





# Workplan for Arsenic Hot Spot Subsurface Investigation and Bench-Scale Studies


Kewaunee Marsh  
Kewaunee, Wisconsin

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*Prepared For*  
*Wisconsin Department of Natural Resources*

  
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# Section 1

## Background

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Approximately 15 acres of the Kewaunee Marsh Beady Wildlife Area, in Kewaunee, Wisconsin, are contaminated with arsenic. The source of the arsenic is likely a spill from the adjacent railroad that occurred in the 1940s. An interim action was completed in 1996 to limit the threat of direct contact with the arsenic, during which approximately 4 acres of the marsh were capped, and all 15 acres were enclosed in a fence.

In 2002, STS Consultants completed a Phase II Site Investigation (SI), which defined the broad distribution of arsenic in the marsh (STS, 2004 and 2006); and in 2007, RMT, Inc. (RMT), completed a treatability study and a remedial options analysis for the marsh (RMT, 2007). During the treatability study, RMT noted that a high, and relatively isolated, area of elevated arsenic concentrations was present in groundwater at monitoring well MW04-10. Consequently, RMT completed an additional groundwater investigation near MW04-10 to test the hypothesis that a hot spot of dissolved-phase arsenic was present within the railroad ballast near the location of a railroad spill. The results of the additional investigation confirmed that a hot spot of dissolved-phase arsenic was present below the railroad ballast and to the east of the ballast near MW 04-10; however, additional work is required to delineate the depth and lateral extent of the high-level arsenic contamination.

## Section 2

# Sampling Objectives

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As part of the remedial options analysis, RMT concluded that remediation of the hot spot area is critical for the overall remediation of the site because the hot spot may provide an ongoing source of arsenic to the marsh. Several remedial approaches were evaluated for the hot spot, and these options were presented to the WDNR in the treatability study report (RMT, 2007). The WDNR selected two options to be evaluated further in field trials: (1) *in situ* treatment using a site-specific stabilization chemistry, and (2) pumping and off-site disposal of contaminated groundwater through a groundwater extraction trench.

Prior to designing and implementing the field trials for the remedial options for the hot spot, additional characterization of the arsenic hot spot is needed. The additional investigation will provide the following information that is critical for the field trial selection and designs:

- The depth and the lateral extent of the high-level arsenic contamination
- Cross-section of the hot spot, from which we can confirm or revise the conceptual model of ballast material contained in a low permeability “bowl”
- An understanding of the leaching and stabilization behavior of the highly contaminated material, for better evaluating the cost and effectiveness of the selected remedial options

Once the investigation is completed, RMT will complete and discuss with the WDNR, the decision process, shown on the flow chart on Figure 1, to select the appropriate remedial options to pursue in the field trial phase.

## Section 3

# Subsurface Investigation

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RMT plans to construct 30 borings in the arsenic hot spot at the locations proposed on Figure 2. The dense sampling network proposed for this scope of work is intended to provide sufficient data to delineate the extent of the high-level arsenic contamination.

RMT will subcontract with a Geoprobe® operator to construct the 30 borings. Details on the soil sampling are as follows:

- **Depth:** The proposed depth of each boring (15 or 30 feet) is shown on Figure 2. Those borings constructed on the former railroad ballast, which is elevated approximately 10 feet above the grade of the marsh, will extend to a depth of 30 feet below ground surface (bgs) (13 borings), and those borings constructed within the marsh will extend to a depth of 15 feet bgs (17 borings).
- **Name:**
- **Alternate borings:** The locations of borings M1-B, M1-C, and M1-D have been selected to define the western edge of the hot spot. However, these borings are located in a section of the marsh that typically has standing water and may not be accessible. If these borings cannot be completed near the proposed locations, RMT may select to construct alternate borings M3-A, M3-E, and M5-E to further refine the arsenic distribution in the marsh to the east of the ballast.
- **Sample log:** The soil from each boring will be logged in the field. The specific focus of the log will be to define the depth of the interface between the ballast and the native marsh soil, and to characterize the nature of each material.
- **Sample name:** Each sample will be named according to the grid location shown on Figure 2, and will include the depth interval (e.g., B1-C [4-6'] or M4A [4-8']). Sample locations in the ballast area are labeled with a "B," while those from the marsh are labeled with a "M."
- **Sample collection:**
  - **Arsenic samples:** Soil samples will be collected from 2-foot intervals in the upper 15 feet of each boring, and from each 4-foot interval in the 15- to 30- foot depth (below the ballast) in the deeper borings constructed in the ballast. Each soil sample (up to 220 samples) will be submitted to Pace Analytical Services, Inc. (Pace), for arsenic analysis.
  - **Samples for RMT's Applied Chemistry Laboratory:** Excess soil from each sample interval (i.e., not submitted to Pace for arsenic analysis) will be containerized in a

plastic Ziploc® bags, and labeled as described above. These samples will be returned to RMT's Applied Chemistry Laboratory. The samples will be refrigerated pending the results from the arsenic analysis from Pace. Following receipt of the arsenic results, samples will be selected for ash content analysis and bench-scale studies (see Section 4).

- **Borehole abandonment:** All boreholes will be abandoned with bentonite chips per Wisconsin Administrative Code NR 141, except B1-B, B3-B, B1-C, B3-C, B1-D, and B3-D, which will be converted to temporary 1-inch wells.
- **Temporary wells:** As shown on Figure 2, borings B1-B, B3-B, B1-C, B3-C, B1-D, and B3-D will be converted to temporary 1-inch flush-mount wells. The wells will be screened between 5 and 15 feet below grade, across the water table with 10-slot PVC screen. The wells will be used to monitor the response of the water table in the ballast during the field trial for the groundwater extraction trench. The field trial for the groundwater extraction trench will be described in a workplan to be submitted to the WDNR at a later date.
- **Waste disposal:** All soil not submitted to Pace will be brought back to RMT's Applied Chemistry Laboratory for potential use in the ash content analysis and bench-scale studies. Any excess soil that remains at the end of the bench-scale studies will be containerized and disposed by Veolia under the hazardous waste disposal contract they hold with the State of Wisconsin.

# Section 4

## RMT Laboratory Analyses

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RMT will select specific soil samples from which to complete ash content analysis, and bench-scale studies for leaching and *in situ* stabilization in RMT's Applied Chemistry Laboratory. The purpose and method for these tests are described below.

### 4.1 Ash Content

#### 4.1.1 Purpose

The ash content of the soil will provide another measure for confirming the depth of the interface between the ballast material and the native marsh soil (in addition to the field observations). Soil with relatively low ash content is associated with ballast material, and soil with relatively high ash content is associated with native marsh material. The depth of this interface is needed for developing a cross section and conceptual model of the hot spot area, and for understanding the relative distribution of arsenic between the ballast and the marsh material. The ash content analysis will be used to confirm the depth of the ballast/marsh interface as logged in the field.

#### 4.1.2 Method

The boring logs will be reviewed and the approximate depth of the ballast/marsh interface will be determined for each of the 13 borings collected from the ballast. In addition, the results of the arsenic analysis by Pace will be reviewed to determine if there is a correlation between the arsenic concentration and the soil type (sand ballast and marsh material). On the basis of the review of the boring logs and arsenic data, RMT will select at least two depth intervals above the ballast/marsh interface (presumably with high arsenic concentrations), and two depth intervals from below the ballast/marsh interface from which to complete the ash content analysis.

The soil samples will be collected from the excess soil that was refrigerated at RMT's Applied Chemistry Laboratory as described in Section 3. The selected soil will be analyzed for ash content using ASTM Method D2974-07a (Standard Test Methods for Moisture, Ash, and Organic Matter of Peat and Other Organic Soils), using an ashing temperature of 650°C. This temperature is consistent with the previous ash analyses that were completed at the site.

## 4.2 Leaching Test

### 4.2.1 Purpose

100 ug/L  
A leaching test will be completed on the ballast material in order to approximate the number of pore volumes that must be flushed through the soil in order to achieve a concentration of 0.1 milligram/liter (mg/L) arsenic. These data are critical for evaluating the cost, time, and overall effectiveness of the groundwater extraction trench pump-and-dispose remedial option.

### 4.2.2 Method

On the basis of the review of the arsenic data from Pace, RMT will select at least two samples of highly contaminated material from which to complete the leaching test. If high concentrations are present in both the marsh and the ballast material, discrete leaching tests will be completed on at least two samples of each soil type to evaluate differences in leaching behavior.

The leaching test will be completed as follows:

- 5, 10, and 20 g of soil (wet) will be placed in a 50 mL centrifuge tube.
- 35, 30, and 20 mL (respectively) DI water will be placed in the tubes to bring the total weight to 40 g.
- The sample will be tumbled in a rotary shaker overnight (~18 hrs).
- The samples will be centrifuged to settle the solids. The supernatant will be decanted, and an aliquot will be filtered for arsenic analysis. pH will be measured on the unfiltered supernatant. The arsenic and pH will be analyzed in RMT's laboratory.
- A fresh aliquot of DI will be added to each tube (using the same volume as added in the first elution), and steps 3 and 4 will be repeated until the arsenic concentration in the extractant is <0.1 mg/L. The arsenic and pH will be analyzed in RMT's laboratory.
- The moisture content of each saturated sample will be measured in RMT's Soils Laboratory by method ASTM D2216. The moisture content will be used to approximate the total pore volume available in each sample.
- The leaching results will be presented on a plot of arsenic concentration versus pore volume. The approximate number of pore volumes required to reduce arsenic concentrations below target values can be determined from these plots.



## 4.3 Stabilization Test

### 4.3.1 Purpose

RMT previously completed treatability studies on the highly contaminated groundwater collected from the site, in which we showed that the arsenic can be removed from the groundwater using a stabilization process that includes the addition of hydrogen peroxide, ferric sulfate, and limestone (RMT, 2007). The previous bench-scale studies did not evaluate if this treatment is effective in immobilizing arsenic when soil is included in the process. At the field trial and full-scale level, the *in situ* stabilization approach will rely on the effectiveness realized when these chemicals are mixed into saturated soil. Therefore, additional bench-scale testing on saturated soil samples is needed to confirm the effectiveness of the *in situ* stabilization option.

### 4.3.2 Method

On the basis of a review of the arsenic data, RMT will select at least two samples of highly contaminated material from which to complete the leaching test. If high concentrations are present in both the marsh and the ballast material, discrete stabilization tests will be completed on at least two samples of each soil type.

In general, RMT will complete the stabilization of the saturated soil samples by adding the chemical doses of hydrogen peroxide, limestone, and ferric sulfates as recommended in Subsection 3.2 of the treatability study report (RMT, 2007). The test will be completed as follows:

- A subsample will be collected from each material to be tested. The subsample will be left untreated. RMT will extract the pore water from the saturated sample for arsenic analysis, and the solids will be screened by RMT's Applied Chemistry Laboratory for leachable arsenic using both the Toxicity Characteristic Leaching Procedures (TCLP) and the screening Synthetic Precipitation Leaching Procedure (SPLP) tests. These results will be used to compare against the results of each treated sample.
- The prescribed amounts of the hydrogen peroxide, limestone, and ferric sulfate will be added to each sample to be treated, and the material will be allowed to react.
- General observations on the mixing ability and reaction response will be recorded.
- Following the addition of the chemicals, pore water will be extracted and analyzed for dissolved arsenic by RMT's Applied Chemistry Laboratory to determine if the arsenic has been removed from the water.

- The solids that remain following the addition of chemicals will be screened by RMT's Applied Chemistry Laboratory for leachable arsenic using both the screening TCLP and the screening SPLP tests.
- The results of the untreated versus treated samples will be compared to evaluate the effectiveness of the *in situ* stabilization on saturated soil.

## Section 5

# Evaluation and Reporting

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RMT will evaluate the results of the arsenic analysis by Pace, and will use these data to delineate the lateral extent and depth of the hot spot contamination. In addition, RMT will evaluate the soil boring logs and ash content analysis to develop a detailed cross section of the ballast. The arsenic data and the detailed cross section will be reviewed together in order to confirm or redefine the conceptual model of the hot spot area that has been presented for the site. Any data gaps that remain at the end of this evaluation will be presented to the WDNR.

RMT will also evaluate the results of the leaching and *in situ* stabilization bench-scale studies, to confirm the relative effectiveness of the groundwater extraction trench and *in situ* stabilization options, respectively.

The decision to pursue the field trials for the groundwater extraction trench will be based on the newly defined conceptual model and the results from the leaching bench-scale study. RMT will follow the decision flow chart presented on Figure 1, to determine if the groundwater extraction trench should undergo further evaluation in the field trial phase.

On the basis of these evaluations, RMT will present to the WDNR justification for eliminating or pursuing the groundwater extraction trench and/or *in situ* stabilization field trials. Assuming that field trials will be recommended for both options, RMT will use the data gathered during previous investigations, prior treatability studies, the additional hot spot investigation, and the recent bench-scale studies to develop detailed designs and approaches for each field trial.

The details for the field trials will be presented in a workplan to be submitted to the WDNR for approval. This workplan will be a comprehensive document that will also include the results and evaluations of the hot spot investigation and bench-scale studies.

## Section 6 References

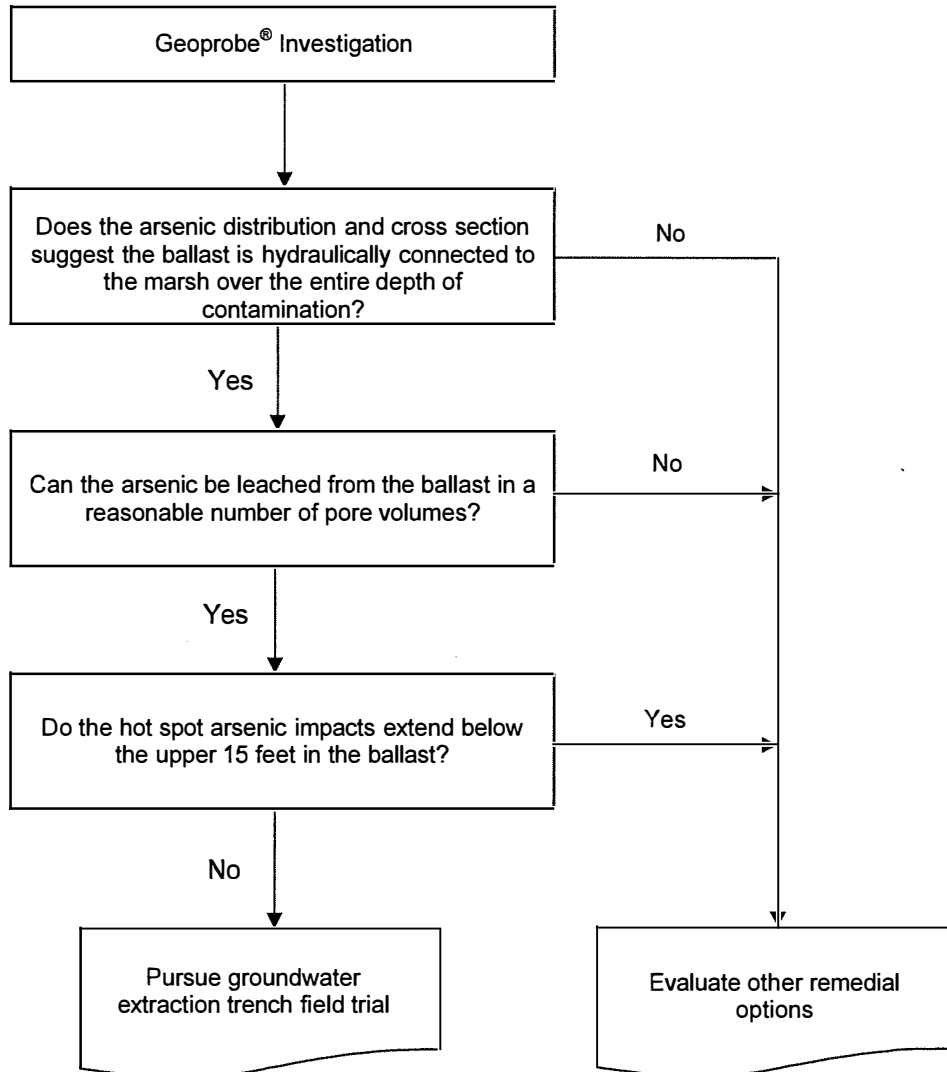
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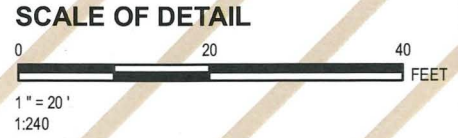
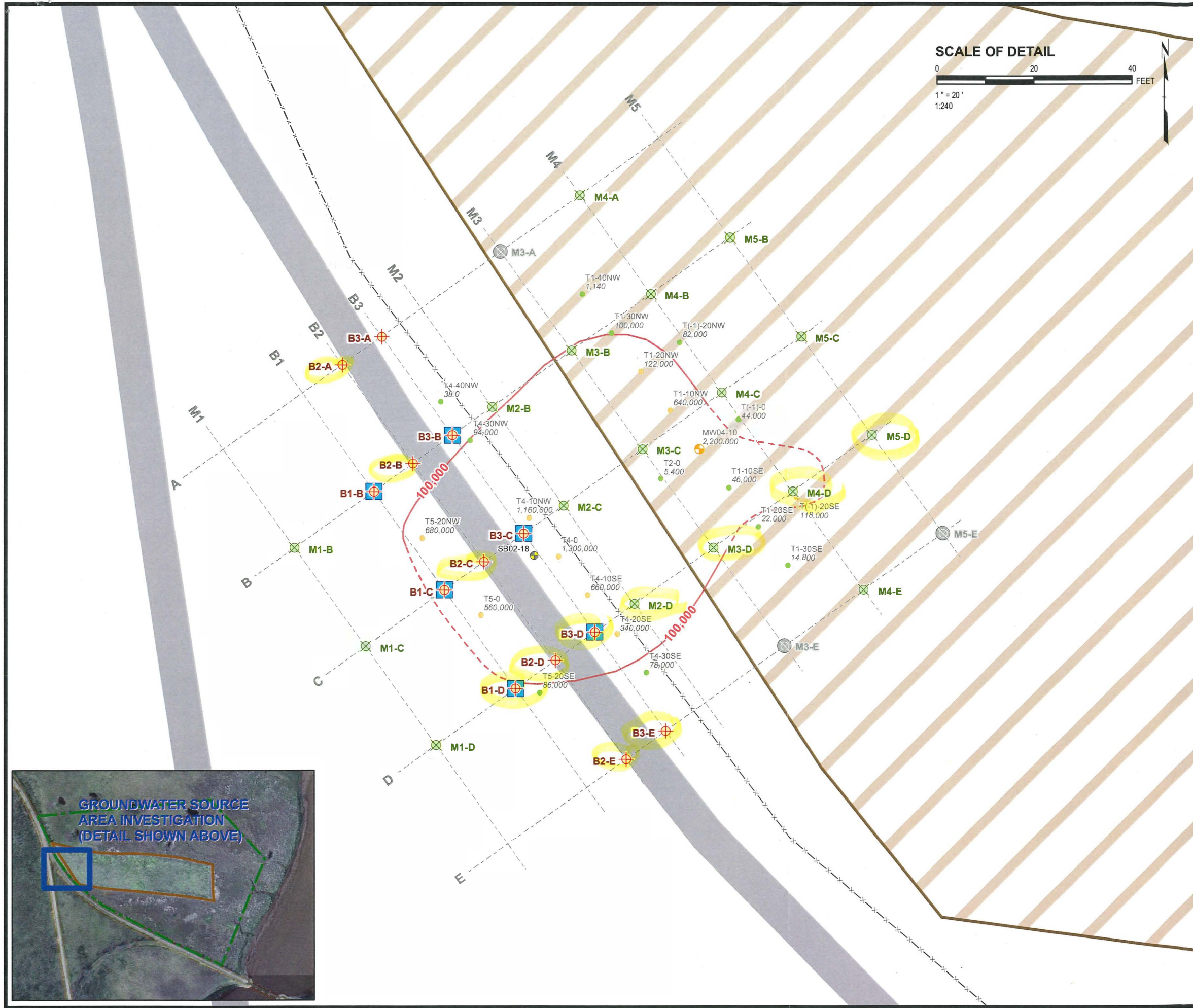
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STS Consultants. 2006. Site assessment and remediation action alternatives report addendum: Kewaunee Marsh. Report to Wisconsin Department of Natural Resources. September 2006.

**Figure 1**  
**Decision Flow Chart for Groundwater Extraction Trench Field Trial Evaluation**





**LEGEND**

- M1-B PROPOSED MARSH GEOPROBE LOCATION (15ft)
- B1-B PROPOSED BALLAST GEOPROBE LOCATION (30ft)
- PROPOSED ALTERNATE GEOPROBE LOCATION
- PROPOSED TEMPORARY MONITORING WELL LOCATION
- SOIL BORING (STS HISTORICAL SAMPLE LOCATION)
- MONITORING WELL LOCATION
- ARSENIC ISOCONCENTRATION IN SHALLOW GROUNDWATER (100,000 µg/L) - DASHED WHERE INFERRED

RMT TEMPORARY WELL LOCATION (APRIL 2007)  
(ARSENIC CONCENTRATION COLOR CODE)

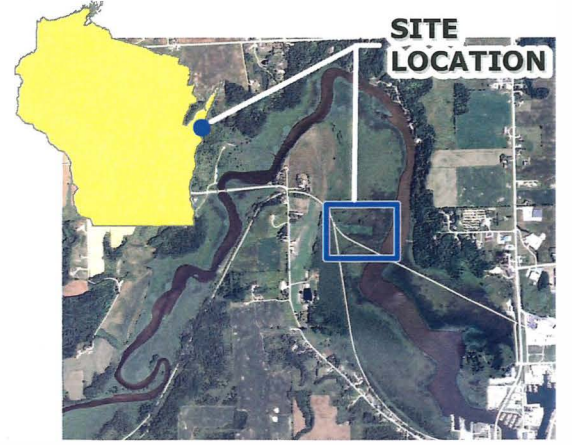
- < 100,000 µg/L
- > 100,000 µg/L

(94,000 ARSENIC CONCENTRATION IN µg/L)

- FENCE
- CAPPED AREA
- BIKE PATH (FORMER RAILROAD TRACKS)

**NOTES:**

- IF BORING M1-B, M1-C, & M1-D CANNOT BE CONSTRUCTED BECAUSE OF WET MARSH CONDITIONS TO THE WEST OF THE BALLAST, THE 3 ALTERNATE BORINGS (M3A, M3E, AND M5E) WILL BE CONSTRUCTED.



PROJECT:		<b>WISCONSIN DEPARTMENT OF NATURAL RESOURCES KEWAUNEE MARSH</b>	
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