

Wisconsin Department of Natural Resources



2013 Low Level Mercury Sampling in Duluth-Superior Harbor,
St Louis River Area of Concern, Superior, Wisconsin

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Background:

The United States Army Corps of Engineers (USACE) is working with St Louis River Area of Concern (AOC) partners on a pilot project for open water placement of dredge material to restore degraded aquatic habitats. The 3-year pilot for placement of dredge material from the federal navigation channel of Duluth-Superior Harbor is taking place in the 21st Avenue West embayment, on the Minnesota side of the AOC. The first year of the pilot was 2013. USACE, Minnesota, and other entities monitored various parameters during the pilot; however, most of those efforts included mostly physical and biological parameters. Collection of chemical parameters was somewhat limited. To help fill this data need Wisconsin DNR conducted surface water sampling for low-level mercury from several locations in the harbor during and after the 2013 dredging and placement operations.

Methods:

Surface water grab sampling was conducted in Duluth-Superior Harbor on September 23, 2013 during mechanical dredging and placement of material via surface diffuser. Sample locations are shown in Figure 1. A photograph of the diffuser is included as Figure 2. Sometime after September 23 and prior to the end of 2013 placement activities a bubble curtain was installed in place of a section of the silt curtain to allow scow access and mechanical placement of material. The USACE dredging contractor stopped dredging and placement operations around November 16, 2013. The silt curtain across the 21st Avenue embayment was removed on November 18, 2013 after visual inspection of turbidity levels. WDNR sampled again on November 19, 2013. Samples were not collected prior to placement activities due to constraints in timing and budget.

The WDNR field crew consisted of Joe Graham and Matt Steiger. Sample locations are summarized in Table 1. The location of Site 2 was moved from the desired mid-channel at the Blatnik Bridge due to heavy ship traffic and difficulty anchoring. Upon arrival at a station, the bow of the boat was pointed into the wind and anchors were set. Samples were collected using standard WDNR protocols with additional clean techniques for trace metals (DNR 101.2). A non-metallic boat was not available for sampling so plastic sheeting was draped over and fastened to the side and the deck of the boat. Grab samples were collected by filling the bottles underwater after emptying dilute acid solution. A duplicate sample and field blank were collected and analyzed for each day of sampling.

Field parameters were collected with a multiprobe sonde (Hydrolab MS5) at 1 meter and near bottom at each station during the September sampling event. Sonde readings were not done in November due to an equipment malfunction. All samples were sent to the Wisconsin State Laboratory of Hygiene in Madison, Wisconsin for analysis. The field analyses and laboratory parameters are listed in Table 2. All locations were sampled during both events except site 3, which was not sampled in November because dredging was complete in that location.

Table 1: Sample Locations for 2013 Low Level Mercury Sampling in Duluth-Superior Harbor

Site	Location	Latitude	Longitude	SWIMS STATION
1	Bong Bridge	46.73267	-92.14292	10041152
2	Blatnik Bridge / Interstate Island	46.74986	-92.10425	10041153
3	Downwind of Dredge	46.72539	-92.06191	10041154
4	Outside Curtain	46.75806	-92.11846	10041155
5	Inside Curtain	46.76138	-92.11729	10041156
5D	Inside Curtain Duplicate	46.76138	-92.11729	10041156
Field Blank	Blank	46.76138	-92.11729	10041156

Figure 1: Sample Locations

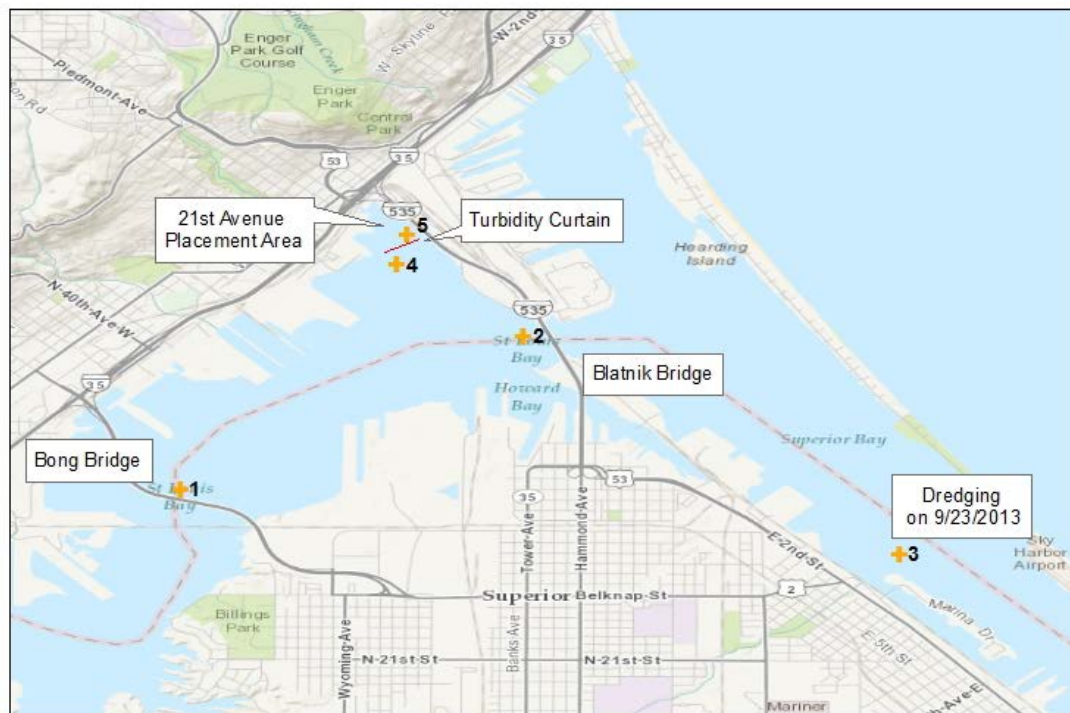


Table 2: Field and Laboratory Parameters

Lab	Field
Total Mercury (THg) EPA 1631 – CVAFS	Water Depth*, Secchi Depth, Temperature*
Methyl Mercury (MeHg) EPA 1631 – CVAFS	Dissolved Oxygen
Total Suspended Solids	Conductivity
Turbidity	

(*11/19/13 readings from Lowrance unit on boat)

Result & Discussion:

Lab analytical results and field parameters for during and post placement sampling events are in Tables 3/3A and 4/4A, respectively. Total mercury ranged from 1.9 ng/L at the Blatnick/Interstate Island location and was highest inside the silt curtain at the placement site with concentrations of 10.6 to 13.2 ng/L. The mean mercury concentration for samples outside the curtain is about 3.0 ng/L. Comparing this mean to the levels detected inside the curtain shows that mercury was at least 3 to 4 times higher than background during dredge material placement operations. Turbidity and TSS levels were also higher within the placement area and show a strong correlation to mercury levels (Figure 3). The differences in turbidity and mercury levels inside (Site 5) and immediately outside (Site 4) the curtain demonstrates the effectiveness of turbidity barriers and indicates their importance to mitigate off-site impacts. Samples collected several days after dredge material placement were only slightly elevated compared to background and may be influenced by residual suspended material, tributary inputs, or WLSSD’s wastewater outfall. Methyl mercury was only detected in one sample at concentration of 0.1 ng/L at the Bong Bridge. Mercury was not detected in any of the field blanks indicating effective use of clean sampling techniques by the sampling crew.

Conclusions & Recommendations:

Mercury levels in the placement area near the diffuser were 3 to 4 times higher than background mercury on the day of sample collection. Open water placement of dredge material results in elevated total mercury concentrations, at least temporarily while particulates remain in suspension.

Mercury concentrations are strongly correlated to total suspended solids and turbidity levels. While this may suggest that impacts of mercury may be short-lived, repeated and prolonged placement activities coupled with uncertainty in the final deposition and resuspension of suspended sediments and mercury further investigation may be warranted to assess cumulative impacts.

The differences in turbidity and mercury levels inside (Site 5) and immediately outside (Site 4) the curtain demonstrates the effectiveness of turbidity barriers and indicates their importance to mitigate off-site impacts. Sediment curtains appear to have been effective on the day samples were collected when the surface diffuser was being used to place dredge material. Turbidity control BMPs should be considered for open water placement of dredge material in the harbor. The use of additional silt curtains around individual smaller placement units should also be considered to keep material on targeted placement areas. Turbidity control would be required for work in Wisconsin waters.

Additional monitoring is recommended to further examine temporal and spatial variation of mercury concentrations with the estuary/harbor, before, during and after dredging and placement operations. Recommend expanding the list to include sulfate, dissolved organic carbon (DOC), chlorophyll a, filtered total mercury, filtered methyl mercury. Particulate total mercury and methyl mercury should be considered as additional parameters.

Consideration should be given for conducting comprehensive independent studies of bioaccumulation and cumulative effects of open water placement of dredge material during the pilot project. Results could be compiled in a single assessment report for informed stakeholder engagement.

Table 3: Lab Analytical Results for September 23, 2013 Sampling – During Operations

Site	Location	Total Hg (ng/L)	Methyl Hg (ng/L)	TSS (mg/L)	Turbidity (NTU)
1	Bong Bridge	2.58	< 0.1	10.5	11.9
2	Blatnick/Interstate Island	1.9	< 0.1	10.3	9.16
3	Downwind of Dredge	2.41	< 0.1	8.25	9.55
4	Outside Curtain	3.02	< 0.1	13	16.7
5	Inside Curtain	10.6	< 0.1	27.5	35
5D	Inside Curtain Duplicate	13.2	< 0.1	33	52.7
Field Blank	Blank	< 0.14			

Table 3A : Field Parameters for September 23, 2013 Sampling – During Operations

Site	Location	Field Chemistry at 1 meter depth					
		Water Depth (m)	Secchi Depth (m)	Temp (°C)	DO (mg/L)	DO (% Sat)	Cond. (uS)
1	Bong Bridge	8.1	0.61	16.7	8.98	94.4	218
2	Blatnick/Interstate Island	7.7	0.67	16.6	8.80	92.3	203
3	Downwind of Dredge	8.9	0.82	16.3	9.06	96.9	177
4	Outside Curtain	2.2	0.61	17.2	8.63	91.5	254
5	Inside Curtain	2.2	0.27	17.1	7.60	81.4	303
5D	Inside Curtain Duplicate	2.2	0.27	17.1	7.46	79.9	304

Table 4: Lab Analytical Results for November 19, 2013 Sampling – Post Operations

Site	Location	Total Hg (ng/L)	Methyl Hg (ng/L)	TSS (mg/L)	Turbidity (NTU)
1	Bong Bridge	3.84	0.1	5	10.3
2	Blatnick/Interstate Island	3.17	< 0.1	4.4	12
3	Downwind of Dredge				
4	Outside Curtain	4.34	< 0.1	8	13.8
5	Inside Curtain	4.19	< 0.1	6.6	14.8
5D	Inside Curtain Duplicate	4.3	< 0.1	6.8	14.7
Field Blank	Blank	< 0.14			

Table 4A : Field Parameters for November 19, 2013 Sampling – Post Operations

		Water Depth (m)	Temp (°C)
1	Bong Bridge	8.1	1.7
2	Blatnick/Interstate Island	8.4	2.8
3	Downwind of Dredge		
4	Outside Curtain	2.2	3.2
5	Inside Curtain	2.4	2.9
5D	Inside Curtain Duplicate	2.3	2.7

Figure 2: Surface Diffuser Used for Placement of Material



Figure 3: TSS and Total Mercury

