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Site Investigation Work Plan

C.D. Besadny Fish and Wildlife Area
Kewaunee Marsh Arsenic Area
Kewaunee, Wisconsin

STS Project No. 4-27393
July 15, 2002

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Wisconsin Department of Natural Resources
1125 North Military Avenue (54303)
P.O. Box 10448
Green Bay, Wisconsin 54307-0448

THE INFRASTRUCTURE IMPERATIVE

STS CONSULTANTS

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July 15, 2002

Ms. Annette Weissbach, Hydrogeologist/Project Manager
Wisconsin Department of Natural Resources
1125 North Military Avenue (54303)
P.O. Box 10448
Green Bay, Wisconsin 54307-0448

Re: Site Investigation Work Plan, C.D. Besadny Fish and Wildlife Area (Kewaunee Marsh Arsenic Area) -- STS Project No. 4-27393

Dear Ms. Weissbach:

STS Consultants, Ltd. (STS), has completed this Site Investigation Work Plan outlining the scope and procedures for completing a Phase II Subsurface Assessment including remedial action alternative analysis for the arsenic-impacted portion of the C.D. Besadny Fish and Wildlife Area (Kewaunee Marsh). This Work Plan was prepared in substantial accordance with conditions of Chapter NR 716.09 of the Wisconsin Administrative Code and includes significant elements of the Substantially Completed Work Plan dated September 10, 2001. The Work Plan includes a Sampling and Analyses Plan, a Data Management Plan, a Health and Safety Plan, and a Preliminary Project Schedule.

We appreciate the opportunity to provide professional consulting services to the Wisconsin Department of Natural Resources and look forward to working together on this project.

Sincerely,

STS CONSULTANTS, LTD.

Jan Tesch

Jan J. Tesch
Project Scientist

Paul J. Killian, P.E.
Principal Engineer

Copy: Ms. Marie Stewart
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Madison, Wisconsin 53707-7921

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Work Plan for Soil and Water Sampling and Analyses
C.D. Besadny Wildlife Area - Kewaunee Marsh Arsenic-Impacted Site
Town of Pierce, Kewaunee County, Wisconsin

1.0 INTRODUCTION

This Site Investigation Work Plan outlines the anticipated scope and procedures of a site investigation that will be implemented to characterize the distribution of arsenic in soil, sediment, surface water, and groundwater in an arsenic-impacted site within the C. D. Besadny Fish and Wildlife Area in the Kewaunee Marsh. This Work Plan includes sampling objectives, scope, procedures, equipment, quality control (QC) and documentation, and management procedures for wastes derived from sampling and related investigative work.

The site is located in the SW 1/4, Section 7, T23N, R25E, Town of Pierce, Kewaunee County, Wisconsin, approximately 1 mile northwest of State Highway 42 and 1/4 mile east of County Trunk Highway E, along a Fox Valley & Western Railroad corridor formerly known as the "ferry yard lead." The site is approximately 1,000 feet northwest of the Kewaunee River. The location of the site appears on Figure 1.

The site investigation includes the following elements:

- Define current arsenic concentrations in soil, sediment, surface water, and groundwater.
- Develop a conceptual site model and evaluate applicable exposure pathways through the analysis of arsenic fate and transport in the marsh/river system.
- Document the condition of the interim action cover, evaluate the influence of the interim action on the movement and stabilization of arsenic in the area, and provide an opinion as to whether the interim action will function as an effective final remedy.
- Present feasible remedial action options in accordance with Wisconsin Administrative Code Chapter NR 722.
- Evaluate the previous modeling efforts conducted and provide an opinion on whether additional modeling would be an advantage to predicting the environmental fate of arsenic.

2.0 BACKGROUND INFORMATION

2.1 Physiography

C.D. Besadny Fish and Wildlife Area consists of over 22,000 acres of state-owned property located in Pierce Township, Kewaunee County, Wisconsin. The impacted site is located in the Lake Michigan basin near the banks of the Kewaunee River. The area is marshy with surficial soils consisting mostly of soft peat and mucky peat, with thicknesses ranging from 15 to 25 feet (STS Consultants, Ltd. [STS], 1995). Ground moraine clay till underlies the peat deposits. These glacial soils are estimated to be approximately 50 to 100 feet thick in this area. Bedrock below Kewaunee County consists of undifferentiated dolomite (Skinner and Borman, 1973). Drainage at the site is generally to the east, toward the Kewaunee River. The ground surface at the marsh is frequently inundated with surface water, especially when the Kewaunee River is flowing at high water levels in the spring. Low flow conditions generally occur in the summer months.

2.2 Previous Investigative Work and Interim Remedial Action

The WDNR was made aware of the impacted area in the early 1990s and conducted initial sampling in October 1992. The area of impact appears to have been present since the 1940s near the railroad track based on aerial photographs. During the 1930s and 1940s, sodium arsenite was a common component of pesticides used to control insects at the cherry producing orchards of Door County.

A preliminary assessment of the site was performed in 1994 by STS, which included completing shallow soil borings to a maximum depth of 1.5 feet. A subsequent investigation included collecting surface water samples, groundwater samples from the shallow monitoring wells, sediment samples, and soil pore water. The WDNR also sampled soil, surface water, groundwater, and plant and animal tissue at the site in 1996 and 1997.

In 1996, an interim remedial cover, consisting of geotextile covered with woodchips, bark, and organic yard waste was placed over areas of the site with the highest documented arsenic concentrations to prevent direct contact exposure to arsenic-containing sediments. A security fence was installed around the impacted area, including the interim covered areas. The area of the interim cover was approximately 3.25 acres, lying within an approximate 15-acre fenced area.

Before the cover was constructed, shallow groundwater monitoring points were installed near the cover area, and a staff gauge was installed nearby in the Kewaunee River. Groundwater and river elevations were measured, and groundwater samples were collected from the monitoring points. Surface water samples were also collected from the Kewaunee River. Monitoring Points MP-1 through MP-4 were installed downgradient of the cover area within the security fence, and Monitoring Points MP-5 and MP-6 were installed outside the fence, sidegradient of the cover. The groundwater and surface water sample results indicated:

- Arsenic concentrations above the NR 140 enforcement standard (ES) of 50 micrograms per liter (µg/L) were detected at MP-1 through MP-4 in April and October 1996. At MP-5, the NR 140 ES was not exceeded, but concentrations were greater than the NR 140 preventive action limit (PAL) of 5 µg/L. At MP-6, the April 1996 sample was above the ES, but the October 1996 sample was between the PAL and the ES.
- Arsenic concentrations in surface water samples collected in April, May, and June 1996 were above the NR 105 Table 9 Arsenic Human Cancer Criterion of 50 µg/L, but below the NR 105 Table 1 Acute Toxicity Criterion of 339.8 µg/L and the NR 105 Table 5 Chronic Toxicity Criterion of 153.2 µg/L. Arsenic concentrations in samples of river water collected in July and October 1996 and June 1997 were well below the NR 105 criterion. In August of 1997, NR 105 criteria for arsenic were revised. The Acute Toxicity Criterion was lowered to 0.185 µg/L. Arsenic concentrations in samples collected in August 1997 were below the method of detection. Previous upstream sampling of the river indicates that background concentrations are on the order of 1 to 4 µg/L. These background concentrations are above the NR 105 Human Cancer Criteria.

The WDNR also performed several rounds of sampling of various environmental media. Soil and groundwater were collected and analyzed, both prior to and subsequent to the interim action. A summary of analytical results from the sampling conducted in 1994 through 1997 is presented in Table 1. Sample locations are shown on Figures 3A, 4A, and 5A. Plant and animal tissue samples were collected, and this data was used to complete a baseline ecological risk assessment for the site. A summary of baseline ecological risk assessment appears in Table 2.

2.3 Previous Groundwater and Surface Water Modeling

Groundwater and surface water modeling of the expected fate and transport of arsenic at the site was performed by STS in 1997 using the BIO1D model, which simulated the transport of organic, inorganic, and radioactive groundwater constituents. The model indicated that the transport of arsenic in the groundwater at the site is very slow, with the model predicting that the maximum concentration of arsenic in the groundwater would reach the Kewaunee River in approximately 2,800 years. The groundwater model generally simulated dissolved arsenic migration based on estimated sorption through the saturated organic soil.

A (HydroCAD) surface water model was utilized to evaluate transport of the arsenic in stormwater. The results indicated that the maximum stormwater arsenic concentration was 28.3 µg/L; the highest downstream arsenic concentration calculated was 15.6 µg/L. The surface water model predicted arsenic migration in surface water using the ratio of arsenic mass and total runoff from regional sub-basins.

Arsenic migration in the surface and subsurface environment is a complex combination of chemical specification, mass transfer, and interaction between surface water and groundwater. Accordingly, numerical fate and transport modeling is inherently limited. In a memo dated July 16, 1998, the WDNR outlined some of the limitations of the 1997 modeling efforts. A copy of the July 1998 memo is provided in Appendix A.

2.4 Baseline Ecological Risk Assessment

In April 2000, the WNDR published its Baseline Ecological Risk Assessment (BERA) of the Arsenic Contaminated Wetland Associated with the C.D. Besadny Fish and Wildlife Area and the Kewaunee River. The BERA was conducted to determine the present and future risks to wildlife, birds, and aquatic resources from exposures to arsenic in the soil, sediment, groundwater, and surface water following implementation of the interim action at the site. The BERA also documented the degree of uncertainty and quality of the data available in performing the risk assessment and indicated that further investigation of soil, sediment, groundwater, and surface water is warranted to determine if the interim action cover is sufficient to protect the environment and public health.

2.5 2001 WDNR Sampling Effort

In May and June of 2001, the WDNR Bureau of Watershed Management (BWM) conducted additional investigation at the site. Ten groundwater monitoring wells were installed at the site, and ten surface water samples and ten soil/sediment samples were collected. In addition, the WDNR installed a continuous water level tracker on the former railroad bridge located adjacent to the site.

The new surface water data indicated that the actual system of transport of arsenic in the wetland environment is probably more complicated than assumed by the 1997 modeling. With the exception of two wells, concentrations of arsenic in groundwater samples were generally comparable to or lower than concentrations from samples collected from 1994 through 1997. In one of the two wells that contained higher concentrations, there was very little groundwater present in the well at the time of the sampling. The other well was very near one of the sloughs that drain the area to the Kewaunee River, and it may have been influenced by the strong surface water gradient associated with drainage of the slough.

The automated water level tracker on the nearby former railroad bridge collected data nearly continuously at a rate of one data/second and logged at 15-minute intervals. This data was compared to Kewaunee River water level data collected by United States Geological Survey (USGS) at a location approximately 6 miles upstream, and also to Lake Michigan water level data collected by National Oceanic and Atmospheric Administration (NOAA). This comparison clearly indicates that the river elevation at this location varies directly with fluctuations in Lake Michigan levels. There is no evident relationship between the USGS measured river levels and the water levels near the site. This indicates that the hydrology of the marsh at this location is more aptly described by estuarine dynamics than by typical channel flow. In addition, the WDNR has moved its level tracker to several groundwater monitoring wells on the site. The data in the wells indicated that the estuarine character of the water level fluctuations at this site appear to extend westward into the groundwater regime for some distance.

Sampling results of the May-June 2001 BWM investigation are summarized on Table 3. The BWM data also included water levels from monitoring wells and from the water level data logger maintained by the WDNR. This information will be reviewed and incorporated into the Geographic Information System (GIS) database. The BWM data does not redirect the proposed sampling effort outlined in this Work Plan. Rather, the data, along with other historical environmental sampling results, will assist in documenting changes and trends in groundwater, surface water, and sediment quality.

3.0 SITE INVESTIGATION

The site investigation will consist of a soil investigation, a surface water investigation, a groundwater investigation, a site survey, and interim cap evaluation. The site investigation will be performed in accordance with the Sampling and Analysis Plan (Appendix B), the Data Management Plan (Appendix C), and the Site-Specific Safety Plan (Appendix D).

STS will retain U.S. Filter/Environscan Services, 301 West Military Road, Rothschild, Wisconsin, to perform analytical services on the project. The laboratory Standard Operating Procedures (SOP) is attached as Appendix E. STS will complete soil boring/sample collection and monitoring well installation using in-house drilling capabilities. A 48-hour advance notification must be given to the WDNR Project Manager (Ms. Annette Weissbach at [902] 492-5865) before any significant activities will be performed at the site. In her absence, contact Mr. Jim Killian of WDNR Madison at (608) 264-6123. A project organization chart is included as Figure 6. Ms. Jan Tesch will contact Ms. Weissbach and Mr. Killian on a weekly basis during the sampling with a progress update.

3.1 Soil/Sediment Investigation

The scope of the soil/sediment investigation will consist of the following:

- Twenty-two surface wetland sediment samples will be collected using a trowel or shovel. Ten of these samples will be submitted to the laboratory for phase separation into pore water and sediment solids and for analysis of arsenic to determine partitioning of arsenic at the site between soil and water (Figure 2).
- Twenty-two soil borings will be advanced to an approximate depth of 5 feet. Samples will be collected using a piston sampler, because of the low solids content expected in the peaty near-surface soils. Eight of these samples will be submitted for phase separation and analysis (Figure 2).
- Soil samples will be analyzed for arsenic, iron, aluminum, manganese, organic matter, percent solids, pH, cation exchange capacity (CEC), and phase separation; arsenic, soil, grain size analysis, and water.

Table 4 is a summary of the environmental sampling that will occur at the project site.

3.2 Surface Water Investigation

The scope of the surface water investigation will consist of the following:

- Collect 26 surface water samples at the locations indicated on Figure 4.

- Collect 9 spring-thaw surface water samples at the locations indicated on Figure 4.
- Surface water samples will be submitted to the laboratory for analysis of hardness, arsenic, iron, aluminum, calcium, magnesium, manganese, and sulfate. At approximately one-quarter of the sample locations, duplicate paired samples will be collected. One of these duplicate samples will be field-filtered, and the other will remain unfiltered. Both samples will be submitted for laboratory analysis.
- Field measurements will include pH, conductivity, redox potential (eh), and temperature.
- Two stream gauges will be installed in the Kewaunee River. Locations of the stream gauges are show in Figure 4.
- A continuous-monitoring automated water level tracker will be installed on the former railroad bridge, adjacent to the site.

3.3 Groundwater Investigation

The scope of the groundwater investigation will consist of the following:

- Install and develop the following list of groundwater monitoring wells and piezometers in accordance with NR 141 in selected soil boring locations.
- Install four groundwater monitoring well nests, each consisting of three wells with screen depths of 5, 10, and 20 feet (Figure 3).
- Install three groundwater monitoring wells nests, each consisting of two wells with screen depths of 5 and 10 feet (Figure 3).
- Advance five soil borings to a depth of 10 feet to obtain soil samples and install groundwater monitoring wells (Figure 3).
- Advance four soil borings to an approximate depth of 20 feet to obtain soil samples and install groundwater monitoring wells (Figure 3).
- Sample the wells and piezometers. Perform field analyses on samples, including pH, conductivity, redox potential, dissolved oxygen, and temperature. Analyze groundwater for arsenic, iron, aluminum, calcium, magnesium, manganese, and sulfate. The majority of samples will be field-filtered. However, analogous to the surface water investigation, approximately 1/4 of the samples will be duplicated and submitted both for "dissolved" and "total" analysis as a basis for evaluation of transport of suspended solids.
- Measure groundwater levels in the wells and piezometers to determine horizontal and vertical gradients on the site. Elevation of the Kewaunee River, as measured by the stream gauges, will be recorded on the same date as the groundwater levels.
- Advance an automatic water level tracker (In-situ Inc. miniTROLL) in two monitoring wells. One of these will be installed in a well on the eastern portion of the site (near the Kewaunee River) and one will be installed in a well in the western portion of the site. In-situ, Inc. produces high quality, accurate water level meters at reasonable cost. Information about the miniTROLL is included in Appendix F.

- Perform in-field hydraulic conductivity testing in selected wells and piezometers.
- Conduct groundwater/surface water elevations and groundwater sampling on a quarterly basis for one year.
- Monitor weather conditions.

Monitoring well locations are shown on Figure 3.

3.4 Survey/Interim Cap Evaluation

The scope of the subject site survey/interim cap evaluation was defined to include the following:

1. Verify subject site limits and physical features.
2. Document the location and surface elevation of each soil boring and sediment and surface water sample location.
3. Document the location and elevation of stream gauges and water level tracker installed in the Kewaunee River.
4. Document the location of ground surface and top of casing elevation of each groundwater monitoring well and piezometer.
5. Document and map topography of the site, including the interim action cover.
6. Visually assess the condition of the cover, including measuring the thickness of the wood chip/yard waste mixture covering the geotextile.

In January 2002, STS completed field elements of the site survey/interim cap evaluation. Thickness of the wood chip/yard waste layer over the geotextile was found to range from 0.6 foot to 2.7 feet at approximately 20 sampling points throughout the cover. Field observations suggest that the majority of the wood chips had decayed in all areas, making the interior cover resemble organic soil.

4.0 CONCEPTUAL MODEL DEVELOPMENT

Arsenic can be present in the subsurface environment in several forms, depending on several geochemical conditions including the amount of absorbent components of the soil, mineral composition in soil, pH, and redox potential. Arsenic occurs frequently in both the pentavalent state (+5) and in the trivalent state (+3) in the subsurface. Arsenic +3 (or arsenite) is the reduced state of inorganic arsenic and is considerably more toxic, more soluble, and more mobile than the oxidized state (arsenate). Accordingly, from a risk assessment perspective, oxidizing conditions encouraging the formation of arsenate, typically represent less of a threat to public health and the environment. Unfortunately, arsenite is likely prevalent in low eH and pH environments, which are typical of a flooded soil system.

Water levels within the Kewaunee Marsh fluctuate in response to seasonal influences. Low water level conditions may create an oxidizing environment in the shallow unsubmerged soil encouraging the oxidation of arsenite to a less mobile, less toxic arsenate. Soluble arsenic significantly increases with decreasing eH and pH. Additionally, the presence of iron or manganese hydroxides generally increases the adsorption rate of arsenate on soils. The addition of agricultural lime (calcium chloride) during interim corrective action was presumably done to increase pH and promote the formation of arsenate. This would generally suggest that the migration of arsenic in an oxidized environment would be limited. However, it is possible that arsenic co-precipitates with iron, manganese, or aluminum oxides and is present as suspended solids in surface water runoff. Reported desorption and remobilization of arsenic from the suspended solids may occur during periods of flooding or as seasonal water levels increase, and oxidation and pH adjustment may actually be increasing arsenic transported through suspended sediment.

To confirm this conceptual model, sampling and analysis will be conducted to evaluate the potential contaminant transport mechanisms at the Kewaunee Marsh. The wetland conditions at the marsh suggest that there may be little distinction between groundwater/surface water and soil/sediment. In completing the proposed study, we will attempt to define the groundwater/surface water interface to the extent that it influences contaminant migration. Additionally, the organic and inorganic material transported as suspended solids by surface water will be considered as a contaminant transport mechanism. Geochemical conditions near the interim action cover near the Kewanee River and at areas surrounding the cover will be defined.

As indicated previously, numerical modeling of arsenic fate and transport is very complex, particularly under the biological and geochemical conditions represented by the Kewaunee Marsh. STS will review previous modeling efforts, including WDNR comments of July 1998, and provide an opinion regarding the potential benefits of future fate and transport modeling.

4.1 CTIS Methodology

All environmental data, including both historic and newly acquired data, will be managed in a geodatabase using Microsoft Access and ESRI ArcGIS 8.2. Water elevations and arsenic concentrations from groundwater and surface water samples will be displayed using symbols proportionate to results. This will allow for a visual assessment of current versus past conditions. As sampling points have not remained the same over time, a more in-depth analysis of temporal change requires interpolating the data.

The proposed interpolation scheme utilizes the "Inverse Distance Weighted (IDW)" method combined with barrier lines representing the direct contact prevention cap and the river. The data from each sampling period will be interpolated using the above methodology. Grids from different epochs can then be subtracted, allowing for a visual assessment of changes over time. The sparseness of the data will be taken into consideration when interpreting these grids. Conceptual models of contaminant transport will be provided, utilizing the above analyses and all data acquired.

All historic data, as well as newly acquired data, will be provided to the WDNR in ESRI geodatabase format. This format utilizes a Microsoft Access database as its storage mechanism, so all data will be accessible using the Access application. Layers can also be provided in GIS shapefile format, if desired. Interpolation results will be in grid format.

4.2 Weather Monitoring

Precipitation and barometric records will be obtained for the project area from the National Oceanic and Atmospheric Administration (NOAA) weather monitoring station nearest the site. The weather data will be used in conjunction with on-site monitoring devices to evaluate availability.

5.0 SITE INVESTIGATION/REMEDIAL ACTION OPTIONS REPORT

Pursuant to NR 722, Wisconsin Administrative Code, remedial action options will be developed and evaluated for applicable human health and environmental exposure pathways. This evaluation will include the review of the available literature for similar sites (similar types of contaminants in freshwater wetland and surface water environments). The remedial action options review will also include an opinion regarding the effectiveness of the interim action cap.

The interpretation and analysis of environmental data will be completed enhanced using a GIS platform. Through query and interpolation methods, a GIS allows comparison of contaminant concentrations over space and time. The ability to electronically layer various environmental variables and perform queries and analysis between them provides insight to understanding the conditions impacting contaminant migration. The effectiveness of the interim cap and any future corrective action can also be evaluated using similar methods.

We propose to provide full data management and GIS services employing the sweep of ESRI products. Historical environmental data provided by WDNR will be incorporated into a GIS for the Kewaunee March project site. All additional space data generated during the course of this investigation will be incorporated into the common GIS. This will allow rapid visualization of the data to assist in decision making and site condition interpretations.

The Site Investigation report will include site maps, figures, cross-sections, and graphs, as necessary, to effectively convey and summarize site conditions. These drawings are expected to include, but are not necessarily limited to:

- Interim cap Isopach and cross-sections (3).
- Groundwater elevation contour map(s) (high water/low water).
- Distribution of arsenic in groundwater (1).
- Geochemical site characteristics (1).
- Distribution of arsenic in sediment/soil (3 maps at 1 per level).
- Geologic cross-sections (3).

Site Investigation/Remedial Actions Options Report will be prepared in accordance with Chapters NR 716 and NR 722, Wisconsin Administrative Code. If applicable, the report will include recommendations for further remedial action at the site or justification that the interim action will continue to function as an effective final remedy.

6.0 SCHEDULE

A preliminary schedule of the anticipated tasks to complete the site investigation is appended to this Work Plan. The majority of the surface soil/sediment and groundwater well installation will be performed in the spring and summer of 2002. Soil borings located near or through the interim cover will be performed using drill rigs and support vehicles, if surface conditions will support the vehicle. Boring and well installation performed in the marsh areas beyond the interim cover area will be completed by hand drilling techniques. Surface water samples SW02-1 through SW02-9 will be collected during the spring thaw in 2003. Other surface water samples will be collected during the summer of 2002. Quarterly groundwater monitoring will continue through March 2003, assuming the wells are installed by June 2002. It is anticipated that the Site Investigation /Remedial Action Options Report will be completed by April 2003.

7.0 INVOICING

Work performed on the project will be prepared following information contained in the purchase order. Invoices will be submitted on a monthly basis to Ms. Weissbach at the WDNR Green Bay District office.

8.0 REFERENCES

Skinner, E.L., and Borman, R.G. (1973), Water Resources of Wisconsin - Lake Michigan Basin, United States Geological Survey, Hydrologic Investigations Atlas HA-432.

STS Consultants, Ltd. (1994), Preliminary Assessment Report, Arsenic Spill Site, Kewaunee County, Wisconsin

STS Consultants, Ltd. (1995) Assessment Report, Kewaunee Marsh Arsenic-Impacted Site, Kewaunee County, Wisconsin

STS Consultants, Ltd. (1997) Final Report, Kewaunee Marsh Arsenic Site, Kewaunee, Wisconsin.

United States Environmental Protection Agency (1992), Supplemental Guidance to RAGS: Calculating the Concentration Term, OSWER 9285.7-081.

United States Geological Survey (1978), Kewaunee, Wisconsin Quadrangle 7.5-Minute Series Topographic Map.

Wisconsin Department of Natural Resources (2000), Baseline Ecological Risk Assessment for the Arsenic-Contaminated Wetland Associated with the C.D. Besadny Fish and Wildlife Area and the Kewaunee River.

Wisconsin Department of Natural Resources
STS Project No. 4-27393

List of Tables

Table 1

Previous Sampling Results

CARROL D. BEDSADNY FISH AND WILDLIFE AREA
Kewaunee Marsh Arsenic Area
Kewaunee, Wisconsin

1. Surface Water

Sample	Date	As (ug/L)	Comment
BKG-1	Nov. 94	35.5	marsh surface water
BKG-2	Nov. 94	398	marsh surface water
BKG-3	Nov. 94	690	marsh surface water
BKG-4	Nov. 94	64.1	marsh surface water
H-1	Nov. 94	19300	marsh surface water
H-2	Nov. 94	5660	marsh surface water
H-3	Nov. 94	148000	marsh surface water
H-4	Nov. 94	920000	marsh surface water
H-5	Nov. 94	24800	
H-6	Nov. 94	19100	marsh surface water
R-1	Feb. 95	< 1.0	river water
R-1A	Mar. 95	< 1.0	river water
R-1B	Mar. 95	< 1.0	river water
R-1C	Mar. 95	< 1.0	river water
R-1D	Apr. 95	2.7	river water
R-1E	Apr. 95	< 1.0	river water
R-2	Feb. 95	4.1	river water
R-3	Feb. 95	1.2	river water
P-1*	Feb. 95	17200	marsh pore water (filtered)
P-2*	Feb. 95	800000	marsh pore water (filtered)
P-3*	Feb. 95	21000	marsh pore water (filtered)
P-4*	Feb. 95	6.6	marsh pore water (filtered)
P-5*	Feb. 95	< 1.0	marsh pore water (filtered)

ID	Date	As (ug/L)	Comment
Water			
wat95-1	Jun-95	3	reference site upstream wetland s. side of Co. Hwy E
wat95-2	Jun-95	500	dug pit s. side of rr tracks, s. of spur
wat95-3	Jun-95	370	SE of dead area, outer pond remnant
wat95-4	Jun-95	62	wildlife pond #6
wat95-5	Jun-95	3400	wildlife pond #12
wat95-6	Jun-95	860	SE of dead area, inner pond remnant

ID	Date	As (ug/L)	Comment
wt-01	5/22/96	1	reference site
wt-02	5/22/96	8300	SW of cap, north of tracks
wt-03	5/22/96	1400	S of cap, NE of where spur meets tracks
wt-04	5/22/96	2400	SE of cap, south of STS MP-3
wt-05	5/29/96	430	S slough to river, near ST-05
wt-06	5/22/96	37	south of tracks

Table 1

Previous Sampling Results

CARROL D. BEDSADNY FISH AND WILDLIFE AREA
Kewaunee Marsh Arsenic Area
Kewaunee, Wisconsin

ID	Date	As (ug/L)	Al(mg/Kg)	Ca (mg/kg)	Fe (mg/kg)	Mg (mg/kg)	S (mg/kg)	Comment
pw-01-01	5/21/96	7.6						south of tracks, towards river (pit water)
pw-01-02	5/21/96	1.4						south of tracks, towards river (filtered pit water)
pw-01-03	5/23/96	1.6						sampled two days later (pit water)
pw-02-01	5/21/96	8500						north side of tracks, off spur (pit water)
pw-02-02	5/23/96	9900						sampled two days later (pit water)
pw-03-01	5/22/96	2400	1700	93	4.6	35	4.2	NE of cap, between ponds #12 and #6 (filtered pit water)
pw-03-02	5/22/96	1900						NE of cap, between ponds #12 and #6 (filtered pit water)
pw-03-03	5/23/96	3000						NE of cap, between ponds #12 and #6 (filtered pit water)
pw-04-01	9/11/96	3.7						reference site for s. of tracks (it water)

Table 1

Previous Sampling Results

CARROL D. BEDSADNY FISH AND WILDLIFE AREA
Kewaunee Marsh Arsenic Area
Kewaunee, Wisconsin

ID	Date	As (ug/L)	Comment
sw-01-01	5/21/96	1.5	grab from pond 1
sw-02-01	5/21/96	180	s side of tracks, between spur. surface water grab
sw-03-01	5/21/96	360	s side of pond 10
sw-04-01	5/21/96	2.4	grab from kew. river dwnstrm. of rr bridge
swshk-04	4/8/96	8100	sw of cap (near WT-02, unfiltered)
sw-05-01	9/11/96	76	north end of small channel near well gw-09
sw-06-01	9/11/96	60	pond 6
sw-07-01	9/11/96	110	pond 7
sw-08-01	9/11/96	4.6	south end of small channel near well gw-09

ID	Date	As (ug/L)	Comment
sts-r1	4/23/96	118	unfiltered sample taken from river bank
sts-r2	5/20/96	108	unfiltered sample taken from river bank
sts-r3	6/18/96	50	unfiltered sample taken from river bank
sts-r4	6/18/96	< 16	unfiltered sample taken from river channel
sts-r5	7/12/96	3.7	unfiltered sample taken from river bank
sts-r6	10/23/96	3.2	unfiltered sample taken from river bank

Sample Site	Date	As (ug/L)	Comments
KMWT-01	Jun-97	< 1.0	Upriver background site
KMWT-02	Jun-97	24	North slough-upper reach at fence
KMWT-03	Jun-97	7	North slough-mouth at juncture with river
KMWT-04	Jun-97	9	South slough-upper reach at fence
KMWT-05	Jun-97	2	South slough-mouth at juncture with river
KMWT-06	Jun-97	1.0	Downstream south of railroad bridge

Sample Site	Date	As (ug/L)	Comments
SW-9	Jun-97	260	Between cap and railroad
SW-10	Jun-97	86	50 ft SE of cap
SW-11	Jun-97	120	50 ft east of cap
SW-12	Jun-97	320	Depressed area in filled Pond 12
SW-13	Jun-97	530	N. of cap, midway between Pond 7 and cap
SW-14	Jun-97	810	30 ft NW of Pond 10
SW-15	Jun-97	26	Collected in Pond 9

All samples unfiltered unless noted

Table 1 (continued)

PREVIOUS SAMPLING RESULTS

CARROL D. BESADNY FISH AND WILDLIFE AREA

Kewaunne Marsh Arsenic Area
Kewaunee, Wisconsin

2. Groundwater

ID	Date	As (ug/L)	Al (ug/L)	Ca (mg/L)	Fe (mg/L)	Mg (mg/L)	S(mg/L)	Comments
gw-01	4/8/96	0.9						south of rr (filtered)
gw-02	4/8/96	0.9						south of rr (filtered)
gw-03	4/8/96	0.9						south of rr (filtered)
gw-05	5/21/96	60						south of rr (filtered)
gw-06-01	5/22/96	89						north of cap (filtered)
gw-06-02	5/22/96	220						north of cap (unfiltered)
gw-07-01	5/22/96	91	ND	100	2.2	40	0.9	NE of cap (filtered)
gw-07-02	5/22/96	65						NE of cap (unfiltered)
gw-08-01	5/22/96	310	31.00	39.00	0.87	16.00		east of cap (filtered)
gw-08-02	5/22/96	220	440.00	38.00	2.10	14.00		east of cap (unfiltered)
gw-09	5/22/96	28						SE of cap (filtered)
gw-10	5/21/96	310						south of cap (filtered)
gw-11	5/21/96	0.7	ND	92	2.7	32	0.8	south of rr (filtered)

		As Concentration	As Concentration	pH	Conductivity	Temp	Redox	DO
ID	Date	Unfiltered	Filtered			(Celsius)	(mV)	(mg/L)
sts-mp1	4/23/96	771	763	7.2	282	8.7		
	6/12/96	983	733					
	10/23/96	486	318	6.65	595	10.4	-17	0.5
sts-mp2	4/23/96	837	877	6.58	527	10.1		
	6/12/96	643	436					
	10/23/96	170	65.8	6.64	927	10.2	-181	0.5
sts-mp3	4/23/96	282	333	6.86	640	10.6		
	6/12/96	167	136					
	10/23/96	175	156	6.35	856	10.5	-105	0.5
sts-mp4	4/23/96							
	6/12/96	454	358					
	10/23/96	391	311	6.59	707	11.4	-179	0
sts-mp5	4/23/96	<16	<16					
	6/12/96	12.2	9.9					
	10/23/96	5.1	5.7	6.45	800	10.6	-21	0.5
sts-mp6	4/23/96	67	46					
	6/12/96	393	415					
	10/23/96	48.1	19	6.87	902	10.9	-56	0.5

		pH	Conductivity	Temp	Redox	DO
Well	Date	(Celsius)	(mV)	(mg/L)		
gw-01	10/23/96	6.71	725	10.2	44	1.5
gw-02	10/23/96	6.8	643	9.7	30	0.5
gw-10	10/23/96	6.63	751	9.2	32	1
gw-11	10/23/96	6.54	652	9	25	1

Table 1 (continued)

PREVIOUS SAMPLING RESULTS

CARROL D. BESADNY FISH AND WILDLIFE AREA
Kewaunne Marsh Arsenic Area
Kewaunee, Wisconsin

3. Soil/Sediment

Boring	Date	Depth	As (mg/kg)	Comment
B-1	1994	15-16cm	2	15' below water surface in river channel
B-2	1994	4-6cm	2	4' below water surface in river channel
B-3	1994	0-2cm	5.5	
B-4	1994	0-2cm	4	
B-5	1994	0-2cm	4.1	
B-6	1994	0-2cm	no recovery	
	1994	2-4cm	4.3	
	1994	4-6cm	4.95	
	1994	6-8cm	7.15	
B-7	1994	0-2cm	no recovery	2' below ice on river bank
	1994	2-4cm	4.65	
	1994	4-6cm	16.1	
	1994	6-8cm	0.81	
B-8	1994	0-2cm	no recovery	2' below ice on river bank
	1994	2-4cm	1.7	
B-9	1994	0-2cm	249	
B-10	1994	0-2cm	897	
	1994	2-4cm	290	
	1994	4-6cm	85.6	
B-11	1994	0-2cm	943	
B-12	1994	0-2cm	324	
B-13	1994	0-2cm	3290	
	1994	2-4cm	23.7	
	1994	4-6cm	32.7	
	1994	6-8cm	< 0.72	
B-14	1994	0-2cm	858	
B-15	1994	0-2cm	1660	
B-16	1994	0-2cm	1220	
	1994	2-4cm	390	
	1994	4-6cm	12.2	
	1994	6-8cm	0.93	
B-17	1994	0-2cm	no recovery	
	1994	2-4cm	29	
	1994	4-6cm	15.1	
	1994	6-8cm	1.46	
B-18	1994	0-2cm	1400	
B-19	1994	0-2cm	768	
	1994	2-4cm	874	
	1994	4-6cm	181	
	1994	6-8cm	29.5	

TABLE 2

SUMMARY OF BASELINE ECOLOGICAL RISK ASSESSMENT RESULTS

CARROLL D. BESADNY FISH AND WILDLIFE AREA
Kewaunee Marsh Arsenic Area
Kewaunee, Wisconsin

RECEPTOR GROUP	EXPOSURE POINT/AREA OF CONCERN	RELATIVE RISK CHARACTERIZATION
Human Health (Based on NR 105)	River	Low (NearTerm) High (Far Term)
	Wetland	Low
Emergent Marsh and Sedge	Wetland	Low
Algal-, Phyto- and Periphyton	Wetland	Low
Fish Community	River	Minimal
	Wetland	Low
Reptiles and Amphibians	Wetland	Moderate to High
Benthic Macroinvertebrates	River	Minimal
	Wetland	Low to Moderate
Surface Water Macroinvertebrates	River	Minimal
	Wetland	Low
Large Mammals	Wetland	Low
Small Mammals	Wetland	Low
Birds	Wetland	Low
Possible NR 105 Criteria - Wildlife and Domestic Animals	Wetland	High
Microbial Community - Decomposers and Detrivores	Wetland	Low to Moderate
Aquatic Life (Based on NR 105)	River	High (Near Term)
	Wetland	Low

TABLE 3
2001 WDNR-BWM SAMPLING RESULTS
C.D. Besadney Fish and Wildlife Area
Kewaunee, Wisconsin

WATER ANALYSIS RESULTS

FIELD ID	X (WTM83/91)	Y (WTM83/91)	DATE	ALKALINITY TOTAL TOTAL CACO3(MG/L)	ALUMINUM TOTAL RECOVERABLE(UG/L)	ARSENIC TOTAL RECOVERABLE(UG/L)	CALCIUM TOTAL RECOVERABLE(MG/L)	CONDUCTIVITY AT 25C(UMHOS/CM)	IRON TOTAL RECOVERABLE(MG/L)	MAGNESIUM TOTAL RECOVERABLE(MG/L)	MANGANESE ICP TOTAL RECOVERABLE(UG/L)	PH LAB(SU)	PHOSPHORUS TOTAL(MG/L)	SULFATE TOTAL(MG/L)
BACK01-1	717366.8183	448664.7375	26-Jul-01	229	138	ND	62.1	603	0.2	31.9	17	8.44	0.166	28.8
GW01-1	717533.633	447789.300	11-Jun-01	512	160	15	96	945	1.4	35	39	6.84	0.499	9.8
GW01-10	717636.185	447524.804	5-Jun-01	388	830	2.9	100	600	4.1	34	110	6.68	0.421	<4.5
GW01-2	717573.166	447730.342	11-Jun-01	356	130	150	130	708	2.4	51	45	6.72	0.233	11
GW01-3	717699.717	447722.498	11-Jun-01	324	270	260	91	655	2	32	29	6.67	0.371	11.3
GW01-4	717765.352	447755.687	11-Jun-01	264	180	17	76	528	1.7	25	34	6.59	0.492	11.4
GW01-5	717736.946	447705.511	11-Jun-01	276	110	130	78	566	1.7	26	45	6.63	0.327	11.5
GW01-6	717743.792	447649.859	5-Jun-01	215	1300	7000	92	741	2.1	36	52	6.45	2.68	85.9
GW01-7	717726.495	447579.253	5-Jun-01	203	2600	150	77	485	4.2	24	67	6.69	1.2	28.4
GW01-8	717670.936	447597.358	5-Jun-01	347	180	230	97	658	1.8	34	80	6.76	0.811	9.7
GW01-9	717500.957	447642.312	5-Jun-01		11000	7100	540	1210	77	87	3000	6.95	1.48	8.4
GW01-3	717699.717	447722.498	16-Aug-01	322	ND	91.7	92.1	664	1.4	31.7	19	7.09	0.295	11.8
GW01-5	717736.946	447705.511	16-Aug-01	277	2350	135	102	564	5.8	28.5	69	6.87	0.19	12.6
GW01-6	717743.792	447649.859	16-Aug-01	235	283	2380	83.7	671	1.1	30.4	26	6.99	0.953	52.2
GW01-7	717726.495	447579.253	16-Aug-01	205	1590	27.7	70.7	434	2.9	22.7	42	7.4	0.522	19.7
GW01-8	717670.936	447597.358	16-Aug-01	313	202	28.1	101	579	2.4	32.6	53	7.16	0.639	9.9
KM01-CNTRB	717779.4082	447477.3321	26-Jul-01	221	277	ND	58.4	575	0.3	33.4	34	8.48	0.178	27.8
KM01-NSLU	717806.9164	447639.0504	26-Jul-01	244	3990	52.6	97	589	6.1	40.2	180	8.11	2.62	29.5
KM01-SSLU	717768.9305	447570.1828	26-Jul-01	225	1260	25.1	67.8	596	1.6	33.7	73	8.17	0.484	28.6
KM01-WBRIG	717762.7012	447477.0696	26-Jul-01	221	306	1.2	58.4	579	0.4	33.5	35	8.53	0.199	28.6
SW01-1	717452.752	447634.565	30-May-01	260	200	98	85	510	6.4		3100	7.21	0.738	11.1
SW01-10	717629.475	447726.027	31-May-01	373	580	720	100	892	3.8		790	7.5	6.86	23.1
SW01-2	717548.167	447570.954	30-May-01	84	39	ND	24	179	0.68		870	6.71	0.455	12.1
SW01-3	717557.887	447614.081	30-May-01	412	160	1200	140	752	6.9		520	7.66	5.36	11.5
SW01-4	717638.000	447608.819	30-May-01	336	94	1900	84	712	1.3		220	7.51	2.81	16.6
SW01-5	717671.368	447551.281	30-May-01	503	2600	13000	390	717	260		5900	7.43	18.8	7.2
SW01-6	717748.069	447590.073	31-May-01	314	6400	3100	140	721	33		840	7.12	8.72	31.9
SW01-7	717726.936	447640.348	30-May-01	637	17000	8200	330	1280	56		1400	7.38	13.5	113
SW01-8	717771.179	447646.084	31-May-01	222	520	4600	77	628	7.8		55	6.94	2.23	36.6
SW01-816	717691.09	447613.05	16-Aug-01	197	89	938	87.1	425	1.4	19.6	34	6.95	0.94	17.6
SW01-9	717768.699	447689.862	30-May-01	327	7000	1400	140	445	32		1800	7.55	11	18.3

SEDIMENT SAMPLING RESULTS

ID	X (WTM83/91)	Y (WTM83/91)	DATE	ALUMINUM TOTAL(MG/KG)	ARSENIC TOTAL(MG/KG)	CALCIUM (MG/KG)	IRON ICP(MG/KG)	MAGNESIUM (MG/KG)	MANGANESE (MG/KG)	PHORPHORUS (MG/KG)	SULFATE (MG/KG)	SOLIDS % CLAY	SOLIDS % SAND	SOLIDS % SILT	SOLIDS PERCENT
KMSED01-A	717749.0065	447522.9538	23-Aug-01	7680	ND	45400	10100	10600	113	521	310				21.7
KMSED01-B	717763.4582	447571.9235	23-Aug-01	7870	64	31900	6800	5400	76.4	782	1900				16.6
KMSED01-C	717801.704	447638.7253	23-Aug-01	8790	102	34500	10300	4680	107	632	460				17.6
KMSED01-D	717824.5716	447687.0436	23-Aug-01	8910	ND	29500	9800	3990	93.7	673	670				21.5
SED01-1	717659.709	447521.138	11-Jun-01	2600	31	20500	14400	3040	226	924	ND	33	8	59	11.2
SED01-2	717737.987	447542.247	11-Jun-01	14000	51	20700	16300	6460	173	1060	110	23	19	58	22.9
SED01-3	717779.765	447615.688	11-Jun-01	7700	243	20000	9800	4450	139	1020	210	23	29	48	18.6
SED01-4	717795.597	447685.171	11-Jun-01	8740	126	19200	8540	4710	85.1	497	88	23	32	45	31.4
SED01-5	717598.141	447617.887	11-Jun-01	3940	438	31700	7670	7310	125	794	64	24	56	20	17.2
SED01-6	717701.047	447602.055	11-Jun-01	3320	110	27400	6670	3770	35.7	980	130	24	32	44	10.6
SED01-7	717766.572	447664.942	11-Jun-01	3980	255	19200	6590	4360	89.5	1200	120	32	28	40	10.6
SED01-9	717598.581	447723.431	11-Jun-01	2780	320	23600	5040	4920	62.3	1150	97	30	50	20	12.1
SED01-10	717531.736	447583.145	11-Jun-01	1690	25	41500	4120	3930	53.1	524	120	23	61	16	12.3
SED01-10D	717531.736	447583.145	11-Jun-01	1950	30	38400	4820	4030	70.2	456	100	26	48	26	13.2

TABLE 4
Summary of Environmental Sampling
C.D. Besadny Fish and Wildlife Area
Kewaunee Marsh Arsenic Area
Kewaunee, Wisconsin

Sample ID	Depth	Number of Samples Collected	Samples for Phase Separation	Monitoring Well
SS02-1	0-2 cm	1	1	
SS02-2	0-2 cm	1	0	
SS02-3	0-2 cm	1	1	
SS02-4	0-2 cm	1	0	
SS02-5	0-2 cm	1	1	
SS02-6	0-2 cm	1	0	
SS02-7	0-2cm	1	1	
SS02-8	0-2 cm	1	0	
SS02-9	0-2 cm	1	1	
SS02-10	0-2 cm	1	0	
SS02-11	0-2cm	1	1	
SS02-12	0-2 cm	1	0	
SS02-13	0-2 cm	1	1	
SS02-14	0-2 cm	1	0	
SS02-15	0-2 cm	1	1	
SS02-16	0-2 cm	1	0	
SS02-17	0-2 cm	1	1	
SS02-18	0-2 cm	1	0	
SS02-19	0-2 cm	1	1	
SS02-20	0-2 cm	1	0	
SS02-21	0-2 cm	1	0	
SS02-22	0-2 cm	1	0	
Total		22	10	

Sample ID	Depth	Number of Samples Collected	Samples for Phase Separation	Samples for Grain Size Distribution	Monitoring Well
SB02-1	5 feet	0	1	1	MW02-1
SB02-2	5 feet	3	0		
SB02-3	5 feet	3	0		
SB02-4	5 feet	0	1	1	MW02-2
SB02-5	5 feet	3	0		
SB02-6	5 feet	3	0		
SB02-7	5 feet	3	0		
SB02-8	5 feet	3	0		
SB02-9	5 feet	0	1	1	MW02-7
SB02-10	5 feet	0	1	1	MW02-5
SB02-11	5 feet	3	0		
SB02-12	5 feet	3	0		
SB02-13	5 feet	3	0		
SB02-14	5 feet	0	1	1	MW02-6
SB02-15	5 feet	3	0		
SB02-16	5 feet	3	1		
SB02-17	5 feet	3	0		
SB02-18	5 feet	3	0		
SB02-19	5 feet	3	0		
SB02-20	5 feet	3	0		
SB02-21	5 feet	3	0		
SB02-22	5 feet	3	0		
	5 feet	0	1	1	MW02-3
	10 feet	0	0	1	MW02-3I
	20 feet	10	0	1	MW02-3d
	5 feet	0	1	1	MW02-4
	10 feet	0	0	1	MW02-4I
	20 feet	10	0	1	MW02-4d
IB02-1	10 feet	0	0	1	MW02-1i
IB02-2	10 feet	5	0	1	MW02-2i
IB02-3	10 feet	0	0	1	MW02-7i
IB02-4	10 feet	5	0	1	MW02-5i
IB02-5	10 feet	5	0	1	MW02-6i
DB02-1	20 feet	10	0	1	MW02-1d
DB02-2	20 feet	0	0		
DB02-3	20 feet	10	0	1	MW02-7d
DB02-4	20 feet	0	0		
DB02-5	20 feet	0	0		
Total		106	8	18	18

Soil Analysis:			duplicate (5%)	total
Arsenic, iron, aluminum, manganese, organic matter and % solids	132	soil	7	139
Soil pH	132	soil	7	139
Phase separation, arsenic on soil and water	18	soil/water	1	19
CEC	12	soil		12
Grain size distribution	18	soil		18

Surface Water Samples:				unfiltered duplicate (25%)	
Hardness, arsenic, iron, aluminum, calcium, magnesium, manganese, sulfate	(2002 - Summer)	22	water	6	28
	(2003 - Spring thaw)	9	water	3	12

Groundwater Samples - New Wells			unfiltered duplicate (25%)	
hardness, arsenic, iron, aluminum, calcium, magnesium, manganese, sulfate	18	water	5	23

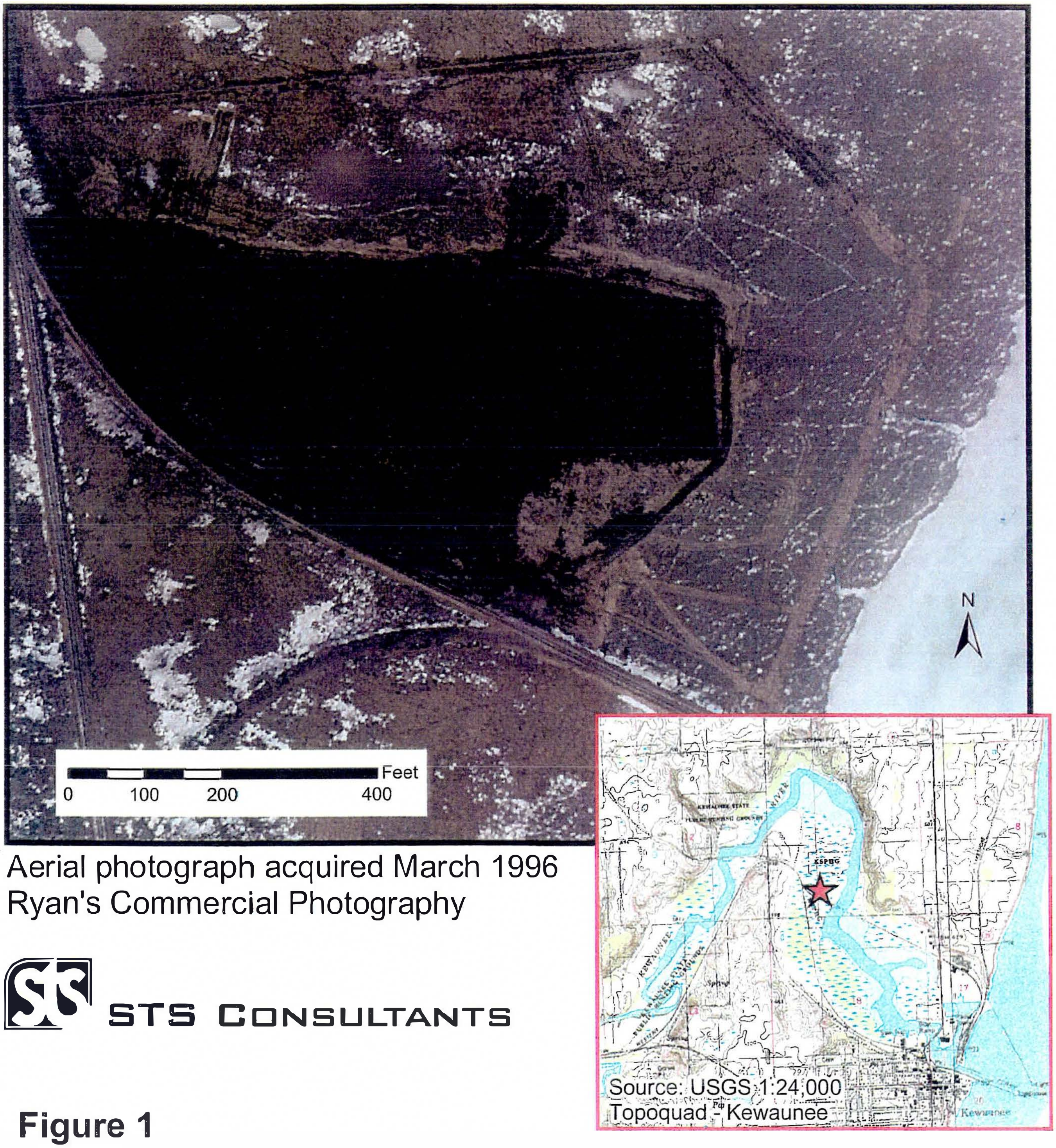
Revision Notes:

1) Added surface water sampling table 4-11-02
2) Added grain-size distribution (18) 4-24-02

List of Figures

Kewaunee Marsh Arsenic Area

C. D. Besadny Fish and Wildlife Area
Kewaunee, Wisconsin

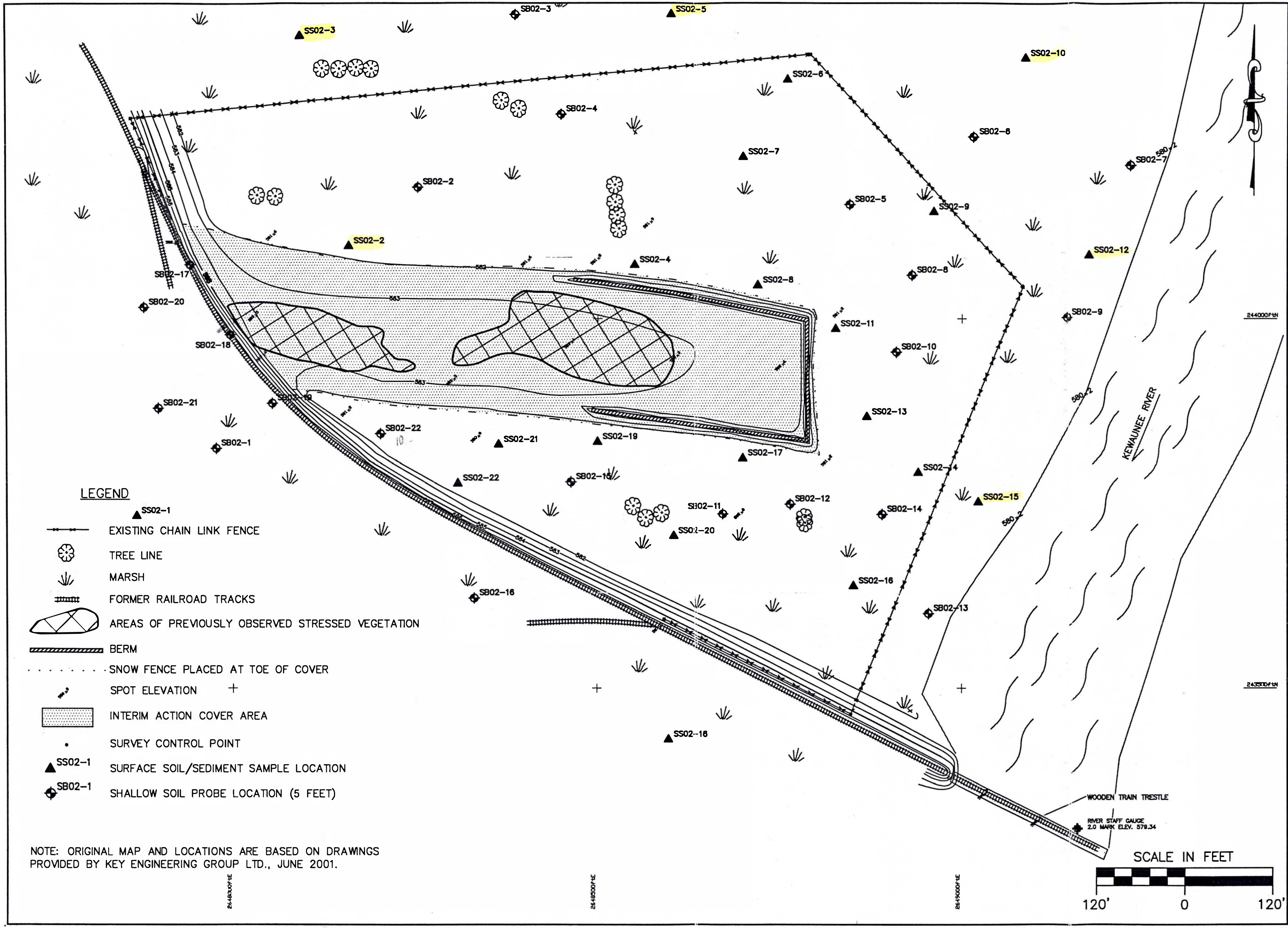


Aerial photograph acquired March 1996
Ryan's Commercial Photography

Source: USGS 1:24,000
Topoquad - Kewaunee

STS CONSULTANTS

Figure 1



NOTE: ORIGINAL MAP AND LOCATIONS ARE BASED ON DRAWINGS PROVIDED BY KEY ENGINEERING GROUP LTD., JUNE 2001.

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DRAWN BY	J.L.C.	DATE 4/4/02
APPROVED BY	P.J.K.	DATE 4/4/02
CADFILE	x:2002/27277/dwg/test/fig3	
XREF		

FIGURE 2 REVISED 4/3/02 STS
PROPOSED SOIL / SEDIMENT SAMPLE LOCATIONS
C.D. BESADNY FISH AND WILDLIFE AREA
KEWAUNEE, WISCONSIN

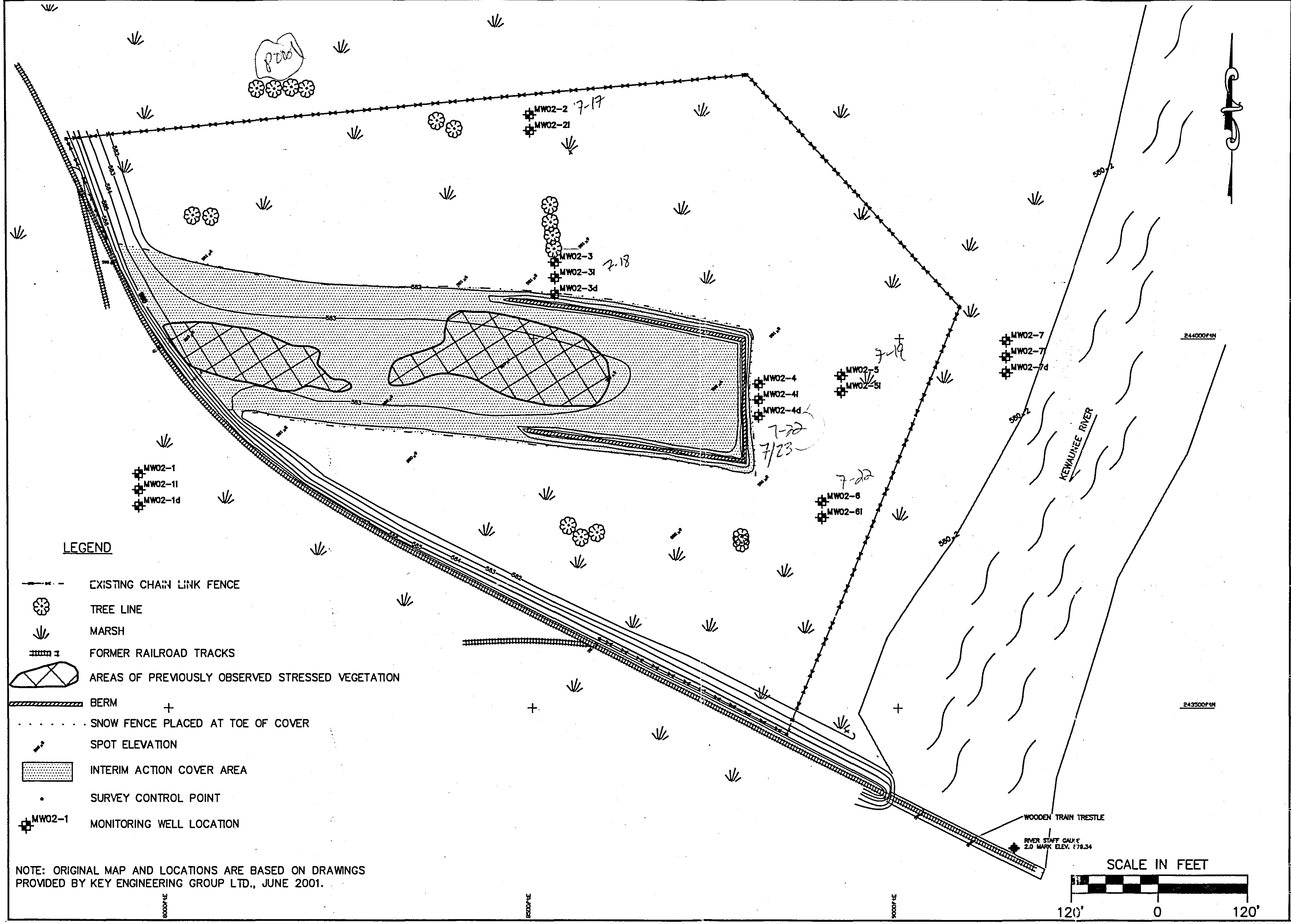
1035 Kepler Dr.
Green Bay, WI 54311
920.468.1978

STS PROJECT NO. 27277

STS PROJECT FILE 27277

SCALE 1"=120'

FIGURE NO. 2



NOTE: ORIGINAL MAP AND LOCATIONS ARE BASED ON DRAWINGS PROVIDED BY KEY ENGINEERING GROUP LTD., JUNE 2001.

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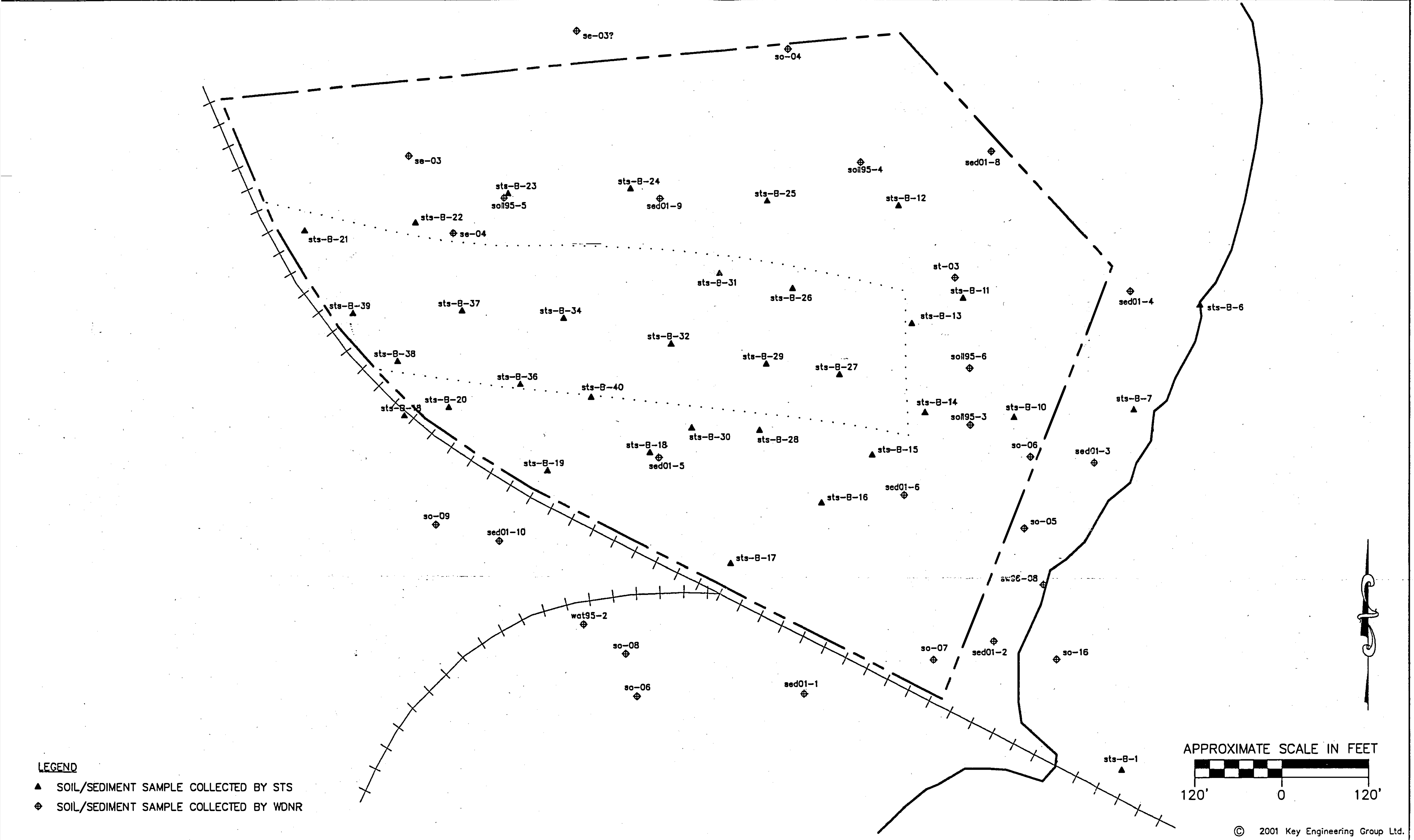
APPROVED BY P.J.K.	DATE 4/4/02
CADFILE x:2002/27277/dwg/test/fig5	
XREF	

FIGURE 3 REVISED 12/19/01 (KEY)
PROPOSED GROUNDWATER SAMPLE LOCATIONS WITH WELLS
C.D. BESADNY FISH AND WILDLIFE AREA
KEWAUNEE, WISCONSIN

STS

1035 Kepler Dr.
Green Bay, WI 54311
920.468.1978

STS PROJECT NO.	27277
STS PROJECT FILE	27277
SCALE	1"=120'
FIGURE NO.	3



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SIGNED BY DPH	DATE 08/01/01
DRAWN BY CS	PROJECT R1103004
APPROVED BY CLJ	SHEET NO. 3A

CADFILE G:\ACAD\R1103004\R11030044.dwg
XREF
LWAN

FIGURE 3A
PREVIOUS SOIL/SEDIMENT SAMPLING LOCATIONS

C. D. BESADNY FISH AND WILDLIFE AREA
KEWAUNEE, WISCONSIN

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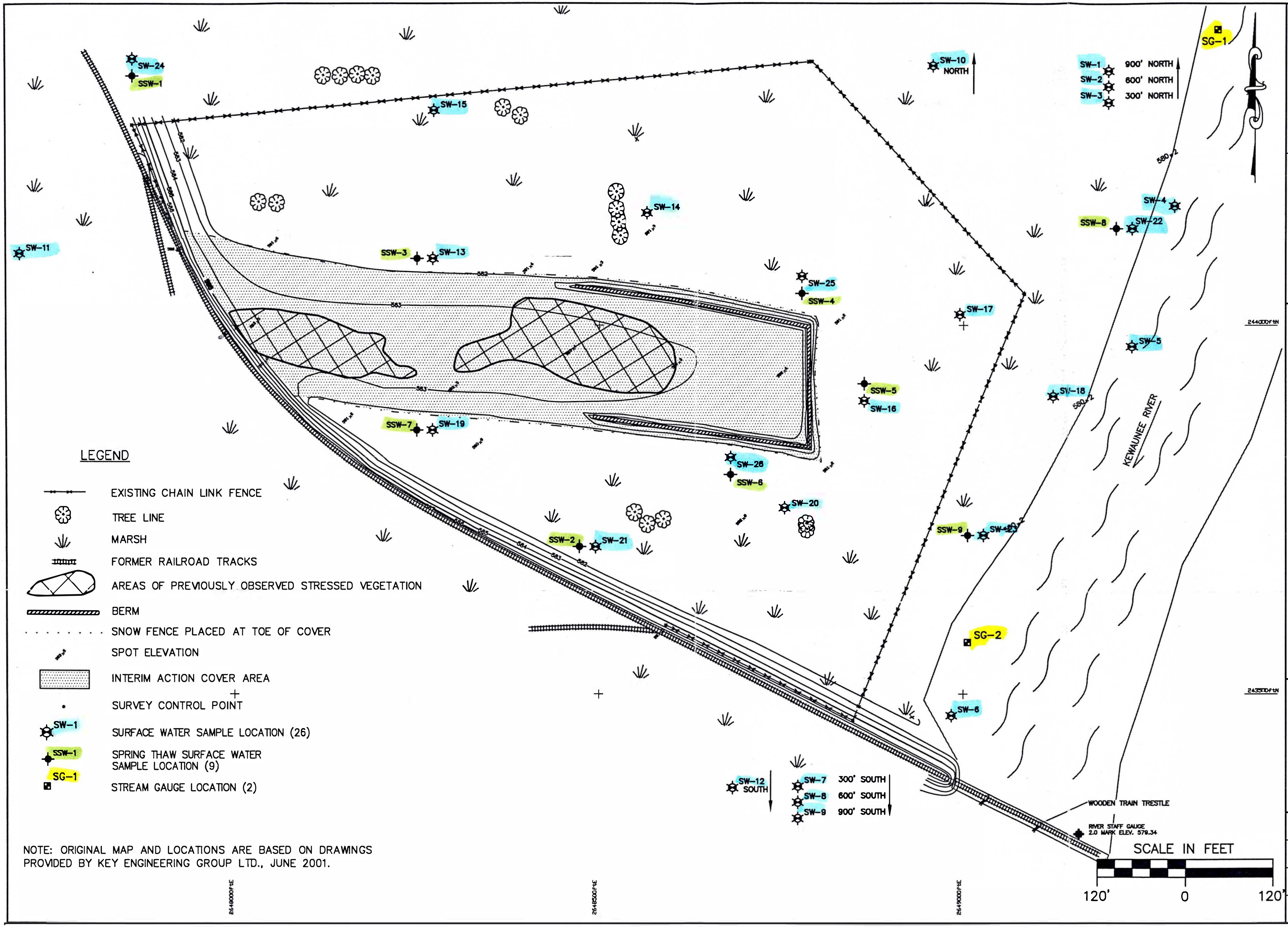

NOTE: ORIGINAL MAP AND LOCATIONS ARE BASED ON DRAWINGS PROVIDED BY KEY ENGINEERING GROUP LTD., JUNE 2001.

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APPROVED BY P.J.K.	DATE 4/4/02
CADFILE x:2002/27277/dwg/test/fig4 XREF	

FIGURE 4 REVISED 4/3/02 STS
PROPOSED SURFACE WATER SAMPLE LOCATIONS
C.D. BESADNY FISH AND WILDLIFE AREA
KEWAUNEE, WISCONSIN

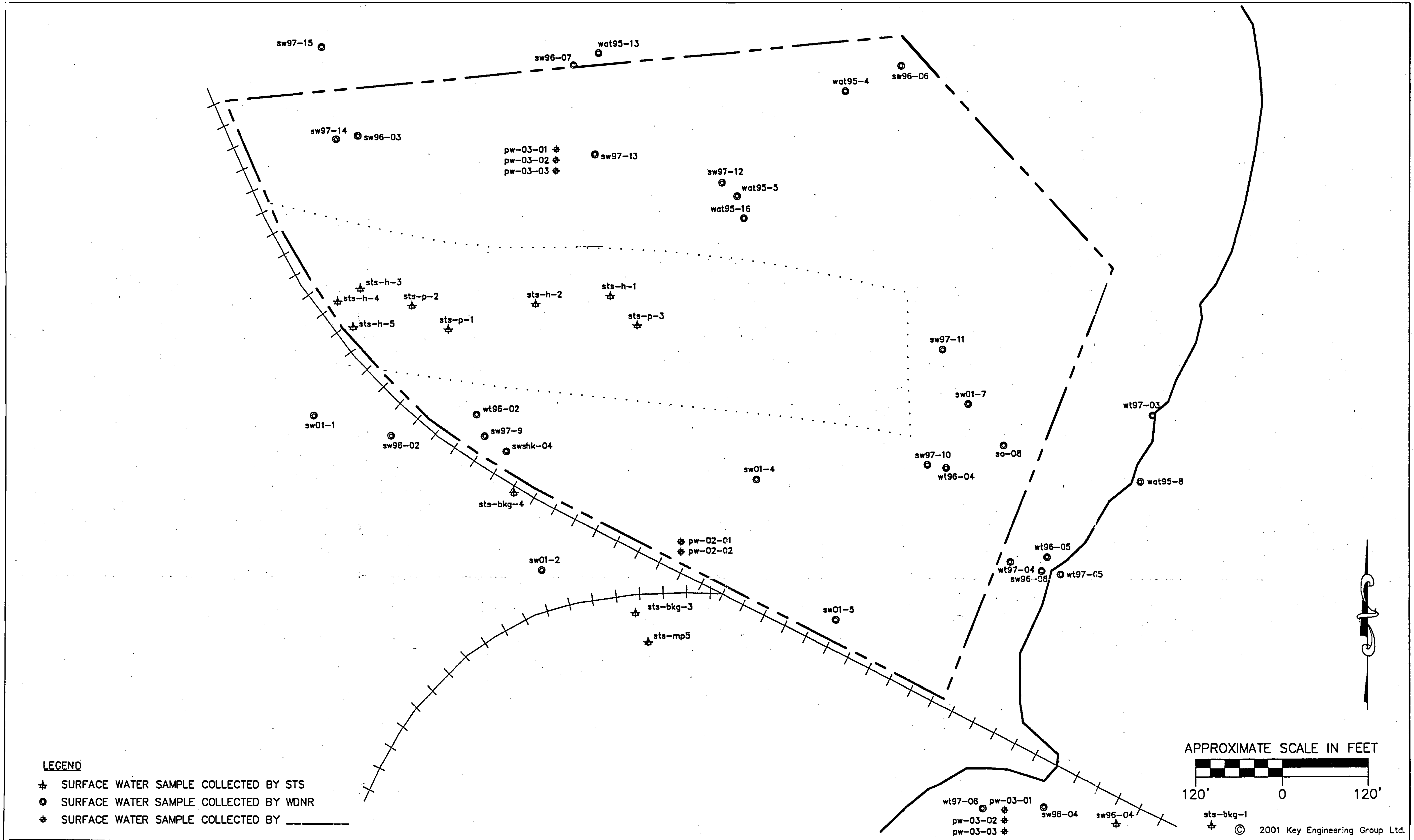
STS
1035 Kepler Dr.
Green Bay, WI 54311
920.468.1978

STS PROJECT NO. 27277

STS PROJECT FILE 27277

SCALE 1"=120'

FIGURE NO. 4



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DRAWN BY CS	PROJECT R1103004
ROVED BY GLJ	SHEET NO. 4A

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FIGURE 4A
PREVIOUS SURFACE WATER SAMPLING LOCATIONS

C. D. BESADNY FISH AND WILDLIFE AREA
KEWAUNEE, WISCONSIN

KEY ENGINEERING GROUP LTD.
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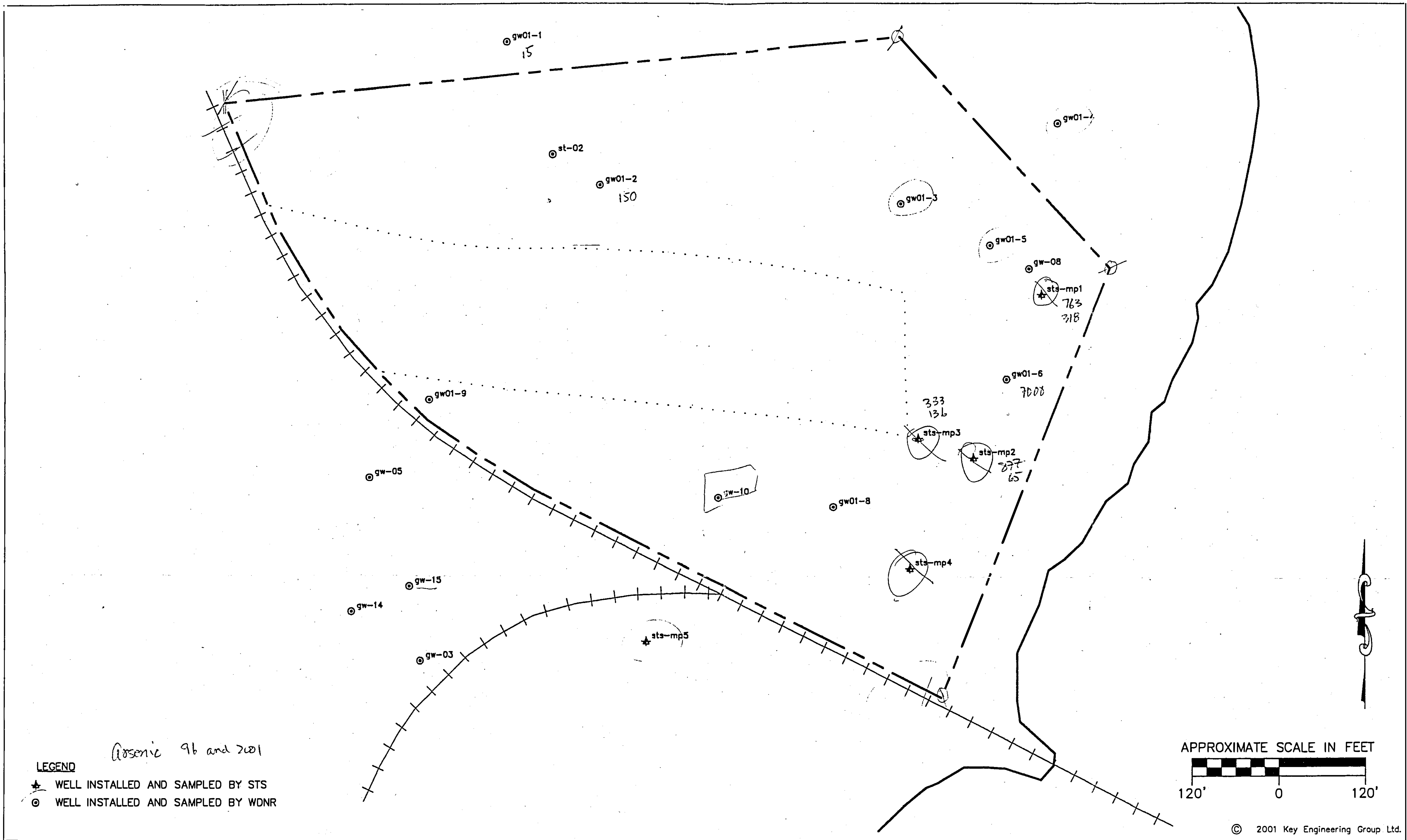

Arsenic 96 and 2001

LEGEND

- ★ WELL INSTALLED AND SAMPLED BY STS
- ⊙ WELL INSTALLED AND SAMPLED BY WDNR

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SIGNED BY DPH	DATE 08/01/01
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FIGURE 5A
PREVIOUS GROUNDWATER SAMPLING LOCATIONS

C. D. BESADNY FISH AND WILDLIFE AREA
KEWAUNEE, WISCONSIN

KEY ENGINEERING GROUP LTD.
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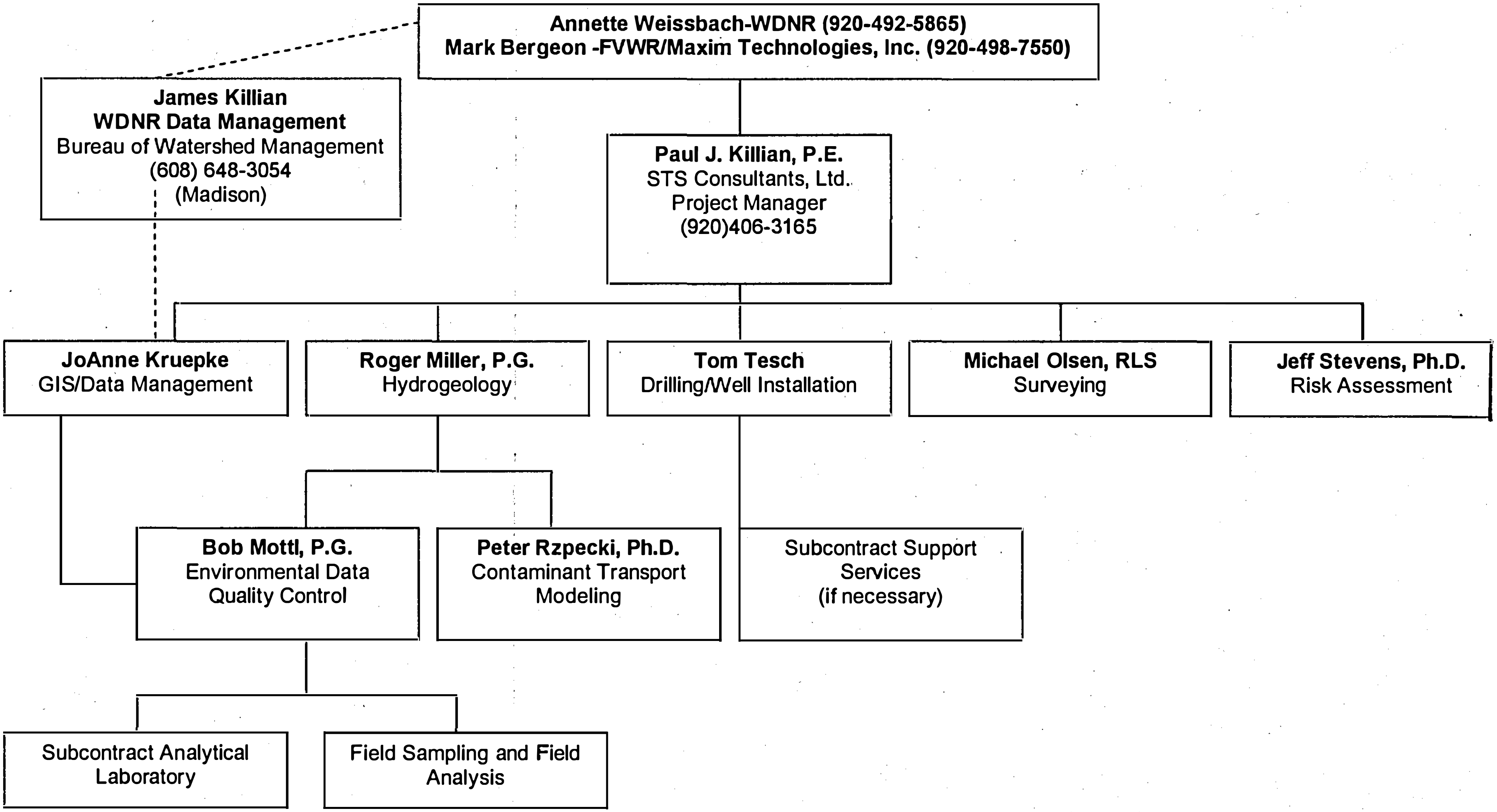
Figure 6

Kewaunee Marsh Site Assessment/Remedial Options Analysis
Kewaunee, Wisconsin
Project Team



27393(ORGCHART.DOC)

Wisconsin Department of Natural Resources
STS Project No. 4-27393

Appendix A

WDNR July 16, 1998, Memo

DATE: July 16, 1998 FILE REF: 3200

TO: Jennifer Huffman - NER/Green Bay

FROM: Tom Janisch - WT/2 Tom Janisch

SUBJECT: Bureau of Watershed Management Comments On the August 14,1997 STS *Final Report, Kewaunee Marsh Arsenic Site, Kewaunee, WI.*

Our comments on the above report are attached. The two main components of the STS report, the GeoTrans groundwater model report and the STS surface water model report, are commented on separately followed by some comments and observations on the site and collected data. A second report will be generated that will incorporate the site data into a screening level ecological risk assessment. A summary of our review comments on the above Final Report are below.

Applicable Surface Water Standards

■ Ambient surface water criteria in NR 105, Wis. Admin. Code, are referenced in the STS report in several places in estimating the impacts of off-site transport of arsenic in the marsh surface waters and groundwater to the Kewaunee River. The NR 105 value used in the report is 50 ug/l based on the human cancer criteria. As of August 1997, the water quality criteria in NR 105 were revised to the following numbers and should be the points of comparison.

Protection of Aquatic Life		Human Cancer Criteria
Acute Toxicity Criteria	Chronic Toxicity Criteria	
339.8 ug/l	148 ug/l	0.185 ug/l

■ Conceptually, the groundwater can be treated as a point source discharge and based on this, effluent limitations applicable to the groundwater can be developed using the above numbers and the groundwater and river discharge volumes. The acute toxicity criteria must be met "end-of-pipe" which is the face of the groundwater plume at the river with no allowance for dilutional mixing in the river as is done in the development of effluent limitations based on the chronic toxicity criteria and human cancer criteria. The controlling arsenic concentration that must be met in the groundwater discharging to the river is 680 ug/l. Outside of any mixing zones, the downstream concentration of arsenic must meet the ambient water quality criteria in the above table.

GeoTrans Groundwater Model

- In the original GeoTrans modeling proposal, it was indicated some sensitivity analyses would be performed to evaluate the sensitivity of the model to changes in the estimated parameter values, such as groundwater velocity and the retardation coefficient. No information on any sensitivity analyses performed was provided in the report. Substitution of the upper end hydraulic conductivity value (1.5 x 10^{-3} cm/s) found in the pump tests performed on the site for the average value (1.7 x 10^{-4} cm/s) would appear to result in significantly reduced time lines when the increasing arsenic concentrations in the groundwater would reach the river. For example, while the GeoTrans model using the average hydraulic conductivity predicts the critical concentration of 680 ug/l will not reach the river for 1,800 years, substitution of the upper end hydraulic conductivity value changes this timeline to 200 years. Based on the characteristics of the organic component in the upper layers of the marsh soils and the presence of the highest arsenic concentrations in these layers, it is believed use of the higher hydraulic conductivity value for the site is appropriate

- Information is not provided in the GeoTrans report on the possible range of retardation coefficients and distribution coefficients that might be applicable in order to analyze what affect the differing values would have on the model output. The limited discussion in the model report seems to focus on the oxyhydroxide/pH/arsenic relationship as controlling the availability for transport in the groundwater in upland soil situations. Literature would appear to indicate that where sediments and wetland soils are involved, other factors may come into play in determining arsenic availability such as redox levels and other factors influencing speciation. These may all be factors that would increase the concentrations of arsenic in the groundwater and thereby decrease the timelines that the increasing concentrations may reach the river compared to the present model outcomes.

- The conclusions of the modeling report were that the arsenic transport rate is extremely slow and that the groundwater concentrations will not peak for 1000's of tears into the future. Based on our comments we would not agree that the transport rate is extremely slow. A rough gauge of the transport rate can be gotten by looking at the current site situation. Based on the groundwater monitoring done by STS at wells MP-1 and MP-2, groundwater concentrations average approximately 650 ug/l of arsenic (close to the critical concentration of 680 ug/l discussed above) 900 feet from the spill site 56 years after the accident. At this rate, the critical concentration plume could reach the river in approximately 11 years. Also, we are not necessarily as interested in knowing when the arsenic concentrations in the groundwater will peak as we are in knowing when the critical concentration of 680 ug/l will reached. Unacceptable arsenic concentrations and loading to the river from the groundwater will occur much sooner than the model predicted maximum concentration of 200 mg/l.

STS Surface Water Model

■ STS has used some conservative assumptions in their model that would tend to overestimate the arsenic in the surface runoff from the site and the downstream concentrations when the arsenic in the surface runoff, groundwater, and river background are mixed during storm events. The STS model is predicting the downstream arsenic concentrations would range from 15.6 to 28.3. Given the flow volumes in the river under a range of conditions compared to the discharge volumes in the groundwater from the site and surface runoff, arsenic from the latter two sources would not appear to contribute significantly to the loading or downstream river arsenic concentrations. The immediate concern is on-site and near-site conditions. Since the ambient water quality criteria based on the human cancer criteria is 0.185 ug/l, the default criteria becomes the background concentration of arsenic in the river. Any source that increases the downriver concentration of arsenic above background levels needs to be looked at.

Other Comments and Observations In Regard to the Site

■ In order to get an idea of the historical off-site transport of arsenic, data related to near-site and downstream levels of arsenic in the sediments and water column were reviewed. Arsenic levels in the marsh soils at the eastern end of the impacted marsh near the river are in the 200 mg/kg range. Generally, arsenic levels in river sediments near the site and downriver are 5 to 13 mg/kg greater than the estimated 4 mg/kg maximum probable background concentration. These levels would appear to indicate that since the original spill, some off-site transport of arsenic to the river has occurred by various means. The elevated concentrations extend up to 56 cm into the river bottom at the most downstream sediment sampling site (3,000 ft below the site). There does not appear to be any trends or differences in elevated concentrations between the near-site and downriver sediment sampling sites. Past sediment sampling data for Kewaunee Harbor does not indicate any elevation of arsenic concentrations above background.

■ No historical water column monitoring for arsenic has taken place in the river. The river sediments essentially serve as a past record of arsenic levels transported in the river in the past. River monitoring was initiated in early 1996. Based on this monitoring, there appeared to be some elevated arsenic concentrations (approximately 100 ug/l) in the river next to the site in early 1996 that were attributed to disturbances on the marsh due to the cap placement. While this may be the case, more long term monitoring would be needed to determine the relationship between conditions on the marsh and river arsenic concentrations. Based on the available sampling, arsenic levels were somewhat elevated associated with the two main slough channels that drain the impacted areas of the marsh. Other than the above, arsenic concentrations in the river near the site and downriver have generally been indistinguishable from background in the available monitoring. But again, more long term monitoring is needed to determine what the relationship is between conditions on the marsh and the river. Some set of conditions has been responsible for off-site transport of arsenic and increased concentrations above background in the river sediments. What these conditions are or how often they are induced is not known.

- Between the period when site investigations began in early 1996 and June of 1997 river levels increased 2.35 feet. This may be related to increased water levels in Lake Michigan. At the increased river levels, the marsh becomes inundated to a greater depth. The increased water levels mean a greater opportunity for interchange between the marsh and the river. The conditions created may result in greater off-site transport of arsenic from the site to the river.

Overall Conclusions

- The overall conclusion is that the timelines for the increasing concentrations of arsenic in the groundwater to reach the river may be significantly shorter than that predicted using the assumptions in the GeoTrans model resulting in critical concentrations reaching the river in decades not centuries as predicted by the model.

- Off-site transport of arsenic from the site to the river has occurred in the past judging by the elevated concentrations in the river sediments. The specific transport route and factors responsible for this transport are not fully known. There is nothing to say that these same factors won't be responsible for continuing off-site transport of arsenic to the river in the future.

- More long term monitoring of the site conditions and arsenic concentrations in the marsh surface waters, groundwater, and river water are needed to understand what site-specific factors may be influencing arsenic availability and off-site transport including more measurements on hydraulic conductivity in various soil segments and locations over the marsh. More groundwater monitoring would include placement of monitoring wells closer to the river.

- More sediment sampling should be conducted in the river to verify the degree and extent of arsenic contamination as indicated by the limited 1997 WDNR sampling.

- In evaluating a sediment remediation project and its ability to practically achieve remedial goals, we ultimately consider and balance a number of factors including sediment quality objectives for the protection of human health, aquatic organisms and wildlife, technical feasibilty of implementing the remedial alternative, net environmental effects, and compliance with applicable laws and regulations. In the case of the contaminated groundwater moving toward the river, a time factor needs to be considered. If reaching the critical concentration of arsenic in the plume at the river will not occur until sometime in the future, do we need to implement some remedy now to prevent any contaminated groundwater from reaching the river or wait until that future date when the critical concentrations is going to begin discharging to the river. Also, the impacts of the in-place pollutants in the soils on-site need to be considered.

■ We would recommend a cross program meeting when the screening level ecological risk assessment has been completed and reviewed to discuss the site status and remediation and/or containment goals for the site.

If you have any questions or would like to discuss the comments, please call me at 608-266-9268.

cc: Duane Schuettpelz - WT/2
Lee Liebenstein - WT/2
Dennis Weisensel - NER/Green Bay
Ron Fassbender - NER/Sturgeon Bay

STS Final Report , Kewaunee Marsh Arsenic Site, Kewaunee, Wisconsin

Applicable Surface Water Standards

The Final Report references in several places that the modeled concentrations of arsenic leaving the site in either the groundwater or the surface waters from rainfall events are not likely to exceed than the NR 105 ambient water quality criteria based on human cancer of 50 ug/l. As of August of 1997, the Human Cancer Criteria (HCC) in NR 105 was revised downward to 0.185 ug/l. Prior to this the 50 ug/l value applied to all stream use classifications. With the revisions in the NR 105 Code based on the Great Lakes Water Quality Initiative, the HCC for Great Lakes tributary streams became 0.185 ug/l. Background concentrations of arsenic in the Kewaunee River upstream of the site range from 1 to 4 ug/l based on past sampling. Since the calculated criteria in the code is less than the background, practicality dictates that the background values be deferred to in discussions of impact where necessary.

The ambient water quality criteria in NR 105 to protect aquatic life is as follows:

	Arsenic as +3 or trivalent form
Acute Toxicity Criteria	339.8 ug/l
Chronic Toxicity Criteria	148 ug/l

Conceptually, the discharge of contaminated groundwater from the site to the Kewaunee River can be treated as a point source discharge i.e. theoretically the discharge can be thought as being discharged from an outfall pipe. Using this approach, water quality based effluent limitations can be calculated using NR 106, Wis. Admin. Code. We have used this concept at other sites involving contaminated groundwater discharges to surface waters.

Development of these conceptual effluent limitations are more appropriate for making comparisons with any modeled or estimated releases in the groundwater from the site. Calculations of effluent limitations takes into account an area of mixing of the river water and the effluent discharge (in this case the groundwater from the site) where the numeric water quality criteria for HCC and chronic toxicity criteria can be exceeded. Outside of this mixing area downstream, the unadjusted ambient water quality criteria must be met. The acute toxicity criteria must be met at the "end-of-pipe" with no adjustments for mixing.

The preliminary effluent limitations for the conceptual discharge of the site groundwater to the river are calculated below.

Effluent Discharge Limits

Acute Toxicity Criteria - 339.8 ug/l x 2 = **679.6 ug/l**

. . . .

Chronic Toxicity Criteria - 148 ug/l x $\frac{1/4\ Q_{7,10} \text{ of Kewaunee R. in cfs}}{\text{Groundwater discharge to River in cfs}}$

148 ug/l x $\frac{1.58 \text{ cfs}}{0.002 \text{ cfs}}$ (Derived from maximum hydraulic conductivity value for site)

116 mg/l

. . . .

Human Cancer Criteria - 0.185 ug/l x $\frac{\text{Annual Mean River Discharge Flow in cfs}}{0.002 \text{ cfs}}$

0.185 ug/l x $\frac{89.2 \text{ cfs}}{0.002 \text{ cfs}}$

44.6 mg/l

. . . .

The above preliminary calculations show that the acute toxicity criteria results in the most stringent effluent limitations and would control the maximum allowable concentration of arsenic in the groundwater discharged to the river at 680 ug/l.

Bureau of Watershed Management Comments on HSI GeoTrans, Inc., Report, "Fate and Transport Modeling of Arsenic at the Kewaunee Marsh" May,1997

While I don't have the expertise to fully assess the use of the BIO1D transport model and the reality of its outcomes, I do have the following comments and observations associated with some components of the model.

1. What is the source of the K_L and A_m parameters values used on page 3-3 of the GeoTrans Report? Similarly, what are the sources of the values for porosity, peat density, and bulk density shown in Table 1 of the Report?

2. Page 2-1 of the Report explains that the derivation of the hydraulic conductivity value used in calculations is based on the results of 6 slug tests for the site. The tests indicated that the permeability of the peat/clay deposits ranged from 6.7 x 10^{-5} to 1.5 x 10^{-3} cm/sec. From these values a geometric mean value of 1.7 x 10^{-4} cm/sec was derived for the hydraulic conductivity based on the four test values after removing the highest and lowest pump test values. It is not explained why the highest and lowest values were eliminated from the test set nor what the remaining four test values actually were that were used to derive the geometric mean value. The question arises of why weren't values that included both the mean and the upper end value for hydraulic conductivity both used in the model to give a range of possible outcomes with regard to timelines for certain arsenic concentrations in the groundwater to reach the river.

Use of the highest hydraulic conductivity of 0.0015 cm/sec translates into a groundwater velocity of 3.29 ft/yr which is almost 9 times faster than the mean velocity (0.37 ft/yr) calculated by GeoTrans and used in the model. The 0.0015 cm/sec hydraulic conductivity translates into values of 4.24 ft/day and 1548.42 ft/year. Based on my March 20, 1997 memo commenting on the preliminary model results, these values are comparable to the hydraulic conductivity found in peat types that are between fibric and hemic peats in terms of decomposition. The upper layers of the marsh soils due to long term seasonal deposition of vegetation are likely in this state of decomposition. Since the greatest levels of arsenic are associated with these upper layers, the arsenic in this zone of greater hydraulic conductivity may be subject to a greater degree of transport than predicted by the model.

It is assumed the use of the higher hydraulic conductivity value will decrease the time lines for the predicted concentrations of arsenic in the groundwater to reach the river. For example, the table below gives the times lines predicted by the GeoTrans model for an increasing range of arsenic concentrations to reach the river based on Figure 8 of their model report and the time lines associated with the upper end measured hydraulic conductivity value. This latter value results in timelines that are in decades rather than centuries. Using appropriate conservative assumptions in a risk assessment, it is appropriate to assume that the actual site groundwater velocities will be somewhere between the mean and maximum value.

Arsenic Concentration in Groundwater at the River (ug/l)	Time for Concentration to reach River From Transport in Site Groundwater (Years)	
	As predicted by GeoTrans using groundwater velocity of 0.37 ft/yr	If the upper end hydraulic conductivity value used which yields a velocity of 3.29 ft/yr
1	200	22.2
10	400	44
50	500	55.6
100	600	66.7
150	700	77.8
700	1800	200
200,000 (model max)	2800	311

An important focus of the model outcome should be to determine at what point the effluent limitation value of 680 ug/l calculated above will reach the river in the groundwater. The GeoTrans model predicts this concentration will be reached at the river in approximately 1,800 years. Using the upper groundwater velocity value of 3.29 ft/yr in the model would mean this concentration could be reached at the river in approximately 200 years or less (see table above). In a worst case scenario, using maximum values (velocity of 3.29 ft/yr and groundwater concentration of 877 ug/l as measured at well MP-2) over the 180 foot distance between the well and the river, the 680 ug/l value could be exceeded in approximately 50 years or less. Another approximation of the possible shortened timeline for increased arsenic concentrations to reach the river can be derived from looking at the current site situation. The average arsenic concentration in the groundwater from STS wells MP-1 and MP-2 over the 1996 monitoring period was 650 ug/l which is close to the critical concentration of 680 ug/l discussed above. It has taken 56 years for the arsenic to reach this concentration in the groundwater 900 feet away from the original spill site. Given the remaining distance between these well sites and the river and assuming the peat soils in this area will have a similar hydraulic conductivity, it will take approximately 11 years for the plume containing the 650 ug/l to reach the river.

3. The model assumes a 0 concentration of arsenic at both the upgradient and downgradient concentration boundaries in the model. The upgradient boundary condition is based on the assumption that arsenic is not entering the model from the upgradient boundary. The measured arsenic concentration in three driven point wells south of the railroad track was 0.9 ug/l. Since the background concentration is approximately 1 ug/l and possibly more, what does this due to the projected time lines of the model. Based on the above table, an arsenic concentration of 1 ug/l was not predicted to reach the river for 200 years based on a starting point of 0. If the concentration is already 1 ug/l or more, does this shorten the time line for the increasing concentrations to reach the river by 200 years e.g. will the 50 ug/l concentration reach the river in 300 years rather than 500 years as predicted by the model? Will this factor along with consideration of the upper end hydraulic conductivity value significantly shorten the timelines predicted by the model for arsenic to reach the river?

4. As a comment on the upgradient concentration of arsenic, it is assumed that STS well MP-6, established to the northwest of the cap, was to serve as the upgradient, unimpacted reference well to establish background concentrations. I don't see it discussed anywhere in the report, but the groundwater in this well is impacted by the site (e.g. the arsenic concentration in the well in the July 1996 sample was 415 ug/l). The well is located approximately 200 ft from the outer isoconcentration line of contaminated soils and almost perpendicular to the groundwater flow direction. It would appear lateral dispersion of groundwater is occurring from the site. How far this lateral dispersion is occurring to the north of the site is unknown. This lateral dispersion could be responsible for elevated levels of arsenic in surface waters and depressions in the marsh to the north of the fenced area at the time of high groundwater table levels. Some lateral dispersion may also be occurring on the south side of the railroad tracks based on the results from WDNR driven point well GW-05 that is located southwest and upgradient of the cap that hadan arsenic concentration in the groundwater of 60 ug/l (filtered) on 5-21-96.

5. The downgradient arsenic concentration of the model is assumed to be 0 at the river. The STS monitoring wells (MP-1, MP-2, and MP-4) are approximately 180 feet to the west of the river. The average arsenic concentrations in the unfiltered samples from these wells during 1996 was 483 ug/l with a maximum concentration of 877 ug/l. No data is available on the arsenic concentration in the groundwater in the area between these wells and the river. For the model, is it assumed that there is no transition in the arsenic concentration in the area from the wells to the river i.e. the front or face of the contaminated plume is assumed to be where the wells are and just beyond the wells the downgradiet concentration of 0 applies from that point to the river? Realistically there probably is a transition in arsenic concentrations in the groundwater between the wells and the river. This transition is assumed to be a decreasing concentration gradient. If this is the case, it may mean arsenic concentrations at increasing levels will be reaching the river on a shorter time scale than the model is predicting.

6. In reviewing Figure 7 of the GeoTrans modeling report which arrays the groundwater monitoring results around each well location, it is noted that a mix of filtered and unfiltered results of arsenic are displayed with some unfiltered results omitted. It is assumed for modeling purposes, the primary focus would be on the unfiltered concentrations. No explanation is given as to why the mix of concentrations and omissions was done. I assume only the arrayed values were used in the model.

7. Page 2-2 of the modeling Report provides a very limited discussion related to arsenic transport properties and limited references to the modeling of arsenic adsorption data in the literature. The discussion of arsenic transport in groundwater mentions only a oxyhydroxide and pH relationship. While the papers cited in the report involving the use of Freundlich and Langmuir isotherms to model arsenic adsorption were not reviewed, by title it appears most of the studies involved upland-type soil. How pertinent is what is discussed and cited to the actual site conditions that may be encountered in the Kewaunee Marsh soils? The marsh soils are hydric, organic soils subject to periodic inundation, saturation and unsaturation in the upper layers, nearly perpetual soil anaerobiosis, and various chemical conditions related to the hydrologic regime of the marsh. Given these conditions, are the oxyhydroxide/pH relationships the only predominating chemical factors controlling arsenic transport in the marsh system? Some perspective on this is contained in the following summary bullets extracted from a limited review of applicable studies in the literature. The references reviewed or pertinent are listed at the end of these comments.

▸ Alterations in the oxidation state of arsenic, as influenced by redox potential and pH, greatly affected its solubility in water. At higher redox levels (200 to 500 mV), arsenic solubility was low and the major part was present as As(V). An alkaline pH, or the reduction of As(V) to As(III), released substantial proportions of arsenic into solution. Under moderately reduced soil conditions (0 to 100 mV), arsenic solubility was controlled by dissolution of iron oxyhydroxides. Arsenic was coprecipitated as As(V) with iron hydroxides and released upon their solubilization. Upon reduction to -200 mV, the soluble arsenic content increased 13-fold as compared to 500 mV.

▸ Numerous studies have dealt with As sorption on specific minerals and soils. Redox potential along with the clay fraction and sesquioxides play a governing role in the speciation and solubility of arsenic in contaminated soils. The transformation of arsenic in the sediment-water system is a function of redox potential and the composition of the sediments, which include mineral colloids, compounds of iron and aluminum, and the organic matter contents of sediments.

▸ Under reducing conditions, arsenite minerals are too soluble to persist in soils but arsenic sulfides were predicted to be stable.

▸ Anaerobic incubation of flooded soils and sediments will increase As concentrations in the pore waters of these materials. A portion of this increased As concentration is As(III) since anaerobic conditions that generally exist in aquatic sediments are conductive to reduction of As(V). The reduced state of As (As^{+3}) has been reported to be 4 - 10 times more soluble in soils than the oxidized state.

- The increase in soluble As as the system traversed from an oxidized to a somewhat reduced environment (+100mV) is attributed to ferric arsenate and other forms of ferric iron which are combined with arsenate, being reduced to the relatively more soluble ferrous form.

- Under oxidized conditions As solubility was low and 87% of the As in solution was present as As(V). Upon reduction, As(III) became the major As species in solution, and As solubility increased. Total As in solution increased approximately 25 times upon reduction of sediment suspensions from 500 to -200 mV.

- More alkaline conditions (pH 7.5) led to greater dissolved As concentrations as compared to more acidic conditions. At a pH of 7.5, As solubility increased significantly under both oxidized and moderately reduced conditions (500, 200, and 0 mV) as compared to more acidic conditions. The large increase of As observed upon reduction was linked to the reductive dissolution of iron oxyhydroxides.

- Examination of sediments in a reservoir show that diagenetic sulfides are important sinks for arsenic in reduced, sulfidic sediments and they control its distribution. During reduction, oxyhydroxides of iron and manganese dissolve and arsenic either precipitates as arsenic sulfides or the arsenic is released to the groundwater system dominantly as As(III). Observed increase in dissolved As upon reduction indicates that As solubility was not limited by the formation of insoluble As sulfide minerals.

- Under reduced conditions (0 to -200mV), As(III) became the major dissolved species. Up to 40% of the total arsenic present in soil became soluble.

- Iron and manganese hydroxides readily absorb As(V) into their matrices. The larger As(III) is probably not as readily absorbed in these structures. This suggests that under reducing pore-water conditions, redox reactions may result in increases in aqueous phase total arsenic concentrations.

- Arsenic complexation by dissolved organic matter prevents adsorptive interactions between the arsenic and solid-phase organic and inorganic materials.

The parameters used in the Modeling Report to define the Langmuir isotherms were determined by manually adjusting the parameter values to obtain the best fit to the arsenic concentrations for the site (page 2-3). The report indicates that there were no paired soil and water sample arsenic concentrations for the site. The soil-sample concentrations were extrapolated to the water sampling locations based on isoconcentration contours developed by STS. Table 1 of the Report is referenced where the water sample arsenic concentrations data and the extrapolated soil concentration points are displayed. It is unclear how this data relates to the parameters used in the Langmuir isotherm of the model. How did the parameters derived from the data base compare to the parameters derived from the literature cited on page 2-2 of the Report? The June 1996 GeoTrans modeling proposal indicated that GeoTrans would perform a literature search to obtain representative estimates of the distribution coefficient (K_d) for arsenic in an organic (marsh) environment. What was the result of this literature search? The modeling proposal also indicated that GeoTrans would use existing concentration data for the site to estimate the in-situ K_d for the marsh/arsenic system. What is this estimated value?

Do the methods of deriving the parameters as discussed above adequately address all the variables made in the bullets above related to potential factors that control arsenic speciation and solubility? It would appear that under the chemical and physical conditions present in the marsh soils that a larger proportion of the arsenic will be present in solution in the sediment interstitial waters compared to more upland soils at a given solid phase arsenic concentration. This in turn would affect the distribution coefficient which in turn would affect the model outputs in terms of timelines and concentrations of arsenic that would be predicted to reach the river boundary at the site.

8. To put some perspective on what the use of the differing groundwater velocities mean to the timelines and loading of arsenic to the river, the following table was constructed. The differing groundwater velocities used were based on the average value used in GeoTrans model and the highest measured velocity as discussed in comment 2 above. To put further perspective on the projected annual arsenic loading to the river from the groundwater under the various scenarios in the table below, the annual background loading of arsenic in the river is 527 lbs/yr based on annual mean discharge flow of 89.2 cfs and an assumed background concentration of arsenic in the river of 3 ug/l.

As discussed above, the critical concentration of arsenic in the groundwater plume at the river based on treating the groundwater discharge conceptually as an effluent discharge is 680 ug/l. Depending on the groundwater velocity used in the model, the time line for this concentration to reach the river is either 1,800 years or 200 years depending on whether the average or maximum hydraulic conductivity value is used. Even with the use of the higher conductivity value, the relative annual percentage contribution of arsenic loading from the site to the river is only 0.5% at the 680 ug/l concentration in the groundwater.

Hydraulic Conductivity		Groundwater Velocity		Volume	Estimated Annual Arsenic Loading to River (lbs/year) Assuming the following Arsenic Concentrations in Groundwater				
ft/day	ft/year	ft/day	ft/year	Gal/year	10 ug/l	50 ug/l	100 ug/l	300 ug/l	700 ug/l
GeoTrans Model Output Using Mean Hydraulic Conductivity									
0.48	176	0.00104	0.37	5.4×10^4	0.005	0.023	0.045	0.135	0.31
Number of Years To Reach River →					400	500	600	1,200	1,800
Substitution of Upper End Hydraulic Conductivity Into Model									
4.24	1,548	0.0090	3.29	4.72×10^5	0.039	0.197	0.39	1.18	2.76
Number of Years To Reach River →					44	56	67	133	200

In calculating the discharge volume of groundwater to the river, it was assumed that the linear and vertical length of the arsenic contaminated plume from the site to the river is 960 ft and 20 ft, respectively. These are values used by STS in their calculations. The 960 ft distance encompasses the northern and central flow paths of the GeoTrans model and a part of the marsh that would include a southern flowpath to the south of the cap that measures 360 ft of the total 960 ft along the river. The above assumes that the model characteristics that apply to the central flow path also apply to the northern and southern flowpaths. It appears from Figure 10 of the GeoTrans model that the concentration points in the groundwater at the river in the northern flowpath reach the river in a shorter period of time compared to the central flowpath. As noted above, the GeoTrans model only modeled the arsenic times lines and transport for the northern and central flowpaths but not the southern flowpath.

The southern flowpath area makes up 20% of the surface area of the site, lies south of the cap, and contains levels of arsenic contamination in the sediments equal to or greater than the contamination in the northern flowpath area included in the model. As noted above, the groundwater from the southern flowpath discharges to the river along a linear distance of 360 ft. The GeoTrans model does not discuss why the timelines and transport for arsenic were not modeled for in the southern flowpath. It is noted that some of the highest concentrations of arsenic in standing surface water over the site where found in this southern flowpath area south of the cap. Based on sampling done in May of 1996, arsenic concentrations were the following in the surface water going in an easterly direction starting in the wedge area between the cap and railroad and ending at the head end of the outlet channel to the river - 8,300 ug/l, 1,400 ug/l, 2,400 ug/l, and 430 ug/l. Also, at the same time the arsenic concentrations in a dug pit (marsh soils dug out and water in pit sampled after a settling period) about the middle of this area had an arsenic concentration of 9,900 ug/l. The relationship of these surface water concentratons to the groundwater is not known, but based on this the southern flowpath could be an area where higher concentrations of arsenic are moving in the groundwater compared to the northern flowpath area.

9. The June 1996 GeoTrans modeling proposal (page 3-7) states that a limited number of sensitivity analyses would be performed to evaluate the sensitivity of the model to changes in the estimated model parameter values, such as groundwater velocity and the retardation coefficient. The sensitivity analysis was to provide a tool for estimating the potential error in the model predicted arsenic concentrations at the river as a result of the estimated range of parameter values. I see nothing in the Appendix B GeoTrans fate and modeling report that indicates that this sensitivity analysis was performed. No sensitivity analyses results are presented.

The importance of looking at the range of hydraulic conductivity values and groundwater velocities is discussed above as it significantly impacts time lines for the estimated concentrations and loading of arsenic to reach the river. It would seem that this type of analyses also needs to be done for the estimates of the distribution coefficient and retardation coefficients. Also, because the decompositional status of the organic matter in the wetland soils varies with depth and the decompositional state impacts the hydraulic conductivity, it would seem that this needs to be looked at more closely. The highest arsenic concentrations in the soils are in the upper segments of the organic soils that have the highest hydraulic conductivity.

Comments on STS Report, "Surface Water Modeling Report" of May 1997

The STS model predicts the amount of runoff and subsequent arsenic contributions to the river from the site under various rainfall event scenarios and saturation conditions in the marsh soils. The outcome of this modeling is integrated with outcomes of the GeoTrans groundwater modeling and consideration of background loading of arsenic concentrations in the river to derive an estimated downstream concentration.
Some comments and observations on the model and outputs:

1. Table 3 of the STS Report indicates that the assumed concentration of arsenic in Subarea 2, which includes the cap, is 0. I'm not sure why a 0 concentration was assumed. While the cap itself is above water, there is an area of Subarea 2 between the cap and the fence of approximately one acre that is subject to inundation.
It appears it would have been appropriate to extrapolate the surface water concentrations from Subareas 1 and 3 and apply them to Subarea 2 for use in the calculations.

2. In Table 3 of the Report it is noted that some WDNR surface water is data is used for model input. For Subarea 3 it is noted that one WDNR data point was used. This sample (SW08) was collected in Sept. 1996 at the mouth of a channel off the marsh. Because this sample was taken at the mouth it is influenced by the river and is probably not representative of the surface water quality on the marsh. However, four WDNR surface water samples were collected across Subarea 3 in May of 1996 at the same time the samples were collected that are used in STS Table 3 for the northern or Subarea 1. The results from the four samples were provided in various reports. The results for the four samples were 8,300, 1,400, 2,400, and 430 ug/l. Use of these values along with the 19,100 value would yield an average concentration (6,326 ug/l) which is actually less less than the average concentration used by STS (9552 ug/l) for the model. Also, the STS value of 19,100 ug/l was collected in the marsh surface waters prior to capping. The higher arsenic concentrations in the surface soils of the"dead" areas prior to capping probably directly influenced this level and it may not be achieved in the surface waters after capping.

It is noted that in Tables 4A and 4B of the STS Surface Water Modeling Report that under scenarios where either the maximum or average concentrations of arsenic are in the runoff from the subareas under the various rainfall events and SCS Runoff Curve Numbers (83 to 95), the concentration of arsenic in the runoff waters is estimated to range from 2,210 to 4,824 ug/l. This estimated range of values exceeds the ambient water quality criteria discussed above meaning aquatic life on the marsh exposed to this water would be at impacted.

However, attributing the measured concentration of arsenic in the standing surface waters of the marsh to the levels in the runoff from the marsh due to precipitation events probably results in an overly conservative estimate of the concentration in the runoff from the marsh to the river. Rainfall events would likely have a dilutional effect on the surface water concentration prior to runoff. Also depending on river levels at the time of the precipitation event, high flows in the river could overflow on to the marsh, further diluting concentrations of arsenic in the surface waters of the marsh. Also as STS notes in their Section 2 Report conclusions, runoff from the surrounding uplands to the marsh could also be a source of dilution water (see discussion below where the arsenic concentration in only the surface water that may reach the river is discussed).

3. Another scenario for a source of arsenic to the river is from arsenic in surface water on the marsh draining to the river that would not necessarily related to a precipitation event. To get a rough estimate of this, the surface water data that was collected in June of 1997 by WDNR can be used. Surface water samples and water depth measurements were collected at eight locations in the marsh from areas around the cap. The resulting average arsenic concentration and loading to the river that is estimated based on this data is calculated in the following table.

	SUBAREA		
	1	2	3
Acres	6.50	0.93	3.10
Square Feet	283,140	40,511	135,036
Ave. Water Depth (ft)	0.36	0.88	0.79
Cubic Feet	101,930	38,333	106,678
Gallons	762,436	286,731	797,951
Total Gallons From 3 Subareas	1,847,118	—	—
Ave. As Concentration (ug/l) In Surface Water Sample from Subarea	553 (n=3)	120 (n=1)	173 (n=2
Pounds As/Subarea Water	3.52	0.29	1.15
Total lbs Arsenic	4.96	—	—
Ave. As Concentration In Combined Subarea Water	0.322 ug/l	—	—

Using the estimated average surface water concentration of arsenic on the marsh from above with some of the other parameters in regard to the river and the groundwater as shown in the following table, a non-precipitation event related downstream arsenic concentration can be estimated. The following assumes all of the standing surface water on the marsh will drain to the river over a seven day period. During the June 1997 sampling event, the surface waters of the marsh were directly connected to the marsh. Due to the uneven topography of the marsh surface, the natural berms paralleling the river, and evapotranspiration during the growing season, it is probably overly conservative to assume that all of the standing water on the marsh will drain to the river. River levels would also have to drop sufficiently for the marsh to drain. The table below shows that for the range of groundwater concentrations used they would contribute minimally to any elevated concentrations of arsenic in downstream waters. The significant contributor would be from drainage events from the surface waters off the marsh to the river. How many times, the duration of these drainage events, and the concentration of arsenic in the drained surface waters would determine their contribution to downstream arsenic concentrations. In the assumptions used below, the drainage event would appear to have only have a minimal short term effect on the background concentrations.

Water Source	A. Flow - cfs	B. Ave. Arsenic Concentration - ug/l	Pounds Arsenic/ year
River	89.2 Annual Mean (21,042 x 10^6 gal / year)	3 Background	527
Surface Water Drainage 1 time / yr over 7 days	0.41 see table above (1.847 x 10^6 gal / year)	322	4.96
Groundwater	0.002 Max. Hydraulic Conductivity (0.472 gal / year)	Concentration at River	
		10	0.039
		100	0.39
		300	1.18
		700	2.76
Downstream Kewaunee R. Arsenic Concentration	<u>Total A x B.</u> Total A. (89.61 cfs) (21,042 x 10^6 gal / year)	3.03 ug/l Varying groundwater does not change downstream arsenic concentrations to any degree.	

4. A conservative component of STSs calculations for estimating the downstream Kewaunee River arsenic concentrations is using the peak concentration of 200 mg/l that the GeoTrans groundwater model predicts will be present in groundwater at the river at some date in the future. It may have been useful to have used some more near term groundwater model-estimated concentrations of arsenic in the calculation of downstream concentrations from the combined sources (river, marsh runoff, and groundwater). Also, the hydraulic conductivity component of the groundwater could have been varied as discussed above in the comments on the groundwater model to get an idea of how this may be estimated to influence the downstream arsenic concentrations from the combined sources.

It is noted that in the STS calculations that under the maximum and average arsenic concentrations from the subarea runoff scenarios, the downriver arsenic concentrations from the combined sources is 28.3 and 15.6 ug/l. respectively. STSs conclusion was that since these values are less than the 50 ug/l Human Cancer Criteria in NR 105, this surface water standard would not be exceeded even using a number of conservative assumptions. However as noted in the initial comment above, the surface water criteria based on Human Cancer Criteria in NR 105 were revised in August 1997 from 50 to 0.185 ug/l for the Great Lakes tributaries. Based on the calculated value of 0.185 ug/l being less than background concentration in the river (estimated to be between 2 - 4 ug/l), the background concentration is essentially the default criteria. The downstream estimated concentrations of 28.3 and 15.6 ug/l that STS calculated are greater than the default background criteria.

Other Comments And Observations In Regard to the Site

Past Off-Site Transport of Arsenic

Sediments

To get a handle of what amount of arsenic may have left the site in the past from the various transport mechanisms, we can look at the arsenic concentrations in the marsh soils near the river, in the river sediments near the marsh, and downstream of the site to the harbor. The sediment samples we have collected in these locations that have been reported on in past memos are summarized in the table below.

Background		ST-05		SO-12		SO-16		SO-17		SO-18		Kewaunee Harbor
Taken in upstream wetlands and river mg/kg		Marsh soils 10 ft S. of South Channel, 20 ft E. of fence		On river bank 20 ft below juncture of south channel slough mg/kg		In river 40 ft off of site, 100 ft below South Channel mg/kg		1,000 ft downstream of site mg/kg		3,300 ft downstream of site mg/kg		Past ACOE sampling for dredging projects in harbor has not found As concentrations > background
0-15 cm	2 - 4	0-15 cm	67	0-16 cm	12.2	0-20 cm	17	0-20 cm	6	0-43 cm	11	
				16-32 cm	9.4	20-49.5 cm	13	20-60 cm	<3	43-56 cm	15	
				33-47 cm	4.2			60-69 cm	<3	55-83 cm	4	

Generally, arsenic levels on the marsh just to the west of the chain link fence that parallels the river are in the 200 mg/kg range (One STS sediment core in this area at site B-10 had 897 mg/kg at 0-2 ft; 290 mg/kg at 2-4 ft; and 85.6 at 4-5 ft.). This area appears to be in the extent of the 200 mg/kg isoconcentration line radiating out from the main area of contamination to the west that is now capped. Sample ST-05 in the above table is about the only sample available to characterize the marsh soils between the chain link fence and the river. The concentration of 67 mg/kg may represent an outer isoconcentration line radiating out from the main area of contamination to the west.

The elevated arsenic concentrations associated with the eastern end of the impacted area are not reflected in the river sediments near the site or downriver from the site. If 4 mg/kg is taken as the maximum probable background concentration in river sediments, it would appear that off-site transport of arsenic has increased the levels in river sediments only from 5 to 13 mg/kg above background (the implications of the elevated levels of background in terms of ecological impacts and effects will be elaborated on in the followup biological assessment). The depth of elevated levels of arsenic in the sediments varies with the sampling location. At sample site SO-17, arsenic concentrations are slightly above background in the 0-20 cm segment compared to S0-18 where arsenic is elevated in the 0-56 cm segment. In the surface strata impacted, there does not seem to be a lot of difference in arsenic concentrations when the upstream or and downstream sample sites are compared. The depositional rate of sediments in the Kewaunee River is not known. It can be conjectured that given the extent of arsenic contamination at river site SO-18 down to 56 cm into the sediment and that the spill event on the marsh occurred approximately 56 years ago, that the depositional rate for sediments in the river was approximately 1 cm per year.

A review of ACOE sampling data from dredging projects in the Kewaunee Harbor from the years 1974, 1982, and 1986 and a WDNR study in Great Lakes Harbors in 1990 indicates that arsenic levels in the harbor sediments were at background levels. It would appear to indicate from the available sampling that the moderately elevated levels of arsenic found in the river channel sediments upstream of the harbor have not been transported to the harbor area.

Information on particle size analysis of the river and water depths and soft sediment depths in transects across the river are in the tables below to put some perspective on the river characteristics at and below the site. The three sites involved below for particle size analysis are the three sites above where arsenic analysis was done. The three transects across the river where done in relationship to these three sample sites. Soft sediment depths were determined with 1 3/4 inch diameter pole marked in 0.1 ft. increments. The pole was pushed into the sediments to the point of refusal and the penetration depth recorded

Sample Transect	Depth	Sediment and Water Depths in Transects Across River (feet)				
		25 ' from west bank	1/3	Middle	2/3	25 ' from east bank
T-1 (SO-16)	Soft Sediments	2.2	2.4	5.0	3.8	3.1
	Water	3.5	6.2	9.5	6.2	3.5
T-2 (SO-17)	Soft Sediments	2.6	3.8	3.5	3.0	2.6
	Water	3.8	5.5	10.5	6.6	3.6
T-3 (SO-18)	Soft Sediments	2.3	2.9	5.5	4.1	1.9
	Water	5.3	8.5	10.5	4.7	4.2

Particle Size Analysis of River Sediment Samples					
Sample Site	Sediment Depth (cm)	% Sand	% Silt	% Clay	Soil Texture
SO-16A	0-20	7	61	31	Slty clay loam
SO-16B	20-49.5	31	48	21	Loam
SO-17A	0-20	54	31	15	Sandy loan
SO-17B	20-60	79	13	8	Loamy sand
SO-17C	60-69	22	56	22	Silt loam
SO-18A	0-20	13	66	21	Silt loam
SO-18B	20-40	18	58	24	Silt loam
SO-18C	40-60	71	18	11	Sandy loam
SO-18D	60-83	24	51	25	Silt loam

Based on the particle size analysis, most of the segments analyzed were dominated by fine-size particles (silts + clays) with the exception of SO-17B and SO-18C which were predominated by sand sized particles.

The bottom line is that various transport mechanisms have been responsible over the years for off-site transport of arsenic from the original spill site on the marsh to deposition and moderate elevation of the arsenic in near-site and downriver sediments from 5 to 13 mg/kg above background. This is based on a limited amount of sampling. Additional sampling would be needed to verify this degree and extent of river contamination.

Surface Water

Arsenic concentrations in surface waters of the precapping dead areas of the marsh were recorded at an astoundingly high level of 920 mg/l based on the STS November 1994 samples. Other sample concentrations ranged from 5.66 to 148 mg/l.

The quarterly river monitoring performed by STS at the site for April, May, and June of 1996 showed elevated levels of arsenic in the water of 118, 108, and 50 ug/l, respectively compared to a background concentration levels of 1 to 3 ug/l. Cap construction and placement took place in February of that year. STS indicates that they believe these elevated concentrations are due to increased surface water transport of arsenic impacted sediments from portions of the area that where vegetation was removed and bottom soils disturbed due to the construction. This may be a partial explanation. WDNR monitoring of surface water quality on the marsh in April and May after the cap construction showed elevated arsenic concentrations. As discussed above, arsenic concentrations in a west to east transect across the marsh south of the cap yielded concentrations of arsenic at 8,300, 1,400, 2,400, and 430 ug/l. Since the marsh vegetation provides a settling and filtering function, some portion of the arsenic being measured either on the marsh or in the river may be in a dissolved state and not associated with suspended solids. Some surface water sampling in 1997 in the area of the 1996 transect showed arsenic levels of 86 and 260 ug/l. These levels appear to show a decrease in surface water concentrations of arsenic in this area. More long term sampling would be needed to determine if placement of the cap had a short term impact on surface water concentrations of arsenic or other mechanisms are involved due to seasonal hydrologies and chemistries.

Arsenic concentrations at the head end of the two slough channels (north and south) just to the west of the chain link fence that parallels the river had arsenic concentrations in them of 76 ug/l (North Channel) and 430 ug/l (South Channel) in the 1996 monitoring.

In 1997, we collected samples from the upper end of both slough channels at the fence and samples from the mouth of the channels at the river. The arsenic concentrations in the paired upstream/downstream site in the north and south channel were 24/7 and 9/2 ug/l, respectively. Observations during the above 1997 sampling indicated that water flow direction varied by going from the river toward the marsh up the slough channels and then reversing itself by going from the marsh towards the river over the period of observation.

The bottom line is that other than the STS finding of elevated concentrations of arsenic in river water next to the site in early 1996, other later samples at the site and downriver, found normal background concentrations of 1 - 3 ug/l. This is based on limited sampling. More long term sampling in the river near the site would be needed to determine what yearly and seasonal patterns may exist for off-site transport from the marsh to the river. This may be pertinent in lieu of a pattern of increasing water levels in the river based on gauge readings first taken in March of 1996 and extending to June of 1997. In this period, river levels gradually increased 2.35 feet. I do not have any river level readings for the period from June of 1997 to the present so I don't know if river levels stabilized at the high levels, continued increasing, or dropped. River water levels are important because at higher levels more interchange will take place between the marsh and the river because of flooded conditions on the marsh. More interchange means the greater opportunity for either arsenic in the dissolved or suspended state to be transported off the marsh to the river. In June of 1997 when the river gauge reading was recorded at 4.35, the cattail areas of the marsh were flooded with 8 to 10 inches of water. Carp , who can access the marsh by going up the slough channels underneath the chain link fence, were seen or heard splashing

on the marsh in areas around the eastern end of the cap. Their roiling activities may be responsible for resuspending arsenic contaminated sediments. Stagnant, standing surface waters over the marsh may become anaerobic which could cause transformation of arsenic into the more soluble, more toxic trivalent form.
It should be noted that based on the STS map establishing the isoconcentration lines for arsenic in marsh sediments that there are areas of arsenic concentration in surface sediments of up to 2,000 mg/kg but mostly up to 1,000 mg/kg that are not covered by the cap. These areas are subject to the carp activities and chemical transformations discussed above.

Site Distribution of Arsenic

Based on the marsh soil sampling conducted in 1994, STS constructed an isoconcentration map for arsenic in the 0 to 2 ft profile. The resulting map shows two concentric areas of elevated arsenic concentration. One area is next to the railroad tracks at what is assumed to be the location where the hopper cars tipped and spilled their loads of arsenic granules. The center of the second area of concentration is approximately 450 ft to the east toward the river. The exact transport mechanisms responsible for the mass movement of arsenic between the two sites will probably never be known. Attempts at doing so should possibly be attempted in order to determine if the causative conditions are uncommon or could possibly reoccur in the marsh.

References

Agget, J. and M.R. Kriegman. 1988. The Extent of Formation of Arsenic(III) in Sediment Interstitial Waters and its Release in Lake Ohakuri. Wat. Res 4:407-411.

Anderson, L.D., and K.W. Bruland. 1991. Biogeochemistry of Arsenic in Natural Waters: The Importance of Methylated Species. Environ. Sci. Technol. 25:420-426.

Brannon, J.M. and W.H. Patrick, Jr. 1987. Fixation, Transformation, and Mobilization of Arsenic in Sediments. Envir. Sci. Technol. 21:450-459.

Deuel, L.E. and A.R. Swoboda. 1972. Arsenic Solubility in a Reduced Environment. Soil Sci. Soc. Amer. Proc. 36:276-278.

Holm, T.R., M.A. Anderson, R.R. Stanforth, and D.G. Iverson. 1980. The Influence of Adsorption on the Rates of Microbial Degradation of Arsenic Species in Sediments. Limnol. Oceanogr. 25: 23-30.

Masscheleyn, P.H., R.D. Delaune, and W.H. Patrick, Jr. 1991. Effect Of Redox Potential and pH on Arsenic Speciation and Solubility in a Contaminated Soil. Environ. Sci. Technol. 25:1414-1419.

Mok, W. and C.M. Wal. 1990. Distribution and Mobilization of Arsenic and Antimony Species in the Coeur D'Alene River, Idaho. Environ. Sci. Technol. 24:102-108.

Moore, J.N., W.H. Ficklin, and C. Johns.1988. Partitioning of Arsenic and Metals in Reducing Sulfidic Sediments.Environ. Sci. Technol. 22:432-437.

Kobayashi, S. and G. Fred Lee. 1978. Accumulation in Sediments of Lakes Treated with Sodium Arsenite. Environ. Sci. Technol. 10:1195-1200.

Pierce, M.L. and C.B. Moore. 1982. Adsorption of Arsenite and Arsenate on Amorphous Iron Hydroxide. Water Res. 16:1247-1253.

Wisconsin Department of Natural Resources
STS Project No. 4-27393

Appendix B

Sampling and Analysis Plan

STS CONSULTANTS, LTD.

Sampling and Analysis Plan

C.D. Besadny Fish and Wildlife Area
Kewaunee Marsh Arsenic Area
Kewaunee, Wisconsin

STS Project No. 4-27393

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1.0 INTRODUCTION

This Sampling and Analysis Plan (SAP) identifies the sampling procedures that will be implemented during the site investigation. This SAP includes sampling objectives, scope, procedures, equipment, quality control (QC), and documentation, as well as management procedures for investigation derived waste.

2.0 FIELD SAMPLING

This section details the field sampling scope, equipment, procedures, decontamination, QC, and documentation protocols.

2.1 Soil/Sediment Investigation

2.1.1 Scope

The scope of the soil/sediment investigation is detailed in the Site Investigation Work Plan. Sample collection and analysis will be consistent with procedures identified in the Wisconsin Administrative Code Chapter NR 700 series of regulations.

2.1.2 Equipment

Equipment and materials to be used during soil investigation will include:

- Drill rig with capability of boring with 4 1/4-inch inner diameter (ID) hollow stem augers (HSAs).
- Piston sampler.
- Field notes form.
- Soil boring logs.
- Stainless steel bowls and spoons.
- Stainless steel trowel or shovel.
- Tap water, distilled water, Alconox®.
- Steam cleaner.
- Sample jars and preservatives.
- Munsell Soil Color Chart.
- Stakes for marking sample locations.
- Chain of Custody forms.
- Sample labels.
- Indelible marking pen.
- Coolers and ice.
- Camera and film.

2.1.3 Procedures

Soil borings will be advanced both with a drilling rig using HSAs, if possible, or with hand drilling equipment. Soil samples from drill rig sampling will be collected at 2 1/2-foot intervals with a 2-foot split-spoon sampler when adequate recovery is possible using this technique. These soil samples will be collected in accordance with American Society of Testing Materials (ASTM) D 1586, "Standard Test Method for Penetration Test and Split-Barrel Sampling of Soils." In some site soils, particularly in peat deposits near the surface, a piston sampler may be required to obtain samples of the soft, peaty soil. Surface soil/sediment samples will be collected by hand, using a stainless steel trowel or shovel. Immediately after sample collection and description, soil samples selected for laboratory analysis will be placed in a stainless steel bowl and mixed with a stainless steel spoon. An aliquot of the homogenized soil sample will be placed in the appropriate sample container. For soil and sediment arsenic analysis, no preservative is required. In addition to the sample for chemical analysis, a separate aliquot from the same sample will be packaged for water content testing. The soil samples will then be placed in a cooler with ice.

In addition to analysis for arsenic, several samples will be collected for processing in the laboratory to determine paired pore water-soil solid arsenic concentrations. These samples will be collected in a manner similar to that described above, but it is important that there be no headspace in the sample jar. Before these samples are collected, packaged, and shipped to the laboratory, it is very important that communication with the laboratory be maintained, so that the laboratory knows to expect the samples and will process them accordingly.

The laboratory will separate pore water from soil/sediment solids by centrifuge using Standard Methods for the Examination of Water and Wastewater (American Public Health Association, 2001) Proposed Method 8080C, “Extraction of Sediment Pore Water.”

A boring log will be maintained for each boring location. Boring logs will include the Standard Penetration Test (spt) blow counts; depth and thickness of each soil stratum; a description of each stratum (including Munsell color); Unified Soil Classification System classification; soil moisture, plasticity, density, or consistency; olfactory observations; sample depth interval and recovery; and the depth at which groundwater is first encountered. For surface soil/sediment samples, soil descriptions will be documented on the field notes form.

2.1.4 Decontamination

The down-hole drilling equipment will be decontaminated prior to mobilization and between boring locations using a high pressure steam cleaner. Decontamination water will be supplied from a potable water source. The split-spoon soil sampler, soil mixing bowls, and spoons will be decontaminated between each use with tap water and detergent (Alconox®) wash, tap water rinse, and a distilled water rinse. Decontamination water will not be contained.

2.1.5 Quality Control

Sampling and analytical QC will take the form of duplicate samples in which two sample aliquots, in separate containers are submitted to the laboratory for analysis. QC of both the field sampling procedures and the analytical procedures will be measured by the degree of agreement of the analytical results of the two samples. These analytical samples will be collected at a rate of one duplicate per twenty soil samples.

In addition to the duplicate sampling, field rinsate blanks will be collected to measure the effectiveness of field decontamination between sample intervals. After decontamination of the sampling equipment (split-spoon, mixing bowl, and mixing spoon), deionized water will be run over the equipment and collected into sample bottles. These samples will be preserved as prescribed by the analytical method and analyzed for arsenic. Rinsate samples will be collected at a rate of one rinsate sample per day of field sampling.

As a QC measure on the laboratory's procedure in which pore water and soil/sediment solids are separated, the laboratory will perform analyses of pore water on both filtered and unfiltered aliquots of the pore water removed from three of the sediment samples. The laboratory must follow the methods, instrumentation, and QC requirements of the United States Environmental Protection Agency (USEPA) Contract Laboratory Program (CLP). The laboratory need not be registered under CLP, but it must meet CLP requirements. The laboratory must be currently certified according to requirement of NR 149 (Laboratory Certification) Wisconsin Administrative Code. STS has selected U.S. Filter/Enviroscan Services of Rothschild, Wisconsin, as the analytical laboratory. Analysis of groundwater samples will follow the Parameters and Methods for Sediment Analyses (WDNR Table 1), to provide consistency in evaluation and reporting analytical results. The Enviroscan 2002 Standard of Practice (SOP) specifies the usual analyses provided by the laboratory. STS will have the laboratory modify the analytical method to coincide with WDNR Table 1 methods.

Soil investigation field documentation will undergo a QC review during and after the completion of field activities. Upon completion of the field program, documentation will be relinquished to the Project Manager.

2.1.6 Documentation

Soil sampling documentation will consist of the following:

- Field Notes Form.
- Soil Boring Log Information Form (WDNR Form 4400-122).
- Well/Drillhole/Borehole Abandonment Form (WDNR Form 3300-5B).
- Photographs.

2.2 Surface Water Sampling

2.2.1 Scope

The scope of the surface water sampling task is detailed in Section 3.2 of the Site Investigation Work Plan. The surface water sampling locations are depicted in Figure 4 of the Site Investigation Work Plan.

2.2.2 Equipment

Equipment that will be used to collect surface water samples is as follows:

- Sample containers and preservatives, supplied by the laboratory.
- Tube-type drum sampler, capable of collecting water from a column approximately 3 feet deep.
- Clean pre-filtration jugs.
- Peristaltic pump and tubing.
- 0.4-um filters.
- Field notes form.
- Down-hole water quality probe which measures pH, temperature, dissolved oxygen, conductivity, and redox potential (Eh).
- Personal protective equipment.

- Decontamination supplies.
- Stakes for marking sample locations.
- Camera and film.

2.2.3 Procedures

Surface water samples will be collected both from areas of standing water in the marsh and from the banks of the Kewaunee River and tributary sloughs in the study area. During collection activities at the river and sloughs, the buddy system will be employed for safety purposes.

Before samples are collected, water quality will be measured at the location, using the down-hole water quality probe. The probe will be inserted into the water at the area to be sampled. Readings for pH, temperature, conductivity, dissolved oxygen, and redox potential will be recorded.

Surface water samples collected from "casual" standing water in the marsh will be collected by dipping the pre-filtration jug directly into the surface water, and allowing it to fill by gravity. Samples will be field-filtered using a peristaltic pump placed in the sample container and preserved. Samples collected from drainage sloughs and the Kewaunee River will be collected using a tube-type drum sampler ("drum thief coliwasa"). The advantage of the drum thief is that it can collect a sample from a length water column, not just from the surface or a particular discrete depth. These samples will also be transferred from the drum sampler into the pre-filtration jug to be filtered and preserved.

2.2.4 Decontamination

Equipment expected to require decontamination for this task is the down-hole water quality probe and the peristaltic pump tubing. The pre-filtration jugs, filters, and drum sampler tubes are designed to be disposable. The probe is decontaminated by rinsing it in tap water, then rinsing with distilled water. The tubing for the peristaltic pump will be decontaminated by running approximately one gallon of distilled water through the pump between sample locations. Personal protective equipment, namely gloves, will be changed between surface water sampling locations to avoid cross-contamination.

2.2.5 Quality Control

Sampling and analytical QC will include duplicate samples in which two sample aliquots (in separate containers) are submitted to the laboratory for analysis. QC of both the field sampling procedures and the analytical procedures will be measured by the degree of agreement of the analytical results of the two samples. These analytical samples will be collected at a rate of one duplicate per twenty samples per analyte. In addition to the duplicate samples, a field rinsate blank will be collected from a drum sampler tube, pre-filtration jug, and peristaltic pump tubing. This field blank will be collected using a clean, unused tube and jug.

Surface water investigation field documentation will undergo a QC review during and after the completion of field activities. Upon completion of the field program, documentation will be relinquished to the Project Manager.

2.2.6 Documentation

Surface water sampling documentation will consist of the following:

- Field Notes Form.
- Photographs.
- Calibration records for the water quality probe.

Analytical procedures will be measured by the degree of agreement of the analytical results of the two samples. These analytical samples will be collected at a rate of one duplicate per twenty samples per analyte. In addition to the duplicate samples, a field rinsate blank will be collected of a drum sampler tube, pre-filtration jug, and peristaltic pump tubing. This field blank will be collected using a clean, unused tube and jug.

Surface water investigation field documentation will undergo a QC review during and after the completion of field activities. Upon completion of the field program, documentation will be relinquished to the Project Manager.

2.3 Groundwater Monitoring Well Installation

2.3.1 Scope

The scope of the surface water sampling task is detailed in the Site Investigation Work Plan.

2.3.2 Equipment

Equipment that will be used to install and develop the monitoring wells are as follows:

- Drill rig with capability of boring with 4 1/4-inch ID HSAs.
- Fiberglass tape of adequate length to reach the bottom of the well.
- Field notes form.
- Soil boring logs, well construction forms, and well development forms.
- Tap water, distilled water, and Alconox®.
- Generator and steam cleaner.
- Brush, buckets, and plastic.
- 2-inch, flush-threaded 0.010-inch slot, and Schedule 40 polyvinyl chloride (PVC) well screens (5 and 10 feet long).
- Locking well caps.
- High solids bentonite grout.
- Bentonite pellets.
- Washed, well sorted silica sand, appropriate size grades for filter pack and fine sand filter pack seal.
- Flush-mount protective casings.
- Keyed-alike locks.
- Bailer.
- Electric water level indicator.
- Camera and film.

Note: The drill rig can only be used if soil will allow adequate support of the drill rig. If adequate support is not available in the area of the proposed well locations or to access the proposed well location, hand drilling methods will be used.

2.3.3 Procedures

The groundwater monitoring well soil borings will be advanced with a drilling rig using HSAs. Soil samples will be collected at 2 1/2-foot intervals with a 2-foot split-spoon sampler. Soil sampling will be in accordance with the procedures detailed in Section 2.1.

The groundwater monitoring wells will be constructed in general accordance with NR 141. The groundwater monitoring wells will be constructed of Schedule 40 PVC. The groundwater monitoring wells will have a 5- or 10-foot length, 0.010-inch, machine-slotted, PVC well screen.

The annular space seal, filter pack, filter pack seal, ground surface seal, and protective cover materials will meet the NR 141 specifications. The annular space between the borehole and the well screen will be backfilled with a clean, washed, sand filter pack to a depth of 1/2-foot above the top of the well screen. Placement of the filter pack will be followed by the installation of approximately 1/2-foot of fine filter sand. A 1-foot bentonite pellet seal will be placed directly above the sand pack where conventional drilling techniques can be utilized. In hand drilling situations, Johnson pre-assembled screens will be inserted in the boreholes at appropriate depths by pushing the well point from the surface.

A protective casing will be placed over the PVC pipe. The well casing and the protective cover will have a "stickup" of approximately 2 to 3 feet above the ground surface.

Each well will be developed to remove sediment produced by construction and to clear out screen slots. The wells will be developed in accordance with NR 141. The wells will be developed utilizing a bailer or pump. For wells that cannot be purged dry, the wells will first be surged and purged. Following well surging and purging, the well will be pumped or bailed until a minimum of ten well volumes is removed or until the well produces sediment free water. For wells that can be purged dry, development will consist of slowly purging the well dry. To measure the well volume, the depth to the static water level and to the bottom of the well will be measured from the survey reference point (the highest point on the well casing). The water level indicator will be decontaminated between measurements.

By using the depth to water, well depth, and well radius, the volume of standing water in the well (well volume) will be calculated using the following equation:

$$V = 3.14\, r^2 \times h \times 7.48$$

V = well volume (gallons)
r = well radius (feet)
h = water height (feet)

2.3.4 Decontamination

The down-hole drilling equipment will be decontaminated prior to mobilization and between boring locations using a high pressure steam cleaner. The split-spoon soil sampler and development equipment will be decontaminated between each use. Decontamination will consist of a tap water and detergent (Alconox®) wash, tap water rinse, and a distilled water rinse. Decontamination water will not be contained.

2.3.5 Quality Control

Groundwater monitoring well installation documentation will undergo a QC review after the completion of field activities. Original field forms and photo documentation will be stored in a secure area until completion of the field program. Upon completion of the field program, documentation will be relinquished to the Project Manager.

2.3.6 Documentation

The drilling and groundwater monitoring well construction and development will be documented in the field by a contractor field scientist using the following field forms:

- Field Notes Form.
- Calibration records for the water quality probe.
- Soil Boring Log Information Form (WDNR Form 4400-122).
- Monitoring Well Construction Form (WDNR Form 4400-113A).
- Monitoring Well Development Form (WDNR Form 4400-113B).
- Well Information Form (WDNR Form 4400-89).

2.4 Groundwater Sampling

2.4.1 Scope

Each monitoring well will be sampled and analyzed for parameters documented in the Site Investigation Work Plan. Sample collection and analyses will be consistent with procedures identified in the Wisconsin Administrative Code NR 700 series of regulations.

2.4.2 Equipment

Equipment used for groundwater sampling include:

- Disposable or dedicated Teflon or polyethylene bailer.
- Electric water level indicator.
- Down-hole water quality probe, which measures pH, temperature, dissolved oxygen, conductivity, and redoxpotential (Eh).
- Pre-filtration jugs.
- Peristaltic pump and tubing.
- 0.4-um filters.
- Field log book and field forms/logs.
- Tap water, distilled water, and Alconox®.
- 5-gallon pails.
- Sample containers and preservatives.
- Chain of Custody forms.
- Sample labels.
- Indelible marking pen.
- Coolers and ice.
- Nylon rope.

2.4.3 Procedures

To prevent potential contamination during transportation to the site, sampling equipment will be stored in clean plastic containers or wrapped with aluminum foil. A new sheet of clean plastic sheeting will be used at each sampling location to provide a clean surface on which to place sampling equipment during sample collection activities.

Prior to sampling, each well will be purged of at least three well volumes. Following the well purging process, groundwater samples will be collected with a dedicated or disposable bailer. The time between the completion of purging and sample collection will not exceed 24 hours, unless the rate of recovery in the well requires more time for groundwater to collect in the well.

All samples requiring preservation will be preserved in the field. Measurements of pH, temperature, conductivity, and redox potential will be made at least three times during purging of the well, and at the time that the sample is collected. Barometric pressure, wind speed, and direction will be recorded in the field notes. Samples will be placed into pre-filtration jugs and filtered using the peristaltic pump.

2.4.4 Decontamination

The bailer will be decontaminated between wells. Decontamination of the bailer will include an Alconox® and tap water wash, a tap water rinse, and distilled water rinse. The decontamination procedure for the down-hole water quality probe will not include the soap and water solution, but it will merely be rinsed with tap water, then with distilled water. Peristaltic pump tubing will be decontaminated by running approximately one gallon of distilled water through the tubing between samples.

2.4.5 Quality Control

To evaluate the effectiveness of the decontamination process, a field rinsate blank will be collected during the sampling process. The bailer will be cleaned and filled with distilled water and subsequently transferred to a new filtration jug, passed through the peristaltic pump and a filter, and placed into laboratory supplied sample containers. The field blank will be maintained with the other groundwater samples. Field blanks will be collected at a rate of one rinsate blank per day of groundwater sampling.

In addition to the field rinsate blanks, duplicate groundwater samples will be collected at a rate of one duplicate sample per twenty groundwater samples. The duplicate sample will be submitted for analysis to evaluate the precision of the laboratory analysis.

2.4.6 Documentation

Data collected and field observations made during groundwater sampling will be recorded on the following field documentation forms:

- Field Notes Form.
- Groundwater Monitoring Form.

2.5 Hydraulic Characterization

2.5.1 Scope

Following the installation and development of the monitoring wells, water levels and in-field hydraulic conductivity testing will be performed to determine aquifer hydraulic characteristics. Water levels will be measured in all of the monitoring wells and hydraulic conductivity tests (slug tests or bail down tests) will be performed in select groundwater monitoring wells. The wells to be tested for hydraulic conductivity include:

MW02-1
MW02-1i
MW02-1d
MW02-04
MW02-4i
MW02-4d
MW02-2
MW02-5
MW02-6i

2.5.2 Equipment

- Solid PVC slug.
- Nylon rope.
- Stop watch (or watch with a second hand).
- Electric water level indicator.
- Water level datalogger with pressure transducer.
- Field forms/logs.
- Tap water, distilled water, Alconox®.
- 5-gallon pails and plastic sheeting.

2.5.3 Procedures

The depth to groundwater in the wells will be measured with a hand-held electric water level indicator.

Slug testing will involve lowering the pressure transducer into the well to a depth that will allow the solid PVC slug to be lowered into the well without coming into contact with the transducer. The maximum transducer depth will be limited by the settings of the datalogger and will be addressed according to the manufacturer's operation manual when setting up the test. The rising water level produced by lowering the slug into the well, as well as the falling water level when the slug is removed and the corresponding time, will be digitally recorded by a datalogger device. Readings will be recorded until the water level has recovered to approximately 90% of the static water level or stabilized.

Bail-down testing will involve purging the well dry with a bailer, measuring the rising water level with a pressure transducer or a water level indicator, and recording the time and water level depth during the return of the water level to the static position for at least 2.5 hours.

Reduction of the test data and calculation of the hydraulic conductivity will be performed by the Bouwer and Rice (1976, 1989) method.

2.5.4 Decontamination

The testing and water level measurement equipment, with the exception of the pressure transducer, will be decontaminated prior to use and at each well location by an Alconox® and tap water wash, a tap water rinse, and a distilled water rinse. A distilled water rinse only (no soap or tap water) will be used to decontaminate the pressure transducer.

2.5.5 Quality Control

Field documentation will undergo a QC review during the field activities. Original field forms will be reviewed for completeness and accuracy. Original field documentation, computer disks, and data plots will be stored in a secure area until completion of the field program. Upon completion of the field program, documentation will be relinquished to the Project Manager.

2.5.6 Documentation

Data collected and field observations made while performing in-field hydraulic conductivity tests and water level measurements will be recorded on the following field documentation forms:

- Field Notes Form.
- Groundwater Level Data Sheet.
- Field Hydrate Conductivity Test Form.

2.6 Survey

2.6.1 Scope

The scope of the survey is detailed in the Site Investigation Work Plan (See Section 3.4 above).

2.6.2 Procedures

The survey will be performed by a Registered Land Surveyor certified in the State of Wisconsin. Horizontal control will be referenced to the NAD 83 system at 0.01-foot accuracy and vertical control to the NAVD88/IGLD1985 referenced to mean sea level at 0.01-foot accuracy.

2.6.3 Quality Control

Survey field documentation will undergo a QC review after the completion of field activities. Upon completion of the field program, documentation will be relinquished to the Project Manager.

2.6.4 Documentation

The survey will be documented in AutoCAD electronic format and also in digital flat file format with (x, y, z) coordinates associated with sample point IDs.

3.0 MANAGEMENT OF INVESTIGATION DERIVED WASTE

Investigative derived waste generated during the field investigation activities will be managed as described below.

3.1 Solid Waste

Personal protective equipment, plastic sheeting, and disposable sampling equipment will be disposed of as solid waste.

3.2 Soil Cuttings

Soil cuttings generated during soil boring drilling and groundwater monitoring well construction will be returned to the boreholes. Cuttings from the upper 5 feet of soil, expected to contain the highest arsenic concentrations, will be segregated from deeper cuttings. Deeper cuttings will be mixed with bentonite chips and returned to the borehole. Cuttings from the upper 5 feet will be returned to the borehole on top of the deep soil/bentonite mixture.

3.3 Well Development and Sampling Water

Water collected during well development and sampling will be discharged to the ground surface.

4.0 REFERENCES

American Public Health Association (2001), *Standard Methods for the Examination of Water and Wastewater*, 21st Edition.

American Society of Testing and Materials, *Practice for Dry Preparation of Soil Samples for Particle-Size Analysis and Determination of Soil Constants*, Designation D 421-85.

American Society of Testing and Materials, *Standard Test Method for Penetration Test and Split-Barrel Sampling of Soils*, Designation D 1586-84.

American Society of Testing and Materials, *Test Method for Particle-Size Analysis of Soils*, Designation D 432-63 (Revised 1990).

Wisconsin Department of Natural Resources, *Leaking Underground Storage Tank and Petroleum Analytical and Quality Assurance Guidance*, PUBL-SW-130-93, July 1993.

Wisconsin Department of Natural Resources, Wisconsin Administrative Code, Environmental Protection, *Groundwater Quality*, Chapter NR 140.

Wisconsin Department of Natural Resources, Wisconsin Administrative Code, Environmental Protection, *Investigation and Remediation of Environmental Contamination*, Chapter NR 700 Series.

WDNR

Table 1 Listed Parameters

Parameter	suggested Analytical Method	Required Detection Limit (ug/g dry)
Inorganics-Metals		
Aluminum	SW846 6010B	
Arsenic	EPA 6010 or 7060	2.0
Cadmium	EPA 7131	0.02
Chromium (total)	EPA 6010 or 7191	5.0
Copper	EPA 6010 or 7211	2.0
Iron	EPA 6010/SW846 6010B	
Lead	EPA 6010 or 7421	5.0
Mercury	EPA 7471	0.02
Nickel	EPA 6010	5.0
Selenium		
Manganese	SW 846 6010B	
Zinc	EPA 6010 or 7951	5.0
Inorganics-Nutrients		
Oil & Grease		
Total Phosphorus	EPA 365.1	
Total Hardness	SM2340B	
Nitrate		
Nitrite		
Ammonia-Nitrogen		
Total K-Nitrogen		
Conduct, Ph, Alk	SM2510B/EPA 150.1/SM2320B	
Total Sulfate	EPA 375.2	
Organics		
Chlordane	EPA 8081, 354440B, 3	0.01
DDT	EPA 8081, 354440B, 3	0.01
DDE	EPA 8081, 354440B, 3	0.01
PCBs (total)		0.05
2,3,7,8-dioxin, 2,3,7,8-furan, and all 2,3,7,8-substituted dioxin and furan congeners		1 ng/kg
Total Organic Carbon	SW 846 EPA 9060	
Polycyclic Aromatic Hydrocarbons (PAHs- 16 unsubstituted Parent Compounds)	EPA 8310	0.03

Wisconsin Department of Natural Resources
STS Project No. 4-27393

Appendix C

Data Management Plan

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Data Management Plan

C.D. Besadny Fish and Wildlife Area
Kewaunee Marsh Arsenic Area
Kewaunee, Wisconsin

STS Project No. 4-27393

Wisconsin Department of Natural Resources
1125 North Military Avenue (54303)
P.O. Box 10448
Green Bay, Wisconsin 54307-0448

THE INFRASTRUCTURE IMPERATIVE

Table of Contents

1.0 INTRODUCTION

This Data Management Plan was prepared to identify the procedures that will be implemented during the site investigation at the C.D. Besadny Fish and Wildlife Area Kewaunee Marsh site to ensure that data collected is recorded, reduced, validated, and reported in an appropriate and consistent manner.

2.0 DATA RECORDKEEPING

2.1 Field Notes Form

The site investigation field activities will be documented on field note forms. The field notes will provide sufficient data and observations, in as much detail as necessary, to reconstruct events that occurred during the site investigation. Information recorded on the field forms will include site conditions, the sequence and duration of events, field sampling information, and field measurements. The field forms will be stored in a secured location when not in use. Each field form will include the name of the field personnel it is assigned to, project name, project start date, and project end date. Each field notes form will include the date, start time, weather, names of field personnel, and the names of site visitors. All measurements made and samples collected will be recorded in ink, and no erasures will be made. If an incorrect entry is made, the information will be crossed out with a single strike mark and initialed by the person making the changed entry. All equipment used to make the measurements will be identified.

2.2 Field Forms

Site investigation data will be recorded on the following field forms.

- Soil Boring Log.
- Well/Drillhole/Borehole Abandonment Form.
- Monitoring Well Construction Form.
- Monitoring Well Development Form.
- Groundwater Monitoring Well Information Form.
- Groundwater Monitoring Form.
- Groundwater Level Data Sheet.
- Field Hydraulic Conductivity Test Form.

2.3 Field Audits

Internal audits of field activities will be conducted. The audits will include an evaluation of data recordkeeping.

2.4 Project File

The original laboratory reports will be assembled by the Project Manager. The laboratory files, along with other relevant records, reports, field notes, photographs, subcontractor reports, and data reviews will be maintained under the custody of the Project Manager.

3.0 FIELD SAMPLE IDENTIFICATION AND LABELING

Each site investigation sample will be identified with a field sample identification number consisting of a sample location, year sampled, and depth interval. Because there have been several environmental sampling events at this site in the past, the year (01 or 02) sampled is included to avoid confusion when sampling results are analyzed as a complete body of data.

3.1 Sample Location Number and Depth Interval

Numeric designation used to identify location and depth interval that the sample was collected. The sample location numbers and designations indicate the type of sample collected. Sample location numbers will include the year of the sampling event to prevent confusion among the various sampling events that have occurred at this site. Sample designations for this site investigation include:

♦ SW	Surface Water Sample.
♦ MW	Monitoring Well (groundwater)Sample.
♦ SS	Surface Sediment Sample.
♦ SB	Shallow Soil (5 feet of depth) Boring Sample.
♦ IB	Intermediate Soil (10 feet of depth) Boring Sample.
♦ DB	Deep Soil (15 to 30 feet of depth) Boring Sample.

3.2 Example

The following is an example of a site-specific field sample identification number: IB02-3/ 5.5-7.5. The interpretation of this sample number is as follows: Intermediate soil boring, collected in 2002, Location IB01-3, sample interval 5.5 feet to 7 feet beneath ground surface.

3.3 Sample Label

Each sample will be labeled. The sample label will include the following information:

- Site Name.
- Name of Sample.
- Date and Time of Collection.
- Field Sample Identification Number.
- Analysis Required.
- Preservation.

4.0 DATA REDUCTION AND REPORTING

Field data will be transcribed onto tables for review and validation. Once validated, the data will be compiled and reported in summary tables. Units will also be provided on all summary tables.

Laboratory deliverables shall include ALL documentation, including, but not limited to:

- Log-in records.
- Bench sheets.
- Chain of Custody forms.
- Instrument read-outs.
- All initial and continuing Quality Control (QC) documentation.
- Analytical and sample preparation standard operating procedures (SOPs).
- Sample results and quality assurance (QA)/QC.
- Summaries of blanks, field duplicates, spikes, surrogates, and laboratory control samples.
- A brief case narrative.

Deliverables will also provide the date of sample receipt, extraction date, and analysis date. The analytical data will be summarized in a format organized to facilitate data review and evaluation. The data summaries will include any data qualifiers provided by the laboratory. The laboratory data qualifiers may include items such as no detects, concentrations detected below the limit of quantitation, and estimated concentrations due to QA/QC results.

Laboratory analytical data will be placed on the website for viewing by authorized parties. Further interpretation of analytical results will be submitted in written report format with appropriate discussion.

Wisconsin Department of Natural Resources
STS Project No. 4-27393

Appendix D

Site-Specific Safety Plan

STS CONSULTANTS, LTD.

Site-Specific Safety Plan

C.D. Besadny Fish and Wildlife Area
Kewaunee Marsh Arsenic Area
Kewaunee, Wisconsin

STS Project No. 4-27393

Wisconsin Department of Natural Resources
1125 North Military Avenue (54303)
P.O. Box 10448
Green Bay, Wisconsin 54307-0448

FOR INTERNAL USE ONLY[1]

STS CONSULTANTS, LTD.

SITE-SPECIFIC SAFETY PLAN

A. GENERAL INFORMATION

PROJECT NAME: Kewaunee Marsh Arsenic Site **STS PROJECT NO.** 27393

LOCATION: Wisconsin Central Ltd. property, Highway County E

PLAN PREPARED BY: Jan Tesch **DATE:** April 1, 2002

Updates will occur as conditions change. The plan will expire at completion of STS involvement.

SITE SAFETY OFFICER: Dan Braatz/Bill Zakowski

REVIEWED BY: ______________________ **DATE:** ____________________

OBJECTIVE(S): To complete surface elevation survey and soil boring location staking, surface water sampling, soil sampling, groundwater sampling, and installation of groundwater monitoring wells.

PROPOSED DATE OF EXPLORATION AND COMPLETION DATE: July 1, 2002 to May 1, 2003

BACKGROUND REVIEW: The Wisconsin Department of Natural Resources (WDNR) was notified of, and subsequently identified arsenic contamination within a wetland adjacent to a former railroad corridor in the C. D. Besadny Wildlife Area, Town of Pierce, Kewaunee County, Wisconsin. The site is security fenced and has been monitored since 1994. In 1996, a cover was placed over the zone of greatest impact as an interim remedial measure, so that additional monitoring and testing could be performed.

Arsenic concentrations in the impacted area were as high as 920,000 micrograms per liter (μg/L) in water, and 10,700 μg/L in soil sediment in 1995. The NR 140 Enforcement Standard (ES) for arsenic is 50 μg/L. The Preventive Action Limit (PAL) is 5 μg/L

Arsenic compounds can be associated with pesticides and herbicide production and use, manufacture of pharmaceuticals, glass, textile printing, tanning, taxidermy, sludge formation control in lubricating oils, and wood treating.

DOCUMENTATION/SUMMARY:

OVERALL HAZARD: Serious: X Moderate: ___ Low: ___ Unknown: ___

The health and safety protocols established in this plan are based on the site conditions and chemical hazards known and/or anticipated to be present from available site data. The possibility of contamination within the site requires a conservative approach to on-site safety procedures. The following site safety plan is intended solely for use by STS during the proposed observation and sampling activities described in the STS Site Exploration Work Plan. Specifications herein are subject to review and revision based on actual conditions encountered in the field.

B. SITE/WASTE CHARACTERISTICS

WASTE TYPE(S): Liquid X Solid X Sludge X Gas ___

CHARACTERISTIC(S): Corrosive ___ Ignitable ___ Radioactive ___ Volatile ___

Toxic X Reactive ___ Unknown ___ Other ___

ROUTES OF ENTRY:

Inhalation X Ingestion X Skin Absorption X

DESCRIPTION:

Principal Disposal Method (type and location):
Unknown Should have no disposal of hazardous waste. The site is a wildlife refuge area. Possible that pesticides containing arsenic may have been dumped at this location.

Unusual Features (dike integrity, power lines, terrain, etc.)
Site is fenced.

Possible unstable walking surface:
The area is a wetland. Possibility of sinking into deep organic or open water.

Status: (active, [✓ inactive], unknown).

History: (Worker or non-work injury, complaints from public; previous agency action):
Hunter contacted Wisconsin Department of Natural Resources (WDNR) about dead vegetation in area. Arsenic impacts may have occurred from a spill incident on the railroad.

Biological Indicators:
Dead trees, animal carcasses (ducks, geese, and muskrats) had been found on site in 1994.

Pathways for Dispersion of Hazardous Materials:
Airborne dust, gas release from bog or under ice, soil, and groundwater transmission. Possible volatile arsenic compounds.

Wind Direction:
To be determined on site.

C. HAZARD EVALUATION

EXPLOSIVES GASES

Types	LEL	Action Level	Required Action

Not applicable.

Airborne contaminants will be kept below 50 parts per million (ppm) Arsine in the breathing zone, thereby controlling against an explosion hazard.

SPECIFIC COMPOUNDS

Types	TLV[1], STEL[3], PEL[4]	IDLH[2]	Symptoms of Overexposure	Odor
Arsenic	.01 mg/cu.m. Carcinogen	Skin and mucous membrane irritant Action		
Arsine Gas	0.2 mg/cu.m.Carcinogen 0.05 ppm TLV	19.1 mg/c.m. 6 ppm	Head, Dizziness	Garlic odor

(Occupational Safety and Health Administration) OSHA Standard 1910.1018 Inorganic arsenic - Requires regulated work areas, hygiene facilities, protective clothing, medical surveillance. See Standard. for further detail.

Arsenic compounds should be regarded as very potent poisons. Their acute toxicity, however, varies greatly as between organic and inorganic compounds, depending on valence and solubility. Acute effects at the point of entry may occur if exposure is excessive. Dermatitis may occur as an acute symptom but is more often the result of sensitization. Cases of acute arsenical poisoning due to inhalation are exceedingly rare. Since soils will not be agitated, airborne dust should be a controlled exposure. Gloves, over-boots, and full body protection will be worn to prevent clothing and skin contamination. Ingestion is the most significant acutely fatal route. The fatal dose of arsenic trioxide has been reported to range from 70 milligrams (mg) to 180 mg. Smoking, eating, and drinking while working at the site is strictly prohibited. The potential of arsine gas also poses a significant and serious need for control of inhalation of the gas, since inhalation at a concentration of 6 parts per million (ppm) can be fatal.

ODOR THRESHOLD

Compound	Concentration at Odor Threshold	Odor
Arsine gas	0.21-0.63 ppm 0.6-2 mg/cu.m.	**INADEQUATE WARNING - 4 X TLV**

GENERAL ORGANIC VAPORS

Health Action Levels	Required PPE Level
Observation from support zone	Level D to be worn continuously Level C for emergency escape
Decontamination	Level D
Drilling of Boreholes	Level D

Surface Water Sampling Level D

Confined Space: Yes ____ No ____

Types:

Contaminants Expected:

Arsenic and arsenic compounds

1. TLV = Threshold limit valve for an 8-hour time-weighted average exposure
2. IDLH = Immediately dangerous to life and death
3. STEL = Short term exposure limit - 15-minute maximum exposure
4. PEL = OSHA Permissible Exposure Level.
5. Skin = Can be absorbed through the intact skin

PHYSICAL HAZARDS

_X_ Weather Related
(Insert Cold injury warning during winter months.)

Other Hazard Identification

Note land features, vehicle movement. Entrapment hazards and drowning hazards may be present due to bog-like conditions in the wetlands and soils/water with high concentrations of arsenicals. Plan includes provisions for emergency rescue for those entrapped in the bog. SEE attached STS Standard Safe Work Practices for Contaminated Sites.

Noise: Noise should not be a problem at this site; therefore, hearing protection would be unnecessary.

SPILL CONTAINMENT PROGRAM

If there is a potential for a spill, a containment program will be included in the Appendix. Most often contaminated solids will be encountered. Visqueen sheeting will be laid out to collect contaminated soils. This material and sheeting will be loaded and disposed of at the completion of the excavation.

D. ON-SITE CONTROL

CONTROL BOUNDARIES: Map/Sketch Attached _X_ Site Secured _X

Safe perimeter has been established as: perimeter outside of fenced area.

The control boundary has been established, and is identified as the area within the fence.
No unauthorized person should be within the impact area.

The support zone is located on the former railroad corridor west of the impact area

GENERAL SAFE WORK PRACTICES ON CONTAMINATED SITES
(Include "STS Safe Work Practices on Contaminated Sites" here or attached at end of Site Safety Plan.)

PERSONAL PROTECTION

The following protective clothing materials are required for the involve substances:

TASK OR JOB: Observations from support zone-air sampling, sediment/subsoil sample collection.

LEVEL OF PROTECTION: ___ A ___ B ___ C _X_ D

Head

__X__ Hardhat (Drilling operations only)

Eye/Face

__X__ Safety Glasses/Goggles
_____ Face Shield
_____ Goggles

Hand

___ Neoprene _X_ Nitrile ___ PVC ___ Viton _X_ Over glove ___ Other
___ Taped

Body

___ Full Encapsulating Suit
___ Two-Piece Rainsuit, Material:
___ One-Piece Splash Suit, Material:
___ Tyvek Suit ___ Tyvek/Saranax Suit _X_ Tyvek/Polyethylene Suit
___ CPF IV Suit with hoods and boots for entry personnel

Respirator

All personnel will comply with STS's written standard operating procedures in the STS Respiratory Protection Program and pages 4-31 through 4-52 in the STS Health and Safety Manual.

___ SCBA (open circuit, pressure demand): 30 minutes for gas monitoring personnel
___ Full Face Respirator, cartridge HEPA and OVA/AG; all other team members
___ Half Mask Respirator, Cartridge
___ Other:

Ear

___ Earplug, type: minimum NRR rating of 25 dBA, if noise level is greater than 85 dBA
___ Earmuff, type

Foot

_X_ Boots, type: Steel toe safety boots with disposable over-boots.

No changes to the specified levels of protection shall be made without the approval of the Site Safety Officer and the Project Engineer.

PERSONAL PROTECTION

The following protective clothing materials are required for the involved substances:

TASK OR JOB: Escape of arsine is detected during site sampling.

LEVEL OF PROTECTION: ___ A ___ B _X_ C ___ D

Head

___ Hardhat

Eye/Face

___ Safety Glasses/Goggles
___ Face Shield
___ Goggles

Hand

___ Neoprene _X_ Nitrile ___ PVC ___ Viton _X_ Over glove ___ Other
___ Taped

Body

___ Full Encapsulating Suit:
___ Two-Piece Rainsuit, Material:
___ One-Piece Splash Suit, Material:
___ Tyvek Suit ___ Tyvek/Saranax Suit _X_ Tyvek/Polyethylene Suit
___ CPF IV Suit with hoods and boots for entry personnel

Respirator

All personnel will comply with STS's written standard operating procedures in the STS Respiratory Protection Program and pages 4-31 through 4-52 in the STS Health and Safety Manual.

___ SCBA (open circuit, pressure demand): 30 minutes for entry personnel.
___ Full Face Respirator, cartridge: or
_X_ Half Mask Respirator, cartridge: AG/OV-HEPA
___ Other

Ear

___ Earplug, type: minimum NRR rating of 25 dBA, if noise level is greater than 85 dBA.
___ Earmuff, type:

Foot

_X_ Boots, type: Steel toe safety boot with disposable overbook

No changes to the specified levels of protection shall be made without the approval of the Site Safety Officer and the Project Engineer.

MONITORING EQUIPMENT AND PROCEDURES:

Sensidyne arsine monitoring tubes are to be used to determine arsine gas concentrations that may be associated with tar-like material.

Personal monitoring will be conducted to determine T.W.A. concentration of Arsine. Pump drawing 0.1-0.2 Lpm through charcoal tube will be undertaken during the soil boring procedures. Sample will be analyzed by independent accredited laboratory and results provided to subcontractors.

PERSONNEL DECONTAMINATION PROCEDURES:

Modified Level D: Wash outer gloves, boots, and sampling equipment with Alconox soap and water, rinse with potable water. Rinse water will not be retained.

EQUIPMENT DECONTAMINATION PROCEDURES:

Decontamination (Decon) boring equipment between each sampled boring location. Decon solution to consist of soap and water. Level D protection will be worn during any decontamination operations.

SITE ENTRY PROCEDURES:

Have a site safety briefing with the field engineer who will explain any procedures and answer any questions. Everyone must understand the plan and emergency signals/signs. Decontaminate all equipment prior to arrival. A mobile telephone will be carried to the site. Wearing Level D protection, the sampling team will enter the marsh to collect samples.

Emergency signals, will be prearranged and discussed with team.

EXPLORATION-DERIVED MATERIAL DISPOSAL:

Clothing that is disposable (e.g., inner gloves and splash suits) should be placed in covered drums onsite. All sampling equipment in contact with subsurface materials shall be decontaminated before removal from site. Water samples, if shown to possess contaminants upon laboratory analyses will be returned to the site.

Emergency Decontamination Procedures:

Flush any wounds immediately and go directly to the hospital for medical attention. Since the expected contaminants are extremely hazardous, decontamination will be essential before instituting life saving first aid procedures (CPR).

Site Entry Procedures: Enter near railroad trestle.

Work Limitations (time of day, heat, cold, etc.): Work to be done during daylight hours only. Stop work if raining or lightning. Follow attached safe work practices for contaminated sites.

* EMERGENCY INFORMATION

EMERGENCY TELEPHONE NUMBERS ARE TO BE VERIFIED PRIOR TO ANY SITE ACTIVITIES

Local Resources:

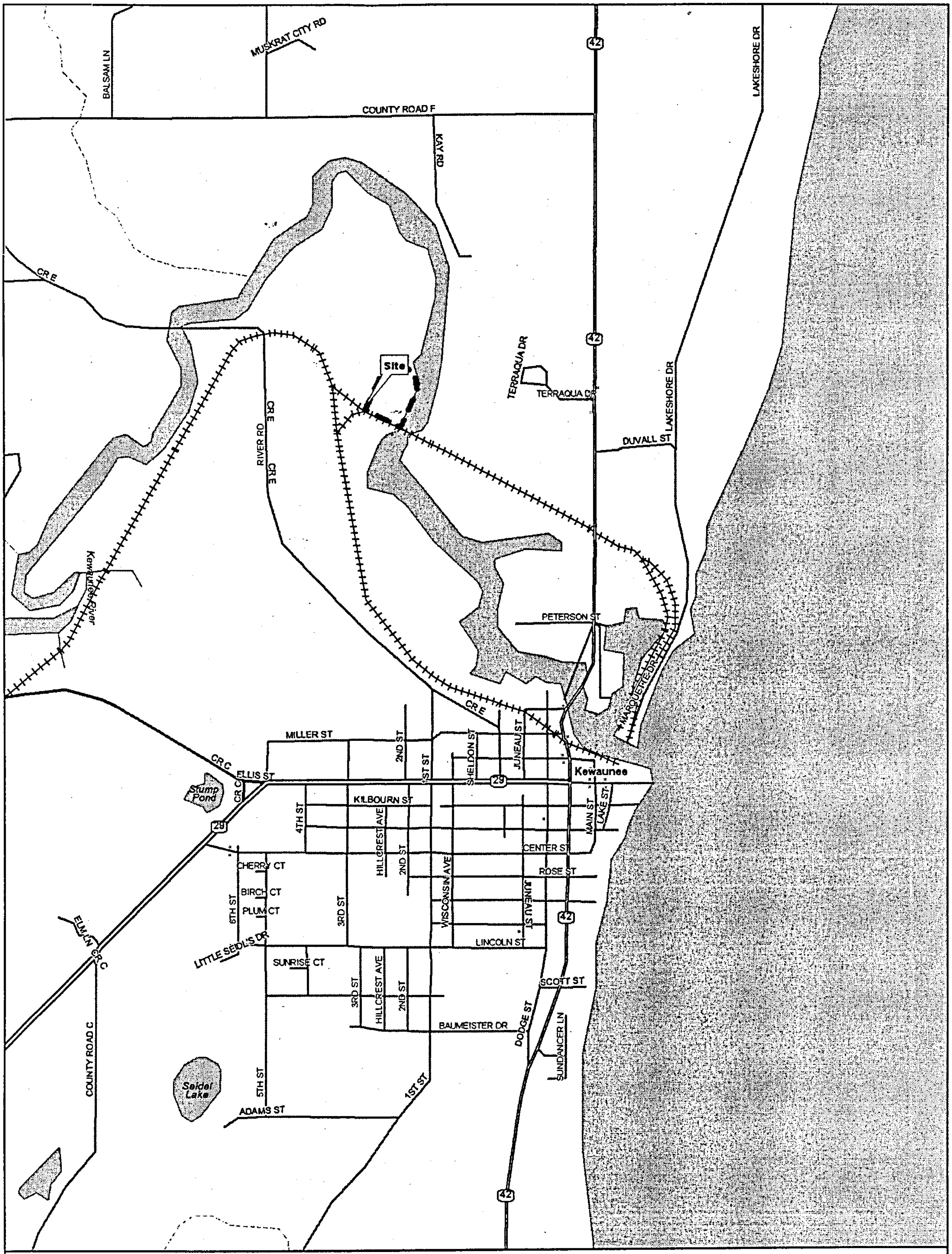
Ambulance: 911
Hospital Emergency Room: Aurora BayCare Medical Center, Green Bay, Wisconsin 920-288-4040
Poison Control Center: 1-414-266-2222
Police: 911
Fire Department: 911
National Response Center (NRC): 1-800-424-8802
EPA Contact:

* Site Resources:

*To be arranged prior to work
Mobile Phone: To be carried on site.
Water Supply: To be carried on site.
Electricity:
Telephone: To be carried on site.
Other:

Emergency Contacts:

Jan Tesch - Project Manager - STS Consultants, Ltd.
Paul Killian - SSO-STS Consultants, Ltd.
Jim Kauer - Regional Health Safety Officer - STS Consultants, Ltd., Green Bay, Wisconsin
National Spill Response 1-800-424-8802



DELORME

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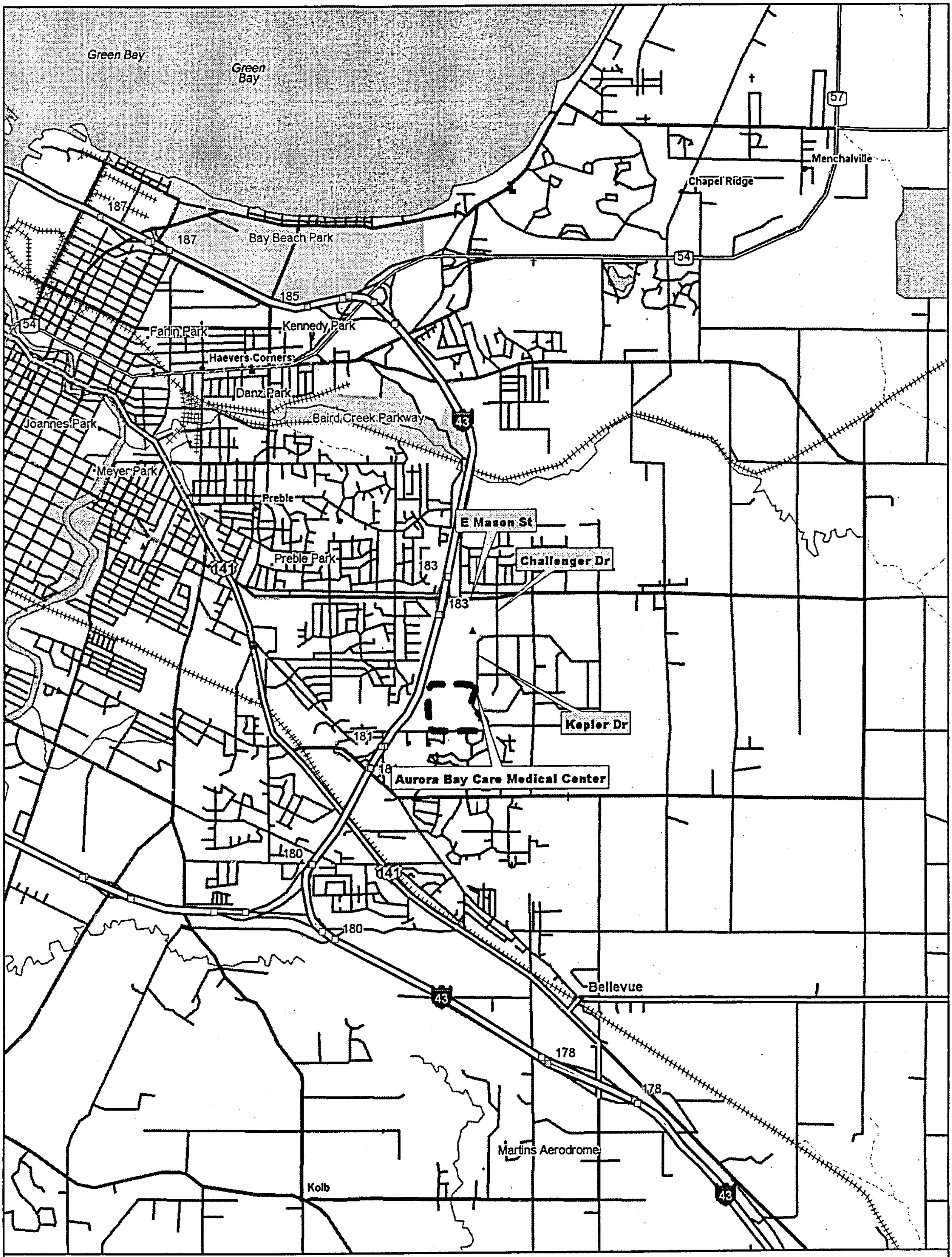
Zoom Level: 13-0 Datum: WGS84

Scale 1 : 25,000
1" = 2080 ft



DELORME

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Zoom Level: 11-6 Datum: WGS84

Scale 1 : 62,500
1" = 5210 ft

TN
MN
3.0°W

EMERGENCY PROCEDURES

The following standard emergency procedures will be used by on-site personnel. The Site Safety Officer shall be notified of any on-site emergencies and be responsible for ensuring that the appropriate procedures are followed.

Personnel Injury in the Impacted Area:

Upon notification of an injury in the Impacted Zone, the designated emergency signal (hands over head or signaling with red flag and other hand signals) will be given. The two-man team will retrieve the injured person with the safety lines and will move as a group to the decontamination area. If there is an air problem with the SCBA or air purifying respiratory protection, rescue personnel must not attempt rescue unprotected (Level B-minimum). The site Safety Officer should evaluate the nature of the injury, and the affected person should be decontaminated to the extent possible prior to movement to the Support Zone. The DESIGNATED FIRST AID PERSON shall initiate the appropriate first aid, and contact should be made for an ambulance and with the designated medical facility (if required). No persons shall re-enter the Impacted Zone. Job shall cease and all return to office.

Personnel Injury in the Support Zone:

Upon notification of an injury in the Support Zone, Site Safety Officer will assess the nature of the injury. Since all STS personnel are needed for support and potential rescue, the operation will cease. The on-site designated first aid person shall initiate the appropriate first aid and necessary follow up as stated above. Since any injury on this site can increase the risk to other all site personnel shall move to the decontamination line for further instructions. Activities on site will stop.

Fire/Explosion:

Upon notification of a fire or explosion on site, the designated emergency signal (shout) shall be sounded and all site personnel assembled at the decontamination line. The Fire Department shall be alerted and all personnel moved to a safe distance from the involved area.

Personnel Protective Equipment Failure:

If any site worker experiences a failure or alteration of protective equipment that affects the protection factor, that person and his/her buddy shall immediately leave the Impacted Zone. Re-entry shall not be permitted until the equipment has been repaired or replaced.

Other Equipment Failure:

If any other equipment on site fails to operate properly, the Project Engineer and Site Safety Officer shall be notified and then determine the effect of this failure on continuing operations on site. If the failure affects the safety of personnel or prevents completion of the assigned tasks, all personnel shall leave the Impacted Zone until the situation is evaluated and appropriate actions taken.

*F. EMERGENCY ROUTES

(Give road or other direction; attach map)

HOSPITAL: St. Mary's Kewaunee Area Memorial Hospital, Inc. - Lincoln Street, Kewaunee

PHONE: (920) 388-2210

*EMERGENCY ROUTES ARE TO BE DRIVEN BY STS PERSONNEL PRIOR TO SITE ACTIVITIES

I have received the Health and Safety Plan for the Kewaunee Marsh Arsenic work site. I have read this plan and had the opportunity to ask questions. I understand the information and instructions in this plan. I have also participated in the education and training programs in compliance with Federal OSHA 29 CFR 1910.120(E): 40 hours of initial instruction and 8 hours of refresher training and am currently in the Medical Health Surveillance Program as outlined in the STS Health and Safety Manual (Appendix II). If specialized training is required for site operations this will be given in addition to the 40-hour training. Daily pre-entry meetings to review the SSP (any given changes) will be held as applicable.

Please note that medicine can potentiate the effects from exposure to toxic chemicals. If you are taking any prescription or over-the-counter medicine, you must advise your supervisor or site safety officer.

Team Member	Signature of Team Member After Reading this Plan	Responsibility

STANDARD SAFE WORK PRACTICES ON CONTAMINATED STS SITES

1. Eating, drinking, chewing tobacco, smoking, and carrying matches or lighters is prohibited in a contaminated or potentially contaminated area or where the possibility for the transfer of contamination exists.
2. Avoid contact with potentially contaminated substances. Do not walk through puddles, pools, mud, etc. Avoid, whenever possible, kneeling on the ground, leaning or sitting on equipment or ground. Do not place monitoring equipment on potentially contaminated surfaces.
3. All field crew members should make use of their senses to alert them to potentially dangerous situations in which they should not become involved (i.e., presence of strong and irritating or nauseating odors). Caution: If you detect the smell of rotten eggs (hydrogen sulfide), evacuate. Hydrogen sulfide causes acute systemic toxicity and deadens the sense of smell. If any unusual colors of gas clouds/emissions are noted, evacuate. Also, if any symptoms or odors are experienced through a respirator, move to the decon line. CALL IN!
4. Field crew members should be familiar with the physical characteristics of investigations, including:
    - Wind direction.
    - Accessibility to associates, equipment, and vehicles.
    - Communication/Emergency signals.
    - Hot zone (areas of known or suspected contamination).
    - Site access.
    - Nearest water sources.
5. All wastes generated during activities on site should be disposed of as directed by the project manager or his on-site representative.
6. Protective equipment, as specified in the section on personal protection, will be utilized by workers during the initial site reconnaissance and other activities.
7. Hands and face must be thoroughly washed upon leaving the work area.
8. Whenever decontamination procedures for outer garments are in effect, the entire body should be thoroughly washed as soon as possible after the protective garment is removed.
9. No facial hair, which interferes with a satisfactory fit of the mask-to-face seal, is allowed on personnel required to wear respirators.
10. Medicine and alcohol can potentiate the effects from exposure to toxic chemicals. Prescribed drugs should not be taken by personnel at hazardous waste operations where the potential for absorption, inhalation, or ingestion of toxic substances exists, unless specifically approved by a qualified physician. Alcoholic beverage intake, during off hours, should be minimized or avoided. If you are taking any prescription or over-the-counter medicine which can impact your work, please advise your supervisor or Site Safety Officer.
11. All personnel must be familiar with standard operating safety procedures and any additional instructions and information contained in the Site Safety Plan.
12. All personnel must adhere to the information contained in the Site Safety Plan.
13. Contact lenses cannot be worn when respiratory protection is required or when the hazard of a splash exists.
14. Personnel will be aware of symptoms of toxic chemicals exposure and for heat or cold stress.

15. Respirators shall be cleaned and disinfected after each day's use or more often if necessary.
16. Prior to donning, respirators will be inspected for worn or deteriorated parts. Emergency respirators or self-contained devices will be inspected at least once a month and after each use.
17. The employee will be familiar with all sections of the STS established respirator program and the site-specific SSP.

Wisconsin Department of Natural Resources
STS Project No. 4-27393

Appendix E

Laboratory Standard Operating Procedure

Determination of:	Sample Preparation of Metals in waters, wastes, and TCLP extracts.
Scope/Purpose:	To provide a standard method for the digestion/preparation of aqueous samples, EP and mobility-procedure extracts, and wastes that contain suspended solids for analysis by GFAAS or ICP. The procedure is used to determine total metals.
Reagents:	Concentrated Nitric Acid Concentrated Hydrochloric Acid
Equipment:	Hot Plates Black Ribbon filter paper
References:	Code of Federal Regulations Title 40, Part 136 Appendix C, U.S. Government Printing Office, Washington D.C. 20402, 1991.

Discussion:

This method describes the procedure for digesting a sample in order to make it suitable for analysis by either Inductively Coupled Plasma (ICP) or Graphite Furnace Atomic Absorption Spectroscopy (GFAAS). The sample is treated with nitric acid and heated to near dryness. It is then subjected to more nitric acid and is refluxed within its beaker. A final treatment of hydrochloric acid and deionized water dissolves any remaining residue. By treating the sample with nitric acid and heating, two things are accomplished. First, the acid and heat combine to break down most organic interferences within a sample's matrix. Second, metals will readily dissolve in nitric acid leaching them away from elements that could form complex interferences. Due to the instruments inability to analyze solids, samples with a high turbidity or a solids content must be digested.

There are two types of liquid sample digestion; total and recoverable. The total prep is a much more vigorous technique and is often needed to destroy metal complexes and leave them susceptible to atomization. Both procedures are described in detail in this document.

Special Interferences:

The analyst should be cautioned that the digestion procedures may not be sufficiently vigorous to destroy some metal complexes.

Precipitation could cause a lowering of concentrations and therefore less accurate results for some elements.

TOTAL METALS DIGESTION METHOD:

1. Samples are evaluated upon receipt to determine if they require a digestion. Floating solids, discolored or murky samples or smelly waters need to be digested prior to analysis. Samples not obviously in need of prepping should be evaluated by checking the turbidity. If the turbidity is > 1.0 NTU then it should be digested.
2. Choose a measured volume of the mixed acid preserved sample appropriate for the expected level of metals. For most waters use 100 ml, for samples such as liquid sludges use 10 ml. It is up to the discretion of the analyst as to the volume of sample used, but the consistency and amount of solids present are key indicators. Pipette the sample if appropriate otherwise use graduated cylinders. Be sure to rinse the graduated cylinder with a 1% acidified nitric acid deionized water solution after every use. If possible wash the cylinder with a small portion of the sample before taking the volume to be used for digestion.
3. Transfer sample to a clean 250 ml beaker.
4. Mark the sample ID on the beaker and write the sample number and dilution on the benchsheet.
5. Add 3.0 ml of concentrated Nitric Acid.

6. Place the beaker on a hot plate set at 4 or 6 depending on the hot plate you are using. Cover with a fluted watch glass and evaporate to near dryness without boiling or allowing the sample to go completely dry.
7. Remove and cool the beaker and add another 5.0 ml portion of concentrated nitric acid.
8. Cover the beaker with a smooth watch glass and return it to the hot plate. Heat so that a gentle reflux action occurs. The 3 or 5 setting on the hot plate should be sufficient.
9. Continue heating and adding acid until the digestate is light in color and does not change in appearance.
10. Again, evaporate to near dryness and cool the beaker.
11. Add 5 ml of concentrated hydrochloric acid and 15 ml of deionized water per 100 ml of final solution and warm the beaker for 15 minutes to dissolve any precipitate or residue resulting from evaporation. If the sample requests furnace lead, do not add the HCL as it negatively interferes with the GFAAS analysis of lead. If this sample in question is being spike for silver, use an excess of HCL. An additional 5 ml should be sufficient. This helps prevent the spike from precipitating which will improve the recovery.
12. Cool beaker and wash down the walls and watch glass with deionized water.
13. Gravity filter the sample through Black Ribbon filter paper to remove any insoluble material that could clog the nebulizer on the ICP. The sample is to be filtered into a 100 ml volumetric flask and diluted to the mark using deionized water.
14. Pour the digested sample into a 120 ml plastic sample cup and mark the sample ID, dilutions and date in permanent pen.

Recoverable Metals Digestion Method:

1. Choose a measured volume of the well mixed, acid preserved sample appropriate for the expected level of elements and transfer to a 250 ml beaker. Be sure to rinse the graduated cylinder with acidified deionized water and a small portion of the sample being digested prior to use.
2. Mark the sample ID on the beaker with the grease pencil, and write the sample number and dilution on the benchsheet.
3. Add 1.0 ml of concentrated nitric acid and 5.0 ml of concentrated hydrochloric acid. Hydrochloric acid is an interferant for low level lead analysis and should be left out of samples requesting furnace recoverable lead.
4. Place the sample on a hot plate set on 4 and evaporate without boiling to about 25 ml.
5. Remove the sample from the hot plate and cool.
6. Gravity filter out any insoluble materials through Black Ribbon paper into a 100 ml volumetric flask. Again, do not filter if the sample requests zinc.
7. Be sure to rinse the sides of the beaker, filter paper, and funnel to get all of the digestate.
8. Adjust the volume to 100 ml with deionized water.
9. Pour into a sample cup labeled to tell the analyst the sample ID, dilution. and date digested.

QA/QC:

1. A reagent blank needs to be prepared every time samples are digested using any of these methods. Measure 100 ml of deionized water into a 250 ml beaker and treat in the same manner as a sample requesting a total prep. This method is much more vigorous and detailed than the recoverable procedure and if contamination was to be introduced during digestion it would more likely show up in the total prep procedure.
2. Matrix spike/matrix spike duplicates (MS/MSDs) are to be done after every ten samples.
3. A LCS/Fortified blank is analyzed per batch of 20 samples, or every analysis day.
4. GFAAS spiking levels need to be 20.0 µg/l for lead, copper, selenium, antimony, thallium, chromium, arsenic, and 2.0 µg/l for cadmium and silver. A spike mix may be prepared in advance to simplify the spiking procedure. This mix can be made by pipeting 1.0 ml of 1000 mg/l stock standard of each of the metals needing 20 µg/l into a 1 liter volumetric, preserving with 10.0 ml of nitric acid, and recording the mix into the reagent logbook. The mix for cadmium and silver is made by pipeting 1.0 ml of a 1000 ml stock standard into a 1 liter volumetric and making a second dilution by pipeting 10.0 ml of the 1.0 mg/l working standard into a 100 ml volumetric. Preserve the mix with 1.0 ml of conc. nitric acid and record all reagents and dilutions into the reagent logbook. From this point, 2.0 ml of the two standards are pipetted into the 250 ml beakers containing equal portions of the sample. They can now be digested using the prep procedure requested for that sample. After the transfer to the 100 ml volumetric, and diluting the sample to mark with deionized water, the final concentration of the spike will be 20.0 µg/l for Pb, Cu, Se, Sb, T1, Cr, As, and 2.0 µg/l for Cd and Ag.
5. Spiking for ICP metals is done at much higher concentrations. Most metals can be spiked with the Quality Control Standard 23,which can be purchased from several vendors. The standard contains 100 mg/l of Sb, As, e, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, Se, Tl, Ti, Sn, Li, P, S, V, and Zn. The spike is made by pipeting 1.0 ml of the standard into the beakers containing the sample. The exact volume used is dependent upon the expected concentrations of the sample and the request of the ICP analyst. A second standard is used to spike for most of the remaining metals. Quality Control Standard 7, which can also purchased from several vendors, contains 1000 mg/l K, 100 mg/l Al, Ba, B, Ag, Na, and 50 mg/l Si. Pipet no more than 1.0 ml of this standard into the sample. The reason for this is that it contains Ag which shows a very poor spike recovery if a larger amount is used. A digestion note, use excess HCL in spikes containing Silver if possible. It seems to aid in the recovery of the spikes. The Si, Na, K, Ca, Mg and Fe spike concentrations are too low using the volumes stated above. They need tO be supplemented to produce a concentration that is discernible from the amount of analyte in the sample. Ca, Mg, Na, and K should be spiked at approximately 50 mg/l, and Fe and Si should be spiked at about 10 mg/l. Spike levels will vary depending on what concentrations are to be expected in the sample being spiked.
6. If a sample needs to be spiked with a metal not contained in either of the mixed standards used, they can be done separately at a concentration dictated by the ICP analyst.

Batches:

1. Samples are given a batch number in order to track the metal digestions in our LIMS computer system. These numbers are written on the upper right corner of the benchsheet, and entered when the dilutions are entered into the computer. Batch numbers are changed at the first of the month and that number is used throughout the month for all liquid metal preps.

Glassware Clean Up and Storage:

1. After use, wash glassware using hot water and a concentrated general laboratory soap.
2. Immerse the washed glass into a nitric acid solution and allow them to soak for 24 hours.
3. The acid solution should be 5Ã10% nitric acid in order to effectively clean all surfaces of the glass.
4. Rinse the glass with distilled water and allow to dry.
5. In order to prevent contamination, label separate glassware for use with contaminated and dirty samples. Keep the two sets of glassware separated through the entire prepping and cleaning process.

Special Note: Separate glassware for metals from that used for total Sulfur or Sulfate. High concentrations of Barium used here would contaminate the metals glassware.

Reviewed by: ____________________

Approved by: ____________________

Determination of: Metals in sediments, cakes, and soils.

Scope/Purpose: To provide a procedure for the acid digestion of solid samples for analysis by Inductively Coupled Plasma and Graphite Furnace Atomic Absorption Spectroscopy.

Reagents:
Reagent grade concentrated nitric acid
Reagent grade concentrated hydrochloric acid
Reagent grade 30% hydrogen peroxide

Equipment:
Hot plates
Analytical balance capable of reading to 0.01 gram
Black ribbon filter paper

References:

Test Methods for Evaluating Solid Waste Laboratory Manual, SW-846. Vol 1A, chapter 3, Method 3050A, Revision 1 July 1992.

Methods for the Determination of Metals in Environmental Samples, EPA-600/4-91-010, Environmental Monitoring Systems Laboratory Office of Research and Development, U.S. Environmental Protection Agency, June 1991.

Discussion:

A representative amount of a sample is digested in nitric acid and hydrogen peroxide. The digestate is then refluxed in hydrochloric acid. These treatments serve to destroy metal complexes with organic substances and leach the metals away from insoluble materials. The insolubles are filtered out and what is left is a strongly acidic liquid that may be analyzed using either the ICP of GFAAS techniques.

Special Interferences:

The analyst should be cautioned that the digestion procedure may not be sufficiently vigorous to destroy some of the metal complexes.

Not using a homogeneous sample could cause less accurate results. It could also cause a large deviation between duplicate samples.

Precipitations could cause a lowering of concentrations and therefore less accurate results for some elements.

SOLID TOTAL METALS DIGESTION METHOD:

1. Mix the sample to achieve homogeneity using a spatula.
2. Weigh out to the nearest 0.01 gram 3 g of soils and sediments, and 1 g of ashes and sludge cakes. Transfer to a 250 ml beaker.
3. Record the exact weight of the sample on the benchsheet as they are weighed out.
4. Add 10 ml of concentrated nitric acid, cover with a watch glass, and place the beaker on the hot plate and heat to 95°C. A setting of 2 should be sufficient. Reflux for 15 min.
5. Cool sample, add 10 ml of concentrated nitric acid, cover with a watch glass and allow the sample to reflux for 30 minutes without boiling. If the sample bumps, turn down the heat and use a glass bump rod to prevent the spattering.
6. Remove the watch glass and allow the solution to evaporate to approximately 5 ml. Do not dry the sample.
7. After cooling the sample, add 2 ml of water and 3 ml of 30% hydrogen peroxide. Cover the sample with the watch glass and return it to the hot plate. Extreme care needs to be taken, as the peroxide will react violently in the beaker and may foam over.

8. Allow the sample to stop effervescing and cool the beaker. Continue to add the peroxide in small portions until the effervescence is minimal or the sample appearance is unchanged. Do not add more than a total of 10ml of peroxide.
9. Add 5 ml of concentrated hydrochloric acid and 10 ml of deionized water and replace the watch glass and return the beaker to the hot plate. Allow the sample to reflux for 15 min. Cool the sample.
10. Filter the sample through Black Ribbon filter paper into a 100 ml volumetric flask. Be sure to thoroughly rinse the beaker, sample, filter paper, and funnel with deionized water.
11. Dilute to the mark with deionized water.
12. Mix the sample and pour it into a sample container labelled with the sample ID, date, and weight of sample digested.

SOLID SAMPLE PREPARARTION - TOTAL RECOVERABLE ELEMENTS:

1. Thoroughly mix the sample to achieve homogeneity.
2. Accurately weigh 3.0 g of the sample and transfer it to a 250 ml beaker.
3. Add 6 ml concentrated nitric acid and 6 ml of concentrated hydrochloric acid.
4. Cover with a watch glass and heat on a hot plate for 30 minutes. A setting of 2 is generally hot enough to reflux the sample without boiling it.
5. Remove from hot plate and cool sample.
6. Filter the sample through black ribbon filter paper into a 100 ml volumetric. Be sure to thoroughly rinse the beaker, sample, filter paper, and furmel.
7. Dilute to 100 ml using deionized water.

QA/QC:

1. A reagent blank needs to be prepared every time solid samples are digested. Treat a beaker with 10 ml of deionized water as you would a normal sample.
2. Duplicates need to be done at a frequency of 10%.
3. Matrix spike/matrix spike duplicates (MS/MSDs) are to be done at a frequency of 5 %.
4. GFAAS spiking levels for Pb, Cu, Se, Sb, Tl, Cr, and As is 20.0 µg/l. Spiking concentrations for Cd and Ag is 2.00 µg/l. A spike mix may be prepared in advance to simplify the spiking procedure. The mix for the 20.0 µg/l metals is made by pipeting 1.0 ml of 1000 mg/l of each element into a 1 liter volumetric and diluting to the mark with deionized water. The mix for Cd and Ag is prepared by pipeting 1.0 ml of standard into a 1000 ml flask and diluting to the mark with deionized water. Prepare a second dilution by pipeting 10 ml of the working standard into a 100 ml volumetric flask and dilute to the mark with deionized water. From this point 2.0 ml can be pipeted from each of the two standards and added to the beaker containing the solid sample.
5. Spiking for ICP metals is done at much higher concentrations. Most metals can be spiked with the Quality Control Standard 23, which can be purchased from different vendors. The standard contains 100 mg/l of

Sb, As, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, Se, T1, Ti, V, and Zn. The spike should be made by pipeting 5.0 ml of the standard into the beakers holding the solid sample. The exact volume may vary depending on the expected concentration of the sample and the requests of the ICP analyst. A second standard is used to spike for most of the remaining metals. Quality Control Standard 7 is also purchased from Spex Industries. This standard contains 1000 mg/l K, 100 mg/l A1, Ba, B, Ag, Na, and 50 mg/l Si. Use no more than 1 ml of this standard as it contains Ag, which shows very poor spike recoveries at higher concentrations of spikes on the ICP. As a digestion note, use excess hydrochloric acid in silver spikes, it seems to improve recovery. An additional 5 ml should be sufficient. The Si, Na, K, Mg, and Fe spike concentrations are too low using these volumes. The concentration of these metals in many samples is normally quite high. Pipet 10 ml of 1000 mg/l stock standard into the beaker to insure an amount of spike that the ICP can detect apart from the samples concentration.

6. If a sample needs to be spiked with a metal not contained in either of the standards normally used they can be done separately at a concentration dictated by the ICP analyst.
7. Record all spike dilutions on the benchsheet and on the sample container.

Batches:

1. Samples are given a batch number in order to track the metal digestions in our LIMS computer system. These numbers are written on the upper right corner of the benchsheet, and entered when the dilutions are entered into the computer, Batch numbers are changed at the first of the month and that number is used throughout the month. There are two different batch numbers issued at the beginning of the month; one for liquid preps and one for solid preps.

Glassware Clean Up and Storage:

1. After use, wash glassware using hot water and a concentrated laboratory soap.
2. Immerse the washed glassware into a nitric acid solution and allow them to soak for 24 hours.
3. The acid solution should be 5Â10% in strength in order to effectively clean all surfaces of the glass.
4. Rinse the glass with distilled water and allow to dry.
5. In order to prevent contamination, label separate glassware for use with solid samples. Keep this set separated from the liquid prep glassware throughout the entire prepping and cleaning process.

Special Note: Separate glassware for metals from glassware used for total Sulfur or Sulfate. High concentrations of Barium used in those procedures would contaminate the metals glassware.

Reviewed by: ______________________

Approved by: ______________________

Determination of: EPA Method 200.7/6010 for the determination of Trace Metals Analysis of Water and Wastes by ICP Emission Spectroscopy. This method describes a technique for the sequential multi-element determination of trace elements in solution.

Scope/Purpose: To provide a method for which soluble, suspended, and total metals in drinking water, surface water, domestic and industrial wastewater can be analyzed. Also, to provide a method for the analysis of total elements in soils, sludges, and other solid wastes.

Reagents:
SPEX Multi-Element Plasma Standards
Single element Standards
Fisher/Baker Standards; Nitric acid

Equipment:
Inductively Couples Plasma (ICP) spectrophotometer by SA Jobin Yvon, Model Ultrace 138
Gilson Autosampler
Gateway P5-120 PC
JYESS Software
Volumetrics
Pipettes
Polyethylene bottles

References:

Code of Federal Regulations Title 40, Part 136, Appendices A and B, U. S. Government Printing Office, Washington, D.C. 20402, 1991; EPA 200.7

Methods for the Determination of Metals in Environmental Samples, EPA/600/4-91/010, Office of Research and Development, June 1991, EPA 200.7

Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020, Environmental Monitoring and Support Laboratory, 26 W. Martin Luther King Drive, Cincinnati, OH 45268, Revised 1983, including EPA-600/4-84-017, March, 1984, EPA 200.7

Test Method for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, EPA, Office of Solid Waste and Emergency Response, 401 M St., S.W., Washinton D.C. 20460, November, 1986, including December 1987 and November 1990 updates. EPA 6010

Quality Assurance/Quality Control Manual, U. S. Filter/Enviroscan, 1997.

JY User's Manual, Reference 31 088 409

Interferences:

Positive Interferences are shown on Table 1: Interference Study on JY-138 Ultrace.

The negative interferences have little significance if the level of interferents is low or analyte concentration is high. The negative responses are a result of baseline fluctuation caused by the interferent or by a peak that occurs on or close to the background point. Most of the time the background points can be changed, but in a few cases they are unavoidable.

In either case (positive or negative interference) the problem usually can be solved by diluting and reporting a higher detection limit for the analyte or by choosing an alternate wavelength. In either case the detection limit will be higher than what is normally reported.

A summary of negative results is below:
1000 ppm Ca, Mg, Al; 400 ppm Fe causes a negative result for the following:
Se (196.090) of -0.058 ppm
Sb (206.833) of -0.027 ppm
Ag (328.068) of -0.027 ppm
Sn (242.170) of -0.062 ppm
Tl (276.787) of -0.085 ppm

100 ppm Cr, Cu, Ni, Ti, V, Mn cause a negative result for the following:
Sn (242.170) of -0.508 ppm Mg (279.079) of -0.797 ppm
Fe (238.204) of -0.153 ppm

400 ppm Fe causes a result for Cu (324.754) of -0.028 ppm

Table 1: Interference Study on JY-138 Ultrace

Element	Interferent	Concentration	Element Result-ppm	Cause of interference:
Zn (213.856)	Cu	100	0.205	Peak of Cu on Zn line
Zn (213.856)	Ni	100	1.243	Peak of Ni on Zn line
As (220.353)	Al	1000	0.600	Tailing of Al causes high reading for As; Cannot use two B.G. points due to other interferences
Pb (220.353)	Al	1000	0.009	Tailing from nearby peak. Problem solved by using two B. G. points.
Be (313.042)	V	100	0.116	V has peak close to Be peak; Causes tailing and high result for Be.
V (292.402)	Fe	400	0.134	Small peak very close to V line causes high result.
V (292.402)	Ti	100	0.100	Small peak close to V line.
Co (228.616)	Ti	100	0.202	Small peak close to Co line.
Sb (206.833)	Cr	100	0.825	Tailing from nearby peak.
Se (196.090)	Cr,Cu,Ti,V,Mn,Ni	100	0.011	Small peak which may be noise at this level.

Sampling, Preservation & Holding Time:

Sample Matrix	Container	Sample Preservation	Holding Time
Drinking Water	100 ml Glass or Plastic	HNO3 to pH <2.0	6 months
Wastewater	100 ml Glass or Plastic	HNO3 to pH <2.0	6 months
Soils	10 g of sample	Glass /no preservation	6 months

Guidelines:

The following steps are outlined for the start up and operation of the JY-138 ICP.

Instrument Start-up:

1. Turn valves on the argon tank to start gas flow (approximately 80 psi)
2. Check pressure on nitrogen tank (@ red line on the gauge.)
3. Press **P1, G1, and NEBU** keys on the front of the instrument to start argon flow
4. Hook up pump tubes and start pump to aspirate water
5. Wait a few minutes, then push the **NEBU** key again.
6. Turn OFF the pump and SLOWLY release the pressure from the argon humidifier using the black handle located on the inside left corner of the torch box.
   Note: The water level in the humidifier should be between the black lines.

7. After completing Steps 1-6, push the **START** key to ignite the torch.
   Note: The nebulizer flow must be **OFF** to start the torch.
8. Wait about one minute and press the **NEBU** key again to restart the pump.

   NOTE: THE INSTRUMENT MUST BE WARMED UP FOR APPROXIMATELY ONE HOUR BEFORE ANALYZING ANY SAMPLES.

Instrument Shutdown:

1. Press the **STOP** key and allow the instrument to cool down.
2. Press **P1, G1,** and **NEBU** keys to shut off.
3. Turn OFF the pump and unhook the pump tubes.
4. Turn the valves on the argon tank to shut off flow.

Computer Software:

This is a summary of the software for the JY-138 ICP. For specifics refer to the J-Yess Version 4.0 Software manual.

1. Turn on the computer and monitor to bring up the Windows screen.
2. Exit or close the messages on the screen. Double click on JY software icon.
3. Continue by touching any key to get the first menu screen
4. Pressing "↵" will give you the Main Menu of the software.
   Note: A zero order search will automatically be done when you press enter.
5. The "Shift F3" with no option change will automatically open the Autosampler option.
6. Press "F10" to choose autosampler.
   Note: This unit has a Gilson 222 autosampler.
7. Press the "esc" key twice to return to the Main Menu.
   The Main Menu contains the following options:
   - Methods
   - Preparation
   - Analysis
   - Results

Methods:

The Methods option is used to set up and modify the analytical files.
The options TMISC, TRCRA, TBESRB, and TWAR are described in detail on **Table 2:** Method Summary for the JY-138 Ultrace

Preparation:

The Preparation option contains: Autoattenuate, Autosearch, Profiles, and Calibration:

Autoattenuate sets the high voltage for the photo-multiplier tube for each element in the file or selected ones. Use the high standard for this option.

Autosearch locates the exact peak position and transfers the information to the software for the location of the offset peaks. Press "F10" to continue with the next element.
Note: This option is used for each method at the beginning of each day's run. If more than one peak appears on the scan the software will give a list of possible elements for each line.

Profiles allow you to see a scan of samples, standards, etc. The background points may be chosen for the analysis from the scans.

Calibration allows for the calibration of the method. Standard concentrations are listed On a separate summary page. Determine which standard will be analyzed by selecting "yes" or "no".

To SAVE the modification press "F8".
To SELECT elements press "F3".
To DISPLAY calibration curve press "F3".
To PRINT press "Shift ,Print Screen".
Note: If a standard is not selected you must exit the current calibration mode and start a new calibration procedure.

THE INSTRUMENT MUST BE CALIBRATED BEFORE SAMPLES MAY BE ANALYZED.

Analysis:

The software program allows for individual analysis or group analysis.
The **Analysis** option allows for a single sample to be analyzed.
The **Sample File** option allows for the analysis of one or more metals.

Results:

The Results option allows for the review of completed analysis.

EXIT SOFTWARE PROGRAM:

To Exit the program, go to the DOS prompt and type "exit". Press "Start/Shut Down" option to turn off computer.
Note: The monitor must be shut off separately.

Instrument Maintenance:

Flush the nebulizer with deionized water and air after each use. Check for clogging or chips and replace, if necessary.

QA/QC Information:

Each sample run (10 samples) shall have a check standard, matrix spike, matrix spike duplicate, calibration blank every ten samples. A reagent blank is analyzed daily for each prepped matrix.
Default limits of 25% for duplicates and 75-125% for matrix spikes are used until enough data has been collected to establish new limits. Samples shall be spiked at various concentrations depending on the elemets of interest and the sample concentration. Spikes or duplicates out of control shall be repeated, or the data shall be flagged on the bench sheet and final report.

NOTE: IF CHECK STANDARDS DO NOT FALL WITHIN THE LIMITS OF 5% AND 10% FOR EPA 200.7 AND EPA 6010, RESPECTIVELY, SAMPLES MAY NOT BE RUN UNTIL PROBLEM IS CORRECTED.

Glassware is washed thoroughly rinsed with acid and then with distilled water.
All quality control data is recorded appropriately and easily retrievable.

Calibration Standards:

The calibration standards are made up from the 1000ppm Plasma stock solutions. Add one ml of 1:1 HNO_3 per one liter of total standard volume. All dilutions are made with Modulab deionized water. The final standard solutions are stored properly labeled polyethylene bottles. The calibration concentration tables used for each task file are listed in Table 2: Method Summary for JY-138 Ultrace.

The calibration standards are verified after every calibration using the SPEX multi-element plasma standards. The standards are analyzed at different concentrations depending on the element being checked and the concentration range of the task file. The SPEX standard must be within 10 % of true value.

Reagent Blanks:

The reagent blanks are prepared by taking 100 ml of deionized water and carrying it through the complete metal digestion process. Blanks are run for the liquid prep, the solid prep, and for the recoverable prep. Reagent blanks are analyzed on every prepped sample run. The reagent blank is dependent on the sample matrix and prep performed.

Check Standards:

A check standard is used for each task file and has a concentration approximately in the middle of the calibration range. The check standard must be within 10% of the true value for EPA 6010 and 5% for EPA 200.7. The check standard is independent of the calibration standards.

Method Detection Limits:

Method detection limits are conducted according to method EPA 200.7, EPA 6010 and 40 CFR Part 136 Appendix B. Current MDL attached to this procedure.

Calibration Instructions:

Calibrate the instrument according to JY-138 Ultrace User's Manual. The system is flushed out with a blank between each standard. An average intensity from three readings of each standard is used to reduce random error.

Reporting Data:

Samples that require dilutions are entered in the autosampler file and the final dilution result is checked against the initial analysis of the concentrated sample and a comparison is made between the two sample results. Data is reported in mg/l to three significant figures.

Summary:

Below is an analyses summary of a sample set:

1. Start instrument, let warm up, and do the zero calibration
2. Choose the Task file desired and set up autosampler file from bench sheet. (see attached.)
3. Calibrate the instrument and verify calibration
4. Analyze the samples. Review data for interferences and initial concentrations.
5. Print out a concentration and dilution report page. Review final data for errors in detection limits and dilution factors.
6. Enter final results into LIMS system.

Bench Sheet and Final Report:

Use the following codes on bench sheets and final report pages:

chkstd:	Check standard
blk	Calibration Blank
RB(DATE)LIQ:	Liquid prep reagent blank with date prepared
RB(DATE)SOL:	Solid prep reagent blank with date prepared
R (Analytical #):	TCLP extract
(Analytical #)r:	Recoverable prep
(Analytical #)FUS:	Fusion
(Analytical #)s:	Soluble metals
(Analytical #)DUP:	Duplicated from the same prepped container
(Analytical #)DUP PRE:	Prepped in duplicate
(Analytical #) + #:	Spiked straight from the container
(Analytical #) + # PRE:	Spiked sample before prepped

Reviewed by: ____________________

Approved by: ____________________

Wisconsin Department of Natural Resources
STS Project No. 4-27393

Appendix F

In-situ, Inc. miniTROLL Datalogger Device

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PRODUCTS
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Did you know that all of In-Situ's instruments can be rented?

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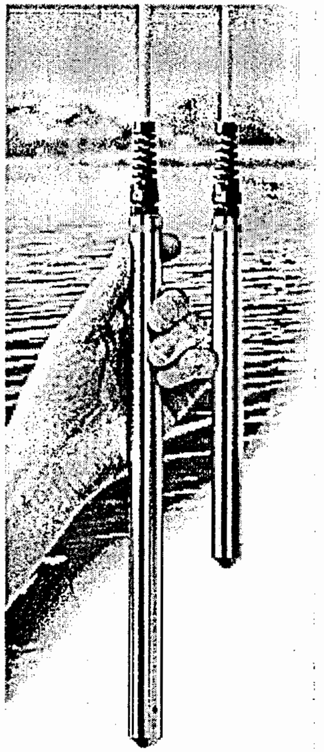
miniTROLL



Need to collect real-time, accurate data for the analysis of water level trends?

The **miniTROLL** is self-contained and completely submersible and it features the smallest diameter at only 0.72 inches (18.3mm)! The **miniTROLL** is used by water professionals around the world to collect real-time information for analysis of both short- and long-term water level trends.

Features:

- **Smallest diameter at only 0.72 inches (18.3mm)**
- Powerful onboard data logger
- Internal memory - up to 1MB (440,000 data points)
- Linear, linear average, logarithmic, and event logging modes
- **User-replaceable AA batteries** - no need to return to the factory!
- High quality **vented Quick-Connect cable** (FEP or Polyurethane) - Fully detachable!
- Ultimate 4-way pressure compensation including **automatic** barometric compensation
- **Optional stainless steel backshell for cableless applications or suspension by low-cost wire**
- Real-time crystal clock
- Networking and telemetry capable
- Accuracy certified to NIST-traceable standards
- Multiple product versions - select only the features you need to match your budget
- Always upgradeable!

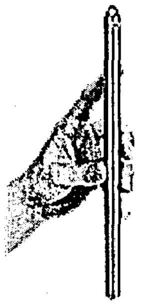
Measures

- **Water level**
- **Temperature**

What makes the miniTROLL the best choice for short-term or long-term water monitoring?

Powerful and Important Features
Easiest To Use
Exceptionally Reliable
Highly Accurate
Useful Features and Field-Upgradable Options
Excellent Value
Powerful Versions for Every Application

NEW! Be sure to check out the low-cost miniTROLL Standard-A! Deploy it without cable by using a stainless steel backshell.



Why do water professionals choose the miniTROLL?

Powerful and Important Features are the reason!

- Completely self contained and fully submersible
- Smallest Diameter - only 0.72 inches (18.3mm)!
- Internal data logger
- Non-volatile memory (up to 1MB - 440,000 data points)
- Temperature compensated pressure sensor
- Optional temperature sensor
- Internal power - user-replacement AA batteries
- Protection for lightning and surges
- Real-time crystal clock
- RS485 and/or SDI-12 communications capabilities

Easiest to use
In-Situ instruments are famous for their ease-of-use and the miniTROLL is no exception. With intuitive Windows-based Win-Situ software you will be able to operate the miniTROLL right out of the box. We have designed the software to be intuitive, with Wizards to step you through every operation. The miniTROLL puts our 25 years of experience into a field-proven tool, used by water professionals in virtually every profession.

- User Replaceable Batteries! **(Most Ecological and Economical Choice)**
- Built-in **Barometric Compensation** options
- More Options!! - **Gauged** (vented) and **Absolute** (non-vented) options
- **Direct-Read** and **Wire Suspension** Options
- No need to merge data sets for temperature and pressure
- Powerful and Easy to Use Software
- Upgradable via the Internet
- Version Upgradable - even downhole!
- Watertight Pocket PC and Windows interface
- 24/7 Customer Service

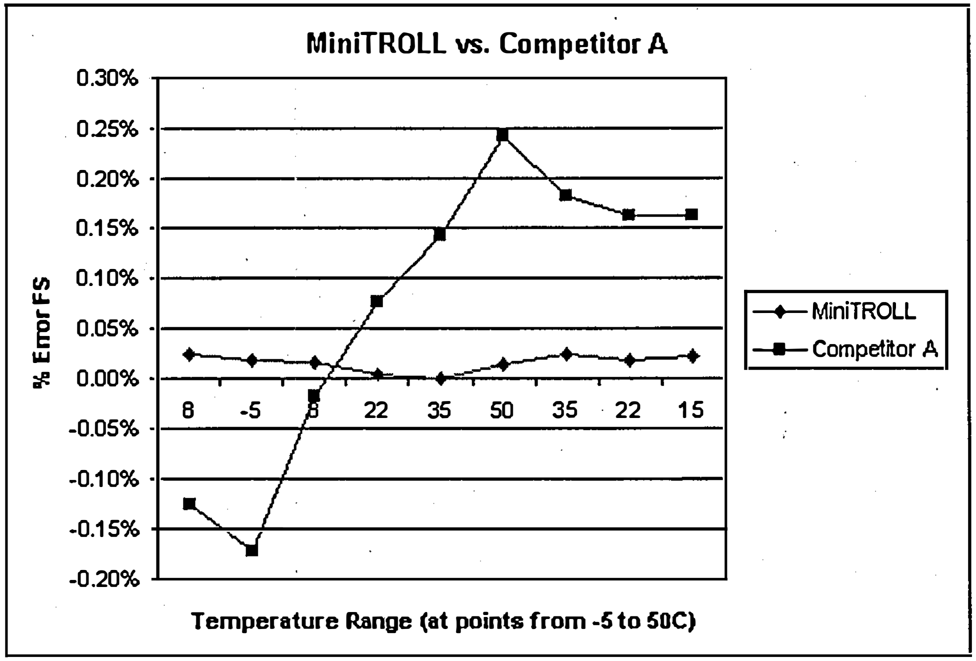
Exceptionally Reliable
The miniTROLL has been deployed for years in all corners of the earth. We continuously improve the miniTROLL in both hardware and software design to give the customer a tool that is the most current, powerful and has the lowest cost of ownership. Many of the features that make miniTROLL reliable are hidden behind the scenes in our extensive Quality Control and manufacturing process. Other items you may be interested in are built-in and designed to give you a tool that is engineered for years of trouble-free and effortless monitoring. These features include:

- 316L Stainless Steel Body (far more durable than plain 316 stainless)
- Non-Volatile memory
- Motorola HC11 Processor
- Super-Accurate, Real-time Crystal Clock (More Accuracy Means Less Error)
- Digitally Compensated, Media Isolated Silicon Strain-gauge Pressure Sensor
- Pressure Rating: 2x range / 3x burst
- Up to 6years of Data Logging Capability at 15 minute intervals
- FEP(Teflon Equiv.) Cable Option for Harsh Environments
- Operating Temperature: -5C to 50C

Highly Accurate - A discussion our competition would rather not have
Our Customers and their clients demand **accuracy** *and* **precision**. The miniTROLL has been extensively tested against competing units in every operating environment known. The result? The miniTROLL is considerably more accurate. Our published specifications are very conservative and reflect our high regard for the integrity of data in all environmental conditions, not just the lab. We stand behind our accuracy by providing a **calibration report** with EVERY miniTROLL. Some competitors do not include an calibration report. Why? Their accuracy is simply an average of poor accuracy readings (see chart below). They can honestly say their Full Scale specification is good due to the "cancellation" of the negative and positive errors or an average of the pressure readings over temperature.

- Pressure Accuracy: **0.05%fs** @15°C and 0.1%FS over entire range
- Temperature Accuracy: +/- 0.25C over entire range
- Resolution: **16-bit** A-D converter: 1mm (0.00531%FS) for a 30-psi sensor
- Automatic Barometric Compensation
- Automatic Temperature Compensation -- across the full temperature range from -5 to 50°C
- Fluid Density Correction
- Gravitational Acceleration Correction
- Liquid Density Correction
- **NIST-Traceable** Calibration

You decide--have a look at a graph below that shows unbiased data from an environmental test between the miniTROLL and a competitor. Even though the written specifications are similar, environmental testing shows there is a substantial difference. WHICH instrument would you trust with YOUR readings? In many cases the accuracy of our instruments will be much greater than our specifications, giving you assurance that you have chosen the right tool for the job.



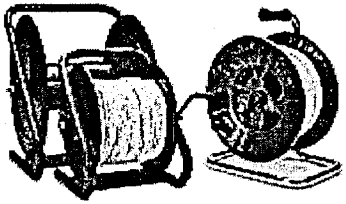
Useful Features and Field-Upgradable Options
In designing the miniTROLL, as well as in our ongoing product support, we incorporate a philosophy of providing features that our customers will use and appreciate. It does not matter whether a product is the shortest, best-looking or most powerful. In the end, the product must perform flawlessly and effortlessly in the harsh environment of the real-world. Our extensive Marketing Research and world-class Research and Development team constantly test new product improvements and options in the real-world, with feedback from real-world users. This effort has enabled In-Situ to provide our customers with a menu of options to suit their needs as well as budget. All of the miniTROLL products share the same proven technology in both body and internal component materials. Our options simply give you the choice of the right tool for the job. The miniTROLL is also field-upgradeable(even downhole!), should the job requirements change. Here are some of the many optional additions to your toolkit.

Sensor Options

- Pressure Only
- Temperature Only
- Temperature and Pressure
- Gauged or Absolute (Vented or Non-vented respectively
- All probes are fully temperature compensated
- 15, 30, 100, 300 and 500-psi (0-351m, 0-1152 ft)

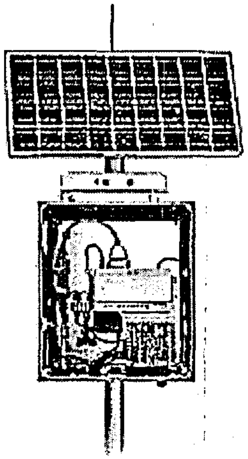
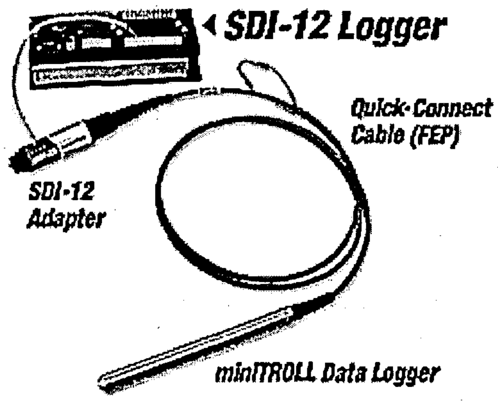
Suspension and Device Integration Options

- Cable Suspension
- Poly or FEP Direct-Read Cable
- NPT Threaded nose cone option for direct-pressure



Communications Options

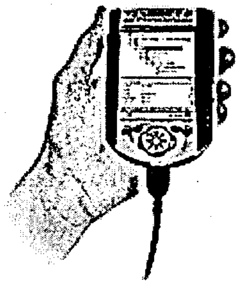
- RS232
- RS485
- SDI-12
- Telemetry (Modem, Radio,
- Internet
- Fully Networkable
- 3rd-Party Integration

Telemetry Systems	SDI-12 Communications
	

Programming and Data Collection Interface Options

- Portable and Watertight Pocket PC
- Laptop/Desktop PC
- Internet
- 3rd-Party Integration
- Open Software Designer Architecture
- Multiple language support
- Microsoft Windows and Pocket PC Interface that is powerful and

Pocket-Situ running on the Compaq iPAQ Pocket PC



Tests and Test Logging Options

- Linear Tests
- Linear Average Tests
- Event Tests
- Log Tests
- Up to 0.5 second minimum sampling rate
- Download only new data (no wrap around)
- Up to 16 tests scheduled to run or stored
- Up to 440,000 data points stored (220,000 x 2 channels)

Excellent Value - Add the features Up, Try it Today!

The answer is simple: The miniTROLL combines powerful functionality and In-Situ reliability with affordable versions. Sure, there are many competitive products. When you add up features & benefits, which unit comes out ahead ? **How important Is your data?**

- ▷ Affordable, Reliable and very Easy-to-use, the **miniTROLL** is being used by water professionals to collect precise information for analysis of both short- and long-term water level trends.

Touch the future. Experience the technology. The miniTROLL will change the way you monitor.

The miniTROLL is now available in four versions
Choose the version best suited to your needs.

miniTroll Versions	**SDI-12 Pressure**	**SDI-12 Press/Temp**	**Low-Cost Standard-A**	**Standard Temperature**	**Standard Pressure**	**Advanced**	**Professional**
Pressure channel	•	•	•		•	•	•
Temperature channel		•		•			•
SDI-12 Communications	•	•	Optional	Optional	Optional	Optional	Optional
Temperature compensation	•	•	•	•	•	•	•
Barometric compensation	•	•			•	•	•
Fluid density compensation						•	•
Internal Data logging			•	•	•	•	•
Memory (data points)			30,000	30,000	30,000	80,000	220,000
Number of tests stored			1	1	1	2	16
Linear tests			•	•	•	•	•
Linear average tests						•	•
Event tests						•	•
Log tests							•
Min sampling rate (sec)			0.5	0.5	0.5	0.5	0.5
SDI-12 Min samp. rate (sec)	2	2	2	2	2	2	2
Telemetry capability						•	•
Networking capability	•	•					•
Download speed				1X	1X	2X	3X
Downloads only new data						•	•
Upgradeable	•	•	•	•	•	•	

- Click here to order a free **miniTROLL** brochure!
- Need more information? Take a guided tour of the miniTROLL

TERMS OF INTEREST

Gauged (vented) Option. Automatically compensates for atmospheric changes:

Vent to atmosphere. Why? - Forces on both sides of the pressure transducer are equalized, providing a more accurate reading relative to ambient atmospheric pressure.

Compensate for Barometric Changes. Why? - As barometric pressure changes, water in an enclosed aquifer will rise and fall in response to the change. This phenomenon will introduce a margin of error in your readings if not compensated and primarily affects tests conducted in enclosed aquifers.

All of the electronics and sensors are completely self contained in the Gauged miniTROLL version. This configuration is exceptionally durable and made to withstand years of exposure to harsh downhole conditions. By using a tool with everything you need built in, it Increases Accuracy, and Reduces Time and Effort to merge barometric data reading corrections to get "True" water levels.

Absolute (non-vented) Option:

No Need to Compensate for barometric changes in some tests. Why? - When monitoring an open body of water, or a pressurized water column, there is no need to compensate for barometric pressure. In the open body of water, the affects of the change in barometric pressure are insignificant, relative to even the high accuracy recorded by the miniTROLL. When monitoring a pressurized water column, changes to outside atmospheric pressure will usually be of no significance to your test.

All of the electronics and sensors are completely self contained in the Absolute (non-vented) miniTROLL version. The Absolute miniTROLL may be suspended by either a stainless steel wire or direct-read cable option. This configuration is exceptionally durable and made to withstand years of exposure to harsh downhole conditions. By using a tool with everything you need built in, it Increases Accuracy and Reliability.

Direct readings

Don't need to remove unit from well to get readings. Why? - In many cases you will not want to disturb the transducer once you have started to take readings downhole. The Reliable, Watertight and Easy to Use direct-read cable option for the miniTROLL allows you to see everything the miniTROLL is detecting and recording with a simple twist of a connector at the wellhead. By utilizing the direct-read cable option to examine either real-time or recorded downhole data, your miniTROLL will remain in the exact same place as when you first positioned it. Your data will be far more accurate. Here are some more reasons to use the simple direct-read option for the miniTROLL:

- Readings may be offset upon reinstallment
- Unit may be contaminated and unwise to handle
- More chances for unit to snag in well
- Difficult to reposition
- Easy to collect data
- Can connect to telemetry systems / 3rd-party data loggers / Online / Automation

Wire Suspension (non-direct reading)

In some cases, you will want to suspend your Absolute (non-vented) miniTROLL by a thin stainless steel wire. You will want to employ this method when:

- Least Cost is an issue
- Very High Security is an issue
- Well contamination may prevent introduction of poly or FEP downhole cable.
- Longer term monitoring is being employed
- Atmospheric compensation is not an issue

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SCHEDULE - KEWAUNEE MARSH SITE
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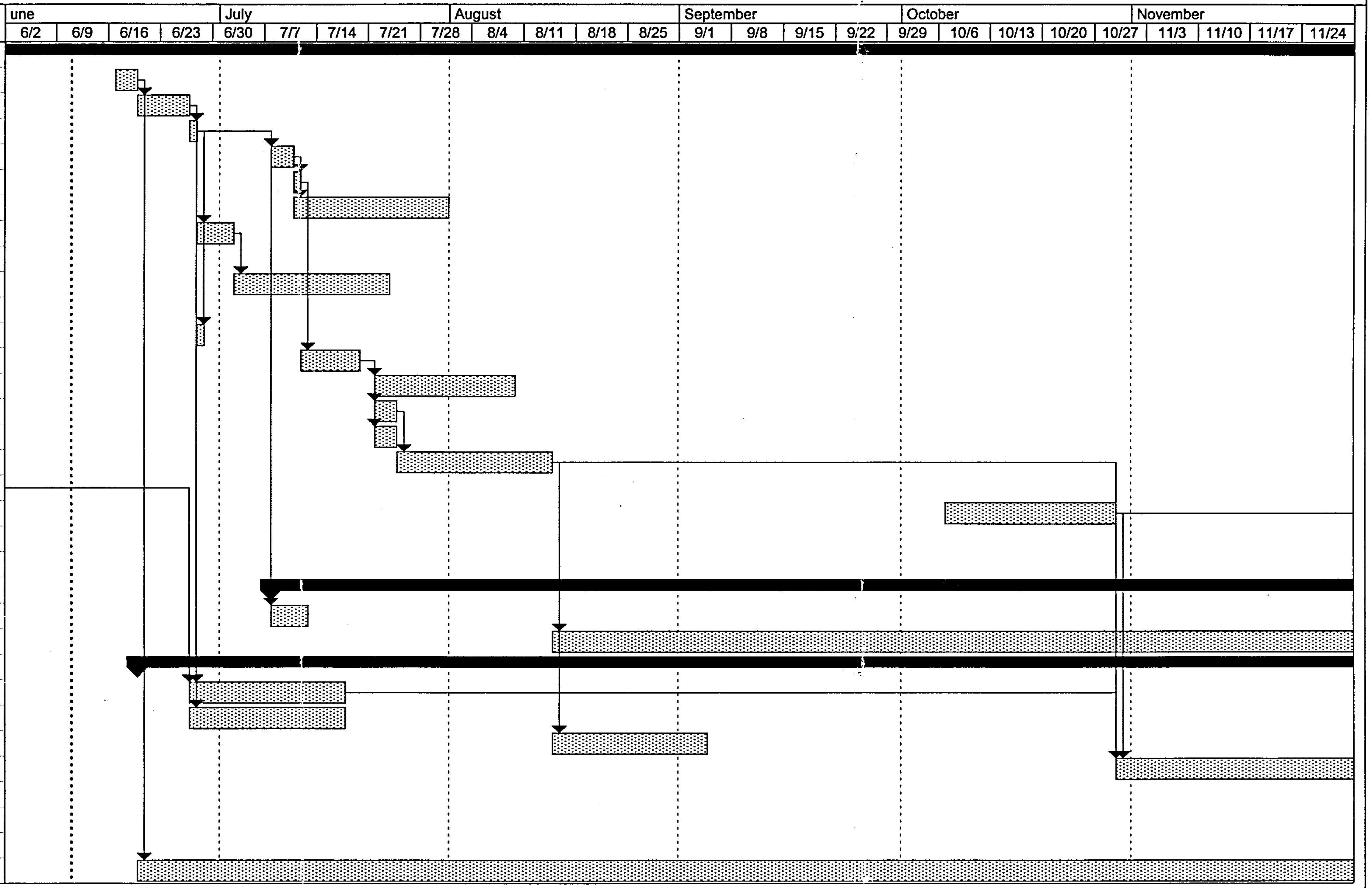
STS CONSULTANTS, LTD.

ID	❶	Task Name	Duration	Start
1		**TASK 2: Site Investigation**	**351 days**	**Tue 1/1/02**
2	▦	Review State Contract Agreement	3 days	Mon 6/17/02
3	▦	Project Set-up/Coordination	5 days	Thu 6/20/02
4	▦	Initial Project Meeting	1 day	Thu 6/27/02
5	▦	Soil Borings and Soil Sampling	3 days	Mon 7/8/02
6	▦	Grain Size Distribution Testing	1 day	Thu 7/11/02
7	▦	Chemical Analysis of Soil Samples	15 days	Thu 7/11/02
8	▦	Surface Water Sampling - Summer/Fall Conditions	3 days	Fri 6/28/02
9	▦	Surface Water Sampling - Spring Runoff Event	2 days	Mon 4/14/03
10	▦	Chemical Analysis of Surface Water Samples - Summer/Fall	15 days	Wed 7/3/02
11	▦	Chemical Analysis of Surface Water Samples - Spring	15 days	Wed 4/16/03
12	▦	Installation of Water Level Indicators (3)	1 day	Fri 6/28/02
13	▦	Groundwater Monitoriong Well Installation	6 days	Fri 7/12/02
14	▦	Groundwater/Surface Water Elevations	15 days	Mon 7/22/02
15	▦	Groundwater Sampling	3 days	Mon 7/22/02
16	▦	Field Hydraulic Conductivity Tests and Data Reduction	3 days	Mon 7/22/02
17	▦	Chemical Analysis of Groundwater Samples	15 days	Thu 7/25/02
18	▦	Survey/Cap Evaluation	5 days	Tue 1/1/02
19	▦	Surface Water Elevations/Groundwater Monitoring - 4Q02	17 days	Mon 10/7/02
20	▦	Surface Water Elevations/Groundwater Monitoring - 1Q03	17 days	Mon 2/10/03
21	▦	Surface Water Elevations/Groundwater Monitoring - 2Q03	17 days	Mon 4/7/03
22		**TASK 4: Data Management**	**118 days**	**Mon 7/8/02**
23	▦	GIS Basemap Development - Historical Data	5 days	Mon 7/8/02
24	▦	GIS Maitenance and Update	90 days	Thu 8/15/02
25		**TASK 5: Report Preparation**	**226 days**	**Thu 6/20/02**
26	▦	Base Map Preparation	15 days	Thu 6/27/02
27	▦	Review Previous Modelling Efforts	15 days	Thu 6/27/02
28	▦	Remediation Alternatives Review	15 days	Thu 8/15/02
29	▦	Prepare Draft Report	45 days	Wed 10/30/02
30	▦	WDNR/FVWR Group Review	10 days	Wed 1/1/03
31	▦	Report Review Meeting	1 day	Wed 1/15/03
32	▦	Finalize Report	37 days	Thu 1/16/03
33	▦	Project Management	226 days	Thu 6/20/02



Project: Schedule_KM
Date: Tue 6/11/02

Task	▨	Milestone	◆	Rolled Up Split	┈┈┈	External Tasks	▨	Deadline	⇩
Split	┈┈┈	Summary	▬	Rolled Up Milestone	◇	Project Summary	▬		
Progress	▬	Rolled Up Task	▨	Rolled Up Progress	▬	External Milestone	◆		