Detailed Investigation of the Minnesota Slip

Featuring Laser Induced Fluorescence

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Minnesota Pollution Control Agency

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Duluth Minnesota

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List of Acronyms and Abbreviations

ACC	Air Combat Command
AMSL	Above Mean Sea Level
AOC	Areas of Concern
COC	chemicals of concern
DECC	Duluth Entertainment and Convention Center
DTI	Dakota Technologies Inc.
GLIN	Great Lakes Information Network
GLNPO	Great Lakes National Program Office
GPS	Global Positioning System
LIF	Laser Induced Fluorescence
MPCA	Minnesota Pollution Control Agency
NTS	Northeast Technical Services
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyls
PEC-Q	probable effect concentration quotient
R-EMAP	Regional Environmental Monitoring and Assessment Program
RL	Reporting Limit
SQT	sediment quality targets
TOC	total organic carbon
USACE	US Army Corps of Engineers
USEPA	U.S Environmental Protection’s Agency
UTM	Universal Transverse Mercator
WCEC	West Central Environmental Consultants

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Photographs were taken by Andrew Streitz, Nicole Barg, and Alex Hokenson. Technical review of the draft report was provided by Steve Hennes (MPCA). The compilation of previous studies was performed by Alex Hokensen and Nicole Barg (MPCA). All analyses, figures, and tables were prepared by Andrew Streitz, except where noted. The authors wish to thank Managers Michael Kanner and Douglas Beckwith (MPCA) for their support.

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Disclaimer

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Executive Summary

A detailed investigation of the sediments of Minnesota Slip was performed in March 2004, using a real-time survey tool in combination with traditional sediment sampling techniques. Although other assessment studies have been conducted at the Slip, sampling limitations experienced during those investigations precluded developing an understanding of the depth of contamination. Building on these previous results, the goal of the current investigation was to survey and sample the full extent and magnitude of sediment contamination with the Slip. Survey locations were accessed through the ice with a Laser Induced Fluorescence (LIF) tool, targeting 29 points spatially distributed throughout the Slip. Continuous LIF records were produced from depths ranging from 0 to 20 feet beneath the water-sediment interface. The results of this survey were then used to locate sites for eight sediment cores, from which 18 sediment samples were collected for laboratory analysis. These borings were extruded, sampled and submitted to chemical analysis for metals, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and various physical parameters. Maximum total PAH concentrations from an individual sample was 270 mg/kg. The maximum concentrations for mercury, lead and zinc were 3.3, 544 and 559 mg/kg respectively. PCBs were not found at a detection limit of 40 ug/kg.

The LIF tool identified a thick sequence of material identified as coal tar constituents in the back half of the Slip, thinning toward the mouth or front of the Slip. Cross-sections based on the LIF profiles reveal the extent and depth of this contamination. Total PAH concentrations were used to correlate laboratory data against the LIF results. The LIF fluorescence response % correlated to 0.9 with total PAHs for samples in the back half of the Slip where the erosional affects of seiche, wave action, and propeller disturbance were at a minimum. This statistical treatment of the data produced a statistical measure of equivalence, allowing the more numerous and better spatially distributed LIF results to be used in the determination of the degree of sediment contamination by PAHs.

In order to place the data results in the context of sediment toxicity for the benthic community the concept of sediment quality targets (SQT) and probable effect concentration quotient (PEC-Q) were introduced. That analysis showed an elevated risk to the benthic community and the potential for contaminated sediment to contribute to compounds that bioaccumulate in the local fish food chain. The Report concludes with a recommendation that a list of viable cleanup alternatives be developed and evaluated in a Feasibility Study, which would then guide the remediation of the Slip.

CHAPTER 1
Introduction

Minnesota Slip, an active manmade slip surrounded by land on three sides, is located at the mouth of the St. Louis River in the Duluth Harbor (Figure 1). The river, which discharges into Lake Superior, has a long history of serving the manufacturing and shipping needs of the very active Duluth-Superior shipping port, and has been home to significant historical heavy industry including paper mills, coal gasification plants and steel processing. The port remains active in the transport of iron ore, coal, limestone and grain, and is the largest on the Great Lakes in terms of shipping volume (Duluth Port Authority 2005).

Figure 1: Location of Minnesota Slip in Duluth Harbor

Due to the considerable contamination in the St. Louis River estuary, the International Joint Commission (IJC) designated the lower St. Louis River as one of 43 Areas of Concern (AOCs) in the Great Lakes basin in the late 1980's. Many sites within the St. Louis River AOC have elevated concentrations of metals, PAHs, PCBs, dioxins, and furans (Schubauer-Berigan and Crane 1997; Crane et al. 1997; Breneman et al. 2000).

Minnesota Slip has been studied in the past as a part of the St. Louis River AOC, see Section 2.4, Sampling History. These investigations showed that the sediments in the Slip are contaminated with PAH, heavy metals and PCBs and other compounds in lesser concentrations. However, there was not enough information on the sediment contamination to complete a risk assessment to human health and the environment. Therefore the MPCA applied for and received a grant in 2003 from the USEPA's GLNPO to perform a complete horizontal and vertical extent and magnitude investigation of contamination in the sediments of the Slip. The 2004 study was developed after it was decided that more information was needed to understand the extent of contamination in the Slip. The objectives of this study were as follows:

1. To delineate the extent and magnitude of contamination throughout the Slip, particularly at depth;
2. To use a sediment screening tool, laser induced fluorescence, to provide qualitative detail as to the presence of PAHs in the sediments at depth in real time;
3. To use LIF to target and reduce the number of collected sediment samples submitted for chemical analyses;
4. To assess the correlation between LIF results and total PAH analytical results; and
5. To conduct a limited screening ecological risk assessment.

Once the dimensions of the chemical characteristics and volume of sediment contamination are better understood, then a risk assessment and comprehensive solution for the remediation of the Slip will be considered.

If an unacceptable risk to human health or the environment is established, the collected data can be used to perform a "Sediments Feasibility Study", which will generate a range of remediation options and costs. At that point, the MPCA and other possible regulators will select a cleanup remedy and seek funding to implement a remedial solution for the contaminated sediments.

CHAPTER 2
Description of Study Site

2.1 Introduction

Minnesota Slip is located in the northern section of the Duluth Harbor basin between Canal Park and the Duluth Entertainment and Convention Center (DECC) (Figure 1). Though the Slip is oriented approximately 30 degrees west of north in its long dimension, for the purposes of this Report when referring to compass directions the Slip will be assumed to be oriented due north. The east side of the Slip is bounded by a parking lot, hotel, restaurant and shops, while the west side is bounded by harbor Avenue, the DECC, and a movie theater. The north end of the Slip is bounded by a sidewalk and the south is open to the harbor. The Slip mouth is spanned by a drawbridge allowing access between the DECC and Canal Park. Both the sidewalk and the foot bridge have considerable pedestrian traffic. The land that borders the Slip to the west is owned by the DECC. The property and the buildings on the eastern half are privately owned. The City of Duluth owns and maintains both the sidewalk on the north side and the draw bridge.

The total area of the Slip is slightly larger than three acres. There are currently three vessels permanently docked in the Slip. They are the former United States Steel (US Steel) flag ship the SS. William A. Irvin, and as of May 26, 2004, the decommissioned US Coast Guard Cutter, Sundew. The US Army Corps of Engineers (USACE) Tug Boat, Lake Superior; is a seasonal resident of the Slip. The Slip has been home to at least one of these floating museums since 1986, providing daily tours in the summer months. Remaining space in the Slip is occupied in the summer by charter fishing boats and docks and a harbor tour boat. The Irvin and the tour boat are docked on the west side of the Slip while the charter fishing boats and the Sundew are docked on the east side (Figure 2). The drawbridge controls entry into and out of the Slip while also acting as a wave retention wall that decreases washout of the Slip.

Figure 2: Looking North into Minnesota Slip from the Drawbridge, July 2004.

Estimates of the volume of contaminated sediments are of limited use due to the incomplete nature of past investigations, but estimates have ranged between 2,000 to 6,000 cubic yards. The main contaminants as determined in the previous investigations are PAHs, PCBs, and mercury. An updated discussion of contaminants and affected sediment horizons based on the current sampling can be found in Chapter 5 of this report.

There are three storm sewers that empty into the Slip and two that empty just outside the mouth of the Slip (Figure 2). Two of the three storm sewers that empty into the Slip are located at both of the east and west corners of the north end of the Slip. The third storm sewer is located approximately 125 feet south of the northern end of the Slip, on the west wall. The pipe leading to this outfall will be replaced by the City in a separate project in 2005. This outfall was identified as a major contributor of sediment to the Slip in this investigation (Water Depth display in Appendix A), and in its new configuration it is built with a sediment trap. Most of the Slip drainage area borders the downtown business area of Duluth and adjacent residential neighborhoods; extending from 2nd Avenue West to 1st Avenue East and up to 14th Street. Storm sewers that drain Canal Park and Commerce Street also discharge into the Slip (Crane et al. 2002).

2.2 Site Hydrogeology

Regional geology in the Duluth area consists primarily of materials deposited during the last glaciation, and more recently as river sediment, overlying Precambrian igneous and sedimentary bedrock. These materials consist of silts, sands, and gravels which were deposited as the glaciers retreated northward. Fine grained sediment, primarily red silt and clay, was deposited in the ancestral glacial Lake Duluth. This red silt and clay occurs over much of the lower elevations in the Duluth area.

Bedrock units underlying the area consist of olivine gabbro and anorthositic gabbro members of the Duluth Complex, and the sedimentary units of the Fond du Lac Formation. The Duluth Complex is lower Precambrian, and the Fond du Lac Formation is upper Precambrian in age. The gabbroic members of the Duluth Complex form the hills to the west of the St. Louis River and Lake Superior shore (MPCA 1995).

2.3 Site History (taken largely from Crane et al. 2002)

Historically, Minnesota Slip has undergone several physical modifications since European settlement of the area. The area encompassing the northern section of the Duluth Harbor was initially swampland. Modern development of the harbor began after 1861. Construction of the Duluth Ship Canal was started in 1870, thereby providing a Duluth entry into the harbor from Lake Superior. As of 1887 a portion of the current Minnesota Slip had already been formed through dredging operations. The Slip formerly was called the Marshall Wells Slip, and a Marshall Wells building was adjacent to it; part of this building is now called the Meierhoff building.

Several historical photos of the Slip are retained at the USACE Maritime Museum in Duluth. A photo taken in 1904 shows a coal yard west of Minnesota Slip that was eventually replaced by a scrap yard. A double train freight shed used to be located just west of the Slip. A May 1, 1929, photo of the Slip shows a pile of material to the north of the Slip that appears to be coal. Another historical photo shows workers dumping wheelbarrows full of material into the Slip, approximately half-way down the east side of the Slip. As of 1931, there was another Slip just west of Minnesota Slip; this area is now filled in and is the current location of the DECC. Over time, parts of Minnesota Slip have been dredged out and filled in. However, none of these historical businesses have been determined to be directly responsible for sediment contamination of Minnesota Slip.

The contamination constituents and proportions found in the Slip sediments are similar to the coal tar wastes found off the US Steel and Interlake/Duluth Tar sites further up the river, especially for average total PAH concentrations (Appendix A, Figure A1). At the US Steel Site the steel process waste stream was contaminated chiefly with metals and PAHs that originated with the large amounts of coal used in the coking process. It may be that coal gasification, which occurred in many places along the harbor including the Canal Park area, was the cause of the similar waste products identified in the Slip.

2.4 Sampling History

In 1993, a survey of sediment quality in the Duluth/Superior Harbor was conducted (Schubauer-Berigan and Crane 1997). The goals of this survey were to quantify the level of sediment contamination of metals, pesticides, PCBs; total organic carbon (TOC), measure vertical distributions of these contaminates and prioritize areas of the Duluth/Superior Harbor for more investigation. This study had one sediment core in the Slip labeled DSH 40, located near the Irvin.

In 1994, a follow-up study to the 1993 sampling was performed. It targeted the 1993 hotspot areas of concern within the Duluth/Superior Harbor, which included the Slip (Crane et al 1997). This study included five sediment cores taken from Minnesota Slip, MNS 1-5, and recommended that the contaminants of concern for this Slip included PAHs, PCBs, and mercury. It also referenced the Ontario Ministry of Environment and Energy Lowest Effect Level guidelines in identifying other contaminants of concern. The MPCA used made use of these guidelines because at that time it did not have state screening levels guidelines.

In 1999, sediment samples were collected for a sediment remediation scoping project (Crane et al. 2002). The main goal was to collect additional samples to further delineate the vertical and horizontal distribution of PAHs, PCBs, lead, mercury, and zinc. A total of 22 core sites were taken from Minnesota Slip. Contamination within the Slip was found to be heterogeneous, with several sites exceeding the corresponding Level I or Level II Sediment Quality Targets. The greatest exceedence of the Level II Sediment Quality Targets occurred with PAHs. Highlights of the Level I and II Sediment Quality Targets are reproduced and discussed in Chapter 8 of this report, and can be found in their entirety in Crane et al. 2000.

Minnesota Slip has also been included in the following MPCA sediment assessment studies for the St. Louis River AOC:

- Regional Environmental Monitoring and Assessment Program (R-EMAP) surveying, sampling and testing: 1995 and 1996 sampling results (Breneman *et al.* 2000 and unpublished data) [one surficial (0-5 cm) site sampled in 1995 and resampled in 1996 in Minnesota Slip];

- Minnesota Slip sampling to assess PAH analytical techniques (unpublished MPCA data 1998) (two core sites and three surficial sites); and
- Bioaccumulation of contaminants in the Duluth-Superior Harbor (AScI Corporation 1999) (four surficial sites in Minnesota Slip).

Finally, in the spring of 2002, a USACE project dredged approximately 750 cubic yards from the back half of the Slip (USACOE 2002). The clam-shell dredging produced sediments to be used in an innovative treatment test performed at Erie Pier (Figure 3).

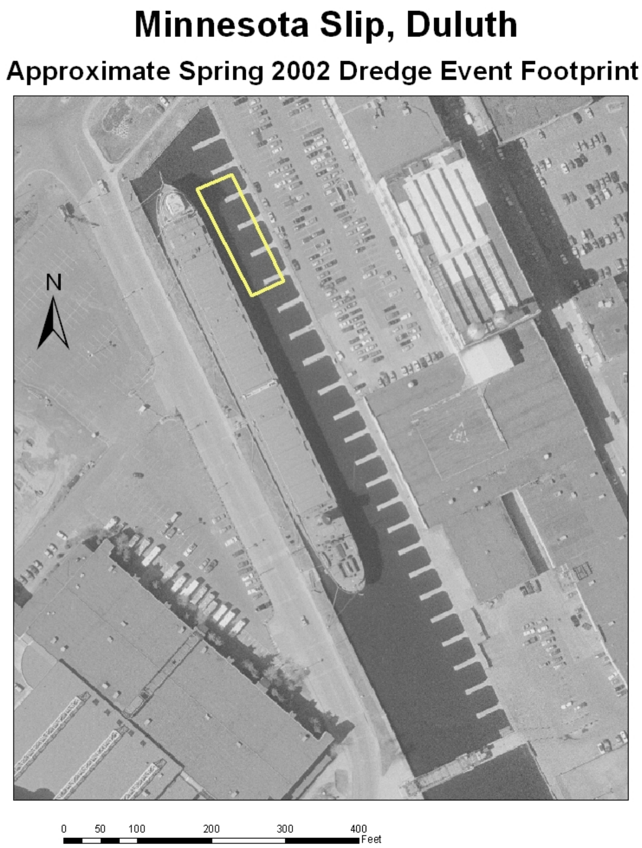


Figure 3: Approximate Area Dredged in Minnesota Slip, Spring 2002

2.5 *Other Associated Projects*

The MPCA and the City of Duluth worked together to submit complimentary grants to GLNPO to ensure that if Minnesota Slip was remediated that it wouldn't suffer degradation from contaminated storm water and sediments emptying into the Slip at several outfall points. Figure 4 shows the network of storm sewers in the neighborhood of the Slip, which is outlined in red. The largest of the storm sewers which empty into the Slip are circled in green. The City received funding to implement the installation of sediment traps to reduce sediment loading, which will be completed in 2005. Identification and implementation of an effective Best Management Practice for dealing with storm water runoff will reduce the quantity of pollutants discharging to the Slip, and therefore to the St. Louis River. An effective project will serve as a model for other similar urbanized areas of Duluth and Superior along the St. Louis River as well as an example to other cold climate lake communities.

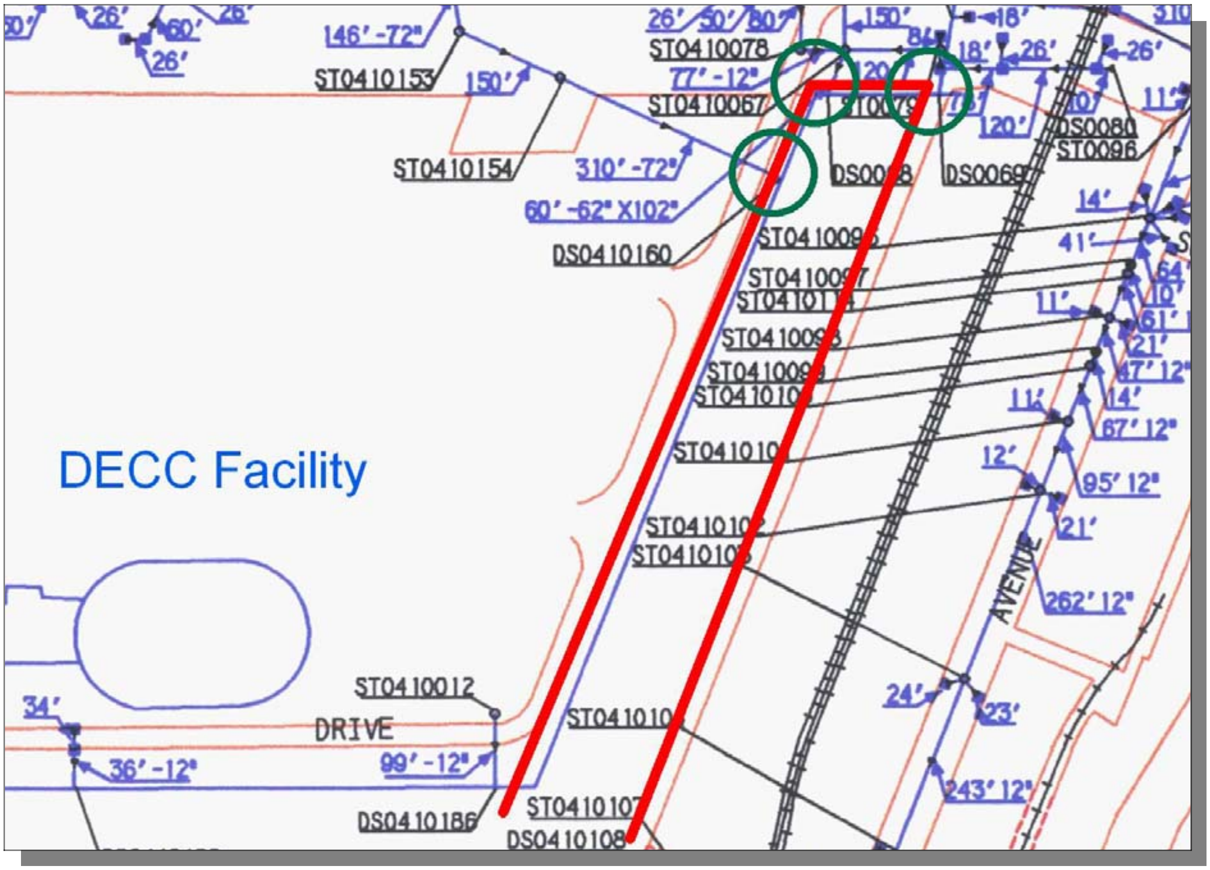


Figure 4: Detail from City of Duluth Storm Sewer System at the Slip

CHAPTER 3
Investigation Strategy and Sampling Methods

3.1 Study Objectives

The 2004 study was developed after it was decided that more information was needed to understand the extent of contamination in the Slip. The objectives of this study were as follows:

1. To delineate the extent and magnitude of contamination throughout the Slip, particularly at depth;
2. To use a sediment screening tool, laser induced fluorescence, to provide qualitative detail as to the presence of PAHs in the sediments at depth in real time;
3. To use LIF to target and reduce the number of collected sediment samples submitted for chemical analyses;
4. To assess the correlation between LIF results and total PAH analytical results; and
5. To conduct a limited screening ecological risk assessment.

When setting the project objectives it was noted that previous investigations of the Slip made use of hand samplers and the USEPA vessel Mudpuppy's vibrocorer drilling system. Unfortunately, due to the depth-limiting constraints of these two methods in the Slip the depth of investigation achieved was no greater than seven feet. A major goal of the current investigation was to collect information on sediments well beyond the depths achieved during investigations, and if possible penetrate into undisturbed, native sediments.

To decide at what depth to investigate the sediments, historical dredging depths were researched. Table 1 shows the changing depth to which the Duluth Harbor has been dredged in the last 150 years (Plass 2002). Given that the Slip was constructed before 1887 (Crane 2002), and remained in active use through the 1960's, this indicates that the Slip itself was most likely dredged to a maximum level of 27 feet. In a personal communication to an MPCA employee, Bill Meierhoff, the President of Marine Iron & Ship Building Company and a longtime owner of land on the east side of the Slip, stated that in 1935, the depth of the Slip was 21 feet (MPCA 2004). This provides support to the timeline laid out in Table 1, therefore it was decided to penetrate beyond that depth in the Slip to ensure a complete investigation of the sediment.

Changing Depth of the Duluth Harbor Shipping Channel	
Year	Dredged Depth (ft)
1873	13
1881	16
1902	20
1960	27

Table 1: Dates of Changes in the Proscribed Dredging Depth in the Duluth Shipping Channel.

The 2004 sampling made use of Geoprobe™ hydraulic push technology, which allows depths of penetration of at least 30 feet of sediment. This tool is capable of sampling the sediment quickly and can be mounted on a small tracked vehicle when maneuverability or weight are issues of concern. An advantage of utilizing this rig was that it could also deploy an innovative survey tool called Laser Induced Fluorescence (LIF). LIF was selected due to its ability to provide detailed coverage of the Slip through probe pushes that can be collected quickly, and which reveal qualitative information on the presence of PAHs in real time. The strategy of the investigation was to first collect the LIF information and study the results on the ice with the goal of strategically selecting the location of the sediment cores. The sediment sampling is the second phase of the field work which includes logging of the geology and collection of sediment samples for laboratory analysis.

Both types of information, the LIF and the chemical analyses of sediment samples were collected because both separately and in combination, the two methods confer important benefits to the investigation. This follows the USEPA system, TRIAD (EPA 2005). From the referenced web link:

> *The United States Environmental Protection Agency (EPA) supports the adoption of streamlined approaches to sampling, analysis, and data management activities conducted during site assessment, characterization, and cleanup. Under the name of "the Triad approach," (this involves) integrating systematic planning, dynamic work plans, and real-time measurement technologies to achieve more cost-effective hazardous waste site cleanup strategies.*

The LIF data collection phase is faster and cheaper to perform than the sediment collection and chemical analysis phase. The sediment collection and laboratory analysis phase produces hard numbers in the form of chemical concentrations, results that are commonly produced at remediation sites. Chemical analysis is expected, accepted and form the basis for remediation decisions. The LIF technique is not well known and its results are not readily accepted as the basis for a remediation decision. Therefore the analytical results will be compared against the corresponding LIF results to produce an analytical equivalence, where a total PAH level corresponds with a specific LIF response number (see Table 2 for a complete list of PAH compounds). In this way the more complete investigation of the Slip by LIF may be leveraged by the fewer analytical results to give a more complete understanding of the three-dimensional extent and magnitude of PAH sediment contamination than would otherwise be possible if only the chemical sediment sampling phase had been employed.

The LIF discussion has focused upon just one of the contaminant types in the Slip, coal tar constituents containing PAHs. This is because the LIF tool measures the fluorescent properties of PAH compounds, a response not shared with metals and PCBs. Therefore the approach taken in this report will be to demonstrate the correlation of the LIF response with the total PAH concentration on the one hand, and to also demonstrate the correlation of the total PAHs with PCB and metal concentrations on the other. Correlations will be generated for both high and low concentration environments.

3.2 Site Preparation- Ice Thickness and Access

Though LIF had been successfully used on the ice in the St. Louis River off of the US Steel Superfund site in West Duluth in March 2002, the Slip presented several potential obstacles. First, unlike the US Steel site where most of the work was done in less than four feet of water, the depth of water beneath the ice in the Slip averaged 15 feet. This depth was a safety concern to all who would work on the site. Though the Slip always freezes in the winter, the ice thickness had never been measured. MPCA contractors hired a local firm to test the thickness of the ice in two-week increments leading up to the planned work in March 2002.

A second problem was identified in December 2002, when an aerator was installed into the northeastern corner of the Slip by employees of the Duluth Steam Plant. The plant was using the aerator to keep a portion of the Slip open, to be used with a pump as a backup water source in case the city water supply to the Plant was ever interrupted. MPCA contractors from West Central Environmental Consultants (WCEC) met with Plant staff and received their support to have the contractors install a dry well for use by the plant. This gave the plant access to water in the case of emergency, while allowing the Slip to freeze completely. Within ten days of the aerator's removal from the water the Slip was completely frozen throughout the extent of the Slip (Figures 5 & 6).

◀ Figure 5: Slip with Bubbler in Operation; January 6, 2004.

Figure 6: Slip after Bubbler ▶ Disconnected; January 22, 2004.

Ice soundings were conducted twice in the month before field work started, on February 18 and 24, 2004 (Appendix A, ice soundings). The soundings revealed an ice thickness greater than 12 inches across the Slip on February 18, and a thickness of at least 18 inches by February 24. Though the ice was not consistently thick enough to support a truck-mounted probe, it was sufficient for the smaller track-mounted probe, which was the approach selected for this project.

The last remaining site access issue was getting the equipment down to the ice. Because the pier wall was three feet above the ice surface, the MPCA contractors worked with a subcontractor to build a wooden ramp to reach the ice. The ramp was built off the western pier, on the DECC property south of the Irvin. It remained in place during the week of field work. Access to the ramp was controlled at night with barricades.

3.3 Collection of Laser Induced Fluorescence Data

WCEC coordinated field activities in the Minnesota Slip for work performed between March 1 and March 7, 2004. Following mobilization of all equipment to the Slip, the first step in the investigation of the Slip was to use the LIF tool to investigate the vertical and horizontal extent of possible sediment contamination across the entire Slip. The LIF equipment fit onto a small tracked rig that was controlled with a remote by an operator walking alongside. The rig easily maneuvered through the snow, slush and ice found throughout the site. The rig was brought by trailer to the site every morning from a nearby garage.

A pre-planned grid of sample points was used as a guide, though in practice site conditions often required a small shifting of grid node position. These conditions included ice conditions, locations suffering Global Positioning System (GPS) blackouts and probe refusal. The field procedure at each new sample location was to first drill a hole through the ice with an ice auger, measure the thickness of the ice, measure the depth to the top of sediment, and then employ the LIF tool. Following completion of the LIF data collection phase, the grid node location was marked with real-time kinematic differential GPS receivers capable of sub-meter accuracy. (A more complete discussion about the LIF can be found in Chapter 4.) Displays were produced using both the thickness of ice and the Slip Bathymetry based on these measurements (Appendix A).

The goal in this phase was to collect LIF information completely through and beneath the contaminated sediments at all points. This was determined in two ways. First, a visual inspection of the LIF response in the field was reviewed in real time as the probe was advanced into the sediment. When the LIF response both dropped below 0.5% and the LIF response color changed to blue or green, the LIF operator signaled that there was no LIF response. The second indicator came from the probe operator who frequently identified a strong contrast in the physical resistance of the sediment to the advancing probe. The accepted field procedure was to advance the LIF probe at least four feet below the last positive coal tar detection.

The first stage of the investigation lasted two days and involved collecting LIF information at 29 locations that were evenly distributed throughout the Slip (Figure 7). The locations of the LIF probe points and sediment cores are listed in Appendix A. The locations are presented in the Universal Transverse Mercator (UTM) Coordinate system. Bathymetry, ice thickness, and sub-bottom material data was also collected during advancement of the LIF probes. The docks pictured in Figure 7 are present in the Slip only in the summer, and consequently were not present during the LIF Survey.

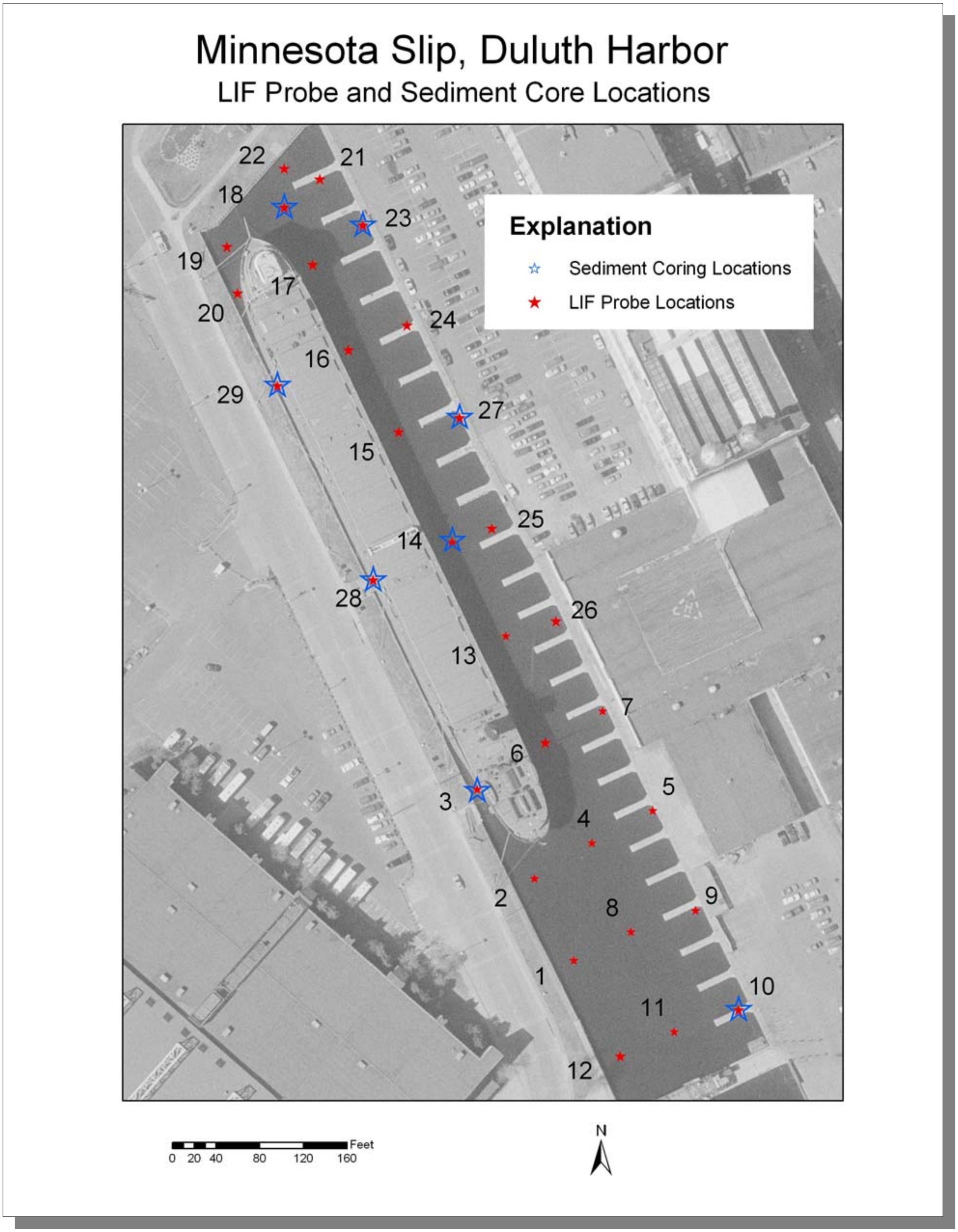


Figure 7: Location of LIF Probes and Sediment Cores.

Figure 8 shows the field collection of LIF information of the sediment through the ice at Grid Node #1. The real time display of depth vs. LIF response is displayed via a portable computer for the operator, and saved as an electronic file (Figure 9). This immediate feedback allowed MPCA staff to identify geologic and contamination patterns, trace possible contaminated sediment horizons, and plot the sediment sampling locations and depths.

◀ Figure 8: Collection of LIF Information in the Slip.

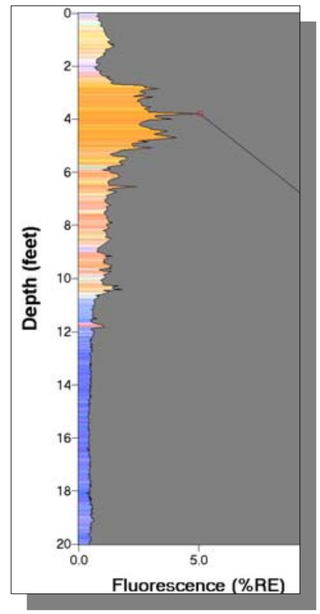


Figure 9: Sample LIF JPG, Point #1 ▶

Figure 9 displays a LIF readout from Probe Point #1, taken close to the Irvin on the west side of the Slip. The strength of the matrix fluorescence is measured on the horizontal scale. The greater the response, the greater deviation of the signal to the right hand of the display. The area encompassed by this signal is also colored using the standard color scheme ROY G BIV (red, orange, yellow, green, blue, indigo and violet) and links the hotter colors of red and orange to the strongest identification of coal tar constituents, and blue to the weakest response. Combining the strength of the amplitude with the color of the response yields an interpretation of whether the matrix is dominated by coal tar constituents. The large amplitude peaks in Figure 9 found between 2 and 6 feet are therefore interpreted as arising from an elevated concentration of coal tar in the sediments. In contrast, the small amplitude, blue colored response below 11 feet is interpreted as having no coal tar constituents. More information on the interpretation of the LIF response is available in Appendix B, where two reports produced by the LIF subcontractor Dakota Technology are on display. The company's main researcher is Randy St. Germain, and it is his pioneering work that has produced a reliable field screening tool (St. Germain 2002).

3.4 Collection of Sediment Cores and Samples for Laboratory Analysis

Following the successful collection of the first 27 LIF probe records, the Geoprobe™ rig was modified to collect sediment cores in two-inch outside-diameter transparent acetate tubes. LIF records and sediment samples were collected at Points 28 and 29 at the end of the week. They were collected out of sequence due to their location between the Irvin and the Slip wall. These points were collected with the truck-mounted push probe. The complete field procedure is described in the document: "Minnesota Slip Site Sediment Sampling and Analysis Plan", prepared for the Minnesota Pollution Control Agency, Duluth, MN, by West Central Environmental Consultants, Morris, MN, on February 19, 2004 (WCEC 2004).

Sediment core locations were selected that ran the range from strong LIF response to weak LIF response, and finally to near zero LIF response (background). In this way, the LIF-analytical PAH relationship could be analyzed across the LIF spectrum, and supposedly across the contaminated sediment concentration range as well. Sediment borings were also balanced spatially throughout the Slip to provide a representative review. Locations of sediment samples are displayed in Figure 7. Seven sediment borings (3, 10, 14, 18, 27, 28, and 29) were placed within inches of the related LIF boring locations. Sediment samples from each sediment boring were submitted to NTS for analysis of PAH, PCB, RCRA metals, Diesel Range Organics (DRO), moisture, and zinc, with a subset run for Total Organic Carbon. The sediment samples were submitted to laboratory analysis for parameters listed in Table 2. In addition, grain size analyses were performed on two samples.

Minnesota Slip Analytical Parameters March 2004	
Metals	**Polycyclic Aromatic Hydrocarbons (PAHs)**
Arsenic	Acenaphthene
Barium	Acenaphthylene
Boron	Anthracene
Cadmium	Benzo (a) anthracene
Chromium	Benzo (a) pyrene
Lead	Benzo (b) fluoranthene
Mercury	Benzo (ghi) perylene
Silver	Benzo (k) fluoranthene
Zinc	Chrysene
Selenium	Dibenzo (a,h) anthracene
	7, 12-Dimethylbenz (a) anthracene
Other	Fluoranthene
Polychlorinated biphenyls (PCB)	Fluorene
Diesel Range Organics (DRO)	Indeno (1,2,3-cd) pyrene
Total Solids (%)	2-Methyl-naphthalene
Total Organic Carbon (TOC)	Naphthalene
Moisture Content	Phenanthrene
	Pyrene

Table 2: Laboratory Parameters for Sediment Samples

CHAPTER 4
LIF Results

4.1 Introduction

The goal of this chapter is to introduce the field screening tool, LIF, describe how this information was collected, and graphically review the results. A more detailed, numerical review of the data will be performed in Chapter 6.

4.2 Introduction to LIF (St. Germain 2002)

Fluorescence is a property of some compounds where absorbed Ultra Violet light stimulates the release of photons (light) of a longer wavelength. Fluorescence, a property of many aromatic hydrocarbons, can be used to detect small amounts of substance in/on a much larger matrix. This method has been used in laboratories for decades. Now with the availability of high power light sources and optical fibers, Dakota Technologies, Inc (DTI) has brought this technology to the field.

The system developed by DTI sends UV light through fiber optic cable strung within rods. The light exits through a window in the side of the probe. As the probe is advanced the soil is exposed to the UV light. If fluorescent compounds exist (i.e., contaminants), light is emitted. The "signal" light is transmitted through a fiber, back uphole to be analyzed. Responses are indicated in real-time on a graph of signal vs. depth. The graph can also display false color logs and waveforms to aid in identification of the contaminant present. LIF responds to virtually all creosotes and coal tars.

4.3 Presentation of LIF Response Results

The LIF data collected on the ice was stored in a variety of computer formats including the JPG format. Printouts of the waveforms for all 29 probes are presented in Appendix D. Typical of these displays is Figure 10, which is the LIF response record for Grid node #9. Below the header information at the top of the record is the continuous waveform which shows the LIF response extending from the water-sediment interface to a depth of 20 feet (left-hand scale). There are four main peaks in the first six feet of the record which show an LIF response of greater than 2% (horizontal scale at the bottom). However not all of these peaks are in response to coal tar. In order to make that judgment it is necessary to consider the waveform color which is diagnostic of PAH compounds.

The color of the waveform comes from the integration of wavelength, fluorescence delay and signal response. To the right are waveform insets corresponding to the depths of 1.97 and 2.47 feet. The inset corresponding to 1.97 shows four normal shaped peaks with central tendencies distributed on the time (horizontal) scale, vs. signal intensity on the vertical scale. The combination of these colors provides the orange color of the signal at 1.97 feet below the water-sediment interface. Red and orange colors are diagnostic of coal tar (St. Germain 2002), and will be identified in this report as an indicator of the presence of coal tar and elevated total PAH concentrations.

In contrast to this interpretation of the strata at a depth of 1.97 feet, the LIF response below six feet is blue/green and has very small amplitude. The interpretation is that this sediment extending from six feet down is probably not contaminated with PAHs. Blue-green is understood to represent a negligible presence of fluorescing compounds. The actual relationship between LIF response and total PAH concentrations will be developed later in this report.

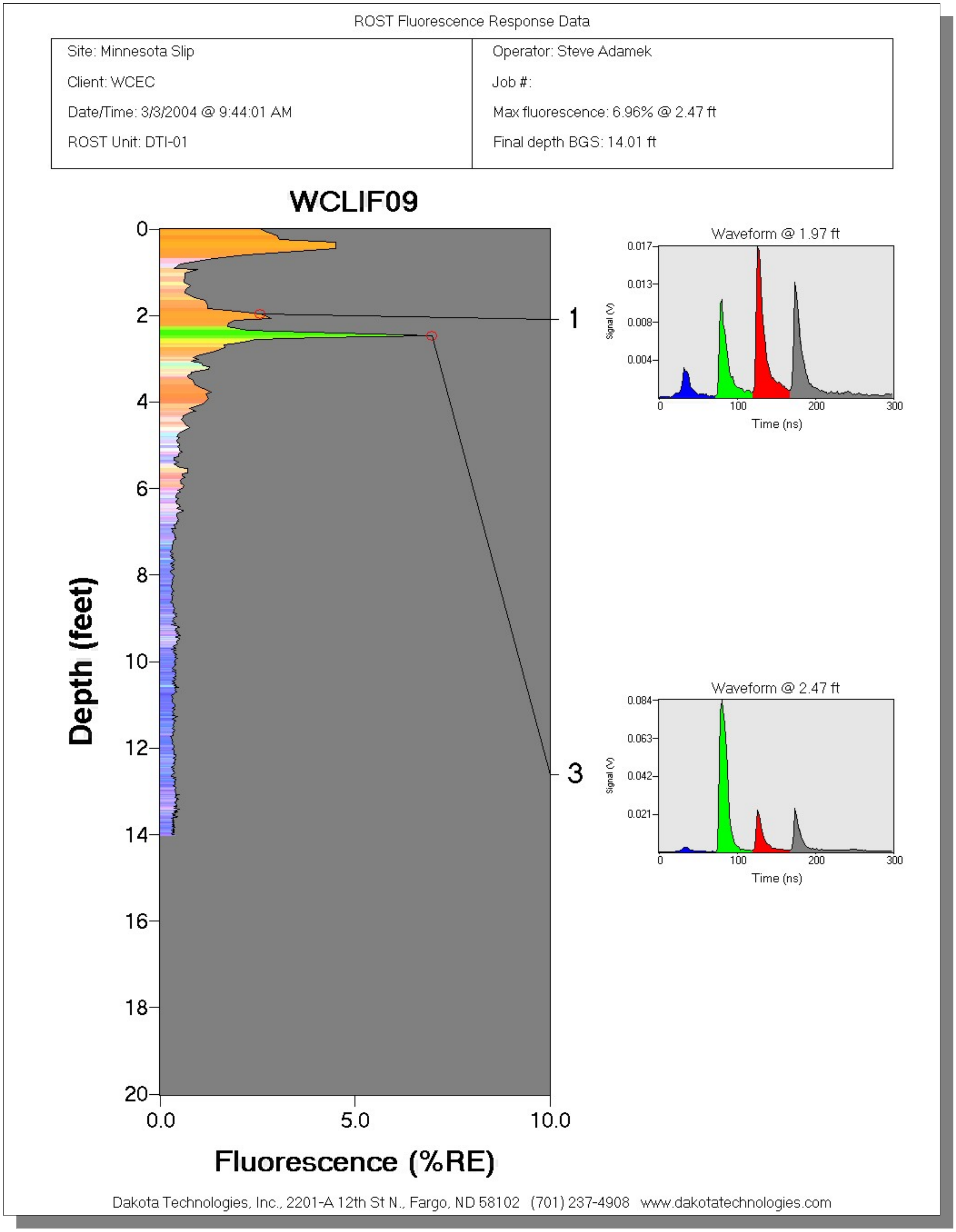


Figure 10: LIF Fluorescence Response Record for Grid Node #9.

That leaves the anomalous green response at 2.47 feet. The LIF response is large (~7%), but narrow, encompassing roughly 0.25 foot. Based on its green color, the narrow spike in the LIF response is disregarded as an indicator of increased PAHs. This anomalous LIF signal is superimposed on top of the orange response corresponding to 2.5% LIF response. The most likely source of this anomalous signal is peat.

4.4 Interpretation of LIF Results

The LIF response records can be used in a variety of ways to investigate the Slip. The simplest approach is to study the records directly as an indicator of what lies below the sediment-water interface. Two examples are presented as Figures 11 and 12. Figure 11 is a display of ten LIF readouts that run in a line down the center of the Slip, roughly north-south (see plan view inset). They are arranged so that the top of the LIF readouts, which each begin at the sediment-water interface, are oriented with the elevation of the sediment surface at the same point in the Slip. Therefore the display can be read as a cross-sectional representation of LIF response along the long dimension of the Slip.

The river surface elevation used in this display is 601 feet Above Mean Sea Level (AMSL), which is an average of reported historic levels. Information on current and historic lake levels was obtained from the Great Lakes Information Network (GLIN 2004).

Several observations on the disposition of the sediments may be made from a study of this display. First, the Slip is deeper at its mouth, shallower in the back. (Note that “front” refers to the southern end of the Slip while “back” refers to the northern end.) Second, all LIF records show a considerably elevated LIF response in the top ten feet of sediment, and third, all push probes penetrating greater than 10 feet display a thick, underlying sequence of sediment characterized by the low fluorescence wavelength (blue color) and low amplitude signal. Combining these observations it can be noted that as the water depth shallows toward the back of the Slip, the thickness of the sediments displaying a high LIF response increases, and the LIF signal of this interval increases in amplitude.

This simple presentation of LIF response provides evidence of the location of the PAH contaminated sediments in a cross-section down the center of the Slip, contamination first identified in previous investigations (Crane et al 2002). Information such as this was used to help select the location of sediment cores and identify targets for analytical sampling. A second, similar display of a parallel line running along the eastern edge of the Slip is presented as Figure 12. This display highlights a cross-section down the eastern wall of the Slip.

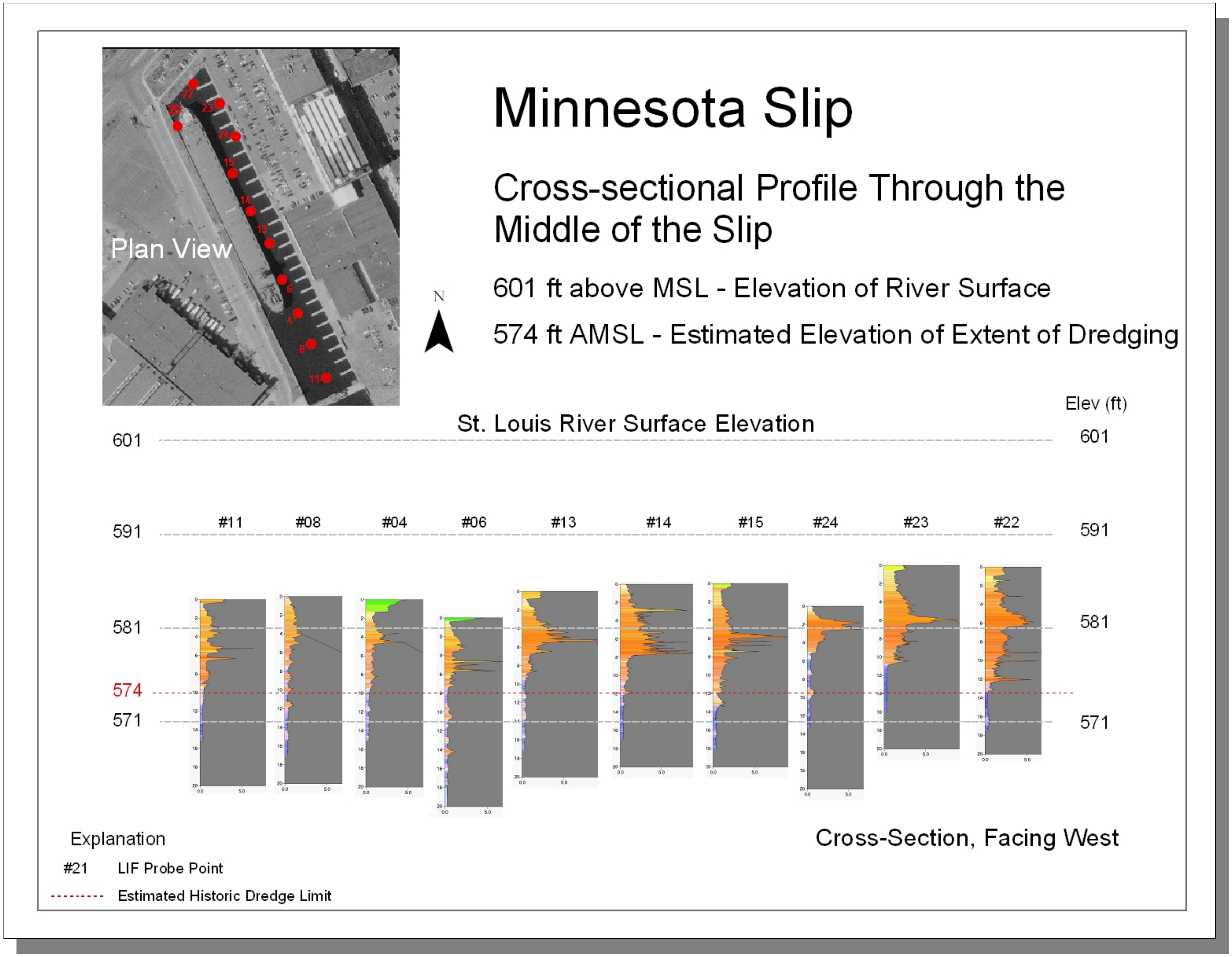


Figure 11: Cross-section through the Middle of the Slip, Featuring LIF Response Records.

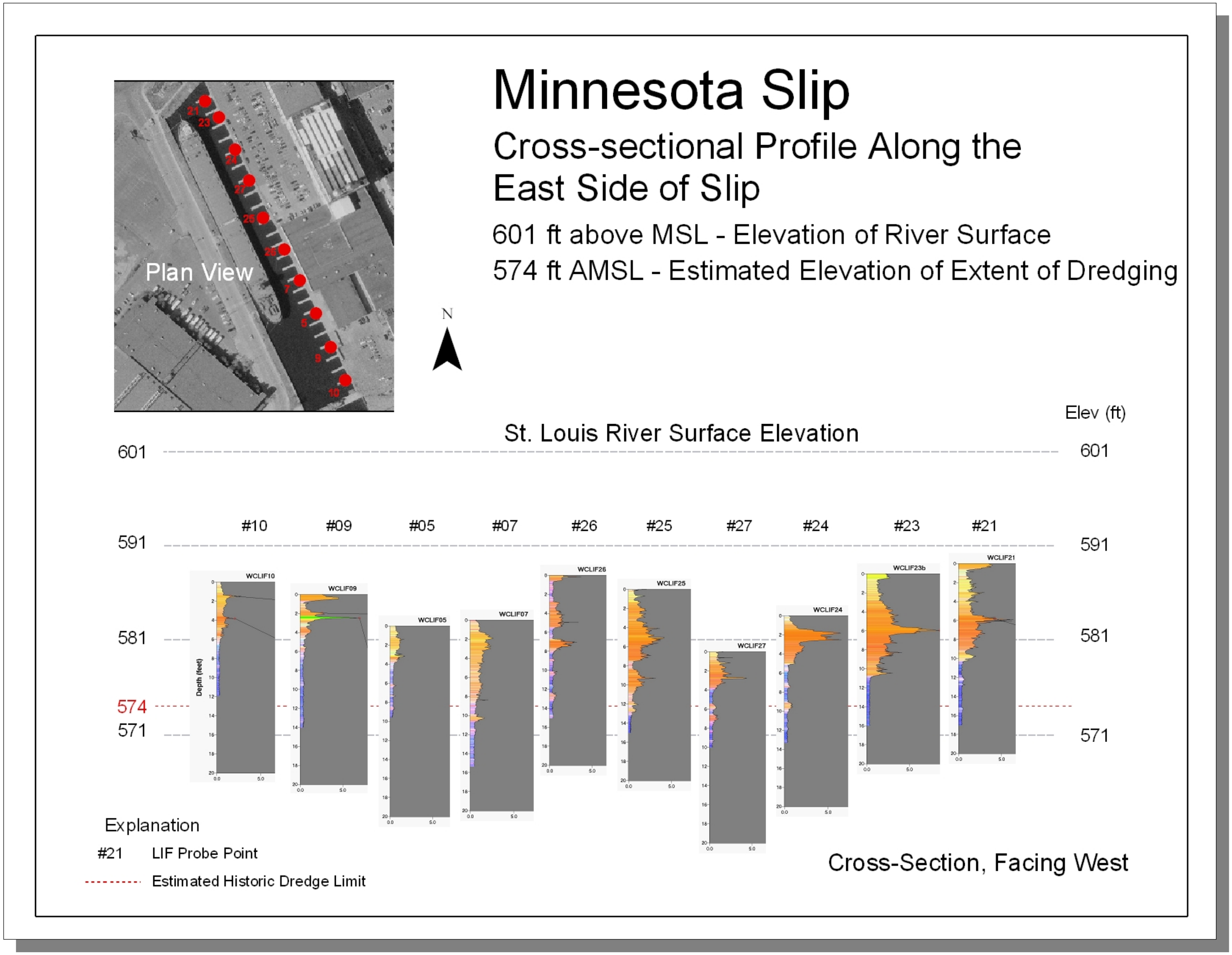


Figure 12: Cross-section Along the Eastern Wall of the Slip, Featuring LIF Response Records.

4.5 Determining Dredging Extent in Slip

Another use of this data is to attempt to identify the pre-industrial bottom of the Slip, where undisturbed refers to sediment that has never been moved or disturbed by human activity in the harbor, river or Slip. If the boundary between disturbed and in-place sediments could be identified, it would provide a lower boundary of possible contamination which would play an important role in the selection of a sediment contamination remedy. The depth of the main shipping channel has steadily increased since the construction of the Slip on or before 1887 (Table 1), giving a maximum probable depth to the Slip of 27 feet.

Two sources of information are available to shed light on the historic limits of dredging in Minnesota Slip: 1) the LIF records which penetrated at least to a depth of 33 feet below the ice surface, and 2) the change in resistance to the hydraulic probing as communicated by the Dakota Technologies driller to Agency staff during field work on the ice.

Looking first at the LIF records, it can be observed that the records in the previous two Figures are underlain by low fluorescing sediment strata. The red dashed line superimposed on the records in both Figures represents the 574 feet above Mean Sea Level (AMSL) datum that corresponds to the 27 foot dredging depth. Only very small amplitude signals of any type are found below this elevation. All of the sediment intervals yielding an LIF response greater than 1% are found above this elevation.

The second form of information is not quantitative, but is useful none-the-less. As the probe was being advanced into the sediment the probe operator reported greater resistance starting roughly 10 feet below the water-sediment interface. This varied point to point, but corresponded with the 574 AMSL datum. For example, when drilling in a spot on the ice that was 17 feet above the sediment-water interface, this resistant layer was encountered approximately 10 feet into the sediment.

It is important to state that harbor dredging is not a precise operation, or at least wasn't until recently. Selected modern dredging techniques can precisely remove sediment to within an inch of a desired datum. And quick depth profiles can be run to check the precise bathymetry with remote sounding techniques. But historically, with cruder tools, it is likely that dredging produced a ragged sediment surface interface. And, depending on how the Slip was used, the official channel depth may not have always been matched in the Slip.

4.6 Numerical Presentation of LIF Response

An alternate, quantitative approach to analyzing the LIF data is to extract the maximum LIF response % from the LIF displays for every 0.5-foot of depth. Referring to Figure 10, the maximum LIF signal within the top 0.5-foot corresponds to 5% LIF response, the smaller peak at 2 feet is approximately 3%, and the small peak at 4 feet is 1%. These numbers can then be analyzed statistically, displayed graphically or compared to other datasets, including the chemical results which are discussed in the next section. Maximum LIF was selected primarily because the 0.5-foot sequence comes closest to matching the interval sampled in the analytical samples, to which they will be compared.

One example of how the LIF can be displayed is seen in Figure 13, where a plan view of the Slip displays the locations of all the LIF probes. The star symbols representing the probe locations are colored according to the maximum LIF response detected in the top one foot of sediment. The color scheme discussed in Sections 4.2 and 4.3, links the hotter color of red to the highest LIF response, and blue to the lowest response. Displays of deeper intervals are presented as Figures 14 and 15. These figures display maximum LIF responses for depth intervals of 1 to 2 feet, 2 to 3 feet, 3 to 4, and 4 to 5 feet respectively.

Combining these plan views with the cross-sectional views (Figures 11 & 12) yields a more complete understanding of the distribution of sediments with suspected coal tar constituents. A quick review of the plan view figures reveals that the highest LIF response in the top foot is near the front of the Slip, with the highest LIF response appearing to shift to the back of the Slip with increasing depth. A more quantitative approach will be described later in this report.

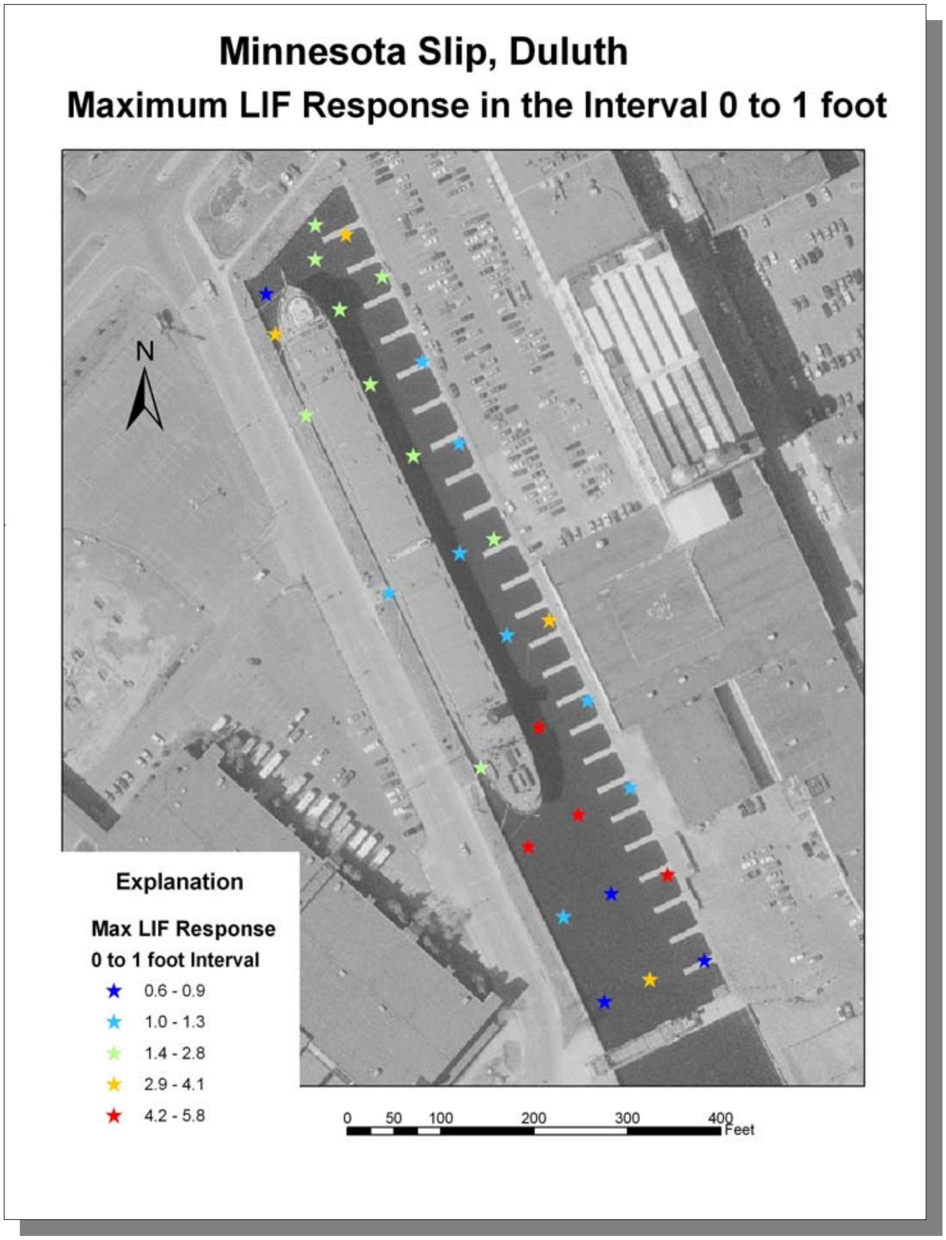
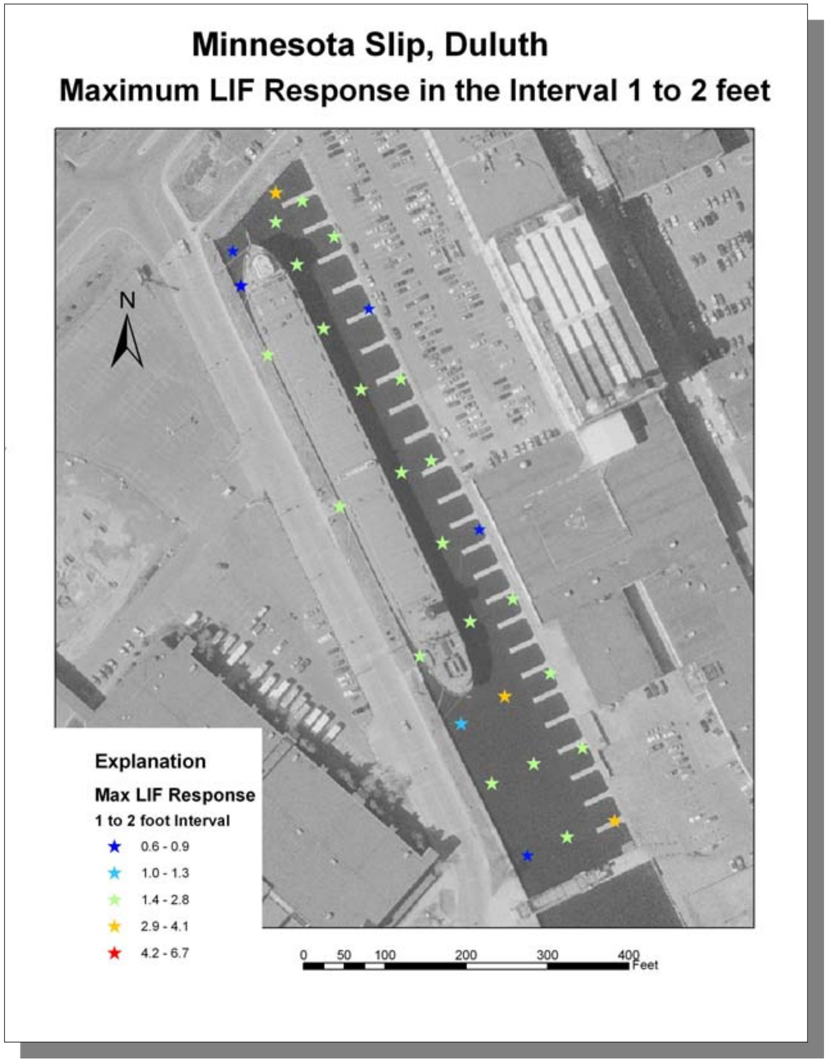


Figure 13: Maximum LIF Response Detected in Top Foot of Sediment



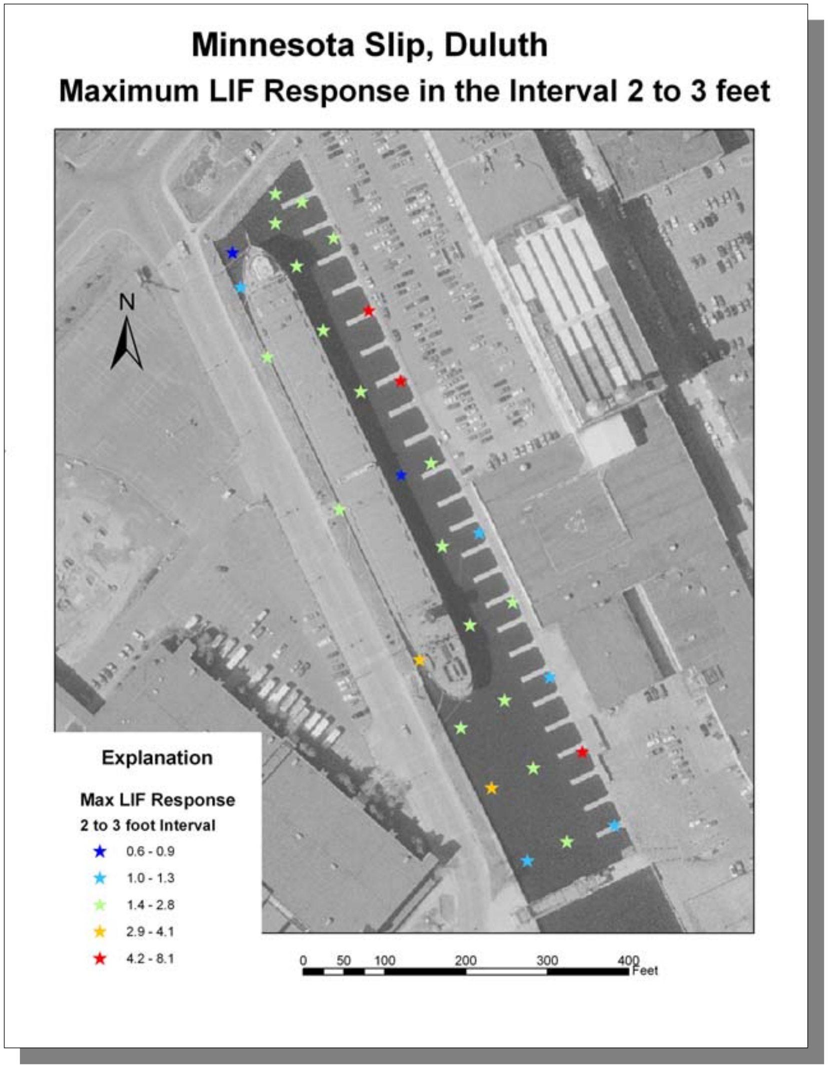
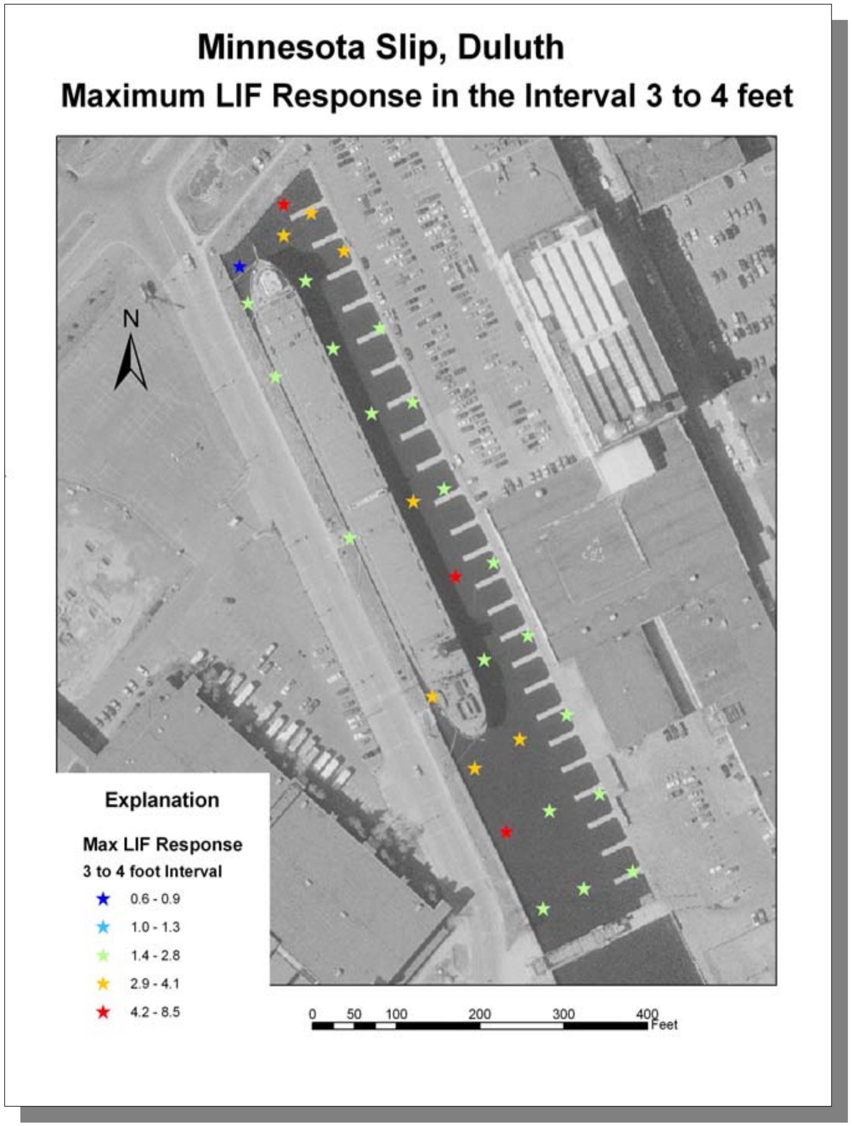


Figure 14: Maximum LIF Response Detected in Second and Third foot of Sediment.



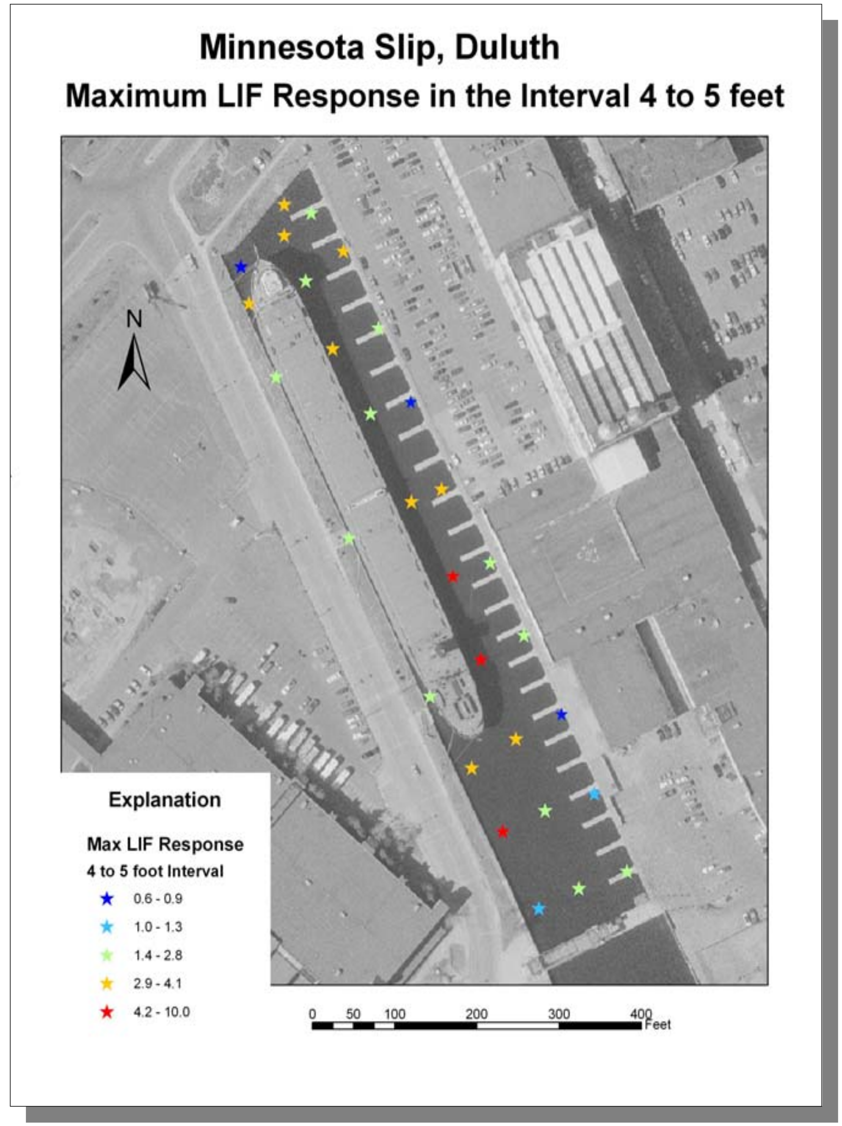


Figure 15: Maximum LIF Response Detected in Fourth and Fifth foot of Sediment.

CHAPTER 5
Sediment Samples Strategy and Results

5.1 Introduction

This chapter describes the process used to select sediment core locations based on the real-time results of the LIF investigation and information gained from past sampling of the Slip. The locations and depths of the cores sampled are presented along with results from the laboratory analysis. A more detailed, numerical review of the data will be performed in Chapter 6.

5.2 LIF Survey Importance to Sediment Sampling

Figure 7 presents the locations of both the LIF probes and the sediment cores that were sampled for analytical testing. Inspection of this figure reveals that most of the sediment borings are clustered in the back half of the Slip. This sample weighting was based on a real time review of the LIF data, presented in Figures 11 & 12. They show that both the amplitude of the LIF response and the thickness of the sediment producing this response increases toward the back of the Slip. But interest in the back of the Slip first arose from a review of sediment data collected in the 1990's (Crane et al. 2002), where an analysis of samples from the back of the Slip showed that there was a strong positive correlation between the contaminants encountered in the sediments and increasing depth of the sample. There was also an inverse correlation between the concentration of contaminants and increasing depth in the front of the Slip. It should be pointed out that this correlation describes an association through a non-parametric ranking of variables, and is not necessarily evidence of a cause and effect. The relationship between sample location and correlation is illustrated in Figure 16 with degree of correlation reflected in the vertical axis and the progression from back of the Slip (left hand) to the front (right hand) expressed on the horizontal axis. All samples from this period were taken from a depth of less than 7 feet, with 75% of the samples coming from less than 4 feet.

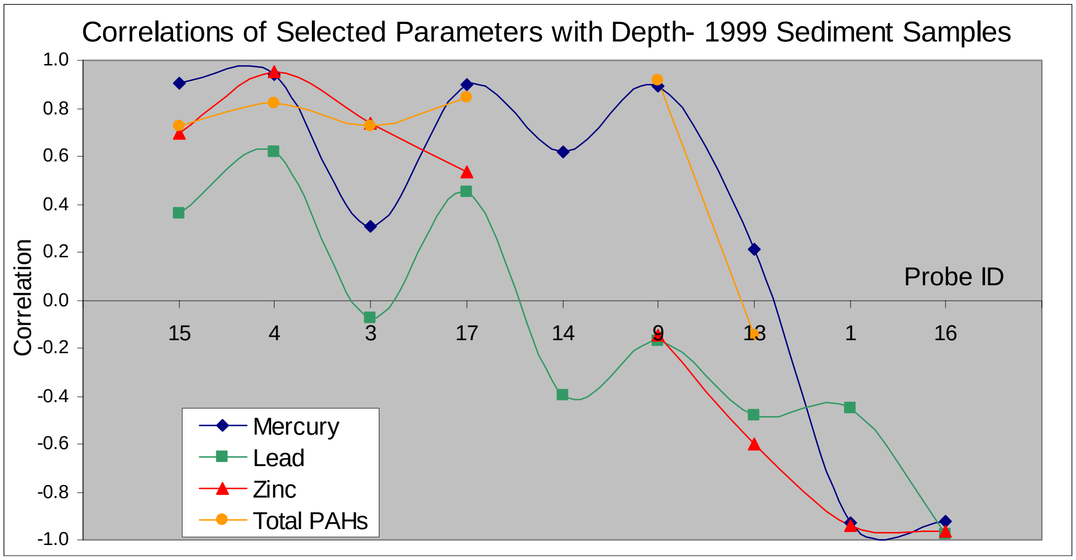


Figure 16: Correlation Between Increasing Sediment Depth and Parameter Concentration for selected cores.

The discussion has been limited to a comparison of total PAHs and LIF response, but as Figure 16 demonstrates, other contaminants such as metals yield similar results, at least in respect to the depth of the sample. This relationship will be developed later in this report.

The positive correlations between depth of sample and contaminant sample concentration of the 1990's data are clustered in the back of the Slip and the inverse correlations in the front. All parameters show the same transition between the back and front of the Slip. Though the transition is not uniform, all parameters move in the same general pattern. This relationship is echoed in the LIF response records on display in Figures 11 & 12, which show a steadily increasing level of LIF response in back-Slip records to a depth of approximately six feet, then a decline in LIF response over the next 4–6 feet. This LIF response pattern is visible in all of the six back Slip LIF response records. Because the previous studies were focused on the top several feet of sediments, calculations showing an increasing level of total PAHs with depth fit these results very well. This evidence provided additional reasons for sampling the sediment in the back of the Slip to target high, moderate and low LIF responses.

The over-all strategy of picking sediment samples to submit to laboratory analysis was to select targets from the LIF records, finding a rough balance between high, medium and low LIF response. A mixture of LIF responses allows for a wide range of comparisons between LIF response values and chemical concentrations. The desired outcome is a clear statement of where the survey and analytical methods were in agreement, and where they are not. For example it was possible that LIF and chemical values could have a strong correlation at LIF values above 1%, but a weaker correlation below that level. Three back-Slip probe locations were sampled at three different depth intervals, while the remaining three were sampled at two intervals.

In the front of the Slip, the initial interpretation of the 1990's data was that there was an inverse relationship between increasing depth and concentration of PAHs (Crane et al. 1997, Crane et al. 2002). Looking at Figure 11, it is clear now that such an interpretation was the artifact of the shallow depth of penetration (two feet), and that the overall nature of the contaminated sediments is similar to the back of the Slip. The main difference is that the front-Slip LIF response is found at a shallower depth and has a reduced response % in comparison to records taken in the back of the Slip.

Besides targeting the back and front of the Slip, the basal, low fluorescence sediment was also of interest. All of the LIF records register a coal tar related fluorescence response in the top 10 feet, and all are underlain by strata that exhibit no LIF response 12–14 feet below the water/sediment interface. This underlying sediment was sampled in different parts of the Slip to check the assumption that these strata were devoid of coal tar-related contamination.

5.3 Collection of Sediment Samples

The distribution of sediment samples are presented graphically in Figure 17 which provides a cross-section of sorts of the Slip. The back of the Slip is to the left, the front to the right. A solid shape refers to the top of a boring, an open shape to the base (where the two are very close together the precise base sampled is unknown). Referring to the figure, Boring 18 is therefore sampled in the intervals 0–4 feet, and 4–8 feet.

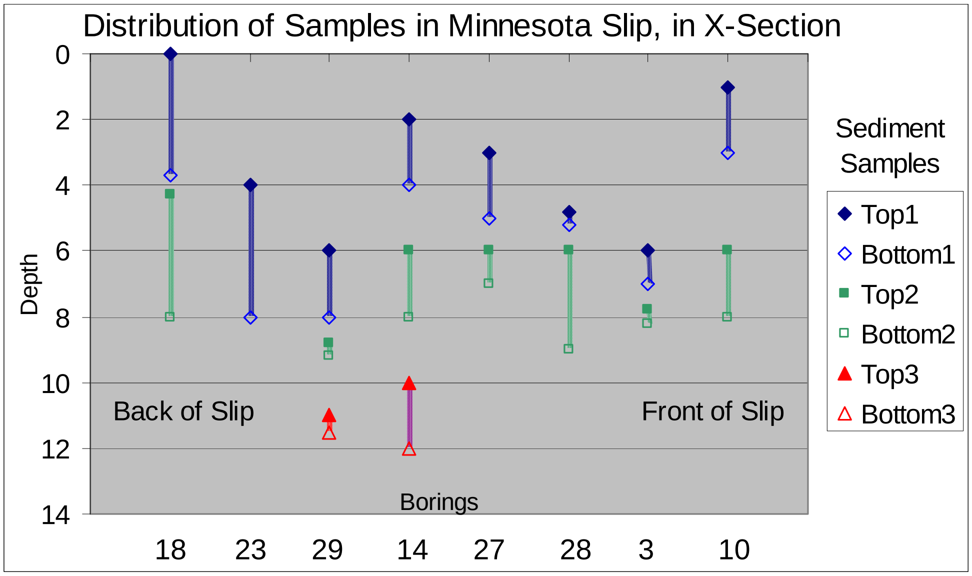


Figure 17: Distribution of Sediment Samples, by Depth and Location in the Slip.

The collection of the sediment samples was completed in four days. The probe operators swapped out the LIF equipment for the sampling equipment, and moved the rig back to the relevant probe locations to collect the sediment sample. Having already drilled a hole in the ice and determined bathymetry in the LIF stage, the field procedure was somewhat simplified for the collection phase. There were the occasional problems in collecting adequate sediment due to low % recovery of solids. In this case borings were repeated providing sufficient sample for the analytical phase of the project. Another problem involved samples collected through a process of heave, where a probe sampling tube was advanced into a pre-existing hole in preparation to pushing it into undisturbed sediments was instead completely filled while stationary by an upward pressure exerted within the sediments. Repeated sampling could not improve on this result, so three “heave” samples were eventually submitted for laboratory analysis. The sediment collected probably originated in the matrix lying immediately below the stationary open tube though this is speculation. The procedure adopted was to assign the samples in question the depth of the open sampling tube.

All sediment samples were handled according to the procedures laid out in the Site Sediment Sampling and Analysis Plan (WCEC 2004).

5.4 Laboratory Analysis Results of Sediment Samples

Metal, PCB and PAH concentrations of sediment samples submitted for laboratory analysis are presented in Appendix A as Tables A3 & A4. The first Table displays the detected concentrations of metals, DRO, total solids, TOC, and PCBs. The column entitled “Sample Location” is the probe location ID, and “Sample Name” provides the sediment interval collected. The second Table displays the PAH results for the same sample intervals.

Some of the highlights of the data presented in Tables A3 & A4 can be summarized as follows:

- PCBs were not detected in any samples at a Reporting Limit of 0.04 ppm,
- Maximum mercury detected was 3.2 ppm,
- Maximum Total PAH detected was 270 ppm,
- Maximum lead detected was 544 ppm.

Particle size distributions were prepared for two Slip sediment samples taken from the Slip. A histogram of the size distribution from sample 14, 6 – 8 foot depth is displayed in Figure 18. Particle size analyses were performed using U.S. Standard Size designated test sieves Number 4 through Number 400, corresponding to particle size diameters of 4.76 mm (Number 4) through 38 micron (Number 400).

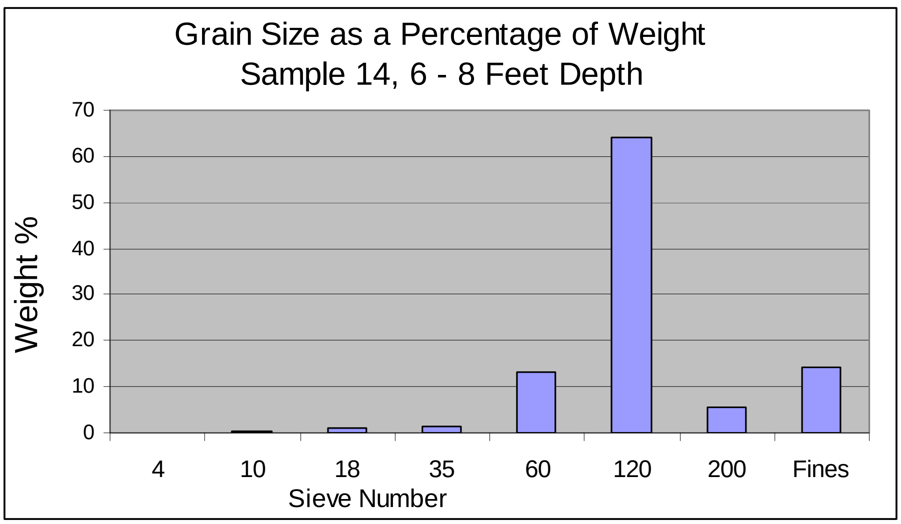


Figure 18: Gain Size Weight Distribution for Sample 14, 6 – 8 feet.

For this sample the matrix is ~75% fine sands, with most of the remainder silts and other smaller particles. The matrix of the second sample is >50% fine particles measuring 50 microns or smaller. More information on the particle sized composition of the two samples analyzed is available in Appendix A, Tables A6 & A7.

Descriptive statistics for selected parameters of all the 2004 samples are presented in Table 3.

Statistics for Selected Parameters of 2004 Samples							
	All results ppm, dry weight concentrations						
	Total PAH	**DRO**	**Arsenic**	**Lead**	**Mercury**	**Zinc**	**TOC (%)**
Mean	32.1	58.8	1.8	117.5	0.4	118.6	1.4
Median	14.5	28.5	1.3	59.4	0.1	66.4	0.0
Standard Dev.	62.7	73.0	1.4	162.9	0.8	167.9	1.6
Range	270.0	225.0	4.4	541.0	3.2	558.6	4.9
Minimum	0.0	5.0	0.6	3.0	0.1	0.4	1.0
Maximum	270.0	230.0	5.0	544.0	3.3	559.0	5.0
Count: 18							

Table 3: Descriptive Statistics for all Samples, Selected Laboratory Parameters.

5.5 Comparison of 2004 Data with Prior Sampling Events

Comparison of sediment samples between those collected in 2004 and those collected in the 1990's is complicated by a dredging of the Slip that occurred in the spring of 2002. Approximately 750 cubic yards were removed from the top of the sediment profile in the back half of the Slip (Figure 3). The sediment was removed to test an innovative remediation technique called Electrochemical Geo-Oxidation. The test was performed in isolated cells dug into the Erie Pier dredge spoil facility in Duluth. Keeping in mind this qualification, the previous studies detected a maximum total PAH of approximately 1,200 ppm, and PCB levels of 0.6 ppm. The highest mercury detection from the 1990's sampling (2.2 ppm) was found in the back of the Slip about 40 feet from the north end, and a depth of 4-6 feet, outside the area dredged in 2002. This is in the same general area and same depth of 2004 sample point 18, interval 4-8 feet. The results from this sample are 3.2 ppm.

5.6 Data Verification

Chemical Data Verification for the Minnesota Slip Project was performed by MPCA contractors Bay West Inc., using standard environmental QC parameters and the criteria listed on the Agency website (MPCA Laboratory Data Checklist). The report, "MN Slip Data Verification Report.doc" is available in Appendix C.

The Verification report concluded, "Overall, while there are indications of low bias on several analyses, the reported results met MPCA checklist guidelines and no results were qualified."

CHAPTER 6
Limited Screening Ecological Comparison Using Sediment Quality Targets and Probable Effect Concentration Quotients

The depth to which benthic organisms can penetrate sediment varies, but at the nearby St. Louis River Interlake Duluth Tar Superfund site, for water depths of less than 2.5 meters, the potential penetration depth was estimated to be 0.15 meters. Taking into account the root penetration of aquatic plants increases the depth of penetration of all flora and fauna to a depth of 1.0 meter. However, where water depths are greater than 2.5 meters, limiting the effect of sunlight, the depth of penetration for plants and benthic organisms into the sediment was estimated to be no greater than 0.5 meters. Since water depths in the Slip were found to be everywhere greater than 2.5 meters except for the immediate vicinity of a stormwater outfall in the northwest corner of the Slip (Appendix A, Section 2), the sediment interval of greatest relevance for ecological exposure is the top 0.5 meter. This interval was well-sampled in previous investigations, and therefore was not closely examined in this investigation. Finally, it should be noted that no recent investigation of the Slip has found the presence of aquatic plants growing in the sediment.

The limited screening ecological risk assessment was conducted by comparing the sediment chemistry results with the Level 1 and Level 2 Sediment Quality Targets (SQTs) (Crane, et al, 2000). SQTs are contaminant values that represent a level of protection of sediment-dwelling organisms. Level 1 SQTs identify chemical concentrations which will provide a high level of protection for designated water uses, specifically for aquatic life. By comparison, a lower level of protection for designated water uses will be provided by the Level 2 SQTs. Goals of the SQT as such for the protection of sediment dwelling organisms:

- Level 1 SQTs are intended to identify contaminant concentrations below which harmful effects on sediment dwelling organisms are unlikely to be observed.

- Level 2 SQTs are intended to identify contaminant concentrations above which harmful effects on sediment-dwelling organisms are likely to be frequently or always observed.

As presented in Appendix A as Tables A3 & A4, the SQT values for some parameters have been added to these Tables in the form of color coding. Where the detected level of a given parameter is above the Level 2 SQT, the value is colored green. Where the level is above Level 1, and below Level 2, it is colored yellow. For all values less than Level 1 the field is uncolored. Table A5 presents the SQT Level 1 and Level 2 values for selected parameters.

6.1 Heavy Metals

Heavy metals are distributed across the Slip, with the highest concentrations detected in the back of the Slip, in samples taken from cores 18 and 23 (Figure 17). The majority of detections were below the Level 1 SQT with the exception of cadmium, lead and zinc. Two samples had cadmium concentrations over Level 1 SQT, of which one was a surface sample (0-4 feet) at point 18. Three samples had zinc concentrations above Level 1 SQT and two above Level 2 SQT. These samples were all at least 4 feet at depth. Lead was found in 11 samples above the Level 1 SQT and four samples above the Level 2 SQT. Three of the samples were in the upper four feet of the sediment. Barium, boron, silver and selenium do not have published SQT levels. Silver was not detected and boron was detected only in one sample.

6.2 Mercury

The 0.20 ppm detection limit selected for lab analysis was above the Level 1 SQT of 0.18 ppm. In consequence, the seven of eighteen samples where mercury was detected were all above the Level 1 SQT, while two were also above the Level 2 SQT. Both of these samples were located far back in the Slip at a depth of 4-8 feet.

6.3 PCB's

No PCB's were detected in any of the chemistry samples. The reporting limit was 0.04 ppm.

6.4 PAHs

Eighteen individual PAH concentrations are presented in Appendix A, Table A4, thirteen of which have derived SQTs. Of these thirteen compounds most exceed the Level 2 SQT value. Total PAH Level 2 SQT values were exceeded at five sample points, where four were at depths great than four feet. The highest value was from sediment core 14, at a depth of 2-4 feet. The 2004 sample points nearest to the 2002 dredge area in the back of the Slip were 14, 27 and 23, with samples taken from 14 and 23 yielding values above the Level 2 SQT. No PAH concentrations exceeded the SQT values in samples taken from sediment below 9 feet.

6.5 Other Parameters

Other parameters analyzed for include DRO, total solids, and TOC. There is no SQT value available for DRO, however the Wisconsin Department of Natural Resources calculated DRO effect concentrations for the nearby St. Louis Estuary site Hog Island/Newton Creek (WDNR 1995). These effect concentrations are used in place of SQT values for DRO in Appendix A, Table A3. Based on this work three samples exceed the Level 1 screening value, and none exceed the Level 2 value. SQT values are not applied to the physical parameters TOC and total solids.

6.6 Summary of SQT Comparison

Based on a comparison of analytical data and SQT values (Appendix A, Tables A3 & A4) several chemical components of the contaminated sediment are considered a risk to the benthic community and the larger ecological environment, where they are found in the top meter of sediment.

Based on exceedences of the SQTs the chemicals that are considered "chemicals of concern" (COC) are cadmium, lead, mercury, zinc, DRO, PCBs and PAHs. PCBs were identified in a previous surface investigation (Crane 2002) and will be carried forward as a COC.

Chapters 7 & 8 will demonstrate the relationship between LIF and total PAHs, bringing the larger LIF dataset to bear on the question of ecological impairment.

6.7 2004 Minnesota Slip Mean PEC-Q Values

PAHs are not the only contaminant found in the Slip, and in fact elevated concentrations of metals are often found in the same sediments as high levels of PAHs. To evaluate the combined effects of multiple contaminants, the mean Probable Effect Concentration Quotient (mean PEC-Q) is calculated by dividing the individual contaminants by their respective Level 2 SQTs and taking the mean of the summed quotients. For the MN Slip site, the PEC-Q contaminant inputs are metals and total PAHs. The mean PEC-Q calculation also includes PCBs, a contaminant not found in the Slip in this round of sampling. Mercury has a known toxic effect but because a reliable consensus-based PEC is not available, it is not included in the quotient. For more information regarding the calculation of the mean PEC-Q see Appendix D.

Mean PEC-Q values for the Slip are presented in Table 4, with samples arranged in increasing order of the Mean PEC-Q level. Only two of the 2004 sediment samples included sediment from the top 0.5 meter, Boring 18 (0-4 feet) and Boring 10 (1-3 feet). The locations of these two Borings are displayed in Figure 19 (next page). The surficial samples both exceed 0.1 (Level 1 SQT) but are less than 0.6 (Level 2 SQT), indicating the potential for moderate toxic effects to the benthic community. A total of five sediment samples from the remaining samples, all deeper than 0.5 meters, were above the 0.6 Mean PEC-Q.

Boring ID	Depth Interval	Mean PEC-Q
10	6-8 ft	0.00
29	11 ft	0.01
27	6-7 ft	0.01
14	10-12 ft	0.02
29	9 ft heave	0.02
29	6-8 ft	0.04
3	6-7 ft	0.11
27	3-5 ft	0.19
10	1-3 ft	0.35
18	0-4 ft	0.45
18	4-8 ft	0.47
28	6-9 ft	0.52
3	8 ft heave	0.64
28	5 ft heave	0.90
14	6-8 ft	0.99
23	4-8 ft	1.07
14	2-4 ft	3.98
Level 1 SQT, mean PEC-Q > 0.1		
Level 2 SQT, mean PEC-Q > 0.6		

Table 4: Calculated Mean PEC-Qs for 2004 Minnesota Slip Samples.

As presented above, the 2004 investigation did not result in an adequate number of surface samples to fully evaluate the top 0.5 meters. There is more information on sediment toxicity in the form of PEC-Q values in the data collected for the Slip in 1998 and 1999. Mean PEC-Qs for surficial samples taken in the top 0 – 5 or 0 – 15 cm interval are displayed in Figure 19. Most of the sample values exceed the Level 2 SQT of 0.6, indicating a high likelihood of significant effects from exposure to surficial sediments throughout the Slip. The complete list of calculated 1998-1999 mean PEC-Q values are presented in Appendix A, Table A8.

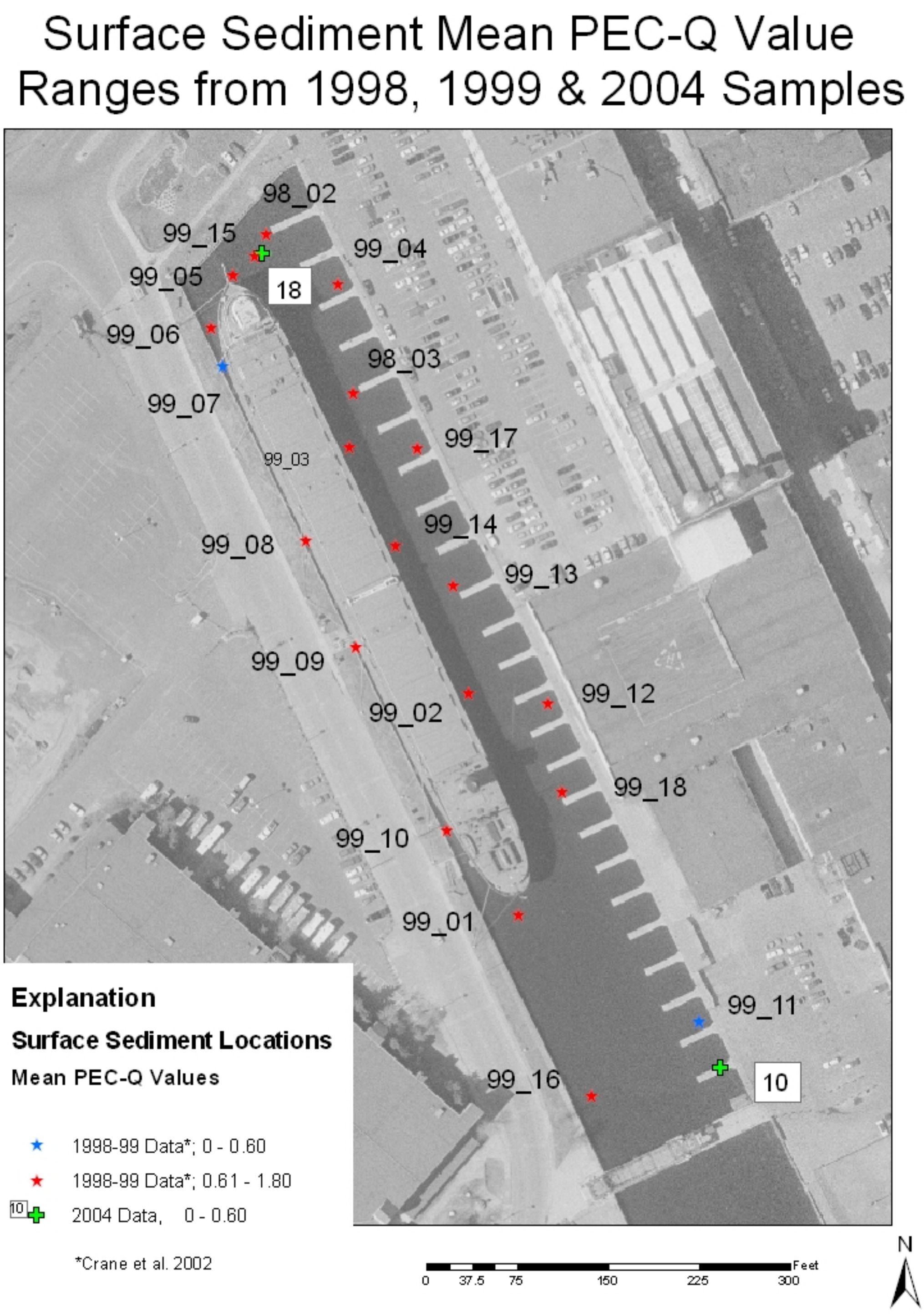


Figure 19: Mean PEC-Q Values from Sediment Samples taken from the Top Two Feet of Sediment; 1998, 1999 & 2004.

The Regional Environmental Monitoring and Assessment Program (R-EMAP), unpublished data collected in 1995 and 1996, revealed that for the testing performed on the one sample taken from the Slip (in the vicinity of LIF point #20, see Figure 7) there was not significant toxicity. But because the bioaccumulation testing showed significant accumulation of PAHs in the oligochaete worm, *Lumbriculus*, it is another indicator of potential impacts to the benthic community.

6.8 Risk to Human Health

Minnesota Slip is within an active harbor surrounded by retail and commercial businesses. More than half the Slip is open to the public year round. The Slip is used for docking of tour boats, museum boats and charter fishing boats. Exposure from contaminated sediments to the public is very limited given the depth of the Slip. No public swimming or wading is permitted or practical. No public water supplies are taken from the Slip. The major contaminants, PAHs, are generally non-volatile and not emitted from the waters of the Slip to the air. Therefore, the remaining pathway for human exposure is fish consumption. This too is limited since the Slip is relatively small and too deep for spawning and foraging for feeder fish. It is thought that larger fish spend a very small amount of time in the Slip because there is limited food supply available. In summary, risk to human health from contaminated sediments in the Slip is assumed to be very low.

CHAPTER 7
Data Interpretation

This purpose of this chapter is to present a detailed analysis of the field and laboratory results through the use of a variety of statistical and graphical tools. The focus is on different subgroups of the full dataset, first an examination of the samples taken in the back of the Slip, then a review of samples taken from the lowest elevation beneath the Slip, and finally a statistical review of subgroups based on LIF response using measures of statistical significance. The goal is to demonstrate the strong relationship between the field and laboratory parameters in the smaller datasets and justify the extrapolation of this relationship to the entire dataset.

7.1 Physical Influences Operating Throughout the Slip

In Chapter 5, in a discussion of historical results the point was made that the Slip is not a homogenus environment for sediment composition. Slip sediments have been moved, mixed and removed by a variety of forces at work on the waters in the bay. Sediments in the front of the Slip exhibited a negative correlation between increasing depth and total PAH concentration while the back of the Slip showed a strong positive correlation (Figure 16). These conclusions were an artifact of the small amount of data available at the time. Figure 11 illustrated that both the positive and negative correlations are most likely the result of thicker sequences of contaminated sediments to be found in the back of the Slip. The depth of penetration of the 1990's sampling was not great enough to reveal this fact. With information gathered in 2004, more complex patterns have become clear, and they continue to show a difference between the front and back of the Slip. An explanation for this difference may come from the difference in both the erosional and depositional forces at work on different parts of the Slip. Figure 11 displayed the bathymetry of the center of the Slip, showing that the Slip is shallowest in the back, and deeper in the front. Erosional forces that may be responsible include wave action in the bay, river flow, seiche-induced flow, storm water flow, and propeller turbulence from boats moving in and out of the Slip. The following discussion describes each of these forces and their effect on the Slip in detail.

7.1.1 Waves

Wave action can be illustrated by an anecdote from the March 2004 field work. The first day of field work was March 2, and in addition to the thick ice in the Slip, the Duluth-Superior bay was also ice-locked, as well as the western end of Lake Superior out to a distance of four or five miles. By the next day strong winds started blowing from the northeast, building up large waves directed down the lake toward the harbor entrance. The wind continued to blow on March 4th, with the waves breaking up the ice in the lake, and eventually moving into the harbor under the Aerial Lift Bridge. Throughout the day waves steadily cleared ice from the harbor, including all the ice up to the mouth of the Slip (Figure 20).

The force of the waves and the direction of the force could be seen in the way the ice broke up surrounding the mouth of the Slip. Waves were propagated and refracted through the inner harbor by the canal walls and docks. Waves that broke the ice at the mouth of the Slip did not penetrate far into the Slip. It may be assumed that whatever the

effect of the waves on the sediment at depth, that it was much less in the back than in the front of the Slip.

Figure 20: Ice Loss in the Bay Adjacent to the Mouth of Minnesota Slip.

7.1.2 The River

The Duluth Shipping Canal is the main mouth for the St. Louis River as it flows into Lake Superior, and is less than 1,000 feet from Minnesota Slip. In general, the maximum velocity of a river is found at the surface, declining to near zero at the stream bed. The average velocity of a river can be found at 0.6 of the depth as measured from the surface (Gupta 2001). For the harbor channel, with a dredged depth of 27 feet, that means that the average river velocity occurs at a depth of 16.2 feet. The water depth at the mouth of the Slip as measured in 2004 ranged from 14–18 feet. The implication for the Slip is that there is considerable energy available in the river at the approximate elevation of the sediment surface at the mouth of the Slip.

7.1.3 Seiche

Seiches are lake wide displacements of water that are wind-induced. Water pushed by the wind can pile up on shore causing noticeable increases in water depth. When the wind is reduced the water mass continues to slosh back and forth like water in a bathtub. Seiches can cause water to flow into the harbor from the lake through the shipping canal, against the flow of the river. The seiche can raise water levels in enclosed bays and Slips throughout the river estuary, with the greatest effect observed closer to the lake. The flow into and out of the Slip could presumably affect the sediment profile in the Slip, but such an effect is not quantifiable at this time.

7.1.4 Ship Movement

The final erosional force is that of ship passage into and out of the Slip. The largest currently operating boat to berth in the Slip is the commercial sight-seeing craft Vista Star. It is 91 feet long and has a draft of seven feet. It berths in the front half of the Slip along the western wall. Its many daily departures and arrivals create some turbulence in the Slip from its propeller action. There are several much smaller boats that also berth in the Slip along the eastern wall extending to the back of the Slip. Wind energy can also be conducted to the sediments via the movement of berthed boats. This might be most important with the Irvin since its hull sits only a few feet above the sediments.

7.1.5 Deposition

Storm water can both deposit new sediment and create a flow out of the Slip. Water depth in the Slip is considerably less in the northwest corner, in the back of the Slip near storm water discharge pipes (Figure 2), suggesting sediment has been deposited at the outfalls. There is considerable evidence that this new sediment has lower contaminant concentrations than sediments found at depth within the Slip. Analysis of the 1990's data shows an increase in most metals and total PAHs with depth in the back of the Slip, where the storm water discharge pipes are located. Figure 16 showed the correlation values for different parameters based on the 1999 dataset, with samples from the back of the Slip on the left, and those from the front of the Slip on the right. Sample numbers are on the horizontal axis. Positive correlations of increasing concentrations with increasing depth in the back of the Slip transition to negative correlations toward the front. This decreasing contaminant load will be augmented by the construction of stormwater sediment traps by the City of Duluth in 2005.

In conclusion, it is reasonable to assume that the erosional forces exert a stronger effect on the front of the Slip, while deposition of new sediment is most apparent in the back of the Slip. Both of these processes increase the likelihood that correlations between field and laboratory parameters are more likely to be found in the relatively undisturbed sediments found in the back of the Slip. Therefore, this is where most of the analysis of the data is directed. Once these relationships have been fully investigated, and regression analyses have been used to quantify the relationship between the LIF response and total PAH concentration in the back of the Slip, then this understanding will be tested for its application throughout the Slip.

7.2 Analysis of Field and Laboratory Data in Back Slip Sediment

The following borings and samples from the back of the Slip will be investigated: Boring 18 (Samples 0-4 & 4-8 ft), Boring 23 (Sample 4-8 ft), Boring 29 (Samples 6-8, 9, & 11 ft) and Boring 27 (Samples 3-5 & 6-7 ft). See Figure 7 for location of these and all other borings. Field LIF and laboratory analytical results for all samples are presented in Appendix A, Table A 9.

The first step is the calculation of correlations between paired LIF response and laboratory parameters from the 2004 data. The results are presented in Figure 21. The parameters displayed are the most critical to the selection of a remedy. One important metal not included is mercury, because more than 60% of the results were below the Reporting Limit of 0.2 ppm, making a correlation analysis difficult. DRO & lead (Pb) had less than 40% "no detection" results, and the remaining parameter results were all above the Reporting Limit.

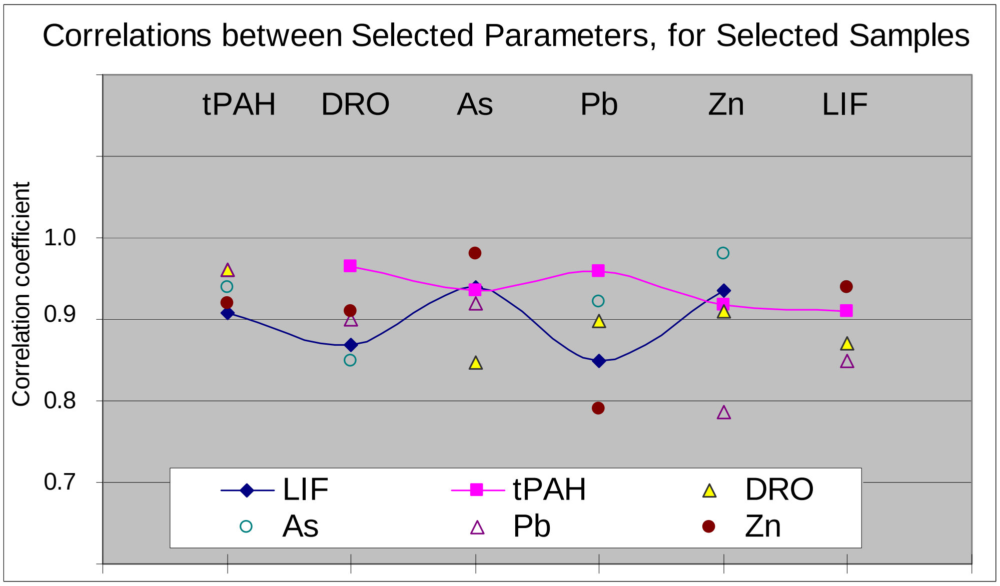


Figure 21: Correlations between 2004 Field and Laboratory Parameters.

The correlations are clustered in the 0.8–1.0 range. The tabular presentation of the data displayed in Figure 19 is included as Table 5. Total PAHs correlate with the other parameters in the 0.9–0.96 range, and LIF response in the 0.85–0.95 range. Correlations of these two parameters are highlighted with colored lines in Figure 21. Such a high degree of agreement between metals, semi-volatiles and the LIF screening tool is encouraging, and will be expanded on later in this chapter. The strong correlation between LIF response and laboratory results is the basis for the premise that the more numerous and spatially distributed LIF response results may be used to predict levels of contamination for most contaminants throughout the Slip.

	LIF	***tPAH***	***DRO***	***As***	***Pb***	***Zn***
LIF		0.91	0.87	0.94	0.85	0.94
Tpah	0.91		0.96	0.94	0.96	0.92
DRO	0.87	0.96		0.85	0.90	0.91
As	0.94	0.94	0.85		0.92	0.98
Pb	0.85	0.96	0.90	0.92		0.79
Zn	0.94	0.92	0.91	0.98	0.79	

Table 5: Matrix of Correlations Between Various Field & Laboratory Values.

The cause of the strong correlation between the different parameters may be a single, dominant contaminant source. Historical records suggest a coal gasification source, but further speculation lies outside the goals of this report.

Figure 22 provides the same analysis as presented in Figure 21, but for the entire dataset, not just the back of the Slip. The contrast between the two datasets is largest for the both the correlation of total PAHs and LIF with all other parameters.

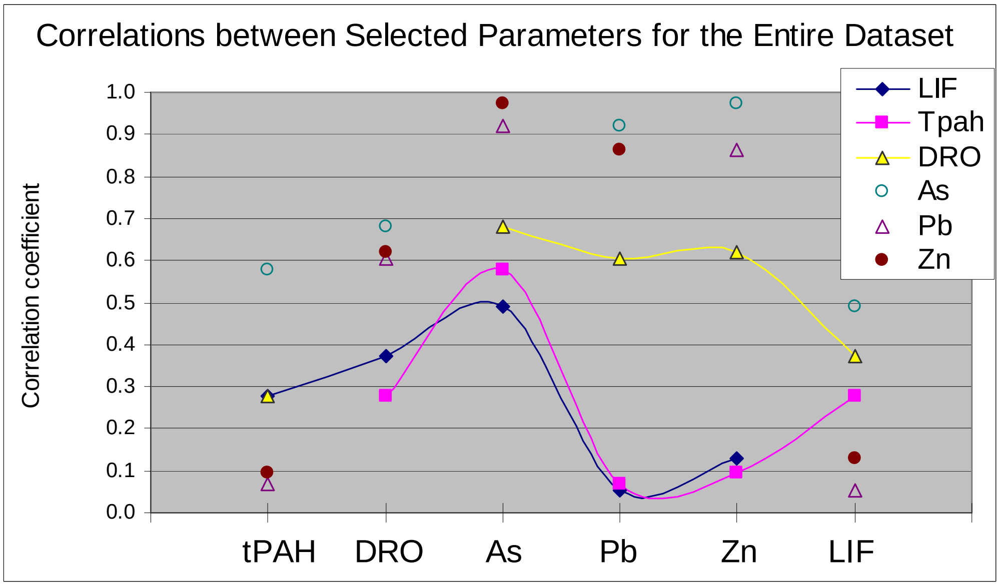


Figure 22: Correlations between 2004 Field and Laboratory Parameters for the Entire 2004 Dataset.

7.3 *Comparison of Sediment Sample Parameters where the LIF Response is Low*

Splitting the Slip into front and back halves is one way of isolating data into groups to facilitate analysis. Returning to the entire Slip dataset, another way to investigate the data is to divide the dataset between native and disturbed sediment. Continuing the argument begun in Chapter 4, in the Section entitled, “Determining Dredging Extent in Slip”, this section presents the analyses of results from sediment samples that share the following characteristics:

1) The samples are taken from the base of four different borings, from strata that was identified by the push probe operator as coming from the more resistant, possibly undisturbed sediment strata;
2) The samples come from the approximate probable depth of the maximum historic dredging depth of 27 feet; and
3) The LIF response associated with the depth of the samples is less than 1.2%.

Table 6 displays the laboratory values for this particular subgroup. Where the concentration is below the Reporting Limit (RL) the entry is highlighted.

		All ppm					
Boring #	Depth	tPAH	DRO	As	Pb	Hg	Zn
27	6-7'	0	<RL	0.8	<RL	<RL	11.8
29	11'	0	<RL	0.6	<RL	<RL	15.2
10	6-8'	0	<RL	0.6	<RL	<RL	7.8
14	10-12'	0.611	<RL	0.9	10.3	<RL	17.4

Table 6: Deep Sediment Samples with LIF response of <1.2%.

This Table shows that a low LIF response correlates well with undisturbed sediments that have contaminant concentrations near or at background levels. The levels of total PAHs, DRO and mercury are all below or near the Reporting Limit. The levels for the remaining parameters are similarly small. It should be noted that all the analytical results for these four deep borings are well below the Level 1 SQT concentrations.

Therefore, a concentration below the Level 1 SQT is below environmental concern. This strongly suggests that a low LIF response is a good predictor of a low analytical concentration for the parameters listed in Table 6.

7.4 Comparison of Sediment Sample Parameters where the LIF Response is High

Deep sediment samples from Borings 27, 29, 10 and 14 were selected as a test of the ability of the LIF survey tool to match analytical results at the low range of LIF response. The next step is to explore the relationship between LIF response and parameter concentrations in sediments that yielded a higher LIF response. Accordingly, returning once more to the full dataset, samples were divided into two groups, separating those having a LIF response greater than 1.2% from those with a LIF response of 1.2% and below. This latter group includes all of the previous subgroups that are thought to be from uncontaminated sediments.

The premise is that these two subgroups form different populations because of the different LIF response percentages. As a test of this premise, the Mann-Whitney Rank Sum Test was employed to test for statistically significant differences between the subgroups for different parameter concentrations. The results are reported in Table 7.

Tests of Statistical Significance on Selected Parameters between High and Low LIF Sample Subgroups								
Parameter	PAH	Pb	DRO	Hg	As	Ba	Cr	Zn
Significant Difference?	Yes	Yes	Yes	NA*	No	No	No	No
** Too few values above Reporting Limit*								

Table 7: Tests of Statistical Significance.

The results show a statistically significant difference for total PAHs, Pb, and DRO. There is not a statistically significant difference between the concentrations of arsenic, barium, chromium, and zinc for the two subgroups. There is not enough information to make this determination for mercury, where six out of seven of the Low level LIF and five out of eleven of the High LIF dataset are below the Reporting Limit. The analyses are presented in full at the end of this Chapter.

The results initially appear to be mixed, with the two datasets registering statistically significant differences for some parameters, and not for others. But the missing context is the environmental significance of the concentration levels of the parameters in question. If the LIF response value predicts the concentrations of parameters that reach a level of environmental concern, while failing to predict other parameters that are not of concern, then the screening tool can be considered a success. In this case because there is a statistically relevant difference between selected parameters for the two LIF subgroups means that LIF as a screening tool is correlating strongly with parameters that represent an ecological risk. On the other hand the screening tool is not correlating with parameter concentrations that do not represent an ecological risk. This is a useful result.

The issue of environmental concern is addressed by comparison of contaminant concentrations to SQTs. SQTs were adopted for the St. Louis River Area of Concern for a variety of parameters (Table 14, Crane *et al.* 2000). The SQT process yields two numbers, Level 1 and Level 2 targets. These values are reproduced in Appendix A, Table A5. A subset of SQT values for relevant parameters is presented in Table 8, below.

	Aquatic Life	
Metals	Level I SQT	Level II SQT
Arsenic	9.8	33
Cadmium	0.99	5
Chromium	43	110
Copper	32	150
Lead	36	130
Mercury	0.18	1.1
Nickel	23	49
Zinc	120	460
Total PAHs	1.6	23
mg/kg dry weight		

Table 8: Recommended Level I and Level II Sediment Quality Targets for the Protection of Sediment-dwelling Organisms.

7.5 Calculations of Statistically Significant Differences for Selected Parameters

Note: All field and laboratory parameter results failed normality tests. The datasets were then analyzed with non-parametric statistics. In general non-parametric tests are more flexible than parametric tests in that they can be applied to all datasets. Tests performed with SIGMASTAT, version 2.03.

Parameter- PAH

Mann-Whitney Rank Sum Test
Normality Test: Failed (P = <0.001)

Group	N	Missing	Median	25%	75%
Col 1	7	0	0.600	0.000	6.925
Col 2	11	0	20.000	14.425	53.600

T = 37.000 n(small)= 7 n(big)= 11 (P = 0.009)

The difference in the median values between the two groups is greater than would be expected by chance; there is a statistically significant difference (P = 0.009)

Parameter- DRO

Mann-Whitney Rank Sum Test
Normality Test: Failed (P = <0.001)

Group	N	Missing	Median	25%	75%
Col 1	7	0	5.000	5.000	14.000
Col 2	11	0	48.000	27.250	134.50

T = 38.000 n(small)= 7 n(big)= 11 (P = 0.011)

The difference in the median values between the two groups is greater than would be expected by chance; there is a statistically significant difference (P = 0.011)

Parameter- Pb

Mann-Whitney Rank Sum Test
Normality Test: Failed (P = <0.001)

Group	N	Missing	Median	25%	75%
Col 1	7	0	3.500	3.500	52.975
Col 2	11	0	87.900	48.375	192.000

T = 44.000 n(small)= 7 n(big)= 11 (P = 0.046)

The difference in the median values between the two groups is greater than would be expected by chance; there is a statistically significant difference (P = 0.046)

Parameter- Zn

Mann-Whitney Rank Sum Test
Normality Test: Failed (P = <0.001)

Group	N	Missing	Median	25%	75%
Col 1	7	0	15.200	12.350	75.375
Col 2	11	0	76.100	51.725	108.750

T = 52.500 n(small)= 7 n(big)= 11 (P = 0.221)

The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.221)

Parameter- As

Mann-Whitney Rank Sum Test Monday, December 20, 2004, 09:54:47
Normality Test: Failed (P = 0.001)

Group	N	Missing	Median	25%	75%
Col 1	7	0	0.800	0.650	1.350
Col 2	11	0	1.500	1.050	2.850

T = 47.500 n(small)= 7 n(big)= 11 (P = 0.094)

The difference in the median values between the two groups is not great enough to exclude the possibility that the difference is due to random sampling variability; there is not a statistically significant difference (P = 0.094)

CHAPTER 8
Setting the Equivalence between LIF Response and Total PAH Concentrations

The chapter focuses on the final step of this investigation: quantifying the relationship between LIF response and total PAH concentration. Previous chapters have shown that there is a strong correlation between total PAH & DRO concentrations, the metal Pb, and LIF response percentages. These analyses culminate with the preparation of a regression calculation that will provide a means for selecting the LIF response equivalent of a corresponding total PAH value. The resulting combined dataset will then be used to make better informed decisions of the extent and magnitude of the Slip's contaminated sediments. This will be necessary when the next stage of the project, the Feasibility Study, evaluates the risk posed to human health and the environment, and selects a protective remedy for the sediments.

8.1 Regression Analysis

Regression is a statistical technique applied to data to determine the degree of correlation of a dependent variable with one or more independent variables, often for predictive purposes. It is a check to see if there is a strong or weak cause and effect relationship between two things or variables. Parametric analysis rules apply for this tool requiring that the data must either be normally distributed or able to be converted into a normal distribution. In this report all of the residual datasets submitted to regression analysis are normally distributed.

Various forms of regression analyses were performed in Excel© using the Solver function, which allows the user to perform an automated, iterative search for a solution to an equation through the location of a global (or local) minimum. The objective function focuses on a target cell which is commonly the sum of squares of the modeled residuals. However the regression can also be based on minimizing the sum of square roots of the residuals, the sum of the cube, cube root, or any other operation. For this analysis, the objective function selected was minimizing the sum of the square of the modeled residuals. A sensitivity analysis was run to look for anomalous regression solutions based on the objective function choice. The solution was found to be not sensitive to the function selected. Figure 23 displays the graphical results of this regression analysis.

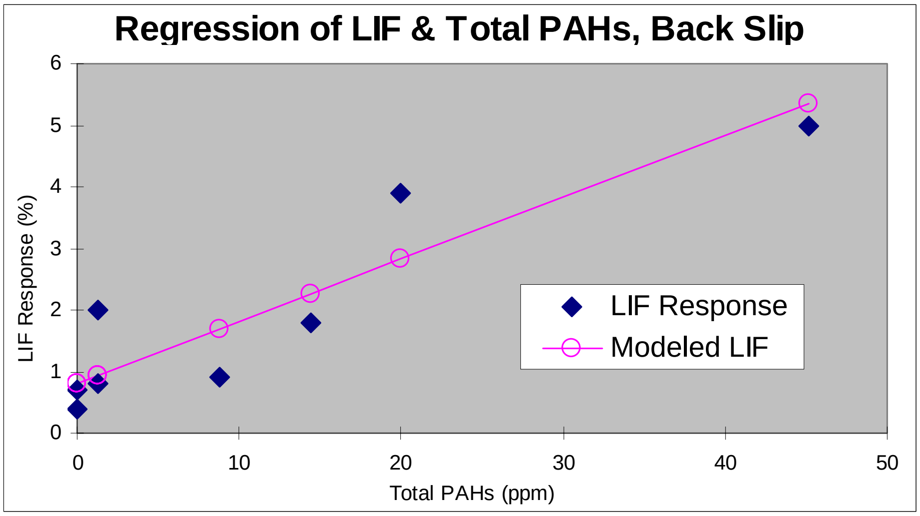


Figure 23: Regression Analysis of LIF Response and Total PAH Concentrations for Samples from the Back Slip.

The actual data is presented as blue diamonds. The purple open circles are the modeled LIF response percentages based on the PAH concentrations. The best fit model minimizes the variation of the modeled points from the actual data by minimizing the differences between the real and the modeled data. The purple linear line connects the modeled points and can be used to predict one variable given a known value of the other variable. Because the regression line closely matches the original data points, this can be considered a good graphical fit.

A more quantifiable measure of the "goodness" of the fit is presented in Table 9. The results of this calculation are positive and point to a well modeled system, which supports the claim that LIF response percentages and total PAH concentrations are closely related at this site in the undisturbed back half of the Slip.

Regression Statistics	
Multiple R	0.91
R Square	0.82
Observations	8

Table 9: Numerical Results of the Regression Analysis of LIF Response and Total PAH Concentrations in the Back Slip.

Chapter 9
Conclusions and Recommendations

9.1 Conclusions

Overall, the objectives of the 2004 Minnesota Slip investigation were achieved. These objectives were as follows:

1. To delineate the extent and magnitude of contamination throughout the Slip, particularly at depth;
2. To use a sediment screening tool, laser induced fluorescence, to provide qualitative detail as to the presence of PAHs in real time and at depth;
3. To use LIF to target a reduced number of sediment sample locations for chemical analysis;
4. To assess the correlation between LIF results and analytical results; and
5. To conduct a limited screening ecological risk assessment.

This report has presented the results of an investigation of the Minnesota Slip in the Duluth Harbor. Both the survey tool LIF and traditional sediment sampling were employed, often in the same spots in order to provide a basis for correlating the field with the laboratory results. The results were analyzed, correlations and regressions performed, and the conclusion was made that the field and laboratory results showed a high degree of correlation for most contaminants of concern. The resulting regression analysis has produced a tool to equate total PAH concentrations with LIF response, which allows Agency staff to use the more numerous and more spatially well distributed LIF results to characterize the extent and magnitude of the sediment contamination in the Slip. In conjunction with PEC-Q analyses and datasets collected prior to this investigation, a much clearer picture of the Slip's sediment contamination has emerged.

The 2004 investigation was carried out primarily to provide information on the sediment at depths greater than the top few feet. Combining this new information on the extent and magnitude of the contamination with the extensive surface sediment samples collected in 1999, the contaminated area that may pose an unacceptable ecological risk has been delineated. The limited screening ecological risk assessment has confirmed that an unacceptable risk to the biota of the Slip and the Duluth Harbor exists from the contaminated sediment in the Slip. The information collected during this study will be used to select cleanup goals and evaluate cleanup alternatives in the Slip.

9.2 Recommendations

1. Calculate an estimated volume of contaminated sediment;
2. Perform a Feasibility Study to provide cleanup goals and remediation options for the Slip cleanup; and
3. Seek funding opportunities such as the Great Lake Legacy Fund for remediation as there is no responsible party to clean-up the Slip.

Staff from the MPCA's Superfund Unit III, based in Duluth, will be coordinating with the USEPA GLNPO and Army Corp of Engineers staff to create a remedial plan and funding opportunities for the Slip. The MPCA currently is contracting for the completion of a Feasibility Study is targeted for September 30, 2005.

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