

Health Consultation

Technical Review of Discrepancies in 2002 Laser Induced Fluorescence
Data, and 2003 and 2004 Analytical Data

ST. LOUIS RIVER SEDIMENTS:
US STEEL SITE

DULUTH, ST. LOUIS COUNTY, MINNESOTA

EPA FACILITY ID: MND039045430

JULY 25, 2006

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Agency for Toxic Substances and Disease Registry
Division of Health Assessment and Consultation
Atlanta, Georgia 30333

Health Consultation: A Note of Explanation

An ATSDR health consultation is a verbal or written response from ATSDR to a specific request for information about health risks related to a specific site, a chemical release, or the presence of hazardous material. In order to prevent or mitigate exposures, a consultation may lead to specific actions, such as restricting use of or replacing water supplies; intensifying environmental sampling; restricting site access; or removing the contaminated material.

In addition, consultations may recommend additional public health actions, such as conducting health surveillance activities to evaluate exposure or trends in adverse health outcomes; conducting biological indicators of exposure studies to assess exposure; and providing health education for health care providers and community members. This concludes the health consultation process for this site, unless additional information is obtained by ATSDR which, in the Agency's opinion, indicates a need to revise or append the conclusions previously issued.

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Prepared By:

Minnesota Department of Health
Environmental Health Division
Under Cooperative Agreement with the
U.S. Department of Health and Human Services
Agency for Toxic Substances and Disease Registry

FOREWORD

This document reviews issues raised by discrepancies in sediment data for the St. Louis River Estuary, St. Louis County, Minnesota. It is based on a formal evaluation prepared by the Minnesota Department of Health (MDH).

- **Evaluating data:** MDH relies on information provided by the Minnesota Pollution Control Agency (MPCA), U.S. Environmental Protection Agency (EPA), and other government agencies, private businesses, and the general public.
- **Developing recommendations:** MDH outlines conclusions and offers recommendations that are directed toward reducing or eliminating human exposure to contaminants. The role of MDH in dealing with individual sites is primarily advisory. For that reason, the evaluation report will typically recommend actions to be taken by other agencies—including EPA and MPCA. However, if an immediate health threat exists, MDH will issue a public health advisory warning people of the danger, and will work to resolve the problem.
- **Soliciting community input:** The evaluation process is interactive. MDH starts by soliciting and evaluating information from various government agencies, the individuals or organizations responsible for cleaning up the site, and community living near the site. Any conclusions about the site are shared with the individuals, groups, and organizations that provided the information. Once an evaluation report has been prepared, MDH seeks feedback from the public. Given the nature of this technical document, direct interaction with the community on this specific topic will be limited.

If you have questions or comments about this report, we encourage you to contact us.

Please write to: Community Relations Specialist
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The Minnesota Pollution Control Agency (MPCA) requested review of sediment data associated with the US Steel site in the St. Louis River by the Minnesota Department of Health (MDH). MDH, and others, have identified problems with these data. This Technical Health Consultation discusses problems with the data and recommends steps that could help to assure that future data will not be plagued by similar problems.

Background

The US Steel site located in the Morgan Park area of Duluth, Minnesota began operation in 1915. The facilities on-site included coke ovens, a coke by-products plant, open-hearth and blast furnaces, a blooming mill, a billet mill, and a merchant mill. Also, a continuous rod mill, wire mill, nail mill, pot annealing equipment, staple and woven fence machines, nail cleaning, bluing and coating facilities, rod and wire cleaning facilities, and galvanizing facilities operated onsite at different times. In addition, from about 1918 until 1929, benzene and toluene were produced on-site. Operation of the steel mill continued until 1975 when open hearth and blast furnaces were shut down. The coking plant ceased operations in 1979 (MPCA 1989). Attachment 1 shows the location of the US Steel Site on the St. Louis River. Attachment 2 is an aerial photo of the US Steel facility in 1951 (from Tweed Museum Exhibition, 1992). Attachment 3 shows surface water and material flowing from the site into the St. Louis River in 1967 (Federal Water Pollution Control Administration 1967-8).

In 1983, the US Steel Site and the St. Louis River Interlake/Duluth Tar Site (SLRIDT) were added to the National Priorities List (NPL) as a single Comprehensive Environmental Response, Compensation, and Liability Information System (CERCLIS; Superfund) site numbered MND039045430. In 1984, MPCA placed both sites on the Minnesota Permanent List of Priorities (PLP) as separate sites. Remediation of some areas of the US Steel site has occurred since the Record of Decision (ROD) was signed in 1989. Sediments were not specifically addressed in the ROD and have not been remediated.

In March 2002, US Steel conducted Laser Induced Fluorescence (LIF) testing of sediments at some 210 locations using an LIF sensor attached to a geoprobe. Data acquired during this testing was used to develop a workplan that was submitted to the MPCA in September 2003 (US Steel 2003). Also in September 2003, in accordance with the workplan, US Steel conducted sediment sampling in the St. Louis River to identify the chemicals of concern in sediments that are likely associated with the site. MPCA staff was present during the sampling; MPCA split samples at 4 locations for independent analyses. In 2004, a small number of additional sediment and soil samples were taken at the site. Samples from 3 locations in 2004 were split and submitted to 3 different laboratories for analyses.

Discussion

MDH reviewed data from the 2003 and 2004 sediment sampling events at the US Steel, St. Louis River site in Duluth. Four 2003 samples were split between US Steel and MPCA for analysis by contracted labs; and three 2004 samples were split three ways, to be analyzed by labs contracted by US Steel, MPCA and Pace Analytical. In addition to analytical work on these samples, Dakota Technologies conducted LIF on samples in their lab, to demonstrate a correlation between the LIF signal and analytical data. This document discusses problems with the split sample data, as well as attempts to correlate LIF signal to analytical data.

2003 Sediment samples

Mean of duplicate sample data were used in calculations and correlations for 1 sample (2003 US Steel – F42). Comparisons of interlaboratory data were made by plotting data from the MPCA on the ordinate and data from US Steel on the abscissa for individual chemicals in chemical groups. PAH data from MPCA was plotted against PAH data from US Steel (Figure 1); dioxin data from MPCA and US Steel were plotted against each other (Figure 2); and, metals data from MPCA and US Steel were plotted against each other (Figure 3). Agreement between the data sets being compared (i.e. between different laboratories) would be expected to result in a best-fit straight line through the data (forced through the origin) having a slope of 1 (± 0.3) and a correlation (R^2) of 0.8 – 1.0. The descriptive statistics for resulting best-fit lines for the 2003 data are noted in Table 1.

Figure 1

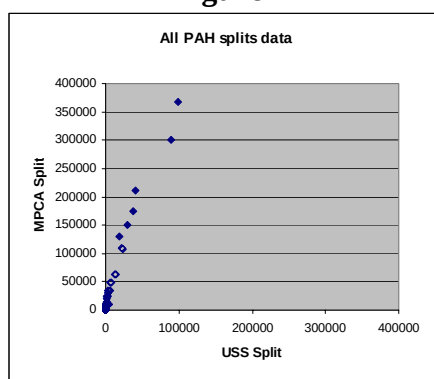


Figure 2

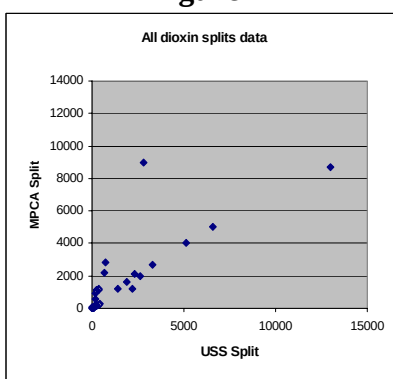


Figure 3

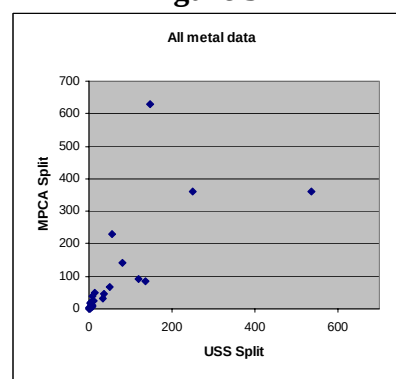


Table 1

MPCA data plotted against US Steel data (best-fit line through the origin)								
PAH (SIM)			Dioxins			Metals		
Slope	R ²	n=	Slope	R ²	n=	Slope	R ²	n=
3.965	0.95	74	0.793	0.67	42	1.027	0.46	32

Note the steep slope of the PAH data and the poor correlations of both the dioxin and the metals data. While the PAH data may suggest some systematic error in one or both of the labs, the lack of correlation found between dioxin data and between metals data do not suggest a particular source of error.

A closer look at the data was conducted by comparing data from each chemical group in each individual sample. The results of these analyses within each chemical group are shown in Table 2.

Table 2

Location	Depth	PAH (SIM)			Dioxins			Metals			% Moisture			% TOC	
		Slope	R ²	n=	Slope	R ²	n=	Slope	R ²	n=	USS	MPCA	Ratio	USS	MPCA
L 08	2-3'	8.8	0.96	18	0.7	0.99	17	0.7	0.99	8	53.3	44.5	0.83	0.013	5.4
F 42 (USS data mean of dups)	0-05'	3.9	0.92	17			3	1.5	0.99	8	19.5	42.4	2.17	0.0058	10
G 14	0-05'	2.1	0.86	18	0.7	0.93	6	1.4	0.96	8	19.8	23.9	1.21	0.0024	< 0.5
K 42	0-05'	17.7	0.92	21	3.3	0.99	16	4.3	1.00	8	29.2	81	2.77	0.0065	17

Note that correlations (between MPCA and US Steel splits) within chemical groups for each individual sample are very good, but that the line slopes range from 0.68 to 17.7; and for 8 out of the 11 samples best-fit line slopes are outside of a reasonable range of confidence (1 ± 0.3). These data suggest that there is some systematic error that changes from sample to sample. The good correlations of individual samples within chemical groups suggest that the problem is not with the analytical chemistry (i.e. the actual output of the analytical instrument – e.g. GC-MS for organics or ICP-MS for metals) but may be in sample preparation or, more generally, in the determination of the denominator term of the concentration. This hypothesis is generally supported by the complete lack of agreement between US Steel and MPCA moisture and Total Organic Carbon (TOC) data. Assuming samples were not mis-identified, these data suggest that critical mistakes were made in either the splitting of the samples (in the field or the laboratories), in handling of the samples, or in determining the % moisture and TOCs of the samples. The US Steel TOCs appear to be in error.

2004 Sample data

Two-way comparisons for split 2004 sample PAH analytical data from US Steel, Pace and MPCA, and comparison of US Steel and MPCA 2004 metals data from these split samples were conducted using similar techniques. One difference in these data compared to the 2003 PAH data is that Full Scan PAH methods were used to analyze the samples, whereas the 2003 data were acquired using Selective Ion Monitoring (SIM). PAH group-specific comparisons between labs are shown in Figures 4, 5 and 6, and 2004 metals analyses from US Steel and MPCA are plotted in Figure 7. The statistical characteristics of best-fit lines are in Table 3. The statistics suggest that there are problems with these data sets as well.

Figure 4

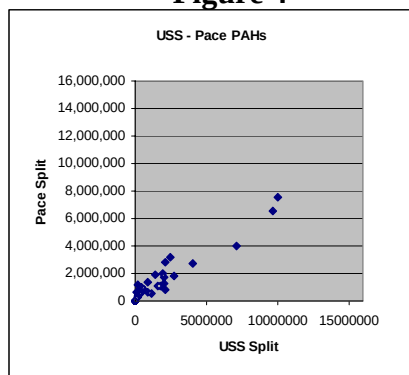


Figure 5

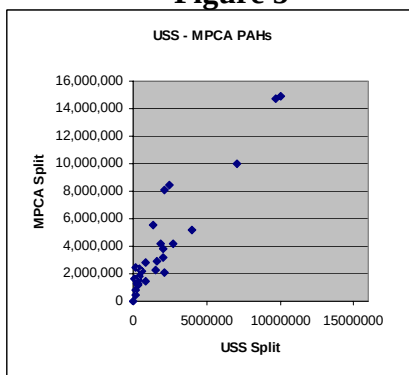


Figure 6

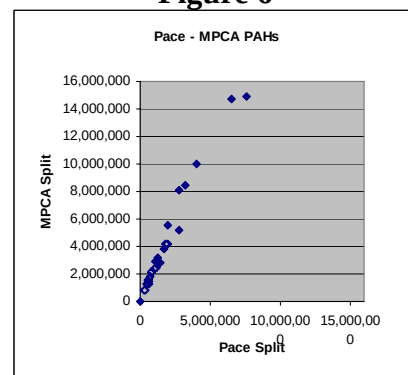


Figure 7

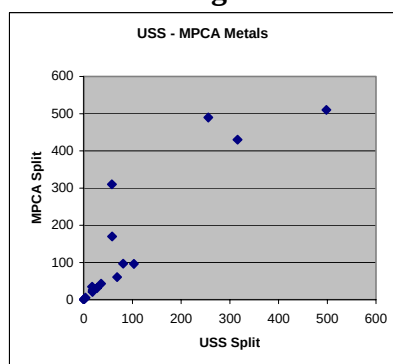


Table 3

Best-line fit statistics							
PAH (Full Scan)						Metals	
USS - Pace			USS - MPCA			Pace - MPCA	
Slope	R ²	n=	Slope	R ²	n=	Slope	R ² n=
0.72	0.91	42	1.59	0.85	41	2.23	0.97 41

When individual samples from within chemical groups are compared (Table 4), problems similar to those described for the 2003 data are apparent. Slopes for these data range from 0.55 to 3.67 with correlations from 0.54 to 0.98. Eight of 12 comparisons result in either or both slope and correlations falling outside the reasonable range (1 ± 0.3 and 0.8 - 1.0, respectively).

Table 4

		PAH (Full Scan)									Metals			% Moisture	
		USS - Pace			USS - MPCA			Pace - MPCA			USS - MPCA				
Location	Depth	Slope	R ²	n=	Slope	R ²	n=	Slope	R ²	n=	Slope	R ²	n=	USS	MPCA
OU-Q-S-4	Soil	1.9	0.67	12	1.14	0.98	12	0.55	0.54	11	1.29	0.61	7	28%	13%
OU-J-S-1	Sediment	1.4	0.97	15	3.67	0.98	14	2.69	0.98	13	1.2	0.97	7	4.8%	39%
CPSB-S-2	Sediment	0.7	0.94	15	1.49	0.96	15	2.14	0.98	13	0.9	0.96	7	6.5%	42%

Note from Table 4 that 1 of the 3 split 2004 samples was a soil sample. US Steel % moisture for

this soil sample was 28%, and yet the % moisture for the 2 sediment samples are 5% and 7%. One would expect that sediment samples would contain much more moisture than soil samples. In addition, note the discrepancies in % moisture analyses between the 2 labs.

2003 SIM vs 2004 Full Scan PAH data

MPCA concluded in their first reviews of these data that Full Scan PAH data is more reliable than SIM data. Sample surrogates (similar chemicals spiked into field samples) are typically lost with the dilution of SIM samples, resulting in the loss of one means of validating PAH data. However, instrument validation was still conducted using spikes. As a result, the only error that could not be checked in the SIM samples was dilution error. Dilution error should be below 5% per dilution. The good correlation between MPCA and US Steel individual sample PAH SIM data (Table 2) shows good analytical agreement between laboratories. However, a small amount of the 2003 split sample difference, shown in the slope of the best-fit line (MPCA and US Steel individual sample PAH SIM data: Table 2), may be the result of laboratory dilution error (likely < 5% per dilution). Full Scan PAH data (from 2004 samples) has been reviewed, and presumably corrected for dilution error.

MDH relies on SIM data to determine the potential cancer risks from a number of carcinogenic PAHs that cannot typically be seen using Full Scan. Therefore, a representative set of SIM data can be important for developing an understanding of the potential cancer risk to people. If PAH contamination at a site is characterized by a consistent PAH fingerprint (ratio of constituent PAHs) containing most of the carcinogenic PAHs (likely with SIM GC-MS data), it should be possible to compute the risk at different locations on the same site from a shorter list of PAHs that may be analyzed by an alternative method. Because a fingerprint shows the relative concentration of different PAHs and not the absolute concentrations, and because the ratios of PAH concentrations resulting from SIM analysis are consistent between laboratories (i.e. good correlations for individual samples between US Steel and MPCA laboratories), fingerprints developed from SIM analysis data for the US Steel site can be applied to Full Scan data from the site.

Correlating LIF signal response with analytical data

This analysis reviews only data from surficial sediment samples (n=29). Duplicate samples are treated as individual samples.

When aromatic rings in chemical compounds are exposed to photons at some specific energy levels, they respond by fluorescing, emitting photons at a specific, lower energy level. Therefore, an instrument using the appropriate wave-length laser and measuring laser-induced fluorescence (LIF) at the proper wavelengths should be able to measure total PAH concentrations in an environmental media. LIF response was measured in the laboratory to the 2003 sediment samples. Two measures of LIF signal were reported: total LIF response; and an alternative, filtered response described as LIF PAH 1,2,3 response. Table 5 shows the correlation coefficients (R^2) when both LIF data sets are matched with US Steel PAH analytical data.

Note, in Table 5, that there is no correlation between either filtered or unfiltered LIF response and PAH concentration. Also note that the correlation between filtered and unfiltered response

is excellent. This may suggest: that the signal is not filtered enough to isolate the portion of the signal that is sensitive to the PAH fluorescence with minimum interference; or, that the relationship between the signal and tPAH concentration has not been appropriately described (e.g. linear or non-linear). In addition, methods have not been described to determine if the tPAH concentration is outside of the LIF range of sensitivity. Problems with PAH analysis were described in the above sections. These problems may also contribute to the lack of correlation between LIF and analytical results.

Table 5
Correlation between 2003 sediment PAH data and LIF (all surficial data)

tPAH range correlated (2003 SIM data)	Max Min	1,000,000 ppb 0 ppb				
n =		Total LIF Scan	Adjusted LIF (PAH 1,2,3)	tPAHs	cPAHs	cPAHs- PEQ
Total LIF Scan	29	1.00				
Adjusted LIF (PAH 1,2,3)	27	0.98	1.00			
tPAHs	29	0.03	0.10	1.00		
cPAHs	29	0.06	0.14	0.98	1.00	
cPAHs-PEQ	29	0.07	0.15	0.97	1.00	1.00

It is likely that the range of sensitivity of LIF is somewhat less than the range of quantitation for chemical analysis of PAHs. Therefore, while there may be a correlation within a range of PAH concentrations, there may not be a correlation over the entire range of PAHs found in sediments at this site. Table 6 shows the correlation coefficients between LIF and samples containing 0.5 to 50 mg/kg PAHs (US Steel analytical data), which is likely to be an important range at this site.

Table 6
Correlation between 2003 surficial sediment PAH data LIF, over a limited PAH concentration range
(500 µg/kg – 50,000 µg/kg: US Steel analytical data)

tPAH range correlated (2003 SIM data)	Max Min	50,000 ppb 500 ppb				
n =		Total LIF Scan	Adjusted LIF (PAH 1,2,3)	tPAHs	cPAHs	cPAHs- PEQ
Total LIF Scan	19	1.00				
Adjusted LIF (PAH 1,2,3)	18	0.97	1.00			
tPAHs	19	0.18	0.29	1.00		
cPAHs	19	0.14	0.23	1.00	1.00	
cPAHs-PEQ	19	0.21	0.31	0.97	0.96	1.00

Note that 10 fewer samples are included in the correlation, but that the results are not much better than the results shown over the entire range of samples collected (Table 5). In addition, the filtered and unfiltered LIF responses continue to correlate well.

These data suggest that, in spite of the theoretical promise of LIF technology, current filtering of the signal does not seem to optimize (or even elicit) a response that is correlated with laboratory measured PAH concentration of environmental samples.

MDH Conclusions and Recommendations

- 1) **Sediment data for the US Steel Site:** The US Steel 2003 data are adequate to determine the chemicals of concern (or chemicals of interest) at the site. This was the primary purpose for collecting these samples. In addition, these data are likely sufficient for fingerprinting chemical signatures of separate chemical groups on the site. However, information derived from these data are not sufficient to describe the extent and magnitude of any specific chemical contamination at this site. **Recommendation:** MDH recommends that either additional information be collected prior to remediation, or that more extensive sampling, analyses and data validation be conducted during cleanup activities to assure that cleanup goals are met.
- 2) **PAH Analytical Method:** Proper methods were reportedly used when splitting samples in the field. Therefore, it is likely that at least 1 laboratory had significant problems in determining the denominator when conducting chemical analysis of these sediment samples. There are likely problems with moisture determinations in at least 1 laboratory; TOC data from US Steel are suspect. In addition, both the individual sample PAH SIM data from 2003 and the individual sample PAH Full Scan data from 2004 correlated between labs, suggesting that the analytical side of the laboratory analysis was consistent between labs. MDH believes that SIM data can be similar to Full Scan PAH data in accuracy. While dilution error may be increased in SIM as a result of additional dilutions and the loss of surrogates, there are still sufficient QA/QC measures to assure reasonable accuracy in SIMs analyses. **Recommendation:** SIM data may be used to determine a PAH fingerprint for the site.
- 3) **Analytical Methods and Data:** The problems with the 2003 and 2004 data are likely the result of errors in the denominator of the reported concentrations. Causes of this could include; poor methods or techniques when the samples were split (field or laboratory), or problems with determining the dry weight of the samples. **Recommendation:** MPCA should develop proposals to assure that future analytical data are reliable. MDH staff will assist on request.
- 4) **LIF:** While LIF technology has promise, there was poor agreement between LIF and analytical laboratory data. This could be because:
 - a) the range of PAH concentrations through which LIF is sensitive is much smaller than the range of PAHs found at this site;
 - b) a good description of the relationship between LIF signal and tPAH concentration has not been established (e.g. linearity vs non-linearity, indications in signal response that the concentration is outside the range of sensitivity);
 - c) the important aspects of the LIF signal that correlate with PAH concentration have not been identified; or,
 - d) the PAH laboratory analytical data are not reliable enough to develop a reasonable correlation with LIF.

Recommendation: MDH encourages MPCA and US Steel to work with the LIF manufacturer to optimize LIF response to PAHs prior to conducting additional work with this tool.

Public Health Action Plan

The Minnesota Department of Health will continue to assist the MPCA in their assessment of the US Steel site. In addition, MDH will assist the MPCA develop methods or controls that will increase the reliability of site data.

References

Federal Water Pollution Control Administration (1967-8). Aerial Photographs of US Steel Facility and St. Louis River. US EPA, Courtesy G. Glass, Duluth, MN.

Minnesota Pollution Control Agency (1989). Record of Decision (US Steel Site). St. Paul, MN. Declaration, Administrative Record Index, Summary of remedial alternative selection, February, 22, 1989.

US Steel (2003). Former Duluth Works Sediment Characterization and Tier I Risk Assessment Work Plan. Prepared by URS Corporation, Pittsburgh, PA. September 5, 2003.

Certification

This Minnesota Public Health Consultation, Technical review of discrepancies in 2002 Laser Induced Fluorescence data, and 2003 and 2004 analytical data, St. Louis River Sediments: US Steel Site, Duluth, MN, was prepared by the Minnesota Department of Health under a cooperative agreement with the federal Agency for Toxic Substances and Disease Registry (ATSDR). It was completed in accordance with approved methodologies and procedures existing at the time the health consultation was initiated. Editorial review was completed by the Cooperative Agreement partner.



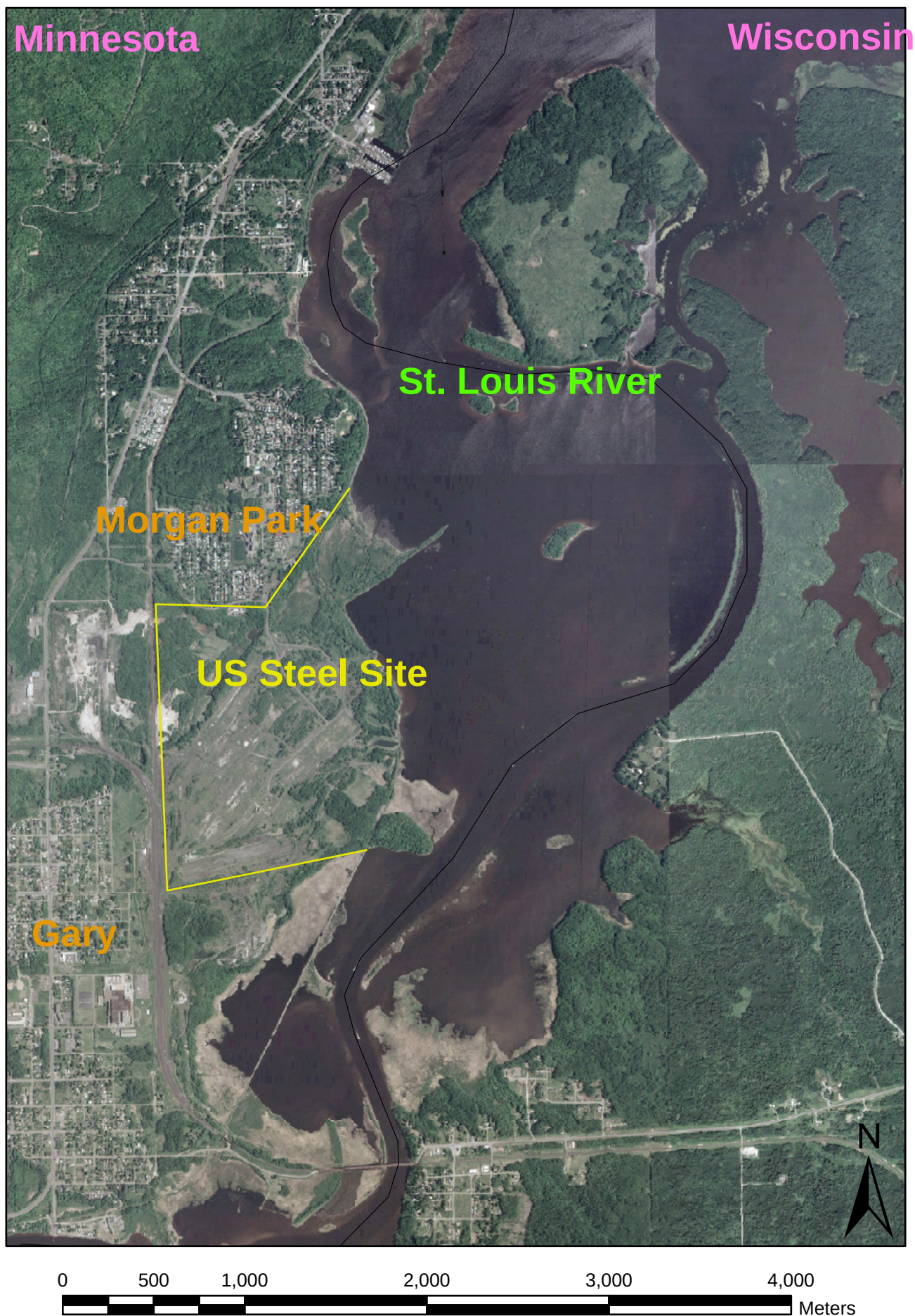
Technical Project Officer, CAT, SPAB, DHAC

The Division of Health Assessment and Consultation (DHAC), ATSDR, has reviewed this health consultation and concurs with its findings.



Team Lead, CAT, SPAB, DHAC, ATSDR

Attachment 1



Attachment 2



Attachment 3

