State of Wisconsin

CORRESPONDENCE/MEMORANDUM

Date: July 28, 2005

To: Bureau of Watershed Management
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Bob Masnado – WT/2 Water Quality Standards Section
Candy Schrank – WT/5 Fisheries Management and Habitat Protection Section
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Subject: Recommendation for Threshold Bound Effect Concentration Range for Arsenic in the Sediments of the Turning Basin Area and 6th Street Slip Areas of the Menominee River to be Used to Select a Remedial Goal to Protect Site-Specific Aquatic-Related Assessment Endpoints

Background

This memo was written by a workgroup consisting of Kristin DuFresne – NER/Green Bay, Steve Galarneau – SER/Plymouth, Jim Killian – WT/2, and Tom Janisch – RR/3. The latter three individuals are members of the WDNR's Contaminated Sediment Standing Team (CSST) and have had experience with contaminated sediment sites around the state and arsenic sites in particular.

Given the present state of the ERA and HHRA documents for the aquatic portion of the Ansul site that calls for significant revision and supplementation of the contents, our workgroup used a modified process below in the development of a range of effect-based threshold concentrations for arsenic in the sediments of the Turning Basin Area and 6th Street Slip Area of the Menominee River. The range of effect-based threshold concentrations was derived in a risk characterization process and from reference sources. Ultimately one value within the range needs to be selected in the risk management process as a value to be used as a cleanup goal that would be protective as possible of the assessment endpoints and receptors associated with those endpoints for the site. Once WDNR has established this arsenic sediment cleanup goal, it will be provided to U.S. EPA – Region V as a recommended sediment cleanup goal for the Ansul site. EPA is ultimately responsible for negotiating with Ansul to determine the final cleanup goal for the arsenic contaminated sediments at the site.

The site-specific aquatic-related assessment endpoints/receptors that were considered as contained in the URS ecological risk assessment were:

1) Assessment Endpoint # 1: Survival, growth, and reproduction of benthic macroinvertebrates and maintenance of community structure and function.

2) Assessment Endpoint # 2: Survival, growth, and reproduction of aquatic biota associated with the sediments, including rooted aquatic plants, amphibians, and fish, and maintenance of community structure and function.

3) Assessment Endpoint #3: Survival, growth, and reproduction of aquatic feeding mammals, omnivorous waterfowl and carnivorous birds and maintenance of their community structure and function.

Human health site exposures come from possible contacts with site sediments and water and from food such as fish that have spent time over the site. Some previous WDNR memos as listed in the reference section of this memo have commented on human health issues as related to fish consumption. On July 19, 2005 Rob Thiboldeaux, Wisconsin Department of Health & Family Services, and Candy Schrank, Fisheries Management and Habitat Protection – Monitoring and Assessment Section, were asked to respond to the comments made in these memos. They were also asked to provide a recommendation regarding the risk to humans from consuming fish caught from the Menominee River.

Each of the assessment endpoints in turn has measurement endpoints and measures of effects associated with them. Each of the measurement endpoints and measures of effects associated with the endpoints are to be taken as individual lines of evidence to be weighed in the risk characterization process. The measurement endpoints and the results of the measures of effects are integrated and interpreted in the risk assessment process to yield upper and lower effect-bound threshold concentrations using consistent conservative assumptions as called for in the U.S. EPA (1997) Ecological Risk Assessment Guidance.

The summary of the measures of effects as lines-of-evidence discussed below are in Table 1 that follows. The effect-threshold concentrations or reference point concentrations for each measure of effect in the sediment medium may be expressed as a range of concentrations where applicable in the Table. As indicated, the development of the effect concentrations associated with each measurement endpoint is discussed below. Since this risk characterization process represents a modified, truncated process, it may not fully follow the steps and considerations usually done in a risk characterization as per the guidance but is believed that the results can be supported and used with confidence as science-based effect-based numbers to make risk management decisions on.

Some of the previous memos listed in the reference section of this memo contained preliminary discussions of the measures of effects as lines of evidence and effect threshold concentrations associated with those measures of effects. The purpose of this memo is to consolidate and summarize the preliminary discussions of the most viable lines of evidence and related effect concentrations from the previous memos. Due considerations and further weighting of the information may have resulted in somewhat different effect concentrations related to a line-of-evidence between the previous memos and this memo. The effect concentrations in this memo are to be used as the final and over riding recommended effect concentrations.

Summary of Recommendations/Conclusions

Based on considering and weighing the effect concentrations associated with the measures of effect in Table 1, the lower and upper bound effect concentrations we are recommending to EPA for consideration by risk managers to select a remediation goal for arsenic in the sediments associated with the Ansul site is from 10 – 20 mg/kg. The upper and lower values in Table 1 range from essentially background concentrations to 23 mg/kg. We believe the 10 – 20 mg/kg range is the most relevant and protective range from which to select the remediation goal value for the sediments of the site.

Workgroup Request to Programs

The workgroup requests that the above programs to which this memo is addressed provide their written comments and/or concurrence with the 10 – 20 mg/kg range as being protective of their environmental endpoints of interest. Once comments and/or concurrence have been received, the workgroup will provide EPA and then the responsible party with WDNR's recommended sediment cleanup goal.

The Menominee River is one of Wisconsin's designated Great Lakes Areas of Concern because of contaminated sediment issues and the impacts of those sediments on the aquatic habitat and receptors. Studies and cleanup discussions for the site sediments have been on going for a number of years and EPA has requested WDNR provide a recommended arsenic sediment cleanup goal in effort to bring the issue to resolution for the protection and restoration of the Menominee River and Lake Michigan resources.

Table 1. Summary of Lower and Upper Bound Effect Thresholds and Reference Points Associated With the Measurement Endpoints for Sediments at the Ansul Site.				
Assessment Endpoint	**Measurement Endpoint or Reference Point (Line-of-Evidence)**	**Measure of Effect**	**Lower and Upper Bound Effect Thresholds Or Reference Points For Arsenic mg/kg**	**Relative Weight Given in the Integration of Measurement Endpoint and Reference Point Results in the Risk Characterization Process**
1. Site Specific - Survival, growth, and reproduction of benthic invertebrates	Sediment concentration-endpoint responses of test organisms in toxicity testing	Compare toxicity of Turning Basin sediments to reference area toxicity to amphipods and midges	**9 - 18**	No formal weighting process was used (e.g., Menzie et al. 1996) to assign a relative weight or level of confidence to each individual measurement endpoint or reference point relative to its contribution in characterizing and estimating risks to receptors from exposure to sediments and water from the site. Measurement endpoints in this table are generally ordered from those that would qualitatively be given the most weight (e.g, site specific measures of effect) to those given somewhat lower weight (e.g., concentration-response relationships established at other sites). In the approach used, measurement endpoint results and other information and data lines-of-evidence are used in a strength-of-evidence approach which is inclusive in nature and integrates and evaluates all pertinent information in the risk characterization process.
2. Site Specific – Survival, growth, and reproduction of benthic invertebrates	Arsenic sediment pore water concentrations	Compare concentrations of arsenic in sediment porewater to the water only chronic toxicity value to protect benthic species).	**16**	
3. Site Specific Survival, growth, and reproduction of waterfowl	Protect waterfowl utilizing the site	Comparison of exposure concentrations in food and water ingested from the site with LOAEC associated with growth and survival	**9 - 23**	
4. Predicted toxic effects to survival, growth, and reproduction of benthic invertebrates	WDNR CBSQGs	Comparison of Arsenic concentrations in site sediments with TEC and MEC Concentrations in the CBSQGs	**10 - 21**	
5. Site Specific Human Health based on NR 105 assumptions for humans ingesting Menominee R. water and fish from those waters	Protect human health based on NR 105 Water Quality Criteria	Compare arsenic concentrations in site surface waters and downstream river water to NR 105 Water Quality Criteria to protect human health	**4 - 7**	
6. Various ERA and HHRA assessment endpoints for other sediment arsenic contaminated sites in Wisconsin	Kewaunee Marsh ERA and HHRA	Integration of endpoints to yield protective level	**19**	
	Lower Fox River ERA	Protect benthic invertebrates	**12.1**	
7. Various ERA and HHRA assessment endpoints for other sediment arsenic contaminated sites outside of Wisconsin	Site # 1	Ecological Receptors	**19**	
	Site # 2	Human Health	**12**	
	Site # 3	Human Health, secondarily ecological	**20**	
	Site # 4	Ecological Receptors	**9 - 20**	
	Site # 5	Human and Ecological Receptors	**3**	
	Site # 6	Human Health	**20**	
Recommended Effect Threshold Concentration Range to Be Used to Derive an Arsenic Cleanup Number For Sediments at the Ansul Site in the Risk Management Process			**10 - 20**	

Line-of-Evidence # 1 - Site-Specific Toxicity Testing

The site-specific toxicity testing results performed on site sediments using *Hyalella azteca* and *Chironomus tentans* test organisms in February and October of 2001 and reported in the 2003 URS ERA are shown in Tables 7 and 8 below. The February 2001 round of toxicity testing yielded a NOAEC of 26.5 mg/kg for both the *Hyalella* and *Chironomus* tests based on the arsenic concentrations in the sediments tested. The NOAEC value was based on no differences in endpoint results between this study sediment and organisms exposed to the reference sediments. There was a large concentration gap between 26.5 mg/kg and 324 mg/kg that was not used in the exposures. The October 2001 round of testing using only *Hyalella* included sediment with 89 mg/kg of arsenic in it. No sediment with a higher concentration of arsenic in it was tested in this round. In the October round of testing using *Hyalella*, the 89 mg/kg value was the NOAEC value (the highest concentration tested that showed no differences in results when compared to the results from the reference sediment). The concentration gaps in the test sediment did not allow the calculation of an LC50 concentration or that concentration that would be associated with 50% mortality in the test organism.

I've discussed the details and uncertainties of the derivation of this NOAEC value in my June 25, 2003 comments to the URS ERA (pages 29-31). One of the difficulties is that dependence on a test result from testing of short duration and an acute endpoint such as mortality may underestimate the risks to benthic organisms exposed to lower concentrations of arsenic in sediment over longer periods.

The following is from my June 25, 2003 comments:

> Toxicity testing of short duration using the acute endpoint of survival and concentrations related to the effect levels (NOAEC or LOAEC) or calculated LC50 concentrations, if the data allows calculation, may result in concentrations that limit their utility in risk assessments. The effect concentrations derived from short-term toxicity tests may not be sufficiently sensitive to detect the early stages of ecosystem stress. Significant effects on populations can occur at much lower concentrations than those related to acute effects. Longer term studies have shown how species populations such as amphipods (*Hyalella*) can suffer eventual extinction at contaminant levels below those that effect survival (Ingersoll et al. 1997). Short term acute toxicity test results as exemplified by LC50 values or NOAECs may not be sufficiently sensitive to measure or detect the early stages of stresses to populations that can occur from chronic, longer term exposures to lower contaminant levels. What this may mean is that at arsenic concentrations less than the NOAEC of 89 mg/kg of arsenic in sediments based on the acute endpoint of survival in short term tests, significant chronic toxicity effects related to reductions in growth or reproduction may be occurring over longer durations of exposure to arsenic. While discussed in the context of developing wildlife TRVs on page 3 of 6 of Appendix D of the BERA, the following statement also applies to developing effect concentrations from toxicity testing involving invertebrates: *"Test-species doses from chronic studies are used preferentially over data from acute and subchronic studies."*

The 2003 ERA 89 mg/kg arsenic NOAEC value in sediments was the only value based on a sediment concentration-endpoint response relationship from the five measures of effects used to assess the benthic community assessment endpoint. No other threshold effect concentrations were derived from the other measures of effects. No weighting of the endpoints results or integration of the results can be done to derive a range of threshold effect values associated with no to low effects to ensure all the measurement endpoints are protected. Apparently the singular value of 89 mg/kg of arsenic in sediments as derived from the toxicity testing results is intended to be protective of all measurement endpoints under the benthic community assessment endpoint, and other assessment endpoints for that matter.

There is a need to adjust the 89 mg/kg value based on short term-acute endpoint results to a more chronic-related value based on the above discussions. For water quality criteria values, the standard fallback acute-to chronic ratio for calculating an estimated chronic value from a known acute value for a toxicant is to divide the LC50 value by values ranging from 5 to 10 (e.g., EPA, 1985). As indicated above, the sediment concentration values used in the sediment toxicity testing did not allow the calculation of an LC 50 value. The actual LC50 value would be somewhat greater than 89 mg/kg. Given the need to incorporate uncertainty factors into the results of the toxicity testing, the ratio factors of 5 to 10 applied to the acute endpoint-related 89 mg/kg value yields adjusted concentrations of 9 – 18 to protect chronic endpoints based on long term exposures of benthic invertebrates to arsenic in sediment.

Line-of-Evidence # 2 - Site Specific Pore Water Concentrations of Arsenic Related to Bulk Sediment Concentration and Effect Levels to Benthic Invertebrates Exposed to Pore Water

The site-specific toxicity reference value (TRV) used in the URS 2003 ERA as a NOEC for benthic invertebrates exposed to arsenic in the sediment pore water was the NR 105 chronic toxicity criteria value of 153 ug/L to protect aquatic organisms. The corresponding acute toxicity criteria is 340 ug/L. The use of the ambient surface water quality criteria value to protect benthic organisms exposed to arsenic in the pore water assumes benthic organisms are equally as sensitive as organisms that inhabit the water column to arsenic exposure. It has generally been demonstrated that organisms in either habitat are as equally sensitive to toxic contaminants.

The bulk sediment-pore concentrations in site sediments used for the February and October 2003 rounds of toxicity testing are shown in Table 6 below. The bulk sediment concentrations are arranged in order of increasing concentrations in the middle column. The corresponding pore water concentrations associated with the bulk sediment concentrations also increase as the bulk sediment concentrations increase (with the exception of the relationship at site 321F). The chronic toxicity value of 154 ug/L of arsenic is interpolated to be associated with bulk sediment concentrations of 16-17 mg/kg. The 16 mg/kg value is used as the bulk sediment concentration needed such that the associated pore water concentration does not exceed the chronic toxicity value for arsenic as applied to pore water. The chemical form of arsenic in pore water will change depending on the physical and chemical factors present at any one time that influence the form, availability, and toxicity. It is assumed that the conditions in sediments are at times conducive for all of the arsenic present to be in a form that is most available and toxic. The role of the arsenic contaminated groundwater upwelling through the sediments at the bottom of the Turning Basin is not analyzed in the above relationships. It is assumed that even with upwelling, the bulk sediment-pore water concentration established above will still be applicable.

The spatially averaged total arsenic pore water concentrations in the sediments from the five sites collected for the February 2001 toxicity testing was 68,979 ug/L on Day 0 and 30,500 ug/L on Day 10. These high levels of arsenic likely diffuse or are carried in discharging groundwater from the sediments to the lower portions of the overlying surface waters. Under stagnant, low flow conditions in the Turning Basin without a lot of mixing and dilution, the concentrations of arsenic in the lower water column likely exceed the 154 ug/L chronic toxicity value. Studies conducted by WDNR in 1990 trapped river water over sediments and allowed for it to equilibrate with the sediment pore water over a period of time. The concentration of total arsenic in the Turning Basin river water collector was 3,900 ug/L.

Line-of-Evidence # 3 - Protection of Waterfowl Utilizing the Site

The details and considerations made to derive effect based thresholds for arsenic in sediment to protect waterfowl ducklings that may ingest invertebrates that may have been associated with the sediments are in the June 25, 2003 comments (pages 12-14) to the URS ERA and the June 29, 2005 memo (page 3). The toxicity reference value, area use factor, and BSAF values used in the calculation are discussed. The assumption is made that waterfowl that have nested in the adjacent wetland area and with their broods will utilize the site area much more than waterfowl without broods. URS's ERA did not take this into consideration. The range of effect based thresholds for arsenic in sediment (9 – 23 mg/kg) is based on average and 90th percentile BASF values (BASF used to calculate sediment to invertebrate uptake of arsenic and then consumption of invertebrates by ducklings).

Line-of Evidence # 4 – WDNR Consensus- Based Sediment Quality Guidelines

There are many views on the role of sediment quality guidelines (SQGs) in establishing cleanup numbers for contaminated sediments. The listing of uses of the particular set of SQGs the WDNR has adapted are contained in Section 4 of our Consensus-Based Sediment Quality Guidelines document (WDNR, 2003).

Table 2 contains the specific effect level ranges for arsenic that are in the CBSQG document. Table 3 below compares the effect level concentrations for arsenic in the WDNR CBSQGs with the effect levels in a number of other sets of SQGs developed by several agencies, states, and Canada. Generally, all are derived from toxicity databases and some from benthic community studies and are designed to protect the endpoint of benthic macroinvertebrates. Some things to note:

- Note that the states of Minnesota and Massachusetts have also adopted the MacDonald et al. (2000) CBSQGs as the WDNR has.
- SQGs numbered 1 – 5 in Table 3 were integrated by MacDonald et al. to derive their CBSQG effect concentrations.
- It can be seen from the effect levels in the guidelines in Table 2 that were developed using a number of different approaches that there is a general concurrence of the range of concentrations that are in the lower, mid, and upper effect concentration ranges when the effect levels from all the SQGs are combined.
- The concurrence of the effect ranges amongst the different guidelines gives weight and confidence in using the CBSQG values to predict the likelihood of adverse effects to benthic macroinvertebrates.
- As noted in the note to Table 3, the Midpoint Effect concentration is not a derived effect level that is part of any of the SQGs in Table 3 with the exception of the WDNR CBSQGs. The Midpoint effect concentrations were calculated to compare the values amongst the SQGs.
- Use of the CBSQGs alone or an integration of all the guidelines would result in a lower bound effect concentration for arsenic of approximately 10 mg/kg (no or limited exposure risks or NOAEC) and an upper bound effect concentration of approximately 21 mg/kg (some exposure risks, some possible adverse effects, would equate with a LOAEC). The CBSQG probable effect concentration (PEC) of 33 mg/kg arsenic is not suitable as a LOAEC as or an upper bound effect concentration as it does not equate with the lowest concentration that adverse effects would first be noted. Adverse effects to some portion of benthic organisms would be noted at lower concentrations which here are equated with the CBSQG MEC concentration of 21 mg/kg.
- As clearly stated in the CBSQG document, WDNR cannot require RPs to use the CBSQG values as a sole basis for sediment cleanup numbers unless the RP agrees to use them for that purpose. However, a case can be made for their use in the risk assessment process as a line of evidence in establishing those numbers when integrated with the results of other lines of evidence from other measurement endpoints.

The specific role of the WDNR CBSQGs in the ERA process are discussed in Section 4 of the CBSQG document as noted above and is shown in Table 4 below. The CBSQGs are used in Step 1, the screening level ERA, and in Step 7, where the CBSQGs as a measurement endpoint are integrated with the results of the other measurement endpoints for the benthic community assessment endpoint in the risk characterization process.

The argument can be made that site-specific testing and endpoints based on exposing test organisms in the laboratory to site sediments are likely more representative for estimating potential risk than effect-based values from sets of sediment quality guidelines. One reason given is that SQGs do not account for the specific physical and chemical conditions that may be found at a site that may influence the contaminant forms and bioavailability to benthic organisms. There are many uncertainties that need to be considered any time the results of laboratory testing are extrapolated to the field setting based on the changes that sediments undergo between the time they are collected in the field and used in toxicity testing setups. The URS 2003 ERA did not discuss these extrapolation uncertainties Just as there is likely a range of physical and chemical characteristics in the sediments of any one site spatially at a given time, the results used in establishing effect-based concentrations for SQG from toxicity databases represents sites with variable physical and chemical characteristics. Based on this, the environmental variable argument for weighting site-specific toxicity testing results greater than SQG values may only hold true if there was much more site-specific toxicity testing than just one or two rounds to derive a larger database to be representative of variable conditions across the site. The results of limited rounds of toxicity testing conducted at a site using tests of short duration (10-d) and only looking at acute endpoints such as mortality have to be looked at closely for their likely underestimation of exposure risks compared to longer term exposures at lower concentrations.

Line-of-Evidence # 5 - Protection of NR 105 Water Quality Criteria Based on Human Cancer Criteria Considering Upstream Background Sediment-Surface Water Relationships

Based on NR 105, the ambient water quality criteria for the Menominee River based on Human Cancer Criteria is 0.185 ug/L based on a target cancer risk level of 1×10^{-5}. The upstream background concentration of arsenic in the Menominee River is approximately 1.5 ug/L. With background greater than the criteria means there is some baseline risks greater than 1×10^{-5} to humans due to the background concentrations alone (7.57×10^{-5}). Arsenic concentrations at mouth of the Menominee River ranged from 2.05 to 5.6 ug/L in 1994 and 1995 and averaged 3.64 ug/L. The maximum concentration of arsenic in the surface waters of the site was 19 ug/L. The levels in the lower river out to the mouth which are related to arsenic releases from the Ansul site, add incremental risks to humans ingesting fish or consuming water from the system above that already contributed by upstream background concentrations in the river water based on the assumptions used in deriving the NR 105 values. It is assumed the upstream background concentration of arsenic in the river water is associated with the arsenic levels in the soils and sediments of the watershed. The background arsenic concentrations in sediments average approximately 3 – 4 mg/kg with a maximum concentration of 7 mg/kg.

The average arsenic concentrations out in Lake Michigan is 1.01 ug/L. Arsenic concentrations in seven other tributaries to Lake Michigan had average arsenic concentrations of 1.01 ug/L and ranged from 0.4 to 1.5 ug/L. The annual arsenic loading from the Menominee River to Lake Michigan is approximately twice the loading from other tributaries with comparable flow volumes.

The bottom line is that there is a baseline risk level to humans from the background concentrations of arsenic in the Menominee River water, which for all intents and purposes is uncontrollable due to natural watershed sources. The concern is the unacceptable, controllable incremental risks that are present due to the contribution of arsenic released from sources above background including the Turning Basin sediments to the Menominee River water. If background sediment concentrations ranging from 4 to 7 mg/kg are related to and responsible for the upstream background arsenic concentration in River water of 1.5 ug/L, then to remove incremental risks to humans contributed by site sediment sources of arsenic to the surface waters, the 4 to 7 mg/kg of arsenic in the sediments could be used as effect thresholds to remove the surface water incremental risks to the extent practical assuming there is a flux and equilibrium between arsenic in the background sediments and pore water and the overlying surface waters to yield the background water concentration of 1.5 ug/L.

Generic, conservative assumptions are used for arsenic exposure and uptake in deriving the risk-based water quality criteria based on the human health cancer endpoint. Relationships between arsenic in sediments, pore water, and over lying surface water would need to be demonstrated through sampling and modeling studies. Both of the above add some uncertainty to the Line-of-Evidence # 5.

Line-of-Evidence # 6 – Remedial Action Objectives Established for Other Wisconsin Arsenic Contaminated Sediment Sites.

- Besadny Fish and Wildlife Area – After performing an ERA and a HHRA for the site which largely involves an emergent wetland bordering the Kewaunee River, the recommended cleanup goal for the wetland soils based on the risk assessment and risk management processes is 19 mg/kg. The site was contaminated by spills from derailed railway cars carrying arsenic that at the time was being used as an insecticide in orchards. The spill took place sometime in the 1940's which allowed the arsenic to spread over large portions of the wetland area but has not been detected in sediments of the Kewaunee River.

- A review of the ERA for the Lower Fox River (LFR) Superfund site (ThermoRetec, 1999) was done. One of the COPC identified for the LFR was arsenic. The primary COPC and driver of the cleanup of the LFR are PCBs. The ERA for the LFR was an extensively peer reviewed document. The selected threshold for the protection of benthic invertebrates in the LFP ERA was a value of 12.1 mg/kg of arsenic in sediments. For aquatic dependent wildlife such as birds and mammals, toxicity reference values (TRVs) based on arsenic levels in ingested food items were used. These TRVs were not back calculated into sediment concentrations using a BSAF approach. The background arsenic concentration in the LFR was 5.3 mg/kg, which is similar to the background arsenic concentration in the Menominee River.

- Full details for the deriving the protective endpoints concentrations and remedial action objectives for the above two Wisconsin arsenic contaminated sediment sites are contained in site files for each. Some additional information on these two sites are contained in the June 29 and July 5, 2005 memos listed in the reference section.

Line-of-Evidence # 7 - Remedial Action Objectives Established for Arsenic Contaminated Sediment Sites Outside of Wisconsin

A quick search to see what information is available about sediment remediation projects involving arsenic, what the cleanup numbers were, and the endpoints the cleanup numbers were developed to protect. The only site I found that may have a compilation of all Superfund sites and the ROD-established cleanup numbers was www.cleanuplevel.com. The site gives some information but to view the complete database, fees must be paid. The site indicates that nationwide, there are 113 Superfund sites that arsenic contamination. It is not indicated how many of the sites involve arsenic-contaminated sediments. There was some information on the cleanup of an arsenic contaminated sediment site in Burnett County, WI in 1998. The cleanup level for this site was 9.6 mg/kg. I was not aware of a cleanup at this Burnett County site. Contacts with NOR would provide more information as to what type of site was involved.

Table 5 below shows the results for six sites that I found from a number of sources. Full reports involving the sites would need to be reviewed to understand the details of the risk assessments that were performed to derive the cleanup numbers.

The cleanup goals for the out-of-state sites are based on site-specific and study-specific endpoints and assumptions. As such, they may not be directly applicable to the Ansul site. The results do build up a weight-of-evidence that even with consideration of variable endpoints and using various assumptions, there appears to be a general concurrence of the range of arsenic concentrations that are needed to protect those endpoints as a result of the various studies.

References

MacDonald, D.D., C.G. Ingersoll, and T.A. Berger. 2000. Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. Arch. Environ. Contam. Toxicol. 39:20-31.

Menzie et al. 1996. Special report of the Massachusetts weight-of-evidence workgroup: A weight-of-evidence approach for evaluating ecological risks. Human and Ecological Risk Assessment. 2:277-304.

U.S. EPA. 1997. Ecological risk assessment guidance for Superfund: Process for designing and conducting ecological risk assessments. Interim Final. EPA 540=R-97-006.

U.S. EPA. 1985. Technical support document for water quality-based toxics control. Office of Water. EPA-440/4-85-032.

WDNR. 2003. Consensus-based sediment quality guidelines. Recommendations for use and application. Interim guidance. WT-732 2003.

ThermoRetec. 1999. Baseline Human Health and Ecological Risk Assessment. Lower Fox River, Wisconsin. Prepared by: ThermoRetec Consulting Corporation. Prepared for: Wisconsin Department of Natural Resources.

<u>Past Referenced WDNR Comment Memos From Tom Janisch to NER Ansul Project Managers in Regard to Ansul Documents and Site-Related Subjects</u>

September 22, 1999. Subject: Bureau of Watershed Management Comments on the 1) Quality Assurance Project Plan, 2) Field Sampling Plan, 3) Screening Risk Assessments, 4) Analysis Plan for Quantitative Baseline Ecological Risk Assessment, and Appendices, for the Ansul Inc. Site (ID #WID 006 125 215) as Prepared by Dames & Moore. Submitted March 15, 1999.

June 25, 2003. Subject: Review and Comments on the Ecological Baseline Risk Assessment, TSS-Ansul Stanton Street Site, Marinette, WI. Final Report. Dated February 28, 2003. Prepared by URS Corporation.

July 2, 2003. Subject: Review and Comments on the Human Health Risk Assessment, TSS-Ansul Stanton Street Site, Marinette, WI. Final Report. Dated February 28, 2003. Prepared by URS Corporation'

June 29, 2005. Some considerations for deriving a lower bound effect concentration in sediments for arsenic to protect all the assessment endpoints and to be used as a cleanup goal for the site.

July 5, 2005. Offsite considerations of arsenic releases from the Ansul site to Green Bay sediments.

July 12, 2005. Follow up to yesterday's phone conversation on Ansul fish data.

July 18, 2005. Utilizing lines-of-evidence to establish a risk-based cleanup number for arsenic in the Turning Basin Sediments to protect assessment endpoints.

Table 2. WDNR CBSQGs for Arsenic							
Metal / Descriptors	mg/kg dry wt.++						
	≤ TEC	TEC	> TEC ≤ MEC	MEC	> MEC ≤ PEC	PEC	> PEC
Arsenic	℘	9.8	℘⊗	21.4	℘⊗	33	⊗
Concern Levels	Concern Level 1		Concern Level 2		Concern Level 3		Concern Level 4
Risk Category Description	No risk or some possible limited risk		Some possible risk		Some Probable Risk		Probable risk
Effect Description	≤ Threshold Effect Concentration No or Limited Adverse Effects		As concentrations increase between TEC and PEC, incidences of toxicity (adverse impacts to growth, reproduction, and survival)) also increase. More organisms impacted by chronic toxicity. Acute effects to sensitive organisms may be expected in this range				≥ Probable Effect Concentration Probable Adverse Effects to Survival, Growth, and Reproduction

TEC = Threshold Effect Concentration
MEC = Midpoint Effect Concentration
PEC = Probable Effect Concentration
Based on Macdonald et al (2000), the predictive ability or accuracy of the CBSQG TEC for arsenic is 74%, i.e., the percentage of samples less than 9.8 mg/kg predicted to be nontoxic was 74%. The predictive ability or accuracy of the CBSQG PEC for arsenic is 77%, i.e., the percentage of samples greater than 33 mg/kg predicted to be toxic was 77% accurate.

Table 3. Various Sediment Guideline Effect-Related Concentrations for Arsenic to Protect Benthic Invertebrate Community Endpoint			
Sediment Quality Guideline (Lower and Upper Effect Level Nomenclature)	**mg/kg (dry wt.) Arsenic**		
	No or Low Effect Concentration	**Midpoint Effect Concentrations [1]**	**High or Probable Adverse Effect Concentration**
1. Ontario (1993) (LEL, SEL)	6	19.5	33
2. Smith et al. (1996) (TEL, PEL)	5.9	11.5	17
3. Environment Canada (1992) (MET, TET)	7	12	17
4. Long and Morgan NOAA (1992) (ERL, ERM) (From salt and FW database)	33	59	85
5. U.S. EPA (1996) (TEL-HA28, PEL–HA28)	11	29.5	48
6. WDNR CBSQGs (TEC, PEC) (MacDonald et al. 2000)	CBSQGs are based on the geometric mean values from the above five guidelines		
	9.8	21.4	33
6. Canadian Sediment Quality Guidelines (2003) (ISQG, PEL)	5.9	11.5	17
8. New York (1999) (LEL, SEL)	6	19.5	33
9. State of Florida (1994) (TEL, PEL) (From saltwater database)	7.24	24.4	41.6
10. Minnesota Pollution Control Agency (2000) (Adopted MacDonald et al. CBSQGs) (Level 1 SQT, Level II SQT)	9.8	21.4	33
11. NOAA (1999) (ERL, ERM) (From saltwater database)	8.2	39.1	70
12. British Columbia (2003) ($SedQC_{SCS}$, $SedQC_{TCS}$)	11	15.5	20
13. Massachusetts (2003) (Adopted MacDonald et al. CBSQGs) (TEC, PEC)	9.8	21.4	33
Overall Arithmetic Average (Does not include #6 above)	10	23.7	37.3
Background Arsenic Concentrations In the Menominee River sediments generally upstream of the Ansul Site	Over the years a number of dredging projects (5) have taken place in the Menominee River. Background concentrations in the river sediments associated with these projects based on the NR 347 sampling results were: average of **1) 4.8 mg/kg, 2) 2 – 7 mg/kg, 3) 0.9 – 1.8 mg/kg – utility trench, deeper substrates, 4) 1.7 – 2.1 mg/kg, and 5) and 1.3 – 4.4 mg/kg.**		
1. All of the SQGs, with the exception of the WDNR CBSQGs, do not contain a Midpoint Effect Concentration. Calculation done in the table for comparison purposes between SQGs.			

Table 4

ECOLGICAL RISK ASSESSMENT (ERA) PROCESS IN SUPERFUND and WDNR

Schematic Diagram of the Superfund Eight-Step ERA Process

Compile Existing Information	**Step 1: Screening Level Risk Assessment** - Site Visit - Problem Formulation - Toxicity Evaluation (Use of SQGs[+])	**Risk Manager, Risk Assessor, and Stakeholder Discussion and Agreement**
	Step 2 : Screening Level - Exposure Estimates (Use of SQGs[+]) - Risk Calculation	**SMDP ***
Data Collection	**Step 3 : Baseline Risk Assessment** - Problem Formulation - Conceptual Site Model - Identify Receptors of Concern - Literature Search, Toxicity Evaluation - Identify Assessment Endpoints	**SMDP**
	Step 4 : Study Design and DQO Process - Establish Measurement Endpoints to be used as Lines of Evidence (Use of SQGs[+]) - Study Designs, Sampling and Analysis Plan	**SMDP**
	Step 5 : Field Verification of Sampling Design	**SMDP**
	Step 6 : Site Investigation and Data Analysis - Analysis of Exposures and Effects	**SMDP**
	Step 7 : Risk Characterization and Estimation - Integration of Measurement Endpoints (Includes SQGs[+]) to Characterize Risk and Establish Threshold Effect levels	**SMDP**
	Step 8 : Risk Management - Risk Assessors Convey Results of Risk Characterization to Risk Managers for Use In Making Sediment Management Decisions	**SMDP**

- SMDP - Scientific Management Decision Point
- [+] SQGs includes WDNR CBSQGs

Table 5. Cleanup Levels / Remedial Action Objectives for Arsenic at Some Contaminated Sediment Sites			
Site Location	**Background/Description**	**Basis of Cleanup Numbers (Remedial Action Objectives)**	**Cleanup Number for Arsenic**
1. Gambo Creek Waste Removal and Wetland Restoration, Dahlgren, VA. Trib. to Potomac River	Storage site since 1940's; began filling wetlands in 1950's. Storage and disposal for military. Remediation encompassed 2.7 acres of upland and 3.3 acres of wetland.	Protect ecological receptors from contaminated sediments and control leaching of contaminants into groundwater	**Originally set at 7.3 mg/kg but later revised to 19 mg/kg.**
2. PSC Resources, Palmer, Maine on floodplain of Quaboag River.	Former waste oil and solvent reclamation facility. Wetlands associated with the River are contaminated with arsenic and other contaminants.	The chemical-specific wetlands sediments cleanup number for arsenic is based on health risk standards.	**12 mg/kg**
3. Gibbons Creek remnant channel. State of Washington	Near industrial park. Highest arsenic concentrations below storm sewer from a wood treater.	Sediments from sites in remnant channel ranged from 49 – 62 mg/kg, levels expected to have adverse effects on benthic organisms. Model Toxic Control Act (MTCA) levels for soils applied to sediments. MTCA levels meant primarily to address human health concerns, ecological concerns only secondarily addressed.	**20 mg/kg**
4. Bay Road site, San Francisco Bay. East Palo Alto, CA.	Site used to formulate agricultural chemicals for over 70 years. From the 1920s to 1964, the property was owned by a company that manufactured arsenic-based products, such as herbicides. 25-acre site is defined to include areas with arsenic concentrations greater than 20 mg/kg.	The primary objective of the remediation in the tidal wetlands was to protect ecological resources, especially endangered species such as the Clapper Rail. The average background arsenic concentration in soil at the site was 9 mg/kg. Because individual samples may vary from the average, soil-containing arsenic in excess of 20 mg/kg was considered to be affected by activities at the site. The U.S. F&WS required that "target low levels" for arsenic be set based on ambient levels in San Francisco Bay and maximum levels found in nearby marshes.	**9 – 20 mg/kg**
5. Peninsula Park LLC Wilmington, Delaware.	12 acre site has an industrial history including rail car manufacturing, shipbuilding, and iron foundry.	The remedial action objectives for Operating Unit 1 include control soil erosion and transport of contaminated soil into surface waters and control ecological contact with contaminated soil, sediments, and surface water in the wetland area of OU. The quantitative Remedial Action Objectives were developed using the Delaware Uniform Risk Based Standards for Restricted Use in a Critical Water Resource Area. The RAO for arsenic prevents human and ecological receptor contact with soils or sediments associated with risks. The initial application of the arsenic cleanup level will be for sediments in drainage easements from the property.	**3 mg/kg**
6. JCS Company Austin, TX	Former automotive battery reclamation operations.	Cleanup level based on human health concerns. Contaminated soils and sediments in pond on property to be remediated.	**20 mg/kg**

Table 6. Site Bulk Sediment Concentration Related to Pore Water Toxicity Reference Value to Protect Benthic Invertebrates		
	Reference Site and Site Sediments from Feb. and Oct. and 2001 Toxicity Testing and TRV for Arsenic in Sediment Pore Water to Protect Benthic Invertebrates	
	Arsenic	
Sample Site	**Sediment mg/kg**	**Porewater ug/L**
325 O Ref	0.97	1.74
325 F Ref	0.39	2.61
326 F Ref	1.00	2.54
310 F	4.01	21.7
309 F	14.5	13.2
328 O	16.3	136
Bulk Sediment Concentration related to pore water toxicity reference value	**16 mg/kg**	Approximate Arsenic Concentration in pore water associated with chronic toxicity to benthic invertebrates = 154 ug/L
327 O	17.2	200
321 F	26.5	20.5
326 O	26.9	473
207 O	88.9	4,120
304 F	324	3,450
303 F	3,038	341,100
The O after the site number is associated with the sediments collected for the October round of toxicity testing and the F is associated with the sediments collected for the February round of toxicity testing.		

Table 7. Results for one Round of Toxicity Testing for *Chironomus tentans* in 2001 from URS 2003 ERA.								
	Chironomus tentans– Feb. 2001 Testing							
Sample Site	Arsenic		Mean % Reduction Relative to Reference					
	Sediment mg/kg	Porewater ug/L	Survival	Growth				
325 F Ref	0.39	2.61	Ref	Ref				
326 F Ref	1.00	2.54	Ref	Ref				
310 F	4.01	21.7	7.1	12.5				
309 F	14.5	13.2	7.1	24.7				
321 F	26.5	20.5	5.1	17.1				
	For Oct. tests, 26.5 mg/kg = NOAEC value							
304 F	324	3,450	83.7	26.8				
	For Oct. tests, 324 mg/kg = LOAEC value							
303 F	3,038	341,100	93.9	82.2				

Table 8. Results for Two Rounds of Toxicity Testing for *Hyalella azteca* in 2001 from URS 2003 ERA								
	Hyalella azteca – Feb. 2001 Testing				*Hyalella azteca* – Oct. 2001 Testing			
Sample Site	Arsenic		Mean % Reduction Relative to Reference		Arsenic		Mean % Reduction Relative to Reference	
	Sediment mg/kg	Porewater ug/L	Survival	Growth	Sediment mg/kg	Porewater ug/L	Growth	Survival
325 O Ref	---	---	---	---	0.97	1.74	Ref	Ref
325 F Ref	0.39	2.61	Ref	Ref	---	---	---	---
326 F Ref	1.00	2.54	Ref	Ref	---	---	---	---
310 F	4.01	21.7	7.1	12.5	---	---	---	---
309 F	14.5	13.2	7.1	24.7	---	---	---	---
328 O	---	---	---	---	16.3	136	8.0	2.1
327 O	---	---	---	---	17.2	200	1.1	+ 0.5
321 F	26.5	20.5	5.1	17.1	---	---	---	---
	For Feb. tests, 26.5 mg/kg = NOAEC value							
326 O	---	---	---	---	26.9	473	+ 3.2	0.4
207 O	---	---	---	---	88.9	4,120	0	6.7
304 F	324	3,450	83.7	26.8	For Oct. tests, 88.9 mg/kg = NOAEC			
	For Feb. tests, 324 mg/kg = LOAEC							
303 F	3,038	341,100	93.9	82.2	---	---	---	---
					For Oct. tests, no LOAEC can be determined as no values greater than 88.9 mg/kg tested.			