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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 (1.5×10^{-3} cm/s) found in the pump tests performed on the site for the average value (1.7×10^{-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 years 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 be 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 feasibility 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
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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:

	<u>Arsenic as +3 or trivalent form</u>
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**

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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

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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

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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 6.7×10^{-5} to 1.5×10^{-3} cm/sec. From these values a geometric mean value of 1.7×10^{-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 had an 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 downgradient 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 were 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 concentrations 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 10 100 300 700	0.039 0.39 1.18 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 Past ACOE sampling for dredging projects in harbor has not found As concentrations > background
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		
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 SO-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	Silty clay loam
SO-16B	20-49.5	31	48	21	Loam
SO-17A	0-20	54	31	15	Sandy loam
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.

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