Phase II Baseline Monitoring (Revised – April 27, 2012)
Kewaunee Marsh – Kewaunee, Wisconsin

Purpose

To evaluate if the elevated arsenic concentrations in the water in the treatment area are associated with colloidal particles, and determine if changes are needed in the sampling protocol to obtain representative samples of the dissolved phase arsenic concentrations at the Kewaunee Marsh.

Low Flow Sampling Evaluation

Evaluate options for low flow water collection methods to minimize disturbance of groundwater during sampling. The low hydraulic conductivity and slow recovery of the water in wells at the Kewaunee marsh may require that modified low flow sampling methods be used. TRC proposes evaluating the three general methods described below during the Spring 2012 sampling event. In all cases water levels will need to be monitored closely, using a water level indicator, in order to maintain adequate well volume prior to sampling. The methods listed below would be evaluated such that a low flow sampling protocol could be developed for the site.

1. **Low flow sampling using a peristaltic pump and flow through cell**. Collect sample using standard low flow sampling protocol, but allow for adjustment in pumping rates and frequency of parameter readings due to low well volume yields.
2. **Well volume purge and low flow sampling combination**. Remove initial stagnant well volume, or until well goes dry. Once the well has recovered, perform low flow stabilization/sampling using a peristaltic pump and flow through cell.
3. **Low flow sampling using a peristaltic pump and submerged meter probes**. Collect sample using low flow sampling protocol, but set meter down the well with sample tubing placed just above the meter. This method would allow for a significantly slower pump rates. Decontamination of the meter would be required between each well.

Filter Size Evaluation

Evaluate effect filter size has on the concentration of arsenic in water to determine if elevated arsenic concentrations are associated with colloidal particles (typical colloid size ranges from 0.001 and 1 micron).

1. **Unfiltered:** Collect unfiltered samples and place into 250 mL sample jar preserved with nitric acid. Sample will be analyzed without further filtration.

2. **0.45 and 0.20 micron Field Filter:** Collect samples in series using 0.45 micron and 0.20 micron field filters. Samples collected with a bailer will be filtered off-line. Samples collected using a low flow method will be collected in-line, as site conditions allow, in order to minimize alternation of the iron speciation from its native state in the marsh. If in-line filtration cannot be achieved in the field because of low recovery rates in the monitoring well, off-line filtration will be allowed, and documented in the field notes. Place filtered samples into 250 mL sample jar preserved with nitric acid.
3. **Centrifugal Ultrafiltration at 100kD (0.01 to 0.02 micron):** A 0.20 micron filter is the smallest filter size that can practically be applied in the field, but other methods of filtration are available in the laboratory. In this case centrifugal ultrafiltration will be completed by the Wisconsin State Lab of Hygiene to filter potential colloidal particles. Centrifugal filtration will be completed on both unfiltered and post-0.2-micron filter water samples.
    a) **From Unfiltered Sample**: Collect unfiltered samples and place into 60 mL sample jar, with no preservation. Remove all head space from jar and keep on ice and away from light exposure. Sample to be delivered to laboratory and subject to centrifugal ultrafiltration as quickly as possible after collection.
    b) **From Post 0.2-micron**: Collect sample following filtration through 0.2 micron field filter, and place into 60 mL sample jar, with no preservation. Remove all head space from jar and keep on ice and away from light exposure. Sample to be delivered to laboratory and subject to centrifugal ultrafiltration as quickly as possible after collection.

Sampling Plan

A systematic sampling approach is recommended to isolate components of the water sampling at Kewaunee Marsh that may be contributing to the measurement of elevated arsenic concentrations in the treatment area, and to determine modifications to the sampling protocol, if any, that would be recommended for water sampling at Kewaunee Marsh. The proposed sampling plan is summarized in Table 1 below.

TABLE 1
KEWAUNEE MARSH - PHASE II SAMPLING PROGRAM
MAY 2012

FLOW METHOD	FILTER SAMPLING METHOD	SUGGESTED MONITORING WELLS	ANALYSIS # SAMPLE	PURPOSE
Low Flow 1 Low Flow 2 Low Flow 3	None	MW11-2 MW11-3i MW02-3 (or any well not sampled)	None	Evaluate feasibility of suggested low flow methods on typical wells and select one method to use for sample collection
Selected Low Flow Method	Field Filter: 0.45 µm	MW11-1 (treated) MW11-3 (untreated, high As) MW04-9 (untreated, low As)	As & Fe (3) Preserved	Determine effect flow method on arsenic concentration without altering filter size
	- Unfiltered - Field Filter: 0.2 µm[1]	MW11-1 MW11-3 MW04-9	As & Fe (6) Preserved	Determine effect of combination of flow method and filter size on arsenic concentration
	- Lab Centrifugal Ultrafiltration[2] (a) Unfiltered (b) Post 0.2 µm	MW11-1 MW11-3 MW04-9	As & Fe (6) Unpreserved	
Bailer (Current Method)	Field Filter: 0.45 µm	MW11-1 MW11-3 MW04-9	As & Fe (3) Preserved	Establish control conditions for current method
	- Unfiltered - Field Filter: 0.2 µm[1]	MW11-1 MW11-3 MW04-9	As & Fe (6) Preserved	Determine effect of filter size on arsenic concentration without altering flow method
	- Lab Centrifugal Ultrafiltration[2] (a) Unfiltered (b) Post 0.2 µm		As & Fe (6) Unpreserved	
		Total	**18 Preserved** **12 Unpreserved**	

Notes
[1] The samples should be collected in series from unfiltered to 0.45 micron to 0.2 micron using the suggested flow method.
[2] The samples collected for laboratory centrifugal ultrafiltration will not be preserved in the field (i.e. no acid addition).