715 mg/L. More importantly, a compositional value of around 1060 mg/kg is needed to give a TCLP test concentration of greater than 5 mg/L. In other words, sediments with compositional levels below 1060 are not likely to be hazardous due to arsenic leaching in the TCLP test.

## Conclusion

Based on the compositional analysis and screening leaching test analysis of the Geoprobe samples from the Kewaunee Marsh, **sediments with a compositional value of below 1000 mg/kg are not likely to be hazardous due to arsenic leaching in a TCLP test.**