QUALITY ASSURANCE PROJECT PLAN (QAPP):

MINNESOTA SLIP SEDIMENT REMEDIATION SCOPING PROJECT

(Grant Number GL 985004-01)

REVISION: 0

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Prepared by: Judy L. Crane
Environmental Outcomes Division
Minnesota Pollution Control Agency (MPCA)
520 Lafayette Road North
St. Paul, MN 55155-4194

Lanny Peissig, MPCA Supervisor	9/8/99 Date
Judy Crane, MPCA Principal Investigator	9/7/99 Date
Harold Wiegner, MPCA Field Team Leader	7SEP 99 Date
Kim Sandrock, MPCA Quality Assurance (QA) Coordinator	9/15/99 Date
Keith Lodge, University of Minnesota—Duluth Project Manager	09/20/99 Date
Greg Graf, En Chem, Inc. QA Officer	9-23-99 Date
Cheryl Scholten, Minnesota Department of Health (MDH) QA Officer	9-29-99 Date
Anita Rehner, ENSR QA Coordinator	10-4-99 Date
Scott Cieniawski, Great Lakes National Program Office (GLNPO) Project Officer	10-14-1999 Date
Louis Blume, GLNPO QA Officer	10-14-99 Date

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DISTRIBUTION LIST

Lanny Peissig, MPCA (Supervisor)
Judy Crane, MPCA (Principal Investigator)
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Kim Sandrock, MPCA (QA Coordinator)
Keith Lodge, University of Minnesota—Duluth (Laboratory Activities)
Greg Graf, En Chem, Inc. (QA Officer)
Tod Noltemeyer, En Chem, Inc. (Laboratory Activities)
Cheryl Scholten, Minnesota Department of Health (MDH) (QA Officer)
Paul Swedenborg, MDH (Laboratory Activities)
Keith Peacock, MDH (Laboratory Activities)
Anita Rehner, ENSR (QA Coordinator)
David Pillard, ENSR (Laboratory Activities)
Scott Cieniawski, Great Lakes National Program Office (GLNPO) (Project Officer)
Louis Blume, GLNPO (QA Officer)
Joe Bonem, Deep Ocean Navigation (Field Activities)

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LIST OF ABBREVIATIONS AND ACRONYMS

AA	Atomic Absorption Spectroscopy
ADQ	Audit of Data Quality
AFDW	Ash Free Dry Weight
AOC	Area of Concern
As	Arsenic
ASTM	American Society for Testing and Materials
AVS	Acid Volatile Sulfide
BMP	Best Management Practice
BTEX	Benzene, Toluene, Ethylbenzene, and Xylene
CAC	Citizen's Action Committee
Cd	Cadmium
CDF	Confined Disposal Facility
cm	Centimeter
CO	Colorado
COD	Chemical Oxygen Demand
CPR	Cardiopulmonary Resuscitation
Cr	Chromium
Cs	Cesium
Cu	Copper
DECC	Duluth Entertainment and Convention Center
DO	Dissolved Oxygen
DQA	Data Quality Assessment
DQI	Data Quality Indicator
DQO	Data Quality Objective
DRO	Diesel Range Organics
EPA	Environmental Protection Agency
g	Gram
GC/ECD	Gas Chromatography/Electron Capture Detection
GC/MS	Gas Chromatography/Mass Spectrometry
GC/MS-SIM	Gas Chromatography/Mass Spectrometry Selective Ion Methodology
GFAA	Graphite Furnace Atomic Absorption Spectroscopy
GLNPO	Great Lakes National Program Office
GPS	Global Positioning System
H_a	Alternative Hypothesis
H_o	Null Hypothesis
HCl	Hydrochloric Acid
Hg	Mercury
ICP	Inductively Coupled Plasma Emission Spectroscopy
IJC	International Joint Commission
IL	Illinois

LIST OF ABBREVIATIONS AND ACRONYMS

KCl	Potassium Chloride
kg	Kilogram
L	Liter
L:D	Hours of Light and Dark
LOQ	Limit of Quantification
m	Meter
MDH	Minnesota Department of Health
MDL	Method Detection Limit
mg	Milligram
MI	Michigan
mL	Milliliter
mm	Millimeter
MN	Minnesota
MNS	Minnesota Slip Code Name for Sediment Samples Collected in 1994
MPCA	Minnesota Pollution Control Agency
MS/MSD	Matrix Spike/Matrix Spike Duplicate
MSR	Management Systems Review
N/A	Not Applicable
NaCl	Sodium Chloride
NBS	National Bureau of Standards
ng	Nanogram
Ni	Nickel
NRRI	Natural Resources Research Institute
PAHs	Polycyclic Aromatic Hydrocarbons
Pb	Lead
PCBs	Polychlorinated Biphenyls
PE	Performance Evaluation
PEC	Probable Effect Concentration
PQL	Practical Quantitation Limit
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QA/QC	Quality Assurance/Quality Control
QC	Quality Control
RAP	Remedial Action Plan
R-EMAP	Regional Environmental Monitoring and Assessment Program
RFP	Request for Proposal
RPD	Relative Percent Difference
RSD	Relative Standard Deviation

LIST OF ABBREVIATIONS AND ACRONYMS

R/V	Research Vessel
Se	Selenium
SEH	Short Elliot Hendrickson
SEM	Simultaneously Extractable Metals
SETAC	Society of Environmental Toxicology and Chemistry
SOP	Standard Operating Procedure
SRM	Standard Reference Material
TCDD	Tetrachlorodibenzo-p-dioxin
TCDF	Tetrachlorodibenzo-p-furan
TDL	Target Detection Limit
TEC	Threshold Effect Concentration
TOC	Total Organic Carbon
TSA	Technical Systems Audit
µg	Microgram
UMD	University of Minnesota--Duluth
U.S.	United States
USACOE	U.S. Army Corps of Engineers
USEPA	U.S. Environmental Protection Agency
WDNR	Wisconsin Department of Natural Resources
WI	Wisconsin
Zn	Zinc

A PROJECT MANAGEMENT

A1 PROJECT/TASK ORGANIZATION

A1.1 Purpose/Background

The Great Lakes National Program Office (GLNPO) has funded a study by the Minnesota Pollution Control Agency (MPCA) to conduct a sediment remediation scoping project in Minnesota Slip, Duluth Harbor. In order to ensure that high quality data are collected, it is essential that quality assurance/quality control (QA/QC) steps be adhered to while collecting, handling, and analyzing sediment samples. This document provides the Quality Assurance Project Plan (QAPP) which will be followed during this investigation. As part of the QAPP, a detailed work plan is given in Section B for the field sampling component of this study.

The MPCA Principal Investigator will have overall responsibility for all phases of this project. The various quality assurance and management responsibilities of key project personnel are defined in the following section.

A1.2 Roles and Responsibilities

The overall lines of authority for this specific project can be found in Figure A-1. Figures A-2 through A-4 provide the specific lines of authority for contractual laboratories at ENSR, En Chem, Inc., and Minnesota Department of Health (MDH), respectively. These charts include all of the individuals discussed in the following subsections.

A1.2.1 MPCA Personnel

The MPCA staff associated with this project can be reached at the following address:

Environmental Outcomes Division
Minnesota Pollution Control Agency
520 Lafayette Road
St. Paul, MN 55155-4194
General Phone: 1-800-657-3864
Fax: 651-297-7790

Person:	***Responsibilities:***
Lanny Peissig, Supervisor Standards Development & Application Unit Environmental Research & Reporting Section Phone: 651-297-1781 Email: lanny.peissig@pca.state.mn.us	Supervise Principal Investigator Approve contracts for technical services Approve QAPP

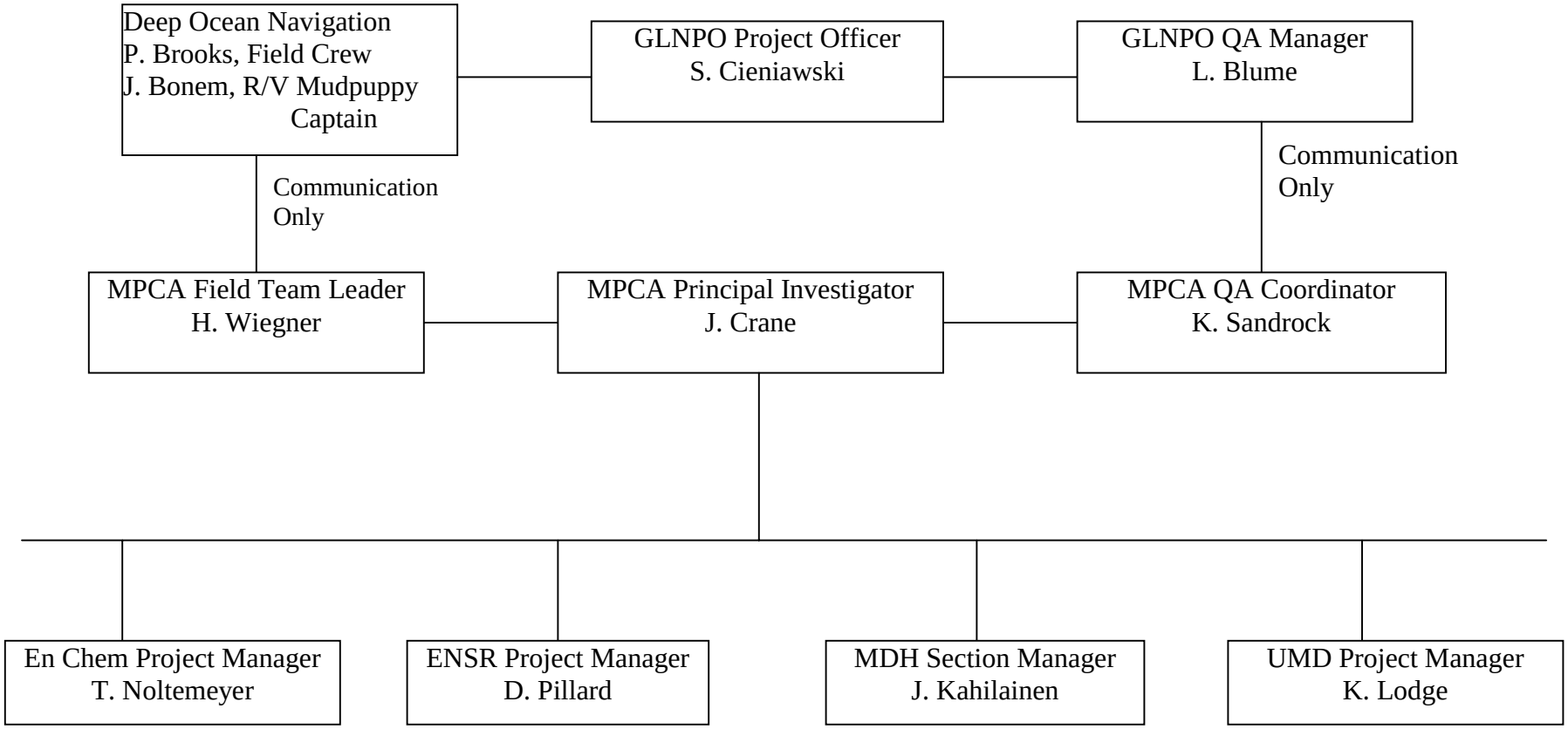

Figure A-1. General project organization chart.

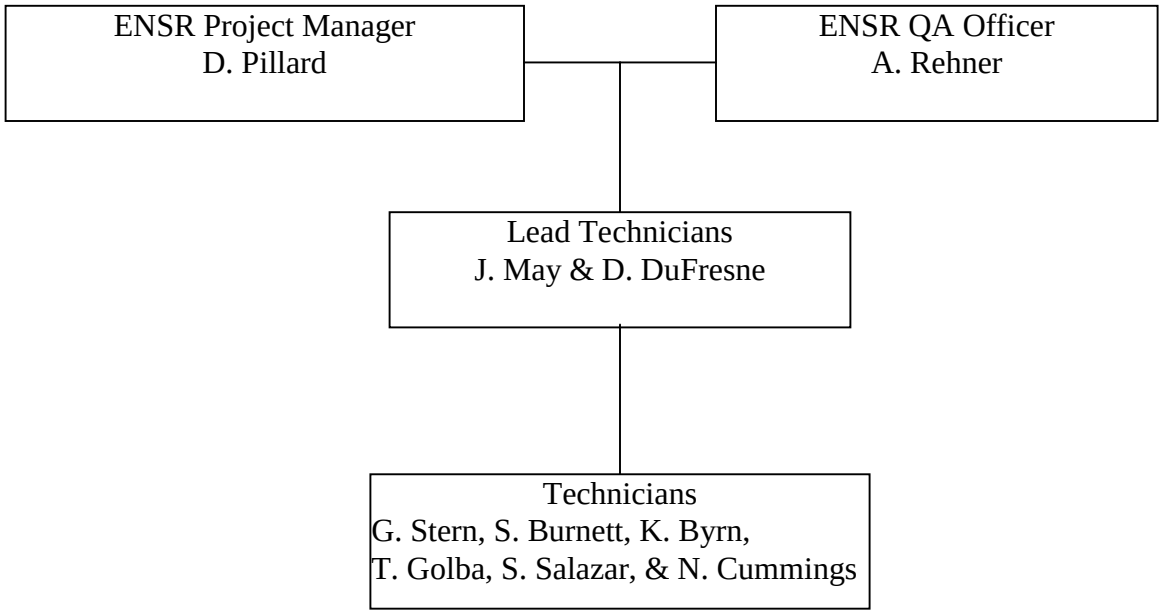

Figure A-2. Project organization chart for ENSR.

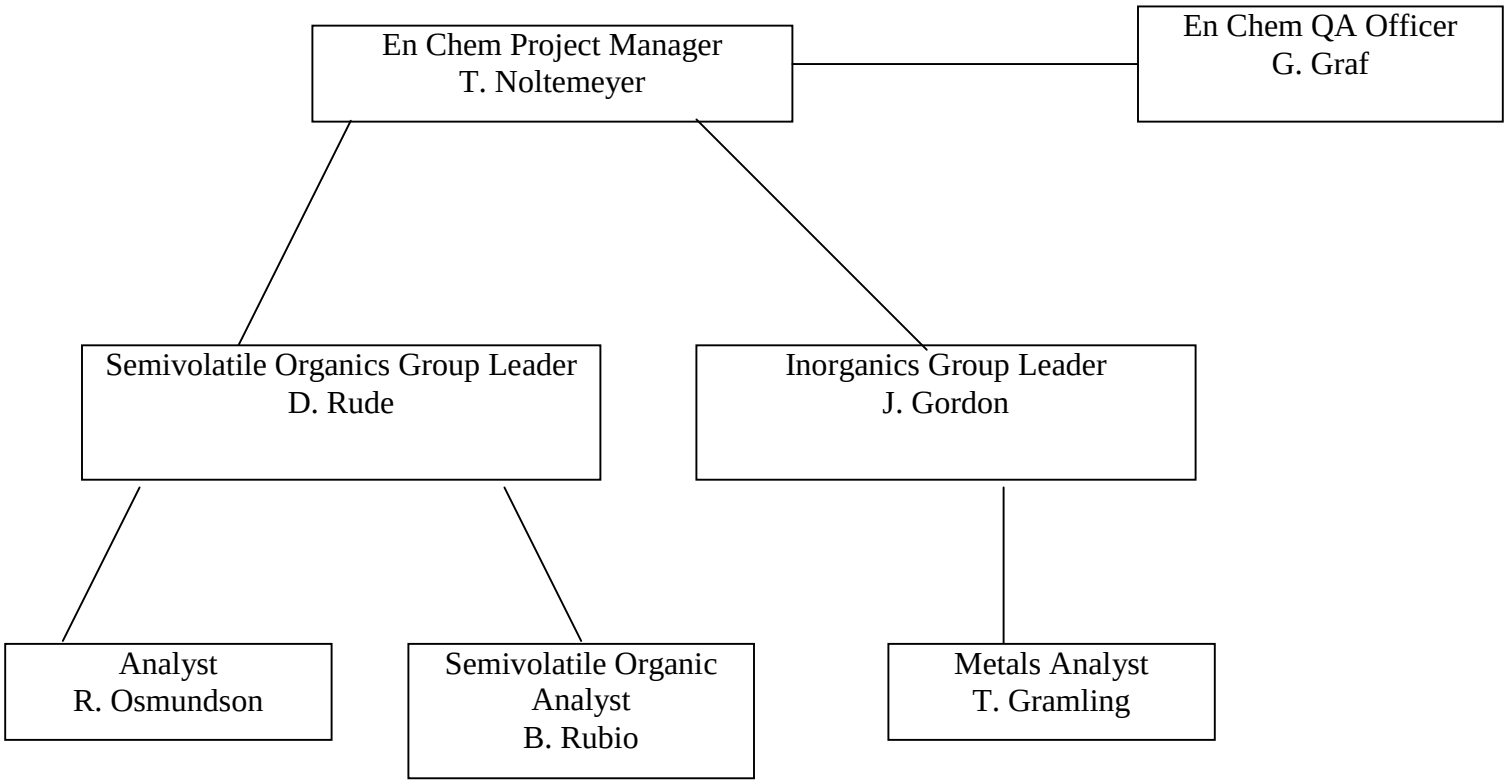

Figure A-3. Project organization chart for En Chem, Inc.

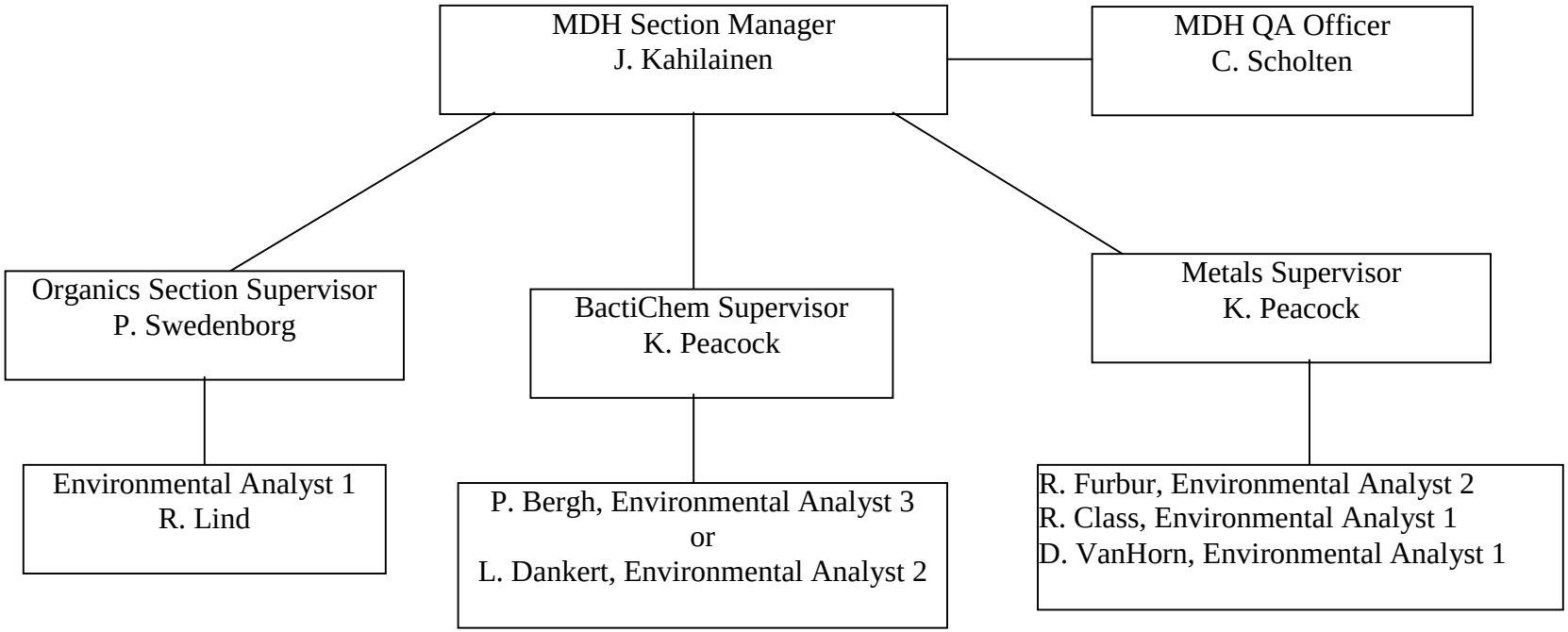

Figure A-4. Project organization chart for MDH.

Person:	***Responsibilities:***
Judy Crane, Principal Investigator Standards Development & Application Unit Environmental Research & Reporting Section Phone: 651-297-4068 Email: judy.crane@pca.state.mn.us	Develop request for proposals (RFPs) Review responder proposals Contract out toxicology and analytical work Develop work plan and QAPP Order supplies Conduct field work Analyze data and write report Perform project and grant management tasks
Harold Wiegner, Field Team Leader Ground Water & Toxics Unit Environmental Monitoring & Analysis Section Phone: 651-296-9315 Email: harold.wiegner@pca.state.mn.us	Assemble supplies Coordinate field sampling Coordinate sending samples to contract laboratories
Kim Sandrock, QA Coordinator Biological Monitoring Unit Environmental Monitoring & Analysis Section Phone: 651-296-7387 Email: kim.sandrock@pca.state.mn.us	Review and approve QAPP Conduct field and laboratory audits, as needed Respond to QA/QC questions

A1.2.2 <u>GLNPO Personnel</u>

The GLNPO staff and other contractors associated with this project are as follows:

Person:	***Responsibilities:***
Scott Cieniawski, Project Officer U.S. EPA GLNPO 17G 77 West Jackson Boulevard Chicago, IL 60604 Phone: 312-353-9184 Fax: 312-353-2018 Email: cieniawski.scott@epamail.gov	Coordinate grant requests Review work plan and QAPP Provide technical assistance, as needed Prepare GLNPO field safety plan Coordinate use of R/V Mudpuppy for field sampling Assist with field sampling Review quarterly progress reports Review draft and final reports

Person:	***Responsibilities:***
Louis Blume, QA Officer Same address as S. Cieniawski Phone: 312-353-2317 Fax: 312-353-2018 Email: blume.louis@epamail.epa.gov	Review and approve QAPP Conduct field and lab audits, as needed Provide technical assistance for QA/QC questions
Joe Bonem, R/V Mudpuppy Captain Deep Ocean Navigation c/o EPA Warehouse 102 9th St. Bay City, MI 48708 Phone: 517-895-6182 Fax: 517-895-6183	Help transport and set-up R/V Mudpuppy at site Operate the R/V Mudpuppy during field sampling
Polly Brooks, Field Crew Deep Ocean Navigation (same address, phone, fax as J. Bonem)	Help transport and set-up R/V Mudpuppy at site Assist with field sampling of sediments

A1.2.3 Contract Laboratories

Three different analytical laboratories will be used to analyze chemical and physical properties of sediment samples, whereas ENSR will be used to conduct toxicological studies of selected sediment samples. Each laboratory will have their own provision for conducting an internal QA/QC review of the data before it is released to the MPCA. The Laboratory Project Manager will contact the MPCA Principal Investigator with any data concerns.

QA/QC information will be included in the data packages and/or reports submitted to the MPCA. Corrective actions will be reported to the MPCA. Corrective actions will be reported to the MPCA Principal Investigator with the QA/QC section. The contract laboratories may be contacted by the MPCA Principal Investigator, GLNPO Project Officer, GLNPO QA Officer, or MPCA QA Coordinator at any time to discuss QA/QC concerns.

ENSR Staff

Staff from ENSR will be responsible for conducting two kinds of sediment toxicity tests: 10-day sediment toxicity tests using the midge, *Chironomus tentans*, and 42-day toxicity tests using the amphipod, *Hyalella azteca*. The ENSR staff associated with this project (Figure A-2) can be reached at the following address:

ENSR
4303 West LaPorte Avenue
Fort Collins, CO 80521
Phone: 970-416-0916
Fax: 970-493-8935

Person:	***Responsibilities:***
David Pillard, Project Manager Email: dpillard@ensr.com	Ensure the tests are conducted according to the applicable test guidelines and appropriate Standard Operating Procedures (SOPs) Coordinate statistical analysis of data Coordinate preparations and review of toxicity test reports
Anita Rehner, QA/QC Coordinator	Review study protocols prior to study initiation Conduct phase audits of the laboratory Ensure proper implementation of applicable SOPs Review and validate laboratory data Review toxicity test reports
Jeff May and Doree DuFresne, Lead Technicians	Lead the set-up, maintenance and tear-down of sediment toxicity tests Coordinate the performance of other project tasks by other technicians Conduct routine monitoring of physico-chemical conditions during the tests Conduct statistical comparisons of sample results with the negative control Oversee data review and preparation of toxicity testing sections of report
Gina Stern, Susan Burnett, Kerry Byrn, Tim Golba, Sandy Salazar, and Nicole Cummings Technicians	Clean glassware and test vessels Feed organisms and maintain cultures Conduct routine monitoring of physico-chemical conditions during the tests Perform other tasks as assigned by the Principal Technicians or Project Manager

En Chem, Inc. Staff

Staff from En Chem, Inc. will be responsible for measuring the following analytes in sediment samples: acid volatile sulfides (AVS), simultaneously extractable metals (SEM), and polychlorinated biphenyl (PCB) congeners. The En Chem staff associated with this project (Figure A-3) can be reached at the following address:

En Chem, Inc.
525 Science Drive
Madison, WI 53711
Phone: 608-232-3300
Fax: 608-233-0502

Person:	***Responsibilities:***
Tod Noltemeyer, Project Manager Phone: 608-232-3310 Email: tnolteme@enchemmd.enchem.com	Manage client projects to ensure that the analytical objectives of the project are met by the laboratory staff Schedule sample analysis and assign resources Communicate issues/questions between the client and analytical staff Oversee the preparation of data packages Respond to the clients technical questions
Greg Graf, QA Officer	Provide oversight of laboratory QA program Prepare and distribute SOPs and quality documents Provide resolution of out-of-control events Maintain laboratory certifications and agency approvals
Daniel Rude, Semivolatile Organics Group Leader	Supervise the Semivolatile Organics Group Schedule analyses Monitor status of projects Maintain semivolatile organic section SOPs Monitor EPA methods for updates Develop new methodologies based on regulatory demands

Person:	***Responsibilities:***
Robert Osmundson, Analyst	Conduct PCB analyses of sediment samples including: sample tracking, sample preparation, analysis by electron capture gas chromatography (GC), interpretation, and data package formation Maintain GC and computer systems
Barbara Rubio, Semivolatile Organics Analyst	Responsible for all BNA analyses by GC/mass spectrometry (MS) Develop and implement BNA methods Update SOPs and QC limits, as needed
Jeffrey Gordon, Inorganics Group Leader	Supervise the Inorganics group Schedule analyses Monitor status of projects Maintain inorganic section SOPs Monitor EPA methods for updates Develop new methodologies based on regulatory demands
Timothy Gramling, Metals Analyst	Perform AVS and SEM analyses Maintain standards

MDH Staff

Staff from the Minnesota Department of Health (MDH) will be responsible for measuring the following analytes in sediment samples: polycyclic aromatic hydrocarbons (PAHs), mercury (Hg), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni), selenium (Se), Zinc (Zn), ammonia, total organic carbon (TOC), and percent moisture. The MDH staff associated with this project (Figure A-4) can be reached at the following address:

Minnesota Department of Health
Public Health Laboratory Division
Chemical Laboratory
717 Delaware Street Southeast
Minneapolis, MN 55414
Phone: 612-623-5200
Fax: 612-676-5514

Person:	***Responsibilities:***
Jean Kahilainen, Section Manager Phone: 612-676-5300 Email: jean.kahilainen@health.state.mn.us	Manager of Chemical Laboratory Ensure laboratory resources are available on an as required basis Overview final analytical reports
Cheryl Scholten, QA Officer Phone: 612-676-5127 Email: cheryl.scholten@health.state.mn.us	Provide oversight of laboratory QA program Prepare and distribute SOPs and quality documents Provide resolution of out-of-control events Maintain laboratory certifications and agency approvals
Paul Swedenborg, Supervisor Phone: 612-676-5452 Email: paul.swedenborg@health.state.mn.us	Supervisor of Organics Section Schedule analyses Monitor status of projects Oversee data review and preparation of analytical reports
Robert Lind, Environmental Analyst 1 Phone: 612-676-5452 Email: robert.lind@health.state.mn.us	Conduct PAH analyses of sediment samples, including: sample preparation, analysis by GC/MS-Selective Ion Monitoring (SIM), Interpretation, and data package formation Maintain GC/MS and GC/MS-SIM
Keith Peacock, Supervisor Phone: 612-676-5305 Email: keith.peacock@health.state.mn.us	Supervisor of BactiChem and Metals Sections Schedule analyses Monitor status of projects Conduct TOC analyses Oversee data review and preparation of analytical reports
Robert Furbur, Environmental Analyst 2	Conduct mercury analyses Report results
Robert Class, Environmental Analyst 1 or Daniel Van Horn, Environmental Analyst 1	Conduct metal analyses Report results

Person:	***Responsibilities:***
Paul Bergh, Environmental Analyst 3 or Lisa Dankert, Environmental Analyst 2	Conduct ammonia analyses Report results
Daniel Van Horn, Environmental Analyst 1	Conduct metal digestions and percent moisture analyses Coordinate transfer of samples to other Analysts

UMD Staff

The University of Minnesota-Duluth (UMD) Trace Organic Analytical Laboratory will be responsible for the particle size analysis of sediment samples into sand, silt, and clay fractions. The UMD staff associated with this project can be reached at the following address:

Chemical Engineering
University of Minnesota-Duluth
10 University Drive
Duluth, MN 55812-2496
Phone: 218-726-6164
Fax: 218-726-6585 or 6907

Person:	***Responsibilities:***
Keith Lodge, Associate Professor Email: klodge@d.umn.edu	Supervisor of Trace Organic Analytical Laboratory Provide technical assistance with particle size method development Provide QA review of data and prepare analytical report
Student Worker (to be determined)	Conduct particle size analyses Prepare electronic spreadsheet of results

A2 PROBLEM DEFINITION/BACKGROUND

A2.1 Purpose/Background

The Duluth-Superior Harbor is one of the busiest ports in the Great Lakes area. However, this vital harbor has seen a degree of environmental degradation. Historic and ongoing land use and water-related activities have contributed a variety of pollutants to the St. Louis River, including the harbor. This contamination has led to several impaired uses including: fish consumption

advisories, restrictions on dredging, and habitat impairments. In 1987, concerns over environmental quality conditions prompted the designation of the lower St. Louis River as one of 43 Great Lakes Areas of Concern (AOCs) (IJC, 1989). This includes the area from Cloquet, MN to its entrance to Lake Superior (Figure A-5).

The International Joint Commission (IJC) is in charge of reviewing Remedial Action Plans (RAPs) for each AOC. The RAPs are being prepared in a staged approach to: 1) assess the severity and extent of contamination, 2) to develop and implement a plan for restoring beneficial uses, and 3) to evaluate the success of any remedial (i.e., clean up) measures that are conducted. Importantly, the RAP process includes substantial citizen participation. The St. Louis River Citizen's Action Committee (CAC) is working to restore and protect the St. Louis River by moving the RAP process forward (MPCA/WDNR, 1992; 1995).

The Sediment Contamination Work Group of the St. Louis River CAC has recommended a three-phase sediment strategy to reduce impairments associated with sediment contamination (MPCA/WDNR, 1995). This strategy consists of: 1) assessment studies to locate sediment hot spots, 2) development of hot spot management plans, and 3) implementation of remediation (i.e., clean up) actions. This strategy provides an incentive to remediate upstream sites first so that downstream sites will not be recontaminated.

Since 1992, the Minnesota Pollution Control Agency (MPCA) has conducted several sediment investigations in the St. Louis River AOC to implement the RAP sediment strategy (Schubauer-Berigan and Crane, 1996, 1997; Crane et al., 1997; Crane 1999a, Breneman et al., In review). These projects have been conducted with the cooperation and financial assistance of either the U.S. Environmental Protection Agency (EPA) or the EPA's Great Lakes National Program Office (GLNPO). The MPCA has also worked with interested stakeholders [e.g., Wisconsin Department of Natural Resources, CAC work groups, industry, consultants, laboratory contractors, and collaborators (e.g., Natural Resources Research Institute)]. Thus, an ecosystem-based management approach is being used to involve all stakeholders in the decision-making process of how contaminated sediment sites are assessed, managed, and remediated (MacDonald and Crane, 1999).

The sediment data assembled to support Stage I of the RAP, and collected thereafter (Table A-1), indicate that several areas in the St. Louis River AOC are contaminated by a variety of toxic and bioaccumulative substances. Sediment assessment projects in the reservoirs downstream of Cloquet, MN, and in the lower estuary, have been conducted to determine the spatial extent of contamination and to assess impacts to benthic biota and fish. The weight-of-evidence data that have been collected to date show a range of biological and chemical impacts in the reservoirs and lower estuary of the St. Louis River AOC. The primary surficial contaminant of concern in the

Figure A-5. Map of the St. Louis River Area of Concern.

Table A-1. Contaminated Sediment Studies Conducted in the St. Louis River AOC since 1992

Location	Sampling Year(s)	Toxicity Tests	Sediment Chemistry	Benthic Data	Reference
Thomson, Forbay, Fond du Lac Reservoirs	1992, 1993	Amphipod	Hg, PCBs, TCDD, Cs-137	No	Schubauer-Berigan & Crane (1996)
Duluth-Superior Harbor	1993	Amphipod, Midge, Microtox, Mutatox	Metals, Hg, PAHs, PCBs, TCDDs, TCDFs, Pesticides, Ammonia, TOC, Cs-137	No	Schubauer-Berigan & Crane (1997)
USX Superfund Site	1993	Amphipod, Midge, Microtox, Mutatox	Metals, Hg, PAHs, Ammonia, Cyanide, Oil & Grease, TOC, Phenol	No	MPCA (unpublished data)
Newton Creek/Hog Island Inlet	1993, 1994	Amphipod, Midge, Cladoceran, Fathead Minnow	Metals, Hg, DROs, PAHs, Oil & Grease, Ammonia, Cyanide, TOC, Particle Size	Yes	Redman & Janisch (1995)
Duluth-Superior Harbor	1994	Amphipod, Midge	SEM Metals, AVS, As, Pb, Hg, TCDDs, TCDFs, Pesticides, PAHs, PCBs, Ammonia, TOC, Tributyltin, Particle Size	Yes	Crane et al. (1997)
Lakehead Pipe Line (North of Hog Island Inlet)	1995	Amphipod, Midge, Cladoceran	Metals, Hg, DROs, PAHs, Oil & Grease, Ammonia, TOC, Particle Size	No	Wenck Associates (1995)

Table A-1. Continued

Location	Sampling Year(s)	Toxicity Tests	Sediment Chemistry	Benthic Data	Reference
Upper St. Louis River; Thomson and Forbay Reservoirs	1995	No	Hg, methyl Hg, grain size	No	ENSR (1996)
Knife Falls, Potlatch, Scanlon, Thomson, Forbay, and Fond du Lac Reservoirs	1995, 1996	No	Hg	Yes	Glass et al. (1998)
St. Louis River AOC	1995, 1996	Amphipod, Midge, Microtox	SEM Metals, AVS, Hg, PAHs, TOC, Particle Size	Yes	Breneman et al. (In review) and USEPA (In prep.)
Duluth-Superior Harbor	1995, 1996	Amphipod, Midge, Cladoceran, Fathead Minnow, Lumbriculus Bioaccumulation	Metals, Hg, Ammonia Phosphorus, Cyanide, COD, TOC, Oil & Grease, PCBs, PAHs, Pesticides, Particle Size	No	TMA (1996)
Vicinity of WLSSD, Duluth Harbor	1996	No	Toxaphene	No	MPCA (unpublished data)
Interlake/Duluth Tar Superfund Site	1996	Amphipod, Midge, Microtox	SEM Metals, AVS, PAHs, TOC, Metals, Hg, Ammonia, Cyanide, BTEX, Particle Size	Yes	IT Corporation (1997)
Slip C, Duluth Harbor	1997	No	Hg, Pb, PAHs, PCBs, TOC, Particle Size	No	Crane (1999a)

Table A-1. Continued

Location	Sampling Year(s)	Toxicity Tests	Sediment Chemistry	Benthic Data	Reference
Minnesota Slip, Duluth Harbor	1998	No	Hg, Pb, PAHs, TOC	No	MPCA (unpublished data)
Duluth-Superior Harbor	1999	Lumbriculus Screening, Bioaccumulation	Hg, PAHs, PCBs, TOC	No	Crane (1999b)
Dakota Pier, Duluth Harbor	1999	No	Metals, Hg, PAHs, Ammonia, Cyanide, Sulfate, TOC	No	MPCA (unpublished data)
Minnesota Slip, Duluth Harbor	1999	Amphipod, Midge	Metals, Hg, PAHs, PCBs, AVS, SEM, TOC, Particle Size	No	Crane (1999c)
Lower St. Louis River Estuary	1999	No	Toxaphene, Cs-137 Pb-210, TOC	No	King (1999)

Sediment Chemistry: As = arsenic; Cs = cesium; Hg = mercury; Pb = lead; PAHs = polycyclic aromatic hydrocarbons; PCBs = polychlorinated biphenyls; TCDDs and TCDFs = tetrachlorodibenzo-p-dioxins and - furans; DROs = diesel range organics; SEM = simultaneously extractable metals; AVS = acid volatile sulfides; BTEX = benzene, toluene, ethylbenzene, and xylene; TOC = total organic carbon; COD = chemical oxygen demand.

Thomson, Forbay, and Fond du Lac Reservoir sediments is mercury (Glass et al., 1990, 1998; Schubauer-Berigan and Crane, 1996), while historical sources of PCBs and 2,3,7,8-TCDD (dioxin) have contaminated deeper sediments in these reservoirs (Schubauer-Berigan and Crane, 1996).

Mercury and PAHs are widespread contaminants of concern in depositional areas of the lower St. Louis River estuary, whereas metals, PCBs, dioxins and furans, organochlorine pesticides, tributyltin, and diesel range organics (DROs) tend to be more localized contaminants of concern (MPCA/WDNR, 1992; Redman and Janisch, 1995; Schubauer-Berigan and Crane, 1997; Crane et al., 1997; Crane, 1999a; Breneman et al., In review). The most highly contaminated sediments occur within two Superfund sites (i.e., USX and Interlake/Duluth Tar) in the inner Duluth Harbor (Schubauer-Berigan and Crane, 1997; IT Corporation, 1997). Other contaminated areas in the Duluth-Superior Harbor include: Hog Island Inlet/Newton Creek in Superior, WI (Redman and Janisch, 1995), as well as several boat slips (e.g., Slip C, Minnesota Slip), areas adjacent to wastewater treatment plants, and other areas with historical sources of contamination (Figure A-6) (Schubauer-Berigan and Crane, 1997; Crane et al., 1997; Crane, 1999a). The data from these sediment studies will be included in the next update of the U.S. EPA's National Sediment Inventory; this inventory will provide comparisons of the national incidence and severity of sediment contamination (USEPA, 1997).

Sediments from several hot spot sites in the AOC have been shown to be toxic to sediment-dwelling organisms and/or associated with alterations of benthic invertebrate community structure (Prater and Anderson, 1977; Redman and Janisch, 1995; Crane et al., 1997; Schubauer-Berigan and Crane, 1996, 1997; Breneman et al., In review; USEPA, In prep.). Furthermore, fish consumption advisories are in effect for selected fish species in the St. Louis River AOC because of mercury contamination. Most of these advisories limit fish consumption to one meal per week for the protection of human health (MDH, 1999); more restrictive advisories are in effect for women of child bearing age and young children. In addition, health advisories are also in effect for the consumption of carp and lake sturgeon due to PCB contamination (MDH, 1999).

Action is currently being taken to implement source control measures and remediate contaminated sediments at the most contaminated areas in the Duluth-Superior Harbor. Remediation options such as natural recovery, *in situ* treatment, capping, incineration, and/or confined disposal of dredged materials are being considered at both Superfund sites. At the Hog Island Inlet/Newton Creek site, some sediments have already been dredged and disposed of in a designated landfill as the first phase of the clean-up efforts. A remediation scoping project at Slip C, in the Duluth Harbor, has been completed to further delineate the extent of contamination and to develop a short-list of potential remediation options (Crane, 1999a).

The results of some of these recent sediment investigations have shown that several areas within the St. Louis River AOC are relatively clean. For example, the areas located in the estuary

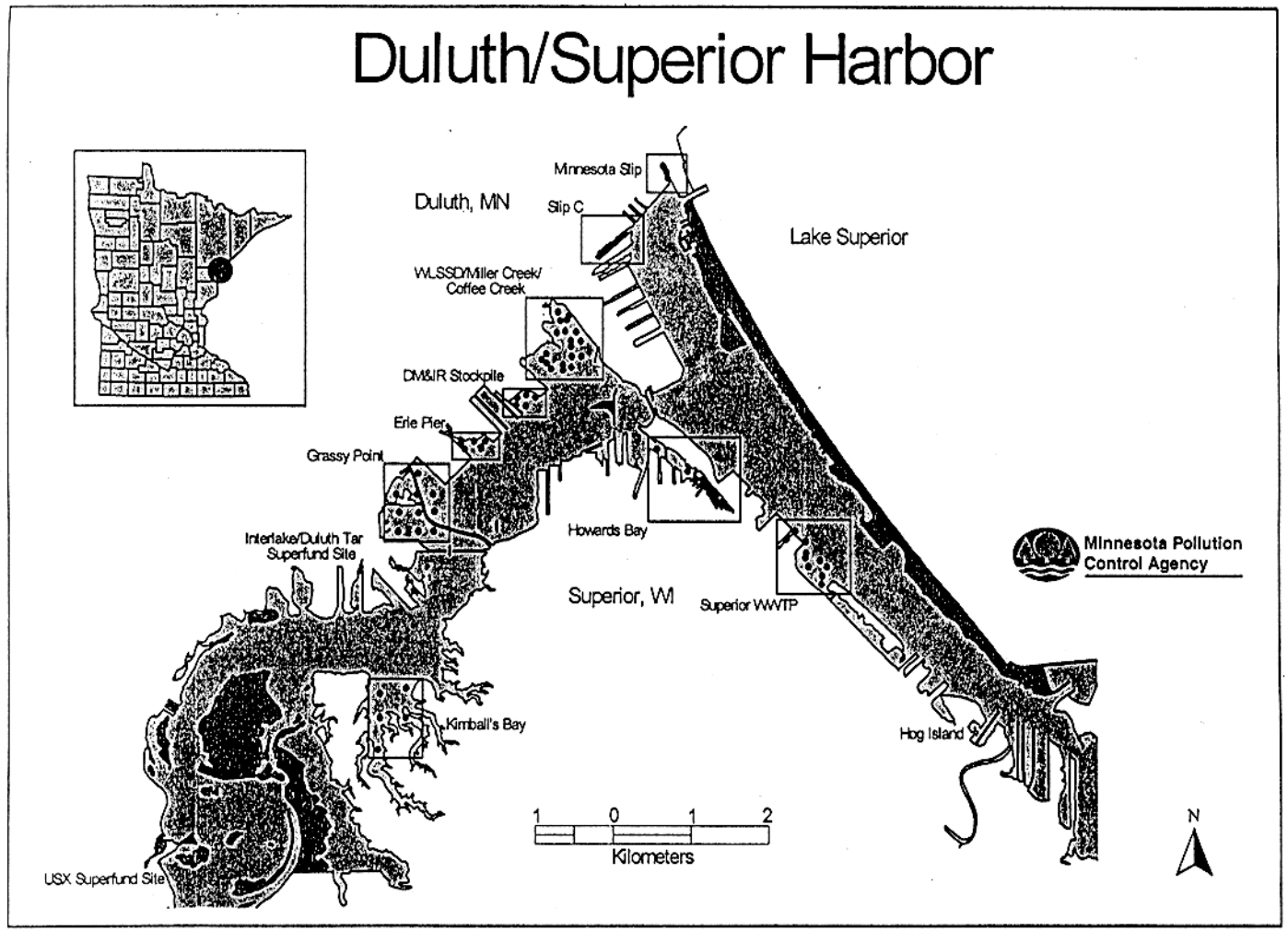

Figure A-6. Location of known contaminated areas in the Duluth-Superior Harbor. Boxes denote sites sampled in 1994, including a reference site at Kimball's Bay (Crane et al., 1997).

upstream of the USX Superfund site in Morgan Park, MN and Allouez Bay in Superior, WI, have low concentrations of contaminants (MPCA and WDNR, 1992; Schubauer-Berigan and Crane, 1997; Breneman et al., In review). These areas provide important fisheries and wildlife habitat. These clean sites also represent reference areas for determining background levels of anthropogenic contaminants in the lower estuary. In addition, the Duluth-Superior Harbor shipping channels contain substantial quantities of relatively clean materials. These dredged materials are washed at the Erie Pier confined disposal facility (CDF) in Duluth, and the sand-sized particles are re-used for beach nourishment, habitat development, highway construction, and other beneficial uses (USACOE, 1997).

A2.2 Problem Statement and Background

A2.2.1 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 A-7). Previous sediment assessment studies have shown that portions of the slip are contaminated with moderately high levels of bioaccumulative contaminants (e.g., PAHs, PCBs, and mercury) and other contaminants (e.g., metals) (Schubauer-Berigan and Crane, 1997; Crane et al., 1997; unpublished R-EMAP and MPCA data; AScI Corporation, 1999). This contamination is of additional concern because of the close proximity of Minnesota Slip to the Duluth entry of Lake Superior.

Past studies of the Duluth-Superior Harbor have not allowed the opportunity to examine the full extent of contamination, and associated bioeffects, in Minnesota Slip. This is partly due to the great expense associated with carrying out these investigations. In order to fully quantify the degree of contamination, and potential for toxicity, the MPCA will be conducting a sediment remediation scoping project in Minnesota Slip.

A2.2.2 Site Description

The present day land use around Minnesota Slip is geared toward tourism. The northeast side of the slip is bounded by a parking lot and commercial businesses in Canal Park (e.g., restaurants and small retail stores), whereas the southwest side of the slip is bounded by Harbor Avenue and the DECC. The slip itself is used to permanently dock the SS William A. Irvin, a former flagship of U.S. Steel's fleet of ore carriers. Since 1986, it has been used as a floating museum administered by the DECC. The Irvin takes up about one-third of the slip as shown in Figure A-8. The rest of the slip houses a marina for commercial and private boat owners. In addition, one of the Vista fleet boats is docked in the outer part of the slip; the Vista fleet boats offer harbor and dinner cruises. Entry into the slip is restricted by a drawbridge. The bridge acts as a wave retention wall that decreases washout of the slip.

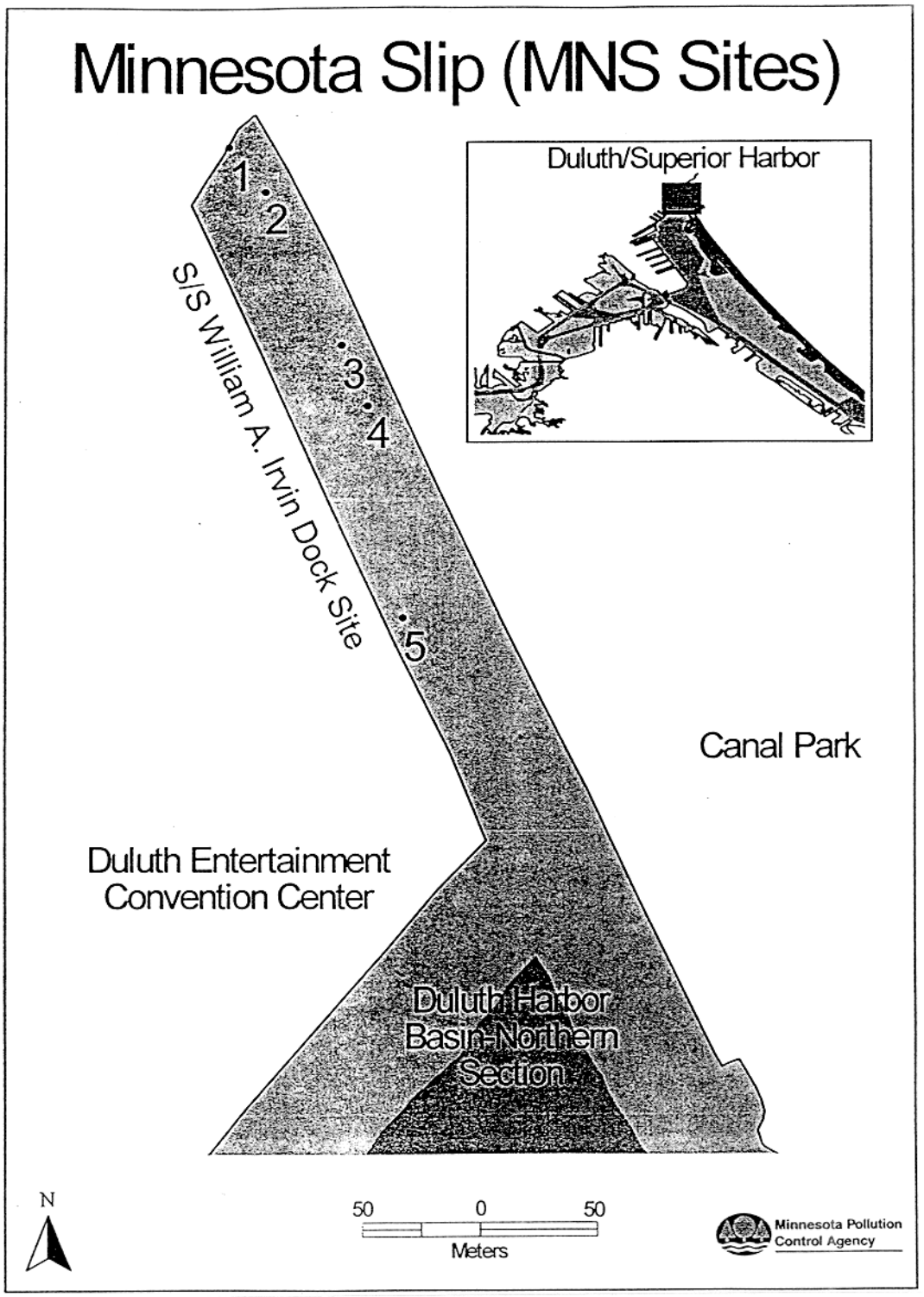

Figure A-7. Location of Minnesota Slip in the Duluth Harbor. Sampling points denote sediment sampling stations for a 1994 study (Crane et al., 1997).

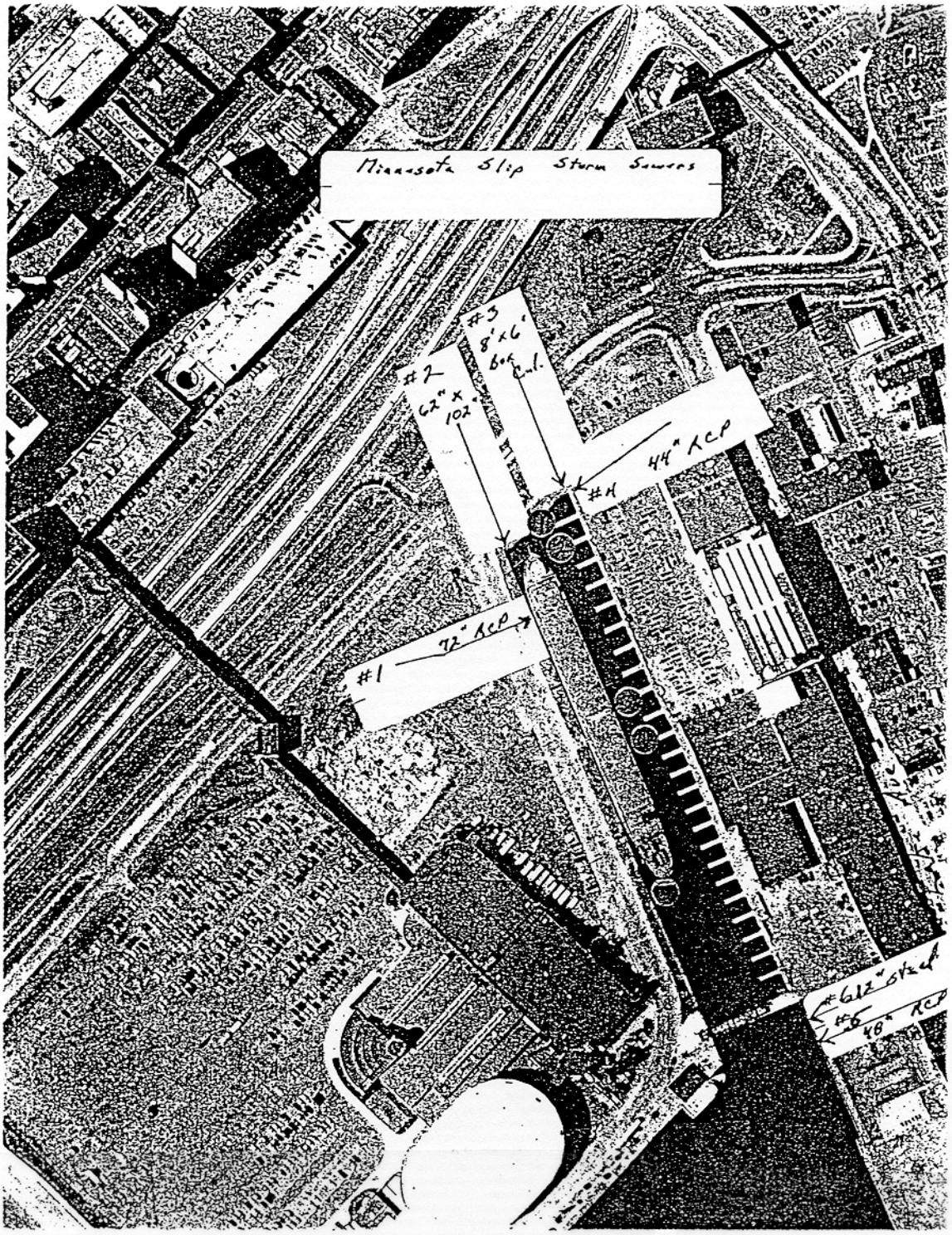

Figure A-8. Aerial photograph of Minnesota Slip. Note the placement of the SS William A. Irvin and nearby boat slips.

Four known storm sewers, and one unknown storm sewer, drain into Minnesota Slip. Two other storm sewers discharge from the breakwall immediately outside of the slip. The City of Duluth, Department of Public Works--Sewer Division, has provided the MPCA with a map of the known storm water drainage into Minnesota Slip (Appendix A). Most of the drainage area borders the downtown business area of Duluth and adjacent residential neighborhoods; this area extends from 2nd Avenue West to 1st Avenue East up to 14th Street. Storm sewers that drain Canal Park and Commerce Street also discharge into the slip.

Local charter boat operators have called the U.S. Coast Guard on several occasions to report oil slicks on the water after rainstorm events. Oil and grease, as well as garbage, appear to be flushed into the slip primarily from the most inland storm sewers. The city of Duluth has created a Storm Water Utility that will seek out funding to update the maps of the storm water system and make improvements to the system. This would include the implementation of best management practices (BMPs) such as the use of sediment traps, retention ponds and filters. A pre-proposal submitted to GLNPO last year, by the city of Duluth, was unsuccessful in obtaining funding for a contaminant loading study in Minnesota Slip. This type of study would have helped to determine the direction and types of emphasis required for the selection of BMPs.

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 (Walker and Hall, 1976). Construction of the Duluth Ship Canal was started in 1870, thereby providing a Duluth entry into the harbor from Lake Superior. A map of the harbor, circa 1887, shows that some of the current slip had already been formed through dredging operations (Figure A-9). The slip used to be called the Marshall Wells slip, and there was a Marshall Wells building adjacent to it; part of this building is now called the Meyerhoff building.

Several historical photos of the slip are retained at the Corps of Engineers Maritime Museum in Duluth. A photo taken in 1904 shows a coal yard just south of Minnesota Slip that was eventually replaced by a scrap yard. The slip used to also have a double train freight shed 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 northeast side of the slip. As of 1931, there was another slip just southwest of Minnesota Slip; this area is now filled in. Over time, parts of Minnesota Slip have been dredged out and filled in. Additional historical information about surrounding land uses in the vicinity of Minnesota Slip is given in Table A-2 (D. Kellner, Duluth, personal communication, August, 1999).

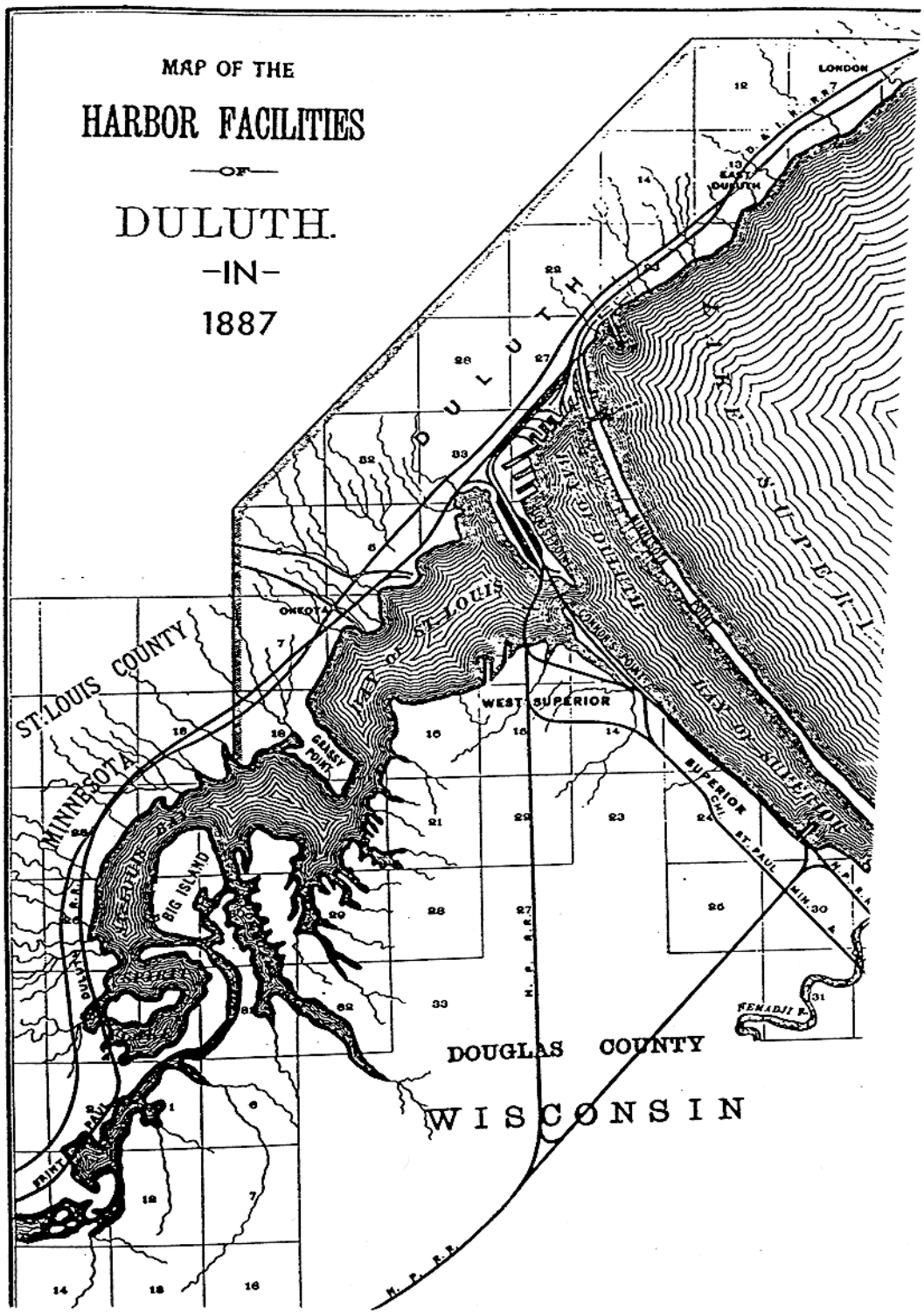

Figure A-9. Map of the Duluth Harbor facilities in 1887 (Walker and Hall, 1976).

Table A-2. Inventory of Historical Land Uses around Minnesota Slip

Property Name	Date of Develop-ment	Beginning Date of Operation	Ending Date of Operation	Address
A.H. Thompson Planing Mill (Geo. Lautenschlager)	1872	1872	1890	7610 - 7614 Lake Ave.
Gowan-Lenning Brown Co. Grocery Wharf		1878	1935	525 S. Lake Ave.
Crowley-Brown Sandstone Wharf		1878	1895	
N. Grigon Shipyard, Shipbuilding and Repair Wharf	1880	1880	1895	
Northern Pacific No. 5 & No. 6	1883	1883	1950	Industrial Slip (E side) and Minnesota Slip (W side)
Scott & Holston Planing Mill	c. 1880	1884		1501 - 1520 Lake Ave.
St. Paul & Duluth Railroad Cos. Warehouse		1884		2nd Ave. W. & Waterfront (west side of Minnesota Slip)
Marquis De Mares- Cold Storage House	1884	1884		7607 Lake Avenue
Stone & Ordean Wholesale Grocery Warehouses	1884	1884	1940	1604 Lake Ave.; later 525 Lake Ave. S.
C. H. Graves & Co. Salt Lime Cement & Plaster Warehouses		1884	1924	1604-1706 Lake Ave.
Asa Dailey's Lumber Yard	c. 1885	1885	1890	
Marshall Wells Hardware Company and Dock	1889	1889	1950	301 or 325 Lake Ave. S.
Booth Fisheries Co. Fish & Merchandise Wharf	1894	1894	1940	20 W. Morse
Whitney Materials Co. Sand & Gravel Wharf	1895	1895	1940	15 Buchanan
Standard Salt & Cement Co. Wharf		1895	1960	237-245 Lake Ave.
White Line Transportation Co. Freight & Passenger Wharf		1895	1940	
Christiansen & Sons, Inc. Fish Wharf		1905	1935	20 W. Morse
Scandia Fish Co. Wharf		1908	1920	
City of Duluth Public Wharf		1910	1940	
Rust-Parker Co. Grocery Wharf		1911	1940	217-219 Lake Ave. S.
City of Duluth Public Wharf		1915	1940	
Christiansen & Sons		1927		20 W. Morse
Johnson, Sam & Sons, Fisheries		1927		19. W Morse
United States & Doninin Trans. Co.		1930		20 W Morse
Duluth Ice & Fuel Co.		1935		102 Buchanan
MacAskill-Monaghan Co.		1950	1960	227 Lake Ave. S.
Stone & Ordean Building	1884	1950	1960	1604 Lake Ave.; later 525 Lake Ave. S.
Jeno's Inc.	1884	1970	1970	1604 Lake Ave.; later 525 Lake Ave. S.

A2.2.3 Past Data Collection Activities

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

- Survey of sediment quality in the Duluth-Superior Harbor: 1993 sampling results (Schubauer-Berigan and Crane, 1997) (one core site in Minnesota Slip).

- Sediment assessment of hot spot areas in the Duluth-Superior Harbor (Crane et al., 1997) (five core sites in Minnesota Slip).

- Regional Environmental Monitoring and Assessment Program (R-EMAP) surveying, sampling and testing: 1995 and 1996 sampling [one surficial (0-5cm) 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)

- Bioaccumulation of contaminants in the Duluth-Superior Harbor (AScI Corporation, 1999) (four surficial sites).

The aforementioned studies have provided bits of information about sediment quality conditions in Minnesota Slip. Taken together, these bits of information provide a "weight-of-evidence" about: contaminants of concern, potential for short-term and long-term toxicity to bottom feeding (i.e., benthic) organisms living in the sediments, potential for changes in the community structure of naturally occurring benthic organisms, and potential for bioaccumulation of certain contaminants (like mercury) in the base of the aquatic food chain.

These studies have given rise to concerns of extensive contamination in Minnesota Slip sediments. The most contaminated sediments are located in the inner part of the slip. Some sites are contaminated with oil to as deep as 1.6 m. Contaminants of concern include: PAHs, PCBs, mercury, cadmium, chromium, copper, lead, nickel, zinc, acid volatile sulfides (AVS), simultaneously extractable metals (SEM), toxaphene, p,p'-DDD and o,p'-DDT, and KCI-extractable ammonia (Schubauer-Berigan and Crane, 1997; Crane et al., 1997; unpublished R-EMAP and MPCA data; AScI Corporation, 1999). The concentration ranges of contaminants of concern, and other parameters, are given in Table A-3.

A limited number of 10-day toxicity tests, with *Hyalella azteca* and *Chironomus tentans*, have not revealed significant acute toxicity to the sediments, although sediments from the most contaminated area of the slip have not been tested (Schubauer-Berigan and Crane, 1997; Crane et

Table A-3. Ranges of Contaminant Concentrations in Minnesota Slip (Schubauer-Berigan and Crane, 1997; Crane et al., 1997; unpublished R-EMAP and MPCA data)

Contaminant	Concentration
Total PAHs	5.7-320 mg/kg
PCBs	7.8-612 µg/kg
Mercury	0.075-1.6 mg/kg
Lead	31-280 mg/kg
Cadmium	2.6 mg/kg
Chromium	49.8 mg/kg
Copper	83.2 mg/kg
Nickel	30.7 mg/kg
Zinc	214 mg/kg
AVS	1.43-1.54 µmol/g
SEM	5.36-7.59 µmol/g
Toxaphene	147-204 µg/kg
p,p'-DDD & o,p'-DDT	10 µg/kg
KCI-extractable ammonia	10.2-138 mg/kg
<u>Other Parameters</u>	
TOC	0.67-8.3%
Particle Size	
Sand	48.2-96.9%
Silt	2.0-40%

al., 1997). The surficial sediments are populated primarily with pollutant tolerant worms (i.e., oligochaetes) (Crane et al., 1997). The results of some bioaccumulation studies indicated that benthic worms accumulated PAH compounds in their tissues, but little PCBs or mercury were accumulated (AScI Corporation, 1999). Thus, this slip has been designated as a hot spot area of elevated contamination where there is the potential for biological impairments to the benthic community.

A2.2.4 Intended Data Usages

The MPCA anticipates using the results of this project to determine the spatial extent of contaminants of concern, as well as the potential toxicity of the sediments to benthic invertebrates through short-term and long-term toxicity tests. Intended data usages are to provide information to assist in the development of possible remediation options for Minnesota Slip, including natural recovery. The decisions to be applied from this project will encompass sediment management activities at Minnesota Slip. These activities could include: implementation of point/nonpoint source controls, sediment remediation, and/or dredged material management. The MPCA's Remediation Unit in the North District will be responsible for taking over this site for the implementation of any remediation options.

Other expected data users are the members of the St. Louis River CAC and CAC Sediment Contamination Work Group in developing recommendations for sediment management alternatives. The city of Duluth Sewer Division, university researchers, local planning agencies, and environmental groups may also use these sediment data. The data will be added to GLNPO's sediment database for the St. Louis River AOC, as well as to the Corps of Engineer's sediment database for the Duluth-Superior Harbor.

A3 PROJECT/TASK DESCRIPTION AND SCHEDULE

A3.1 Purpose/Background

In order to conduct a sediment remediation scoping project in Minnesota Slip, the following project objectives will be met:

- Delineate the extent and depth of selected sediment contaminants in Minnesota Slip.
- Determine the acute and chronic toxicity of surficial sediments to selected benthic invertebrates.
- Estimate the volume of contaminated sediments in the inner 75% of the slip.
- Develop a short list of sediment remediation options for further consideration.

The following section will describe the work tasks to be conducted and the associated QA/QC goals, procedures, and timetables for collecting the measurements.

A3.2 Description of the Work to be Performed

Specific work tasks (and responsible organizations for completing tasks) include the following:

- Inform the Minnesota Department of Health that the MPCA will use them for PAH, mercury, cadmium, chromium, copper, lead, nickel, selenium, zinc, ammonia, TOC, and percent moisture analyses (no contract required). (MPCA)

- Prepare contracts, per MPCA requirements, for other analytical and toxicity testing services, including:

    - Develop and distribute Request for Proposals (RFPs) for soliciting toxicity testing laboratory and analytical laboratory bids for work exceeding $10,000. Review responder proposals and select the laboratories (En Chem, Inc. and ENSR). Put together MPCA contracts with laboratories. (MPCA)

    - Prepare letter contracts for work under $5,000. This will include separate letter contracts for the University of Minnesota-Duluth (UMD) for particle size analyses and for Short Elliot Hendrickson (SEH) Inc. to map sediment contaminant isopleths for similar core segments. (MPCA)

- Obtain information on historical and current sources of contamination to Minnesota Slip, as well as historical and current land use patterns for the area surrounding the slip. Information from Sanborn Insurance maps that date back to the late 1800s will be accessed from microfiche copies at the MPCA. Information on past commercial/industrial operations will be available from the Sanborn maps. Land use patterns will also be determined from historical photos of the slip maintained by the Corps of Engineers Maritime Museum in Duluth. Information will also be obtained from the St. Louis River CAC for a project they are conducting to develop a historical reconstruction of land uses in the lower St. Louis River (Karen Plass, St. Louis River CAC, personal communication, 1998). (MPCA)

- Develop a detailed work plan and quality assurance project plan (QAPP) to delineate the horizontal and vertical profile of contaminants of concern in Minnesota Slip, as well as assess sediment toxicity to benthic invertebrates. (MPCA)

- Collect sediment samples in Minnesota Slip using GLNPO's assistance with the R/V Mudpuppy and Vibrocoring system. Ship samples to the appropriate toxicity testing and analytical laboratories. (MPCA and GLNPO)

- Conduct 28-day sediment toxicity tests with *Hyalella azteca*, followed by a 14-day exposure period in clean water to further assess reproduction. The endpoints for these tests will be survival, reproduction, and growth (e.g., dry weight). In addition, 10-day tests with *Chironomus tentans* will be conducted to assess survival and growth (i.e., weight). Overlying water quality measurements of alkalinity, hardness, pH, dissolved oxygen, conductivity, and unionized ammonia will be made. Prepare toxicity test reports and submit to MPCA. (ENSR)

- Analyze sediment samples for the parameters listed in Table A-4 and report results to MPCA. (En Chem, Inc., MDH, UMD)

- Interpolate the contaminant data in similar core segments using sediment kriging. The volume of contaminants in selected core segments will be estimated by combining all available contaminant data for the slip from previous sediment investigations. (SEH)

- Compare the surficial sediment data to background contaminant levels in the St. Louis River AOC (as determined by the R-EMAP project). The data will also be compared to biologically-based Sediment Quality Objective values (Ingersoll and MacDonald, 1998). (MPCA)

- Present the results at a national conference (e.g., SETAC) and through other public forums. (MPCA)

- Develop a short-list of possible remediation scenarios (e.g., natural recovery, capping, *in situ* treatment, sediment removal) for future consideration. (MPCA)

- Prepare a draft and final manuscript for peer-review publication. (MPCA)

Sediment samples will be collected from Minnesota Slip during September 21-23, 1999 and from September 28 to October 1, 1999. The GLNPO R/V Mudpuppy and crew will be used to assist MPCA staff with this effort during the last week of September. A schedule of the major milestones for this project are given in Table A-5.

Table A-4. Chemical and Physical Parameters to be Measured in Minnesota Slip

Parameter
PCBs: 107 congeners [same group as measured in Slip C (Crane 1999a)]
PAH compounds: acenaphthene, acenaphthylene, anthracene, benzo[a]anthracene, benzo[a]pyrene, benzo[b & j]fluoranthene, benzo[e]pyrene, benzo[g, h, i]perylene, benzo[k]fluoranthene, chrysene, dibenzo[a, h]anthracene, fluoranthene, fluorene, indeno[1, 2, 3-cd]pyrene, 2-methylnaphthalene, naphthalene, phenanthrene, and pyrene
Mercury
Metals: cadmium, chromium, copper, lead, nickel, selenium, zinc
Acid Volatile Sulfides
Simultaneously Extractable Metals: cadmium, copper, mercury, lead, nickel, zinc
Ammonia
TOC
Particle Size: percent of sand and gravel (>53 µm), coarse silt (53-20 µm), medium silt (20-5 µm), fine silt (5-2 µm), coarse clay (2-0.2 µm), medium clay (0.2-0.08 µm), and fine clay (<0.08 µm)
Percent Moisture

Table A-5. Schedule of Major Milestones

MAJOR TASKS	1999 March	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	2000 Jan.	Feb.	March	April	May	June	July	Aug.	Sept.
Request for Proposals: Agency Approval and Posting	XXXX	XXXX	XXX																
Review Proposals				XX															
Contracts: Agency Approval					X	XXXX	XX					XXXX							
Work Plan/QAPP	X					X	XXXXX												
Sediment Sampling							XX												
Toxicity Testing & Lab Report								XXXX	XXXX	XXXX									
Analytical Analyses & Results								XXXX	XXXX	XXXX	XXXX	XXXX	XXXX	XXXX					
Sediment Kriging													XXX	XXXX	XXX				
Data Analysis												XX		XXXX	XXXX	X			
Short List: Remediation Options																	XX		
Draft Manuscript																XXXX	XXXX	X	
GLNPO Review																		XXXXX	
Final Report																			XX

A4 QUALITY OBJECTIVES AND CRITERIA FOR MEASUREMENT DATA

A4.1 Purpose/Background

The purpose of this section is to document the Data Quality Objectives (DQOs) of the project. In addition, performance criteria will be established for the planning process and measurement system that will be employed in generating the data.

A4.2 Specifying Quality Objectives

The DQO Process is a series of planning steps based on the Scientific Method that is designed to ensure that the type, quality, and quantity of environmental data used in decision making are appropriate for the intended application. DQOs are qualitative and quantitative statements derived from outputs of each step of the DQO Process that:

- Clarify the intended use of the data
- Define the type of data needed to support the decision
- Identify the conditions under which the data should be collected
- Specify tolerable limits on the probablility of making a decision error due to uncertainty in the data.

The DQO process consists of the following seven steps:

1. State the problem
2. Identify the decision
3. Identify inputs to the decision
4. Define the study boundaries
5. Develop a decision rule
6. Specify limits on decision errors
7. Optimize the design for obtaining data.

Data Quality Indicators (DQIs) can be evolved from DQOs for a sampling activity through the use of the DQO process (USEPA, 1998).

For this project, the individual steps of the DQO process are listed below.

1. <u>State the Problem</u>

    - The members of the project team were previously described in Section A1.2.
    - The primary decision maker for this project is the MPCA Principal Investigator, who will solicit input from expected data users.

- The description of contamination problems in Minnesota Slip were identified in Section A2.2
    - The financial resources available to carry-out this project include GLNPO grant number GL985004-01 for $128,600 plus a state match of $6,770. In addition, staff support from the MPCA and GLNPO will be available for sampling and other project assistance. The timeline for meeting major project deliverables is provided in Table A-5. The entire project will be completed by September 30, 2000.

2. Identify the Decision

- The principal study question is based on using a weight-of-evidence approach to determine: what is the spatial extent of contamination in Minnesota Slip and do acute and/or chronic effects result from benthic organisms exposed to the sediments?
- Alternative actions that could result from resolution of the principal study question include:
    - Implementation of a storm water loading study to quantitate contaminant loads entering the slip and to develop Best Management Practices to reduce contaminant inputs to the slip.
    - Evaluation of groundwater inputs of contaminants to the slip.
    - Implementation of a human health and/or ecological risk assessment for Minnesota Slip.
    - Implementation of a feasibility study to better quantitate remediation options for this study.
    - No action.
- A decision statement for this site would be to ensure all possible source control measures are taken before any potential sediment remediation options are carried out.
- Multiple decisions about source control measures may be necessary to address sediment contamination problems in Minnesota Slip. However, this will be based on the availability of funding opportunities to pay for this work.

3. Identify Inputs to the Decision

- To resolve the decision statement, measurements of the chemical and physical parameters given in Table A-4 need to be made. Selenium was added to the list because it has not been measured in the slip before, and it has been found to be a contaminant of concern in nearby soil sites along the waterfront. This list excludes the previously determined contaminants of concern of toxaphene and

p,p'-DDD and o,p'-DDT (Schubauer-Berigan and Crane, 1997). These contaminants were excluded because of their high analytical costs, and because PAHs are the greatest contaminant of concern at this site (Schubauer-Berigan and Crane, 1997; Crane et al., 1997). Any remediation actions taken at this site to reduce PAH contamination will most likely take care of most of the other contaminants of concern. In addition to chemical measurements, an assessment of acute and chronic sediment toxicity needs to be made to provide another piece of information in the weight-of-evidence approach. The results of a recent bioaccumulation study (GL985604-01), in which two sites were sampled in Minnesota Slip for 28-day bioaccumulation tests with *Lumbriculus variegatus* (AScI Corporation, 1999) will also be used to resolve the decision statement. A benthological survey will not be conducted, as part of the weight-of-evidence approach, because a previous survey showed the slip is consistently dominated with pollutant-tolerant oligochaetes (e.g., Tubificids and naidid oligochaetes) (Crane et al., 1997).

- To determine the sources for each item of information identified above, the sediment will be analyzed for chemical and physical parameters as detailed in Section B. In addition, acute and chronic toxicity tests, with representative benthic organism, will be conducted according to EPA protocols. Previous sediment investigations provided information about the limited spatial distribution of some contaminants and potential for acute toxicity (Schubauer-Berigan and Crane, 1997; Crane et al., 1997; unpublished R-EMAP and MPCA data; AScI Corporation, 1999), but these studies did not provide enough information to resolve the decision statement.
- For contaminated sediments, the MPCA has not established specific information needs that must be acquired to establish action levels. Instead, a weight-of-evidence approach will be used to establish next steps for Minnesota Slip.
    - The appropriate measurement methods exist to provide the necessary data for this project. Last year, a small number of Minnesota Slip sediment samples were submitted to MDH in order to refine their PAH methods for these samples. Due to the moderately high levels of PAHs in the samples, it was determined that the less expensive GC/MS (rather than GC/MS-SIM) method could be used with a minimal loss of information about certain PAH compounds that comprised less than 2% of the total PAHs (P. Swedenborg, MDH, personal communication, 1998). For the toxicity tests, the 42-day *Hyallela azteca* test is a fairly new method. The contract laboratory will run one negative control with each sample as an extra measure to ensure the success of these tests.

4. Define the Boundaries of the Study

- The characteristics that define the population of interest are the chemical and physical parameters listed in Table A-4, and the acute and chronic endpoints of the sediment toxicity tests. The endpoint for the acute, 10-day *Chironomus tentans* toxicity tests is survival; growth (i.e., weight) will be measured as a chronic endpoint. The chronic endpoints for the 42-day *Hyalella azteca* tests are survival (after 28, 35, and 42 days), reproduction, and growth (28 and 42 days as dry weight).
- The spatial boundary of the decision statement will be limited to:
    - The geographic area of Minnesota Slip down to a maximum depth of 1.5 m.
    - Consistent sediment core sections will be obtained to allow comparisons within subsets of data and to determine if the surficial sediments are less contaminated than deeper sections. This will involve the collection of sediments in the biologically active layer (i.e., 0-5 cm) to be composited and split for sediment chemistry and toxicity tests. In addition, the following core sections will be obtained for various chemical and physical parameters: 0-15 cm, 15-30 cm, 30-45 cm, 45-60 cm, 60-75 cm, 75-90 cm, 60-90 cm (one site), 90-120 cm, and 120-150 cm. Due to the high cost of the analytical measurements, more data will be collected with less expensive parameters like lead, zinc, and mercury. As done at Slip C (Crane, 1999a), regression relationships between these less expensive parameters and PAHs will be sought that may lead to extrapolations of PAH concentrations in deeper core segments. A suite of other metals will be measured in only the 0-5 cm core segments to allow additional validation of recently developed sediment quality objectives for the St. Louis River Area of Concern (GL985604-01), with the sediment toxicity testing results.
    - The temporal boundary of the problem will be limited to a distinct period of time from September 21-23, 1999 to September 28-October 1, 1999. The data will be used to reflect the sediment quality conditions from which a decision can be made concerning future management actions at Minnesota Slip. The data is being collected at the end of September because it will be less disruptive to the charter boat operators in Minnesota Slip at that time. In addition, more private boats may be pulled out of the marina by that time which will make sampling easier.
    - The scale of decision making will be based on the analytical results from all core segments to enable volume estimates of PAHs, mercury, lead, and

zinc to be made. The surficial analytical data (i.e., 0-5 cm and 0-15 cm) will be compared to sediment quality objectives to determine if exceedances of threshold effect concentrations (TECs) and probable effect concentrations (PECs) occur. In addition, a weight-of-evidence approach will be used to assess the chemical and bioeffects data available from this, and previous studies, for the surficial sediments.

- Potential practical constraints on data collection include the following: weather conditions such as severe weather or snow, inability to gain access to pre-determined sampling sites because of physical obstructions (e.g., other boats) or non-cohesive sediments (i.e., high sand content), equipment failure, or unavailability of personnel, time, or equipment.

5. Develop a Decision Rule

- The statistical parameter that characterizes the populations of interest are the true mean contaminant concentrations for each sediment section and the true mean toxicological endpoints.
- Since action levels have not been set for contaminated sediment sites in Minnesota, all of the available chemical and bioeffects data will be evaluated using a weight-of-evidence approach.
- If...then statements for the decision rule will follow the sediment assessment framework and contingency table of MacDonald et al. (1998) (Appendix B).

6. Specify Tolerable Limits on Decision Errors

- From previous sediment investigations, the possible range of most of the chemical parameters is given in Table A-3. In some instances, not enough data have been collected to determine appropriate ranges of certain heavy metals.
- The decision errors and null hypothesis are as follows:
    - The two decision errors are (i) deciding the weight-of-evidence data indicates the sediments are contaminated enough to warrant remediation when it truly does not, and (ii) deciding the weight-of- evidence data indicates the sediments are not contaminated enough to warrant remediation when it truly does.
        - The true state of nature for decision error (i) is that the slip does not need remediation.
        - The true state of nature for decision error (ii) is that the slip needs to be remediated.

- The potential consequences of each decision error are:
    - The consequences of deciding that Minnesota Slip warrants remediation, when it truly does not, will be that the MPCA will have to spend additional fiscal and personnel resources to assess the human health and ecological risks at the site, as well as to conduct a feasibility study of possible remediation scenarios. In addition, the involvement of various stakeholders would be wasted and may lead to mistrust of MPCA actions at this and other St. Louis River AOC hot spot sites.
    - The consequences of deciding that Minnesota Slip does not warrant remediation, when it truly does, will be that aquatic biota, and possibly humans, may be exposed to unacceptable risks at this site. In addition, it would make it more difficult for the city of Duluth to solicit funds to implement BMPs for the stormwater outfalls draining into Minnesota Slip.
- Decision error (ii) has more severe consequences since that risk of jeopardizing human health and ecological stability outweighs the consequence of having to devote more staff and fiscal resources to evaluating remediation options.
- The null hypothesis (baseline condition) and the alternative hypothesis are as follows:
    - The baseline condition, or null hypothesis (H_o), is that the weight-of-evidence of available data indicates the sediments require remediation.
    - The alternative hypothesis (H_a) is that the weight-of-evidence of available data indicates the sediments do not require remediation.
- The false positive decision error occurs when the null hypothesis is rejected when it is true. The false negative decision error occurs when the null hypothesis is not rejected when it is false.

- The range of possible values of the parameter of interest, where the consequences of decision errors are relatively minor (gray region) must be specified on a case-by-case basis.

7. <u>Optimize the Design</u>

- Guidance on "Statistical Techniques Applied to Sediment Sampling (STATSS)" (Lubin et al., 1995) will be used to optimize the experimental design.

- Additional consideration will be made to optimize the use of sediment kriging to develop isopleths of chemical contaminants for different core segments. The samples need to be collected in a triangulation pattern to make the kriging most effective.

A4.3 Specifying Measurement Performance Criteria

An important feature of the QAPP is that it links the data user's quality objectives to verifiable measurement performance criteria. Once these measurement performance criteria have been established, sampling and analytical methods criteria can be specified in Section B.

Data Quality Indicators (DQIs) are qualitative and quantitative descriptors used in interpreting the degree of acceptability or utility of data. The principal DQIs are precision, bias, representativeness, comparability, and completeness. Establishing acceptance criteria for the DQIs sets quantitative goals for the quality of data generated in the analytical measurement process.

A4.3.1 Precision

Precision is a measure of agreement among replicate measurements of the same property, under prescribed similar conditions. This agreement is calculated as either the range (R) or as the standard deviation (s). It may also be expressed as a percentage of the mean of the measurements, such as relative percent difference (RPD) or relative standard deviation (RSD) (for three or more replicates).

Field precision is assessed through the collection and measurement of field replicates at a rate of one replicate per ten analytical samples. This allows intralaboratory precision information to be obtained on sample acquisition, handling, shipping, storage, preparation, and analysis. Both samples can be carried through the steps in the measurement process together to provide an estimate of short-term precision. An estimate of long-term precision can be obtained by separating the two samples and processing them at different times or by different people and/or analyzed using different instruments. Precision control limits are given in Table A-6.

For duplicate measurements, relative percent difference (RPD) is calculated as follows:

$$RPD = \frac{D_1 - D_2 \times 100\%}{(D_1 + D_2)/2}$$

RPD = relative percent difference
D_1 = sample value
D_2 = duplicate sample value

Table A-6. Summary of Analytical Data Quality Indicators for Sediment Samples

Analyte	Precision (% RPD)	Accuracy (%)	Completeness (%)
PCB Congeners	<50	40-150	95
Individual PAHs	<50	50-130	95
Mercury	<20	70-130	95
Metals (Cd, Cr, Cu, Ni, Pb, Zn)	<10	85-115	95
Selenium	<10	80-120	95
AVS	<20	65-125	95
SEM	<20	80-120	95
Ammonia	<20	80-120	95
Particle Size	<50	N/A	95
TOC	<20	80-120	95
Percent Moisture	<20	80-120	95

N/A = Not Applicable
RPD = Relative Percent Difference

For three or more replicates:

$$RSD = (s/x) \times 100$$

RSD = relative standard deviation
s = standard deviation of three or more results
x = mean of three or more results

Standard deviation is defined as follows:

$$s = ((\sum(y_i - \text{mean } y)^2 \times 1/(n-1)))^{0.5}$$

s = standard deviation
y_i = measured value of the ith replicate
mean y = mean of replicate measurements
n = number of replicates

A4.3.2 Bias

Bias is the systematic or persistent distortion of a measurement process that causes errors in one direction. Bias assessments for environmental measurements are made using personnel, equipment, and spiking materials or reference materials as independent as possible from those used in the calibration of the measurement system. When possible, bias assessments should be based on analysis of spiked samples rather than reference materials so that the effect of the matrix on recovery is incorporated into the assessment. A documented spiking protocol and consistency in following that protocol are important to obtaining meaningful data quality estimates. Spikes should be added at different concentration levels to cover the range of expected sample concentrations. The use of spiked surrogate compounds for GC and GC/MS procedures for PCB congeners and PAH compounds, respectively, will be used to assess for bias.

A4.3.3 Accuracy

Accuracy is a measure of the closeness of an individual measurement of the average of a number of measurements to the true value. Accuracy includes a combination of random error (precision) and systematic error (bias) components that result from sampling and analytical operations.

Accuracy in the field is assessed through the adherence to all sample handling, preservation, and holding times. In order to assure the accuracy of the analytical procedures, an environmental sample will be randomly selected from each sample shipment received at the laboratory, and spiked with a known amount of the analytes to be evaluated. In general, a sample spike will be included in every set of 20 samples tested on each instrument. The spike sample will then be analyzed. The increase in concentration of the analyte observed in the spiked sample, due to the addition of a known quantity of the analyte, compared to the reported value of the same analyte

in the unspiked sample determines the percent recovery. The percent recovery for a spiked sample is calculated according to the following formula:

$$\%R = 100\% \times (S-U)/C_{sa}$$

%R = percent recovery
S = measured concentration in spiked sample
U = measured concentration in unspiked sample
C_{sa} = actual concentration of spike added

For situations where a standard reference material is used in addition to a matrix spike:

$$\%R = 100\% \times C_m/C_{srm}$$

%R = percent recovery
C_m = measured concentration of SRM
C_{srm} = actual concentration of SRM

The analytical DQIs for accuracy are given in Table A-6.

A4.3.4 Representativeness

Representativeness expresses the degree to which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition. Representativeness is a qualitative term that should be evaluated to determine whether *in situ* and other measurements are made and physical samples collected in such a manner that the resulting data appropriately reflect the media and phenomenon measured or studied.

For field data, representativeness is dependent upon the proper design of the sampling program and will be satisfied by ensuring that the field sampling plan is followed and that proper sampling techniques are used. The sampling design of this project is representative of moderately contaminated sediments in Minnesota Slip.

Representativeness in the laboratory is ensured by using the proper analytical and toxicity testing procedures; meeting sample holding times; and analyzing and assessing laboratory duplicates for the chemistry samples.

A4.3.5 Comparability

Comparability is the qualitative term that expresses the confidence that two data sets can contribute to a common analysis and interpolation. Comparability must be carefully evaluated to establish whether two data sets can be considered equivalent in regard to the measurement of a

specific variable or groups of variables. In a laboratory analysis, the term comparability focuses on method type comparison, holding times, stability issues, and aspects of overall analytical quantitation.

There are a number of issues that can make two data sets comparable, and the presence of each of the following items enhances their comparability:

- Two data sets should contain the same set of variables of interest
- Units in which these variables were measured should be convertible to a common metric
- Similar analytical procedures and quality assurance should be used to collect data for both data sets
- Time measurements of certain characteristics (variables) should be similar for both data sets
- Measuring devices used for both data sets should have approximately similar detection levels
- Rules for excluding certain types of observations from both samples should be similar
- Samples within data sets should be selected in a similar manner
- Sampling frames from which the samples were selected should be similar
- Number of observations in both data sets should be of the same order or magnitude.

These characteristics vary in importance depending on the final use of the data. The closer two data sets are with regard to these characteristics, the more appropriate it will be to compare them. Large differences between characteristics may be of only minor importance, depending on the decision that is to be made from the data.

For this investigation, comparability will be satisfied by ensuring that the field sampling plan is followed and that proper sampling techniques are used. The analytical data obtained from this study will be as comparable, as possible, to data collected from recent sampling efforts in Minnesota Slip.

A4.3.6 Completeness

Completeness is a measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under normal conditions. Field completeness is a measure of the amount of valid measurements obtained from all the measurements taken in the project. Field completeness for this project will be greater than 90%. Laboratory completeness is a measure of the amount of valid measurements obtained from all the measurements taken in the project. Laboratory completeness for this project will be greater than 95% of the total number of samples submitted to the analytical laboratories (Table A-6).

The calculation for percent completeness is as follows:

$$\%C = 100\% \times (V/n)$$

%C = percent completeness
V = number of valid measurements
n = number of measurements planned

A5 SPECIAL TRAINING REQUIREMENTS/CERTIFICATION

A5.1 Purpose/Background

The purpose of this section is to ensure that any specialized training requirements necessary to complete this project are known and described below. In addition, the procedures are described in enough detail to ensure that specific training skills can be verified, documented, and updated as necessary.

A5.2 Training

Training, as described here, is limited to field sampling activities. Each of the contract laboratories will have their own training requirements for their staff. The MPCA Principal Investigator and Field Team Leader have both had boat and water safety training, as well as right-to-know training for working with hazardous substances. In addition, the MPCA Field Team Leader has had 40-hour OSHA Hazardous Waste Training and subsequent refresher courses.

GLNPO field staff, and their contractors, must take a 40-hour OSHA required (29 CFR 1910.120) health and safety course for hazardous waste workers, plus an annual refresher course. In addition, they are required to be fitted to a respirator and to have annual or bi-annual medical monitoring.

A5.3 Certification

GLNPO field staff, and their contractors, must be certified in first aid and CPR. The captain of the R/V Mudpuppy is required to have a 100-ton marine mariners license.

A6 DOCUMENTATION AND RECORDS

A6.1 Purpose/Background

This section defines which records are critical to the project and what information needs to be included in the reports. In addition, the data reporting format and the document control procedures to be used are described.

A6.2 Information Included in the Reporting Packages

A6.2.1 Field Operation Records

The information contained in these records document overall field operations and generally consist of the following:

- *Sample collection records*. A bound, water proof field notebook will be used to record raw data and to make references to prescribed procedures and changes in planned activities. This notebook includes pre-numbered pages with date and signature lines. The information recorded in this notebook show that proper sampling protocols were performed in the field. This documentation will include the names of the field crew, date, time, weather conditions, sample site code, water depth, sediment sounding, core slice descriptions, equipment/method used, maps and diagrams, and unusual observations.

- *Sample tracking records*. Legal chain-of-custody records will not be required for this investigation. Instead, sample tracking forms will document the progression of samples as they travel from the original sampling location to the various contract laboratories.

- *QC sample records*. These records will be documented in the field notebook for field sample replicates and for recording which samples should be used for analytical duplicates and matrix spikes. Each contract laboratory will record its own QC samples, and this should include information on the frequency, conditions, level of standards, and instrument calibration history. The contract laboratories will also include documentation on sample integrity and preservation, as well as include documentation on the calibration and standards' traceability.

- *General field procedures.* General field procedures on how the data were collected will be recorded in the field notebook.

- *Corrective action reports.* Corrective action reports show what methods were used in cases where general field practices or other standard procedures were violated and include the methods used to resolve noncompliance.

A6.2.2 Laboratory Records

The following laboratory-specific records should be compiled if available and appropriate:

- *Sample Data.* These records contain the times that samples were analyzed to verify that they met holding times prescribed in the analytical methods. Included should be the overall number of samples, sample location information, any deviations from the

SOPs, time of day, and date. Corrective action procedures to replace samples violating the protocol also should be noted.

- *Sample Management Records.* Sample management records document sample receipt, handling and storage, and scheduling of analyses. The records verify that sample tracking and proper preservation were maintained, reflect any anomalies in the samples (such as receipt of damaged samples), note proper log-in of samples into the laboratory, and address procedures used to ensure that holding time requirements were met.

- *Test Methods.* Unless analyses are performed exactly as prescribed by SOPs, this documentation will describe how the analyses were carried out in the laboratory. This includes sample preparation and analysis, instrument standardization, detection and reporting limits, and test-specific QC criteria. Documentation demonstrating laboratory proficiency with each method used could be included.

- *QA/QC Reports*. These reports will include the general QC records, such as initial demonstration of capability, instrument calibration, routine monitoring of analytical performance, calibration verification, etc. Project-specific information from the QA/QC checks such as blanks (e.g., reagent, method), spikes (e.g., matrix, matrix spike duplicate, surrogate spike), calibration check samples (e.g., zero check, span check, and mid-range check), replicates, and so on should be included in these reports to facilitate data quality analysis.

A6.2.3 Data Handling Records

These records document protocols used in data reduction, verification, and validation. Data reduction addresses data transformation operations such as converting raw data into reportable quantities and units, use of significant figures, recording of extreme values, blank corrections, etc. Data verification ensures the accuracy of data transcription and calculations, if necessary, by checking a set of computer calculations manually. Data validation ensures that QC criteria have been met.

A6.3 Data Reporting Package Format and Documentation Control

The format of all data reporting packages must be consistent with the requirements and procedures used for data validation and data assessment described in Sections B, C, and D of the QAPP. The MPCA Principal Investigator will ensure that data are being recorded appropriately on the sample labels, sample tracking forms, and in the field notebook. All entries will be made using permanent ink, signed, and dated, and no erasures will be made. If an incorrect entry is made, the information will be crossed out with a single strike mark that is signed and dated by the sampler. A similar data entry process will be followed by the contract laboratories.

The analytical laboratories will be expected to provide a data package with the following components:

- Case Narrative:
    - Date of issuance
    - Laboratory analyses performed
    - Any deviations from intended analytical strategy
    - Laboratory batch number
    - Numbers of samples and respective matrices
    - Quality control procedures utilized and also references to the acceptance criteria
    - Laboratory report contents
    - Project name and number
    - Condition of samples "as received"
    - Discussion of whether or not sample holding times were met
    - Discussion of technical problems or other observations which may have created analytical difficulties
    - Discussion of any laboratory QC checks which failed to meet project criteria
    - Signature of the Laboratory QA Manager.
- Chemistry Data Package:
    - Case narrative for each analyzed batch of samples
    - Summary page indicating dates of analyses for samples and laboratory quality control checks
    - Cross referencing of laboratory sample to project sample identification numbers
    - Descriptions of data qualifiers
    - Sample preparation and analyses for samples
    - Sample and laboratory quality control results
    - Results of (dated) initial and continuing calibration checks
    - Matrix spike and matrix spike duplicate recoveries, laboratory control samples, method blank results, calibration check compounds, and system performance check compound results
    - Results of tentatively identified compounds.

An electronic copy of the analytical data will be submitted in a format compatible with the MPCA's software (e.g., Excel 5.0 or Excel '97).

The toxicity testing laboratory (ENSR) will be required to submit toxicity test reports, which contain the following components:

- Introduction (brief)
- Sample collection and handling
- Methods, including:

    - exposure system
    - test organisms
    - test performance
    - water chemistry
    - data analysis procedures
    - reference toxicity testing
- Results, including:
    - toxicity tests
    - reference toxicant tests
- References
- Appendices, including:
    - laboratory data sheets and any associated quality assurance/quality control (QA/QC) review
    - statistical printouts
    - reference toxicant control chart(s).

The toxicity testing laboratory will not be expected to interpret the toxicity data; this will be done by the MPCA. An electronic copy of the toxicity test report and associated data files will be submitted in a format compatible with the MPCA's software (e.g., Word 6.0, Word '97, or WordPerfect 6.1; Excel 5.0 or Excel '97).

The Laboratory QA Officers at each contact laboratory must perform a final review of the report to determine whether it meets project requirements. The Project Managers, or their delegated staff, would make any necessary changes to the reports. The Laboratory QA Officers will have the final authority for implementing corrections and/or revisions to their respective QA management plans and SOPs. The MPCA Principal Investigator will have final authority for making revisions to the draft project report, after soliciting review comments from GLNPO and interested stakeholders.

A6.4 Data Reporting Package Archiving and Retrieval

Each contract laboratory has their own policy for the storage of, access to, and final disposal of all records. It is anticipated that all necessary records will be provided to the MPCA with the laboratory data package/report. The MPCA will retain the data for five years after which time it will be sent to the Minnesota Records Center for 30 years. When that time period is up, the Center will contact the MPCA to check if they want to retain the information. If not, the files will be turned over to the Minnesota Historical Society. They will retain the files they are interested in and dispose of the other files.

B MEASUREMENT/DATA ACQUISITION

B1 SAMPLING PROCESS DESIGN (EXPERIMENTAL DESIGN)

B1.1 Purpose/Background

The purpose of this section is to describe all relevant components of the experimental design; define the key parameters to be estimated; indicate the number and type of samples expected; and describe where, when, and how samples are to be taken from Minnesota Slip.

B1.2 Scheduled Project Activities, Including Measurement Activities

Sediment sampling will take place during September 21-23, 1999 (MPCA staff only) and September 28 - October 1, 1999 (MPCA, GLNPO, Deep Ocean Navigation staff). It is anticipated that the MPCA will ship all of the sediment samples to the contract laboratories by October 5, 1999.

ENSR will initiate all toxicity tests within two weeks of sample receipt. ENSR's standard turn around time for producing final, quality assured toxicity reports is four weeks following completion of the toxicity tests. En Chem, Inc. anticipates having a four week turn around time for AVS/SEM and six weeks for the PCB congener work. MDH will have a longer turn around time for reporting their analytical results as they will be working with the MPCA to put the data in an electronic format compatible with GLNPO's sediment database. UMD will also have a longer turn around time with reporting the results of the particle size analyses due to the long (six month) holding time that will be allowed for these samples. A bar chart showing the time of various QAPP milestones was provided in Table A-5.

B1.3 Rationale for the Design

The U.S. EPA Region 5 document on "Statistical Techniques Applied to Sediment Sampling (STATSS)" (Lubin et al., 1995) was referred to when designing this study. Based on the budget available for this project, a nonrandom sampling plan was used to select sites to delineate the vertical and horizontal distribution of selected contaminants in the inner 75% of the slip. Sediment sampling of the outer 25% of the slip will be done to confirm the sediments have low contamination. Synoptic sediment toxicity tests will be used to assess acute and chronic effects to benthic invertebrates for six sites.

The field design of this project will meet the problem statement given in Section A2.2 and the project objectives described in Section A3.1.

B1.4 Design Assumptions

The design assumptions for this study are the following:

- Problems will potentially be encountered with sampling the designated sample sites due to non-cohesive sediments or obstructions/litter in the sediments.
- Problems will potentially be encountered with taking GPS measurements in Minnesota Slip, due to interference caused by the SS William A. Irvin.
- Marina obstructions may prevent field sampling or change the order of sample collection.
- Weather conditions may prevent field sampling from occurring.
- Sediment samples may be very heterogeneous.

These assumptions are based on previous sediment investigations in Minnesota Slip in which problems were encountered, especially due to the sandy, noncohesive nature of the sediments in some locations. It is anticipated that flexibility will be needed in the field sampling plan in case some sites cannot be sampled. Landmark observations of sampling sites will be made to an aerial photograph of Minnesota Slip. This aerial photograph shows the placement of all boat docks in the marina and of the Irvin.

B1.5 Procedures for Locating and Selecting Environmental Samples

For this study, eighteen sites will be sampled in a triangulation pattern in Minnesota Slip (Figure B-1). The triangulation pattern will maximize the use of sediment kriging to generate isopleths of chemical contaminants at various depth intervals. More samples will be collected in the inner 75% area of the slip, based on the results of previous investigations (Schubauer-Berigan and Crane, 1997; Crane et al., 1997; unpublished R-EMAP and MPCA data; AScI Corporation, 1999). Maps of the sampling sites from these previous investigations are given in Figures A-7 and B-2 to B-5. Not all of these sites had similar depth intervals sampled for chemical parameters, as will be done in this investigation.

The sediment sampling will occur over a two-week period from September 21 to October 1, 1999. Surficial (0-5cm) samples will be collected at six sites for concurrent sediment chemistry and toxicity testing analyses (Figure B-1); one of these sites will be used as a field replicate for analytical parameters. Sediment cores will also be collected at all eighteen sites. The cores will be sliced into increments as shown in Table B-1. One long core will be obtained at the bow of the Irvin, and in the vicinity of two stormwater outfalls, for detailed sectioning of the core for PAHs, PCBs, mercury, lead, zinc, TOC, and particle size. This will be done to give an effective vertical profile of these contaminants at one area of the slip that is known to be contaminated. The budget of this project will not support doing this detailed of a core assessment for all these

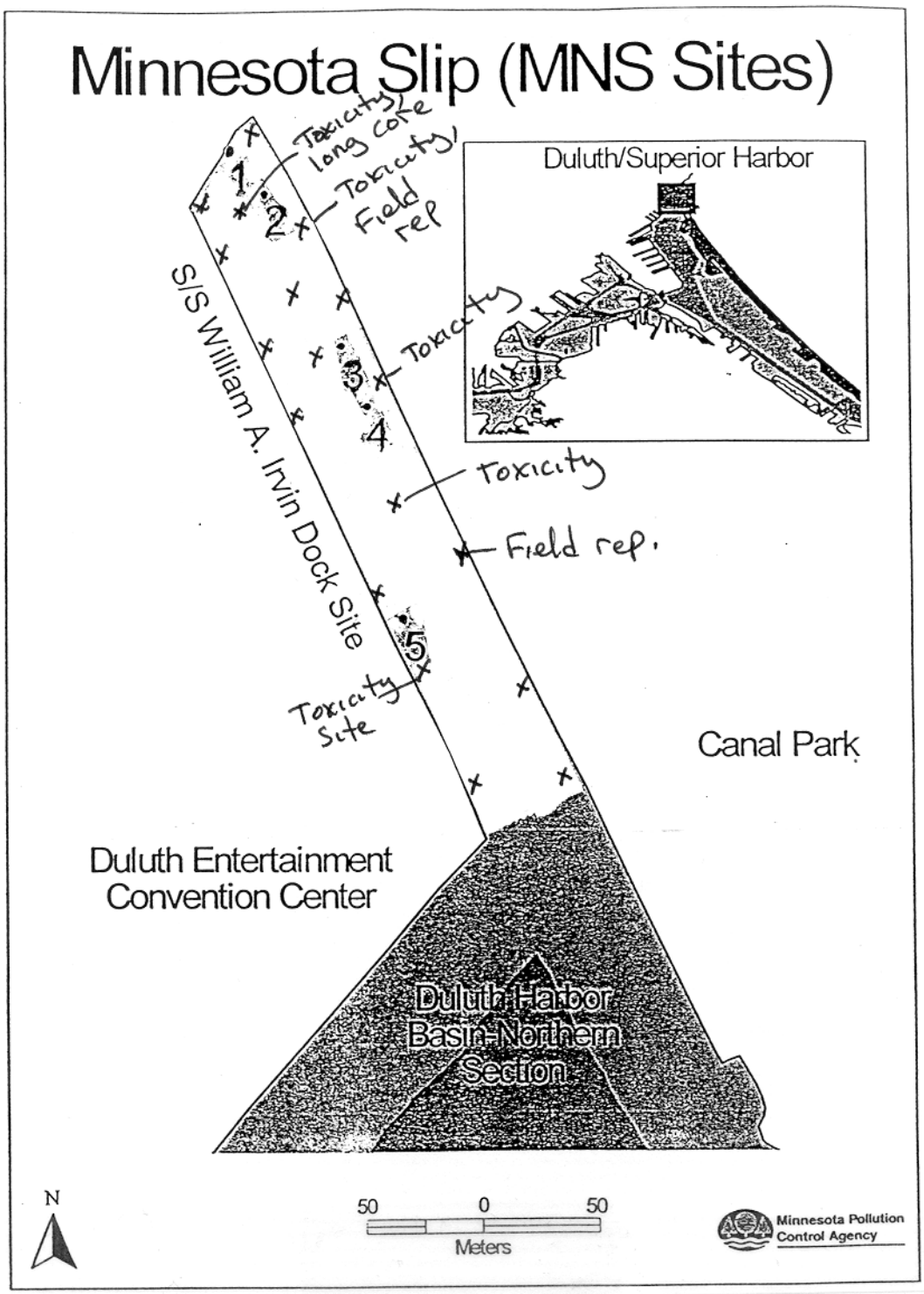

Figure B-1. Proposed sediment sampling sites for the Minnesota Slip sediment remediation scoping project.

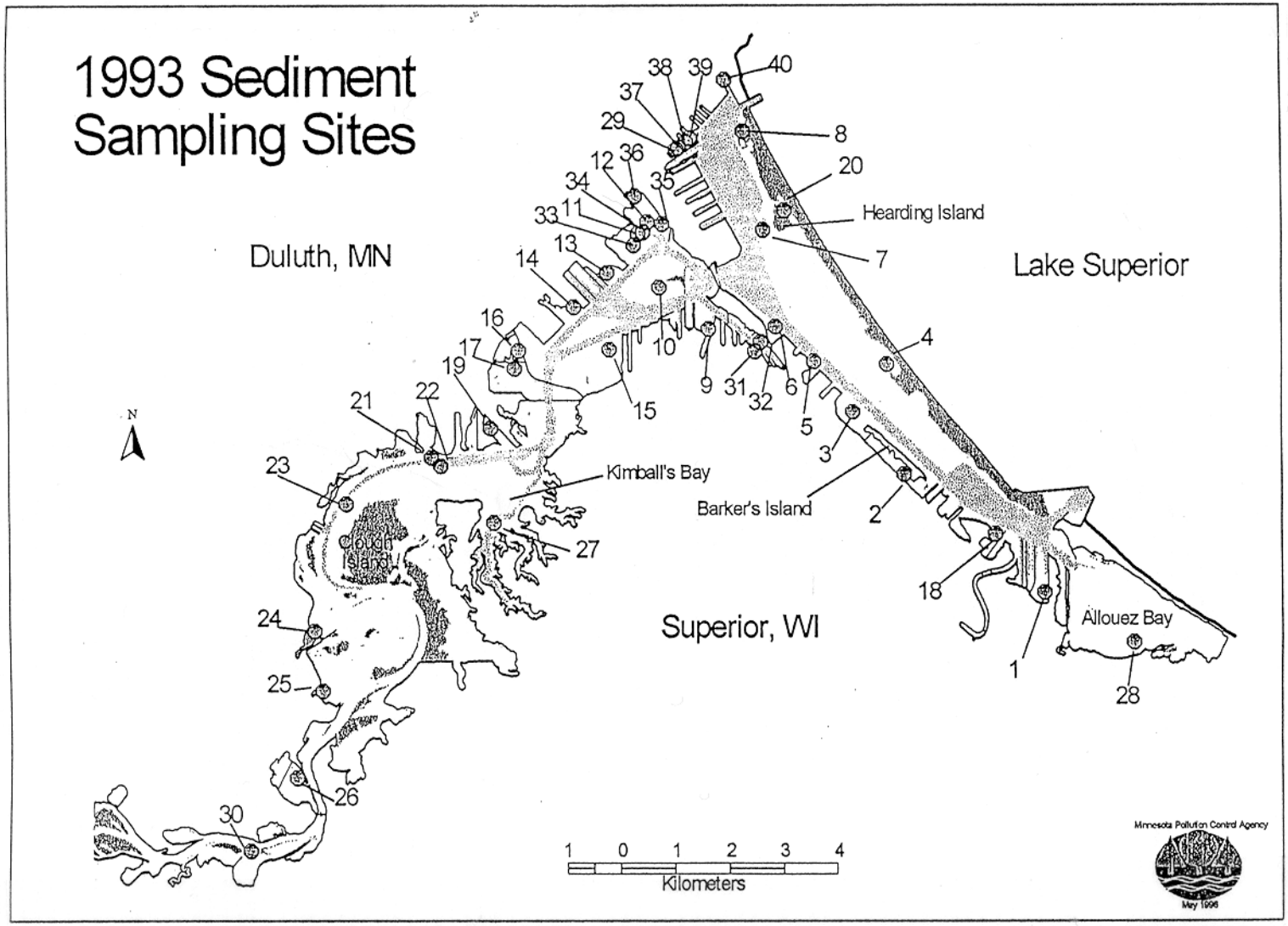

Figure B-2. Location of a sediment sampling site in Minnesota Slip as part of a 1993 sediment survey in the Duluth-Superior Harbor (Schubauer-Berigan and Crane, 1997).

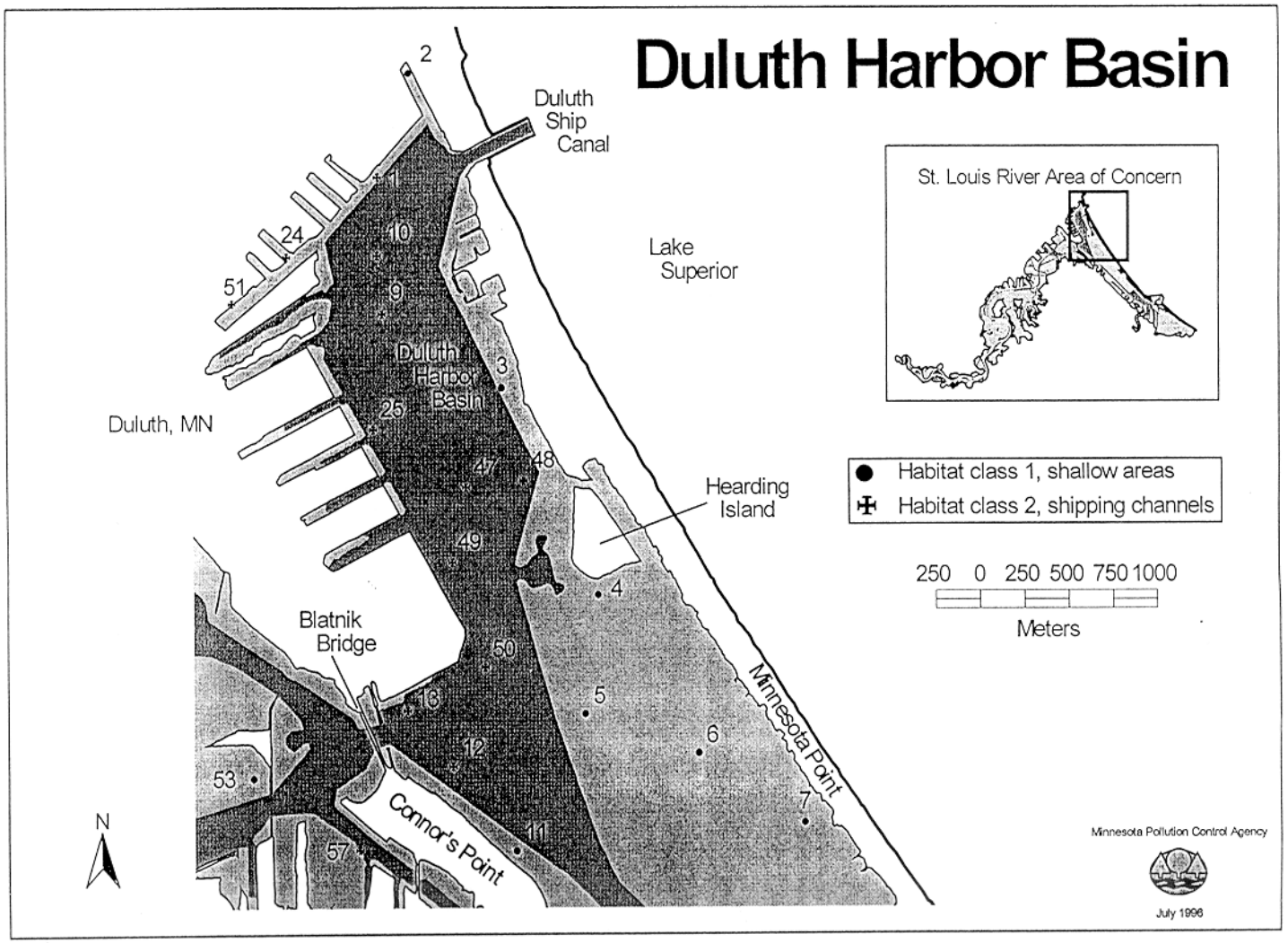

Figure B-3. Location of a sediment sampling location in Minnesota Slip as part of the 1995 R-EMAP sampling effort.

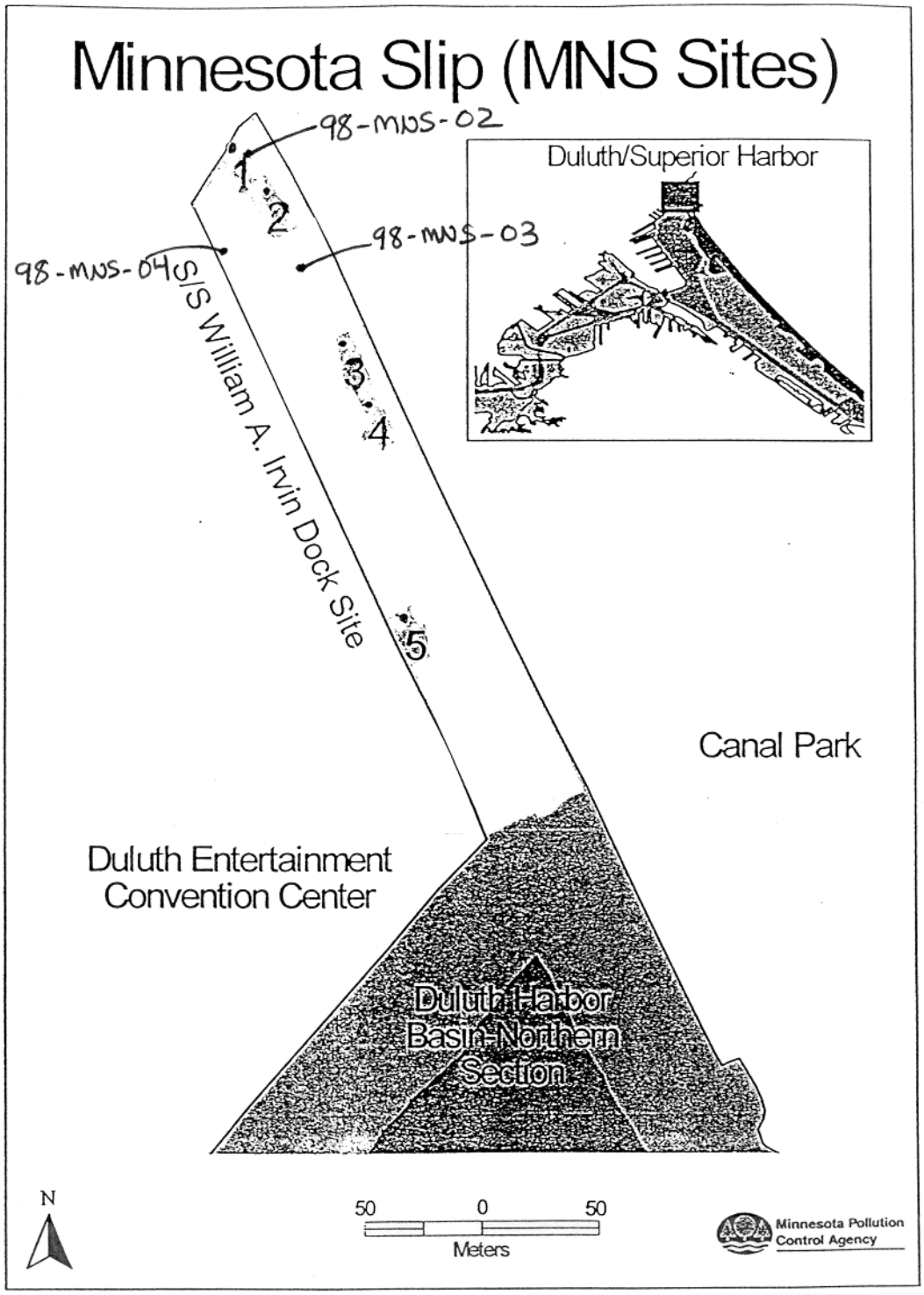

Figure B-4. Location of sediment stations sampled in Minnesota Slip during August 1998.

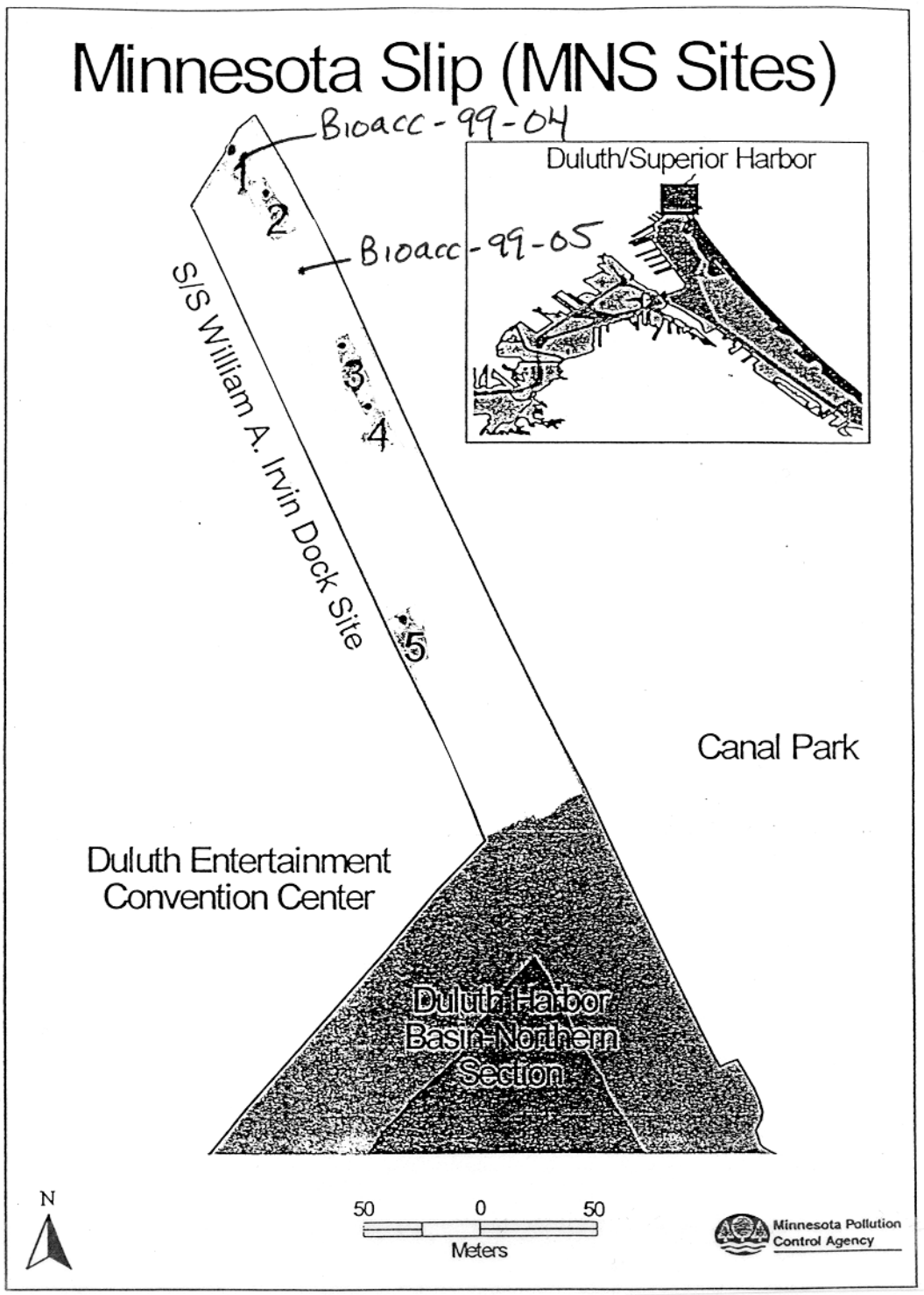

Figure B-5. Location of sediment sampling stations used in Minnesota Slip for a sediment bioaccumulation study.

Table B-1. Sediment Sampling Scheme for Sectioning Sediment Cores and Collecting Field Replicates from Minnesota Slip

	Number of Samples to be Analyzed for Chemical/Physical Parameters											
Core Section (cm)	PAHs	PCBs	TOC	Particle Size	Lead	Zinc	Digestion	% Moisture	Mercury	Other Metals*	Ammonia	AVS/SEM
0-5	6	6	6	6	6	6	6	6	6	6	6	6
field replicate	1	1	1	1	1	1	1	1	1	1	1	1
0-15	18	18	18	18	18	18	18	18	18			
field replicate	2	2	2	2	2	2	2	2	2			
15-30	14	1	14	14	18	18	18	18	18			
field replicate	2		2	2	2	2	2	2	2			
30-45	10	1	10	10	18	18	18	18	18			
field replicate	1		1	1	2	2	2	2	2			
45-60	6	1	6	6	14	14	14	14	14			
field replicate	1		1	1	2	2	2	2	2			
60-75					14	14	14	14	10			
field replicate					2	2	2	2	1			
75-90					10	10	10	10	1			
field replicate					1	1	1	1				
60-90	1	1	1	1								
90-120	1	1	1	1	10	10	10	10	1			
field replicate				1	1	1	1	1				
120-150	1	1	1	1	10	10	10	10	1			
field replicate				1	1	1	1	1				
TOTAL NUMBER OF SAMPLES	64	33	64	66	132	132	132	132	97	7	7	7

*Cadmium, Chromium, Copper, Nickel, and Selenium

parameters at other locations in the harbor. Radioisotope dating will not be done on any of the core segments because this slip has a history of being filled in with dredged material, and the sediments would likely give a smeared dating profile.

In case prescribed locations turn out to be inaccessible during field sampling, professional judgment will be used to select a new site near the original site. Any deviations from the sampling plan will be recorded in the field notebook.

B1.6 Classification of Measurements as Critical or Noncritical

The following measurements will be critical to this study: PAHs, PCB congeners, mercury, lead, zinc, TOC, and particle size. The following measurements are noncritical to this study but will provide a useful data set that can be used to verify sediment quality objectives for the St. Louis River AOC: cadmium, chromium, copper, nickel, selenium, and ammonia. The two types of sediment toxicity tests being used in this study are also critical measurements. It was previously decided that conducting a benthological community survey was a noncritical measurement that could be excluded from this study.

B1.7 Validation of any Nonstandard Methods

No nonstandard sampling, analytical, or toxicological methods will be used in this study. The 42-day *Hyalella azteca* test has had less usage of the other tests; as a conservative measure, one negative control sample will be run with each sample.

B2 SAMPLING METHODS REQUIREMENTS

B2.1 Purpose/Background

This section will describe the procedures for collecting samples and identifying the sampling methods and equipment. In addition, the process for preparing and decontaminating sampling equipment, including disposing of decontamination by-products; selecting and preparing sample containers, sample volumes, preservation methods, and maximum holding times for sampling and/or analysis will be described. Finally, corrective action procedures will be described.

B2.2 Sample Collection, Preparation, and Decontamination Procedures

B2.2.1 <u>Sampling Methods</u>

Sediment samples will be collected from Minnesota Slip using three different methods. Grab samples of surficial sediments (0-5 cm) will be collected using a Shipek grab sampler on the MPCA's R/V Naiad. This sampler was recently used for another GLNPO-sponsored sediment

investigation in the Duluth Harbor (Crane, 1999b). Short sediment cores will be collected between the slip wall and the Irvine using a Livingston corer. This coring device has been used in other MPCA investigations in the Duluth Harbor (Crane et al., 1994; unpublished MPCA data, 1998). Long sediment cores will be collected in other parts of the slip using GLNPO's Vibrocorer on the R/V Mudpuppy. GLNPO's SOP for use of the Vibrocorer is contained in Appendix C. GLNPO's Field Safety Plan is located in Appendix D.

The depth of the soft sediments at each site will be measured by using sediment sounding poles (WDNR, 1995). These poles will also be used to determine the depth of the water column at each site.

A global positioning system (GPS) will be used on-board both the MPCA and GLNPO vessels during the field sampling. Operation of the GPS units will be per the manufacturing instruction manuals for both instruments.

B2.2.2 Sampling Method Requirements

The planned sampling locations for this study are shown in Figure B-1. The Shipek grab sampler will be used to collect composite grab samples of surficial sediments; each composited sample will be split for synoptic sediment chemistry and toxicity testing analyses. For each site, multiple grab samples will be collected from a relatively homogeneous sediment deposit (i.e., all grabs should be of similar sand/silt content). Each grab sample will be collected from an undisturbed area of sediment. From the R/V Naiad, a winch (with a rotating arm) will be used to lower and raise the Shipek grab sampler out of the water. Since this sampler is very heavy, it will be lowered into a "cradle" onboard the boat prior to opening it to reveal the sediments. Although some slumping of the sediments may occur, the MPCA Principal Investigator and Field Team Leader have determined that this sampler works better than a Ponar grab sampler in terms of collecting a more cohesive sample. The approximate upper 5 cm layer of sediment will be removed using a Teflon -lined spatula. The sample will be placed into a 4-L acid and solvent-rinsed Pyrex measuring cup. Any large objects such as twigs, wood chunks, or stones will be removed, and observations about the sediments (e.g., color, odor, appearance of oil sheens, sand/silt/clay content) will be recorded. The sediments will be briefly mixed and transferred into pre-cleaned sample jars.

The Livingston corer will be used from shore to sample the sediments in the approximate one meter band of water between the south wall of Minnesota Slip and the SS William A Irvin; approximately four sediment cores will be collected in this area. As cohesive sediment core sections are extruded from the core, the outer 1-2 mm of sediment will be scraped off, using a Teflon -lined spatula. The outer layer of sediment will be disposed of in the water. The sample will be transferred into a 4-L acid and solvent-rinsed Pyrex measuring cup, observations will be

made, and the sediments will be mixed. The sample will then be split between pre-cleaned analytical jars for various parameters.

Smith et al. (1993) provided a detailed description of the R/V Mudpuppy and its operation, positioning and sampling procedures. The Vibrocorer system on the R/V Mudpuppy will be used at 14 sampling sites in Minnesota Slip. Although the Vibrocorer is designed to collect cores of up to 6 m in depth (Smith et al., 1993), the practical limit of this sampler in the Duluth-Superior Harbor is approximately 2 m (Schubauer-Berigan and Crane, 1997; Crane et al., 1997). GLNPO staff will pre-cut the core tubes to 1.6 m for use in this investigation. Cores will be processed on-board the R/V Mudpuppy immediately after collection. The core will be sectioned by sawing off the top section (0-15 cm) and subsequent sections according to the sampling scheme given in Table B-1.

After sectioning the cores, the Vibrocorer samples will be decontaminated by scraping the outer 1-2 mm of sediment from the core section with an acid- and solvent-rinsed spatula, and discarding it prior to sample homogenization. Samples will be placed into a 4-L acid and solvent-rinsed Pyrex® measuring cup and homogenized by stirring. Homogenized samples will be apportioned into pre-cleaned sample jars for delivery to the appropriate analytical lab.

B2.2.3 Decontamination Procedures

All field sampling personnel will be required to wear steel-toed shoes and gloves; this should protect most staff against contamination of their extremities. Tyvex suits will be worn by the field crew working on the deck of the R/V Mudpuppy.

Equipment (e.g., Pyrex mixing bowls, spatulas, spoons) will be decontaminated by using slip water to rinse off gross amounts of sediments. Next, the equipment will be scrubbed with phosphate-free soap. Finally, the equipment will be rinsed with 10% HCl, hexane, acetone, and distilled water. This procedure follows the general Equipment Decontamination SOP given in Appendix E. This SOP was obtained from U.S. EPA (1995) and has not been adopted as an official MPCA SOP yet. Metal equipment will not be rinsed with 10% HCl. Acid rinsate will be stored in a one gallon screw top empty solvent jug held in a Nalgene plastic safety bottle carrier. At the end of each sample day, the acid and solvent wastes will be transferred to similar containment in the MPCA vehicle. The waste will be transported to the MPCA office in St. Paul for disposal. One deviation from the Equipment Decontamination SOP is that equipment blanks will not be collected for this study.

The sounding poles will not need to be decontaminated, except for a water rinse to remove gross amounts of sediment. These poles will only be used to measure the depth to refusal in the sediments, and thus constitute a physical measurement.

The Shipek grab sampler and Livingston corer will be decontaminated by rinsing them in the slip water to remove gross amounts of sediments. Next, each sampler will be scrubbed with phosphate-free soap, followed by a rinse of distilled water. Next, the Shipek sampler will be rinsed with hexane, acetone, and distilled water. This full procedure will be done between sites. Within each site, only gross amounts of sediment will be removed from the Shipek grab sampler after each composite sample is collected.

For the Vibrocorer, a new lexan core tube will be used for each sediment core. Thus, a detailed decontamination procedure will not be necessary.

B2.3 Support Facilities for Sampling Methods

The capabilities of the analytical laboratories and toxicology laboratory for this project are commensurate with the requirements of the sampling plan.

B2.4 Sampling/Measurement System Failure Response and Corrective Action Process

B2.4.1 Corrective Action Process

Corrective action is the process of identifying, recommending, approving, and implementing measures to counter unacceptable procedures or out of quality control performance which can affect data quality. Corrective action can occur during field activities, laboratory analyses, data validation, and data assessment. All corrective actions proposed and implemented will be documented in the regular quality assurance reports to management. Corrective actions should only be implemented after approval by the MPCA Principal Investigator, or her designee, the Field Team Leader. If immediate corrective action is required, approvals secured by telephone from the MPCA Principal Investigator should be documented in an additional memorandum.

For noncompliance problems, a formal corrective action program will be determined and implemented at the time the problem is identified. The person who identifies the problem will be responsible for notifying the MPCA Principal Investigator, who in turn will notify the GLNPO Project Officer. Implementation of corrective actions will be confirmed in writing through the same channels.

Any noncompliance with the established quality control procedures in the QAPP will be identified and corrected in accordance with the QAPP. The GLNPO Project Officer, or her designee, will issue a nonconformance report for each nonconformance condition.

B2.4.2 Field Corrective Action

Corrective action in the field may be needed when the sample network is changed (i.e., more/less samples, sampling locations other than those specified in the QAPP, etc.), or when sampling procedures and/or field analytical procedures require modification due to unexpected conditions. Technical staff and project personnel will be responsible for reporting all suspected technical or QA nonconformances, or suspected deficiencies of any activity or issued document, by reporting the situation to the Field Team Leader or designee. This person will be responsible for assessing the suspected problems, in consultation with the MPCA Principal Investigator, and making a decision based on the potential for the situation to impact the quality of the data. If it is determined that the situation warrants a reportable nonconformance requiring corrective action, then a nonconformance report will be initiated by the MPCA Principal Investigator.

The MPCA Principal Investigator will be responsible for ensuring that corrective actions for nonconformances are initiated by:

- Evaluating all reported nonconformances
- Controlling additional work on nonconforming items
- Determining disposition or action to be taken
- Maintaining a log of nonconformances
- Reviewing nonconformance reports and corrective actions taken
- Ensuring nonconformance reports are included in the final report files.

If appropriate, the Field Team Leader will ensure that no additional work, that is dependent on the nonconforming activity, is performed until the corrective actions are completed. Corrective actions for field measurements may include:

- Repeat the measurement to check the error
- Re-calibration
- Replace the instrument or measurement device
- Stop work (if necessary).

The Field Team Leader, or his designee, is responsible for all field work activities. In case the sampling program changes, the Field Team Leader will implement the changes after obtaining approval from the MPCA Principal Investigator.

Corrective actions resulting from internal field audits will be implemented immediately if data may be adversely affected due to unapproved or improper use of approved methods. The MPCA QA Officer will identify deficiencies and recommend corrective actions to the MPCA Principal Investigator. Implementation of corrective actions will be performed by the Field Team Leader.

Corrective actions will be documented in quality assurance reports to the entire project management.

Corrective actions will be implemented and documented in the field notebook. No staff member will initiate corrective actions without prior communication of findings through the proper channels. If corrective actions are insufficient, work may be stopped by the GLNPO Project Officer.

B2.5 Sampling Equipment, Preservation, and Holding Time Requirements

The procedures to prevent sample contamination were described in section B2.2.2. Composited sediment samples from each site will be split for various chemical and physical analyses. In addition, applicable composite samples will be split for toxicity testing.

The sample containers for organics will be 250-mL solvent rinsed glass jars with Teflon -lined lids. En Chem, Inc. will use one such jar for PCB congeners, AVS, and SEM determinations for each sample. Mercury, metals, TOC, ammonia, and percent moisture will all be run on the same sample jars at MDH; this will be a half-filled 250-mL pre-cleaned polyethylene jar. Sediments for particle size analysis will be collected in 60-mL pre-cleaned glass jars with Teflon -lined lids. The sediment samples for toxicity testing will be collected in pre-cleaned 4-L high density polyethylene bottles with Teflon -lined lids. The sample integrity will be preserved by keeping the samples cold at 4 °C; organic samples will be kept in the dark. The maximum holding times given in Table B-2 will be used as a general guideline for sediment samples.

B3 SAMPLE HANDLING AND CUSTODY REQUIREMENTS

B3.1 Purpose/Background

This section of the QAPP will describe all procedures that are necessary for ensuring that:

- Samples are collected, transferred, stored, and analyzed by authorized personnel.
- Sampling integrity is maintained during all phases of sample handling and analyses.
- An accurate written record is maintained of sample handling and treatment from the time of its collection through laboratory procedures to disposal.

B3.2 Sample Custody Procedure

Sample tracking will be an important component of this project to ensure that samples are not misplaced or lost during field collection and transport to the contract laboratories. Legal chain-of-custody procedures will not be followed for this project because the data will not be used for

Table B-2. Sediment Sample Volume, Container, Preservation, and Holding Time Requirements

Analyte*	Amount Required for Sample Analysis (g)	Size/Type of Jar	Preservation	Holding Time
PAHs	100	250 mL, glass	Cool/dark, 4 °C	42 days
PCBs	100	250 mL, glass	Cool/dark, 4 °C	42 days
Mercury	5	250 mL, plastic	Cool, 4 °C	30 days
Metals (Cd, Cr, Cu, Ni, Pb, Se, Zn)	5	250 mL, plastic	Cool, 4 °C	30 days
AVS	30	250 mL, glass	Cool, 4 °C	14 days
SEM	Sample extract of AVS	250 mL, glass	Cool, 4 °C	30 days
Ammonia	20	250 mL, plastic	Cool, 4 °C	30 days
Particle Size	20	60 mL, glass	Cool, 4 °C	6 months
TOC	0.2	250 mL, plastic	Cool, 4 °C	40 days
Percent Moisture	40	250 mL, plastic	Cool, 4 °C	40 days

* Note: Sediment samples for PCBs, AVS, and SEM will be collected in the same jar. Also, sediment samples for mercury, metals, ammonia, TOC, and percent moisture will be collected in the same container.

enforcement purposes. A sampling tracking system will be in place using modified chain-of-custody procedures and associated paperwork (Table B-3). ENSR's chain-of-custody forms will be used for samples sent to them (Table B-4). For sediment samples sent to MDH, the MPCA's Sediment MDH Lab Sheet (Tables B-5 and B-6) will be used. This form contains a chain-of-custody record which will not be legally binding. The use of different tracking forms will help to separate the samples being sent to different contract laboratories.

All samples will be assigned a unique identifying code that identifies the project sample site (MNS), year of sampling (1999), and sample number (01 through 18). Since all of the samples will be of a sediment matrix, a matrix identifier will not be included in the sample code. Also, since sampling will occur during one temporal time period, the entire date will not be included in the code. In order to facilitate the ease with which the sample identifiers are written on the jar labels, the codes will be as such: MNS-99-01 through MNS-99-18. In addition, the core depth interval will be recorded on the jar label under the sample name. An example label is given in Figure B-6. Sample labels are to be completed for each sample using waterproof ink unless prohibited by weather conditions. For example, a logbook notation would explain that a pencil was used to fill out the sample label because the pen would not function.

During each field sampling day, samples will be stored on ice in a cooler. The samples will be stored in a refrigerator at the MPCA's Duluth Regional Office at the end of each day. The MPCA Principal Investigator will be personally responsible for the care and custody of the samples until they are transferred or properly dispatched. As few people as possible will handle the samples.

After field sampling is completed on September 23 and October 1, 1999, the particle size samples will be hand delivered to Keith Lodge (UMD) by MPCA staff. The rest of the sediment samples will be transported, in coolers, by MPCA staff to the Field Operations Center in St. Paul. Ed Norwig, MPCA, will be responsible for transporting the MDH samples to the MDH laboratory in Minneapolis.

Both En Chem and ENSR will provide the MPCA with sample kits, including sample bottles, coolers, packaging materials, and chain-of-custody forms. The MPCA Principal Investigator will ensure the samples are packaged properly by keeping them cold (i.e., through use of blue ice packs) and are immobilized with packing material (e.g., bubble-pack) to reduce the risk of breakage. A copy of the chain-of-custody form will be placed in a zip-loc bag and taped to the inside lid of the cooler. The outside of the container will be shut using fiberglass tape. The laboratory name and address, as well as the return name and address, will be clearly labeled on the outside of the container. The labels "Environmental Samples" and "This End Up" will be clearly printed on the top of the shipping cooler. The samples are not anticipated to be classified as hazardous waste; therefore, Department of Transportation regulations will not apply for shipment. These samples will be sent to the contract laboratories by a common courier.

Table B-3. MPCA Environmental Outcomes Division Sample Tracking/Test Request Form

MPCA ENVIRONMENTAL OUTCOMES DIVISION SAMPLE TRACKING/TEST REQUEST FORM

Shaded areas to be completed by laboratory upon sample receipt. Laboratory: make 1 copy for your file and return the original to Judy Crane, MPCA Environmental Outcomes Division, 520 Lafayette Rd. N., St. Paul, MN 55155-4194.

Project Name: _____ Ship to: _____
MPCA Contact Name: _____ _____
Sampled By: _____ Atten: _____ Ship Date: _____

Sample Collection Date (m/d/y)	Time (military)	Sample Identification (Indicate name, location and type of each sample: receiving water, effluent, elutiate, sediment)	Sample Method (Indicate grab, composite, batch or other)	Sample Temperature (°C) and Condition Upon Receipt	Number of Sample Containers x Volume of Sample Per Container	Test(s) Requested					Comments/Instructions (Indicate container type: collapsible carboy, glass jar, jerry can, other)

Allotment # Sample Storage Temperature (°C)

1) Released by: Date: Time:	2) Rec'd by: Date: Time:	3) Released by: Date: Time:	4) Rec'd by: Date: Time:

Table B-4. ENSR's Chain-of-Custody Record Form

M901376

ENSR **CHAIN OF CUSTODY RECORD** Page ___ of ___

Client/Project Name:	Project Location:	Analysis Requested
Project Number:	Field Logbook No.:	
Sampler: (Print Name) /Affiliation:	Chain of Custody Tape No.:	
Signature:	Send Results/Report to:	

Field Sample No./ Identification	Date	Time	Grab	Comp	Sample Container (Size/Mat'l)	Sample Type (Liquid, Sludge, Etc.)	Preservative	Field Filtered							Lab I.D.	Remarks

Relinquished by: (Print Name)	Date:	Received by: (Print Name)	Date:	Analytical Laboratory (Destination):
Signature:	Time:	Signature:	Time:	
Relinquished by: (Print Name)	Date:	Received by: (Print Name)	Date:	ENSR 4303 W. LaPorte Ave. Fort Collins, CO 80521 (970) 416-0916
Signature:	Time:	Signature:	Time:	
Relinquished by: (Print Name)	Date:	Received by: (Print Name)	Date:	
Signature:	Time:	Signature:	Time:	Serial No. 34482

Table B-5. Front Page of MPCA's Sediment MDH Lab Sheet

A)	B)	C)	D)	E)

MINNESOTA POLLUTION CONTROL AGENCY WQD / *Sediment* MDH Lab Sheet

Samples Collected by:_____(Name / QA ID) Date Received by Lab: _____

Report to:_____(Name) Phone: _____ Billing Code: PCA-_____

STORET STATION #	FIELD CODE	Q.A. 84183*	DATE YYMMDD	TIME MILITARY	SAMPLE DEPTH (Meters) C/D* *	(T) 82047	(B) 82048
A)							
B)							
C)							
D)							
E)							

SITE ID 00029	LAB ID 00028				
A)	*1200*				
B)	*1200*				
C)	*1200*				
D)	*1200*				
E)	*1200*				

*** FD = Field Dup, SB = Sampler Blank, TB = Trip Blank, BB = Bottle Blank. * * C = Core D = Dredge.**

TABLE OF MDH PARAMETERS FOR INDIVIDUAL SELECTION / MARK WITH AN 'X'

METALS	STORET #	MDH #	A	B	C	D	E	BACTICHEM	STORET #	MDH #	A	B	C	D	E
Cadmium, Sed mg/kg	01028	**126**													
Carbon, Tot Org, Sed		**267**													
Chromium, Sed mg/kg	01029	**134**													
Copper, Sed mg/kg	01043	**149**													
Digestion, Sed	00172	**206**													
Lead, Sed mg/kg	01052	**161**						**ORGANICS**	**STORET #**	**MDH #**	**A**	**B**	**C**	**D**	**E**
Mercury, Sed mg/kg	71921	**201**													
Nickel, Sed mg/kg	01068	**176**													
Percent Moisture, Sed	70320	**204**													
Percent Volatiles, Sed	70322	**203**													
Phosphorus, Sed mg/kg	00668	**262**													
Selenium, Sed mg/kg	01148	**184**						Civil Chain of Custody		**990**					
Zinc, Sed mg/kg	01093	**196**						Criminal Chain of Custody		**991**					

MDH Copy

⇓ SEE BACK FOR CHAIN OF CUSTODY RECORD and BILLING CODES ⇓

Table B-6. Back Page of MPCA's Sediment MDH Lab Sheet

CHAIN-OF-CUSTODY RECORD for SAMPLE TRANSFERRAL

1) Collected / Relinquished by:	Date: _____ Time:	Received by:	Date: _____ Time:	Comments:
2) Relinquished by:	Date: _____ Time:	Received by:	Date: _____ Time:	Comments:
3) Relinquished by:	Date: _____ Time:	Received by:	Date: _____ Time:	Comments:

Means of Delivery to Laboratory: _____ Delivered by: _____

Samples Intact Upon Arrival at Laboratory: Yes - ☐ No - ☐ Unknown - ☐ Date: _____ Time: _____

BILLING CODES

PB - MPCA-21 PS Compliance Mon.	**PZ** - MPCA-21R PS Compliance Mon. (REG)
PC - MPCA-21 Lake Monitoring	**QX** - NPS Compliance Monitoring
PG - MPCA-27 Minnesota Milestones	**QZ** - Lake Pepin
PH - MPCA-28 Toxics	**RA** - Wetland Use Support
PN - MPCA-33 Clean Water Act/Clean Lakes	**RC** - Feedlot Research
PO - MPCA-34 Use Attainment	**RD** - Statistically Based Monitoring

Revised September 1997

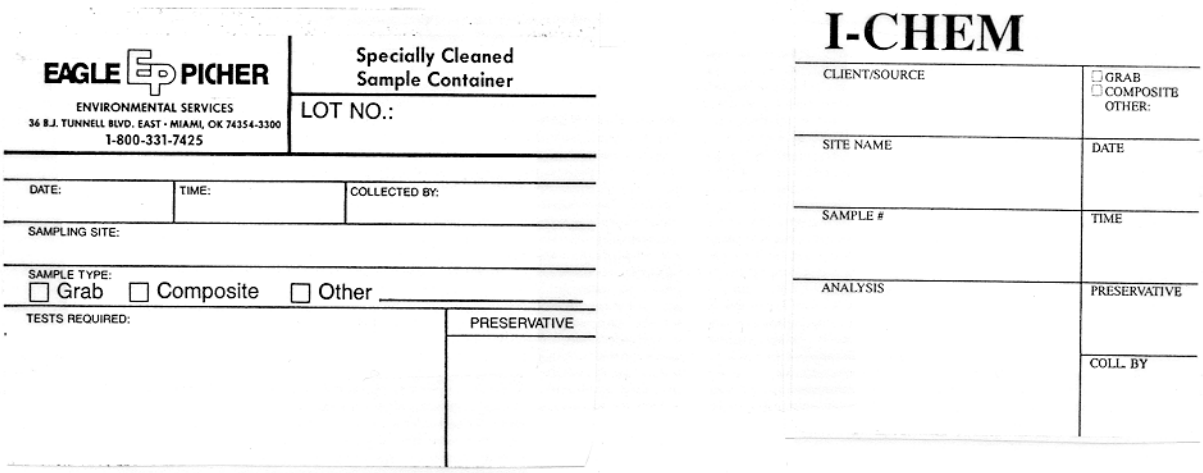

Figure B-6. Examples of sample labels to be used for this study.

Receipts of bills of lading will be retained as part of the permanent documentation. Commercial couriers are not required to sign off on the sample tracking form as long as it is sealed inside the sample cooler.

Laboratory custody procedures for sample receiving and log-in, sample storage and numbering, tracking during sample preparation and analysis, and storage of data will follow each contract laboratories internal procedures. Upon receipt by the contract laboratory, samples will be checked against the sample tracking forms to ensure sample integrity and completeness of shipment. Samples will be tracked through each lab, using forms for sample handling at each phase. The "paper trail" thus formed will include the steps performed on each sample, as well as the person handling the sample. The MPCA will be notified immediately if any difficulties in sample identification, or concerns of sample integrity, are encountered during sample log-in. The samples will be stored in darkness and refrigerated between 1 and 4 °C until they are prepared for testing.

All original field and laboratory processing notes will be stored by the MPCA Principal Investigator. These files will contain field notes, processing information for sediments, and the original copies of data and reports sent from the contract laboratories. All sample tracking forms (field, and in-lab) will be delivered to the MPCA Principal Investigator along with the final data, where they will become part of the official file on these samples.

When the contract laboratories (except UMD) are done using the sediments, they will dispose of the sediments per their in-house requirements. UMD will return the sample jars to the MPCA for disposal.

B4 ANALYTICAL METHODS REQUIREMENTS

B4.1 Purpose/Background

The purpose of this section is to identify the analytical methods and equipment required, including sub-sampling or extraction methods, laboratory decontamination procedures, waste disposal requirements, and specific performance requirements. In addition, corrective actions for laboratory operations will be discussed.

B4.2 Subsampling

Some of the sediment sample jars will be used for more than one analysis. This will require that the sample be homogenized so that a representative subsample can be obtained. This will apply to the analytes that En Chem will analyze for (i.e., PCB congeners, AVS/SEM), and for the inorganic parameters, TOC, and ammonia that will be analyzed by MDH.

B4.3 Preparation of the Samples

Information on the sampling containers, methods of preservation, holding times, holding conditions, and names of laboratories was given in Table B-2. The number of field replicates was given in Table A-2. The preparation of the samples, prior to analysis, is given in the contract laboratories SOPs for analytical (Appendix F) and toxicological procedures (Appendix G).

B4.4 Analytical Methods

Table B-7 summarizes the methods used to measure PAH compounds, PCB congeners, mercury, metals (cadmium, chromium, copper, lead, nickel, selenium, zinc), AVS, SEM, TOC, ammonia, particle size, and percent moisture. Each laboratory will implement the project required SOPs (Appendices F and G). These SOPs provide sufficient details for sample preparation, cleanup, and analysis applicable to this investigation. ENSR's QA Manual, MDH's QA Manual, and En Chem's Statement of Qualifications are provided in Appendices H, I, and J, respectively.

B4.5 Toxicity Testing Methods

The 10-day sediment toxicity tests with *Chironomus tentans* will be conducted to assess survival and growth (i.e., weight) according to U.S. EPA (1994). The 28-day sediment toxicity tests with

Table B-7. Summary of Analytical Methods for Sediment Samples

Analyte	Method # (description)	Sample Clean-up	Blanks	MDL*
PCBs	En Chem SOP (capillary column GC/ECD)	Florisil (or other clean-up method as needed)	Every 20 samples	96-823 ng/kg
PAHs	Method MDH 513 (capillary column GC/MS or GC/MS-SIM)	Gel-permeation clean-up or sulfur clean-up, as needed	Every 20 samples	30-270 ng/kg
Mercury	based on EPA 245.1 A (cold vapor AA)	N/A	10% of total samples	0.005 mg/kg
Metals (Cd, Cr, Cu, Ni, Pb, Se, Zn)	based on EPA 200.7 (extraction) and MDH Methods (graphite furnace AA)	N/A	Every 20 samples	0.1 mg/kg
AVS	En Chem SOP (spectrophotometer)	N/A	Every 20 samples	
SEM	En Chem SOP (ICP and cold vapor AA)	N/A	Every 20 samples	
Ammonia	QuickChem Method 12-107-06-1-A (Lachat instrument)	EDTA or Filtration, as needed	N/A	

* See MDH QA Manual (Appendix I) for reporting limits for PAHs, mercury, and conventional metals.

Table B-7. Continued

Analyte	Method # (description)	Sample Clean-up	Blanks	MDL
TOC	MDH Sample Ignition Method (Dohrmann DC-80 TOC analyzer)	N/A	Every 20 samples	0.1%
Particle Size	UMD SOP (Horiba LA-900 Analyzer)	N/A	N/A	N/A
Percent Moisture	MDH Method based on Standard Method 208G (gravimetric technique)	N/A	N/A	N/A

Hyalella azteca will be conducted according to Ingersoll et al. (1998); this publication will be included as a revision to the U.S. EPA (1994) sediment toxicity testing methods and the revision to ASTM E1706. Table B-8 summaries the recommended test conditions for conducting the 10-day *Chironomus tentans* toxicity test, whereas Table B-9 provides the test acceptability requirements for this test. The test conditions, general activity schedule, and test acceptability requirements for the 42-day *Hyalella azteca* toxicity test are provided in Tables B-10 through B-12, respectively.

B5 QUALITY CONTROL REQUIREMENTS

B5.1 Purpose/Background

The purpose of this section is to identify required measurement QC checks for both the field and the laboratory. QC is "the overall system of technical activities that measures the attributes and performance of a process item, or service against defined standards to verify that they meet the stated requirements established by the customer" (USEPA, 1998). QC is both corrective and proactive in establishing techniques to prevent the generation of unacceptable data. Thus, the policy for corrective action will be discussed.

B5.2 QC Procedures

Most of the QC procedures for this project were defined in Section A4.3. Other elements of the QAPP that contained related sampling and analytical QC requirements included:

- **Sampling Process Design** (B1), which identified the planned field QC samples, as well as procedures for QC sample preparation and handling.

- **Sampling Method Requirements** (B2), which included requirements for determining if the collected samples accurately represented the population of interest.

- **Sample Handling and Custody Requirements** (B3), which discussed any QC devices employed to ensure samples will not be tampered with (e.g., custody seals) or subjected to other unacceptable conditions during transport.

- **Analytical Methods Requirements** (B4), which included information on the subsampling methods and information on the preparation of QC samples in the sample matrix (e.g., spikes, replicates).

- **Instrument Calibration and Frequency** (B7), which defined prescribed criteria for triggering recalibration (e.g., failed calibration checks).

Table B-8. Recommended Test Conditions for Conducting a 10-day Sediment Toxicity Test with *Chironomus tentans*

Parameter	Conditions
1. Test type:	Whole-sediment toxicity test with renewal of overlying water
2. Temperature:	23 ± 1°C
3. Light quality:	Wide-spectrum fluorescent lights
4. Illuminance:	About 500 to 1000 lux
5. Photoperiod:	16L:8D
6. Test chamber:	300-mL high-form lipless beaker
7. Sediment volume:	100 mL
8. Overlying water volume:	175 mL
9. Renewal of overlying water:	2 volume additions/day; continuous or intermittent (e.g., one volume addition every 12 hours)
10. Age of organisms:	Second- to third-instar larvae (All organisms must be third instar or younger with at least 50% of the organisms at third instar)
11. Number of organisms/chamber:	10
12. Number of replicate chambers/treatment:	Depends on the objective of the test. Eight replicates are recommended for routine testing
13. Feeding:	Tetrafin® goldfish food, fed 1.5 mL daily to each test chamber (1.5 mL contains 6.0 mg of dry solids)
14. Aeration:	None, unless dissolved oxygen in overlying water drops below 2.5 mg/L.
15. Overlying water:	Culture water, well water, surface water, site water, or reconstituted water
16. Test chamber cleaning:	If screens become clogged during a test; gently brush the *outside* of the screen
17. Overlying water quality:	Hardness, alkalinity, conductivity, pH, and ammonia at the beginning and end of a test. Temperature and dissolved oxygen daily
18. Test duration:	10 days
19. Endpoints:	Survival and growth (ash-free dry weight; AFDW)
20. Test acceptability:	Minimum mean control survival must be 70% with minimum mean weight per surviving control organism of 0.48 mg AFDW.

Table B-9. Test Acceptability Requirements for a 10-day Sediment Toxicity Test with *Chironomus tentans*

A. It is recommended for conducting a 10-day test with *C. tentans* that the following performance criteria be met:

1. Tests must be started with second- to third-instar larvae (about 10-day-old larvae). At least 50% of the larvae must be in the third instar at the start of the test.
2. Average survival of *C. tentans* in the control sediment must be greater than or equal to 70% at the end of the test.
3. Average size of *C. tentans* in the control sediment must be at least 0.48 mg AFDW at the end of the test.
4. Hardness, alkalinity, and ammonia in the overlying water typically should not vary by more than 50% during the test, and dissolved oxygen should be maintained above 2.5 mg/L in the overlying water.

B. Performance-based criteria for culturing *C. tentans* include the following

1. It may be desirable for laboratories to periodically perform 96-h water-only reference-toxicity tests to assess the sensitivity of culture organisms. Data from these reference toxicity tests could be used to assess genetic strain or life-stage sensitivity of test organisms to select chemicals.
2. The commercial supplier providing organisms to the laboratories should keep a record of time to first emergence for each culture and record this information using control charts. Records should also be kept on the frequency of restarting cultures.
3. The commercial supplier should record the following water-quality characteristics of the cultures at least quarterly: pH, hardness, alkalinity, and ammonia. Dissolved oxygen in the cultures should be measured weekly. Temperature in the cultures should be recorded daily. If static cultures are used, it may be desirable to measure water quality more frequently.
4. The commercial supplier should characterize and monitor background contamination and nutrient quality of food if problems are observed in culturing or testing organisms.
5. Physiological measurements such as lipid content might provide useful information regarding the health of the cultures.

C. Additional requirements:

1. All organisms in a test must be from the same source.
2. Storage of sediments collected from the field should follow ASTM guidance.
3. All test chambers (and compartments) should be identical and should contain the same amount of sediment and overlying water.
4. Negative-control sediment and appropriate solvent controls must be included in a test. The concentration of solvent used must not adversely affect test organisms.
5. Test organisms must be cultured and tested at 23°C (+1 °C).
6. The daily mean test temperature must be within ±1°C of 23°C. The instantaneous temperature must always be within ±3°C of 23°C.
7. Natural physico-chemical characteristics of test sediment collected from the field should be within the tolerance limits of the test organisms.

Table B-10. Test Conditions for Conducting a 42-day Sediment Toxicity Test with *Hyalella azteca*

Parameter	Conditions
1. Test type:	Whole-sediment toxicity test with renewal of overlying water
2. Temperature:	23 ± 1°C
3. Light quality:	Wide-spectrum fluorescent lights
4. Illuminance:	About 500 to 1000 lux
5. Photoperiod:	16L:8D
6. Test chamber:	300-mL high-form lipless beaker
7. Sediment volume:	100 mL
8. Overlying water volume:	175 mL in the sediment exposure from Day 0 to Day 28 (175 to 275 mL in the water-only exposure from Day 28 to Day 42)
9. Renewal of overlying water:	2 volume additions/day; continuous or intermittent (e.g., one volume addition every 12 hours)
10. Age of organisms:	7- to 8-day old at the start of the test
11. Number of organisms/chamber:	10
12. Number of replicate chambers/treatment:	12 (4 for 28-day survival and growth and 8 for 35- and 42-day survival, growth, and reproduction). Reproduction is more variable than growth or survival; hence, more replicates might be needed to establish statistical differences among treatments.
13. Feeding:	YCT food, fed 1.0 mL (1800 mg/L stock) daily to each test chamber
14. Aeration:	None, unless dissolved oxygen in overlying water drops below 2.5 mg/L.
15. Overlying water:	Culture water, well water, surface water or site water. Use of reconstituted water is not recommended.
16. Test chamber cleaning:	If screens become clogged during a test; gently brush the *outside* of the screen
17. Overlying water quality:	Hardness, alkalinity, conductivity, and ammonia at the beginning and end of a sediment exposure (Day 0 and 28). Temperature daily. Conductivity weekly. Dissolved oxygen (DO) and pH three times/week. Concentrations of DO should be measured more often if DO drops more than 1 mg/L since the previous measurement.
18. Test duration:	42 days
19. Endpoints:	28-day survival and growth; 35- and 42-day survival, growth, reproduction, and number of adult males and females on Day 42.
20. Test acceptability:	Minimum mean control survival of 80% on Day 28.

Table B-11. General Activity Schedule for Conducting a 42-day Sediment Toxicity Test with *Hyalella azteca*

Day	Activity
Pre-Test	
-8	Separate known-age amphipods from the cultures and place in holding chambers. Begin preparing food for the test. The <24-hour amphipods are fed 10 mL of YCT (1800 mg/L stock solution) and 10 mL of *Selenastrum capricornutum* (about 3.0 x 10^7 cells/mL) on the first day of isolation and 5 mL of both YCT and *S. capricornutum* on the 3rd and 5th day after isolation.
-7	Remove adults and isolate <24-hour old amphipods.
-6 to -2	Feed and observe isolated amphipods, monitor water quality (e.g., temperature and dissolved oxygen).
-1	Feed and observe isolated amphipods, monitor water quality. Add sediment into each test chamber, place chambers into exposure system, and start renewing overlying water.
Sediment Test	
0	Measure total water quality (pH, temperature, dissolved oxygen, hardness, alkalinity, conductivity, ammonia). Transfer ten 7- to 8-day old amphipods into each test chamber. Release organisms under the surface of the water. Add 1.0 mL of YCT (1800 mg/L stock) into each test chamber. Archive 20 test organisms for length determination or archive 80 amphipods for dry weight determination. Observe behavior of test organisms.
1 to 27	Add 1.0 mL of YCT to each test beaker. Measure temperature daily, conductivity weekly, and dissolved oxygen (DO) and pH three times/week. Observe behavior of test organisms.
28	Measure temperature, dissolved oxygen, pH, hardness, alkalinity, conductivity and ammonia. End the sediment-exposure portion of the test by collecting the amphipods with a #40 mesh sieve (425-µm mesh; U.S. standard size sieve). Use four replicates for growth measurements: count survivors and preserve organisms in sugar formalin for growth measurements. Eight replicates for reproduction measurements: place survivors in individual replicate water-only beakers and add 1.0 mL of YCT to each test beaker/day and 2 volume additions/day of overlying water.
Reproduction Phase	
29 to 35	Feed daily. Measure temperature daily, conductivity weekly, DO, and pH three times a week. Measure hardness and alkalinity weekly. Observe behavior of test organisms.
35	Record the number of surviving adults and remove offspring. Return adults to their original individual beakers and add food.
36 to 41	Feed daily. Measure temperature daily, conductivity weekly, DO, and pH three times a week. Measure hardness and alkalinity weekly. Observe behavior of test organisms.
42	Same as Day 1. Measure total water quality (pH, temperature, dissolved oxygen, hardness, alkalinity, conductivity, ammonia). Record the number of surviving adults and offspring. Surviving adult amphipods on Day 42 are preserved in sugar formalin solution. The number of adult males in each beaker is determined from this archived sample. This information is used to calculate the number of young produced per female per replicate from Day 28 to day 42.

Table B-12. Test Acceptability Requirements for a 42-day Sediment Toxicity Test with *Hyalella azteca*

A. It is recommended for conducting the 42-day test with *H. azteca* that the following performance criteria be met:

1. Age of *H. azteca* at the start of the test should be 7- to 8-days old. Starting a test with substantially younger or older organisms may compromise the reproductive endpoint.

2. Average survival of *H. azteca* in the control sediment on Day 28 should be greater than or equal to 80%.

3. Laboratories participating in round-robin testing reported after 28-day sediment exposures in a control sediment (West Bearskin), survival >80% for >88% of the laboratories; length >3.2 mm/individual for >92% of the laboratories; and dry weight >0.15 mg/individual for 72% of the laboratories. Reproduction from Day 28 to Day 42 was >2 young/female for 63% of the laboratories participating in the round-robin testing. Reproduction was more variable within and among laboratories; hence, more replicates might be needed to establish statistical differences among treatments with this endpoint.

4. Hardness, alkalinity, and ammonia in the overlying water typically should not vary by more than 50% during the sediment exposure, and dissolved oxygen should be maintained above 2.5 mg/L in the overlying water.

B. Performance-based criteria for culturing *H. azteca* include the following

1. It may be desirable for laboratories to periodically perform 96-hour water-only reference-toxicity tests to assess the sensitivity of culture organisms. Data from these reference toxicity tests could be used to assess genetic strain or life-stage sensitivity of test organisms to select chemicals.

2. The commercial supplier providing organisms to the laboratories should track parental survival in the cultures and record this information using control charts if known-age cultures are maintained. Records should also be kept on the frequency of restarting cultures and the age of brood organisms.

3. The commercial supplier should record the following water-quality characteristics of the cultures at least quarterly: pH, hardness, alkalinity, and ammonia. Dissolved oxygen in the cultures should be measured weekly. Temperature in the cultures should be recorded daily. If static cultures are used, it may be desirable to measure water quality more frequently.

4. The commercial supplier should characterize and monitor background contamination and nutrient quality of food if problems are observed in culturing or testing organisms.

5. Physiological measurements such as lipid content might provide useful information regarding the health of the cultures.

C. Additional requirements:

1. All organisms in a test must be from the same source.

2. Storage of sediments collected from the field should follow ASTM guidance.

3. All test chambers (and compartments) should be identical and should contain the same amount of sediment and overlying water.

4. Negative-control sediment and appropriate solvent controls must be included in a test. The concentration of solvent used must not adversely affect test organisms.

5. Test organisms must be cultured and tested at 23°C (+1 °C).

Table B-12. Continued

C. Additional requirements:

6. The mean of the daily test temperature must be within ±1°C of 23°C. The instantaneous temperature must always be within ±3°C of 23°C.

7. Natural physico-chemical characteristics of test sediment collected from the field should be within the tolerance limits of the test organisms.

For the toxicity tests, QC procedures will include using several replicates for each sediment sample, setting up negative controls with the toxicity tests, and running reference toxicant tests to check on the health of the organisms. Control charts for the reference toxicant tests will be one way to document the toxicological QC results.

For the field quality control checks, the only field measurements planned for this project are those related to positioning the boat (i.e., GPS unit). Attainable precision is approximately 1-10 m. To verify this precision, the "marking" method can be used to find known geographical locations (e.g., benchmarks) using only the tracking capabilities of the GPS unit.

The Vibrocorer will be lined with 6 mil polyethylene, which will be removed with each core sample and replaced. The sediment core samples will be decontaminated by removing the outer 2-4 mm of sample prior to homogenization. This will serve as a quality control check to reduce contamination of the core from the liner.

For the laboratory quality control checks, each of the laboratories identified in this QAPP have a QC program they use to ensure the reliability and validity of the analyses performed at the laboratory. All analytical procedures are documented in writing as SOPs and each SOP includes QC information which addresses the minimum QC requirements for the procedure. The internal quality control checks might differ slightly for each individual procedure, but in general, the QC requirements include the following:

- Method blanks
- Reagent/preparation blanks (applicable to inorganic analysis)
- Instrument blanks
- Matrix spikes/matrix spike duplicates (for organic analysis)
- Surrogate spikes
- Analytical spikes (graphite furnace)
- Field replicates
- Laboratory duplicates
- Laboratory control standards
- Internal standard areas for GC/MS or GC/ECD analysis; control limits.

Table B-13 summarizes the internal quality control checks used for each of the critical analyses. Details on the use of each QC check are provided in the analytical SOPs provided for each measurement (see Appendix F). Method detection limits will be calculated for each analyte.

The analyses for PCBs and PAHs use a method blank (consisting of an extracted matrix or solvent phase sample with "zero" known concentration of the analytes), and a matrix spike (a control uncontaminated sediment spiked with known analyte concentration), which are subjected to analyses identical to the samples. Analytical duplicate samples will be run after every 20

Table B-13. Summary of Analytical Quality Control Checks for Critical Measurements

Analyte	Number of Field Replicates	Spikes	Blanks	Analytical Duplicates	Standards
PCBs	3	Matrix	Solvent, Method	Every 20 samples	see SOP
PAHs	7	Matrix	Solvent, Method	Every 20 samples	see SOP
Mercury	10	N/A	Method	Every 10 samples	see SOP
Metals	14 (Pb, Zn) 1 (other metals)	Fortified Sample Matrix	Method	Every 10 samples	see SOP
AVS	1	Matrix	Method	Every 20 samples	see SOP
SEM	1	N/A	N/A	N/A	N/A
Ammonia	1	N/A	N/A	Every 10 samples	see SOP
TOC	7	N/A	Method	Every 10 samples	see SOP
Percent Moisture	14	N/A	N/A	Every 10 samples	N/A
Particle Size	9	N/A	N/A	Every 12 samples	N/A

samples. These analyses will also include measurement of a surrogate internal standard. Acceptance criteria for these internal QC checks are: a "clean" procedural blank, recoveries within the control limits specified in the SOPs for both blank and matrix spike recovery, as well as for the surrogate standard recoveries (Appendix F). Relative error for duplicate samples must be less than 50% relative percent difference (RPD) (Table A-6).

Internal QC checks for metals include the use of blanks, a measured standard NBS reference material (for metals) or NIST standard (for Hg). Analytical duplicate measurements will be made after at least every 10 samples to measure precision. Acceptable precision and accuracy limits for mercury and the metals are given in Table A-6. In addition, the precision and accuracy limits for other parameters (AVS, SEM, ammonia, particle size, TOC, and percent moisture) are given in Table A-6.

All data obtained will be properly recorded. The data package will include a full deliverable package capable of allowing the recipient to reconstruct QC information and compare it to QC criteria. Any samples analyzed in nonconformance with the QC criteria will be reanalyzed by the laboratory if sufficient volume is available. It is expected that sufficient volumes/weights of samples will be collected to allow for reanalysis when necessary.

B6 INSTRUMENT/EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE REQUIREMENTS

B6.1 Purpose/Background

The purpose of this section is to discuss the procedures used to verify that all instruments and equipment are maintained in sound operating condition and are capable of operating at acceptable performance levels.

B6.2 Testing, Inspection, and Maintenance

The success of this project is dependent on well functioning field, analytical, and toxicological equipment. Preventative maintenance of this equipment is the key to reduce possible project delays due to faulty equipment.

B6.2.1 Field Activities

The field equipment for this project includes the GPS units (MPCA/GLNPO), Shipek grab sampler (MPCA), Livingston corer (MPCA), modified drop corer (MPCA), Vibrocorer (GLNPO), and sediment sounding poles. In addition, two different research vessels will be utilized for sediment sampling: the MPCA's R/V Naiad and GLNPO's R/V Mudpuppy. Preventative maintenance procedures for MPCA equipment will follow the professional judgment of the MPCA Field Team Leader. GLNPO's preventative maintenance procedures

will be followed for their equipment. The sounding poles are metal rods which do not require any preventative maintenance.

Corrective action in the field may be needed when the sample network is changed (i.e., more/less samples, sampling locations other than those specified in the QAPP, etc.), or when sampling procedures and/or field analytical procedures require modification due to unexpected conditions. Technical staff and project personnel will be responsible for reporting all suspected technical or QA nonconformances, or suspected deficiencies of any activity or issued document, by reporting the situation to the Field Team Leader or designee. This person will be responsible for assessing the suspected problems, in consultation with the MPCA Principal Investigator, and making a decision based on the potential for the situation to impact the quality of the data. If it is determined that the situation warrants a reportable nonconformance requiring corrective action, then a nonconformance report will be initiated by the MPCA Principal Investigator.

The MPCA Principal Investigator will be responsible for ensuring that corrective actions for nonconformances are initiated by:

- Evaluating all reported nonconformances
- Controlling additional work on nonconforming items
- Determining disposition or action to be taken
- Maintaining a log of nonconformances
- Reviewing nonconformance reports and corrective actions taken
- Ensuring nonconformance reports are included in the final report files.

If appropriate, the Field Team Leader will ensure that no additional work, that is dependent on the nonconforming activity, is performed until the corrective actions are completed. Corrective actions for field measurements may include:

- Repeat the measurement to check the error
- Re-calibration
- Replace the instrument or measurement device
- Stop work (if necessary).

The Field Team Leader, or his designee, is responsible for leading all field work activities. In case the sampling program changes, the Field Team Leader will implement the changes after obtaining approval from the MPCA Principal Investigator.

Corrective actions resulting from internal field audits will be implemented immediately if data may be adversely affected due to unapproved or improper use of approved methods. The MPCA QA Officer will identify deficiencies and recommend corrective actions to the MPCA Principal Investigator. Implementation of corrective actions will be performed by the Field Team Leader.

Corrective actions will be documented in quality assurance reports to the entire project management.

Corrective actions will be implemented and documented in the field notebook. No staff member will initiate corrective actions without prior communication of findings through the proper channels. If corrective actions are insufficient, work may be stopped by the GLNPO Project Officer.

B6.2.2 Laboratory Activities

As part of each contract laboratories QA/QC program, a routine preventative maintenance program will be conducted by them to minimize the occurrence of instrument failure and other system malfunctions. All laboratory instruments are maintained in accordance with manufacturer's specifications and the requirements of the specific method employed. This maintenance is carried out on a regular, scheduled basis and is documented in the laboratory instrument service logbook for each instrument.

Corrective actions in the laboratory may occur prior to, during, and after initial analysis. A number of conditions such as broken sample containers, multiple phases, and potentially high concentration samples may be identified during sample log-in or just prior to analysis. Following consultation with laboratory analysts and section leaders, it may be necessary for the Laboratory QA Manager to approve the implementation of corrective actions. The submitted SOPs specify some conditions during or after analysis that may automatically trigger corrective actions of samples, including additional sample extract cleanup and automatic reinjection/reanalysis when certain quality control criteria are not met (Appendix F).

Corrective actions are required whenever an out-of-control event or potential out-of-control event is noted. The investigative action taken is somewhat dependent on the analysis and the event.

Laboratory personnel are alerted that corrective actions may be necessary if:

- QC data are outside the warning or acceptable windows for precision and accuracy
- Blanks contain target analytes above acceptable levels
- Undesirable trends are detected in spike recoveries or RPD between duplicates
- There are unusual changes in detection limits
- QC limits for sediment toxicity tests are not met
- Deficiencies are detected by the Laboratory, MPCA, and/or GLNPO QA Officer(s) during any internal or external audits or from the results of performance evaluation samples
- Inquires concerning data quality are received.

Corrective action procedures are often handled at the bench level by the analyst, who reviews the preparation or extraction procedure for possible errors, checks the instrument calibration, spike

and calibration mixes, instrument sensitivity, experimental set-up for toxicity tests, and so on. If the problem persists or cannot be identified, the matter is referred to the Laboratory Manager and/or Laboratory QA Officer for further investigation. Once resolved, full documentation of the corrective action procedure will be filed with the Laboratory QA Officer.

These corrective actions are performed prior to release of the data from the laboratory. The corrective actions will be documented in both the laboratories corrective action log and the narrative data report sent from the laboratory to the MPCA Principal Investigator. If corrective action does not rectify the situation, the laboratory will contact the MPCA Principal Investigator.

B7 INSTRUMENT CALIBRATION AND FREQUENCY

B7.1 Purpose/Background

This section concerns the calibration procedures that will be used for instrumental analytical methods and other measurement methods that are used in environmental measurements. Calibration is defined as checking physical measurements against accepted standards.

B7.2 Instrumentation Requiring Calibration

The only field instruments that will require calibration are the GPS units owned by the MPCA and GLNPO. All of the equipment used to analyze the sediment samples will require calibration, as will the water quality equipment used to monitor overlying water quality parameters in the sediment toxicity tests.

B7.3 Calibration Methods that will be Used for Each Instrument

B7.3.1 Field Instrument Calibration

A SOP for the calibration and use of the MPCA GPS unit is not available. Instead, the operating manual for the GPS Pathfinder Basic™ Receivers will be used to calibrate the GPS unit (Trimble Navigation, 1992). Calibration and use of GLNPO's GPS units will be per their procedures.

B7.3.2 Laboratory Instrument Calibration

Calibration of analytical instruments is essential because it is the means by which the instrument responses are properly translated into chemical concentrations. Instrument calibration is performed before sample analysis begins and is continued during sample analysis at the intervals specified in Table B-14 to ensure that the data quality objectives are met. Initial calibration is

Table B-14. Summary of Calibration Methods for Analytes in Sediment Samples and Toxicity Testing Water Column Samples

Matrix	Analyte	Initial Calibration	Ongoing Calibration
Sediment	PCBs	5 pt. curve of 11 congeners	Every 5 samples
Sediment	PAHs	6 pt. curve	Every 12 hours
Sediment	Mercury	4 pt. curve	Every 20 samples
Sediment	Metals	4 pt. curve (GFAA)	Every 10 samples
Sediment	AVS	9 pt. curve	Every 20 samples
Sediment	SEM	2 pt. curve (ICP)	Every 20 samples
Sediment	Ammonia	7 pt. curve	Every 20 samples
Sediment	TOC	single pt.	Every 20 samples
Water	Ammonia	3 pt. curve	Daily
Water	Conductivity	2 calibration standards	Daily
Water	DO	saturated oxygen reading	Daily
Water	pH	standard pH 7.0 and 10.0 buffers	Every 3 hours with a pH 7.0 buffer

performed prior to sample analysis to determine whether the response of the instrument is linear across a range of target analyte concentrations (i.e., the working linear range).

For this study, instrument calibration procedures are described in Table B-14 and in the analytical SOPs (Appendix F). All ongoing calibration measurements must be within 20% of the initial calibration measurement to be considered adequate.

B7.4 Calibration Apparatus

None of the analytical instruments will be calibrated using a calibration apparatus.

B7.5 Calibration Standards

The working linear range of an instrument should be established prior to performing sample analyses. A minimum of five calibration standards for the analysis of organic compounds, and three calibration standards for the analysis of inorganic compounds, should be used when establishing the working linear range for all target analytes of concern. Generally, the working linear range of an instrument for a specific analysis should bracket the expected concentrations of the target analyte in the samples to be analyzed. The calibration standards used to establish the working linear range should encompass a factor of 20 (i.e., 1 to 20, with the lowest concentration equal to 1 and the highest concentration equal to 20 times the concentration of the lowest concentration used).

B7.6 Calibration Frequency

It is critical that the stability of the instrument response be verified during the course of ongoing sample analyses. The verification of instrument stability is assessed by analyzing continuing calibration standards at regular intervals during the period that sample analyses are performed. It is recommended that, at a minimum, calibration standards be analyzed at the beginning of each analytical sequence, after every tenth sample, and at the end of the analytical sequence for all organic and inorganic compound analyses performed. The concentration of the continuing calibration standard should be equivalent to the concentration of the midpoint established during initial calibration of the working linear range of the instrument.

Equipment logbooks will be maintained at each contract laboratory, in which will be recorded the usage, maintenance, calibration, and repair of instrumentation. These logbooks will be available to the MPCA or GLNPO during any audits that may be conducted.

B8 INSPECTION/ACCEPTANCE REQUIREMENTS FOR SUPPLIES AND CONSUMABLES

B8.1 Purpose

The purpose of this section is to establish and document a system for inspecting and accepting all supplies and consumables that may directly or indirectly affect the quality of the project or task.

B8.2 Identification of Critical Supplies and Consumables

Critical supplies and consumables include sample bottles, calibration gases, reagents, hoses, materials for decontamination activities, deionized water, and Milli-Q water. Only pre-cleaned sample bottles will be used for this investigation as obtained by En Chem, Inc., ENSR, and MDH. Sample jars (60 mL) for particle-size analysis were purchased from VWR and were certified clean to EPA standards.

Each of the contract laboratories will utilize high quality supplies and consumables to reduce the chances of contaminating the samples. All water supply systems are tested on a regular basis, for necessary procedures, to ensure it is acceptable for use. Solvent blanks are run to verify the purity of solvents used in the organic analyses. The contract laboratories may also incorporate other measures, such as the dedicated use of glassware for certain analyses (e.g., inorganics, organics) or toxicity tests. In addition, En Chem, Inc. has a specially designed air handling system and temperature controls to protect against contamination of samples and to keep instruments functioning at their highest performance levels.

B8.3 Establishing Acceptance Criteria

Acceptance criteria must be consistent with overall project technical and quality criteria. Each of the contract laboratories should utilize their own acceptance criteria for normal operations with analyzing and/or testing contaminated sediments.

B8.4 Inspection of Acceptance Testing Requirements and Procedures

Each contract laboratory should document inspections of acceptance testing, including procedures to be followed, individuals responsible, and frequency of evaluation. In addition, handling and storage conditions for supplies and consumables should be documented.

B8.5 Tracking and Quality Verification of Supplies and Consumables

Procedures should be established to ensure that inspections or acceptance testing of supplies and consumables are adequately documented by permanent, dated, and signed records or logs that uniquely identify the critical supplies or consumables, the date received, the date tested, the date to be retested (if applicable), and the expiration date. These records should be kept by the

responsible individual(s) at each contract laboratory. In order to track supplies and consumables, labels with the information on receipt and testing should be used.

These or similar procedures should be established to enable project personnel to: 1) verify, prior to use, that critical supplies and consumables meet the project objectives; and 2) ensure that supplies and consumables that have not been tested, have expired, or do not meet acceptance criteria are not used for the project.

B9 DATA ACQUISITION REQUIREMENTS (NON-DIRECT MEASUREMENTS)

B9.1 Purpose/Background

Data collected from other MPCA investigations involving Minnesota Slip will be utilized in this study. These previously collected data will include the results of various sediment chemistry and particle size analyses, sediment toxicity tests, benthological community surveys, and sediment bioaccumulation tests (Schubauer-Berigan and Crane, 1997; Crane et al., 1997; unpublished R-EMAP and MPCA data; AScI Corporation, 1999). These data will be utilized in a weight-of-evidence approach, with the data collected from this study, to make recommendations for further actions (e.g., remediation) at Minnesota Slip.

Past data collection efforts in which the depth intervals of sediment chemistry analyses were similar to this study will be combined in the analysis of the data through sediment kriging. The computer-generated kriging will result in color isopleths of contaminant concentrations for various depth intervals in the sediment.

B9.2 Acquisition of Non-Direct Measurement Data

The use of non-direct measurement data will be such that it is representative of newly acquired data from Minnesota Slip, is not biased, and meets the precision specifications for this study. The non-direct measurement data will also be checked for any qualifiers. Since these previously collected data have been summarized in reports by the MPCA, the data summarization process is consistent with the goals of this project.

B10 DATA MANAGEMENT

B10.1 Purpose/Background

This section will present an overview of all mathematical operations and analyses performed on raw data to change their form of expression, location, quantity, or dimensionality. These operations include data recording, validation, transformation, transmittal, reduction, analysis, management, storage, and retrieval.

B10.2 Data Recording

B10.2.1 Field Data Recording

Field logbooks will be used to record data collection activities. As such, entries will be described in as much detail as possible. The field logbooks will be bound notebooks with waterproof paper. For this survey, one field notebook will be sufficient. The notebook will be assigned to the MPCA Principal Investigator and will be used by both her and the Field Crew Leader to record information. The title page of the filed notebook will contain the following information:

- Person to whom the notebook is assigned
- Project name
- Project start date and end date.

Entries into the notebook will contain a variety of information. At the beginning of each entry, the date, start time, weather, names of all sampling team members present, level of personal protection being used, and the signature of the person making the entry will be entered. The names of visitors to the site will also be recorded in the field notebook.

The types of measurements made (e.g., GPS coordinates) and samples collected will be recorded. All entries will be made using permanent black ink, signed, and dated, and no erasures will be made. If an incorrect entry is made, the information will be crossed out with a single strike mark that is signed and dated by the sampler. Whenever a sample is collected, or a measurement is made, a detailed description of the location of the station, which includes GPS coordinates, will be recorded. The number of photographs taken of the station, if any, will also be noted. All equipment used to make measurements will be identified. A site-specific identification number (e.g., MNS-99-01) will be assigned to sampling sites prior to sample collection.

B10.2.2 Laboratory Data Recording

All raw analytical and toxicity data will be recorded in numerically identified laboratory notebooks or data sheets. The data will be promptly recorded in black ink on appropriate forms that are initialed and dated by the person collecting the data. Changes to recorded data are made in black ink, with a single line cross-out, initials, and date. No “whiteout” will be allowed.

If a laboratory has the capability to directly enter or download the data into a computerized data logger, then this is preferable. Sample data are recorded along with other pertinent information, such as the sample identification number. Other details which will also be recorded include: the analytical method used (SOP #), name of analyst, the date of analysis or toxicity test, matrix sampled, reagent concentrations, instrument settings, and the raw data. Each page of the notebook or data sheet will be signed and dated by the analyst. Copies of any strip chart printouts (such as gas chromatograms) will be maintained on file. Periodic review of these

notebooks by the Laboratory QA Officer will take place prior to final data reporting. Records of notebook entry inspections are maintained by the Laboratory QA Officer.

B10.3 Data Validation

This section addresses how the method, instrument, or system performs the function it is intended to consistently, reliably, and accurately in generating the data. This type of data validation would be shown by meeting acceptable QC limits for analytical parameters and sediment toxicity tests. In addition, the application of preventative maintenance activities and internal QA/QC auditing will ensure that field and laboratory generated data will be valid.

Quality control data (e.g., laboratory duplicates, matrix spikes, matrix spike duplicates, and performance of negative controls) will be compared to the method acceptance criteria. Data considered to be acceptable will be entered into the laboratory computer system. Data summaries will be sent to the Laboratory QA Officer for review. If approved, data are logged into the project database format. Unacceptable data will be appropriately qualified in the project report.

B10.4 Data Transformation

Data transformations result from calculations based on instrument output, readings, or responses. The procedures for converting calibration readings into an equation that will be applied to measurement readings are given in the SOPs for analytical parameters (Appendix F).

B10.5 Data Transmittal

Data transmittal occurs when data are transferred from one person or location to another or when data are copied from one form to another. Some examples of data transmittal are copying raw data from a notebook onto a data entry form for keying into a computer file and electronic transfer of data over a computer network. The transmittal of field data will be double-checked by the MPCA Principal Investigator. The transmittal of laboratory data will be checked by the individual analyst with periodic checks by the Laboratory Project Manager and/or QA Officer.

B10.6 Data Reduction

Data reduction includes all processes that change the number of data items. Each contract laboratory has their own data reduction techniques, as is usually documented in their QA Manual (Appendices H and I). For the toxicity tests, data reduction will involve taking the arithmetic mean of replicate data (e.g., number of surviving organisms). For the analytical results, data reduction will involve calculating the arithmetic mean and standard deviation of field and laboratory replicates.

B10.7 Data Analysis

Data analysis will involve comparing the surficial contaminant concentrations to consensus-based sediment quality guidelines (Ingersoll and MacDonald, 1998) to look for exceedances of threshold effect concentrations (TECs) and probable effect concentrations (PECs). SigmaPlot® will be used to examine possible regression relationships between contaminant concentrations and TOC and/or particle size. In addition, other chemical regression relationships, as done in Crane (1999a), will be investigated. The chemical data from this study will be merged with analogous chemical data from previous sediment investigations in Minnesota Slip to allow sediment kriging to be done. The kriging relies on a triangulation of data points to generate contaminant isopleths for similar depth intervals.

The sediment toxicity data will be analyzed statistically, by ENSR, to evaluate whether significant, adverse effects to biotic endpoints (e.g., survival, growth, reproduction) occur when the test organisms are exposed to Minnesota Slip sediments. The statistical analysis techniques are documented in the individual toxicity test SOPs (Appendix G).

B10.8 Data Tracking

Data management includes tracking the status of data as they are collected, transmitted, and processed. Each contract laboratory will have their own data tracking system in place.

B10.9 Data Storage and Retrieval

Each contract laboratory will have their own data storage and retrieval protocols. For example, data storage procedures at ENSR are documented in Section 8.4 of their QA Manual (Appendix H). The MPCA will retain all the analytical data packages and toxicity test reports in the project files for this study. The time period for storage of MPCA files was given in Section A6.4. In addition, the sediment contaminant data will be added to GLNPO's contaminated sediment database. This will allow for several retrieval options of the database.

C ASSESSMENT/OVERSIGHT

C1 ASSESSMENT

C1.1 Purpose/Background

During the planning process, many options for sampling design, sample handling, sample cleanup and analysis, and data reduction are evaluated and chosen for the project. In order to ensure that the data collection is conducted as planned, a process of evaluation and validation is necessary. This section of the QAPP describes the internal and external checks necessary to ensure that:

- All elements of the QAPP are correctly implemented as prescribed.
- The quality of the data generated by implementation of the QAPP is adequate.
- Corrective actions, when needed, are implemented in a timely manner and their effectiveness is confirmed.

The most important part of this section is documenting all planned internal assessments. Generally, internal assessments are initiated or performed by the Laboratory QA Officer.

C1.2 Assessment Activities and Project Planning

C1.2.1 Assessment of the Subsidiary Organizations

Two types of assessments of the subsidiary organizations can be performed as described below.

- *Management Systems Review (MSR).* A form of management assessment, this process is a qualitative assessment of a data collection operation or organization to establish whether the prevailing quality management structure, policies, practices, and procedures are adequate for ensuring that the type and quality of data needed are obtained. The MSR is used to ensure that sufficient management controls are in place and carried out by the organization to adequately plan, implement, and assess the results of the project.
- *Readiness Reviews.* A readiness review is a technical check to determine if all components of the project are in place so that work can commence on a specific phase.

It is anticipated that a readiness review by each contract laboratory project manager will be sufficient for this project.

C1.2.2 Assessment of Project Activities

Assessment of project activities can involve the following tasks:

- Surveillance

- Technical Systems Audit (TSA)
- Performance Evaluation (PE)
- Audit of Data Quality (ADQ)
- Peer Review
- Data Quality Assessment.

It is anticipated that surveillance will be the primary assessment technique of project activities. This will most readily occur by the Project Manager and QA Officer of each contract laboratory.

C1.3 Documentation of Assessments

C1.3.1 Number, Frequency, and Types of Assessments

Due to the short-term nature of this project for the contract laboratories, no types of assessments are planned other than general surveillance. Section 10.0 of ENSR's QA Manual (Appendix H) and Section 13 of MDH's QA Manual (Appendix I) provide more information about the performance and systems audits they do on an internal basis. En Chem, Inc. also performs regular internal audits (Appendix J).

C1.3.2 Assessment Personnel

Internal audits of the contract laboratories are regularly performed by their respective QA Officers, except for UMD which is a small laboratory. MDH, En Chem, Inc., and ENSR have all undergone certification programs, as detailed in their QA Manuals or Statement of Qualifications (Appendices H - J), which has involved external auditing.

C1.3.3 Schedule of Assessment Activities

No external audits, by the MPCA, will be conducted for this project. External audits, by the GLNPO QA Officer, is up to his discretion. The scheduling of regular internal audits at MDH, En Chem, Inc., and ENSR is at the discretion of the respective QA Officers. However, a special audit will not be needed for this project.

C1.3.4 Reporting and Resolution of Issues

Any audits or other assessments that reveal findings of practice or procedure that do not conform to the written QAPP need to be corrected as soon as possible. The Laboratory Project Manager and QA Officer need to be informed immediately of critical deviations that compromise the acceptability of the test. For noncritical deviations, they need to be informed by the next business day.

Corrective actions should only be implemented after approval by the MPCA Principal Investigator, or her designee, the Field Team Leader. If immediate corrective action is required,

approvals secured by telephone from the MPCA Principal Investigator should be documented in an additional memorandum.

For noncompliance problems, a formal corrective action program will be determined and implemented at the time the problem is identified. The person who identifies the problem will be responsible for notifying the MPCA Principal Investigator, who in turn will notify the GLNPO Project Officer. Implementation of corrective actions will be confirmed in writing through the same channels.

Any nonconformance with the established quality control procedures in the QAPP will be identified and corrected in accordance with the QAPP. The GLNPO Project Officer, or his designee, will issue a nonconformance report for each nonconformance condition.

Corrective actions in the laboratory may occur prior to, during, and after initial analysis. A number of conditions, such as broken sample containers, multiple phases, and potentially high concentration samples may be identified during sample log-in or just prior to analysis. Following consultation with laboratory analysts and section leaders, it may be necessary for the Laboratory QA Officer to approve the implementation of corrective actions. The submitted SOPs specify some conditions during or after analysis that may automatically trigger corrective actions of samples, including additional sample extract cleanup and automatic reinjection/reanalysis when certain quality control criteria are not met (Appendix F).

Corrective actions are required whenever an out-of-control event or potential out-of-control event is noted. The investigative action taken is somewhat dependent on the analysis and the event.

Laboratory personnel are alerted that corrective actions may be necessary if:

- QC data are outside the warning or acceptable windows for precision and accuracy
- Blanks contain target analytes above acceptable levels
- Undesirable trends are detected in spike recoveries or RPD between duplicates
- There are unusual changes in detection limits
- QC limits for sediment toxicity tests are not met
- Deficiencies are detected by the Laboratory, MPCA, and/or GLNPO QA Officer(s) during any internal or external audits or from the results of performance evaluation samples
- Inquires concerning data quality are received.

Corrective action procedures are often handled at the bench level by the analyst, who reviews the preparation or extraction procedure for possible errors, checks the instrument calibration, spike and calibration mixes, instrument sensitivity, experimental set-up for toxicity tests, and so on. If the problem persists or cannot be identified, the matter is referred to the Laboratory Project Manager and/or Laboratory QA Officer for further investigation. Once resolved, full documentation of the corrective action procedure is filed with the Laboratory QA Officer.

These corrective actions are performed prior to release of the data from the laboratory. The corrective actions will be documented in both the laboratories corrective action log and the narrative data report sent from the laboratory to the MPCA Principal Investigator. If corrective action does not rectify the situation, the laboratory will contact the MPCA Principal Investigator.

C2 REPORTS TO MANAGEMENT

C2.1 Purpose/Background

This section will identify the frequency and distribution of reports issued to inform management of the status of the project, including QA/QC issues.

C2.2 Frequency, Content, and Distribution of Reports

The MPCA Principal Investigator will submit quarterly reports to the GLNPO Project Officer for the quarters ending on September 30, December 31, March 31, and June 30. Each of the contract laboratory Project Managers will need to submit a short project update to the MPCA Principal Investigator by December 31, 1999; March 31, 2000; and June 30, 2000. The project updates can be sent via email and need to document how many samples have been analyzed for various parameters or how many toxicity tests have been run. In addition, any problems encountered should be documented, and plans for the next quarter need to be mentioned.

C2.3 Identify Responsible Organizations

Written QC reports will be provided to the MPCA Principal Investigator, by the persons identified in Section A1.2, whenever sample measurements are reported. These reports will summarize QA/QC programs, give detailed results of analysis of QC samples, and provide information on the precision, accuracy, and completeness for each sample run. These written reports will note any significant QA/QC problems encountered during sample analyses, as well as state the corrective actions taken. Any serious QA problems needing immediate decisions will be discussed orally between MPCA personnel and contract staff, with such discussions denoted in writing; these problems will be noted in the quarterly reports to the GLNPO Project Officer.

MPCA will provide summary QA/QC information in the final written report to GLNPO. This report will include information on adherence of measurements to the QA objectives. The final report will contain detailed discussions of QA/QC issues, including any changes in the QAPP, a summary of the contract laboratories QA/QC reports, results of any internal performance audits,

any significant QA/QC problems, detailed information on how well the QA objectives were met, and their ultimate impact on decision making. The following is a list of items to be included in the final project report:

- Changes in the QAPP
- Results of any internal system audits
- Significant QA/QC problems, recommended solutions, and results of corrective actions
- Data quality assessment in terms of precision, accuracy, representativeness, completeness, and sensitivity
- Indication of fulfillment of QA objectives
- Limitations on the use of the measurement data.

D DATA VALIDATION AND USABILITY

D1 DATA REVIEW, VALIDATION, AND VERIFICATION REQUIREMENTS

D1.1 Purpose/Background

The purpose of this section is to state the criteria for deciding the degree to which each data item has met its quality specifications as described in Section B. The potential effect that each deviation from a QAPP may have on the usability of the associated data item, its contribution to the quality of the reduced and analyzed data, and its effect on the decision should be estimated.

D1.2 Sampling Design

How closely a measurement represents the actual environment at a given time and location is a complex issue that is considered during development of Section B1. Acceptable tolerances for each critical sample coordinate and the action to be taken if the tolerances are exceeded should be specified in Section B1.

Each sample should be checked for conformity to the specifications, including type and location (spatial and temporal). By noting the deviations in sufficient detail, subsequent data users will be able to determine the data's usability under scenarios different from those included in project planning.

D1.3 Sample Collection Procedures

Details of how a sample is separated from its native time/space location are important for properly interpreting the measurement results. Section B2 provided these details, which included sampling and ancillary equipment and procedures (including equipment decontamination). Acceptable departures (for example, alternative equipment) from the QAPP, and the action if the requirements cannot be satisfied, should be specified for each critical aspect. Validation activities should note potentially unacceptable departures from the QAPP. Comments from field surveillance on deviations from written sampling plans also should be noted.

D1.4 Sample Handling

Details of how a sample is physically treated and handled during relocation from its original site to the actual measurement site are extremely important. Correct interpretation of the subsequent measurement results requires that deviations from Section B3 of the QAPP and the actions taken to minimize or control the changes, be detailed. Data collection activities should indicate events that occur during sampling handling that may affect the integrity of the samples.

The MPCA Principal Investigator has evaluated the sample containers and the preservation methods to be used and has ensured that they are appropriate to the nature of this project.

Checks on the identity of the sample (e.g., proper labeling and chain-of-custody records), as well as proper physical storage conditions (e.g., chain-of-custody and storage records) will be made to ensure that the sample continues to be representative of its native environment as it moves through the analytical process.

D1.5 Analytical Procedures

Each sample will be verified to ensure that the procedures used to generate the data (as identified in Section B4 of the QAPP) were implemented as specified. Acceptance criteria will be developed for important components of the procedures, along with suitable codes for characterizing each sample's deviation from the procedure. Data validation activities should determine how seriously a sample deviated beyond the acceptable limit so that the potential effects of the deviation can be evaluated during DQA.

D1.6 Quality Control

Section B5 of the QAPP specified the QC checks that are to be performed during sample collection, handling, and analysis. These include analysis of check standards, blanks, spikes, and replicates, which provide indications of the quality of data being produced by specified components of the measurement process. For each specified QC check, the procedure, acceptance criteria, and corrective action (and changes) should be specified. Data validation should document the corrective actions that were taken, which samples were affected, and the potential effect of the actions on the validity of the data.

D1.7 Calibration

Section B7 addressed the calibration of instruments and equipment and the information that should be presented to ensure that the calibrations:

- Were performed within an acceptable time prior to generation of measurement data
- Were performed in the proper sequence
- Included the proper number of calibration points
- Were performed using standards that "bracketed" the range of reported measurement results (otherwise, results falling outside the calibration range are flagged as such)
- Had acceptable linearity checks and other checks to ensure that the measurement system was stable when the calibration was performed.

When calibration problems are identified, any data produced between the suspect calibration event and any subsequent recalibration should be flagged to alert data users.

D1.8 Data Reduction and Processing

Checks on data integrity evaluate the accuracy of "raw" data and include the comparison of important events and the duplicate rekeying of data to identify data entry errors.

Data reduction is an irreversible process that involves a loss of detail in the data and, for this project, will involve averaging across space (e.g., compositing results from field replicates). For this project, all contract laboratory calculations will be checked by the Laboratory Project Manager. Errors will be noted and corrected by crossing out the original notations. Analytical results for sediment samples will be calculated and reported on a dry weight basis.

Any manipulations of the data (e.g., normalization of organic data to TOC, comparisons to sediment quality objectives resulting in the calculation of relative contamination factors, or summary statistics of chemical parameters for different depth intervals) will be double-checked that the formulas were set up correctly in the Excel spreadsheets. In addition, sediment kriging figures, that will be generated in color, will be double-checked that the contaminant isopleths are representative of the sampling point data.

Various tables and charts will be used to synthesize the project results in the draft report. The MPCA Principal Investigator will be responsible for double-checking the information contained in these tables and figures.

D2 VALIDATION AND VERIFICATION METHODS

D2.1 Purpose/Background

The purpose of this section is to describe, in detail, the process for validating (determining if data satisfy QAPP-defined user requirements) and verifying (ensuring that conclusions can be correctly drawn) project data. The amount of data validated is directly related to the DQOs developed for the project.

D2.2 Process for Validating and Verifying Data

D2.2.1 Procedures Used to Validate Field Data

Procedures to evaluate field data for this project primarily include checking for transcription errors and reviewing field notebooks. This task will be the responsibility of the MPCA Principal Investigator.

D2.2.2 Procedures Used to Validate Laboratory Data

The respective Laboratory QA Officer will conduct a systematic review of the analytical data for compliance with the established QC criteria based on the spike, duplicate, and blank results

provided by the laboratory. All technical holding times will be reviewed, the GC/MS and GC/ECD instrument performance check sample results will be evaluated, and results of initial and continuing calibration will be reviewed and evaluated. The ENSR Laboratory QA Officer will conduct a similar systematic review of the toxicity data to ensure the test acceptability requirements listed in Table B-9 and B-12 have been met. One hundred percent of the analytical and toxicity data will be validated.

The data review will identify any out-of-control data points and data omissions, and the Laboratory QA Officer will interact with the laboratory to correct data deficiencies. Decisions to repeat sample collection and analysis may be made by the MPCA Principal Investigator based on the extent of the deficiencies and their importance in the overall context of the project.

D3 RECONCILIATION WITH DATA QUALITY OBJECTIVES

D3.1 Purpose/Background

The purpose of this section is to outline and specify, if possible, the acceptable methods for evaluating the results obtained from the project. This section includes scientific and statistical evaluations of data to determine if the data are of the right type, quantity, and quality to support their intended use.

D3.2 Reconciling Results with DQOs

Data quality assessment (DQA) follows the data validation and verification steps. As such, DQA determines how well the validated data can support their intended use. The MPCA Principal Investigator will evaluate the data to determine if it will meet the data quality objectives specified in Section A4.

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APPENDIX A

DOCUMENTED STORM WATER DISCHARGES TO MINNESOTA SLIP

APPENDIX B

CONTINGENCY TABLES (MACDONALD ET AL., 1998)

APPENDIX C

GLNPO's SOP FOR OPERATING THE VIBROCORER

APPENDIX D

GLNPO's FIELD SAFETY PLAN FOR MINNESOTA SLIP

APPENDIX E

MPCA EQUIPMENT DECONTAMINATION SOP

Minnesota Pollution Control Agency's Decontamination SOP

The purpose of this standard operating procedure (SOP) is to define decontamination procedures for field equipment used for collecting soil, sediment, and water samples. Techniques for ridding equipment of both metals and organic contaminants are discussed. Sampling equipment is decontaminated between each sampling event to avoid cross contamination of samples and to help maintain a healthy working environment. Protective clothing is worn by all field technicians during sampling and decontamination as described in the health and safety plan.

It is the responsibility of the field sampling coordinator to assure that proper decontamination procedures are followed and that all waste materials produced by decontamination are properly managed. It is the responsibility of the project safety officer to draft and enforce safety measures that provide the best protection for all person involved directly with sampling or decontamination. All subcontractors (e.g., drilling contractors) are required to follow the decontamination procedures specified in the contract, the health and safety plan, and this SOP. Individuals involved in sampling and /or decontamination are responsible for maintaining a clean working environment and ensuring that contaminants are not introduced to the environment

All equipment will be decontaminated using a series of washes and rinses designed to remove materials of interest without leaving residues that will in any way interfere with analysis of the samples taken with that equipment. In addition, the decontamination site will be set up at a location separate from the sampling area in order to isolate these two activities.

Field equipment blanks will be taken at a frequency of 5 percent of samples and sent to the laboratory(s) for analysis along with regular samples. These blanks will serve as a quality assurance indicator of possible cross contamination of samples. When feasible, samples to be taken with the same equipment will be taken in order from lowest to highest suspected contaminant levels to minimize the chances of cross contamination.

The following is a list of materials that are required on site to support decontamination. The quantity and actual use of each item will be dependent on the overall size and nature of the sampling effort.

- Cleaning liquids and dispensers: soap and/or phosphate free detergent solutions, tap water, methanol, 10 percent nitric acid, distilled/deionized water
- Personal safety gear as defined in the project health and safety plan
- Chemical-free paper towels and/or tissues
- Powder-free disposable latex gloves

- Waste storage containers: drums, boxes, plastic bags
- Plastic ground cloth on which to lay clean equipment
- Cleaning containers: plastic and/or galvanized steel tubs and buckets
- Cleaning brushes with non-contaminating stiff bristles
- Steam cleaning apparatus (supplied by drilling contractor).

The materials used in decontamination activities are located a minimum of 15-30 feet downwind of the sampling site as designated by the task leader. Decontamination will be carried out before moving to the next sampling site to avoid transporting contaminants.

PROCEDURES

Regardless of the type of contamination that requires removal, the basic steps involved are the same. Procedures unique to organic, metal, and organic/metal combined contamination are discussed in their respective sections that follow.

Step 1: Gross Removal of Material

Steam Cleaning

Depending on the availability of apparatus (e.g., drilling operations), steam cleaning combined with brushing is the preferred method of initial material removal. Using steam alone introduces little further contamination, and is a very efficient way of removing materials. Equipment such as spatulas, split spoons, and drill flights are placed in and/or suspended over tubs that catch contaminated wash waters for proper disposal.

Detergent Wash

In cases where steam apparatus is not available, a phosphate free detergent wash and tap water rinse may be used. A detergent bath is formulated in a tub large enough to hold the equipment to be washed leaving enough volume to hold the tap water rinses. All material is brushed from the equipment into the tub. The equipment is rinsed with tap water while suspended over the wash tub. Because detergents can contain low levels of interfering contaminants for both organic and metals analysis, the thoroughness of the final rinse in this step is of utmost importance. When the analyte levels in the samples to be taken by the decontaminated equipment are suspected to be very low (e.g., background level), it is recommended that the detergent wash be replaced by a distilled water wash or steam cleaning when available, followed by a decontamination equipment blank as described below.

Step 2: Specific Contaminant Removal

Organic Contaminants

For removal of general organic contaminants, the solvent of choice is methanol because a) it dissolves all contaminants of concern and b) it is miscible with water which means it can be removed with a water rinse. The equipment is suspended over a tub and rinsed from the top down with high purity methanol delivered by peristaltic pump for large pieces, or a squirt bottle for smaller pieces. Rinse wastes are disposed of according to the project health and safety plan.

Metal Contaminants

Metals require acid solvents for efficient removal. Nitric acid is the acid of choice because of its ability to dissolve all of the metals of concern. The equipment is suspended over a tub and rinsed from the top down with 10 percent nitric acid delivered by peristaltic pump for large pieces, or a squirt bottle for smaller pieces. Rinse wastes are disposed of according to the project health and safety plan.

Combined Organic/Metals Contaminants

When equipment will be used to take samples that will be analyzed for both metal and organic constituents, the acid rinse is performed followed by the methanol rinse, each as described above. Due to the difficulty in obtaining organics free acids, and the ease of obtaining metals free methanol, the order of the two rinses must not be reversed.

Step 3: Final Distilled/Deionized Water Rinse

A final rinse with distilled/deionized water is carried out last to remove the contaminant specific solvents (i.e., nitric acid and/or methanol). Because these solvents may themselves interfere with sample analyses, this step is very important and must be carried out thoroughly. The equipment is suspended over a waste tub, and rinsed from the top down with distilled/deionized water delivered by pump of squirt bottle, depending on equipment size. In the case of metals decontamination, a simple pH monitoring technique (e.g., pH paper) may be used to monitor rinse water in determining rinse completion.

Step 4: Air Dry

Before an equipment blank is taken, the equipment is laid out on a clean plastic ground cloth and allowed to dry. The equipment should be protected from gross contamination during the drying process.

Equipment Blanks

Equipment Blanks are taken between selected samplings as described in the sampling and Analysis Plan. Equipment is rinsed with distilled water that is subsequently collected in a sample container. The rinsate sample is then labeled and shipped as a blind sample to the laboratory(s) with regular samples. One blank is created in this way for each analysis to be performed on samples taken with this equipment unless otherwise stated in the quality assurance plan. The equipment should be protected from contamination between the time the blank is taken and the time the next sample is collected.

APPENDIX F

ANALYTICAL SOPs

APPENDIX G

TOXICITY TESTING SOPS

APPENDIX H

ENSR'S QA MANUAL

APPENDIX I

MDH'S QA MANUAL

APPENDIX J

EN CHEM, INC.'s STATEMENT OF QUALIFICATIONS