CORRESPONDENCE/MEMORANDUM — **State of Wisconsin**

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FROM: Tom Janisch - WR/2 Tom J.
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SUBJECT: Update on the June 26-27, 1995 Soil and Water Sample Analytical and Toxicity Testing Results and Other Observations from the C.D. Besadny Wildlife Area

We have received the arsenic results for the soil and water samples collected from the Kewaunee Marsh on the above dates. We have also received the toxicity testing results where organisms were exposed to the collected soil and water samples. The objectives for the sampling design were outlined in our earlier July 6, 1995 memo.

This memo will briefly discuss the results of the chemical testing and other observations. The toxicity testing results are currently undergoing statistical evaluation to determine the significance of the results and we will provide these at a later date. All of the biological and chemical data, when available, will need to be integrated and interpreted to determine its ecological significance.

Soil Arsenic Levels

Soil samples were collected at five study sites and one upstream reference site. The sample locations are shown in Figure 1. The reference site was in a wetland 200 feet upstream of County Highway E along the right downstream side and approximately 50 feet from the river. A site was selected that had similar soil and vegetation characteristics to the study sites. The objective of the selection of the study site sampling locations was to expose the organisms in the toxicity testing to a range of arsenic concentrations in the soil and water. Previous STS soil sampling results were used to select sites that had a range of arsenic concentrations in the soil. A shovel was used to collect 6-8 inches of surficial soil material to fill a five gallon bucket. The soil material in the bucket was homogenized at the toxicity testing lab prior to placement in the test chambers. A subsample of the mixed soils was taken for chemical analysis. The results of the soil arsenic analysis at the six sites is shown in Table 1 and placed on Figure 1 to show the spacial relationships of the sampling sites. The previous STS sampling results that were used to select the WDNR sampling sites are also shown in Table 1.

Soil sample sites KM-2, KM-4, and KM-5 were located in sedge (Carex sp.) dominated vegetational areas. Sites KM-3 and KM-6 were in cattail (Typha latifolia). The reference site was in a reed canary grass (Phalaris arundinacea) - cattail area (Typha latifolia). The particle size fractions and percent solids of the samples is shown in Table 2.

The percent solids of the soil samples in Table 2 appear low based on the visual appearance of the collected material in the field. The collected materials were generally above the water table and appeared to have a consolidated structure. A sediment sample taken in a river at this low a level of solids content would be much more fluid. One way to explain this is the tremendously high water absorptive capacity of the organic material in the soil samples along with roots and plant detritus allows the material to wick up and hold water from the groundwater and retain its structure.

The sand size particle fraction makes up approximately 50% of the soil particles in the samples except for KM-1. The soil textural designation in Table 2 is based only on the relative percent of the particle size fractions present and does not consider organic matter content. The actual soil classification for the site does consider the organic matter content and formation processes. Based on visual appearance and texture in the field, coarse sands were not noticed so sands in the samples must have been of a small size, not much larger than silt size particles.

While the DNR samples were a composite of the top 6-8 inches of soil, the STS samples were a composite of the top 24 inches of soil. The differences in the thickness of the soil segments composited may account for the differences in arsenic concentrations between the DNR and STS results. The DNR samples were collected as close as possible to the STS sampling locations as could be determined. The DNR samples showed arsenic in the top 6-8 inches were less than the arsenic levels in the STS composited 24 inches. This may mean that within the 24 inch segments, arsenic concentrations are greater in the lower portions of the segment than in the surface levels. Based on a weighted average calculation, the possible arsenic concentrations in the lower 18 inches of the 24 inch segments is shown in Table 1 in parentheses under the STS soil column. Also the ordering of the sites from highest to lowest arsenic concentrations changes when surface values are compared to the 24 inch segment values. While the DNR arsenic results in the top 6-8 inches were less than the STS composited 24 inch segments, they still provided a range of arsenic concentrations, although somewhat lower, to expose the test organisms to.

The soil samples taken at KM-2 which is south of the tracks, off of the spur, has arsenic (91 mg/kg) at a comparable level than what was found earlier by STS to the east along the south side of the main tracks (93 and 112 mg/kg). All of these levels in the soil on the south side of the tracks are approximately 25 times greater than background. The association of relatively high groundwater levels of arsenic at sites south of the tracks may mean that arsenic is being transported in groundwater from the main impact area north of the tracks and being absorbed to and contaminating wetland soils south of the tracks. This will be further discussed below.

<u>Water Arsenic Levels</u>

With the exception of KM-2, water and soil samples were not collected at the same sites. At KM-2, the groundwater table was just below the ground surface and the water sample was collected in the hole excavated when soil samples were collected. At other study site sample locations on the north side of the tracks, the water table was below the 6-8 inch excavated soil depth. For water sample sites KM-3 and KM-6 between the impact area and the river, water samples were taken in remnants of dug ponds that were present. The ponds were apparently dug in the past for waterfowl and have filled in with floating mats of cattail. However, water samples could be collected from surface water above the mats. Water sample sites KM-4 and KM-5 were taken in two of the series of twelve wildlife ponds that are to the north of the impact area.

These ponds generally have not filled in with floating mats of emergent vegetation, as the ponds to the east. Figure 2 shows the general locations and numbers that have been assigned to the ponds for reference purposes along with water sample site designations.

The upstream water sample reference site was taken in the Kewaunee River near the reference wetland soil sample site. Arsenic analysis was run on unfiltered water samples at all sites. This is appropriate based on the need to apply water quality criteria to total arsenic values. On a visual basis, the water sample taken at KM-2 had the highest total suspended solids based on collecting the water sample from the dug hole.

The results of the water sampling are shown on Table 1 and displayed on Figure 2. The results are the first to give some idea of the surface water quality on the site aside from the most impacted area and the river previously reported by STS. The background level of arsenic in water was found to be 3 ug/l. The sampling result of 500 ug/l in the groundwater at KM-2 south of the railroad tracks is comparable to and confirms STS's earlier finding. A contaminated arsenic plume appears to be moving off the impacted area north of the tracks and moving in an easterly to southeasterly direction. At sampling sites east of the impacted area, arsenic levels in the remnant pond water goes from 860 ug/l at KM-6 to 370 ug/l at KM-3. If the pond arsenic concentrations are somewhat reflective of groundwater quality, concentrations appear to decrease as the river is approached. It is noted that a past STS water sample (BKG-2) taken on the south side of the tracks near the river had an arsenic concentration of 398 ug/l. It would appear the wetland near-river groundwater concentrations to the east and southeast of the impact area approach 400 ug/l.

Whether the pond water quality represents groundwater quality will have to be further assessed. Arsenic levels in the pond water may be subject to different physico-chemical conditions than present in the groundwater.

To the north, the water sample in Pond 12 (KM-5), which is nearest to the second dead area had an arsenic concentration of 3400 ug/l. The arsenic levels in the pond to the north of Pond 12, Pond 6 (KM-4), was 62 ug/l. This represents a considerable decrease in water arsenic concentrations. It should be noted that based on STS soil samples between Ponds 12 and 6, arsenic soil levels are still elevated in this general area (B-12, 324 mg/kg in 0-24 in segment, where WDNR surface sample had 35 mg/kg).

The hydraulic conductivity of the arsenic contaminated groundwater depends on the physical and resulting hydrological characteristics of the organic peat materials in the wetlands soil profile at depth. The hydrological characteristics of the organic material are closely related to the degree of decomposition and compaction of the material. Fibric peats can have a hydraulic conductivity as high as 4.0×10^{-2} cm/sec (120 feet/day). Well decomposed sapric mucks can have a hydraulic conductivity as low as 7.0×10^{-6} cm/sec (0.02 foot/day) or 1000 times less than fibric peats. Hydraulic conductivity may decrease with depth in the soil profile because the most decomposed and compacted muck is potentially found there. The STS data generally shows that in core samples the greatest arsenic soil contamination in the top 2 feet of the soil profile and gradually decreasing through the 4-6 foot substratum levels. At the 6-8 foot depth, arsenic concentrations decrease in most cases to background levels. The STS textural description generally indicates the 6-8 foot depth is made up of mucky peats and organic material above this is described as peats. It can be conjectured that arsenic contaminated groundwater is moving horizontally through the 0-6 foot depth of the soil profile, made up conductive fibric and hemic organic matter and moving minimally or not at all in lower substrata dominated by sapric organic material. Based on our limited observations, it appears the groundwater table is below the soil surface for a large part of the year (may vary from year to year). This may be the reason why surficial soil levels of arsenic are lower than deeper horizon concentrations. There is not a constant movement of contaminated groundwater horizontally through surficial (6-12 inches) soil materials. When standing surface waters are present in the wetland they may originate primarily from precipitation or high river levels.

For comparison purposes, water quality criteria values for arsenic generated by Beth Goodman, the Water Quality Unit Toxicologist, in a July 25, 1995, memo are shown in Table 2 compared to the June water sample arsenic levels. Generally all results except KM-1 represent potential problem levels to aquatic life and wild and domestic animals. Human health concerns are generally not as great for ingestion because neither site waters nor aquatic life are ingested by humans. However, there are concerns with direct dermal contact with soils and inhalation of dusts containing high arsenic levels. Movement of arsenic off-site and into the river and uptake of fish and uptake by arsenic by waterfowl on-site and subsequent ingestion by humans needs to be further assessed.

It is not known if the conditions are ever present in the soils and water of the site, especially in the high arsenic concentration areas, for the potential generation of toxic levels of arsine gas. Generally, arsine gas (arsenic hydride) can exist only in acidic, oxygen depleted environments. While the latter is present, soils and water in the wetland are generally alkaline. Some ponds where Sphagnum sp. moss was present may indicate more acidic conditions. The high arsenic areas may also alter the media pH. Sulfate reduction may also influence acidity. Conditions may be present for the generation of other gaseous forms of arsenic.

We have recommended in our suggestions on the draft consent order language that the railroad be required to fill in ponds such as numbers 6 and 12 and the pond remnants to the east of the impacted area if they are judged to present potential routes of exposure to wildlife and aquatic life at harmful levels. The water arsenic levels would indicate this to be the case. The results of toxicity testing may further back this up.

Other Site Observations

We had the opportunity to visit the site in April, May, June, August, and November during 1995. The April and November trips were primarily to observe the status of water levels in the dead areas and over vegetated areas of the wetland, amount of migratory waterfowl use, and if any freshly killed carcasses were present. Other than the herring gull picked up in May just off the first dead area, no other dead water birds were observed. The greatest amount of surface water seen on the first dead area was approximately 30% coverage in April and again in November. The rest of the first dead area remained unvegetated and the soil surface level was above the water table. Our August visit was preceded by at least a month with no rain and the entire soil surface of the dead areas were dry and cracked. We augured holes at approximately at 100 foot intervals along a transit from the east end of the second dead area to the river and found the water table at 1.3, 1.4, 1.3, 0.7, and 0.9 feet below the soil surface. If we would have allowed adequate time for the water level to equilibrate in the augured holes, the water table elevation may have been slightly closer to the soil surface. At the same time, water levels in the ponds were checked. Some ponds had hydrology dominated by groundwater and other ponds were dominated by surface water. Most of the pond levels were down showing a summer drawdown effect. In some ponds the water level had dropped below the bottom of the ponds leaving them dry or almost dry (Ponds 6 and 10). Some ponds, such as Pond 12, appear to have a stable water level with no drawdown effect. Some ponds have evidence of being in areas of groundwater discharge such as Ponds 1 and 9 on the west side which were either dominated by Chara sp., had high clarity, or were moderately stained.

The seasonal ground and surface water table fluctuations will play a role in the availability of arsenic and opportunity for exposure by water birds, wild and domestic animals, and aquatic organisms. In flooded and waterlogged soil conditions, the reduced, trivalent more toxic form of arsenic (arsenite, As^{+3}) which is soluble, is formed and dominates. In its reduced state, arsenic is 4-10 times more soluble than in the oxidized state in soils. Assuming conditions in the peat below the water table are anaerobic, arsenic will be in its more soluble reduced form and move with the groundwater flow. The presence of sulfides and phosphates in the anaerobic wetland soils may reduce the amount of soluble arsenic.

On our August visit to the site we took some baseline water chemistry measurements from the ponds and the river. This data is shown in Table 4. Also included in Table 4 are pH, alkalinity, and hardness readings from the June water sample sites. These latter measurements were taken in the lab two days after the water samples were collected and may be slightly different than if they had been taken in situ.

The values in Table 4 reflect typical values for wetlands in carbonate rich fertile areas of the state. The majority of total dissolved solids measured by specific conductance are contributed by components that make up alkalinity. Specific conductance is fairly well correlated with the fixed CO_2, pH, calcium and magnesium content of water. Conductance parallels the seasonal fluctuations of total alkalinity. High specific conductance beyond what would be expected from a given alkalinity would indicate the presence of ionic components other than carbonates. From the readings in Table 4 there is nothing to distinguish that specific conductance for some of the sites such as KM-5 (Pond 12 at 3400 ug/l arsenic) with high arsenic water levels are contributing perceptively to the specific conductance measurements. This may change if water samples were taken on or near the main arsenic impact area.

Dissolved oxygen levels in the ponds vary depending on the vegetation and surface water cover. Ponds (Ponds 1, 2, 9) with the highest oxygen levels (generated by photosynthesizing plants) have dense stands of submergents (Utricularia sp. and Chara sp.) in clear water. Ponds with relatively low dissolved oxygen levels (Ponds 7, 8 , 12) generally have dense covers of vegetation on the surface (such a duckweed and algae) that prevent light penetration and submergent plant photosynthetic oxygen generation. The lowest oxygen level in all the ponds tested was found in Pond 12. Of the ponds tested for arsenic, Pond 12 had the highest arsenic concentrations in the water. Since this pond's oxygen levels are approaching anaerobic and may already be anaerobic in the lower portions of the water column, the reduced more toxic form of arsenic may be present. For the above reasons, it will be important as part of the interim action to fill pond 12 to eliminate the open waters in this pond and potential exposure to the more toxic forms of arsenic by aquatic organisms and wildlife.

Future Work

1. When soil and water toxicity testing results are available, they will be integrated with the chemical data and a preliminary ecological risk assessment report will be generated.

2. BWRM has committed to doing, at a minimum, $30,000 of in-time services for pre- and post-interim action implementation monitoring. Chemical and biological components will be a part of the monitoring design. Design of biological and chemical monitoring studies are currently under consideration.

3. We have suggested wording for the draft consent order to Joe Renville for the partnered monitoring for the railroad. We are depending on the railroad to do most of the groundwater and river water monitoring for arsenic. To collect needed information, we may need to install our own driven point wells, survey them in and conduct the monitoring as in-time monies allow. Gaining information on the hydrology and potential contaminated ground water arsenic loading, direction, and movement is critical for this site. It will be important to know the groundwater characteristics and site hydrology to assess the impact of the interim action. On a worst case basis, it can be speculated that the weight of the wood chips placed on the high arsenic concentration areas will a) push the highly contaminated surface materials deeper and into more prolonged contact with the groundwater table, and b) the wood chip coverage will promote highly anaerobic conditions and very low redox conditions which in turn will increase the reduced more soluble, toxic form of arsenic to be picked up in the groundwater flow and reach surface water areas of the wetland and river.

4. A wetland assessment is currently being conducted which will document existing conditions. The wetland assessment will include a general description of the hydrology, soils and vegetation within the wetland complex. It will also describe the wetlands' functional values. The wetland assessment will fulfill the requirements of analysis under NR 103 which is needed for the issuance of the U.S. Army Corps of Engineers section 404 permit. Additional information regarding available alternatives, potential impacts and floodplain analysis will be required to adequately document NR 103 compliance.

If you have any comments or questions or would like to discuss the future status of the site, please give us a call.

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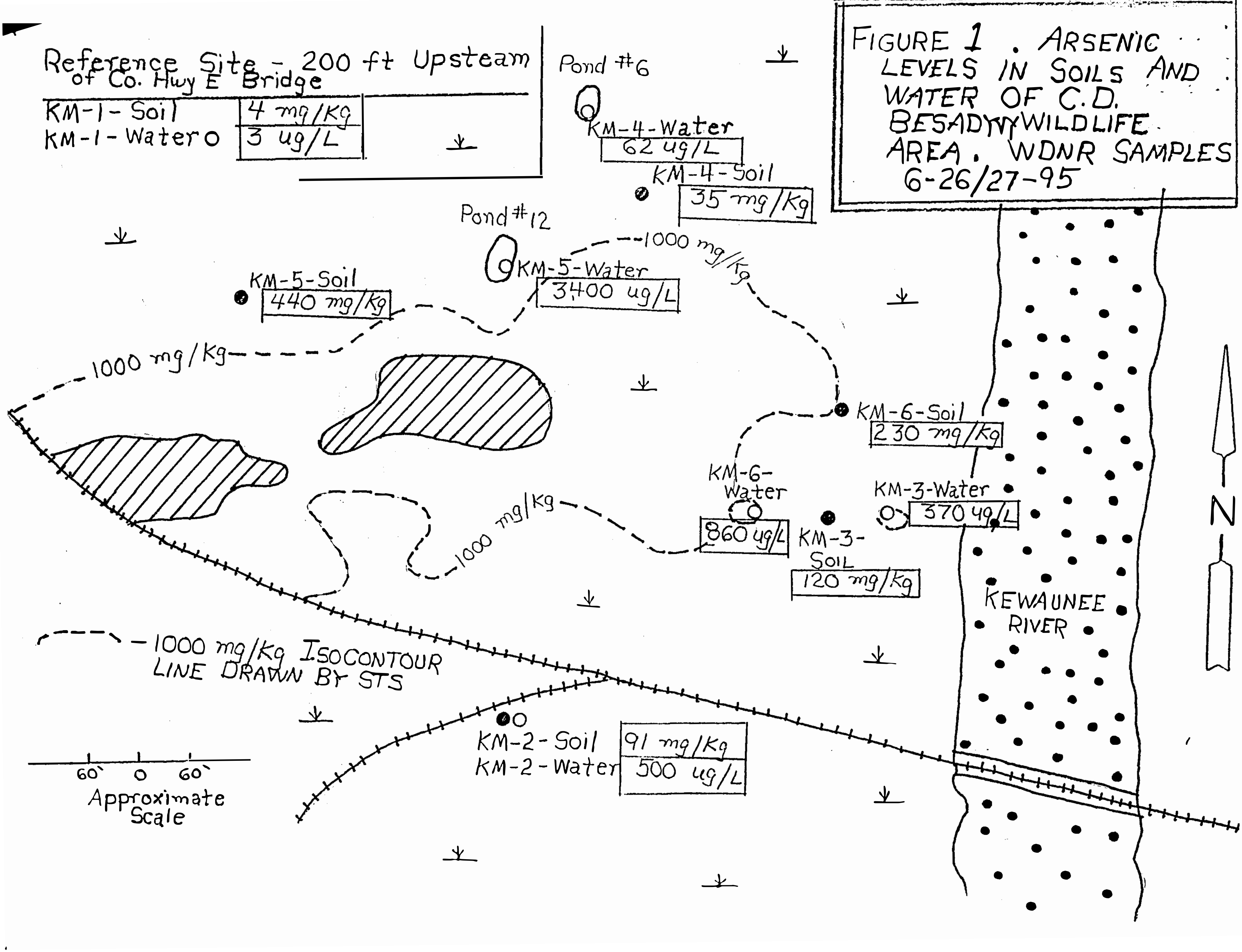

FIGURE 1. ARSENIC LEVELS IN SOILS AND WATER OF C.D. BESADNY WILDLIFE AREA. WDNR SAMPLES 6-26/27-95

Figure 2. Locations and Assigned Numbers to Dug Wildlife Ponds on C.D. Besadny Wildlife Area

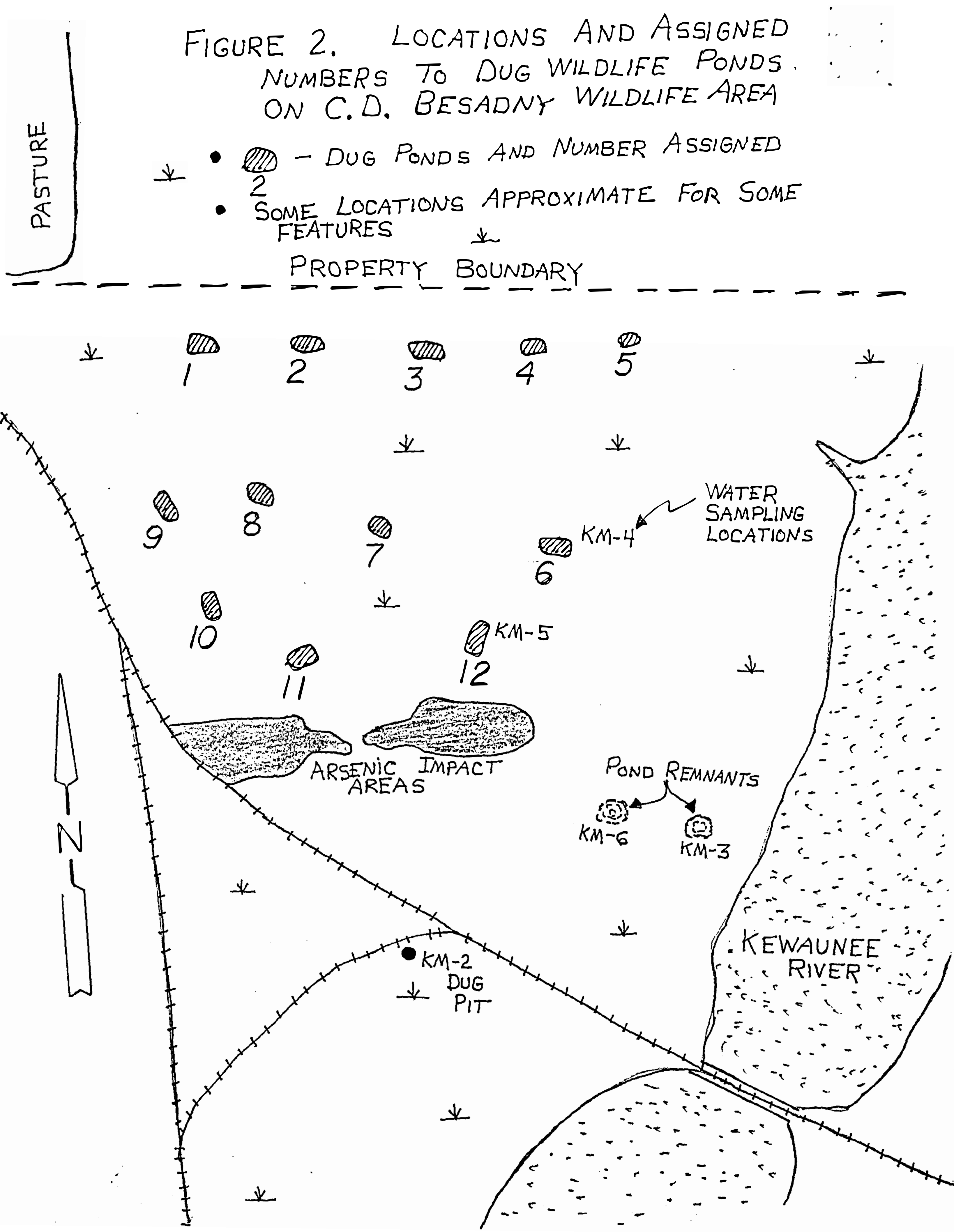

Table 1. Arsenic Levels in Soil and Water Samples from C.D. Besadny Wildlife Area. WDNR 6-26/27-95 Samples Compared with Previous STS Samples.

WDNR 6-26/27-95				STS			
Station	**Water (ug/L)**	**Soil (mg/Kg)**	**Soil Sample Depth (inches)**	**Station**	**Water (ug/L)**	**Soil (mg/Kg)**	**Soil Sample Depth (inches)**
KM-1 (reference site)	3 Kewaunee R.	4 Wetland	0-8	As indicated (Reference sites)	4.1 (R-2) 6.6 (P-4)	2.0 (B-2) 5.5 (B-3) 4.0 (B-4) 4.1 (B-5)	
KM-2	500 Dug Pit	91	0-8	As indicated	398 (BKG-2) 690 (BKG-3)	93.4 (BG-1) 112 (BG-2)	
KM-3	370 Pond Remnant	120	0-8	B-9	NA	249 (292) *	0-24
KM-4	62 Pond #6	35	0-8	B-12	NA	324 (420) *	0-24
KM-5	3400 Pond #12	440	0-8	B-23	NA	636 (701) *	0-24
KM-6	860 Pond Remnant	230	0-8	B-10	NA	897 (1119) *	0-24

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* calculated 8-24 inches

Table 2. Total Solids and Particle Size Analysis for Soils Samples Collected from C.D. Besadny Wildlife Area By WDNR June 1995.

Sample No.	% Solids	% Sand	% Silt	% Clay	Soil Texture
KM-1	28.9	27	55	18	Silt Loam
KM-2	12.1	62	26	12	Sandy Loam
KM-3	14.6	42	48	10	Loam
KM-4	12.1	49	43	8	Loam
KM-5	14.4	53	39	8	Sandy Loam
KM-6	13.1	45	49	6	Sandy Loam

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Table 3. Water Quality Criteria for Arsenic and Comparison with Levels in WDNR June 26/27, 1995 Water Samples.

NR 105 Criteria			WDNR Sample Values	
Human Health		50 ug/L	KM-1	3 ug/L
Wild and Domestic Animal Life		32-50 ug/L	KM-2	500 ug/L
			KM-3	370 ug/L
Aquatic Life -			KM-4	62 ug/L
	Acute	364 ug/L	KM-5	3400 ug/L
	Chronic	153 ug/L	KM-6	230 ug/L
Other Values				
EPA's 1980 human health water quality criterion for consumption of aquatic organisms living in Arsenic contaminated waters		0.175 ug/L		
Death and malformation of toad embryos		40 ug/L		

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Table 4. Basic Water Chemistry Measurements Taken in Ponds of C.D. Besadny Wildlife Area and Kewaunee River.

Sample Site	Temp[1.] °C	Specific[1.] Conductanc umhos/cm^3	Dissolved[1.] Oxygen mg/L	Alkalinity[2.] ppm as $CaCO_3$	Hardness[2.] ppm as $CaCO_3$	pH[2.] su
Kewaunee R. KM-1	26.4	633	5.1	245	286	8.1
Kewaunee R. Adjacent to impacted wetland	27.3	513	7.5	--	--	--
Lake Mich. Pioneer Park	25.1	282.3	15.8	--	--	--
Pond 1	29.8	653	10.7	--	--	--
Pond 2	30.1	615	11.2	--	--	--
Pond 3	28.4	430	3.0	--	--	--
Pond 7	25.6	591	0.4	--	--	--
Pond 8	26.1	636	2.6	--	--	--
Pond 9	33.2	579	8.3	--	--	--
Pond 12 (KM-5)	27.7	499	0.25	147	276	8.01
KM-2	--	--	--	192	214	7.92
KM-3	--	--	--	236	356	7.99
KM-4 (Pond 6)	--	--	--	159	182	7.95
KM-6	--	--	--	226	257	8.00

1. Measured August 7-8, 1995
2. Measured June 29, 1995

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