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Sampling Plan

Kewaunee Marsh Treatability Study

Kewaunee, Wisconsin

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Prepared For Wisconsin Department of Natural Resources

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Section 1 Background and Introduction

Approximately 15 acres of marsh soil/sediment and groundwater in the Besadny Wildlife Area in Kewaunee, Wisconsin (Kewaunee Marsh), are impacted with arsenic. The source of the arsenic is likely a spill of sodium arsenate from the adjacent railroad that occurred in the 1940s. In 1996, following identification and confirmation of the impacts, an interim action was completed to limit the threat of direct contact to the arsenic. Specifically, the most highly impacted area (approximately 4 acres) was capped, and the 15 acres known to contain arsenic impacts were enclosed in a fence. Following the interim action, a Phase II Site Investigation (SI) was completed by STS Consultants, Ltd. (STS), and site-specific cleanup standards were established (19 mg/kg for soil and 148 µg/L for groundwater/surface water).

On the basis of the results of the SI and the site-specific cleanup standards, the WDNR identified three potential remedial options for the site, specifically *in situ* solidification or stabilization, construction of a permeable reactive barrier (PRB), and mechanical removal of "hot spot" contamination. In August 2005, the WDNR requested proposals for conducting treatability and feasibility studies on the potential remedial options. RMT, Inc. (RMT), has been awarded the project.

The WDNR has requested that the treatability studies be completed by next spring 2006. To meet this schedule, soil/sediment and groundwater samples need to be collected in the near future, before the soil and shallow groundwater freeze. In light of the short time period involved and the necessity of collecting samples before the ground freezes, RMT is proposing to collect the samples prior to the preparation of the comprehensive workplan. Therefore, this sampling plan addresses only the collection of soil/sediment and water samples from the site and has been prepared as an addendum to the Quality Assurance Project Plan (QAPP) prepared for the site by STS in December 2004.

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Section 2 Project/Task Organization

The project organization for the treatablity/feasibility studies is similar to that presented in the original QAPP, with the exceptions that RMT has replaced STS as the primary consultant for this phase of work, and that RMT has selected Pace Analytical (Pace) to perform any groundwater and surface water chemical analysis needed by a certified laboratory. An organization chart that reflects these changes is presented on Figure 1. The Quality Manual for Pace will be included in the workplan.

The organizational chart (Figure 1) presents the key members of the project team for the entire treatablity/feasibility study (not just the sampling component, which is the focus of this document). The primary roles and responsibilities of the key members, not described in the original QAPP, include the following:

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Mr. Richard Fish, Senior Project Manager

- Coordinate work and provide status reports to the WDNR Project Manager.
- Coordinate activities of RMT personnel.
- Prepare a Site Health and Safety Plan.
- Track progress of treatablity/feasibility studies
- Review data from treatablity/feasibility studies.
- Report results of treatablity/feasibility studies to the WDNR.

Mr. Thomas Stolzenberg, Quality Assurance

• Provide overall quality assurance for the treatablity studies.

Mr. Robert Stanforth, Senior Chemist

- Develop scope for treatablity studies.
- Coordinate and oversee laboratory work for treatablity studies.
- Analyze data from treatablity studies.
- Provide conclusions and recommendations from results of treatablity studies.

Mr. Paul Turpin, Senior Engineer

- Review reports and workplans for treatability/feasibility study.
- Develop design criteria for engineering components of feasibility study.

Mr. Jeff Macri, Construction Management

- Outline constructibility issues for the remedial options.
- Assist in the cost estimates for the feasibility study.

Mr. John Rice, Senior Hydrologist

• Assess hydrogeologic impacts of the remedial options to the Kewaunee Marsh.

Mr. Rob Hanley

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• Coordinate assessment of wetland restoration/mitigation.

Ms. Alyssa Sellwood, Staff Engineer

- Prepare sampling plan and treatability study workplan.
- Collect samples for the treatability studies.
- Assist with the laboratory treatability studies.
- Prepare treatability/feasibility study documentation report.

Pace Analytical Services

 Provide groundwater and sediment/soil analysis as necessary to verify the results obtained by RMT's Applied Chemistry Laboratory.

Section 3 Sample Quality Objectives

Soil/Sediment samples will be collected from the Kewaunee Marsh during a sampling event in November 2005. The samples will be stored pending the preparation and approval of a comprehensive workplan for the treatability studies. Following such contracting and approval, the samples will be used in the treatability studies to evaluate the effectiveness of various stabilizing agents and adsorption agents on the marsh material. The samples will be collected and stored in a manner that will preserve the *in situ* chemical conditions, particularly the redox status, of the samples. This will be accomplished by collecting soil/sediment and soil pore water for those samples that are below the groundwater table and storing them together, and collecting only soil/sediment for those samples that are above the groundwater table. Samples will be collected in opaque 1-gallon plastic (HDPE) plastic buckets. The sample containers will be filled to the top, and then sealed with airtight covers. Since the samples will be stored in a manner that maintains the saturation conditions of the field (i.e., either saturated or unsaturated), and since the samples will be stored under conditions that minimize biological activity and that are typical for the site during late November/December (*i.e.*, slightly above freezing), minimal disruption of the redox conditions of the soil environment is expected. Minor changes in the speciation of the dissolved arsenic are not of concern, since the samples will be used for treatability studies and the treatment process needs to be sufficiently robust to account for changes in arsenic speciation. The samples will be refrigerated until used in the treatability study, which should be within a few weeks of sample collection.

Groundwater samples will be collected at a later date, following approval of the comprehensive workplan for the treatability studies. The groundwater samples will be collected to provide uncontaminated site groundwater for use in the treatability studies. The WDNR has been collecting groundwater from the monitoring wells on-site to evaluate the trends in the concentration of arsenic in the groundwater, and it is not RMT's intention to duplicate these efforts.

Section 4 Sample Locations

The previous investigations have shown the presence of an area of higher arsenic contamination, which is currently under a 2- to 3-foot cap, and which is surrounded by a larger area of low to moderate arsenic levels in the soil/sediment (from background to around 1,000 mg/kg). Sample locations will be classified into one of three groups, based on arsenic compositional levels, as follows:

High arsenic (arsenic > 1,000, mg/kg)

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- Moderate arsenic (1,000 > arsenic > 200, mg/kg)
- Lower arsenic (200 > arsenic, mg/kg)

Samples will be collected from the contaminated area under the cap, from the moderately contaminated area immediately surrounding the cap, and from the less contaminated areas away from the cap. Approximate locations of the proposed sampling points are indicated on Figure 2.

Soil/Sediment contamination is generally shallow (1-2 feet), so samples will be collected from this interval. The samples will be analyzed individually, and select samples will then be combined into two composite samples, one a composite of the highly contaminated samples and representing the highly contaminated soil/sediment and the other a composite of moderately contaminated samples and representing the moderately contaminated soil/sediment. These two composites will be used for evaluating the different treatment options. Composites are used to provide a large, homogenized sample of contaminated material representing either the highly contaminated or the moderately contaminated areas.

Uncontaminated and unfiltered site groundwater will be used in the treatability studies, and will be collected from one of the upgradient monitoring wells. In addition, groundwater samples may be collected from several of the on-site wells for arsenic speciation analysis, particularly for determining if significant concentrations of the methylated arsenates (monomethyl arsenic acid and dimethyl arsenic acid) are present in the groundwater.

Section 5 Sample Identification and Storage

The sample containers will be marked with the sample numbers, as shown on Figure 2, along with the time and date of the sample collection. The sample containers will be identified on both the side and lid using sample labels showing the project name and number, sample number, and collection date. Since these samples are for use only in treatability studies, to be conducted by the staff collecting the samples, the samples will not be transferred to another party and no Chain-of-Custody forms will be filled out.

The samples will be transported to the RMT Applied Chemistry Laboratory on the day of collection, and will be stored in a refrigerator until (and during) the treatability studies. The refrigerator is in a locked area, with access only by Applied Chemistry Laboratory staff.

Section 6 Field Analysis

Screening analysis for arsenic will be performed using a Niton XLO 703S X-ray fluorescence (XRF) unit. Analysis will be performed by a trained operator. The operator (Robert Stanforth) attended the 1-day Niton training program in Davenport, Iowa, on November 8, 2005. The certificate of training will be available shortly. No other field analysis will be performed. The screening analysis will be used to determine if the samples collected have arsenic concentrations in the desired range for the collection site.

The XRF will be warmed up and calibrated, following the manufacturer's instructions. Standardization will be done using standard NIST soil samples (NIST 2709 – 2711) supplied by the XRF manufacturer. The standards represent low (17.7 mg/kg), moderate (105 mg/kg), and high (626 mg/kg) arsenic levels in the soil. No corrections will be made for the soil matrix; rather, the XRF readings will be used to provide estimates of the soil arsenic range. Samples will be placed in plastic bags, and homogenized by hand by squeezing the plastic bag. The XRF readings will then be made by placing the instrument on the plastic bag and taking readings. The XRF results will be compared with laboratory compositional analysis after the latter is completed, so that a correction factor can be determined for the matrix effect of the marsh soil/sediment for any further in-field analysis using the XRF.

Section 7 Sampling Procedures

7.1 Soil/Sediment Samples

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RMT will collect the soil/sediment samples in order of the least contaminated to the most contaminated areas. Specifically, the soil/sediment samples outside of the capped area will be collected first, and the soil/sediment samples under the cap will be collected from the less (east side) to the more contaminated area (west side).

For the soil/sediment not under cap (TS-05 to TS-15):

- 1. Identify sampling location using a global positioning system (GPS) unit. Record coordinates in field notebook.
- 2. Remove standing vegetation with clippers and sheers, and remove fallen surface vegetation that is not sufficiently decomposed to lose shape.
- 3. Dig into soil/sediment approximately 1-1.5 feet using a shovel and/or post-hole digger. Place a sample of soil/sediment in a plastic bag, and measure the arsenic concentration using an XRF unit. If arsenic is in the desired concentration range, collect soil sample in 2-liter bucket. Fill the bucket to approximately %10 full. If the arsenic concentration is below the desired range, then the soil/sediment will be returned to the hole, the vegetative cover placed over the surface, and a new sample location chosen.
- 4. If water fills hole, fill the 2-liter bucket with the site water using a plastic sampling ladle, bringing the water up to the level of the soil/sediment sample in the bucket.
- 5. Fill hole with cut vegetation and soil from the area immediately adjacent to the sampling location.
- 6. Deliver sample to central location.
- 7. Clean sampling equipment with phosphate-free detergent and water, using a brush to scrub dirt from equipment, as discussed in the decontamination section.

For soil/sediment under cap (TS-01 to TS-04):

- 1. Determine sample location using a GPS unit. Record coordinates in field notebook.
- 2. Clear vegetation from sampling site and surrounding area, and spread out plastic sheet in surrounding area.

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3. Dig through the cap with a shovel, placing the cap material on a plastic sheet.

- 4. Collect soil/sediment sample from underneath the cap, going 1-1.5 feet into soil/sediment using a shovel and/or a post-hole digger. Place sample in a plastic bag, and determine the arsenic concentration with an XRF unit. If arsenic is in the desired range, place sample in 2-liter bucket. Fill the bucket to approximately %10 full. If the arsenic is below the desired range, the soil/sediment will be returned to the hole, the hole closed as in Step 6 below, and a new location chosen.
- 5. If water collects in hole, fill bucket with site water using a plastic sampling ladle, bringing the water level up to the surface of the soil/sediment in the bucket.
- 6. Fill hole with Styrofoam[®] to the level of geotextile. Place new geotextile over Styrofoam[®], and then replace cap material. Cover disturbed soil/sediment with removed vegetation.
- 7. Clean sampling equipment with phosphate-free detergent and water, using a brush to scrub dirt from the equipment.

7.2 Groundwater Samples (uncontaminated)

- 1. Open the monitoring well, and measure the water level in the well.
- 2. Insert dedicated HDPE tubing into the well. The lower end of the tubing will be placed approximately 1 foot below the top of the well screen. Add approximately 1 foot of silicon tubing to the upper end of the HDPE tubing. The silicon tubing will be inserted in the peristaltic pump, since it provides better suction than HDPE tubing.
- 3. Purge the well at a flow rate of between 0.1 and 0.5 L/min, as measured with a graduated container and clock. Measure drawdown as induced by pumping. Purge waters will be disposed on-site (note that this is an upgradient and uncontaminated well). If drawdown is less than 5 feet, continue as described below.
- 4. Purge an estimated three well volumes from the well, and then collect the sample in 20-L carboy until 60 liters have been collected. Do not filter sample.
- 5. Cap the well, and close and lock the protective casing, as appropriate.
- 6. Dispose the purge waters on-site.

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7.3 Decontamination Procedures

A decontamination area will be established at the site for cleaning the sampling equipment. A plastic sheet will be placed on the ground on which two 5-gallon buckets will be placed, one containing a non-phosphate-based detergent and the other used for collecting rinse water. Sampling equipment (spades and trowels) will be washed in the detergent solution using a brush to remove large particles, and then rinsed with clean water from a spray bottle. The water will be collected in the second bucket. The buckets will be capped, and the solutions will be disposed in a municipal sewer system after sampling is completed. The City of Kewaunee

Sewerage Utility gave verbal approval in a telephone conversation on November 16, 2005, for the disposal of the wash water in the local sewer system. Given the small volumes of water involved, the City said that disposal in the sewer system would be acceptable without testing.

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Figure 1 Project Organization Chart Kewaunee Marsh Treatability Study



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