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Lake Michigan Mass Balance Study (LMMB) Methods Compendium

Volume 1: Sample Collection Techniques

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Disclaimer

This document describes sampling and analytical methods used by PIs participating in the LMMB Study. Due to the nature and low concentrations of pollutants monitored in the study, many of the methods used in the LMMB Study represent state-of-the art techniques that will be refined further as new technology is developed and as necessary to resolve matrix interferences. Therefore, the procedures described in this compendium should be considered to accurately reflect procedures in use by the LMMB Study PIs at the time of publication. Users of this document should recognize that these procedures are subject to change.

Users of this document also should recognize that these methods do not constitute "approved EPA methods" for use in compliance monitoring programs. Publication of these methods is intended to assist users of LMMB Study data and to provide a reference tool for researchers interested in building upon LMMB Study findings. Mention of company names, trade names, or commercial products does not constitute endorsement or recommendation for use

Foreword

The Lake Michigan Mass Budget/Mass Balance (LMMB) Study was initiated in late 1993 as part of the Lakewide Management Plan (LaMP) for Lake Michigan. The Lake Michigan LaMP and the LMMB Study were developed to meet requirements mandated by Section 118 of the Clean Water Act (CWA); Title III, Section 112(m) of the Clean Air Act Amendments; and Annex 2 of the Great Lakes Water Quality Agreement. Organizations participating in the development of these programs included: EPA Region 5, the EPA Great Lakes National Program Office, the National Oceanic and Atmospheric Administration, the U.S. Geological Survey, the U.S. Fish and Wildlife Service, the Michigan Department of Natural Resources, the Wisconsin Department of Natural Resources, the Illinois Department of Natural Resources, and the Indiana Department of Environmental Management. In general, the primary goal of the LaMP and the LMMB Study is to develop a sound, scientific base of information with which to guide future toxic load reduction efforts at the federal, state, and local levels.

This compendium describes the sampling and analytical methods used in the LMMB Study. For ease of use, the compendium is organized into three volumes. Volume 1 describes sampling procedures used in the study; Volumes 2 and 3 describe analytical procedures used by each PI. Because sampling apparatus and techniques are generally geared towards specific matrices, Volume 1 is organized according to sample matrix (e.g., air, water, sediment, tissue, etc). Volumes 2 and 3 are organized by pollutant type (e.g, organics, metals, biologicals) because laboratories and instrumentation are typically set up to address specific pollutants rather than specific matrices.

Each Principal Investigator (PI) was required to follow specific quality control requirements necessary to meet data quality and measurement quality objectives for the LMMB Study. To assist users of this document, Appendix A provides the measurement quality objectives (MQOs) established by each PI for his/her sampling and analysis program.

Finally, EPA has made no attempt to standardize the procedures submitted by PIs for publication in this compendium. Therefore, the methods provided in this document contain varying levels of detail. Appendix B provides names, addresses and phone numbers for each PI and for each EPA Project Officer (PO). Specific questions about the procedures used in the study should be directed to the appropriate PI or PO listed in Appendix B.

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Volume 1

Chapter 1: Air

Standard Operating Procedure for Air Sampling for Semivolatile Organic Contaminants Using the Organics High-Volume Sampler

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December 1993

Standard Operating Procedure for Air Sampling for Semivolatile Organic Contaminants Using the Organics High-Volume Sampler

1.0 Overview

This SOP is intended to provide a step by step procedure for collecting airborne suspended particles on quartz fiber filters and airborne semivolatile organic contaminants on XAD-2 resin cartridges using a High-Volume (Hi-Vol) sampler.

The data collected from analyses of 20.3 x 25.4 cm quartz filters and XAD-2 cartridges from the organics Hi-Vol samplers will be used primarily for the Lake Michigan Loading Study (LMLS) and the Integrated Atmospheric Deposition Network (IADN) programs. Samples at the Sleeping Bear Dunes site, which is part of the Integrated Atmospheric Deposition Network, were sampled and analyzed by Indiana University. The sampling method is identical apart from a few minor differences in QC samples. This site represents 10 % of the samples for this method. The objectives of the programs are to determine the loadings of persistent toxic contaminants from the atmosphere to the Great Lakes from both urban and regional sources. Sampling sites have been strategically located around the Great Lakes basin to provide these estimates.

A modified Hi-Vol sampler is used for the collection of suspended particles and organic contaminants in air. The modification consists of an aluminum cylinder behind the filter holding a XAD-2 cartridge. Specific analytes of interest that will be collected from this sampler are listed in Table 1. The sampler operates for one 24-hour period every 12 days. Samples are collected during the week following the installation of filters. Therefore, every other week, the sampler will not contain filters or a cartridge, unless blanks are run.

The flow rate through the sampler is 34 cubic meters per hour. This interval is used because of the need to collect about 800 cubic meters of air in order to get a reliable measurement of the target contaminants at the remote sites in the network. Because of the low concentrations of target compounds, the operator must follow this protocol carefully to insure sample integrity.

This sample will be collected by passing air through a 20.3 x 25.4 cm quartz filter and then through an XAD-2 resin cartridge. The sampler inlet is a standard TSP shelter. The filters, which are pre-cleaned and pre-weighed at the Illinois State Water Survey (ISWS), and the XAD-2 cartridge are shipped to the site, and returned to ISWS for analyses. The analytical methods are documented in laboratory SOPs.

The following procedure is used by the field operator to maintain the organics Hi-Vol sampler, and to remove and replace glass fiber filters and XAD-2 cartridges in a manner that will maintain sample integrity. Dates of operation and sample collection will be provided in the monthly site operation protocol. Generally one filter and cartridge sample will be collected every 12 days. The site must be visited each week to collect samples and set-up samplers for the next week's sample collection. Any questions on the sampling methods or operation of equipment should be directed to the following individuals. The Principal Investigator will be the prime contact for all methodological and general questions. The EPA Project Lead is the second contact if the Principal Investigator cannot be contacted.

Table 1. Elements/Contaminants to be Determine on Glass Fiber Filters and XAD-2 Resin

Filter	Parameter
Glass fiber	Total suspended particles Organic Carbon
XAD-2	PCB Congeners Chlorinated Pesticides a-HCH g-HCH p,p' DDT and metabolites HCB Dieldrin Alpha-chlordane Gamma-chlordane Trans-nonachlor Atrazine PAHs acenaphthylene acenaphthene fluorene phenanthrene anthracene fluoranthene pyrene chrysene benzo(a)anthracene benzo(b)fluoranthene benzo(k)fluoranthene benzo(a)pyrene indeno(123cd)pyrene dibenzo(a,h)anthracene benzo(ghi)perylene retene coronene benzo(e)pyrene

Sampling Protocol and General Operations
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2.0 Summary of Method

Site operators will visit the site weekly to check for proper functioning of equipment and to either collect a sample or set-up the sample collector. Samples will be collected on the prescribed day. If it is raining or snowing, or hazardous conditions prevail, samples may be collected later in the day at the discretion of the site operator. If the sample can not be collected on the prescribed sampling day, the Principal Investigator must be notified. The following sampling activities will take place in the order listed.

1) Initial equipment inspection and testing.
2) Filter/cartridge removal and labeling.
3) Packaging filter/cartridge and sample report form for shipment.
4) Installation of a new filter/cartridge and setting flow rate.
5) Resetting the sampler timer.
6) Waste disposal and clean up.
7) Sample shipment

Steps 1 through 3, 6 and 7 will be conducted when the filters are changed and Steps 1 and 4 through 6 during collector set-up. Each of these steps will be detailed in the following sections.

3.0 Sample Handling and Preservation

Due to the expense of sampling and analyzing the quartz filters and XAD-2 cartridges, a limited number of sites have been selected in order to achieve the goals of this study. Therefore, every sample is important and represents a significant portion of that site's yearly estimate. Any contamination through mishandling or lack of preservation could cause a bias in the program estimates. The filter/cartridge should only be removed from, and installed into the holders in an enclosed area. The cartridges should be at the same temperature as the holders to avoid a tight fit due to thermal expansion.

Once in place, the filters should not be removed until the end of the sampling cycle (one 24-hour sampling period over a 12-day period). Follow all procedures for filter removal, packaging and shipment.

4.0 Interferences

Due to the nature of the chemicals being collected, all precautions should be taken to avoid contamination of the sample and sampler during weekly visits and sample collection. The sampler functions to collect samples of airborne particles that will be analyzed for the parameters list in Table 1. It is very important to avoid touching the filters and to prevent any dust or dirt from contaminating the deposit on the filter. The surfaces on the organics hi-vol inlet should be inspected each week and any dust or dirt wiped away with a damp cloth.

5.0 Safety

In any field operation, emphasis must be place on safety. Site operators must be aware of the potential safety hazards to which they are subjected. Follow all safety protocols and equipment guidelines, and be prepared for emergency situations. The site operator is responsible for his/her safety from potential hazards including but not limited to:

5.1 Travel: When traveling to the site be sure to check on road conditions and weather advisories. Carry emergency supplies (warm clothing, food, water) when traveling in the winter. Always let someone know where you're going and when you expect to be back. Always carry a first aid kit.

5.2 Electrical: For obvious problems (fire, scorching, blown fuses), turn off the power for the circuit involved and notify ISWS. Never attempt electrical repairs other than replacing fuses and circuit boards. Unplug the sampler before making replacements. Be especially cautious if conditions are wet.

5.3 Insect pests: If you are allergic to insect stings, you should carry a kit prescribed by a physician. Be especially cautious if nests or large numbers of stinging insects are present. Notify ISWS of all problems.

6.0 Equipment and Supplies

Careful use, proper maintenance and cleaning extends the life of serviceable field equipment. Permission should be obtained from the Principal Investigator to use anything other than the equipment and supplies mentioned in this list (supplied by ISWS).

6.1 Serviceable Equipment

These items will stay at the site at all times.

-Modified Hi-Vol sampler for organics (pump and timer unit, inlet shelter)
-Filter holder with snap-on cover
-XAD-2 cartridge holder
-Fine forceps

6.2 Consumable Equipment

These items will be sent to the site operator in bulk or once every four weeks.

-Pre-weighed, numbered quartz fiber filters
-XAD-2 cartridges
-XAD-2 transport tins
-Teflon tape
-Black electrical tape
-Latex gloves
-Spare fuses
-Kimwipes

7.0 Calibration and Standardization

The Hi-Vol sampler will be checked quarterly against a standard orifice by ISWS personnel. A magnehelic gauge provides a flow check before and after each sampling run.

7.1 Sampler Inlet

Each week check the condition of the sampler inlet and the quartz fiber filter cover plate. Wipe up any dust and dirt using a damp Kimwipe.

7.2 Timer and Pump Unit

Figure 1 shows the mechanical timer and Figure 2 shows the electronic timer. Each week check the operation of the timer and pump. The following checks should be made:

1) The time of day should be correct to local time.
2) The "Total Sampling Time" should have advanced 24 hours (1440 minutes) from the previous week, if a sample period was programmed during the preceding week.

Turn on the pump manually (see Section 8.1) and let it run for two minutes to determine magnehelic reading.

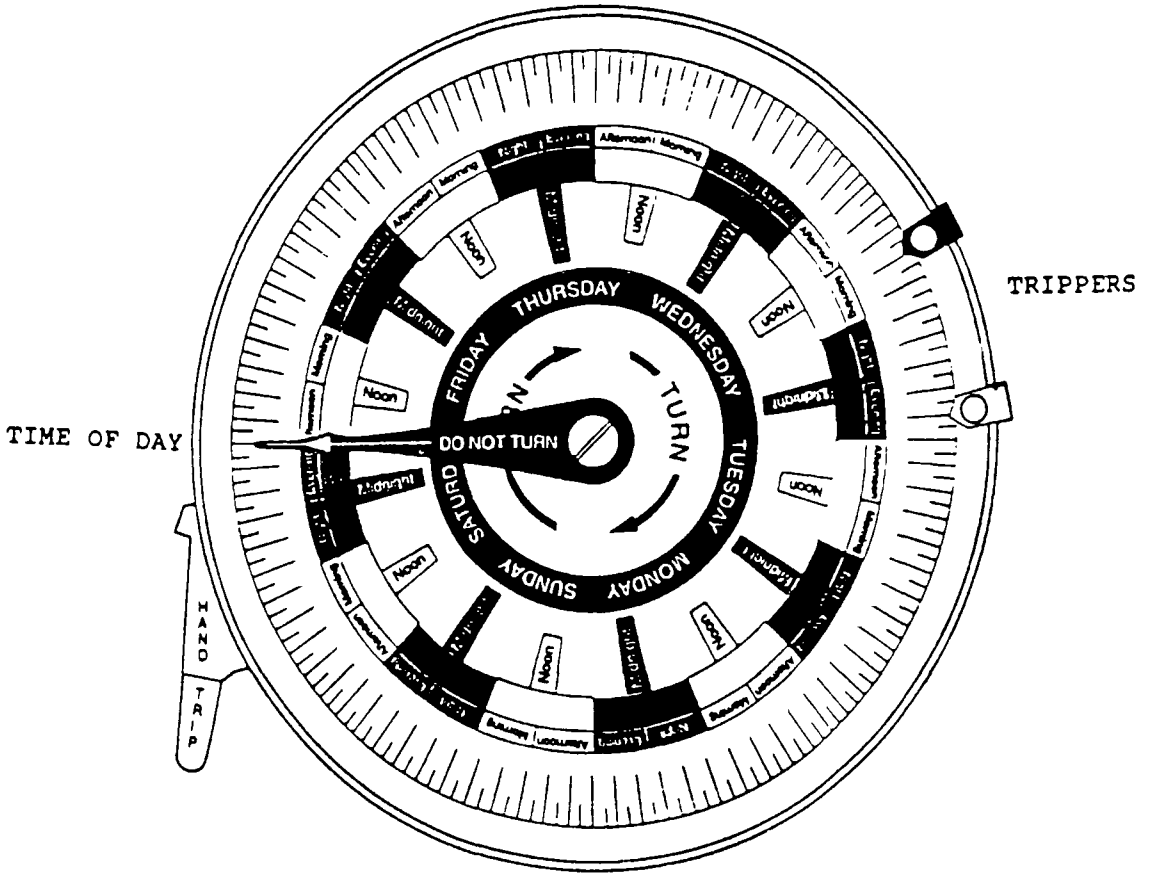

Figure 1. Mechanical Timer

8.0 Procedures

The following procedures will be discussed:

1) Initial Inspection.
2) Filter/cartridge removal and labeling.
3) Filter/cartridge packaging for shipment.
4) Installation of new filter/cartridge.
5) Setting the clock and sample timer.
6) Waste disposal/clean-up.
7) Sample shipment.

Steps 1 through 3, 6 and 7 will be conducted when the filters are changed (every two weeks) and Steps 1 and 4 through 6 during collector set-up. Each of these steps will be detailed in the following sections.

8.1 Initial Inspection (mechanical timer).

Note: This timer is on most of the Organics Hi-Vols.

Upon arrival at the site, make an initial inspection of the equipment to determine proper operation for the week. This procedure is accomplished every week. When a sample is set up, this procedure should be used to check final settings before leaving the site. Refer to Figure 1 for timer details. Check the elapsed time counter reading on the lower left corner of the timer. Record this number on the Data Reporting Form. The counter reads in hundredths of an hour. The large red arrow should point to the correct day and time.

Turn on the sampler by moving the "*Hand Trip*" switch to the "*On*" position and note whether the pump is running normally. After two minutes, record the value on the magnehelic on the Sample data Sheet and the Weekly Site Visit Sheet. Turn the sampler off after two minutes.

This inspection, which should be entered into the Weekly Site Visit Sheet and the Sample Data Sheet, will include:

1) General comments. Comments that might affect the sample collection that week, i.e., fire in the area, wind storms, abnormal precipitation, vandalism, etc.

2) Equipment evaluation. Note any damage to equipment. If the sampler is not operating properly, notify ISWS as soon as possible.

3) Magnehelic reading.

4) Total Sampling Time reading.

8.2 Initial Inspection (electronic timer).

Note: This timer is installed in most of the TSP Hi-vols and some of the organics Hi-vols.

Upon arrival at the site, make an initial inspection of the equipment to determine proper operation for the week. This procedure is accomplished every week. When a sample is set up, this procedure should be used to check final settings before leaving the site. Refer to Figure 2 for timer details. Check the timer to confirm that the following settings:

The "*Power*" switch should be "*On*"

- The "*Set*" switch should be on "*Display*"
- The "*Display*" switch should be in "*Time of the Day*" position
- The "*Sampler*" switch should be in "*Timer*" position
- The "*Sample After*" should be on the setting required on the previous week.
- The "*Sample Every*" switch should be on nine day setting.
- The "*SampleFor*" switch should be on the 24 hour setting.

If, on the prior week, the sampler was set to collect a sample, *the Total Sampling Time* reading on the timer should have advanced 1440 minutes. Check this reading and record it on the Data Reporting Form.

Turn on the sampler by moving the "*Sampler*" switch to the "*On*"position and note whether the pump is running normally. After two minutes, record the value on the magnehelic on the Weekly Site Visit Sheet and the Sample Data Sheet. Turn the sampler off after two minutes.

This inspection, which should be entered into the Weekly Site Visit Sheet and the Sample Data Sheet, will include:

1) General comments. Comments that might affect the sample collection that week, i.e., fire in the area, wind storms, abnormal precipitation, vandalism, etc.

2) Equipment evaluation. Note any damage to equipment. If the sampler is not operating properly, notify ISWS as soon as possible.

3) Magnehelic reading.

4) *Total Sampling Time* reading.

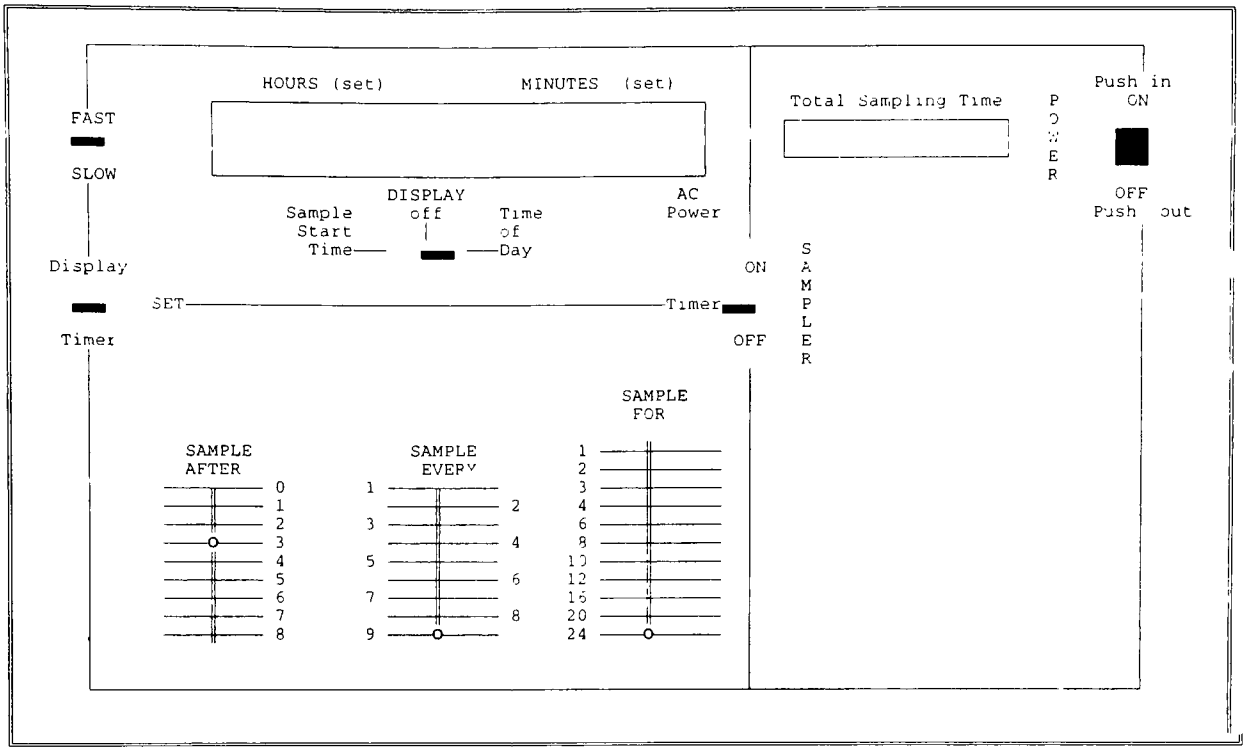

Figure 2. Electronic Timer

8.3 Filter/Cartridge Removal and Labeling

At the end of a sampling cycle, the filter and cartridge are removed by the following procedure. The quartz fiber filter should not be touched, and should be placed in aluminum foil as soon as possible. The following procedures are accomplished only during the replacement of the filter/cartridge.

8.3.1 Glass Fiber Filter Removal

1) Turn on the sampler manually and record the magnehelic gauge reading after two minutes.

2) Lift the triangular hood of the sampler in order to extract the filter holder. The filter is protected by a filter cover plate that exposes the filter during the sampling period. This plate should be covering the filter. While unscrewing the filter holder leave this plate down. Remove the filter holder from the sampler by unscrewing the nuts on the corners of the holder in a diagonal pattern. Let the nuts fall to side, freeing the filter holder.

3) Lift the filter cover plate and remove the filter holder. Place the snap-on filter cover over the filter holder to protect the filter from dust when transporting it to the enclosure. Close the sampler hood and transport the filter holder to an enclosed area.

4) Once in an enclosed area, remove the snap-on filter cover. Remove the quartz fiber filter by unscrewing the outer casing of the filter holder which is held on by nuts on the short sides of the filter holder.

5) Place latex gloves on. Remove the filter and fold it in half lengthwise with the deposit side facing in. Wrap the filter securely in the same piece of aluminum foil that the filter originally came in (the dull side of the foil should face the filter). Attach a label on the outside of the aluminum foil and place the filter in a zip-lock plastic bag.

8.3.2 XAD-2 Cartridge Removal

Refer to Figure 3.

1) Open the front door of the sampler, exposing the cartridge holder. To remove holder, loosen the hand screw nut on the *top* of the cartridge holder. Once the top has been completely loosened and off, proceed to unscrew the *bottom* nut. This nut remains on the cartridge holder. Remove the cartridge holder and transport the holder to an enclosed area.

2) Once inside the enclosure, turn the cartridge holder upside down in order to remove the stainless steel cartridge containing the XAD-2 resin.

Wrap the XAD-2 cartridge in aluminum foil and place the resin cartridge into the resin cartridge transport tin. Seal the tin by placing a piece of Teflon tape around the area where the top and bottom meet. Cover this with black electrical tape. Place a label on the tin

8.3.3 Sample Labeling

All organics Hi-Vol air samples should be labeled using the same alphanumeric system. The label includes:

The "Site ID" letter for the site,
The "Sample" which will be "H" for Hi-Vol samples and "T" for TSP samples.
The "Sample Type", designating either a routine sample (01), duplicate (02), or a QA sample,
The "Matrix" designation, "F" for the glass fiber filter and "C" for the XAD-2 resin cartridge and,
The "Date" of collection in a year-month-day format.

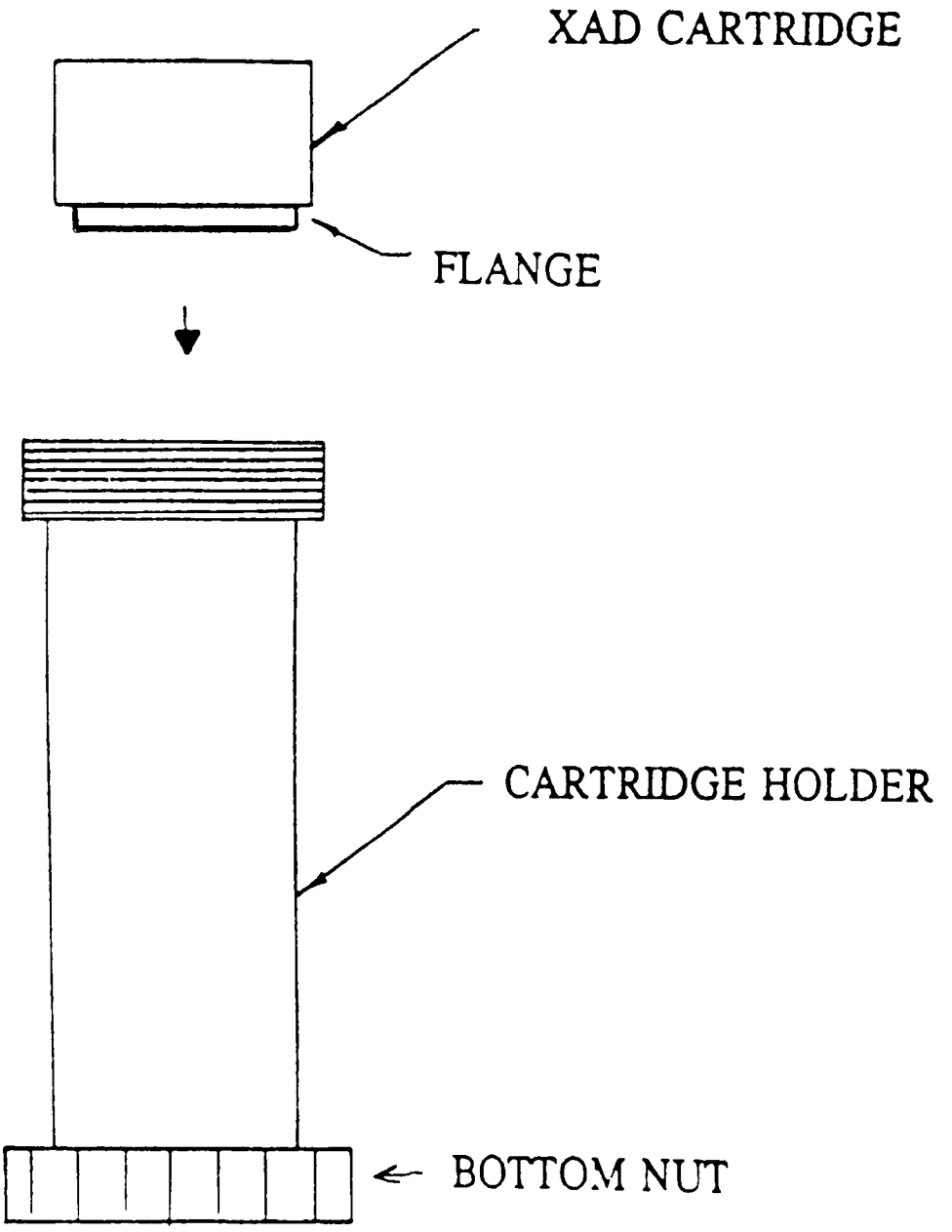

Figure 3. XAD-2 Cartridge and Cartridge Holder

An example label and the valid codes are listed below.

Hi-Vol Sample

Site	Sample	Samp.Type	Matrix	Year	Month	Day				
____	____	____	____	____	____	____	____	____	____	____

Valid Codes

Site ID		Sample	Sample Type
U-Brule River	S-Sleeping Bear Dunes	H- Hi-Vol	01- Routine Sample
C-Champaign	B-Beaver Is.	T- TSP	02-Duplicate Sample
N-Manitowoc	E-Eagle Harbor		TB- Trip Blank
W-Chiwaukee	T-Sturgeon Point	Matrix	FB- Field Blank
V-South Haven	I-Indiana Dunes		
M-Muskegon	J-IIT Chicago	C- XAD Cartridge	
L-Lake Guardian		F- Filter	

Example: SH-01C-930119 is the code for a routine organics Hi-Vol XAD-2 sample collected at the Sleeping Bear Dunes site on January 19, 1993.

8.4 Filter Packaging for Shipment

The filter and cartridge should be shipped in a in a box with packing material. They may be shipped together with other samples.

8.5 Installation of New Filter/Cartridge

At the start of a new sampling cycle, a new filter and cartridge should be installed. The monthly site protocol will list the dates that installation of the filter and cartridge is to take place.

8.5.1 Quartz Fiber Filter Installation

1) Examine the filter holder. It should be wiped clean with a damp (DI water) cloth if necessary.

2) Place on a pair of latex gloves. Within the enclosure, unwrap one of the pre-weighed and place it in the filter holder, *numbered side facing up*. Save the aluminum foil in a plastic bag for use when returning the exposed filter.

3) Close the filter holder by tightening the screw nuts on either side of the holder.

4) Place the snap-on filter covering over the filter holder for transport to the sampling device.

5) At the sampling device, lift up the sampler hood and the filter cover plate. Remove the snap-on filter covering and place the filter holder into the proper position.

6) Place the filter holder nuts onto the filter holder and tighten diagonally. Place the filter cover plate over the filter holder and close the sampler hood.

8.5.2 XAD-2 Cartridge Installation: Refer to Figure 3.

1) Place on a pair of latex gloves. Within the enclosure, open a new resin cartridge sampling tin and unwrap the aluminum foil.

2) Place the XAD-2 cartridge into the cartridge holder *with the flange facing down.* Transport the cartridge holder to the sampler.

3) At the sampler, open the sampling door, make sure the orange o-ring at the bottom of the cartridge holder is seated in the proper groove. Install the cartridge holder, *bottom end first,* screwing the hand screw nut on the cartridge onto the threaded pump device.

4) Make sure the orange o-ring at the top of the cartridge holder is in place and screw the top of the cartridge holder into place by holding the cartridge holder steady and using the hand screw nut to tighten onto the threaded end of the cartridge holder.

5) Turn the sampler on. If the motor does not run smoothly, there may be a leak. Retighten the fittings on the filter and cartridge holders. Once the motor is running smoothly, record the magnehelic reading after two minutes.

8.6 Setting the Clock and the Timer

8.6.1. Mechanical Timer

This procedure is used during sample set-up in samplers with mechanical timers. Refer to Figure 1 for timer details.

1) Turn the large ring clockwise so that the red pointer points to the correct day and time.

2) Attach the switch trippers to the timer ring. The *silver*-colored tripper should be positioned at the start day and time and the *black* tripper on the end day and time specified in the monthly site protocol. The trippers should be attached so that the thumb screw is to the front. The screws should be hand tightened so that the trippers rest firmly against the rim of the ring.

3) Be sure to record the elapsed time reading.

8.6.2 Electronic Timer

This procedure is used during sample set-up in samplers (TSP samplers and a few of the organics Hi-vols) with electronic timers. Refer to Figure 2 for timer details.

1) Check whether the "*Time of the Day*" display is correct. Toggle to the "*Sample Start Time*" and see if this reads "09.00" Record any deviations on the site log and on the sample data sheet. To reset either setting, place the "*Display*" switch to the proper setting and use the "*Fast/Slow*" toggle to make adjustments. The "*Time of the Day*" should be the current time using military units. The "*Sample Start Time*" should be set to "09.00". The sample start time must be at least 30 minutes after the time of day and *the function switch must be left in the "Time of the Day" position.*

To set up the sample run:

2) Position the "*Sample After*" switch to the number of days to be skipped before the start of the first sampling period. This position will change each week and will need to be calculated from the sampling date specified in the monthly site protocol. Position "0" will initiate sampling the first time the "*Time of Day*" equals "*Sample Start Time*" For example if the present time is 10:00 and the sample start time is 09:00 sampling will start 23 hours later. If position "1" is selected, sampling will start one day + 23 hours later at 09:00.

3) The "*Sample Every*" switch sets the sampler to repeat the sampling cycle after the indicated number of days. This switch should be left in the maximum position (nine days) unless otherwise directed.

4) The "*Sample For*" switch sets the sampling time in hours and should be left at the 24-hour setting unless directed otherwise.

Note: Some of the samplers have positive detent switches rather than knobs. These must be seated in the detent to control the sampler.

5) Set the "*Sampler*" switch to the "*Timer*" position. Finally, push the "*Set*" switch down to the "*Timer*" position momentarily and release. This enters the new sampling program. This initializes all timing functions. These steps must be done last, after all other switches have been set.

6) Be sure to record the *Total Sampling Time* reading.

Check the timer to confirm that the following settings:

- The "POWER" switch should be "ON"
- The "SET" switch should be on "DISPLAY"
- The "DISPLAY" switch should be in "TIME OF DAY" position

- The "SAMPLER" switch should be in "TIMER" position
- The "SAMPLE AFTER" should be on the setting required for the next sampling period.
- The "SAMPLE EVERY" switch should be on nine day setting.
- The "SAMPLE FOR" switch should be on the 24 hour setting.

8.7 Waste Disposal and Clean-up

Waste may include materials used to clean the inlet and packaging materials. Dispose of these properly.

8.8 Sample Shipping

Once they are properly packaged (8.4), send the samples, Sample Data Sheets, and the Weekly Site Visit Sheet to the Principal Investigator. Keep a copy of the both Sheets in the site log book. UPS 2nd day delivery is the preferred shipping method. U.S. Priority mail may also be used.

8.9 Quality Assurance Samples

Occasionally the protocol will require collection of quality assurance samples. Travel blanks are filters that are shipped with regular sample filters and stored at the site during the collection period. They should be returned to ISWS unopened after the specified period. Field blanks are filters that are installed in the sampler during the sampling period. The sampler should be unplugged or the silver tripper removed so that the sampler does not run. On samplers with electronic timers, the "SAMPLER" switch is turned off so that the sampler does not run. These samples should have a "TB" or "FB" in the sample code (Section 8.3.3). They are run to assess overall contamination during periods when the cartridge and filter are installed in the sampler but no air is being sampled. Specific instructions will be included in the shipping box for the implementation requirements of these samples.

8.10 Equipment Maintenance and Trouble Shooting

The sampler is exposed to weather, and wind-blown dust and should be cleaned each week by wiping dirty surfaces with a clean damp cloth.

The operation of the sampler should be checked each week. If the pump does not run or there is a problem with the timer display, consult the trouble shooting guide below and contact ISWS. For more information, consult the site operator's manual or contact the manufacturer, Andersen Samplers Inc., 4215 Wendell Dr., Atlanta, GA, 800-241-6898. Table 3 includes some trouble shooting information.

On samplers with electronic timers, a flashing timer indicates that a power failure has occurred. Reset the timer and notify ISWS.

Table 3. Trouble shooting

SYMPTOM/CAUSE	REMEDY
Collector fails to operate No power to instrument	Check switches and power source. Reset circuit breaker.
Circuit breaker continues to break Electrical short	Instrument needs servicing
Motor speed not steady Air leak	Tighten filter holder screws and cartridge holder nuts
Timing or programming error "SAMPLER" switch not on "TIMED", or "SAMPLE EVERY" not in proper position "DISPLAY" switch not on "TIME OF DAY"	Check that the switches are in detents and all instructions have been followed (see Section 2.4.2)

Occasionally motor replacement may be necessary. Figure 4 gives a step-by step description for removal of the old motor. Follow the sequence in reverse to install a new motor. This diagram applies only to IADN master sites (Eagle Harbor, Sleeping Bear, and Sturgeon Point).

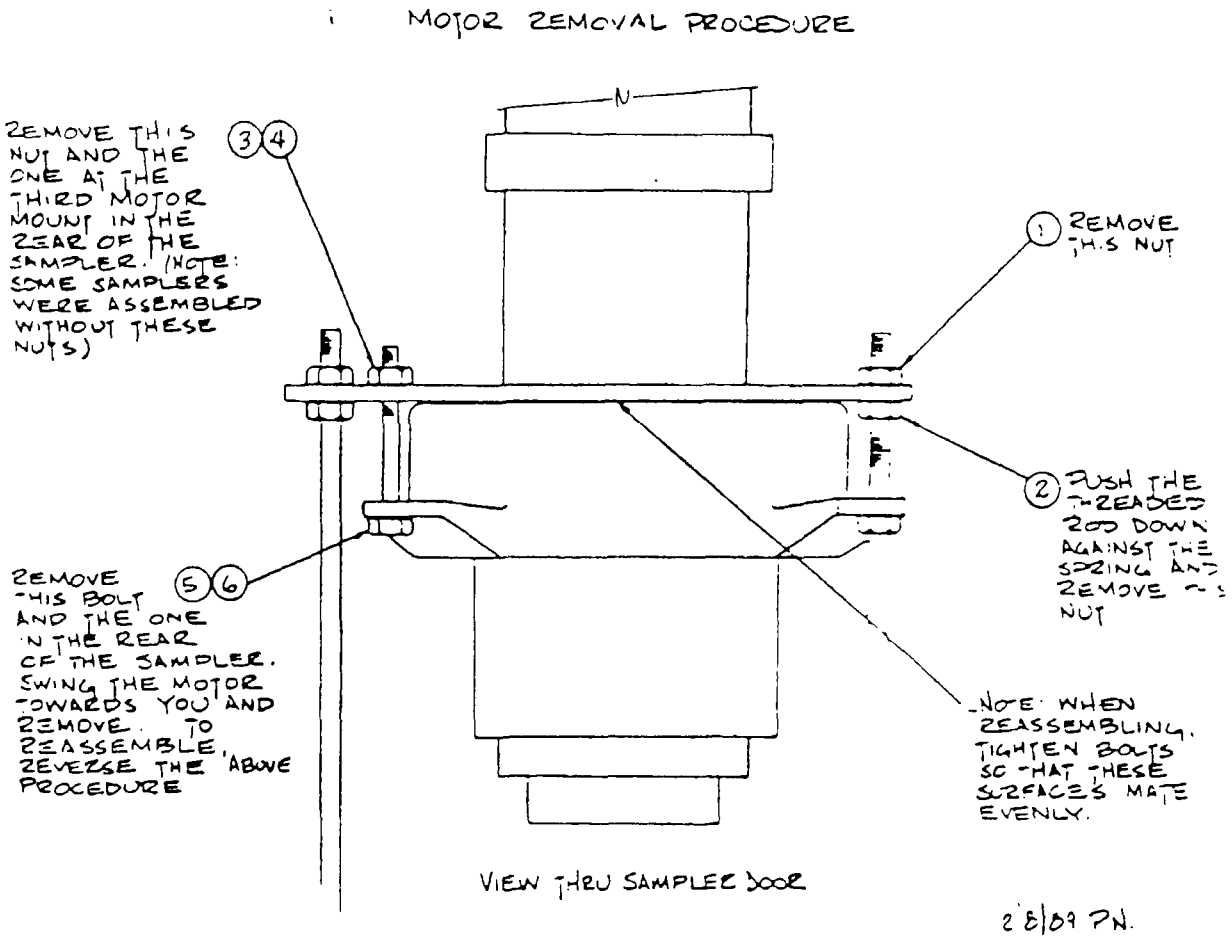

Figure 4. Motor Installation

High-Volume Summary

This summary does not take the place of the detailed SOP and should be used strictly to reinforce the procedure when in the field. Steps 1 through 3 will be conducted when the filters are changed, and Steps 1, 4 and 5 during collector set-up.

1.0 Initial Inspection

Upon arrival at the site, make an initial inspection of the equipment to determine proper operation for the week. This inspection will be entered into the Weekly Site Visit Sheet.

1.1 General comments. Comments that might affect the sample collection that week, i.e., fire in the area, wind storms, abnormal precipitation, vandalism, etc.

1.2 Equipment evaluation. Note any damage to equipment. If the sampler is not operating properly, notify ISWS as soon as possible.

1.3 Clean sampler inlet.

1.4 Magnehelic reading.

1.5 Total Sampling Time reading.

2.0 Filter/Cartridge Removal and Labeling

2.1 Glass Fiber Filter Removal

2.1.1 Turn on the sampler and record the magnehelic reading after two minutes.

2.1.2 Lift the triangular hood of the sampler in order to extract the filter holder. The filter is protected by a filter cover plate that exposes the filter during the sampling period. This plate should be covering the filter. While unscrewing the filter holder leave this plate down. Remove the filter holder from the sampler by unscrewing the nuts on the corners of the holder in a diagonal pattern. Let the nuts fall to side, freeing the filter holder.

2.1.3 Lift the filter cover plate and remove the filter holder. Quickly place the snap-on filter covering over the filter holder to protect the filter from dust when transporting it to the enclosure. Close the filter hood and transport the filter holder to an enclosed area.

2.1.4 Once in an enclosed area, remove the snap-on filter cover. Remove the quartz fiber filter by unscrewing the outer casing of the filter holder which is held on by nuts on the short sides of the filter holder.

2.1.5 *Place latex gloves on.* Remove the filter and fold the filter in half lengthwise with the deposit side facing in. Wrap the filter securely in the same piece of aluminum foil the filter came with, attach a label to the aluminum foil, and place the filter in a zip-lock plastic bag.

2.2 XAD-2 Cartridge Removal

2.2.1 Open the front door of the sampler, exposing the cartridge holder. To remove holder, loosen the hand screw nut on the *top* of the cartridge holder. Once the top has been completely loosened and off, proceed to unscrew the *bottom* nut. This nut remains on the cartridge holder. Remove the cartridge holder and transport the holder to an enclosed area.

2.2.2 Once inside the enclosure, turn the cartridge holder upside down in order to remove the stainless steel cartridge containing the XAD-2 resin. Wrap the XAD-2 cartridge in aluminum foil and place the resin cartridge into the resin cartridge transport tin. Seal the tin by placing a piece of Teflon tape around the area where the top and bottom meet then secure with electrical tape. Attach a label to the outside of the transport tin.

3.0 Filter Packaging for Shipment

The filter and cartridge should be shipped in a box with packing material. They may be shipped together with other samples.

4.0 Installation of New Filter/Cartridge

At the start of a new sampling cycle, a new filter and cartridge should be installed. The monthly site protocol lists the dates for installation and sampling.

4.1. Glass Fiber Filter Installation

4.1.1 Place on a pair of latex gloves. Within the enclosure, unwrap the aluminum foil from a pre-weighed filter and place it in the filter holder, *numbered side facing up.* Save the aluminum foil in a plastic bag.

4.1.2 Close the filter holder by tightening the screw nuts on either side of the holder.

4.1.3 Place the snap-on filter covering over the filter holder for transport to the Hi-vol sampler.

4.1.4 Lift up the sampler hood and the filter cover plate. Remove the snap-on filter covering and place the filter holder into the proper position.

4.1.5 Place the filter holder nuts (1-4) onto the filter holder and tighten diagonally. Place the filter cover plate over the filter holder and close the sampler hood.

4.2 XAD-2 Cartridge Installation

4.2.1 Within the enclosure, open a new resin cartridge sampling tin and unwrap the aluminum foil.

4.2.2 Place the XAD-2 cartridge into the cartridge holder with the flange facing down. Transport the cartridge holder to the sampler.

4.2.3 At the sampler, open the sampling door, make sure the bottom o-ring is properly seated, and install the cartridge holder, bottom end first, screwing the hand screw nut on the cartridge onto the threaded pump device.

4.2.4 Make sure the top o-ring is properly seated. Screw the top of the cartridge holder into place by holding the cartridge holder steady and using the hand screw nut to tighten onto the threaded end of the cartridge holder.

4.2.5 Turn on the sampler to check for leaks; record the magnehelic reading two minutes after the motor is running smoothly.

5.0 Setting the Clock and the Timer

Mechanical timer. Turn the timer ring so that the red pointer points to the correct day and time. Position the switch trippers so that the *Silver*-colored tripper is at the start day and time and the *Black* tripper at the end day and time specified in the site protocol. Make sure the thumb screws face out and are hand-tightened so that the trippers are firmly attached to the rim of the ring. Be sure to record the reading on the elapsed time counter.

For samplers with electronic timers refer to Section 8.6.2.

Appendix A
SAMPLE DATA SHEET

1. Station Name BRULE RIVER 2. Operator _____

3. Sample Start _____ End _____
Yr Mo Da Time Yr Mo Da Time

4. Sample Type Sample Codes

Precipitation Column UP – _____ – _____ Total Vol: _____ L

TSP/TOC Sampler Filter UT – _____ Filter ID _____

Timer End _____ Magnehelic End _____

Timer Start _____ Magnehelic Start _____

Set-up Date _____, + _____ days

Organics High Volume Sampler Filter UH – F– _____ Filter ID _____

Cartridge UH – C– _____

Timer End _____ Magnehelic End _____

Timer Start _____ Magnehelic Start _____

Dichot Sampler Codes UD– _____ UD– _____

Filter IDs: Fine _____ Coarse _____

1st Timer end _____ Rotameters _____ (C) _____ (T)
start _____

2nd Timer end _____ Rotameters _____ (C) _____ (T)
start _____

3rd Timer end _____ Rotameters _____ (C) _____ (T)
start _____

4th Timer end _____ Rotameters _____ (C) _____ (T)
start _____

5. Comments on sample condition or site operation

6. Date Shipped. _____ _____ Received. _____ _____ _____
Yr Mo Da initials Yr Mo Da initials

Appendix B
WEEKLY SITE VISIT SHEET

INSTRUCTIONS: Fill in all applicable space, enter general weather conditions (sunny, raining, etc.) and approximate values for weather variables. Enter "OK" after OPERATION for each sampler tested if the sampler is operating properly; if there is a problem, enter "X" and describe the problem at the bottom of the page. For the Hi-Vols and Dichots, fill in the TIMER, MAGNEHELIC, or ROTAMETER (Coarse and Total) readings in the appropriate spaces. For the MICs and metals AEROCHEM, enter the temperature inside the sampler and the approximate volume in the overflow container (MIC only). For all samplers, indicate with an "X" whether a sample was collected this week and if the sampler was set up for another run. Indicate with an "OK" whether the wind vane is pointing in the proper direction and whether the anemometer is turning.

SITE _____ DATE _____ TIME _____

WEATHER _____ TEMP _____ WIND DIR____ WIND SP ____

ORGANICS HIVOL #1 OPERATION ___ TIMER ____ MAGN ____

Sample: Collected ___ Set up ____

ORGANICS HIVOL #2 OPERATION ___ TIMER ____ MAGN ____

Sample: Collected ___ Set up ____

TSP HIVOL OPERATION ___ TIMER ____ MAGN ____

Sample: Collected ___ Set up ____

DICHOT #1 OPERATION ___ TIMER ____ C ____ T_____

Sample: Collected ___ Set up ____

DICHOT #2 OPERATION ___ TIMER ____ C ____ T_____

Sample: Collected ___ Set up ____

MIC #1 OPERATION ___ TEMP ____ VOL ____

Sample: Collected ___ Set up ____

MIC #2 OPERATION ___ TEMP ____ VOL ____

Sample: Collected ___ Set up ____

METALS AEROCHEM OPERATION ___ TEMP ____

Sample: Collected ___ Set up ____

STANDARD AEROCHEM OPERATION ___

Sample: Collected ___ Set up ____

MET SYSTEM WIND VANE ____ ANEMOMETER ____

PROBLEMS AND GENERAL OBSERVATIONS

OPERATOR ____

Standard Operating Procedure for Precipitation Sampling Using XAD-2 and MIC Collectors

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December 1993

Standard Operating Procedure for Precipitation Sampling Using XAD-2 and MIC Collectors

1.0 Overview

This SOP is intended to provide a step by step procedure for collecting and replacing an XAD-2 column in an MIC-B sampler.

The data collected from analyses of XAD-2 columns from the MIC (Meteorological Instruments of Canada) samplers will be used primarily for the Lake Michigan Loading Study (LMLS) and the Integrated Atmospheric Deposition Network (IADN) programs. Samples at the Sleeping Bear Dunes site, which is part of the Integrated Atmospheric Deposition Network, were sampled and analyzed by Indiana University. The sampling method is identical apart from a few minor differences in QC samples. This site represents 10 % of the samples for this method. The objectives of the programs are to determine the loadings of persistent toxic contaminants from the atmosphere to the Great Lakes from both urban and regional sources. Sampling sites have been strategically located around the Great Lakes basin to provide these estimates.

The MIC sampler is used for the collection of toxic organic compounds (PCBs, pesticides, and PAHs) in precipitation. Specific analytes of interest that will be collected from this sampler are listed in Table 1. The sampler operates continuously for four weeks. This interval is used because of the need to collect at least 5 L of precipitation (equivalent to about 1 inch of rainfall) in order to get a reliable measurement of the target chemicals. Because of the low concentrations of target compounds, the operator must follow this protocol carefully to insure sample integrity.

The sample will be collected by passing the precipitation through a column containing a 10 cm bed of XAD-2 resin. The column is prepared at the Illinois State Water Survey (ISWS), shipped to the site for exposure to the precipitation, and returned to ISWS for extraction and analysis of the chemicals listed in Table 1. These methods are documented in laboratory SOPs.

The following procedure is used by the field operator to maintain the MIC sampler, and to remove and replace XAD-2 columns in a manner that will improve sampler integrity. Although a sample will be collected every four weeks, the collector must be checked each week to ensure proper operation and to empty the overflow container if necessary. Any questions on the sampling methods or operation of equipment should be directed to the following individuals. The Principal Investigator will be responsible for informing the Project Lead at U.S.EPA of changes in this procedure and any problems that develop.

Table 1. Analytes Analyzed from XAD-2 Column

Parameter	Specific
PCB Congeners	To be determined
Chlorinated Pesticides	a-HCH g-HCH p,p' DDT and metabolites HCB Dieldrin Alpha-chlordane *Gamma-chlordane* Trans-nonachlor Atrazine
PAHs	acenaphthalene acenapthene fluorene phenanthrene anthracene fluoranthene pyrene chrysene benzo(a)anthrene benzo(b)fluoranthene benzo(k)fluoranthene benzo(a)pyrene indeno(123cd)pyrene dibenzo(a,h)anthracene benzo(ghi)perylene retene coronene benzo(e)pyrene

Sampling Protocol and General Operations

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Illinois State Water Survey
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Supplies and Packaging:
Mike Snider
Illinois State Water Survey
Phone: 217-244-8716

2.0 Summary of Method

Site operators will visit the site weekly to check for proper functioning of equipment and to ensure that the overflow container is less than ¾ full. Samples will be collected on the prescribed day at, or as close to 10:00 a.m. local time as practical. If it is raining or snowing, or hazardous conditions prevail, samples may be collected later in the day at the discretion of the site operator. If the sample can not be collected on the prescribed sampling day, the Principal Investigator must be notified. The following sampling activities will take place in the order listed.

1) Initial equipment inspection.
2) Check overflow container; measurement of precipitation volume if necessary.
3) Rinsing and cleaning of the precipitation collection surface with deionized (DI) water (from ISWS).
4) XAD column removal and labeling.
5) Packaging XAD column and sample report form for shipment.
6) Cleaning collection surface with methanol (supplied by ISWS).
7) Installation of a new column and setting flow rate.
8) Waste disposal and clean up.
9) Sample shipment.

Steps 1 and 2 will be conducted weekly; Steps 1 through 7 will be conducted when an XAD-2 column is changed (every four weeks). Each of these steps will be detailed in the following sections.

3.0 Sample Handling and Preservation

Due to the expense of sampling and analyzing the XAD-2 columns, a limited number of sites have been selected in order to achieve the goals of this study. Therefore, every sample is important and represents a significant portion of that site's yearly estimate. Any contamination through mishandling or lack of preservation could cause a bias in the program estimates. The XAD-2 column should remain moist with the water level between the top of the resin bed and the top of

the column. If the column is broken or dry on arrival, contact the Principal Investigator immediately. If the column drys out during the sampling period, DI water should be added. This must be noted in the site log and on the sample sheet. Before removal, DI water will be added to the column.

Once in place, the column should be wrapped tightly in aluminum foil to exclude light and should remain wrapped for removal and shipment. Follow all procedures for sample removal, packaging and shipment.

4.0 Interferences

Due to the nature of the chemicals being collected, all precautions should be take to avoid contamination of the sample and sampler during weekly visits and sample collection. The sampler functions to collect *precipitation samples*. Therefore, the sample collection surface and

the XAD column should not be exposed more than is necessary. This will minimize contamination from dry deposition of atmospheric particles. The sampler should be inspected weekly to verify that the sealing pad is mating properly with the top of the sampler. The XAD columns should be plugged at both ends and sealed in a plastic bag as soon as they are removed from the sampler.

Exposure of the XAD column to light can cause the degradation of some of the PAHs. Once installed, the XAD column must remain wrapped in aluminum foil.

Heaters and fans are included in the sampler to avoid temperature extremes that might damage the columns or degrade the samples. Proper maintenance of the heating unit is required, and it should be checked weekly when temperatures below freezing are possible (see Section 6.2).

5.0 Safety

In any field operation, emphasis must be place on safety. Site operators must be aware of the potential safety hazards to which they are subjected. Follow all safety protocols and equipment guidelines, and be prepared for emergency situations. The site operator is responsible for his/her safety from potential hazards including but not limited to:

Travel: When traveling to the site be sure to check on road conditions and weather advisories. Carry emergency supplies (warm clothing, food, water) when traveling in the winter. Always let someone know where you're going and when you expect to be back. Always carry a first aid kit.

Electrical: For obvious problems (fire, scorching, blown fuses), turn off the power for the circuit involved and notify ISWS. Unplug the sampler before replacing fuses and circuit boards. Do not attempt other electrical repairs. Be especially cautious if conditions are wet.

Insect pests. If you are allergic to insect stings, you should carry a kit prescribed by a physician. Be especially cautious if nests or large numbers of stinging insects are present. Notify ISWS of all problems.

Samp. Proc.: Never force glassware with unprotected hands. If the column arrives broken, return it to ISWS. Do not attempt to remove the Teflon plugs.

Chemicals: Methanol is toxic and should not be ingested, inhaled, or come into contact with bare skin.

6.0 Equipment and Supplies

Careful use, proper maintenance and cleaning extends the life of serviceable field equipment. Permission should be obtained from the Principal Investigator to use anything other than the equipment and supplies mentioned in these lists (supplied by ISWS).

6.1 Serviceable Equipment

These items will stay at the site at all times.

MIC Sampler (frame, motor, rain sensor, fan assembly)
Overflow tubing, funnel, and overflow container (25 L plastic carboy)
Space heater
Maximum/minimum thermometer
Graduated cylinders (2 L and 10 mL)
Precleaned Pyrex beaker (2 L)
Forceps
Teflon wash bottles (DI water and methanol)
Standard wash bottle (tap water)
Plastic bucket
Spare o-rings
Plastic bags
Teflon column outlet valve
Latex gloves
Log book
Report forms
Sample labels and marker
Kleen Guard coveralls
Kimwipes

A diagram of the MIC sampler and XAD column assembly is shown in Figure 1. General maintenance and trouble shooting are covered in Section 9.0.

6.2 Consumable Equipment

These items will be shipped to the site operator every 4 weeks.

XAD columns and Teflon plugs
Glass fiber filter pieces
Sample jar
Test tube brush
Shipping box and packaging materials
Freezer packs (summer only)

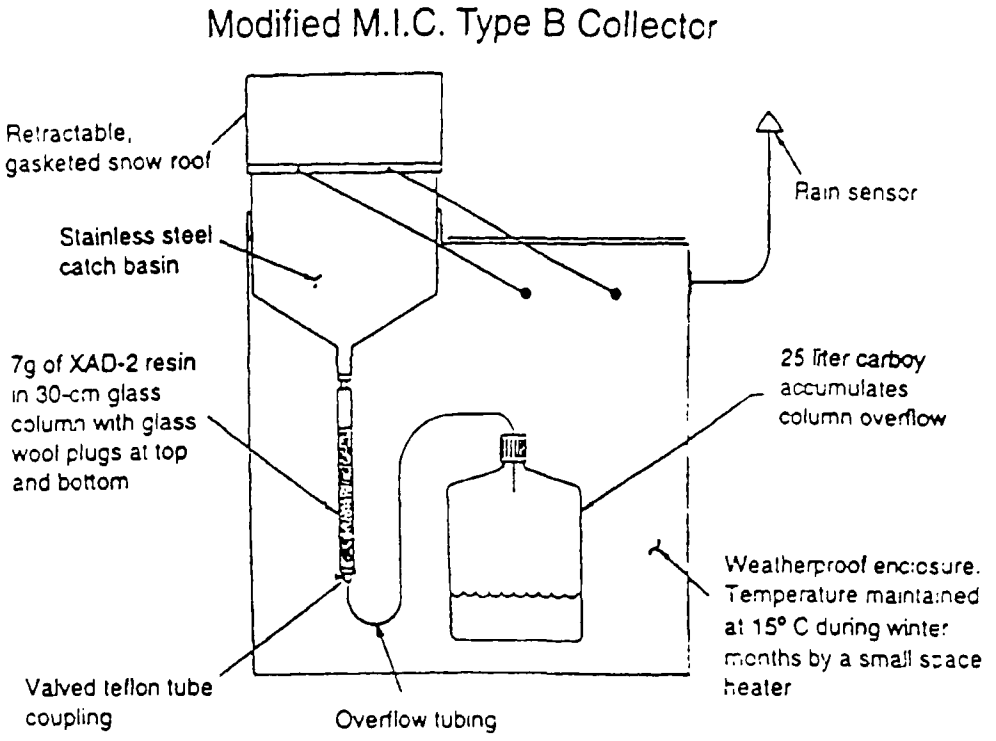

Figure 1. Schematic of the MIC Precipitation Collector

7.0 Calibration and Standardization

7.1 Rain sensor

Each week check the operation of the MIC sampler. If it is dry, wet the sensor with DI water; the cover should open immediately and close within five minutes if no additional wetting occurs. Clean any accumulated dirt off the sensor. Do not allow the sampler to remain open any longer than necessary. See Section 9.0 for more information.

7.2 Heater and Fan

The heater must operate properly in freezing temperatures to maintain proper operation of sampling equipment. The heater should maintain a $5^{\circ} \pm 10^{\circ}C$ temperature in the sampling enclosure. The heater will be calibrated at ISWS. When cold weather is expected, check that the heater is operational by turning up the heater thermostat until the heater comes on; set this thermostat at the calibration mark. During warm weather, make sure that the fan is operational by turning down the fan thermostat; set this thermostat at the calibration mark. Reset the maximum/minimum thermometer and record the temperatures each week.

8.0 Procedures

The following procedures will be discussed:

1) Initial equipment inspection
2) Measurement of precipitation volume in overflow containers
3) Rinsing precipitation collection surface
4) XAD column removal and labeling
5) XAD column packaging for shipment
6) Cleaning collector surface and funnel outlet
7) Installation of new column
8) Waste disposal/clean-up
9) Sample shipment

Steps 1 will be conducted weekly, Step 2 will be conducted as necessary, Steps 1 through 7 will all be conducted every four weeks when the column is changed.

8.1 Initial Inspection

Upon arrival at the site, make an initial inspection of the equipment to determine proper operation for the week. This inspection will be entered on the Weekly Site Visit Sheet and will include:

1) General comments. Comments that might affect the sample collection that week, i.e., fire in the area, wind storms, abnormal precipitation, vandalism, etc. If it is raining or snowing during the visit, note whether the sampler is open. If there is standing water in the funnel see Section 8.2 or if the column has gone dry.

2) Equipment evaluation. Note any damage to equipment. Check operation of the rain sensor if it's not raining (Section 6.1) and the heater or fan (Section 6.2). Check for interferences (Section 3.0). Check the Teflon sealing pad on the cover of the MIC. If it is loose, cracked, or holding water notify ISWS.

3) Record minimum/maximum temperature and reset thermometer.

8.2 Measurement of Precipitation Volume

This procedure will be done on a weekly basis if the overflow container is more than ¾ full. It will always be done when changing an XAD column. If possible do not perform this step during a precipitation event, since this will affect the volume estimate.

If this step has to be done during an event, immediately replace the overflow container with the plastic bucket; and record the amount of precipitation that passes through the column while the water in the full container is being measured. Measure the volume in 1 L increments using the large graduated cylinder. All measurements should be recorded in the Weekly Site Visit and Sample Data Sheets.

If there is standing water in the collection funnel, check that water is flowing through the column. If water is not flowing or flowing very slowly, close the valve on the column and remove it from the funnel catching the precipitation in the pre-cleaned beaker. Check for debris blocking the funnel outlet or the column outlet valve. Use the cleaning wire if necessary. Reconnect the column, adjust the flow (Section 8.8), and allow the water collected in the beaker to pass through the column. Return the beaker to ISWS for recleaning. If flow can not be restored, notify the Principal Investigator.

If the column has gone dry, add DI water from the Teflon wash bottle and try to determine where the leak is. Replace o-rings or tighten fittings as necessary. Note this and the approximate volume of DI water added on both the Weekly Site Visit Sheet and the Sample Data Sheet.

8.3 Rinsing the Precipitation Collection Surface

This procedure is carried out only during XAD column removal and replacement (every four weeks). If possible, do not perform this step during a precipitation event. Wait until all precipitation has drained from the collection funnel. Wear latex gloves at all times. If the system is plugged, see Section 8.2.

If the sample must be collected during a rain event, wear Kleen Guard coveralls making sure that all clothing extending over the collection surface is covered. If practicable, stand downwind of the instrument. Do not lean over the collecting surface.

1) Squirt DI water onto the rain sensor to open the sampler. Turn off the switch on the front of the sampler so that it remains open during the procedure.

2) Wearing latex gloves (and tyvex jacket if necessary), remove any obvious debris (bird droppings, leaves, etc.) from the collection funnel. The presence of debris should be noted on the Data Sheet.

3) Rinse the collection surface with about 200 mL of DI water (one wash bottle full) while wiping with the piece of precleaned glass fiber filter sent with the monthly supplies. This step removes adhering particles from the collection surface. Allow rinsings to pass through the column until the water level is halfway between the top of the resin bed and the top of the column (see Figure 1). If the temperature is so cold that water freezes on contact with the funnel, simply wipe of the collection surface with a dry piece of filter and go to Step 4.

4) Turn off the column outlet valve to maintain the water level in the column.

5) Seal the filter used to clean the collection surface in the glass jar.

6) Be sure to turn the power switch on the front of the sampler back on. Proceed to Section 8.4.

8.4 Column Removal and Labeling

The aluminum foil should remain on the column.

1) Unscrew the XAD column from the fitting at the base of the collection funnel. Cap the column with a Teflon plug. Make sure the black o-ring is in place.

2) Remove the overflow tube while turning the column upside down. Remove the outlet valve fitting and replace it with a Teflon plug. Make sure the black o-ring is in place.

3) Label the column (on the outside of the aluminum foil) and the glass sample jar containing the filter wipe using the same ID number (see Section 8.5).

4) Place the column in a plastic bag and proceed to Section 8.6.

8.5 Labeling Codes

All precipitation samples should be labeled using the same alphanumeric system.

- The "Site ID" letter for the site
- The "Sample" which will be "P" for precipitation samples
- The "Sample Type", designating either a routine sample (01), a duplicate (02), or a QA sample, field blank or travel blank (FB, TB)
- The "Date" of collection (end date of sample period) in a year-month-day format

An example label and the valid codes are listed below.

Precipitation Sample									
___	___	___	___	___	___	___	___	___	___
Site	Sample	Samp.Type		Year		Month		Day	

Site ID		Sample	Sample Type
U-Brule River	S-Sleeping Bear Dunes	P-Precipitation	01- Routine Sample
C-Champaign	B-Beaver Is.		02- Duplicate sample
N-Manitowoc	E-Eagle Harbor		TB- Trip Blank
W-Chiwaukee	T-Sturgeon Point		FB- Field Blank
V-South Haven	I-Indiana Dunes		
M-Muskegon	J-IIT Chicago		
L-Lake Guardian			

Example: SP-02-930119 is the code for a duplicate precipitation sample collected at the Sleeping Bear Dunes site on January 19, 1993. Both the column and the filter wipe should be labeled with this code.

8.6 Column Packaging for Shipment

The columns should be packed in the shipping containers provided by ISWS. Normally supplies for each sampling period will come in these boxes and they can be reused to return the samples. The columns and glass jars should be carefully packed using styrofoam "peanuts" so that the contents do not shift when the package is moved. During the winter (November through April), the box should be clearly labeled "*Do Not Freeze*" so that the shipper does not store the packages outside. During the summer (May to October), three pre-frozen freezer packs (supplied by ISWS) and a reset max/min thermometer should be included in the package.

8.7 Cleaning Collector Surface and Funnel Outlet

Prior to installation of a new column, the collection surface and funnel outlet must be cleaned.

8.7.1 Put on a new pair of gloves.

8.7.2 Place the white plastic bucket under the funnel outlet.

8.7.3 Clean the collector surface by rinsing with 200 mL of pesticide-free methanol (supplied by ISWS) with additional scrubbing with a clean Kimwipe if necessary. Clean the funnel outlet using the test tube brush.

8.7.4 Follow with a rinse of 1 L of tap water from the plastic wash bottle.

8.7.5 Follow with a rinse of 200 mL of DI water from the Teflon wash bottle.

8.7.6 Rinse the funnel outlet fitting and o-ring with methanol and DI water.

8.7.7 Proceed to Section 8.8.

8.8 Installation of a New XAD Column

8.8.1 Remove the aluminum foil to make sure the XAD bed in the column has not separated and is packed between the glass wool plugs. If it has separated, notify ISWS

8.8.2 Replace the aluminum foil and remove the Teflon plug on the bottom (unmarked) of the XAD column and replace it with the column outlet valve. Make sure the black o-ring is in place. Wrap the plug in aluminum foil and put it in a clean plastic bag for reuse when removing the cartridge.

8.8.3 Remove the top Teflon plug (marked red) and place it, wrapped in aluminum foil, in the plastic bag. Rinse the funnel outlet fitting with methanol. Screw the top of the column into the funnel outlet fitting. Make sure the black o-ring is in place.

8.8.4 Open the collector lid by moistening the rain sensor. Add about 50 mL of DI water to the collection funnel (these steps may not be necessary if rain is falling). Make sure water is flowing from the column outlet valve at the bottom of the column. Adjust the flow to between 10 and 15 mL/min using the column outlet valve. Measure the flow using the small graduated cylinder. Connect the outlet tube to the overflow container. The water level should come to rest between the top of the resin bed and the top of the column.

8.8.5 Empty all water from the overflow container and make sure the column is wrapped with aluminum foil.

8.9 Waste Disposal Clean-up

Waste may include materials (water, methanol) and glass fiber filter used to clean the collection surface. Empty any leftover liquid from the Teflon wash bottles into the plastic bucket and seal them in a plastic bag until the next column change. Return the test tube brush with the samples. The water-methanol mixture in the plastic bucket is biodegradable and can be put down the drain.

8.10 Sample Shipping

Once they are properly packaged (Section 8.6), send the samples, Sample Data Sheets, and Weekly Site Visit Sheet to the Principal Investigator. Keep a copy of both Sheets in the site log book. UPS 2nd day delivery is the preferred shipping method. U.S. Priority mail may also be used.

9.0 Quality Assurance Samples

Occasionally the protocol will require collection of quality assurance samples. Travel blanks are columns that are shipped with regular sample columns and stored unopened in the sampler during the collection period. They should be returned to ISWS unopened after the specified period. Field blanks are columns that are connected to the sampler funnel during the sampling period. The switch on the front of the sampler is turned off so that the sampler does not open and no rain passes over the column. Field blanks should include a funnel rinse just like regular samples. Travel blanks are run to assess the amount of sample contamination that occurs during shipment and storage. Field blanks assess overall contamination including shipment, storage, and passive contamination in the sampler during dry periods. These samples should have a "TB" or "FB" in the sample code (Section 8.5).

10.0 Equipment Maintenance and Trouble Shooting

The rain sensor grids are exposed to weather, dust, dirt, and pollutants and must be kept clean to avoid malfunctions. The grids should be cleaned every week by wiping the exposed side with a damp sponge or cloth, using a mild detergent if necessary. If a detergent is used, be sure to wipe off the grid thoroughly to ensure that a detergent film does not build up.

The operation of the sampler should be checked each week. If the cover is not seating properly on either side or if the movement of the cover is not smooth, refer to the trouble-shooting guide below. For more information, contact the manufacturer, MIC Co. 216 Duncan Rd, Richmond Hill, Ontario, Canada, 416-889-6653.

Cause	*Remedy*
Collector fails to operate	
No power to instrument	Check switches and power source
Blown fuse	Replace fuse
Faulty sensor board	Change sensor board
Faulty PC board	Change PC board
Motor will not switch off	
Limit switch and or cam out of adjustment	Readjust limit switch or cam
Limit switch broken	Replace limit switch
MIC Heater fails to operate	
Heater element burnt out	Change sensor board
Faulty component on PC board	Change PC board
Moving cover drops once it moves over top center	
Loose set-screw on motor sprocket	Tighten set-screw
Chain loose	Tighten chain
Cover does not return to funnel	
Dirt on sensor board	Clean sensor board
Heater on the sensor not operating	See "Heater fails to operate"

MIC Summary SOP

This summary does not take the place of the detailed SOP and should be used strictly to reinforce the procedure when in the field. Steps 1 and 2 will be conducted weekly; Steps 1 through 7 will be conducted when an XAD-2 sample is required (monthly).

1.0 Initial Equipment Inspection

Upon arrival at the site make an initial inspection of the equipment to determine proper operation for the week. This inspection which will be entered into the site operator's weekly activity sheet would include:

1.1 *General Comments* - Comments that might effect the sample collection activity that week.

1.2 *Equipment Evaluation* Determine whether the rain sensor and heater (see Section 6.1 and 6.2) or other mechanical devices are operating properly. Check the Teflon sealing pad.

1.3 *Record minimum/maximum temperature and reset thermometer.*

2.0 Overflow Container Measurement for Precipitation Volume

2.1 Remove overflow tubing from overflow container. If precipitation is occurring, place overflow tubing into spare overflow container.

2.2 Pour the contents of the overflow container into a graduated cylinder. Record each 1 L increment and discard contents of cylinder. Repeat procedure until contents of overflow container are empty. If the column is being changed, add any additional sample in the spare overflow container, reading the final portion to the nearest 10 mL.

2.3 Record the total volume estimate on the Weekly Site Visit Sheet. If the container is less than ¾ full, indicate an "N" in the appropriate space. If the visit is for removal and replacement of an XAD-column, record the total from that week on the Weekly Site Visit Sheet, and record the total (the summation of any weekly overflow measurement during the four-week sample collection period) on the Sample Data Sheet.

3.0 Rinsing and Cleaning of Precipitation Collection Surface

This procedure occurs only during XAD-2 cartridge removal and replacement (monthly).

3.1 Squirt DI water onto the rain sensor to open sampling lid and turn off the power.

3.2 Wearing latex gloves (and Kleen Guard coveralls if necessary), remove debris from the collection funnel. Rinse the collection surface with about 200 mL of DI water while scrubbing with a piece of glass fiber filter to remove deposited particles. Allow rinsings to pass over the column until the water level is between top of the column and the top of the resin bed (Figure 1). Close the column outlet valve to maintain water level in column and remove the outlet tubing. If the temperature is very cold, simply dry wipe with the filter.

3.3 Place glass fiber filter in sample jar.

4.0 XAD-2 Column Removal and Labeling

4.1 Unscrew the XAD-2 column from the collection funnel. Once removed, close the top with a Teflon plug. Make sure black O-ring is in place.

4.2 Remove column outlet valve and replace with Teflon plug. Make sure black O-ring is in place.

4.3 Place the column, wrapped in aluminum foil, into a plastic sampling bag.

4.4 Label cartridge (on the outside the aluminum foil) and sample jar (containing glass fiber filter) with the appropriate sample code (see Section 8.5). Place samples into shipping container for protection.

5.0 XAD Column Packaging for Shipment

5.1 Carefully pack the columns in the shipping box with styrofoam "peanuts." Enclose a reset max/min thermometer in the package and pre-frozen freezer packs (May through October only). During the winter (November through April), label the outside of the package *Do Not Freeze.*"

5.2 Ship to ISWS as soon as possible.

6.0 Cleaning Collector Surface and Funnel Outlet

6.1 Place new pair of gloves on.

6.2 Place the plastic bucket under funnel outlet.

6.3 Clean the collector surface by rinsing with 200 mL of pesticide-free methanol.

6.4 Follow with rinse of 1 L tap water. Scrub with a clean Kimwipe if necessary and use the test tube brush to clean the funnel outlet.

6.5 Follow with 200 mL rinse of DI water. Discard contents of overflow Container #2.

6.6 Rinse funnel outlet with methanol.

7.0 Installation of New XAD-2 Column

7.1 Remove the Teflon plug from the bottom (unmarked) of the new column and attach the column outlet valve. Make sure black o-rings are in place. Wrap the plug in aluminum foil and put it into plastic bag until the column is removed.

7.2 Remove the top plug (marked with red and wrap it with aluminum foil and place it in the plastic bag. Screw the top of the column into the funnel outlet. Make sure the black o-ring is in place.

7.3 Open collector lid by moistening rain sensor. Add about 50 mL DI water to the sample collection surface. Open the column outlet valve and adjust the flow to between 10 and 15 mL/min. using the small graduated cylinder to measure the volume. If it is raining, allow the rain to flow through the system. Connect the column outlet to the overflow container using the overflow tubing.

7.4 Wrap the XAD-2 column tightly with aluminum foil.

7.5 Keep the Teflon plugs in a plastic bag within enclosure for next column removal.

8.0 Waste Disposal/Clean-up

Waste includes water, methanol, glass fiber filter, test tube brush used to clean the collector after the XAD-2 column had been removed. Pour all liquids from wash bottles and bucket into the spare overflow container, cap and dispose of properly. Enclose the DI and methanol wash bottles in a plastic bag, and return the test tube scrub brush in the sample shipment to ISWS. The glass fiber filter, gloves, and other trash can be properly disposed.

9.0 Sample Shipping

Once packaged properly (see Section 8.6 of detailed SOP) send the samples (XAD-2 column and glass fiber filter from Sections 8.3 and 8.4 of detailed SOP), the Weekly Site Visit Sheet, the Sample Data Sheets to ISWS.

Appendix A

SAMPLE DATA SHEET

1. Station Name BRULE RIVER 2. Operator _____

3. Sample Start _____ End _____
Yr Mo Da Time Yr Mo Da Time

4. Sample Type Sample Codes

Precipitation Column UP – – _____ Total Vol: _____L

TSP/TOC Sampler Filter UT – _____ Filter ID _____

Timer End _____ Magnehelic End _____

Timer Start _____ Magnehelic Start _____

Set-up Date _____, + _____ days

Organics High Volume Sampler Filter UH – F– _____ Filter ID _____

Cartridge UH – C– _____

Timer End _____ Magnehelic End _____

Timer Start _____ Magnehelic Start _____

Dichot Sampler Codes UD– _____ UD– _____

Filter IDs: Fine _____ Coarse _____

1st Timer end _____ Rotameters _____ (C) _____(T)
start _____

2nd Timer end _____ Rotameters _____ (C) _____(T)
start _____

3rd Timer end _____ Rotameters _____ (C) _____(T)
start _____

4th Timer end _____ Rotameters _____ (C) _____(T)
start _____

5. Comments on sample condition or site operation:

6. Date Shipped: _____ _____ Received: _____ _____
Yr Mo Da initials Yr Mo Da initials

Appendix B

WEEKLY SITE VISIT SHEET

INSTRUCTIONS: Fill in all applicable space, enter general weather conditions (sunny, raining, etc.) and approximate values for weather variables. Enter "OK" after OPERATION for each sampler tested if the sampler is operating properly; if there is a problem, enter "X" and describe the problem at the bottom of the page. For the Hi-Vols and Dichots, fill in the TIMER, MAGNEHELIC, or ROTAMETER (Coarse and Total) readings in the appropriate spaces. For the MICs and metals AEROCHEM, enter the temperature inside the sampler and the approximate volume in the overflow container (MIC only). For all samplers, indicate with an "X" whether a sample was collected this week and if the sampler was set up for another run. Indicate with an "OK" whether the wind vane is pointing in the proper direction and whether the anemometer is turning.

SITE _____ DATE _____ TIME _____

WEATHER _____ TEMP _____ WIND DIR____ WIND SP ____

ORGANICS HIVOL #1 OPERATION ___ TIMER ____ MAGN ____

Sample: Collected ___ Set up ____

ORGANICS HIVOL #2 OPERATION ___ TIMER ____ MAGN ____

Sample: Collected ___ Set up ____

TSP HIVOL OPERATION ___ TIMER ____ MAGN ____

Sample: Collected ___ Set up ____

DICHOT #1 OPERATION ___ TIMER ____ C ____ T____

Sample: Collected ___ Set up ____

DICHOT #2 OPERATION ___ TIMER ____ C ____ T____

Sample: Collected ___ Set up ____

MIC #1 OPERATION ___ TEMP ____ VOL ____

Sample: Collected ___ Set up ____

MIC #2 OPERATION ___ TEMP ____ VOL ____

Sample: Collected ___ Set up ____

METALS AEROCHEM OPERATION ___ TEMP ____

Sample: Collected ___ Set up ____

STANDARD AEROCHEM OPERATION ___

Sample: Collected ___ Set up ____

MET SYSTEM WIND VANE ____ ANEMOMETER ____

PROBLEMS AND GENERAL OBSERVATIONS: OPERATOR_____

Standard Operating Procedure for Air Sampling for Metals Using the Dichotomous Sampler

Clyde W. Sweet
Office of Air Quality
Illinois State Water Survey
2204 Griffith Drive
Champaign, IL 61820

December 1993

Standard Operating Procedure for Air Sampling for Metals Using the Dichotomous Sampler

1.0 Overview

This SOP is intended to provide a step by step procedure for collecting samples of airborne particles on Teflon filters for metals analysis using the dichotomous sampler.

The data collected from analyses of 37 mm Teflon filters from the dichotomous samplers will be used primarily for the Lake Michigan Loading Study (LMLS) and the Integrated Atmospheric Deposition Network (IADN) programs. Samples at the Sleeping Bear Dunes site, which is part of the Integrated Atmospheric Deposition Network, were sampled and analyzed by Indiana University. The sampling method is identical apart from a few minor differences in QC samples. This site represents 10 % of the samples for this method. The objectives of the programs are to determine the loadings of persistent toxic contaminants from the atmosphere to the Great Lakes from both urban and regional sources. Sampling sites have been strategically located around the Great Lakes basin to provide these estimates.

The dichotomous sampler is used for the collection of airborne particles for analysis of trace elements. Specific analytes of interest that will be collected from this sampler are listed in Table 1. The sampler operates for four 24-hour periods during each four-week sampling cycle. The flow rate through the sampler is 1 cubic meter per hour. This interval is used because of the need to collect about 100 cubic meters of air in order to get a reliable measurement of the target chemicals at the remote sites in the network. Because of the low concentrations, the operator must follow this protocol carefully to insure sample integrity.

The samples will be collected by passing air through a 37 mm Teflon filter. The sampler inlet is mounted in a standard Hi-Vol shelter. The filters are pre-weighed at the Illinois State Water Survey (ISWS), shipped to the site for collection of airborne particles, and returned to ISWS, weighed, and shipped to the U.S.EPA labs in North Carolina for analysis of the trace elements listed in Table 1 by X-ray fluorescence (XRF) methods. These methods are documented in laboratory SOPs.

The following procedure is used by the field operator to maintain the dichotomous sampler, and to remove and replace Teflon filters in a manner that will maintain sample integrity. Although a single composite sample will be collected every four weeks, the collector must be checked and reset each week to ensure proper operation and to collect samples on the prescribed sampling periods. Any questions on the sampling methods or operation of equipment should be directed to the following individuals. The Principal Investigator will be the prime contact for all methodological and general questions. The EPA Project Lead is the second contact if the Principal Investigator cannot be contacted.

Sampling Protocol and General Operations

Principal Investigator:
Clyde W. Sweet
Illinois State Water Survey
2204 Griffith Dr.
Champaign, IL 61820

phone: 217-333-7191
Fax: 217-333-6540

Project Lead:
Angela Bandemehr
USEPA/GLNPO
77 W. Jackson
Chicago, IL 60604

phone: 312-886-6858
Fax: 312-353-2018

Equipment Operation and Maintenance

Paul Nelson
Illinois State Water Survey
phone: 217-244-8719
Fax: 217-333-6540

Supplies and Packaging

Mike Snider
Illinois State Water Survey
phone: 217-244-8716

Table 1. Trace Elements Determined on Teflon Filters

Aluminum	Silicon	Phosphorus	Sulfur	Chlorine
Potassium	Calcium	Titanium	Vanadium	Chromium
Manganese	Iron	Cobalt	Nickel	Copper
Zinc	Arsenic	Selenium	Bromine	Lead
Strontium	Tin	Iodine	Cadmium	

2.0 Summary of Method

Site operators will visit the site weekly to check for proper functioning of equipment and to set the sampler timer for the next prescribed sampling day. If it is raining or snowing, or hazardous conditions prevail, samples may be collected later in the day at the discretion of the site operator. If the sample can not be collected on the prescribed sampling day, the Principal Investigator must be notified. The following sampling activities will take place in the order listed.

1) Initial equipment inspection and testing.
2) Resetting the sampler timer (weekly).
3) Changing the Teflon filters (every four weeks).
4) Filling out the Sample Data Sheet (weekly).
5) Packaging filters and sample report form for shipment.
6) Installation of a new filters and setting flow rate.
7) Waste disposal and clean up.
8) Sample shipment.

Steps 1, 2, and 4 will be conducted weekly; Steps 1 through 8 will be conducted when the filters are changed (every four weeks). Each of these steps will be detailed in the following sections.

3.0 Sample Handling and Preservation

Due to the expense of sampling and analyzing the Teflon filters, a limited number of sites have been selected in order to achieve the goals of this study. Therefore, every sample is important and represents a significant portion of that site's yearly estimate. Any contamination through mishandling or lack of preservation could cause a bias in the program estimates. The filters are very fragile and should not be removed from the polypropylene filter holders. As the new filters are being installed, if a hole is discovered, the filter should not be installed but returned to ISWS.

Once in place, the filters should not be removed until the end of the sampling cycle (four 24-hour sampling periods over a four-week period). Follow all procedures for filter removal, packaging and shipment.

4.0 Interferences

Due to the nature of the chemicals being collected, all precautions should be taken to avoid contamination of the sample and sampler during weekly visits and sample collection. The sampler functions to collect samples of airborne particles that will be analyzed for trace elements. It is very important to avoid touching the filters and to prevent any dust or dirt from contaminating the deposit on the filter. The surfaces on the inlet should be inspected each week and any dust or dirt wiped away with a damp cloth.

5.0 Safety

In any field operation, emphasis must be place on safety. Site operators must be aware of the potential safety hazards to which they are subjected. Follow all safety protocols and equipment guidelines, and be prepared for emergency situations. The site operator is responsible for his/her safety from potential hazards including but not limited to:

Travel: When traveling to the site be sure to check on road conditions and weather advisories. Carry emergency supplies (warm clothing, food, water) when traveling in the winter. Always let someone know where you're going and when you expect to be back. Always carry a first aid kit.

Electrical: For obvious problems (fire, scorching, blown fuses), turn off the power for the circuit involved and notify ISWS. Never attempt electrical repairs other than replacing fuses and circuit boards. Unplug the sampler before any replacements are made. Be especially cautious if conditions are wet.

Insect pests: If you are allergic to insect stings, you should carry a kit prescribed by a physician. Be especially cautious if nests or large numbers of stinging insects are present. Notify ISWS of all problems.

6.0 Equipment and Supplies

Careful use, proper maintenance and cleaning extends the life of serviceable field equipment. Permission should be obtained from the Principal Investigator to use anything other than the equipment and supplies mentioned in this list (supplied by ISWS).

Serviceable Equipment

These items will stay at the site at all times.

Dichotomous sampler (pump and timer unit, inlet shelter).
Calibration filters in polypropylene holders.
Pre-weighed Teflon filters in polypropylene holders in snap-lock Petri dishes.
Kimwipes.
Spare fuses.

7.0 Calibration and Standardization

The dichotomous sampler will be recalibrated quarterly against a mass flow meter by ISWS personnel. New rotameter settings will be marked on the instrument and entered in the log book along with the date of recalibration.

7.1 Sampler Inlet

Each week check the condition of the inlet surfaces. Wipe up any dust and dirt using a damp (DI water) Kimwipe.

7.2 Timer and Pump Unit

Figure 1 shows the timer. Each week check the operation of the timer and pump. The following checks should be made:

1) The time of day should be correct to the present local time.
2) The "Total Sampling Time" should have advanced 24 hours (1440 minutes) if a sample period was programmed during the preceding week.

Turn on the pump manually and let it run for one or two minutes. When the filters are changed every four weeks, reset the rotameter using the calibration filters (Section 8.4) before installing the new clean filters.

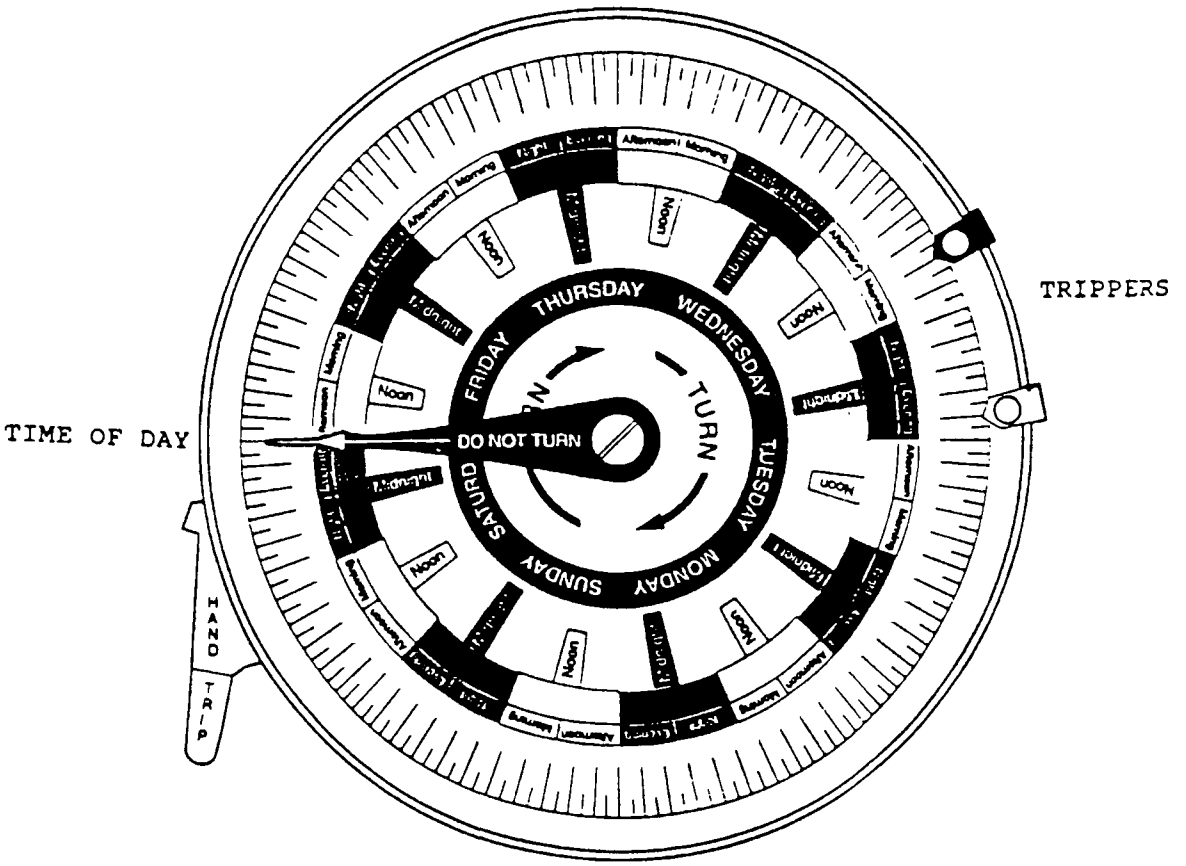

Figure 1. Mechanical Timer

8.0 Procedures

The following procedures will be discussed:

1) Initial Inspection.
2) Setting the clock and timer.
3) Filter removal and labeling.
4) Filter packaging for shipment.
5) Adjusting sampler flow rates.
6) Installation of new filters.
7) Setting the clock and timer.
8) Waste disposal/clean-up.
9) Sample shipment.

Steps 1 and 2 will be conducted weekly; Steps 1 through 8 will all be conducted every four weeks when the filters are changed.

8.1 Initial Inspection

Upon arrival at the site, make an initial inspection of the equipment to determine proper operation for the week. This procedure is accomplished every week. When a sample is set up, this procedure should be used to check final settings before leaving the site. Refer to Figure 1 for timer details. Check the elapsed time counter reading on the lower left corner of the timer. Record this number on the Sample Data Sheet. The counter reads in hundredths of an hour or minutes. The large red arrow should point to the correct day and time. Note any discrepancies on the Sample Data Sheet. The switch trippers should be firmly attached to the timer rim with the silver tripper at the last scheduled start time and the black tripper at the last scheduled stop time.

Turn on the sampler by moving the "Hand Trip" switch to the "On" position and note whether the pump is running normally. After two minutes, record the value on the rotameters on the Sample Data Sheet. Turn the sampler off after two minutes.

This inspection which should be entered onto the Weekly Site Visit Sheet and the Sample Data Sheet will include:

1) General comments. Comments that might affect the sample collection that week, i.e., fire in the area, wind storms, abnormal precipitation, vandalism, etc.

2) Equipment evaluation. Note any damage to equipment. If the sampler is not operating properly, notify ISWS as soon as possible.

3) Rotameter reading.

4) Total Sampling Time reading.

8.2 Setting the Clock and Timer

If a sampling period is scheduled for the next week but no filter change is required, set the clock and timer at this point. Follow the instructions in Section 8.7.

8.3 Filter Removal and Labeling

At the end of a sampling cycle, the filters are removed and replaced by the following procedure. It is extremely important that the filters not be touched, and should be placed in the snap-lock Petri dish as soon as possible. The following procedures are accomplished only during the replacement of filters and not every week.

1) Remove the two Teflon filters by unscrewing the locking nut (Figure 2). The filters must remain in their polypropylene holders. There will be a coarse particle filter in a yellow holder and a fine particle filter in a white holder. Place the each filter and holder in a separate snap-lock Petri dish for shipment. Be careful not to touch the filter.

2) Sample Labeling

All dichotomous (dichot) air samples should be lbeled on the outside of the Petri dish using the same alphanumeric system. The label includes:

- The "Site ID" letter for the site,
- the "Sample" which will always be "D" for dichotomous samples,
- the "Sample Type", designating either a routine sample (01) or a QA sample (FB, TB),
- the "Filter" size designation, a "C" for course or an "F" for fine, and
- the "Date" of collection in a year-month-day format.

An example label and the valid codes are listed below.

Dichotomous Sample

Site	Sample	Samp.Type	Filter	Year	Month	Day
____	____	____	____	____	____	____

Valid Codes

Site ID		Sample	Sample Type	Filter
U-Brule River	S-Sleeping Bear Dunes	D-Dichotomous	01- Routine Sample	C-Coarse
C-Champaign	B-Beaver Is.		FB- Field Blank	F-Fine
N-Manitowoc	E-Eagle Harbor		TB- Trip Blank	
W-Chiwaukee	T-Sturgeon Point			
V-South Haven	I-Indiana Dunes			
M-Muskegon	J-IIT Chicago			
L-Lake Guardian				

Example: SD-01C-930119 is the code for a routine dichot coarse particle sample collected at the Sleeping Bear Dunes site on January 19, 1993 (date filters are removed from the sampler).

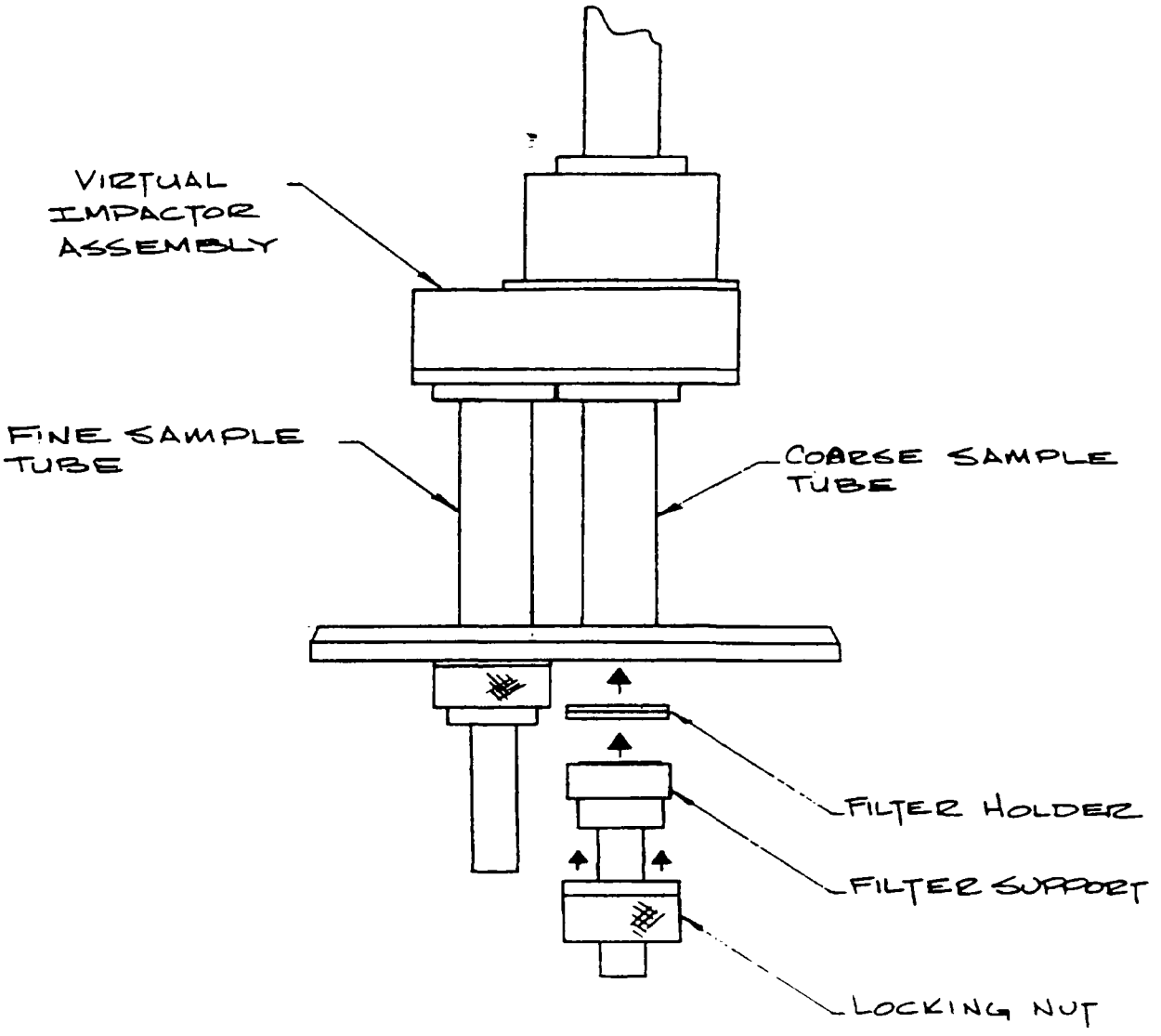

Figure 2. Schematic of the Dichotomous Sampler

8.4 Filter Packaging for Shipment

The filters in labeled Petri dishes should be shipped in a padded envelope or in a box with packing material. They may be shipped together with other samples.

8.5 Adjusting Sampler Flow Rates

8.5.1 Install the calibration filters (labeled side facing up) and tighten the locking nut (Figure 2).

8.5.2 Turn the sampler on using the hand trip switch (Figure 1) and allow it to warm up for at least 10 minutes.

8.5.3 Set the rotameters on the instrument to the most recent calibration set points. These should be marked on the instrument and entered into the site log. The set point on the rotameter scale should be lined up with the center of the metal ball using the adjustment knobs at the base of the rotameters. The rotameter on the left sets the flow to the coarse particle filter and the one on the right sets total flow. If the ball is stuck or there is some other problem with the rotameter, do not attempt to adjust it; but notify ISWS as soon as possible.

8.5.4 Turn off sampler and remove calibration filters.

8.6 Installation of New Filters

At the start of a new sampling cycle (every four weeks), fresh filters should be installed after the flow has been adjusted (Section 8.5).

8.6.1 Place new pre-weighed filters in their color-coded filter holders into the instrument. The labels should face up and the holder color should match the color patch on the instrument (yellow for the coarse position and white for the fine position). Once the filters are in place, tighten the locking nut. Be careful not to touch the filters themselves.

8.6.2 Set the timer for the next sampling period as described in next section.

8.7 Setting the Clock and Timer

8.7.1 Turn the large ring (Figure 1) clockwise so that the red pointer points to the correct day and time.

8.7.2 Attach the switch trippers to the timer ring (see Figure 1). The *silver*-colored tripper should be positioned at the start day and time and the *black* tripper on the end day and time specified in the monthly site protocol. The trippers should be attached so that the thumb screw is to the front. The screws should be hand tightened so that the trippers rest firmly against the rim of the ring.

8.7.3 Be sure to record the elapsed time reading on both the Weekly Site Visit Sheet and the Sample Data Sheet.

8.8 Waste Disposal Clean-up

Waste may include materials used to clean the inlet and packaging materials. Dispose of these properly.

8.9 Sample Shipping

Once they are properly labeled and packaged (Sections 8.3 and 8.4), send the samples, Sample Data Sheet, and Weekly Site Visit Sheet to the Principal Investigator. Keep a copy of both Sheets in the site log book. UPS 2nd day delivery is the preferred shipping method. U.S. Priority mail may also be used.

9.0 Quality Assurance Samples

Occasionally the protocol will require collection of quality assurance samples. Travel blanks are filters that are shipped with regular sample filters and stored at the site during the collection period. They should be returned to ISWS unopened after the specified period. Field blanks are filters that are installed in the sampler during the sampling period. These samples are run to assess contamination of the filters during periods when the sampler is not running. When field blanks are run the sampler should be unplugged. These samples should have a "TB" or "FB" in the sample code (Section 8.3). Specific instructions will be included in the Monthly Site Protocol with the requirements for these samples.

10.0 Equipment Maintenance and Trouble Shooting

The sampler is exposed to weather, and wind-blown dust and should be cleaned each week by wiping dirty surfaces with a clean damp cloth.

The operation of the sampler should be checked each week. If the pump does not run or there is a problem with the timer display, consult the trouble shooting guide below and contact ISWS. For more information, consult the site operator's manual or contact the manufacturer, Andersen Samplers Inc., 4215 Wendell Dr., Atlanta, GA, 800-241-6898. Table 2 includes some trouble shooting information.

Table 2. Trouble shooting

CAUSE	REMEDY
Collector fails to operate No power to instrument	Check switches and power source. Reset circuit breaker.
Circuit breaker continues to break Electrical short	Instrument needs servicing
Operates for a short period then shuts off Overloaded filter or plugged line	Check filters and lines. Call ISWS.

Dichot Air Sample Summary SOP

This summary does not take the place of the detailed SOP and should be used strictly to reinforce the procedure when in the field. Steps 1 and 2 will be conducted weekly; Steps 1 through 8 will be conducted when the filters are changed (every four weeks).

1.0 Initial Inspection

Upon arrival at the site make an initial inspection of the equipment to determine proper operation for the week. This inspection which will be entered into the site operators weekly activity sheet would include:

1.1 Comments on site and area conditions that might have affected the sample collection activity that week.

1.2 Determine whether the pump is operating properly by turning it on and allowing it to operate for two minutes. Record the rotameter and timer readings on the Sample Data Sheet and Weekly Site Visit Sheet.

1.3 Wipe clean the surfaces on the inlet.

2.0 Setting Clock and Sample Timer

This is done when a 24-hour sampling period is scheduled for the coming week and no filter change is required. Follow the procedure in Section 6.0.

3.0 Filter Removal and Labeling

3.1 Unscrew the locking nut (Figure 2) and remove the filters in their plastic holders being careful not to touch the filter. Place each filter directly into its own snap-lock Petri dish.

3.2 Label the Petri dish with the appropriate code (see Section 8.3).

4.0 Filter Packaging for Shipment

Carefully pack the filters in padded containers. Ship to ISWS as soon as possible.

5.0 Adjust Flow Rates

5.1 Install calibration filters.

5.2 Turn the pump on and let it warm up for at least 10 minutes

5.3 Adjust the flows to the latest calibration set point using the adjustment knob at the bottom of the rotameters

5.4 Turn off the pump and remove the calibration filters

6.0 Installation of New Filters

6.1 Install new pre-weighed filters in the sampler. The labels on the filter holders should face up, and the holder color (yellow for coarse and white for fine) should match the color code patches on the sampler. Tighten the locking nut.

6.2 Attach the switch trippers to the timer ring (see Figure 1). The *Silver-colored* tripper should be positioned at the start day and time and the *Black* tripper on the end day and time specified in the monthly site protocol. The trippers should be attached so that the thumb screw is to the front. The screws should be hand tightened so that the trippers rest firmly against the rim of the ring.

7.0 Waste Disposal/Clean-up

Dispose of all trash properly.

8.0 Sample Shipping

Once packaged properly send the samples, the Weekly Site Visit Sheets for the month, the Sample Reporting Forms to ISWS via UPS or Priority Mail.

Appendix A

SAMPLE DATA SHEET

1. Station Name BRULE RIVER 2. Operator _____

3. Sample Start _____ End _____
Yr Mo Da Time Yr Mo Da Time

4. Sample Type Sample Codes

Precipitation Column UP – _____ Total Vol: _____L

TSP/TOC Sampler Filter UT – _____ Filter ID _____

Timer End _____ Magnehelic End _____

Timer Start _____ Magnehelic Start _____

Set-up Date _____, + _____ days

Organics High Volume Sampler Filter UH – F– _____ Filter ID _____

Cartridge UH – C– _____

Timer End _____ Magnehelic End _____

Timer Start _____ Magnehelic Start _____

Dichot Sampler Codes UD– _____ UD– _____

Filter IDs: Fine _____ Coarse _____

1st Timer end _____ Rotameters _____ (C) _____ (T)
start _____

2nd Timer end _____ Rotameters _____ (C) _____ (T)
start _____

3rd Timer end _____ Rotameters _____ (C) _____ (T)
start _____

4th Timer end _____ Rotameters _____ (C) _____ (T)
start _____

5. Comments on sample condition or site operation:

6. Date Shipped: _____ _____ Received: _____ _____
Yr Mo Da initials Yr Mo Da initials

Appendix B

WEEKLY SITE VISIT SHEET

INSTRUCTIONS: Fill in all applicable space, enter general weather conditions (sunny, raining, etc.) and approximate values for weather variables. Enter "OK" after OPERATION for each sampler tested if the sampler is operating properly; if there is a problem, enter "X" and describe the problem at the bottom of the page. For the Hi-Vols and Dichots, fill in the TIMER, MAGNEHELIC, or ROTAMETER (Coarse and Total) readings in the appropriate spaces. For the MICs and metals AEROCHEM, enter the temperature inside the sampler and the approximate volume in the overflow container (MIC only). For all samplers, indicate with an "X" whether a sample was collected this week and if the sampler was set up for another run. Indicate with an "OK" whether the wind vane is pointing in the proper direction and whether the anemometer is turning.

SITE _____ DATE _____ TIME _____

WEATHER _____ TEMP _____ WIND DIR____ WIND SP ____

ORGANICS HIVOL #1 OPERATION ___ TIMER ____ MAGN ____

Sample: Collected ___ Set up ____

ORGANICS HIVOL #2 OPERATION ___ TIMER ____ MAGN ____

Sample: Collected ___ Set up ____

TSP HIVOL OPERATION ___ TIMER ____ MAGN ____

Sample: Collected ___ Set up ____

DICHOT #1 OPERATION ___ TIMER ____ C ____ T____

Sample: Collected ___ Set up ____

DICHOT #2 OPERATION ___ TIMER ____ C ____ T____

Sample: Collected ___ Set up ____

MIC #1 OPERATION ___ TEMP ____ VOL ____

Sample: Collected ___ Set up ____

MIC #2 OPERATION ___ TEMP ____ VOL ____

Sample: Collected ___ Set up ____

METALS AEROCHEM OPERATION ___ TEMP ____

Sample: Collected ___ Set up ____

STANDARD AEROCHEM OPERATION ___

Sample: Collected ___ Set up ____

MET SYSTEM WIND VANE ____ ANEMOMETER ____

PROBLEMS AND GENERAL OBSERVATIONS:

OPERATOR _____

Standard Operating Procedure for Sampling Trace Metals in Precipitation Using Modified Aerochem Collectors

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December 1993

Standard Operating Procedure for Sampling Trace Metals in Precipitation Using Modified Aerochem Collectors

1.0 Overview

This SOP is intended to provide a step by step procedure for the proper collection of a precipitation sample using a modified wet-only Aerochem Metric sampler. Procedures include replacement of the Teflon sampling train and inspection and maintenance of the sampling equipment.

Data collected from analysis of precipitation samples from the modified Aerochem samplers will be primarily used for the Lake Michigan and Lake Superior Load Monitoring Program and for the Integrated Atmospheric Deposition Network (IADN). Samples at the Sleeping Bear Dunes site, which is part of the Integrated Atmospheric Deposition Network, were sampled and analyzed by Indiana University. The sampling method is identical apart from a few minor differences in QC samples. This site represents 10 % of the samples for this method. The data will be used to assess the atmospheric loadings of trace metals to the Great Lakes.

The modified wet-only Aerochem sampler is used to collect weekly precipitation samples for trace metals analysis. Wet-only deposition samplers are designed to open only during a precipitation event in order to minimize contamination from dry deposition and blowing dust, etc. Due to the very high susceptibility of precipitation samples to trace metal contamination, the procedures seek to minimize operator contact with the sample and allow the sample to contact only Teflon surfaces. The Teflon sampling train, which consists of a Teflon-coated funnel, Teflon tubing and Teflon bottle, is shipped to the site each week by Buffalo State University (BUF). After a one week collection period, the entire sampling train is returned to BUF for cleaning and analysis of the precipitation sample. The trace metals listed in Table 1 will be analyzed by ICP/MS as detailed in the laboratory SOP.

Any questions concerning sampling methods or operation of equipment should be directed to the following individuals. The ISWS Contact will be the prime contact for all methodologies and general operation questions. The EPA Project Lead is the second contact if the ISWS Contact cannot be reached. Specific questions should be directed as indicated below.

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Table 1. Analytes from Modified Aerochem Metric Sampler

Parameters:	
Aluminum	Arsenic
Cadmium	Chromium
Copper	Lead
Manganese	Nickel
Sodium	Selenium
Titanium	Vanadium
Zinc	

2.0 Sampling Equipment Description

The Aerochem Metric (ACM) sampler is modified so that the sample will contact only Teflon surfaces to minimize trace metals contamination. The precipitation will be caught in a Teflon-coated aluminum funnel and stored in a 2 L Teflon bottle. The 2 L bottle can collect a volume equivalent to 3 cm of precipitation. The funnel is fitted with a Teflon o-ring and Teflon fitting and is connected to the bottle by Teflon tubing. The metal lid and pad are replaced with a polyethylene lid and Teflon wrapped foam pad. A new polyethylene bag is inserted in the dry bucket each week so that the lid will contact a clean surface. The arms of the ACM are Teflon coated and, at the pivot points, are covered with plastic sleeves to prevent freezing in the winter. The base of the ACM is enclosed with aluminum and insulated to control the temperature and minimize contamination. A heater and fan inside the enclosure operate to regulate the winter temperature to between 5 and 25 °C. In the winter, heat from the enclosure warms the funnel to melt any snow caught by the collector. Summer temperature will be maintained at ambient temperature using the fan.

3.0 Summary of Method

The sampling period, the time between bottle/funnel installation and removal, is one week. The sampling train will be replaced each Tuesday at or about 10:00 am local time. If it is raining or snowing at collection time, the train should be changed after the precipitation stops, but no later than midnight Tuesday. Bottles/funnels are sent to the laboratory even if no precipitation was collected. If the sample can not be collected on the prescribed sampling day, the ISWS Contact must be notified. The following sampling activities will take place in the order listed.

1) Initial inspection
2) Removal of collection bottle
3) Replacement of polyethylene bag over the dry-side bucket
4) Removal of funnel
5) Replacement of sampling train (funnel/tubing/bottle in that order)
6) Sample shipment
7) Field log reporting and sample reporting form completion and submission

All steps will be conducted weekly and are detailed in Sections 9.1 through 9.8. Heavy precipitation may cause the collection bottle to overflow. Changing the bottle during the week to prevent overflow is discussed in Section 9.3.

4.0 Sample Handling and Preservation

Every sample is important and represents a significant portion of that site's yearly estimate. Any contamination through mishandling could cause a bias in the program results. Plastic gloves should be worn while removing, handling, and replacing the Teflon sampling train. (Do not use latex gloves with powder.) All procedures for sample handling, packaging and shipping should be followed.

5.0 Interferences

Ideally, the sampler should collect 100% of the precipitation. However, due to losses of precipitation and/or mechanical malfunctions, not all of the precipitation is collected. The validity of the sample is not based on the amount of precipitation collected but on the integrity of the precipitation collected. The sampler should not remain open for periods greater that 30 minutes after precipitation stops. Any sample exposed to dry deposition for greater than six hours during a standard sampling period will be considered invalid and flagged as such.

Examples of other events which will result in invalid data are malfunctioning of the lid so that continuous cycling occurs during a precipitation event, use of non-standard or modified equipment, or inadequate documentation by operator. Data corresponding to these events will be flagged appropriately.

Samples may also be contaminated by the site operator from water and/or other contaminants entering the sampling train from hands or clothing. Plastic gloves must be worn during all contact with the sampling train. If the sample must be collected during a precipitation event, a Tyvek jacket should be worn and returned to the plastic pouch after completion of sampling.

Extreme temperatures may result in improper operation of the equipment. Freezing temperatures may inhibit flow of precipitation through the funnel opening, while high temperatures may enhance evaporation. A heater and fan are provided to regulate the temperature and should be maintained and inspected weekly. A max-min thermometer is also provided inside the sampler and should be recorded and reset weekly.

6.0 Safety

In any field operation, emphasis must be placed on safety. Site operators must be aware of the potential safety hazards to which they are subjected. Follow all safety protocols and equipment guidelines, and be prepared for emergency situations. The sites operator is responsible for his/her safety from potential hazards including but not limited to:

Travel: When traveling to the site be sure to check on road conditions and weather advisories. Carry emergency supplies (warm clothes, food, water) when traveling in winter. Always let someone know where you are going and when you expect to return. Always carry a first aid kit.

Electrical: For obvious problems (fire, scorching, continuously blowing fuses), turn off the power of the circuit involved and notify ISWS. Never attempt electrical repairs other than replacing fuses and circuit boards. Be sure to unplug the sampler before changing fuses. Be especially cautious if conditions are wet.

Insects/pests: If you are allergic to insect stings, you should carry a kit prescribed by a physician. Be especially cautious if nests or large numbers of stinging insects are present. Notify ISWS of all problems.

7.0 Equipment and Supplies

Proper use, maintenance and cleaning will extend the life of serviceable equipment. The equipment and supplies specified in these lists (supplied by ISWS) should be used at the site. Any modifications or changes must be approved by the ISWS Contact.

7.1 Serviceable Equipment

These items will be maintained at the site at all times:

Modified Aerochem Metric wet/dry precipitation collector (Model 301)
Space heater
Maximum/minimum thermometer
One extra sampling train (Teflon bottle, tubing, and funnel) in packaging as sent by laboratory
One extra Teflon bottle in laboratory packaging
Jack to hold bottle in place
Overflow tray
Enclosure filter
Plastic gloves
Log book
Report forms
Tyvek jacket (in plastic bag)
Kimwipes
Squirt bottle to wet precipitation sensor

A diagram of the Aerochem Metric collector and Teflon sampling train is shown in Figure 1. General maintenance and trouble shooting are covered in Section 11.0.

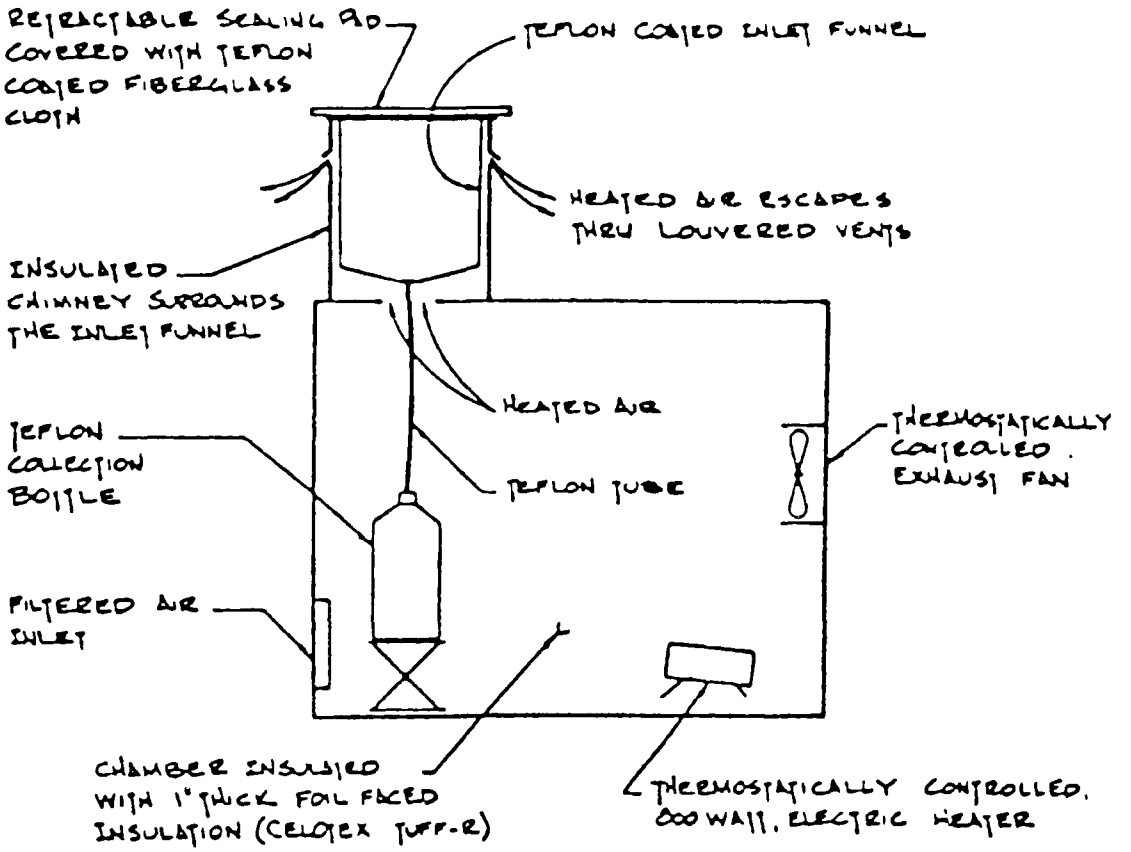

Figure 1. Modified Aerochem Precipitation Sampler (Dry-side bucket not shown)

7.2 Consumable Equipment

These items will be shipped to the operator every week.

Sampling train (Teflon bottle and cap, tubing, and funnel in polyethylene bags)
Shipping box and packaging materials

8.0 Calibration and Standardization

8.1 Rain Sensor

The Aerochem Metric (ACM) sampler consists of a collection container which is covered by a motor-activated lid. In a precipitation event a sensor activates a motor to move the lid off the collector. Each week the sensor should be checked to ensure proper operation. The procedure for this is covered under Section 1.4.4.

8.2 Heater and Fan

The heater must operate properly in freezing temperatures to maintain proper operation of sampling equipment. The heater must maintain a 15° ± 10°C temperature in the sample enclosure. The heater will be calibrated at ISWS. When cold weather is expected, check that the heater is operational by turning up the heater thermostat until the heater comes on; set this thermostat at the calibration mark. During the warm weather, make sure that the fan is operational by turning down the fan thermostat; set this thermostat at the calibration mark. Reset the maximum/minimum thermometer and record the temperatures each week.

9.0 Procedures

The site operator is responsible for maintenance of the site and for weekly sample collection, submission and documentation. The site operator will conduct routine maintenance, request needed supplies or parts in a timely manner, complete the weekly data sheet and maintain the field log book.

In order to ensure a representative wet deposition sample the following detailed procedures on the removal and installation of the sampling train, documentation, and maintenance should be implemented.

The following procedures should be adhered to each week:

1) Initial inspection
2) Removal of collection bottle
3) Replacement of polyethylene bag over dry-side bucket
4) Removal of funnel
5) Replacement of sampling train (funnel/tubing/bottle in that order)
6) Waste disposal and clean up
7) Sample shipment
8) Field log reporting and sample reporting form completion

9.1 Reporting and Labeling

All observations should be recorded on the sample reporting form and in the site log book. All entries should be made with a permanent ink marker. All times will be recorded in local time on 2400 hour clock. Labels are placed only on the sample bottles and only after the sample has been collected.

9.2 Initial Inspection

Carrying a box containing the new sampling train (bottle, tube, and funnel) approach the collector from downwind if possible.

9.2.1 Inspect the immediate site and surrounding area for any conditions which may affect the integrity of the sample, i.e. fire in the area, wind storm, vandalism, etc. Note these in the site log book and on sample reporting form. Also note if it is raining or snowing during sample collection.

9.2.2 Inspect the equipment for any damage and to see that all connections are secure. Remove any snow from top of lid. Operation of the rain sensor and lid will be checked during Section 1.4.4. Check operation of the heater or fan. Check for interferences (Section 1.1.3)

9.2.3 Record minimum and maximum temperatures from inside enclosure and reset thermometer.

9.3 Removal of Bottle from the Previous Week

9.3.1 Put on a clean pair of plastic gloves.

9.3.2 Unscrew the bottle, lower the jack, and recap the exposed collection bottle with the stored cap. (Last week the cap was placed in a plastic bag and stored in the enclosure. Do not put the cap down inside the enclosure unless it is inside a bag.) Place capped bottle inside a plastic bag. Put the label on the out side of the bag.

9.3.3 Remove the tube assembly and place in the plastic bag which was stored inside enclosure last week.

9.3.4 Close door to enclosure, leaving used bottle and tubing in bags inside enclosure. Bottle and tubing will be transferred to shipping box in Section 1.4.4.

9.4 Changing of Bottle for Overflow (During Sampling Period)

Heavy precipitation may result in bottle overflow. To prevent this the bottle may be changed during the sampling period as follows:

9.4.1 Bring one of the extra Teflon bottles in polyethylene bags to field site.

9.4.2 Wearing polyethylene gloves, unscrew the bottle cap, lower the jack, and recap the exposed collection bottle with the cap that was stored in the enclosure. Place the capped bottle inside a plastic bag and leave inside enclosure until Tuesday sampling.

9.4.3 Place the new bottle on the overflow dish. Place the cap inside a polyethylene bag. Raise the jack to position the collection bottle so that Teflon tube is about ½ inch into the collection bottle. Screw on the cap which is part of the tubing assembly. Store the cap in bag inside the enclosure for use at the end of the week.

9.4.4 Both bottles will be shipped to BUF at the end of the sampling period. Indicate on the field report form and in the field notebook that two bottles were shipped.

9.5 Removal and Replacement of the Funnel

9.5.1 Replace the polyethylene bag in the dry side bucket and secure it with a bungee cord. Discard the old bag.

9.5.2 Standing downwind of the sampler, apply enough DI water to the sensor grid for the lid to remain open while changing funnels. Watch as the lid moves over. The lid should move freely with little motor noise. Wipe the underside of the lid with a damp (DI) Kimwipe.

9.5.3 Without leaning over the funnel, note any contamination on the funnel and record this on the site reporting form.

9.5.4 Using the bag as a second glove, remove the exposed funnel and place it in a polyethylene bag.

9.5.5 Retrieve the new funnel from the shipping box and place the used funnel in the shipping box in the same position.

9.5.6 Holding the new funnel through the bag, open the bag, and position the funnel on the wet-side sampler. Do not touch the funnel except when using the bag as a second glove. After the funnel has been properly seated, place the bag inside the enclosure for next week.

9.5.7 Blow any remaining water off the sensor, allowing the lid to close on the wet-side. After the sensor plate has been open, check to see that the sensor plate is warm. Clean any accumulated dirt off the sensor.

9.5.8 Check for a good seal between the lid and funnel.

9.6 Installation of Bottle and Tubing for Next Week

9.6.1 Open the sample enclosure. Put the used bottle and tubing in the shipping box and retrieve the new bottle and tubing.

9.6.2 Copy the weight written on the top of the capped bottle into the log book and onto the sample report form to be submitted *next* week. The dates of the new sampling period should be included with the weight.

9.6.3 Put on a new pair of polyethylene gloves. Using the polyethylene bag as a second glove, remove the new tubing assembly from its bag and slip it onto the bucket nipple from inside the enclosure.

9.6.4 Remove the bottle from the bag and place on the overflow dish. Remove the cap and place it inside a polyethylene bag. Raise the jack to position the collection bottle so that the Teflon tube is about ½ inch into the collection bottle. Screw on the cap which is part of the tubing assembly. Store the bottle cap in a bag inside the enclosure. Place the bags for the bottle and funnel inside the enclosure for next week.

9.7 Waste Disposal and Clean up

Check the site for waste materials such as plastic gloves and Chem wipes prior to leaving site. Take an inventory of equipment and consumables. Notify ISWS of any equipment need repair or replacement of if any supplies are needed.

9.8 Sample Shipping

Once the bottle is detached from the funnel and capped it is not opened again by field personnel. Ensure that sampling train is properly packaged in polyethylene bags and in proper locations in shipping box. Send the contents to: Stephen Vermette, ESSE, Buffalo State University College, 1300 Elmwood Ave., Buffalo, NY 14222. Samples and the sample report form should be sent via UPS or U.S. priority mail to the laboratory no later than the day after collection. Photocopy paperwork so that a copy remains with the site operator. Notify ISWS if any equipment needs repair or replacement or if any supplies are needed.

10.0 Quality Assurance Samples

Occasionally the protocol will require collection of quality assurance samples. Travel blanks are bottles which are shipped with the regular sample trains and stored unopened in the enclosure during the sample period. They should be returned to BUF unopened after the specified period.

The operator will receive a box labeled "system blank" which contains a new sampling train and 250 mL bottle containing DI water. The sampling train should be installed as usual; however, the precipitation sensor is unplugged from the motor box so that the lid remains closed throughout the sampling period. At the end of the sampling period (the following Tuesday), the operator should reconnect the sensor and open the lid by wetting the sensor. The operator should then pour the DI water from the 250 mL bottle into the funnel in circular motions, wetting the sides of the funnel. The lid is then allowed to close. The sampling train is collected according to the procedures for weekly samples, with the exception that the field sheet is labeled "system blank" and the 250 mL bottle is returned

11.0 Equipment Maintenance

Site operators will maintain equipment in good working order at the original location. Site operators should also maintain the area around the collector. Any changes to site conditions should be recorded and reported to ISWS. Modifications at the site or to its equipment must be approved by the ISWS Contact. This includes placing other equipment in close proximity to the existing samplers.

11.1 Check Power Supply

Check all power connections at each visit.

11.2 Routine Cleaning

The housing and top of the lid should be washed periodically with water (distilled water is best) and a clean sponge to remove any residues (i.e. bird feces or accumulated dirt). Also the sensor grid should be scrubbed with a wetted toothbrush to remove accumulated minerals or other contaminants.

11.3 Check Foam Pad Insert

The foam pad should maintain a good seal with the funnel. If there are any gaps blowing dust may enter and contaminate the sample. Over time, the pad will tear and break down and may fall into the sample and cause contamination. This has been the most common maintenance problem. The pad should be replaced at least once a year.

11.4 Enclosure Filter

The enclosure filter is replaced at least once a year.

11.5 Troubleshooting

If the sampler fails to operate when you wet the sensor (lid does not move and motor does not start) there may be an existing power failure. Check that all the line power connections are secure, and that the fuses (found on the motor box) are good (check fuses with a volt meter or spare fuses, as you can't always see that they are blown). A voltage meter or appliance (i.e. radio or light bulb) can be used to check the power supply from the outlet.

If the sampler fails to operate when temperatures are below freezing (the lid does not move and motor is running) the collector lid may be frozen to the bucket, or the support arm pivots may be frozen to the housing, or the weight of snow on the collector lid may prevent the lid from opening. Gently pull at the lid or lid arms to break the ice, or remove the snow from the collector lid. A peaked roof and heating pads can be used to prevent freezing if this problem occurs often.

If the precipitation sampler fails to operator properly, aside from a power failure and freezing there are three components which can fail: the sensor unit, the motor box (containing the drive motor, fuses, and circuitry), or the clutch unit. Common signs of these failures are the continuous cycling of the collector lid, the lid remains on the wet (even when the sensor is wet) or dry-side bucket, or the collector lid stays open long after the precipitation event ends. Signs of these failures well be evident from the event recorder trace on the Belfort raingage drum chart.

11.5.1 Sensor Unit

When the sensor unit is faulty the following symptoms may be observed: The collector lid oscillates non-stop between buckets, or remains on either the wet- or dry-side with the motor running. A quick way to check if the sensor is faulty is to unplug it from the motor box. If the collector lid moves to cover the wet bucket the sensor needs to be replaced.

When the sensor's heater is faulty the lid stays over the dry-side long after precipitation stops and the sensor dries slowly. A faulty heater will not allow the sensor to evaporate water or melt snow, and the collector lid is not triggered to cover the "wet" bucket in a

timely manner. This can be checked by feeling the sensor for heat. A properly operating sensor will feel warm to the touch. If the sensor has cooled the heater probably has failed. If this is the problem, the sensor should be replaced, even though the sensor may continue to activate the lid as the sensor will dry through natural evaporation. If a replacement is not available the sensor may still be used, although the sample may be more susceptible to contamination from dry deposition. Note this on report forms and notify ISWS of the need of a replacement sensor.

11.5.2 Motor Box Unit

When the motor box unit is faulty the collector lid oscillates non-stop between buckets, or rests on the wet- or dry-side without the motor running. If unplugging the sensor (discussed in previous section) doesn't move the lid over to the wet bucket, or if the fuses are found to be good, the motor box will require replacement or repair. ISWS should be contacted. A diagram of the fuse arrangement in the motor box is shown in Figure 2.

11.5.3 Clutch Unit

When the clutch unit is faulty the motor will run but the lid mechanism will not move. In this case the clutch needs to be examined for wear. To do this, remove the clutch arm bolt to separate the clutch from the lid mechanism, and then loosen the thrust collar screw and gently pry the clutch off the motor box. If the thrust collar indent or the clutch tooth appear significantly worn then the clutch should be replaced. If they do not, the tension spring needs to be stretched. To do this, move the tension plate away from the thrust collar. The further away from the thrust collar the plate is pushed, the more tension is produced. Note: the clutch spring should not be stretched so far as to "freeze" the clutch -- it should still be able to pull away ("pop-out") from the motor box. If the clutch cannot be repaired at the site, notify ISWS.

LM/LS Metals Network

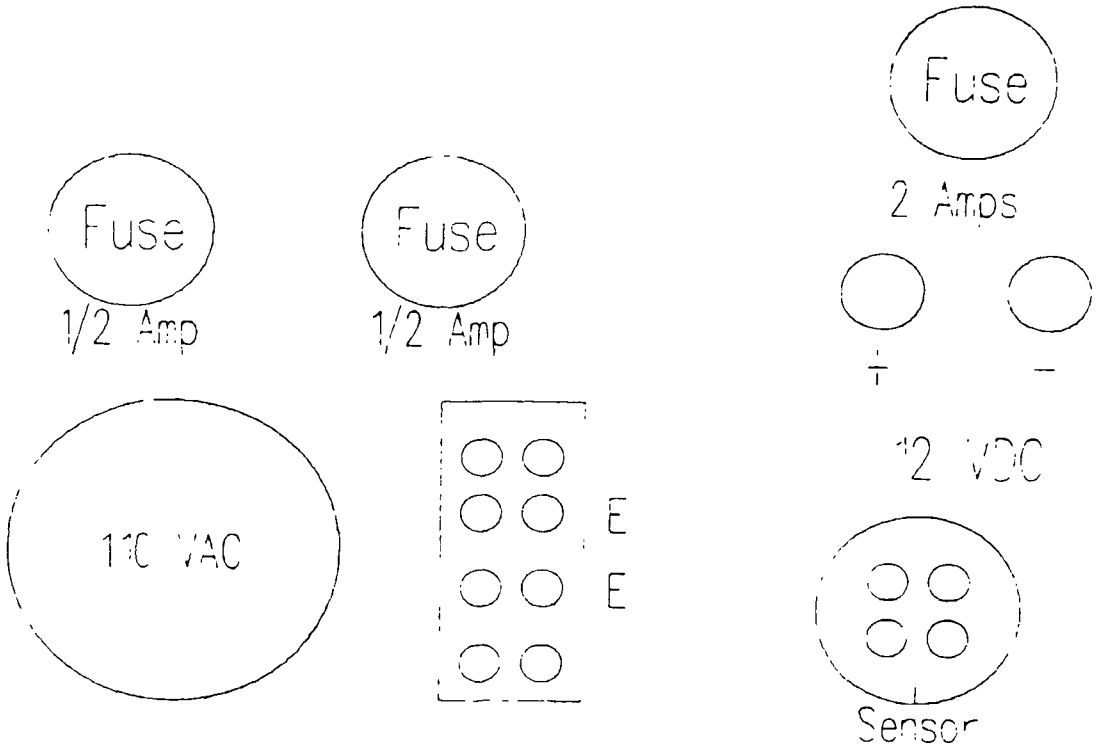

Figure 2. Aerochem Motor Box

Appendix A

SAMPLE REPORTING FORM

1. STATION

Name_____

ID ☐☐☐☐

2. OBSERVER

Name_____

Initials ☐☐☐

3. SAMPLE INTERVAL

Start ☐☐/☐☐/☐☐ (☐☐☐☐)
yr/mo/day/hr(0000-0000)

End ☐☐/☐☐/☐☐ (☐☐☐☐)
yr/mo/day/hr(0000-0000)

4. SAMPLE TYPE

Wet-deposition ☐

System-blank ☐

5. SAMPLE WEIGHT (laboratory use)

Collection Bottle & Sample	☐☐☐☐☐	grams
Collection Bottle	☐☐☐☐☐	grams
Sample Weight	☐☐☐☐☐	grams
Sample Volume	☐☐☐☐☐	mL
Rain Gage Volume	☐☐☐☐☐	mL

6. SAMPLE APPEARANCE

Clear ☐

Cloudy ☐

Floating Material ☐

Settled Out ☐

Other _____

7. REASON FOR BOTTLE CHANGE

End of Sampling Period ☐

To Prevent Overflow ☐

Did Bottle Overflow ☐

8. REMARKS

_____

_____

_____

_____

_____

9. LABORATORY CUSTODY (laboratory use) Ultrapure Acid added _____ mL

Sample Acidified Yes ☐ (if yes, Date ☐☐/☐☐/☐☐) No ☐

Aliquots: Lab I.D. Volume Routing

_____

_____

_____

_____

Metals Cleaning Procedures for Teflon Bottles and Rigid HDPE

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December 1993

Metals Cleaning Procedures for Teflon Bottles and Rigid HDPE

1.0 Teflon Bottles & Rigid HDPE

1.1 Rinse the bottle and cap three times with DI water by filling the bottle approximately ⅓ full, capping, and shaking vigorously. Discard water is poured into cap as part of the cleaning procedure.

1.2 Fill the bottle with 10% reagent nitric acid, screw on the cap and let soak for 24 hours. The bottle should be shaken once at the beginning and once at the end of the 24-hour period.

1.3 Discard the acid solution and rinse three times with DI water, follow same procedure as in Step 1 above.

1.4 Fill the bottle with DI water, screw on cap and let soak for 24 hours. The bottle should be shaken once at the beginning and once at the end of the 24-hour period.

1.5 Discard the DI water and rinse three times with DI water, follow the same procedure as in Step 1 above.

1.6 Shake out excess water, cap snugly, and store for use.

2.0 Teflon Bucket Assembly Cleaning Procedures

2.1 Upon receipt at the ISWS laboratory, the bucket assembly is removed from the polyethylene bag, and the removable components separated from the bucket. These components, the teflon fitting, o-ring, and tubing assembly are placed in a 10% HNO_3 bath.

2.2 The inside of the bucket is wiped with a wet sponge (and DI water) and the inverted bucket is cleaned in a FORMA-FURY laboratory glassware washer using DI water and the same washing sequence and procedures as used for the NADP/NTN collection buckets. A rubbermaid mesh screening is placed under the buckets to prevent abrasion of the teflon coating on the bucket, and prevent contact with the stainless steel interior.

2.3 The bucket and components are washed twice in the Forma-Fury unit. During the first wash, the tube assemblies are set up in the hole atop the inverted bucket, and the partially assembled teflon and o-ring fittings are placed in the washer also. During the second wash, the teflon and o-ring fittings are assembled with the bucket, and the tubing assembly placed next to the buckets vertically.

2.4 Upon removal from the glassware washer, the bucket assembly is shaken to remove excess water. The interior of the assembly is rinsed with 10% reagent grade nitric acid from a squeeze bottle, and then copiously rinsed with DI water

2.5 The bucket assembly is then placed in a closed polyethylene bag and placed in a well padded 16"x16"x16" box for shipment.

2.6 The tubing assembly is placed in a separate 1 gallon resealable single use teflon bag.

3.0 Assembly Package

3.1 A 16"x16"x16" heavy duty cardboard box is assembled and taped with several layers of high quality packaging tape.

3.2 Sufficient packaging to prevent damage is placed in the bottom of the box.

3.3 The following materials are then placed in the box.

Teflon bucket assembly
Tared 2.0 L teflon sample collection bottle
Cleaned tubing assembly in 1 gallon resealable bag
Dry side bag
Data sheet, including shipping date, tare weight, and site ID already completed
Weekly memo - including specific instructions for the week

On occasion, field blank and or system blank bottles and materials are included along with specific instructions.

3.4 The boxes are then filled with packaging materials, sealed, and mailed to the site operators.

4.0 Sample Handling Procedures

4.1 Samples are received at the ISWS from one to seven days after being removed by the operator, with a typical sample arriving three days after sampling. Samples are generally treated on the day of arrival at the ISWS.

4.2 Upon arrival at the ISWS, the sample bottle is taken and reweighed. This and the tare weight are used to calculate the weight and volume of the sample.

4.3 A 0.2% HNO_3 solution is added to each sample based on volume. The sample is then shaken and allowed to equilibrate a minimum of 24 hours, and if possible over a weekend.

4.4 After equilibration, the samples are decanted into previously cleaned 60 mL, 125 mL, 250 mL, or 500 mL sample bottles, based on volume of the sample. The sample bottles are rinsed twice with the sample solution before the entire sample is placed in the bottle. The rinsing procedure is waved in sample of less than 60 mL of solution, as use of the sample would leave too little for analytical analysis.

4.5 Samples are labeled and stored at the ISWS, and taken to the HWRIC for analysis once per month. Samples at the HWRIC are stored at 4 °C both before and after analysis.

Standard Operating Procedure for Sampling of Vapor Phase Mercury

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June 1, 1994

Version 2.0

Standard Operating Procedure for Sampling of Vapor Phase Mercury

1.0 Introduction to Principals of Vapor Phase Mercury Sampling and Analysis

Mercury in the atmosphere exists predominantly in the gas phase in the form of elemental mercury (Schroeder, 1982). Other species of mercury found in the gas phase include methyl and dimethylmercury, and mercuric chloride, mercuric hydroxide and free divalent mercury. Vapor phase mercury is quantitatively removed from an air stream by amalgamation onto gold. While the amalgamation process is believed to remove most vapor phase mercury species with >99% efficiency, the analytical procedure employed determines whether or not 'total mercury' or predominantly elemental mercury is quantified. At the University of Michigan Air Quality Laboratory (UMAQL) vapor phase mercury is collected onto gold-coated borosilicate glass bead traps by drawing air at a low flow rate through a baked glass fiber pre-filter followed by the gold-coated borosilicate glass bead trap. The air is prefiltered to eliminate particles from the gas phase collection traps. After sampling, vapor phase mercury is quantified by cold vapor atomic florescence spectrometry (CVAFS).

In the past, methods for collection of vapor phase mercury have dictated long sampling duration, often from 24 hours up to a week. The collection method employed for the Lake Michigan Loading Study and described in this protocol uses gold-coated borosilicate glass bead traps, which UMAQL has determined to be >99% efficient at collection of vapor phase mercury (at a flow rate <1 lpm). Dual-amalgamation and subsequent analysis by cold-vapor atomic florescence, allows detection of mercury at picogram levels. After thermal desorption, gold-coated bead traps are re-used since they do not exhibit memory effects. Due to the collection efficiency of gold-coated beads and the ability to detect picogram amounts of mercury, sampling strategies using gold-coated bead traps can employ much shorter duration samples than have previously been possible. Short sampling duration provides the resolution necessary to use receptor models in determining sources and source contributions of measured vapor phase mercury.

Preparation and collection of accurate and reliable data on mercury concentrations in environmental samples requires that ultra clean procedures are used. All sampling supplies with which a sample will come into contact must be acid cleaned in a Class 100 Clean Room. At the sampling site, precautions taken to avoid contamination of the sample include storing samples at an outdoor staging area and special operator handling. These and other techniques employed to minimize contamination of the samples are described in detail in this protocol.

2.0 Sample Preparation

2.1 Acid Cleaning Procedure

All Teflon filter packs, Teflon jars, Teflon tubing, gold trap fittings and end plugs (referred to below as 'supplies') are cleaned using an 11-day procedure described by Rossmann and Barres (1991).

Supplies to be acid cleaned are first rinsed in reagent grade acetone under a fume hood, then washed in hot tap water and diluted Alconox. Supplies are rinsed five times in cold tap water then rinsed three times in DI water. The supplies are then heated in 3M hydrochloric acid (EM Science Tracepur HCl in Milli-Q water (18.2 MΩ/cm)) for six hours at 80°C. One liter of 3M HCl is prepared by adding 750 mL of Milli-Q water to 250 mL of concentrated EM Science Tracepur HCl. The 3M HCl can be used several times and is stored for reuse in a polyethylene carboy dedicated for this purpose. The supplies are placed into clean polyethylene tubs which are then filled with the 3M HCl, making sure that all of the surfaces are submersed in the HCl. The tubs are covered and placed in a water bath which is heated to 80°C in a fume hood. The water in the bath is maintained at the level of the acid inside the tubs. After the water in the bath reaches 80°C, the supplies in the tubs are allowed to soak for six hours.

After the six hours, 80°C soak, the tubs are removed from the water bath and allowed to cool in the fume hood. When cool, the 3M HCl is poured back into its polyethylene carboy. The supplies are rinsed in the tubs three times with Milli-Q water. The supplies are then soaked in a 0.56M nitric acid solution (Baker Instra-Analyzed HNO_3 in Milli-Q water) for 72 hours at room temperature in the same polyethylene tubs in which they were heated with HCl. The nitric acid solution is made by adding 35 mL Baker Instra-Analyzed HNO_3 to 965 mL of Milli-Q water. Nitric acid is reused for up to six months and is stored in a carboy dedicated for HNO_3. At the end of the three-day soak, the supplies being cleaned are rinsed three times with Milli-Q water and transferred into a Class 100 Clean Room.

Inside the clean room, the supplies are again rinsed three times with Milli-Q water. The tubs containing the supplies are filled with 0.56M Baker Instra-Analyzed HNO_3 that is kept in the clean room and is dedicated for this final step only. The supplies are then allowed to soak in this acid for seven days. This acid is prepared by adding 35 mL of the Instra-Analyzed HNO_3 to 965 mL of Milli-Q water. At the end of the seven day acid soak inside the clean room, the supplies are rinsed five times with Milli-Q water and allowed to air dry on a clean surface. When the supplies are dry, they are triple bagged in new polyethylene bags and removed from the clean room, ready for use in sampling.

2.2 Preparation of Gold-Coated Bead Traps and Pre-Filters

Gold-coated borosilicate glass bead traps are constructed at The University of Michigan Air Quality Laboratory and tested prior to use in the field. The gold-coated beads used in the traps are made by generating a gold plasma under vacuum conditions that uniformly deposits onto the surface of the beads. The thickness of the coating generated using this process is about 300 Å. The gold-coated beads are contained in a quartz tube which is 10 cm long with an inner diameter of 5 mm and an outer diameter of 7 mm. Teflon heat-shrink tubing is attached to both ends of the tube into which Teflon endplugs are placed when the trap is in storage or connectors when the trap is being used to collect a sample. Each trap contains approximately 0.7 g of gold-coated borosilicate glass beads which are held in place using quartz wool and two sets of three radial indentations in the quartz tube. The gold-coated beads, quartz tubes and quartz wool are baked at 600°C for one hour prior to making the trap. In addition, Teflon endplugs and heat shrink tubing are acid cleaned as previously described. After each trap is made, it is given a unique number identifier in order to chart the history and performance of the trap. New traps are first conditioned by drawing approximately 0.4 m^3 of air through the trap then heating the trap to 500 C for five minutes. Inert gas is purged through the traps at 300 cc/min during heating procedure to remove moisture and other volatile constituents. The conditioning procedure is performed twice prior to

testing the trap. The trap is then tested by injecting a known amount of elemental mercury vapor and comparing the result to an analytical standard. The trap must exhibit duplicate measurements that are within 5% of the standard and the replicate measurements must also be within 5% of each other. Following this test, the trap is then blanked (described below) and stored for seven days. After seven days, the trap is analyzed for a storage blank (sample analysis is described in the *Standard Operating Procedure for Analysis of Vapor Phase Mercury*). The storage blank must be less than 15 pg for the trap to be accepted for use in field sampling. Gold traps are stored with endplugs in place, triple bagged in polyethylene before and after sampling.

Just before going into the field to collect vapor phase mercury samples, gold-coated bead traps are blanked again. Blanking a trap removes all mercury from the gold-coated bead surface and will also remove water vapor and other unwanted constituents. Traps are blanked by placing them in the analytical train and heating them to 500°C for two minutes, identical to a normal sample analysis.

Vapor phase mercury samples collected onto gold-coated borosilicate glass bead traps must be prefiltered to exclude particles. Glass fiber filters (Gelman Sciences) are pre-treated to remove all mercury prior to use in sampling. Glass fiber filters, 47 mm in diameter, are placed in a clean crucible with a lid. The crucible is placed in a muffle furnace which is heated to 500°C and the filters are allowed to bake at this temperature for one hour. While hot, filters are removed from the crucible with acid-cleaned Teflon-coated forceps and placed in an acid-cleaned Teflon jar which is closed and sealed with Teflon tape. The Teflon jar is triple bagged and stored at -40°C until use. Filters are stored no more than three months prior to use and frequent blanks are taken to ensure the filters remain clean.

3.0 Vapor Phase Mercury Sample Collection

During sample collection the filter packs and gold bead traps are housed in a sampling box that is mounted on a pole or tower at least 3 meters above ground level. The sampling boxes were custom-made at UMAQL from fiberglass enclosures (Stahlin Enclosures) using quick connect couplings to connect the vacuum lines from the pump to the sampling devices. Sample intakes are at least 30 cm apart and are not positioned near any potential contaminant sources.

A flow rate of approximately 300 cc/min. is typically used to sample with gold-coated bead traps, however, in highly contaminated areas flow rates less than 300 cc/min. may be desirable. Sample duration and flow rate depend on the study design. The sampling flow rate is maintained with a mass flow controlling device in order to maintain constant flow throughout the sampling period. During the Lake Michigan Loading Study all samples collected will consist of two traps in series. The front trap (A) is used to remove mercury from the air stream and the second trap (B) is used as a back up to characterize any breakthrough from the front trap. The flow rate through the inlet of the front trap must be confirmed before setting up each sample using 'test' traps instead of the sample traps, since any flow measuring device in front of the inlet could potentially contaminate the sample. Air is not drawn into a gold trap without a pre-filter attached since this will result in particle buildup inside the trap. All pumps used for sampling are allowed to warm up for at least 30 minutes prior to use.

3.1 Setting Up Gold-Coated Bead Samples

During all phases of sample set-up and removal, the operator stands downwind of the sample in order not to contaminate the sample by shedding particles from clothing, etc. In addition, particle-free gloves are worn when handling gold bead traps and prefilters. An acid-cleaned filter holder is loaded with a fired glass fiber filter for each new gold bead trap sample to be collected. The filter pack is placed in one of the inner holes in the mercury sampling box (Appendix B). An acid cleaned piece of 0.64 cm Teflon tubing is placed in the ferrule fitting on the outlet of the filter pack and is tightened down with a ferrule nut. The 'test' traps are removed from their plastic tubes, the endplugs are removed from the trap and placed in the plastic tube which is then capped and returned to a clean plastic bag. The Teflon sleeve of the front test trap is placed snugly over the 0.64 cm Teflon tube on the outlet of the filter pack. A piece of 0.64 cm Teflon tubing is placed in the back end of the front trap and a second trap is attached to this piece of Teflon tubing. Another piece of Teflon tubing is secured to the vacuum line and attached to the back end of the second trap (Appendix C). A calibrated rotameter is attached to the inlet of the prefilter pack by a 9 cm long piece of black latex tubing. The flow rate is allowed to stabilize and is then read from the rotameter. After recording the flow rate, the test traps and the rotameter are removed and sample traps are installed in their place in the same manner as described. A trap heating assembly is placed over the front sampling trap. The heating assembly consists of a 12.5 cm length of 0.9 cm ID stainless steel tube wrapped with 1.27 cm silicon heating tape and covered with insulated vinyl tape. A variable transformer is set (~3-4 V) to maintain a constant temperature of 93 °C to prevent condensation of water vapor in the sampling traps. The sample number, date, time, flow rate, meteorological information and any other pertinent information are recorded on a log sheet (Appendix D).

3.2 Taking Down Gold Bead Trap Samples

Particle-free gloves are worn during this procedure. The gold-coated bead traps are removed from the sampling stream and the endplugs are replaced. The juncture of the Teflon plugs/gold trap is wrapped with Teflon tape. The trap is placed in its plastic shield which is capped, and the sample number is placed on the plastic tube. As soon as the trap is removed from the sampling stream, the time is recorded. The tube containing the sample is then sealed in polyethylene bags and is immediately shipped to the UMAQL for analysis. Test traps are placed in line after the filter and the flow rate is read using a calibrated rotameter. All other pertinent information is recorded on the sample log sheet. After the flow rate has been checked, the pump is turned off. The prefilter is discarded.

3.3 Taking Blanks

A minimum of 25% field blanks and 10% shipping/storage blanks are taken to ensure samples are being collected in a contaminant-free manner. Field blanks involve setting up a gold bead trap in the same manner as a sample. The filter pack and attached gold trap are placed in the sampling box for two minutes *without the vacuum line attached.* After the two minutes, the sample is taken off, labeled and stored as described for samples. Shipping/storage blanks are traps that have been blanked, Teflon taped and triple bagged. The traps are then sent to the sampling site along with sample traps but are never removed from the triple bag nor is the Teflon tape removed. The traps are then sent back with sample traps to the UMAQL for analysis.

3.4 Trouble-Shooting

If flow through the gold trap or filter pack sample is low:

3.4.1 Check to make sure that all the connections are sealed tightly (make sure the ferrule nut fittings are tightened down, tubing connectors are tightly inside tubing from gold trap and on filter pack tubing, 'flow check' filter pack is screwed together tightly, tubing from the pump to the sampler is intact and connected securely.)

3.4.2 Make sure that the exhaust of the rotameter is not impeded in any way when using the rotameter to check flow.

3.4.3 Check the black latex tubing in the sampling box for cracks or tears due to weathering.

3.4.4 Make sure the mass flow controller is on and reading the normal output for the sample.

If all systems seem to be working properly and the flow remains low or erratic, operators are instructed to notify Matthew Landis at UMAQL (313) 763-7714 or at home (313) 663-9615 immediately.

4.0 Performance Criteria, Quality Assurance and Quality Control

4.1 Field operators are carefully instructed in the techniques of contaminant-free vapor phase mercury collection. All of the operators are currently operating sampling equipment for either the National Dry Deposition Network, the National Atmospheric Deposition Program, the Integrated Atmospheric Deposition Network or the Great Lakes Acid Deposition Network.

4.2 Every six months UMAQL personnel will inspect the sampling sites to audit the sampling equipment and make all necessary repairs or adjustments.

4.3 Co-located samples are collected from one sampling site during the study to quantify method precision. Reported concentrations are based on the mean of the two co-located samples.

4.4 Precision and accuracy levels will be set and maintained for each type of analysis. A relative precision for total mercury of less than 10% is maintained for samples with values at least three standard deviations greater than the detection limit. Analysis of standards and controls is within 5% of the stated value.

4.5 A minimum of 25% of all samples analyzed are field blanks or analytical blanks to ensure that samples are collected in a contaminant-free manner.

4.6 Every three months maintenance on the CVAFS analyzer is conducted, including replacement of the UV lamp, the Teflon tubing, and the detection cell.

4.7 Gold traps are checked prior to every sample with 0.8 ng of mercury in order to ensure that their use during the previous sample collection has not diminished trap performance.

5.0 References

5.1 Bloom, N.S. and Fitzgerald, W.F (1988) Determination of Volatile Mercury Species at the Picogram Level by Low-Temperature Gas Chromatography with Cold-Vapor Atomic Fluorescence Detection. *Anal. Chem. Acta.* 208, 151.

5.2 Dumarey, R., Temmerman, E., Dams, R. and Hoste, J. (1985) The Accuracy of the Vapour-Injection Calibration of Mercury by Amalgamation/Cold-Vapour Atomic Absorption Spectrometry. *Anal. Chem.. Acta.* 170, 337-340.

5.3 Dumarey, R., Dams, R., and Hoste, J. (1985) Comparison of the collection and desorption efficiency of activated charcoal, silver, and gold for the determination of vapor-phase atmospheric mercury. *Anal. Chem.* 57, 2638-2643.

5.4 Fitzgerald, W.F., and Gill, G.A. (1979) Sub-Nanogram Determination of Mercury by Two-Stage Gold Amalgamation and Gas Phase Detection Applied to Atmospheric Analysis. *Anal. Chem.* 15, 1714.

5.5 Lindberg, S.E. (1981) Author's Reply 'Mercury partitioning in a power plant plume and its influence on atmospheric removal mechanisms.' Atmos. Environ. 15, 631-635.

5.6 Rossmann, R. and Barres, J. (1991) Trace element concentrations in near-surface waters of the Great Lakes and methods of collection, storage, and analysis *J. Great Lakes Res.* 14,:188.

5.7 Schroeder, W.H. (1982) Sampling and analysis of mercury and its compounds in the atmosphere. *Environ. Sci.. Technol.* 16, 394-400.

Appendix A. Facilities, Equipment and Reagents

Following is a list of the required facilities, equipment, supplies and reagents for sample preparation, sample collection and sample analysis that are outlined in this document. The make and model of the following items are those used at The University of Michigan Air Quality Laboratory. Many of these items are available from a variety of sources.

1. Preparation of Field Supplies

Class 100 Clean Room, Work Stations
Clean Room Gloves
Particle-free Wipes
Clean Room Cap, Gown and Boots
Milli-Q Water (18.2MΩ/cm)
Exhaust Hood
Acetone
Alconox
Polyethylene Tubs
EM Science Tracepur and Suprapur Hydrochloric Acid
Polytherm Water Bath (Science/Electronics)
Baker Instra-Analyzed or EM Science Suprapur Nitric Acid
New Polyethylene Bags
20 L Polyethylene Carboys

2. Sample Collection

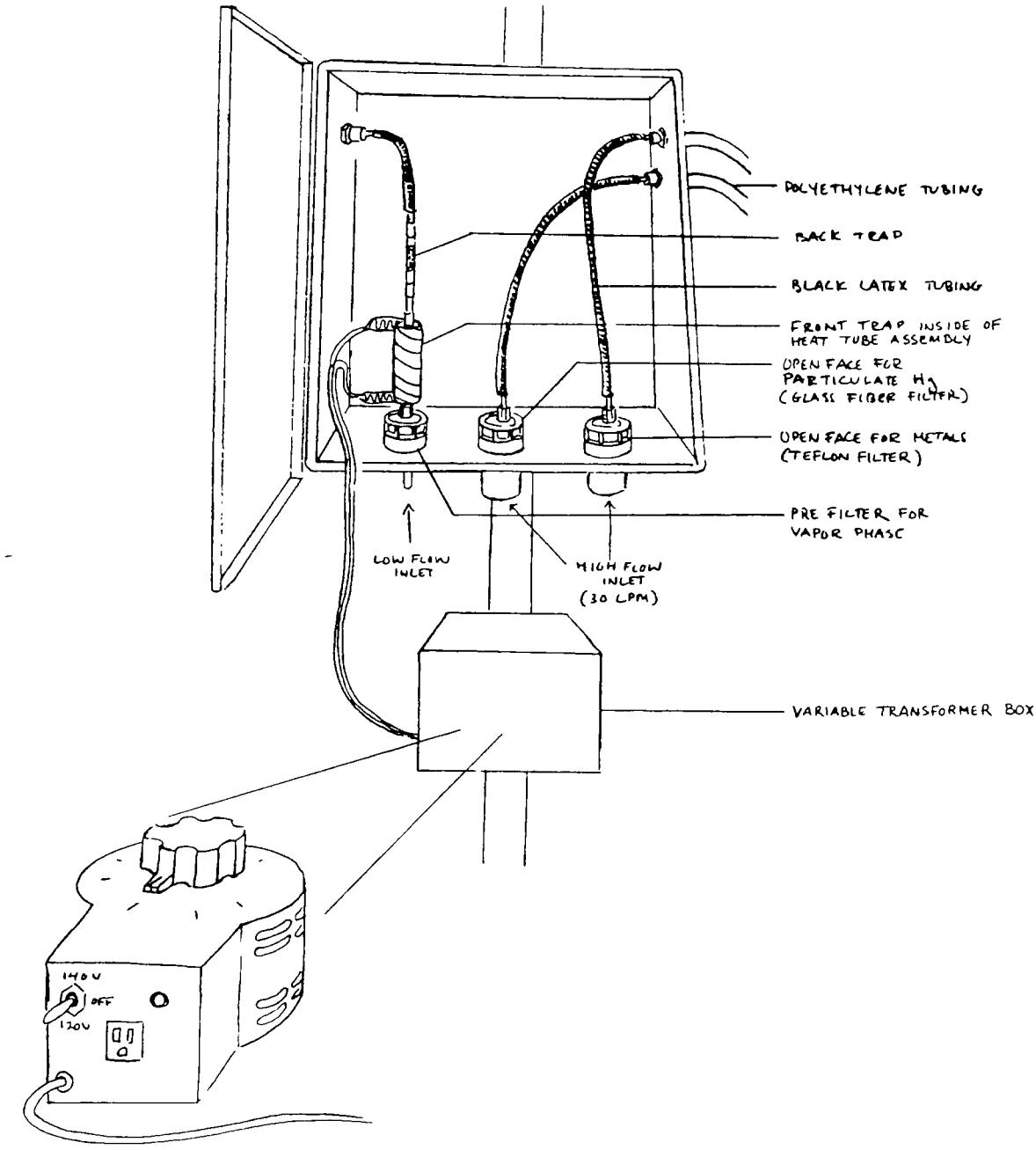
Mass Flow Controlled Vacuum Pump (URG, Model 3000-02M)
Calibrated 300 cc/min. Rotameter (Matheson)
HDPE Tubing with quick connects
Black Latex Tubing
Mercury Sampling Box (UMAQL, See Appendix B)
Acid-Cleaned 47 mm Teflon Filter Holders (Savillex, PFA Labware)
47 mm Preheated Glass Fiber Filters (Gelman Sciences A/E)
Acid-Cleaned Teflon Jars (Savillex, PFA Labware)
Teflon-Coated Forceps
'Blanked' Gold-Bead Traps (UMAQL)
Teflon Endplugs
Trap Heater & Variable Transformer
Acid-Cleaned Teflon Tubing
Particle-Free Gloves
Teflon Tape
Sample Labels
Field Operator Log Book
Shipping Boxes

Appendix A. Facilities, Equipment and Reagents (Cont'd)

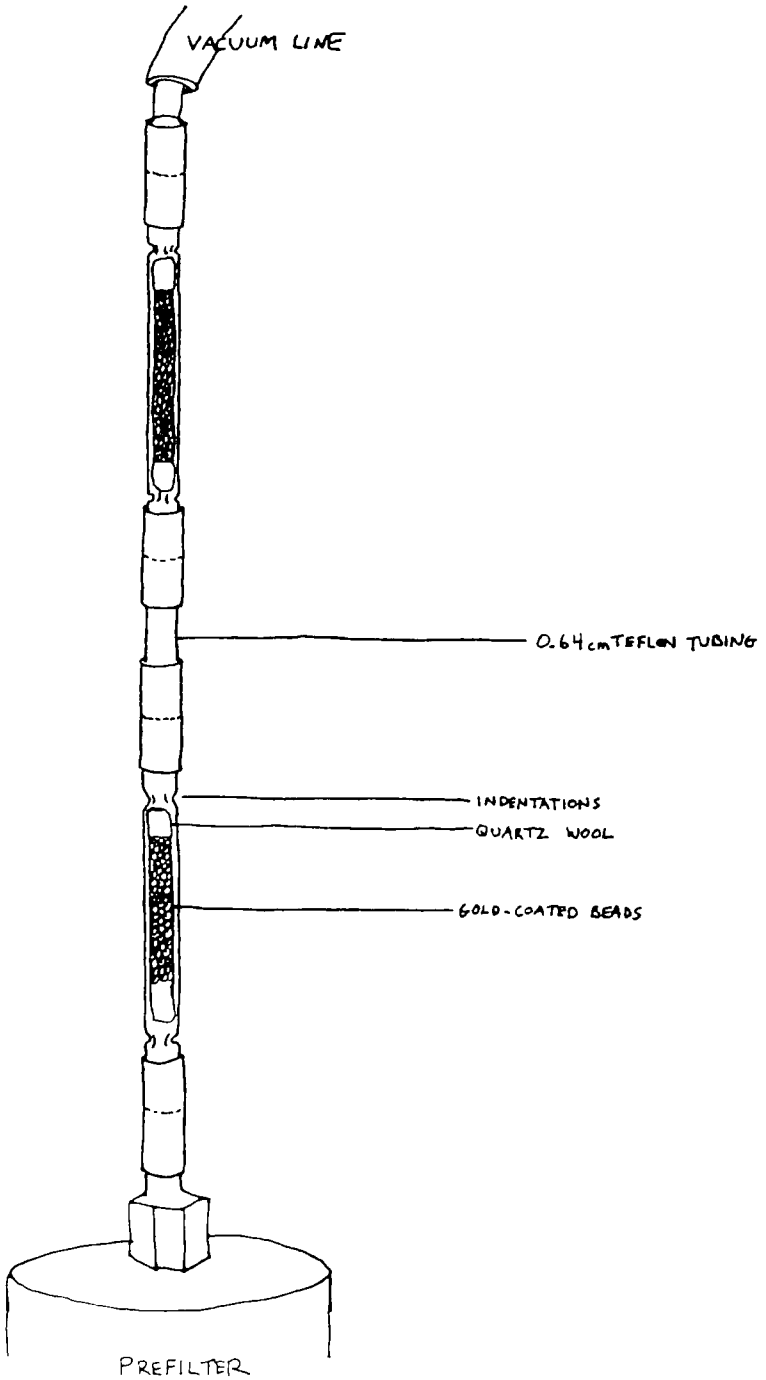
3. Sample Analysis

Cold Vapor Atomic Florescence Detector (Brooks Rand, LTD.)
Line Tamer/Conditioner (Shape Magnetronics Model PCLT 150)
Integrator (Hewlett-Packard Model 3390A)
Helium, Ultra High Purity Grade (99.999%)
Mass Flow Controller (Tylan)
Nichrome Coils (UMAQL)
Electric Leads
Variable Transformers (Staco Energy Products Co. Type 3PN1010)
Cooling Fans
Gold-Coated Glass Bead Traps (UMAQL)
Gas Tight Syringe (Hamilton series 1800)
Injection Port (UMAQL)
Constant Temperature Circulating Water Bath (Fisher Model 901)
Instrument Grade Metallic Mercury (Triple Distilled)
Mercury Flask (UMAQL)
Certified Immersion Thermometer (Kessler Instruments, Inc. 15041A)

Appendix B. Diagram of Mercury Sampling Box



Appendix C. Diagram of Assembled Gold-Coated Bead Traps



Appendix D.

LAKE MICHIGAN LOADING STUDY

IIT-CHICAGO

Vapor Phase Mercury

Sample No.	Au Trap #A/B	Date On/Off	Time On/Off	Flow On (LPM)	Flow Off (LPM)	Wind Speed	Wind Direction	Sky Conditions	Notes	Init.

PUMP SYSTEM USED:_____

ROTAMETER #:_____ CALIBRATION CURVE=_____

Appendix D. (Cont'd)

LAKE MICHIGAN LOADING STUDY *SAMPLE TRACKING FORM*

ITT--CHICAGO

Vapor Phase Mercury Samples: Gold-Coated Bead Trap

Sample Number*:_____
Gold Trap Number:_____
Operator:_____

Date On:_____ Date Off:_____
Time On:_____ Time Off:_____
Rotameter Reading On:_____ Rotameter Reading Off:_____

*If Blank Sample Note Type and How It Was Handled (Shipping Blank, Field Blank, etc.)

_____
_____

Notes: (ambient conditions, anything out of the ordinary, using freshly cleaned filter packs, etc.)

_____
_____
_____
_____

For Use at Univ. Of Michigan Air Quality Lab

Date Sample Received:_____ Rec'd By:_____
Date Sample Analyzed:_____ Rec'd By:_____

Analyzer #:_____

Notes: (Appearance of Sample, Are Endplugs Teflon-taped, etc.)

_____
_____
_____
_____
_____

Standard Operating Procedure for Sampling of Mercury in Precipitation

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Version 2.0

Standard Operating Procedure for Sampling of Mercury in Precipitation

1.0 Introduction/Overview

The objective of the Lake Michigan Loading Study is to assess the contribution of atmospheric deposition to the concentration of mercury and other toxic trace species found in Lake Michigan. The atmosphere has been implicated as one of the dominant sources of mercury and trace elements to bodies of water and it is clear from investigations in remote regions of the globe that long range transport of mercury and other toxics from source regions is occurring. By quantifying the wet deposition and ambient concentrations of mercury it will be possible to determine the relative importance of precipitation and dry deposition in accounting for the atmospheric loading of mercury to Lake Michigan. In addition, investigating other ambient trace species will aid in the identification of significant mercury sources.

2.0 Preparation for Precipitation Sampling

Acid Cleaning Procedure

All field sampling and analytical supplies which will come into contact with the samples are cleaned according to the following procedure.

Supplies to be acid cleaned are first rinsed in reagent grade acetone under a fume hood, then washed in hot tap water and diluted Alconox. Supplies are rinsed five times in cold tap water then rinsed three times in DI water. The supplies are then heated in 3M hydrochloric acid (EM Science Tracepur HCl in Milli-Q water (18.2 MΩ/cm)) for six hours at 80°C. One liter of 3M HCl is prepared by adding 750 mL of Milli-Q water to 250 mL of concentrated EM Science Tracepur HCl. The 3M HCl can be used several times and is stored for reuse in a polyethylene carboy dedicated for this purpose. The supplies are placed into clean polyethylene tubs which are then filled with the 3M HCl, making sure that all of the surfaces are submersed in the HCl. The tubs are covered and placed in a water bath which is heated to 80°C in a fume hood. The water in the bath is maintained at the level of the acid inside the tubs. After the water in the bath reaches 80°C, the supplies in the tubs are allowed to soak for six hours.

After the six hour, 80°C soak, the tubs are removed from the water bath and allowed to cool in the fume hood. When cool, the 3M HCl is poured back into its polyethylene carboy. The supplies are rinsed in the tubs three times with Milli-Q water. The supplies are then soaked in a 0.56M nitric acid solution (Baker Instra-Analyzed HNO_3 in Milli-Q water) for 72 hours at room temperature in the same polyethylene tubs in which they were heated with HCl. The nitric acid solution is made by adding 35 mL Baker Instra-Analyzed HNO_3 to 965 mL of Milli-Q water. Nitric acid is reused for up to six months and is stored in a carboy dedicated for HNO_3. At the end of the three day soak, the supplies being cleaned are rinsed three times with Milli-Q water and transferred into a Class 100 Clean Room.

Inside the clean room, the supplies are again rinsed three times with Milli-Q water. The tubs containing the supplies are filled with 0.56M Baker Instra-Analyzed HNO_3 that is kept in the clean room and is dedicated for this final step only. The supplies are then allowed to soak in this acid for seven days. This acid is prepared by adding 35 mL of the Instra-Analyzed HNO_3 to 965 mL of Milli-Q water. At the end of the seven day acid soak inside the clean room, the supplies are rinsed five times with Milli-Q water and allowed to air dry on a clean surface. When the supplies are dry, they are triple bagged in new polyethylene bags and removed from the clean room, ready for use in sampling.

The Teflon precipitation sampling bottles are not allowed to dry. After the seven day HNO_3 soak, the Teflon bottles are rinsed three times with Milli-Q water and are filled with 0.05M Hydrochloric acid (EM Science Suprapur HCl in Milli-Q water) and allowed to soak in the clean room until needed. When needed, the Teflon bottles are emptied, rinsed with Milli-Q water five times and 20 mL of HCl preservative is added. The bottles are then weighed, sealed with Teflon tape and triple bagged in new polyethylene bags.

3.0 Preparation and Set-up of the MIC-B Precipitation Collector

3.1 Summary

The automatic precipitation collector works by detecting precipitation on a sensor grid. During precipitation the sensor grid energizes a relay which switches on the motor-relay and, in turn, the motor. The motor acts through a chain sprocket drive system to move the cover from the funnel to the wet cover support. The motor is stopped by micro switches which trip as soon as the cover is properly seated on the cover support. When precipitation stops, the sensor grids dry out and the cover returns to seal the collector. This wet only collection prevents dry deposition from contaminating the collection funnel.

A heater is laminated to the underside of the sensor board to accelerate evaporation at the end of precipitation. The temperature of the heater is controlled so that the grid dries at the same rate independent of ambient temperature. To prevent excessive back and forth movement of the lid during extremely light precipitation, a time delay for return of the cover is incorporated into the control circuit.

During sample collection the screen to the right of the funnel reduces rain/snow splash-off into the precipitation collector. The sensor array is mounted two feet away from the collection funnel for the same reason.

The University of Michigan Air Quality Laboratory (UMAQL) has developed a new modified MIC-B collector that enables the installation of up to four discrete precipitation sampling systems. This configuration allows for two mercury sampling trains and two trace element & nutrient sampling trains. A mercury sampling train consists of a Borosilicate glass collection funnel with an effective collection area of 181 cm^2, a Teflon adapter, a glass vapor lock and a 1 L Teflon sample bottle. A trace element sampling train consists of a polypropylene funnel with an effective collection area of 167 cm^2, a polypropylene adapter and a 1 L polypropylene sample bottle (Figure 1). This new sampling configuration allows for the discrete collection and preservation of four independent precipitation samples using one MIC-B sampling instrument.

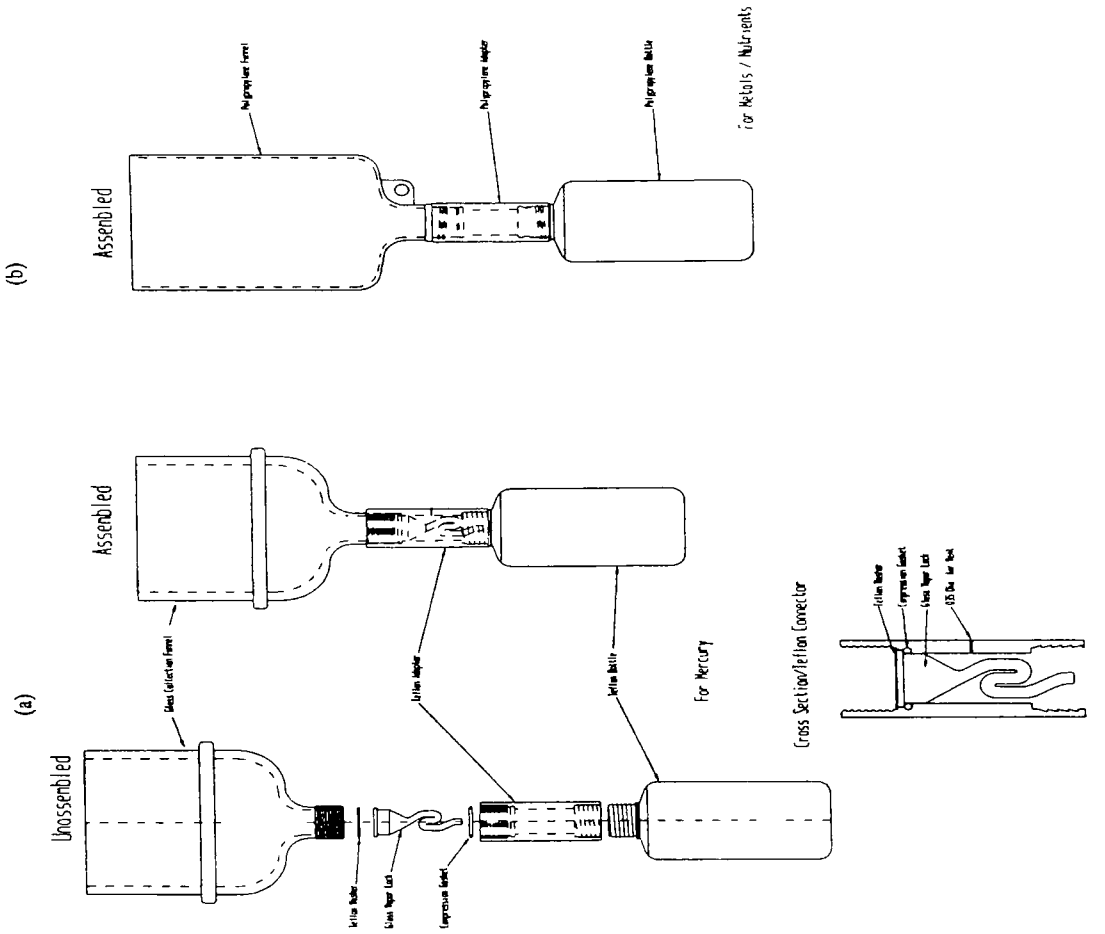

Figure 1. Modified MIC-B1 Sampling Trains for the Collection of Hg(a) and Trace Elements (b)

3.2 Sampler Set-up

The MIC-B collector is placed on a 1 meter tall wooden platform in a location free from obstruction in every direction. The collector cannot be located within 2 meters of other pieces of equipment or splash off may result and contaminate the sample. The sensor grid must also free of any obstruction.

3.3 Sampler Start-up

Connect the instrument to a grounded receptacle. Switch on the main power toggle located on the front of the instrument (only when the hood is in the closed position over the collection funnel insert). Touch one of the sensor grids with a wetted finger. The cover will lift up from the collection funnel insert and over to the rest bar. The motor will then turn off (be sure that you can hear the motor turn off, so that in the event it does not turn off, corrective measures can be taken). Wait one to two minutes and the hood will move back to cover the funnels and the motor will turn off. If the motor does not turn off after seating on the collection funnel insert then refer to the trouble-shooting guide (Section 4.3).

Note: The sampler hood must always be over the collection funnel insert when turning on the instrument's main power!

A space heater and heat tape funnel nests are placed inside the precipitation collector during cold months to melt snow and slush that lands in the funnel and to prevent freezing of the collected sample. The space heater is plugged into the outlet provided inside the sampler cabinet and is maintained on the setting required to keep the cabinet at approximately 10°C.

3.4 Installing the Collection Funnels

The acid-cleaned collection funnels are shipped with the adapters and vapor lock system pre-assembled and packaged in protective polyethylene wrapping. To keep the collector hood open during installation of the funnels into the MIC-B insert, place a wet towel or cloth onto the sensor grid. Open the sampler cabinet, and put on a pair of particle free gloves. Carefully remove the polyethylene wrapping and place each funnel system into the corresponding hole on the funnel support base (Figure 2). Be sure funnels are properly seated into the support base to insure a tight seal. Once all the sampling trains have been installed, cover any unused funnel support bases with the sealing caps provided to prevent water intrusion into the interior of the sampling instrument. Remove the wet towel and allow the collector hood to close.

In order to minimize evaporative loss of mercury from the sample bottle in the collector, a vapor lock system and hydrochloric acid preservative have been incorporated into the new collection system. Each Teflon sample bottle is shipped from UMAQL containing 20 mL of 0.08M HCl preservative. Extreme care is exercised when handling these bottles to avoid spilling the acid and causing personal injury. In the unlikely event that acid does come into contact with exposed skin, the area is immediately flushed with water. Wearing gloves and safety glasses, remove one Teflon sample collection bottle from the three polyethylene bags, unscrew the cap and place it in the inner bag from which you removed the bottle. Reseal the bags to keep the cap clean. Thread the 1 L bottle into the Teflon funnel adapter to complete the mercury sampling train setup. The sample bottles must be snug, however, care must be taken to avoid over tightening. Teflon threads on the sample bottles and the adapters are easily stripped.

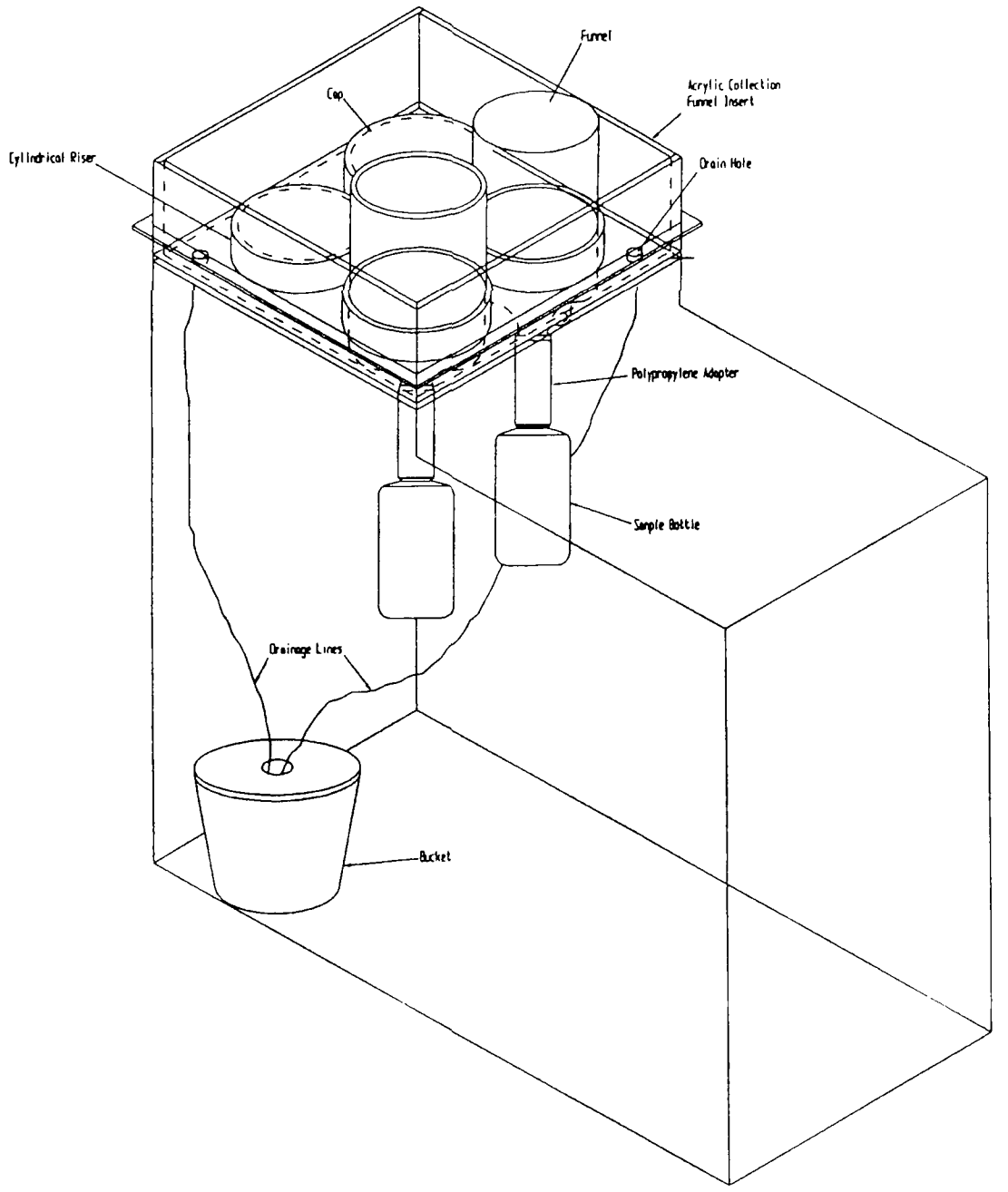

Figure 2. The University of Michigan Custom Acrylic Insert (UM-B)

The other trace elements collected are not volatile, therefore, the sampling train does not utilize a vapor lock or acid for preservation in the field. Wearing particle free gloves, remove one polypropylene sample collection bottle from the three polyethylene bags, unscrew the cap and place it in the inner bag from which you removed the bottle. Reseal the bags to keep the cap clean. Thread the 1 L polypropylene sample collection bottle into the polypropylene funnel adapter to complete the metals sampling train setup.

Note: The funnels and sample bottles have been acid-cleaned in a laborious 11-day procedure and packaged to ensure no particle contamination. Extreme care is exercised when handling the funnels and open sample bottles to prevent anything from falling in or contacting them during installation.

4.0 Sample Collection Procedure

4.1 Daily Site Visit

The operator must arrive at the sampler every morning at 8:00 a.m. local time to perform the following tasks:

1) Check the polypropylene sample bottle for any collected precipitation.
2) Check the Belfort rain gauge for any precipitation and record amount for each event.
3) Fill in information in the daily Sampler/Site Log Book.
4) Check the sampler to make sure, if appropriate, that the heater is working, the funnels are free of obvious contamination and the sampler is operating (by tripping the sensor grid).

If it is raining or snowing when the operator visits the site in the morning, the sample is not collected until the next morning, unless it appears that the sample bottle is going to overfill. If it is still raining the following morning, the site operator collects the sample as usual and replaces the sampling trains. The duration of the rain event is recorded by the operator on the sample log sheet. If it appears that the sample bottle is going to overfill then the operator removes the sample bottle while it is raining/snowing and collects the sample according to the procedure below. If the operator is unclear about what should be done, they are instructed to call Matthew Landis at UMAQL to determine if the sample should be collected.

4.2 Sample Collection

Supplies necessary to collect a sample: (quantities may vary depending on configuration)

1) One triple-bagged acid-cleaned Teflon bottle
2) One triple-bagged acid-cleaned polypropylene bottle
3) Two log books: samples and meteorological data
4) Particle-Free Gloves
5) Teflon Tape
6) Sample Label Stickers

Open the sampler cabinet, put on a pair of particle-free gloves. If there is evidence that precipitation has overflowed the sample bottle, put the two gallon white plastic bucket underneath the funnel before unscrewing the sample bottle from the funnel adapter. Unscrew the bottle from the funnel adapter, screw the cap on tightly and seal it to the bottle using the Teflon tape provided. Place the appropriate sample number label on the vinyl tape that is on the bottle *(This tape will have the bottle weight and a batch number to identify the bottle, avoid placing the sample label over these numbers).* Seal the sample bottle into three successive polyethylene bags.

Fill out a tracking form (Appendix B) to send with each sample, funnel rinse and control. Please note if the sample overflowed. Fill out the Sample Log and Collector Log sheets. Use the note column for important and/or unusual observations/notes (e.g., pesticide spraying nearby, road construction near site, leaves found in collector funnel, etc.). Do not fill in 'Sample Volume' this is for lab use.

The samples are shipped to UMAQL in Ann Arbor the day they are collected. If the operator is unable to do so, the samples are refrigerated until they can be shipped the next day. Do not allow the samples to freeze.

Precipitation samples will be collected on an event basis during the intensive months of May through October and on a weekly basis for the remainder of the sampling period. During event precipitation sampling, collection funnels and funnel adapters will be replaced after every precipitation event or after a period of seven successive calendar days without a precipitation event, whichever occurs first. The old funnels and the funnel adapters are removed and replaced with freshly cleaned ones from UMAQL. The old funnels and funnel adapters are shipped back to UMAQL as soon as possible so they can be cleaned. Site operators log the date and time the funnels are replaced on the sample log (an entire line in the log is used).

4.3 Funnel Blank Collection

In order to confirm that the collection funnel assemblies are free of mercury and other contaminants, 'funnel blank' samples are collected. Particle-free gloves are worn by the operator for this procedure. Clean sample bottles with no HCl preservative are attached to each sampling train and are used to collect the funnel rinses. To keep the collector hood open during this procedure, a wet towel is placed on the sensor grid. An acid-cleaned 1 L Teflon sample bottle and an acid-cleaned 1 L polypropylene sample bottle are filled with Milli-Q water and Control identification sticker labels are affixed. The operators are instructed to positions themselves down wind of the sample before the bottles are opened, to prevent particles from their clothing from being shed into the sample. Each funnel is rinsed with approximately 0.5 L of the water making sure all the surfaces of the funnel are covered, the sample bottles are capped and sealed using the Teflon tape provided. The Teflon and polypropylene bottles are removed from the funnel adapters, the caps are threaded on, the bottles are sealed with Teflon tape and the Rinse identification sticker labels are attached. Care is taken to prevent the mouth of the sample bottles from contacting anything during this procedure. The Rinse and Control solutions are re-bagged and packed into a shipping box. The tracking forms are completed for the Rinses and Controls separately.

4.4 Shipping a Sample

It is very important that samples reach UMAQL as soon as possible after being collected. To ship a sample, wrap the triple bagged sample bottle in a layer of bubble-wrap and place it in a shipping container provided. Any extra space in the container is packed with additional bubble-wrap so the bottles will not move inside.

Sample tracking forms for each sample are completed and sent with the samples to UMAQL.

4.5 Maintenance of MIC-B Precipitation Collector

4.5.1 Routine Maintenance

The precipitation collector sensor array is cleaned every month with a damp cloth and mild detergent (1% Alconox), both of which are provided. The detergent film is rinsed off the sensor array with a second, clean, damp cloth.

An operational check on sampler performance is conducted daily. This is done by placing a wetted finger on one of the sensor grids and waiting to make sure the cover seats in the open rest position properly and that one and a one-half to two and a one-half minutes after the hood returns to cover the funnels the hood is seated properly and the motor turns off. If the cover does not seat properly on either side or if the hood drops over excessively when open, refer to the trouble-shooting guide for the appropriate remedy.

4.5.2 Trouble-Shooting

If a collector fails to operate properly or the operator has to replace a fuse or make adjustments, they are instructed to notify Matthew Landis at UMAQL as soon as possible. Some of the parts that can fail will need to be replaced by UMAQL personnel. These cases are noted below.

1. Collector Fails to Operate:

   a. No Power to Instrument

      Check to make sure the instrument is plugged in and the power source is on (no tripped fuses/breakers etc.).

   b. Blown Fuse

      Replace the blown fuse with appropriate fuse.

   c. Faulty Sensor Board or Faulty Power Control Board

      The sensor board will have to be replaced by UMAQL personnel or sent to the operator for replacement. If you have exhausted the two options above call Matthew Landis or Jerry Keeler as soon as possible so replacement parts can be shipped.

2. Motor Will Not Switch Off

   a. Limit switch adjusting screw and/or cam out of adjustment
   Read just the limit switch cam and/or actuating screw.
   This is done by:

      i) Switching off main power and unplugging the sampler (be sure to do this with the cover seated on the funnel).

      ii) While holding the nut still, loosen the set screw on the appropriate micro-switch cam and readjust it until the switch is depressed. Tighten the set screw and repeat the procedure on the right side. When both sides have been adjusted, test the collector by placing a slightly wetted finger on one of the sensor grids. Wait to see if the motor stops when the hood is seated on the hood support and after the hood returns to its resting position over the funnel.

   b. Limit switch may be broken - if this is the case the switch needs to be replaced.

3. Cover Drops Once It Moves Over Dead Center

   a. The set-screw on the motor sprocket may be loose. Locate the set-screw and tighten it.

   b. The chain may be loose and is tightened.

4. Cover Does Not Return To Collection Funnel Insert

   a. Clean the sensor array with a damp cloth and mild detergent - making sure to wipe the detergent off the sensor array.

   b. Heater on sensors may not be operating. If this is the case the heater element may be burned out in which case the sensor board needs to be replaced or there may be a faulty component on the power control board and the power control board needs to be replaced.

5.0 Clean Room Procedures

5.1 Entering the Clean Room

Shoes are taken off outside the clean room by all UMAQL personnel. Personnel then enter the outer vestibule (changing room). Once inside, the hood is put on followed by the clean room suit and clean room boots. The boots are snapped to the suit at the back of the leg (to hold up the boots) and are buckled in the front. Personnel then step over a dividing bench where they put on clean room gloves and snap the clean room suit at the wrist. Now fully clothed they enter the clean room making sure to securely close the door behind.

5.2 Taking Supplies into the Clean Room

All supplies to be taken into the clean room are double bagged in polyethylene. The supplies to be taken into the clean room are placed in the outer dressing room. Upon entering the clean room, the outer bag is removed and left in the entry room. All supplies that enter the clean room that have not been bagged are rinsed with MQ-water and wiped off with particle-fee wipes.

Appendix A. Facilities, Equipment and Reagents

Following is a list of the required facilities, equipment, supplies and reagents for sample preparation and sample collection that are outlined in this document. The make and model of the following items are those used at The University of Michigan Air Quality Laboratory. Many of these items are available from a variety of sources.

1. Preparation of Field Supplies

-Class 100 Clean Room, Work Stations
-Clean Room Gloves
-Particle-free Wipes
-Clean Room Cap, Gown and Boots
-Milli-Q Water (18.2MΩ/cm)
-Exhaust Hood
-Acetone
-Alconox
-Polyethylene Tubs
-EM Science Tracepur and Suprapur Hydrochloric Acid
-Polytherm Water Bath (Science/Electronics)
-Baker Instra-Analyzed or EM Science Suprapur Nitric Acid
-New Polyethylene Bags
-20 L Polyethylene Carboys

2. Sample Collection

-MIC-B Wet-Only Precipitation Collector (MIC)
-UMAQL Modified Acrylic Insert
-Digital Indoor/Outdoor Recording Thermometer
-BSG Collection Funnels
-Polypropylene Collection Funnels
-Teflon & Polypropylene Precipitation Adapters
-Glass P-trap Vapor Lock
-1 L Teflon & Polypropylene Sample Bottles
-Funnel Heat Tape Nests & Variable Transformer
-Ceramic Space Heater
-2 Gallon HDPE Bucket
-Particle-Free Gloves
-Teflon Tape
-Sample Labels
-Permanent Label Markers
-Field Operator Log Book
-Shipping Crates

Appendix B.

LAKE MICHIGAN LOADING STUDY
PRECIPITATION SAMPLE TRACKING FORM
I.I.T.-CHICAGO

Sample Number:_____ OPERATOR: _____

Date of Precipitation: _____

Date Sample Collected: _____

Time Sample Collected:_____

Date Shipped: _____

Comments: _____

FOR USE AT THE UNIV. of MICH. AIR QUALITY LAB:

Date Received at UMAQL: _____ Rec'd By: _____

Volume of Sample Received: _____

Sample Analyzed in the Following Fractions:

Type of Analysis	Volume of Precip (mL)	Vol. Of HCl, HNO_3, or BrCl (mL)	Lot/Batch of BrCl, HCl or HNO_3	Date Filtered, Acidified, Oxidized	Date Analyzed	Analyzed By
pH/i.c.						
ICP-MS (0.2%)						
Filtered						
Reactive Hg						
Total Hg						

Bottle Type (circle one): BSG Polypropylene Teflon
Bottle Batch: _____ Init. Wt. (g) _____
COMMENTS:_____

Appendix B. (Cont'd)

LAKE MICHIGAN LOADING STUDY

IIT-CHICAGO

Vapor Phase Mercury

DATE	TIME	Outdoor Min Temp (in last 24 hrs)	Cabinet Min Temp (in last 24 hrs)	Outdoor Max Temp (in last 24 hrs)	Cabinet Max Temp (in last 24 hrs)	PRECIP. TYPE	Notes	Initials

Standard Operating Procedure for Sampling of Particulate Phase Mercury

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June 1, 1994

Version 2.0

Standard Operating Procedure for Sampling of Particulate Phase Mercury

1.0 Introduction/Overview

The objective of the Lake Michigan Loading Study is to assess the contribution of atmospheric deposition to the concentration of mercury and other toxic trace species found in Lake Michigan. The atmosphere has been implicated as one of the dominant sources of mercury and trace elements to bodies of water and it is clear from investigations in remote regions of the globe that long range transport of mercury and other toxics from source regions is occurring. By quantifying the wet deposition and ambient concentrations of mercury it will be possible to determine the relative importance of precipitation and dry deposition in accounting for the atmospheric loading of mercury to Lake Michigan. In addition, investigating other ambient trace species will aid in the identification of significant mercury sources.

Particle-phase mercury, Hg(p), generally represents a small but significant fraction of total atmospheric mercury. Recent advances in analytical chemistry have made quantification of the extremely low levels of Hg(p) possible, however, tremendous care must be exercised in all phases of sample handling and analysis. This protocol describes analysis of 'acid-extractable' total mercury from atmospheric particulate samples.

2.0 Preparation for Particulate Mercury Sampling

2.1 Acid Cleaning Procedure

All field sampling and analytical supplies which will come into contact with the samples are cleaned according to the following procedure.

Supplies to be acid cleaned are first rinsed in reagent grade acetone under a fume hood, then washed in hot tap water and diluted Alconox. Supplies are rinsed five times in cold tap water then rinsed three times in DI water. The supplies are then heated in 3M hydrochloric acid (EM Science Tracepur HCl in Milli-Q water (18.2 MΩ/cm)) for six hours at 80°C. One liter of 3M HCl is prepared by adding 750 mL of Milli-Q water to 250 mL of concentrated EM Science Tracepur HCl. The 3M HCl can be used several times and is stored for reuse in a polyethylene carboy dedicated for this purpose. The supplies are placed into clean polyethylene tubs which are then filled with the 3M HCl, making sure that all of the surfaces are submersed in the HCl. The tubs are covered and placed in a water bath which is heated to 80°C in a fume hood. The water in the bath is maintained at the level of the acid inside the tubs. After the water in the bath reaches 80°C, the supplies in the tubs are allowed to soak for six hours.

After the six hours, 80°C soak, the tubs are removed from the water bath and allowed to cool in the fume hood. When cool, the 3M HCl is poured back into its polyethylene carboy. The supplies are rinsed in the tubs three times with Milli-Q water. The supplies are then soaked in a 0.56M nitric acid solution (Baker Instra-Analyzed HNO_3 in Milli-Q water) for 72 hours at room temperature in the same polyethylene tubs in which they were heated with HCl. The nitric acid solution is made by adding 35 mL Baker Instra-Analyzed HNO_3 to 965 mL of Milli-Q water.

Nitric acid is reused for up to 6 months and is stored in a carboy dedicated for HNO_3. At the end of the three-day soak, the supplies being cleaned are rinsed three times with Milli-Q water and transferred into a Class 100 Clean Room.

Inside the clean room, the supplies are again rinsed three times with Milli-Q water. The tubs containing the supplies are filled with 0.56M Baker Instra-Analyzed HNO_3 that is kept in the clean room and is dedicated for this final step only. The supplies are then allowed to soak in this acid for seven days. This acid is prepared by adding 35 mL of the Instra-Analyzed HNO_3 to 965 mL of Milli-Q water. At the end of the seven day acid soak inside the clean room, the supplies are rinsed five times with Milli-Q water and allowed to air dry on a clean surface. When the supplies are dry, they are triple bagged in new polyethylene bags and removed from the clean room, ready for use in sampling.

2.2 Preparation of Glass Fiber Filters

Glass fiber filters (Gelman Sciences) are pre-treated to remove all mercury prior to use in sampling. Glass fiber filters, 47 mm in diameter, are placed in a clean crucible with a lid. The crucible is placed in a muffle furnace which is heated to 500°C and the filters are allowed to bake at this temperature for one hour. While hot, filters are removed from the crucible with acid-cleaned Teflon-coated forceps and placed in an acid-cleaned Teflon jar which is closed and sealed with Teflon tape. The Teflon jar is sealed in three successive polyethylene bags and stored at 40°C until use. Filters are stored no more than three months prior to use and frequent blanks are taken to ensure the filters remain clean.

3.0 Particulate Phase Mercury Sample Collection

During sample collection the filter packs are housed in a sampling box that is mounted on a pole or tower at least 3 meters above ground level. The sampling boxes are custom-made at UMAQL from fiberglass enclosures (Stahlin Enclosures) using quick connect couplings to connect the vacuum lines from the pump to the sampling devices. Sample intakes are at least 30 cm apart and are not close to any potential contaminant sources.

Since particulate mercury occurs at ultra-trace levels in the atmosphere and since mercury has a high vapor pressure, the selection of sampling flow rate and sampling duration has been carefully considered. It is typically necessary to sample at flow rates of 10-30 lpm for a minimum of 12-24 hours to collect enough particulate mercury for analysis.

The volume of air sampled is measured using a calibrated dry test meter (DTM). In addition, the flow rate is confirmed at the sample inlet before each sample using a calibrated rotameter. The pumps used (URG-3000-02M) are specially designed for trace level mercury sampling. They feature high efficiency oil less, brush less pumps. All pumps used for sampling are turned on at least 15 minutes prior to use.

3.1 Setting Up Glass Fiber Filter Samples

All sample preparation including filter pack assembly is done outdoors. In extreme weather conditions, operators may elect to complete some tasks in a clean indoor area, making sure sampling supplies (filter packs, forceps etc.) do not contact any surfaces other than in the clean bags in which they were received. Particle free gloves are worn during all sampling activities. When outdoors, site operators position themselves downwind of the sample at all times.

Before sampling commences, it is necessary to confirm the flow rate through the sampling train using a calibrated 30 lpm rotameter. To prevent potential contamination of the sample by the rotameter a 'flow check' filter pack is utilized. The 'flow check' filter pack is equipped with quick connects on either side for attachment of the vacuum line and the rotameter. The glass fiber filter in the 'flow check' filter pack is changed on a regular basis because is will rip or tear over time. The 'flow check' filter pack is placed into the mercury sampling box (Appendix B) such that the orange clampdown nut is on the inside of the mercury sampling box. The male quick-connect on the designated black latex vacuum line for the particulate mercury sample is secured into the female quick-connect on the back of the 'flow check' filter pack. An audible click is heard when the quick-connects are properly sealed.

The calibrated 30 lpm rotameter is equipped with an air diffusion muffler at the inlet and a 22 cm length of black latex tubing with a male quick connect at the outlet. The male quick connect on the rotameter tubing is connected to the female quick connect on the inlet of the test flow filter pack. The system is allowed to stabilize before taking the reading from the rotameter. The scale on the rotameter is read from the midpoint of the silver ball. The calibration curve and 30 lpm set point are indicated on the side of the rotameter. If the flow is below 30 lpm the operators are referred to the trouble shooting section (3.4) to look for possible remedies. If all systems appear normal, the operator adjusts the pump flow as necessary to achieve 30 lpm before starting the sample. The rotameter and 'flow check' filter pack are then removed and stored it in the plastic box provided.

Note: Once set, the flow on the URG-3000-02M is relatively stable. If frequent adjustments are necessary to achieve the desired flow operators are instructed to contact Matthew Landis at UMAQL immediately.

An 'open face' Teflon filter pack is utilized by UMAQL for particulate phase mercury collection. The filter pack is an assemblage of three main components--a threaded 47 mm opaque Teflon cylinder, a circular opaque Teflon filter support base with a 0.64 cm tube ferule nut, and an orange Teflon clamp down nut. After confirming the flow rate to be 30 lpm an acid-cleaned Teflon 'open-face' filter pack is removed from the field site box and unbagged. The filter pack is disassembled by unscrewing the orange clampdown nut and removing the 47 mm Teflon cylinder. The Teflon jar holding the pre-baked glass fiber filters is carefully opened. One 47 mm baked glass fiber filter is placed on the grid of the filter holder with the 'rough' side up using acid-cleaned Teflon-coated forceps. While holding the filter support base vertically to prevent the filter from falling out, the filter pack is reassembled by attaching the 47 mm Teflon tube and threading it firmly into the orange clampdown nut. The Teflon jar holding the remaining pre-baked glass fiber filters is quickly closed. Operators attempt to have the jar open for as little time as possible.

The sample filter pack is then inserted into the mercury sampling box hole designated for the particulate mercury sample. The quick-connect from the vacuum line to the outlet of the filter pack is secured. The DTM reading is immediately recorded along with the time, sample number, date, unusual meteorological conditions and any problems encountered on the sample log and tracking form.

3.2. Taking Down Glass Fiber Filter Samples

After putting on a new pair of particle free gloves, the black latex vacuum line is disconnected from the sample filter pack by uncoupling the quick connectors. The DTM reading is immediately recorded, along with the time, date, unusual meteorological conditions and any problems encountered, on the sample log and tracking form. The sample filter pack is removed from the mercury sampling box. While holding the filter pack vertically with the open tube facing up, the Teflon inlet cylinder is unscrewed from the orange clampdown nut. The Teflon cylinder is removed and the filter support base is lightly pushed up until the glass fiber filter is just below the top of the orange clampdown nut. The filter is then removed from the filter support base with acid-cleaned Teflon-coated forceps, making sure to only touch the exterior edge of the filter. The filter is carefully inserted into the base of the petri dish. The petri dish cover is replaced and sealed with a length of 1.27 cm Teflon tape around the joint between the lid and the base of the petri dish. The sample identification label is then attached to the cover of the petri dish. The sample filter pack is reassembled and sealed in a clean polyethylene bag and stored in the plastic container provided. The petri dish is triple bagged and shipped to UMAQL the day they it is collected. If the operator is unable to ship the sample, the sample is placed in a freezer until it can be shipped the next day.

3.3. Taking Blanks

A minimum of 25% field blanks and 10% storage blanks are taken to ensure samples are being collected in a contaminant-free manner. Field blanks involve loading a glass fiber filter into the open-face filter pack as described in Section 3.1 for a sample. The filter pack is placed in the mercury sampling box for two minutes *without the vacuum line attached.* After two minutes, the sample is taken down and labeled in the same manner as described in Section 3.2 for samples. Storage blanks are collected by transferring a new, unexposed filter from the Teflon jar into an acid-clean petri dish. The petri dish is sealed with Teflon tape and labeled appropriately. Blanks are shipped to UMAQL along with the samples taken on the same date.

3.4 Trouble Shooting

If flow through the 'flow check' filter pack is low:

- Check to make sure that all the connections are sealed (make sure the 'flow check' filter pack ferule nut fitting is tight, tubing quick connectors are all properly fastened, filter pack is screwed together tightly, tubing from the pump to the sampler is intact and connected securely).

- Make sure that the exhaust of the rotameter is not impeded in any way when using the rotameter to check flow.

- Check the vacuum gauge on the URG-3000-02M. If a high vacuum is indicated, quickly turn off the pump and look for a kink in the tubing or an obstruction in the exhaust tubes.

- Check the black latex tubing in the sampling box for cracks or tears due to weathering.

If all systems seem to be working properly and the flow remains low or erratic the operators are instructed to notify Matthew Landis at UMAQL (313) 763-7714 or at home (313) 663-9615 immediately.

4.0 Clean Room Procedures

4.1 Entering the Clean Room

Shoes are taken off outside the clean room by all UMAQL personnel. Personnel then enter the outer vestibule (changing room). Once inside, the hood is put on followed by the clean room suit and clean room boots. The boots are snapped to the suit at the back of the leg (to hold up the boots) and are buckled in the front. Personnel then step over a dividing bench where they put on clean room gloves and snap the clean room suit at the wrist. Now fully clothed they enter the clean room making sure to securely close the door behind.

4.2 Taking Supplies into the Clean Room

All supplies to be taken into the clean room are double bagged in polyethylene. The supplies to be taken into the clean room are placed in the outer dressing room. Upon entering the clean room, the outer bag is removed and left in the entry room. All supplies that enter the clean room that have not been bagged are rinsed with MQ-water and wiped off with particle-fee wipes.

5.0 Performance Criteria, Quality Assurance and Quality Control

5.1 Field operators are carefully instructed in the techniques of contaminant-free particulate phase mercury sample collection. All of the operators are currently operating sampling equipment for either the National Dry Deposition Network, the National Atmospheric Deposition Program, the Integrated Atmospheric Deposition Network or the Great Lakes Acid Deposition Network.

5.2 Every six months UMAQL personnel inspect each of the sampling sites to audit the performance of the equipment and to make all necessary repairs or adjustments

5.3 Co-located samples are collected from one sampling site during the study to quantify method precision. Reported concentrations for co-located samples are based on the mean of the two samples.

5.4 Precision and accuracy levels will be set and maintained for each type of analysis. A relative precision for total mercury of less than 15% is maintained for samples with values at least three standard deviations greater than the detection limit. Analysis of standards and controls is within 10% of the stated value

A minimum of 25% of all samples are analyzed in duplicate. Reported concentrations are based on the mean of the replicates. Analytical precision averages better than 6%.

5.5 Every three months maintenance on the CVAFS analyzer is conducted, including replacement of the UV lamp, the Teflon tubing, and the detection cell.

Appendix A. Facilities, Equipment and Reagents

Following is a list of the required facilities, equipment, supplies and reagents for sample preparation and sample collection that are outlined in this document. The make and model of the following items are those used at The University of Michigan Air Quality Laboratory. Many of these items are available from a variety of sources.

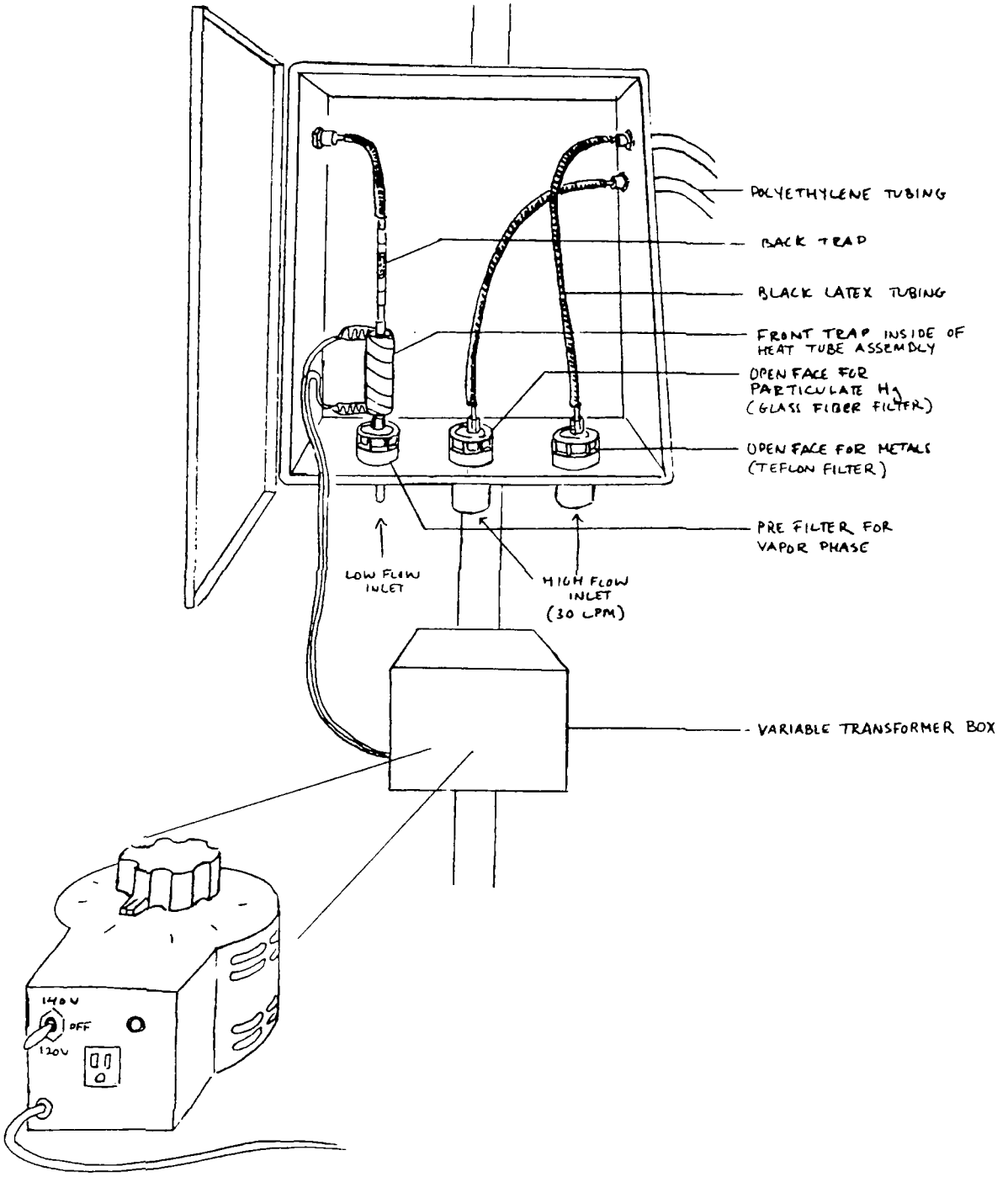
1. Preparation of Field Supplies

Class 100 Clean Room, Work Stations
Clean Room Gloves
Particle-free Wipes
Clean Room Cap, Gown and Boots
Milli-Q Water (18.2MΩ/cm)
Exhaust Hood
Acetone
Alconox
Polyethylene Tubs
EM Science Tracepur and Suprapur Hydrochloric Acid
Polytherm Water Bath (Science/Electronics)
Baker Instra-Analyzed or EM Science Suprapur Nitric Acid
New Polyethylene Bags
20 L Polyethylene Carboys

2. Sample Collection

Vacuum Pump (URG, Model 3000-02M)
Calibrated Dry Test Meter (DTM)
Calibrated 30 lpm Rotameter (Matheson)
HDPE Tubing with quick connects
Black Latex Tubing
Mercury Sampling Box (UMAQL, See Appendix B)
Acid-Cleaned 47mm Teflon Filter Holders (Savillex, PFA Labware)
47mm Preheated Glass Fiber Filters (Gelman Sciences A/E)
Acid-Cleaned Teflon Jars (Savillex, PFA Labware)
Teflon-Coated Forceps
Particle-Free Gloves
Teflon Tape
- Sample Labels
Field Operator Log Book
Sample Tracking Forms
Shipping Boxes

Appendix B.


POLYETHYLENE TUBING
BACK TRAP
BLACK LATEX TUBING
FRONT TRAP INSIDE OF HEAT TUBE ASSEMBLY
OPEN FACE FOR PARTICULATE Hg (GLASS FIBER FILTER)
OPEN FACE FOR METALS (TEFLON FILTER)
PRE FILTER FOR VAPOR PHASE
LOW FLOW INLET
HIGH FLOW INLET (30 LPM)
VARIABLE TRANSFORMER BOX
140V
OFF
120V

Appendix C.

LAKE MICHIGAN LOADING STUDY

IIT-CHICAGO

Open-Face Filter Pack: Particulate Mercury Filter (Glass Fiber)

Sample No.	Date On	Time On	Flow On (LPM)	DTM On	Date Off	Time Off	DTM Off	Notes	Init.

PUMP SYSTEM USED:_____

DTM #:_____

ROTAMETER #:_____ CALIBRATION CURVE=_____

Appendix C. (Cont'd)

LAKE MICHIGAN LOADING STUDY *SAMPLE TRACKING FORM*

ITT--CHICAGO

Particulate Mercury Samples: Glass Fiber Filter

Sample Number*:_____
Gold Trap Number:_____
Operator:_____ _____

Date On:_____ Date Off:_____
Time On:_____ Time Off:_____
Rotameter Reading On:_____ Rotameter Reading Off:_____

*If Blank Sample Note Type and How It Was Handled (Shipping Blank, Field Blank, etc.)

_____
_____

Notes: (ambient conditions, anything out of the ordinary, using freshly cleaned filter packs, etc.)

_____
_____
_____
_____

For Use at Univ. Of Michigan Air Quality Lab

Date Sample Received:_____ Rec'd By:_____
Date Sample Analyzed:_____ Rec'd By:_____

Analyzer #:_____

Notes: (Appearance of Sample, Are Endplugs Teflon-taped, etc.)

_____
_____
_____
_____
_____

Standard Operating Procedure for Dry Deposition Sampling:

Dry Deposition of Atmospheric Particles

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February 10, 1996

Revision 2

Standard Operating Procedure for Dry Deposition Sampling: Dry Deposition of Atmospheric Particles

1.0 Introduction - Principles of Dry Deposition Sampling

Pollution can exist in soil, in the waters of lakes, rivers and streams and in water below the ground. Pollution can also exist in the air, whether it is in the air close to the ground or in the air of the upper atmosphere. Probably every place it has been sought, some form of pollution has been found. "Pollution" is the everyday word used to describe material found anywhere in the environment that would not be there if it were not for mankind's activities. The technical term used to describe pollution is "anthropogenic", which means "man-made"

When the term "atmospheric dry deposition" is used, "atmospheric" refers to the place where pollution may reside and, unfortunately, the place from which pollution may be transferred. In fact, pollution may be transferred among several or all the components of land, water and air. "Dry deposition" refers to one pathway--there are several--through which pollution can be transferred from the component of air to a component of land or water.

This dry deposition pathway is not reserved for man alone. It is part of a natural global process of cycling that has always been there, only now anthropogenic matter--pollution--is being carried alongside natural matter. Dry deposition is defined as the deposition to land or water of particulate matter. If particles are attached to snow or suspended in rain droplets, then the term "wet deposition" is used to describe the process.

So dry deposition is one of several types of atmospheric deposition that occur. But whereas wet deposition is associated with a particular event--rainfall or snowfall--dry deposition can be thought of as occurring year round, even when another kind of deposition is also taking place

It would be difficult or impossible to collect dry deposition during a rainfall event, so the dry deposition sample surface is covered whenever it rains or snows. Doing this manually would require a constant vigil, especially on a cloudy day or overnight. So instead a sampler (the EAGLEII) is used that senses wet conditions and automatically covers the sampling surface until the sensor dries off.

The sampling surface itself is a 1 x 3 inch greased Mylar strip which has been previously mounted onto a clean PVC plate. This plate then holds the strips horizontally so that dry deposition can collect on the strips' greased surfaces. The grease is there to prevent particle bounce which can occur if only a hard surface is used. This collection technique is not unlike the collection of dust by an automobile windshield which is commonly seen even when there has been no precipitation. The grease used (L-Apiezon) is non-volatile, so the difference between before and after sampling weights of the strips is a measure of the amount of deposited material.

The plates on which the greased strips are mounted have a sharp leading edge and are kept pointing into the wind. The sharp leading edge is to provide a laminar or non-turbulent flow of air over the strips (turbulence increases dry deposition). The less turbulence a natural surface creates, the less the deposition. By using a surface which provides a laminar flow of air, the material collected on the strips will be a lowest approximation of the deposition at that sampling location.

The plates are kept pointing into the wind by the large tail on the back of the EagleII. There are two reasons for this. One is to avoid reentrainment of material collected on the sampler which could redeposit on the strips. The other reason is to avoid turbulence created by the structure of the EagleII, which would increase deposition.

Sampling times vary, depending on the ultimate use of the strips. Short-term samples are generally exposed from eight to 72 hours. Short-term samples are usually taken only in urban areas, because of the large amount of dry deposition there. Long-term samples are generally exposed for one to four weeks. These longer sampling times are needed in some non-urban and rural areas, where there may be much lower amounts of dry deposition. The EagleII was designed with long-term sampling in mind.

2.0 Sample Collection: Atmospheric Particulate Dry Deposition

2.1 Preparation for Particle Dry Deposition Sampling

A list of equipment and supplies for field investigations is given in Appendix A. All Mylar strips, strip covers, strip sample box, SP Brand Five-Slide Mailer, dry deposition plates, plate holders and Rubbermaid plate containers are cleaned in double distilled methanol and deionized water in a seven-day procedure before use in sample collection. Apiezon grease-coated strips equilibrate for 24 hours in the strip sample box before weighing. After weighing the four strips are mounted onto each dry deposition plate with strip cover and Teflon-coated clips. Dry deposition plates are stored in the Rubbermaid sample container before and after sampling. Field blanks are also prepared for each sampling period; four preweighed grease-coated Mylar strips are mounted onto the dry deposition plate and kept in the Rubbermaid sample container during the sampling period.

During sample plate set-up and removal, the operator must be very careful not to touch the greased strip surface. This is very important to maintain sample integrity. During sample collection the dry deposition plates are taken out from the Rubbermaid sample container and placed on each side of an automatic dry deposition sampler (EagleII--see Figures 1 and 2) about 2 meters above ground level.

2.2 Particulate Dry Deposition Sampling

During the course of this study atmospheric particles will be collected onto greased Mylar strips each with exposure area 10.3 cm^2 for a total of 41.2 cm^2 on each dry deposition plate. Two dry deposition plates are needed in one sampling period.

2.2.1 Taking Off Dry Deposition Plate Samples

2.2.1.1 Record total sampling time and open sampling time in minutes on the Eagle's log sheets (see Appendix A). These times can be determined by switching the middle switch up and down on the right side of the control box. The times will be displayed on the red display panel. The open time will be preceded by the letters "OPE" and the total time will be preceded by "TOTL". You may have to shade the control box to read the display on a sunny day. Record the rest of the information required in the log sheet.

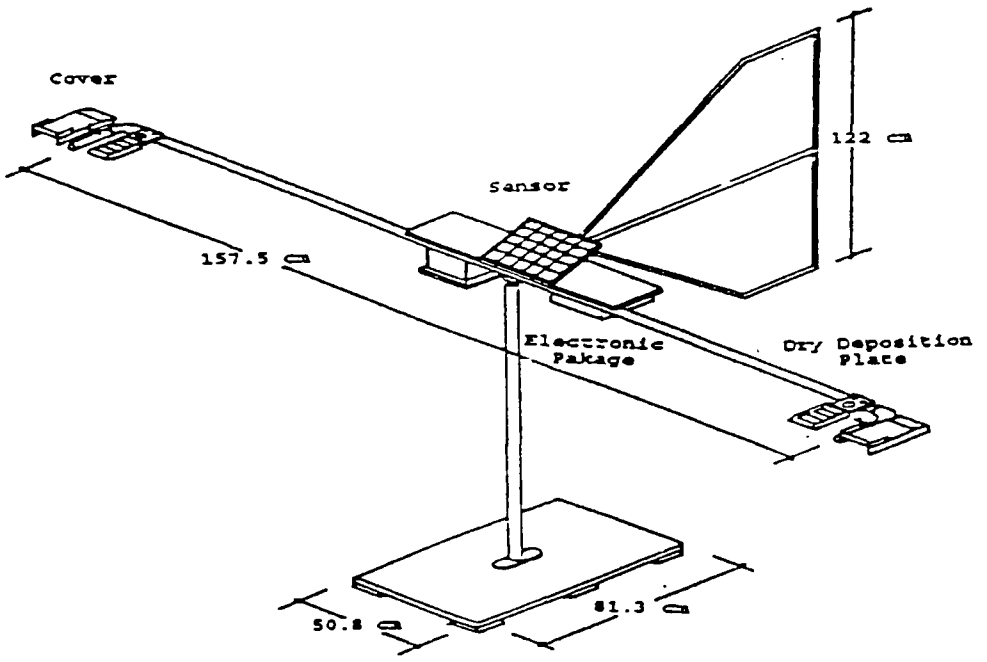

Figure 1. Drawing of Eagle II

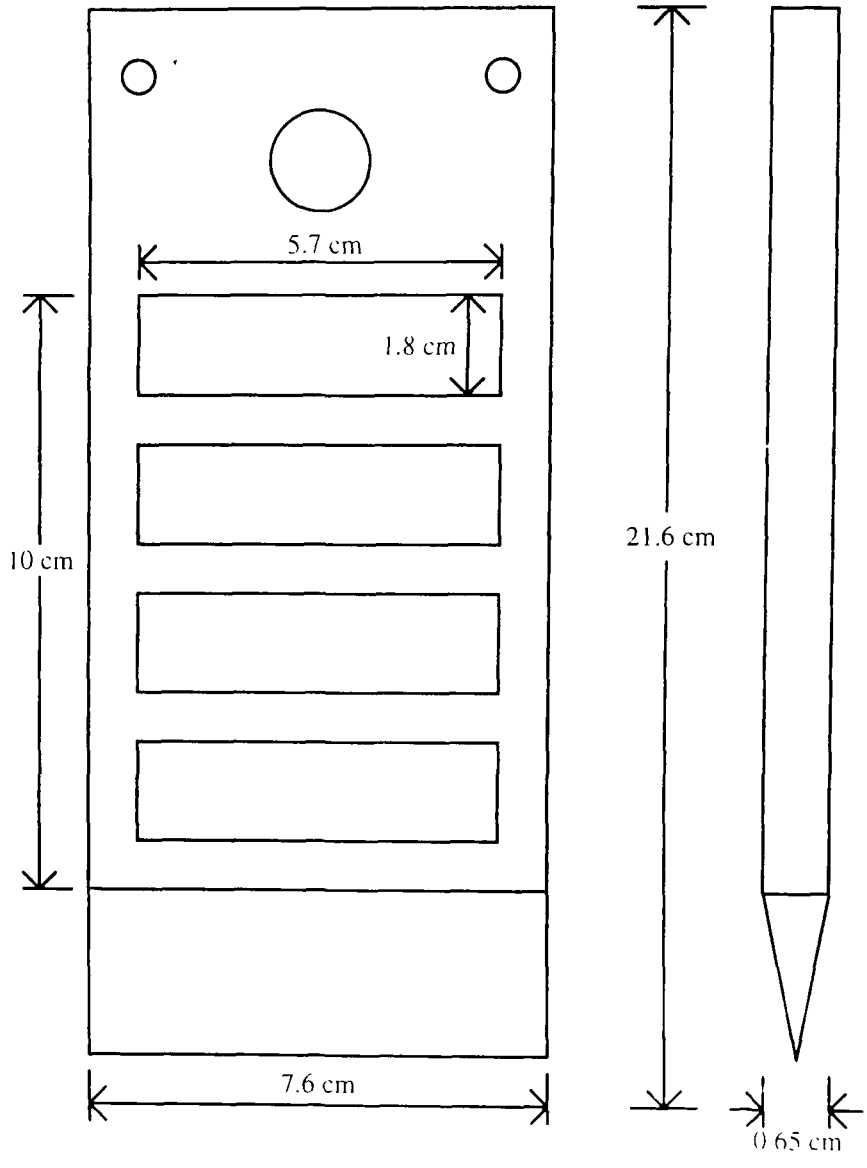

Figure 2. Top View of a Dry Deposition Plate

2.2.1.2 Put on particle-free gloves. Take down the dry deposition plates from both sides of the Eagle by unscrewing the nuts on the bolts. Be careful not to touch the surface of greased strips.

2.2.1.3 Place these two dry deposition plates back into the Rubbermaid sample container along side the field blank. Slide the plates sideways into slots with the sharp edge pointed into the thin slot. Take the Rubbermaid sample box out from the field blank storage box and take it (or send it) back to the Illinois Institute of Technology Air Quality Lab (IITAQL).

2.2.1.4 The rain sensor has to be cleaned at each sample change. Use a Polyester/Cellulose Blend Wiper wetted with deionized water to gently wipe-off the surface of the rain sensor.

2.2.2 Setting up Dry Deposition Plate Samples

2.2.2.1 Turn on the control box (see Figure 3) on the automatic dry deposition sampler by switching up the third switch on right side of the control box (turn it off by switching down).

2.2.2.2 Examine the timer in the control unit by switching the middle switch up and down (see Figure 3) to ensure the correct counting of total sampling time and open sampling time (exact exposure time) of the dry deposition plates. One can ensure the correct running of the timer by comparing the minutes shown on the display with a watch (normal counting test is around two to three minutes).

2.2.2.3 Perform a wet test by putting a little bit of water on the Eagle sensor (see Figure 1) to make sure the Eagle covers on both sides close when the sensor is wet and reopen when it is dry.

2.2.2.4 Put on particle-free gloves. Take dry deposition plates out from Rubbermaid plate container (which are been prestored into the sample holder in the Rubbermaid sample container) and place one plate on each side of the automatic dry deposition sampler using two ¼ inch bolts and nuts.

2.2.2.5 Reset the timer by pressing the red button (press and hold the button for five seconds), which is the first button on the right side of the control box.

2.2.2.6 Place the Rubbermaid sample container (which contains the field blank) into the field blank storage box.

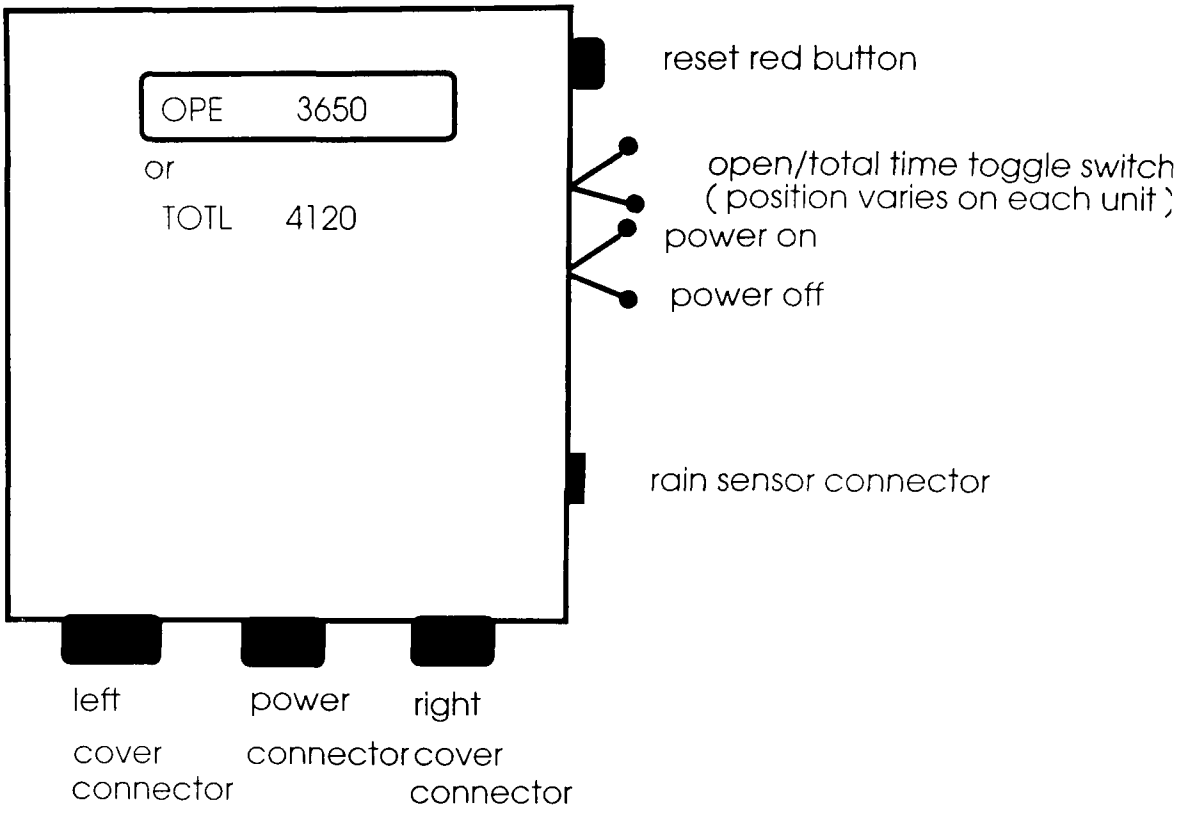

FIGURE 2 CONTROL BOX

Figure 3. Dry Deposition Sampler Control Box

2.2.3 Taking Blanks

Field blanks will be taken during each sampling period of this study. To take a field blank, four preweighed grease-coated Mylar strips will be mounted onto the dry deposition plate and put it in the Rubbermaid sample container along with the sample plates. Unlike the sample plates, the field blank will stay in the Rubbermaid sample container during the entire sampling period. All Field blanks have to be labeled appropriately. Field blanks are given the designation BK after the sample number, such that the field blank is labeled:<site>-01BK. For example the field blank taken with Sample 9 from IIT site will be labeled IIT-8BK.

3.0 Sample Transport

Samples should be transported to the Illinois Institute of Technology Air Quality Lab (IITAQL) immediately after sampling. Samples should be stored in sealed Rubbermaid sample containers during transport. In case the samples cannot be taken to IITAQL immediately after sampling, store the samples at room temperature away from any possible contaminate sources until shipment. Send the sample log sheet along with each of the samples collected. When a sample log sheet is completed, make a photocopy of the sheet, and keep the photocopy in the three-ring binder provided.

Ship samples to:

Dr. Thomas M. Holsen
Associate Professor
10 West 33rd Street
Department of Chemical and Environmental Engineering
Illinois Institute of Technology
Chicago, IL 60616-3793

4.0 Troubleshooting

When troubleshooting the EagleII, follow "secure the sample first" principle. Ideally, no work should be done with samples in place.

When the EagleII is turned off then on again, both covers should cover then uncover the sample area.

4.1 Cover is Loose

The cover can become loose under normal operating conditions after a few months' time. (This problem is being addressed in the next Eagle design, the EagleIII.) Two set screws hold the cover in place. These set screws require an allen key in order to be loosened. One set screw is located on the top and one on the side of the cover pivot shaft. (See Figure 4)

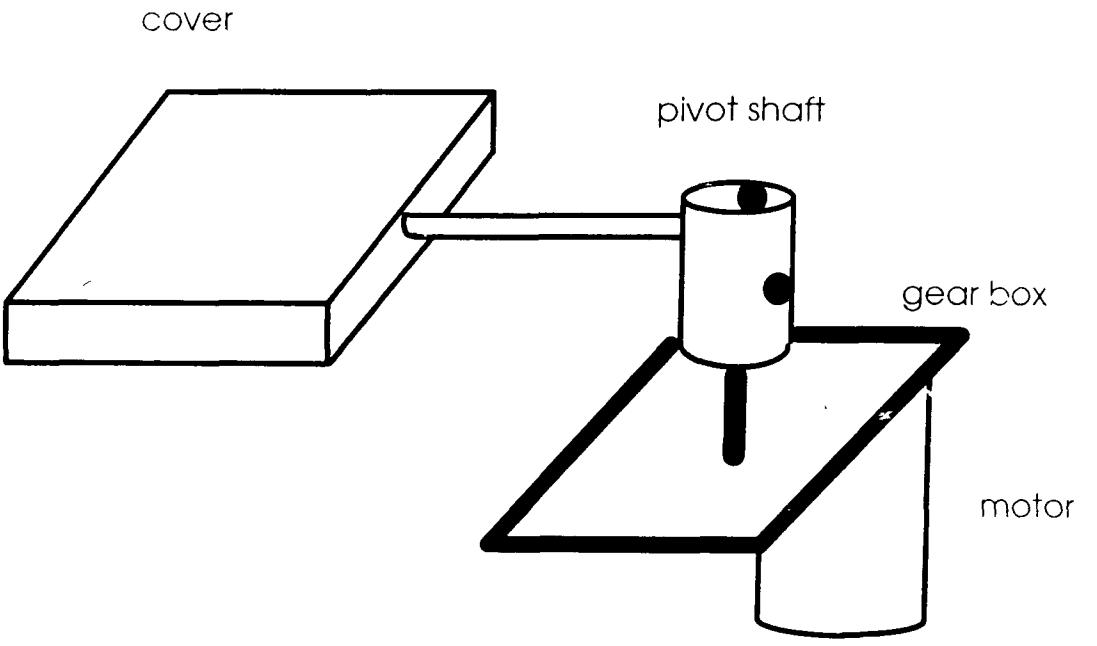

Figure 4. Top and Side View of Plate Cover

4.1.1 Top Set Screw

Rarely needs adjustment and should only be touched if care is taken to ensure that all parts of the cover and the brass shaft on which it is mounted have proper clearance to rotate.

4.1.2 Side Set Screw

This set screw is trouble-prone. Through wear and tear, the set screw wears down the flat part of the cover pivot shaft, and the cover develops greater-than-normal play Normal play is ½ inch of play back and forth (1 inch total) at the end of the cover farthest away from the cover pivot shaft..

4.1.3 Cover Inspection

1) Make sure there is no sample in place.
2) Turn the EagleII off (the on/off switch down).
3) Turn it on long enough to move the covers about halfway, then turn off again.
4) Gently move the covers back and forth to check play. If play is less than 1 inch, turn the EagleII on and take no further action. If play is greater than 1 inch, then call for assistance since the cover may need to be removed and the flat on the cover pivot shaft filed.

4.1.4 Cover Adjustment

The sides of the covers should be about ¼ inch above the sampling surfaces. If a cover is too low, it may touch and ruin a sample. If too high, the cover will not protect the sample. Covers should be horizontal, which can be gauged by the eye.

To adjust a cover:

1) Call for assistance.
2) If the cover is not horizontal, loosen the top set screw and gently tilt the cover until level. Then tighten the set screw.
3) If the cover has been determined to be too high or too low, loosen the side set screw and move the cover into a position where the bottom of the cover sides are about ¼ inch above a dummy plate. This will require the covers be moved above the sampling area, which is accomplished with the on/off switch. Turn it off (down). Turn it on (up). When the covers move into the desired position, turn the switch off again. The cover-to-sampling-plate clearance can now be seen.
4) Before resuming normal operation, turn the switch off then on again to make sure the cover rotates freely, is not loose and does not contact the dummy plate.

4.2 Cover Will Not Move

Call for assistance.

4.2.1 Only One Cover Moves

Check the two wires that connect to the motor. If both connections are good, then either a motor is bad or a connector has become corroded. Replace the motor. 1) Remove the two machine screws that hold the motor to the underside of the pivot shaft gear box. 2) Disconnect the two wires. 3) Install the new motor and reconnect the two wires, disregarding the polarity, since the motor functions either way.

4.2.2 Neither Cover Moves

Perhaps the EagleII has lost power. See the instructions under "No power."

4.3 No Power

4.3.1 If the display is not lit when the on/off switch is on (up), it is likely that there is no power. Two related conditions will cause this. Either one or both of the fuses in the power box are blown, or a power connector is shorting. When a power connector shorts, it will blow a fuse in the power box.

4.3.2 Check power box. Disconnect the power connector from the power box.

Warning: The connectors used on the EagleII are kept in place by a lock ring which only makes a one-quarter turn; care should be taken not to over twist the lock ring, as this will damage the connector. Use a multi-meter set on "DC Volts" to measure the DC Volts output of the power box. If output is 17 VDC, then proceed to check the power connectors. If there is no output, then remove the four machine screws holding down the cover of the power box and remove the cover.

Warning: Unplug the power box before opening it. Use the multi-meter set on "Ohms" to see which fuse is bad. With the multi-meter on "Ohms", put the red and black leads together and zero the needle on the meter. This may not be necessary on some models, for example models with digital readouts. Now put one lead on each end of the fuse to be checked. If the fuse is good, the readout will indicate 0 ohms. If bad, the readout will show infinity. This may be done safely with the fuse in place. After replacing any faulty fuse with one of the same Amp rating (on fuse), replace cover, plug it back in, then check again to see if output is 17 VDC. The power box should work at this point. Before connecting the power connector from the EagleII, both power connectors should be checked for signs of corrosion.

4.3.3 Check power connectors. Disconnect the one power connector from the power box and the other from the control box.

Warning: The connectors used on the EagleII are kept in place by a lock ring which only makes a one-quarter turn; care should be taken not to over twist the lock ring, as this will damage the connector. Use a multi-meter set on "Ohms" to determine if there is continuity from one to the other connector. This is done just like checking a fuse (see preceding paragraph). Zero the multi-meter. Put one lead on one electrode of the connector that goes to the power box. Put the other lead on an electrode of the connector that goes to the control box. If the meter shows infinity, then try touching the lead to the other electrode of the control box connector. If the meter again shows infinity, then there is no continuity between the two connectors and a connector is bad and needs to be replaced. If there is continuity (meter reads 0 ohms), then check across the two electrodes of each connector. If there is continuity, then a connector is bad and needs to be replaced, and the bad connector is probably causing the fuses in the power box to fail. Over twisting the connectors can cause the same problems experienced from a corroded connector.

4.4 Power Cord Wrapping Around Support Pole

The slip ring bearing has a shaft which protrudes into the support pole. The bearing is designed so that while the top rotates, the bottom is stationary. The shaft on the bottom of the bearing has to be secured. If it is not, the bottom and top will rotate together. The power cord which goes to the power box is attached to the bottom of the bearing and will therefore be dragged around and around the support pole. An undue strain would be placed on the power box connector. To avoid this condition, a hole is drilled through the support pole and bearing shaft. A machine screw and nut is placed through this hole.

Note: The hole was not drilled through the exact center of the shaft and pole. If the screw is removed and the shaft turned 180°, the screw will probably not fit back in. This also means that a pole and shaft come as a matched pair, since they were drilled at the same time. *Shafts and poles are not interchangeable.* If a problem arises where the screw will not fit in, a wire or nail can be used to temporarily solve this problem until a nut and bolt can be used.

4.5 No Timer/No Display

If the display is lit, but the timer does not function, or if there is no display but power comes to the control box, call for assistance. The microprocessor in the control box may need to be replaced.

4.6 EagleII is Loose

Each EagleII has a hold down peculiar to the site, but each must be monitored for excess looseness which may cause damage in a high wind to itself, other instruments or may pose a hazard to people. Call for assistance.

4.7 Samples Covered, No Rain

This can occur in very humid conditions, such as when the weather is in a transition period, or when the rain sensor connector has shorted. The connector shorting due to corrosion will make the covers cover the samples. The sensor itself operates on the principle that when rain hits its surface, a short occurs that makes the covers cover the sample. The sensor connector needs to be replaced. Call for assistance.

5.0 Quality Assurance and Quality Control

Field blanks will be collected to ensure samples are being collected and extracted in a contaminant-free manner. Split samples will also be collected and analyzed. See the *Standard Operating Procedures for Preparation, Handling and Extraction of Dry Deposition Plates* for details.

If you have any questions, at any time, please do not hesitate to call Jeff Lu or John Kelly at the Illinois Institute of Technology (312) 567-3553. If you cannot reach someone at the lab phone during business hours, call Prof. Tom Holsen at (312) 567-3559 and leave a message on his machine. We will get back to you as soon as possible.

6.0 Contact List

For questions or problems send a message or call:

Jeff Lu
IIT Air Quality Lab.
(312) 567-3553 (lab)
(312) 791-9649 (home, leave message)

or

Dr. Thomas M. Holsen
Associate Professor
10 West 33rd Street
Department of Chemical and Environmental Engineering
Illinois Institute of Technology
Chicago, IL 60616-3793
Tel (312) 567-3559(leave message)
Fax (312) 567-3548
E-Mail ENVEHOLSEN@MINNA.IIT.EDU

Appendix A. Sample Log Sheet

EAGLE SAMPLE LOG SHEET		DATE	
SAMPLE NUMBER			
SAMPLE LOCATION			
WEATHER CONDITIONS (CIRCLE ONE)	SUNNY	RAINY	CLOUDY
COVER STATUS (CIRCLE ONE)	OPEN	CLOSED	
OPEN TIME, MIN			
TOTAL TIME, MIN			
RESET TIMER?*	YES	NO	
WET TEST RESULTS (CIRCLE ONE)	COVER THEN UNCOVER	NO RESPONSE	OTHER (EXPLAIN BELOW)
* RESET TIMER ONLY WHEN STARTING A NEW SAMPLE			
COMMENTS			

How to fill out the Eagle's log sheet:

Example 1. In this example it is a sunny September 13, 1994, so the site operator enters 09/13/94 into the date, and circles sunny in the weather conditions row. Since it is a sunny day the plate covers should be open and operator should circle open in the cover status row. The open time and the total time should then be recorded. These times can be determined by switching the middle switch up and down on the right side of the control box. The times will be displayed on the red display panel. The open time will be preceded by the letters "OPE" and the total time will be preceded by "TOTL" You may have to shade the control box to read the display on a sunny day. A wet test should then be performed by putting a little bit of water on the Eagle sensor (see Figure 1) to make sure the Eagle covers on both sides close when the sensor is wet and reopen when it is dry. Any comments can be entered at the bottom of the log sheet.

Appendix B. Parts List

One power box (gray; input 120 VAC, output 17 VDC; one 10 amp fuse, one 5 amp fuse)

One control box (white; includes a display, sensor connector, two motor/position-sensor connectors, power connector, on/off switch, total-time/open-time switch, red reset switch, 2 blue relays for the two motors, black microprocessor).

One base

One support pipe

One support pipe screw (prevents rotation of slip ring bearing shaft)

Four set screws

Two cover motors

Two cover motor gear boxes

Two covers (left and right)

Tail

One sensor (for rain and snow)

One sensor holder (mounted on tail)

One slip ring bearing (allows free rotation of upper section, while maintaining a continuous connection to power supply)

Two power connectors (one to power box, one to control box; two-pin connectors)

Two motor/position-sensor connectors (on control box; six-pin connectors)

One sensor connector (on control box)

Four position sensors (two for each cover; not to be confused with rain sensor)

Two sampling plates (dry deposition plates)

One sample blank

Appendix C. Terminology

Sampling area: Where plates get mounted

Cover mount shaft: Horizontal brass shaft from cover

Cover pivot shaft: Vertical steel shaft on which cover pivots to the closed and open positions

Closed cover: The cover is over the sampling area, sampling has been discontinued during a rain or snow event; the timer continues to count total time, but stops counting open time until the cover is again in the open position.

Open cover: The cover is not over the sampling area, the EagleII is in sampling mode; the timer counts open time as well as total time

Dry deposition: Deposition to land or water of particulate matter, both man-made and natural

Anthropogenic: Man-made material found in the environment

Volume 1

Chapter 2: Water

Standard Operating Procedure for Sample Collection of Atrazine and Atrazine Metabolites

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1994

Standard Operating Procedure for Sample Collection of Atrazine and Atrazine Metabolites

1.0 Procedures

1.1 Water will be collected using the method outlined in LMMB 013, *Field Sampling Using the Rosette Sampler*. The rosette will be deployed and retrieved in accordance with standard ship operating procedures.

Sampling locations and depths are outlined in Section 2 with a map provided in Figure 1.

1.2 Sampling Open Water Stations

If the water column is stratified, sampling depths will be the mid-epilimnion and mid-hypolimnion. If the water column is not stratified samples will be collected two feet below the surface and at the mid-water column. The following stations are to be sampled as open water stations: mb63, mb72, mb57, gb24, gb17, 45, 52, 43, mb38, 31, 36, mb26, mb25, mb24, mb21, mb20, mb19m, 340, mb13, mb9, 17, 1, 5, 3.

In addition, duplicate samples should be collected at Station 1 and Station 72m.

1.3 Sampling Master stations

Stations 18 and 41
If the water column is stratified, samples should be collected at the following depths: 2 ft below the surface, 5 ft below the surface, mid-epilimnion, thermocline, mid-hypolimnion, and 5 ft off the bottom. Duplicate samples should be taken at the 2 ft below the surface and 5 ft off the bottom depths.

If the water column is not stratified samples should be taken 2 ft below the surface, mid-water column, 5 ft off the bottom. Duplicates should be collected at all of these depths.

Stations 23, 27, 47
If the water column is stratified, samples should be collected at the following depths: 2 ft below the surface, mid-epilimnion, mid-hypolimnion, and 5 ft off the bottom. In addition, duplicate samples should be collected from all depths at Station 23. These samples will be labeled with "BE Dup.", and are samples to be used in a comparison study.

If the water column is not stratified, samples should be collected 2 ft below the surface, mid-water column and 5 ft off the bottom. Duplicate samples should be collected from all these depths.

1.4 Sample Collection

1.4.1 Objective: Water will be transferred from individual rosette canisters to amber 1 L bottles and placed in cold storage until processed by scientists from the University of Minnesota.

1.4.2 Once the rosette has been carefully positioned to its proper location on the deck of the ship examine the canisters to confirm that all canisters slated for sampling have properly fired.

1.4.3 All operations executed on the deck of the ship require personal flotation devices to be worn.

1.4.4 Remove amber 1 L bottle from storage area and visually inspect for cracks or severely chipped cap threads.

1.4.5 Confirm with marine tech. or other rosette operator which sampling depths correspond to which rosette canisters.

1.4.6 With the sampling depth of each canister noted, vent lower valve on canister allowing water to drain out. Allow several hundred milliliters to drain out before sampling.

1.4.7 Remove cap and aluminum foil from amber one-liter bottle. Rinse bottle and cap three times from the canister discharge stream. Be sure to rinse bottle and cap with the same water that is to be sampled. Use about 200 mL for each rinse, and thoroughly wet all interior surfaces of bottle.

1.4.8 While filling bottle be careful not to place aluminum foil on any dirtv surface or to allow aluminum foil to wash or blow away. While the amber bottle is uncapped the cap should be placed upside down (concave surface up) on clean surface and aluminum foil placed inside of cap.

1.4.9 Once bottle has been thoroughly rinsed carefully fill bottle with water. Fill bottle to within 1 or 2 cm of the very top of the bottle.

1.4.10 While filling bottle be careful not to touch discharge stream before it enters the bottle, and be sure not to let any foreign debris enter the bottle. Avoid all possible contaminants including smoking.

1.4.11 For each depth a 2 L sample is required, therefore, two one liter bottles should be filled for each depth. Each sample must come from the same rosette canister even if two canisters are fired at the same depth.

1.4.12 Label bottle and cap. A label is provided on each bottle. The label has locations marked for the following information: Lake, Station, Date, Depth, and code number. The code number is simply the sequential number of the sample, i.e. the first sample collected is 1, the second 2, etc. Numbering will continue in progressive order throughout the mass balance study, *do not* start renumbering at each location or in each lake, i.e. the last sample collected will nave a code number of about 550.

1.4.13 Since there are two bottles per sample depth, label one sample "a" and one "b", e.g., a code number might be la and 1b or 450a and 450b.

1.4.14 The code number should be written on the cap of each bottle as well as the label. The code number is the only information necessary on the cap. A labeling surface is provided on each cap.

1.4.15 When labeling has been completed move to next canister

1.4.16 Once water from all required depths has been transferred to amber bottles, carefully move bottles to cold storage. Cold storage will be the walk-in cooler provided on board the ship. Storage crates are provided but care should be taken to ensure that crates are secure while ship is moving.

1.4.17 The walk-in cooler should be maintained at approximately 4°C. The cooler should not be any colder than this since it is possible that the samples would freeze and break the bottles. If the cooler goes above 10°C for any period over an hour a note should be made of this in the sample log book.

1.4.18 Once samples are secure in cold storage, information about the samples collected and the sampling site should be entered into the sample log book provided by the University of Minnesota. All information on bottle labels should be entered into the log book as well as a sketch of a temperature depth profile, a note on weather conditions, and who collected the samples.

1.4.19 The temperature depth profile should list the surface temperature of the water the hypolimnion temperature, and the location of any stratification. An accurate temperature depth profile is available from the EBT printout. An example of a sample log sheet is included.

2.0 Sample Locations

Remember:

Rinse three times
Fill two bottles per one sample
Label bottle and cap

2.1 Open Water Stations:

2.1.1 If Stratified
*Mid Epi
*Mid Hypo (If possible sample hypo at depth that corresponds to mean particle mass as measured by transmissometery)

2.1.2 If Not Stratified
*2 ft below surface
*Mid water column

Collect duplicates of two open water stations. One station in Northern LM and one in Southern LM. Put "DUP" on label.

2.2 Master Stations:

2.2.1 If Stratified

Stations 18 and 41
*2 ft below surface *plus duplicate*
*5 ft below surface
*Mid Epi
*Thermo
*Mid Hypo
*5 ft off bottom *plus duplicate*

Stations 23,27, 47
*2 ft below surface
*Mid Epi
*Mid Hypo
*5 ft off bottom

*Plus duplicates of all depths at Station 23 and put "BE DUP" on label

2.2.2 If Not Stratified

All Master Stations (18, 23, 27, 41, 47)
*2 ft below surface
*Mid water column
*5 ft off bottom

*Duplicates of all depths at Stations 18, 23, 41 (put BE on Station 23 label)

Mark Station 18 and Station 41 Duplicates with "DUP", Station 23 with "8E DUP" in addition to regular sample label.

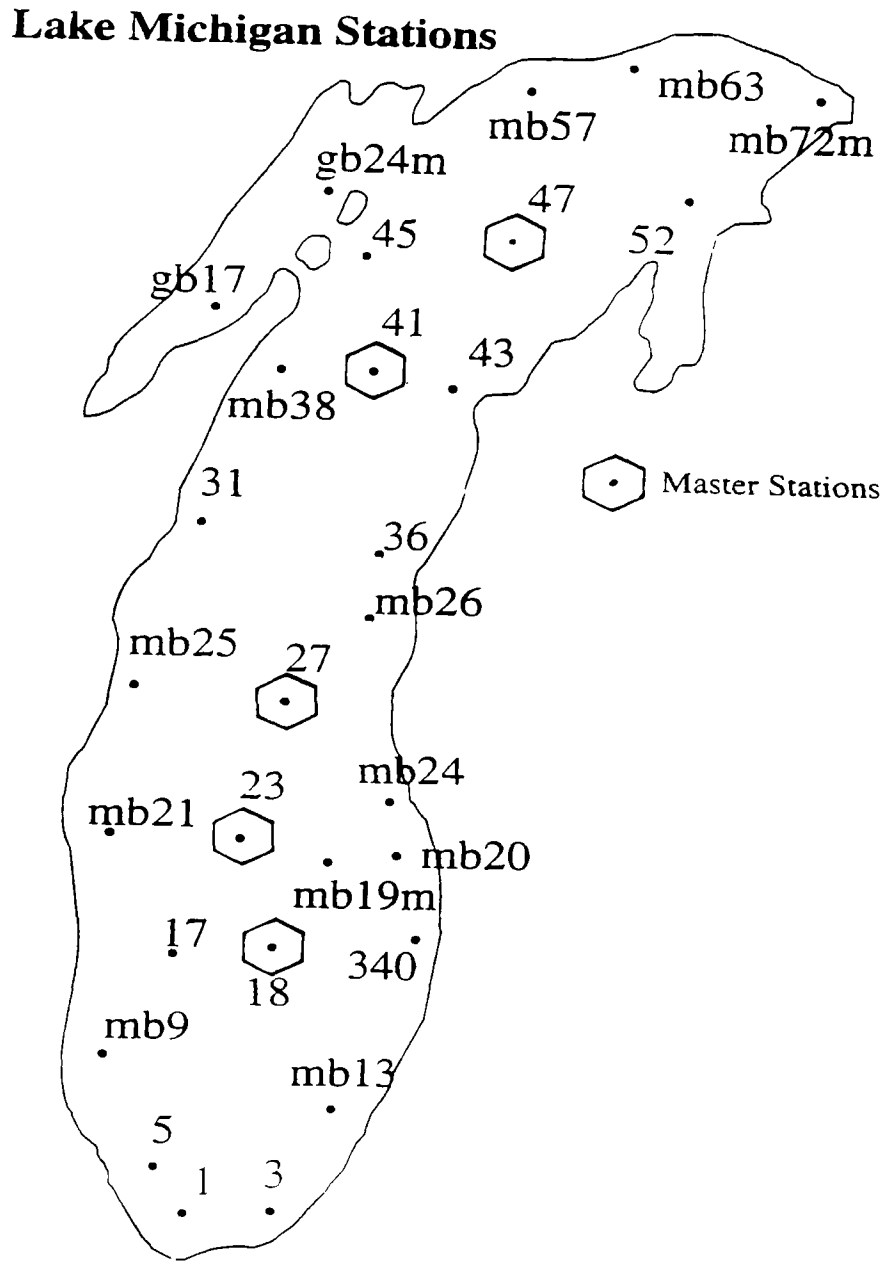


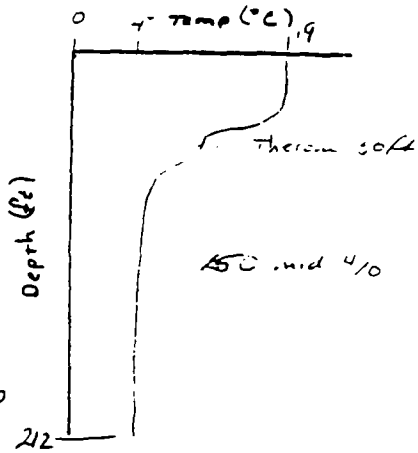
Figure 1
Lake Michigan Stations

Herbicide Sample Log

Date: May 5th 1994
Lake: L. Mich
Station: 18
Collector: SPS

Depth (ft)	Code #
2	12a-b
5	13a-b
12	14a-b
30	15a-b
150	16a-b
212	17a-b
2	18a-b dup
212	19a-b dup

Temp / Depth Profile



Date: May 6th 1994
Lake: L. Mich
Station: 77
Collector: SPS

Depth (ft)	Code #
2	
50	

Temp / Depth Profile

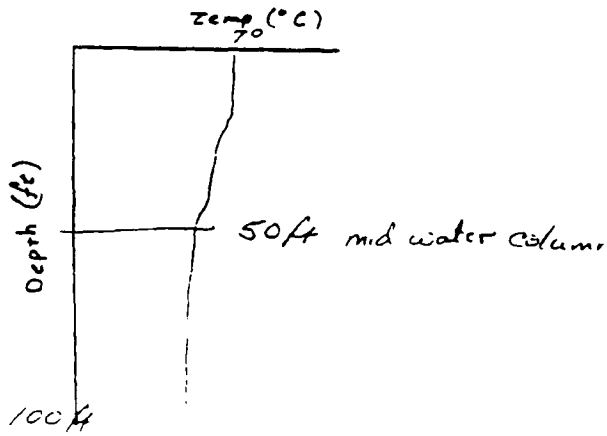


Figure 2
Herbicide Sample Log

HOC Sampling Media Preparation and Handling; XAD-2 Resin and GF/F Filters

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Standard Operating Procedure MSL-M-090-00

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HOC Sampling Media Preparation and Handling; XAD-2 Resin and GF/F Filters

1.0 Scope and Application

This method is applicable to the preparation of sampling media used in the collection of hydrophobic organic compounds (HOCs) from water.

The dissolved HOC phase is collected on XAD-2 resin, a macroreticular resin bead that selectively scavenges HOC from other media such as water and/or air. The manufacturing process of this material results in very dirty product and a very rigorous clean-up procedure is needed to remove these potential interferences. Also, care needs to be taken when handling the resin to avoid damage of the beads which could lead to reintroduction of the original contaminants possibly bound into the beads.

Glass fiber filters are used to filter out the "particulate" fraction of the water. Since HOCs are preferentially bound to particulates in these media, this material needs to be isolated to determine the particulate-bound fraction of HOCs present. Again, special cleaning and handling procedures are required to obtain filters clean enough for trace level HOC analyses.

2.0 Definitions

HOC	Hydrophobic organic contaminants
GF/F	Glass fiber filter
XAD-2	Manufacturers name for a class of polymeric resin beads used to isolate HOCs from water.
LRB	Laboratory Record Book

3.0 Responsible Staff

Laboratory Supervisor. A Technical Specialist or Scientist having expertise in the principles involved with this procedure and in the use of laboratory operations in general. Responsible for ensuring that analysts are trained in the use of the instrument and that maintenance logs are being completed.

Analyst. A Technician, Technical Specialist, or Scientist assigned to utilize the instrument for actual sample analysis using this procedure. Responsible for 1) understanding the proper use of tools and solvents; 2) recording information regarding maintenance of the instrument in the appropriate logbooks; 3) reporting any significant problems with the instrument to the Laboratory Supervisor; and 4) tabulating and reporting sample data to the Laboratory Supervisor.

4.0 Procedure

4.1 XAD-2 Resin

XAD-2 resin can be obtained from a number of different vendors but is manufactured solely by Rohm and Haas. The size of the resin beads is 20-60 mesh. A rigorous clean-up procedure must be applied prior to use of the resin for collection of HOCs.

4.1.1 Apparatus and Reagents

Methylene Chloride, Acetone, Hexane, Methanol; HPLC grade or better
Glass wool/soxhlet extracted in hexane/acetone (50:50)
Amberlite XAD-2 Resin, 20-60 mesh. Rohm and Haas manufacturer

4.1.2 Resin Clean-up Method

The XAD-2 resin is cleaned in the lab by a series of solvent extractions in a large soxhlet apparatus (or in multiple set-ups). The resin is extracted sequentially for 24 hours each in methanol, acetone, hexane and methylene chloride. This is followed by sequential 4-hour extractions in hexane, acetone and methanol which cycles the resin back to a polar solvent. The methanol is then displaced from the resin by numerous rinses with organic-free water. The resin can be stored at this point in clean jars immersed in the water in a dark place for up to three months. The final four-hour hexane extract may be used for a laboratory XAD-2 blank. The last methanol rinse may be used as the starter methanol on the next XAD-2 batch.

4.1.3 QC of Resin/Is it Clean?

A portion of the resin from each clean-up batch must be tested to ensure a thorough clean-up has been performed. As noted above, the final four-hour hexane extract may be used for a laboratory XAD-2 blank. Alternatively, a representative amount of pre-cleaned resin from a given clean-up batch may be extracted using the extraction scheme to be used for the project of interest and the extract analyzed as a resin blank. The cleanliness of the resin will be evaluated on a project specific basis.

4.1.4 XAD-2 Resin Column Preparation

XAD-2 resin must be packed into a column for use as a sampling media for dissolved phase HOCs. The resin columns may be glass, stainless steel or teflon and can vary in size. This procedure is specific to glass columns with dimensions of 300 mm x 50 mm, fitted with nylon end plugs sealed with viton O-rings.

XAD-2 resin columns are prepared by first attaching one teflon adaptor with a swagelock fitting and a 3 inch length of latex tubing to one end of the glass column, and pushing a large plug of cleaned glass wool into the bottom. The column is filled about ½ full with organic free water and clean resin is poured into the column in a slurry to a final packed length of ~19.5 cm (~400 cc). The resin is packed by pumping excess water out from the bottom using a water aspirator peristaltic pump but always maintaining enough water in the colimn to cover the resin. The column should not contain air bubbles or channels.

Glass wool is added at the top to take up the space between the XAD-2 and the column threads. A solid nylon end cap with O-ring is placed on the top and then, after inverting the column and unscrewing the adaptor, the other end is capped in the same fashion.

4.1.5 Column Handling and Storage

Upon receipt of a cleaned batch of resin, the batch is named for the date of receipt and recorded in the project LRB. A copy of the chromatogram of the resulting XAD-2 resin blank that is determined for that batch is also included in the LRB. All columns are assigned individual numbers based on the resin batch number which is written in permanent marker on a piece of tape wrapped around the outside of the column. Columns are stored in a clean, cool place in the dark and can be stored up to 6 months prior to use. After sampling, columns should be stored at 4°C in the dark. There is no holding time for sampled resin columns prior to extraction.

4.2 Glass Fiber Filter

4.2.1 Apparatus and Reagents

Muffle Furnace
Al foil, heavy duty, extra wide
Whatman 293 mm GF/F 0.7µm nominal pore size glass fiber filters

4.2.2 Filter Clean-up Method

Filters are wrapped in a single layer of heavy duty aluminum foil which is sealed around the filter to create a "bag." The filter and aluminum foil are then ashed for four hours at 450°C (±20°C).

4.2.3 QC of Filter/Is it Clean?

One filter (or more, since more than a single filter may be used for a given sample) should be extracted using the extraction scheme to be used for the project of interest and the extract analyzed as a filter blank. The cleanliness of the filter will be evaluated on a project specific basis.

4.2.4 Filter Storage and Handling

Cleaned filters are stored inside of their foil bags in a clean, cool place prior to sampling. Multiple filter/ foil units can be stored in sealed polyethylene bags for storage and/or shipping. The bags containing cleaned filters from the same lot are labeled as the preparation date of filters, the initials of the technician who prepped them, the number of filters in the bag and the page number of the LRB where the preparation information is recorded.

After filters are used for sampling, they are to be folded in quarters (pie shaped) and placed in sealed ashed foil bags and stored frozen in plastic bags. There is no holding time for storage of sampled filters prior to extraction.

4.3 Interferences

Take appropriate precautions to prevent contamination of any equipment associated with this analysis.

5.0 Data Analysis and Calculations

Not applicable.

6.0 Quality Control

6.1 Solvent Blanks. Use only HPLC grade or higher purity solvents for clean-up. Only a single lot number of each solvent should be used. A solvent blank test will be performed upon the start of a new lot number by concentrating a representative volume of solvent to 1 mL and analyzing on the appropriate analytical instrument. Cleanliness of the solvent will be determined on a project specific basis.

6.2 Resin Blank per batch. Resin used for a given project should be isolated to a single manufacturer's lot number since the original level of contamination of the resin can vary significantly with lot. Resin blanks will be analyzed per clean-up batch as specified in Section 4.1.3. Cleanliness of the resin will be determined for each new lot number on a project specific basis.

6.3 One Filter blank per batch. Filters used for a given project should be isolated to a single manufacturers lot number. Filter blanks will be analyzed per clean-up batch as specified in Section 4.2.3. Cleanliness of the filters will be determined on a project specific basis.

6.4 All results will be recorded in an LRB which is reviewed periodically by the laboratory supervisor and monthly by the project manager.

7.0 Safety

All analysts following this procedure should be aware of routine laboratory safety concerns, including the following:

7.1 Protective clothing and eyeglasses should be worn when appropriate.

7.2 Proper care must be exercised when processing samples because volatile and flammable solvents are involved.

8.0 Training Requirements

All staff preparing sampling media described above must first read this SOP and then demonstrate proficiency in the process prior to performing the work under the supervision of the laboratory manager.

9.0 References

MSL-A-006. Marine Sciences Laboratory Training.

Standard Operating Procedure for Site Selection and Sampling for Mercury in Lakewater

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Standard Operating Procedure for Site Selection and Sampling for Mercury in Lakewater

The mercury samples will be collected at all the master stations, as designated within the LMMB/MB plan (Figure 1). Samples will be collected from mid-depth at each station if the water column is unstratified, or from two or three depths during stratification. If a nephloid layer exists at the lake bottom, this will also be sampled. Water will be collected using Teflon-lined Go-Flo bottles that have been rigorously cleaned. All stages of field apparatus cleaning and preparation will be performed within a clean lab following strict trace metal protocols (Patterson and Settle, 1976), as adapted for mercury analysis by Gill and Fitzgerald (1985). This paper, which forms the basis of current sampling procedures and sample collection, is attached as Appendix 1.

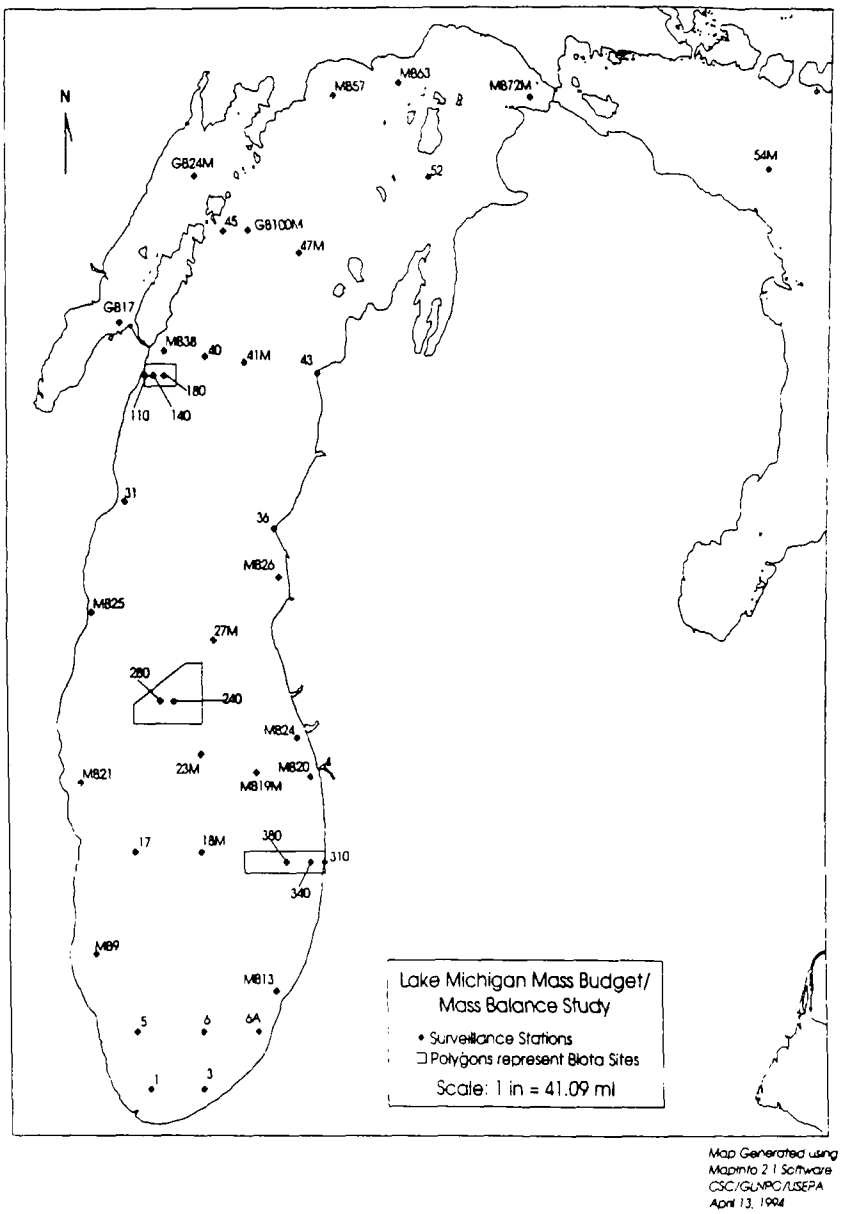
Cleaning consists of an initial soaking in detergent, a MilliQ water rinsing and a further soak in dilute (0.05% HCl). A detailed outline of the cleaning and bottle preparation techniques is contained in Appendix 1. The Go-Flo bottles will be filled with laboratory grade MilliQ water and allowed to sit for six hours (i.e. significantly longer than the expected residence time of the sample in the bottle in the field) before sampling to assess contamination due to leaching of mercury from the Go-Flo bottle walls. Bottles showing any contamination will be recleaned. Initially, two Go-Flo bottles supplied by EPA will be used until additional Go-Flo bottles can be purchased, cleaned and checked. At least three bottles are desirable for periods when three depths are to be sampled per station. Additional bottles are also required as backups in case of loss or contamination.

After cleaning, and between deployment, Go-Flo bottles are stored in two or more polyethylene bags within a tight plastic or wooden container. Prior to storage, bottles will be rinsed with dilute acid and then MilliQ water. If contamination is noted or suspected, bottles will be returned to the UMCBL for cleaning. If the bottles are not to be used within 30 to 60 days, bottles will be shipped back to the UMCBL for rechecking of blanks and for cleaning and maintenance.

Details of sample collection procedures are also contained in Appendix 1. Sample collection will only be performed by personnel trained by UMCBL or another recognized laboratory in the methods of the so-called "clean techniques." Improper use of the Go-Flo bottles can result in permanent contamination. Handling procedures are detailed in Appendix 1. The PI, or a designated substitute, will be on site during each deployment and will be in charge of the planning and co-ordination of on-site activities. The PI will determine when to collect the mercury samples, after consultation with the ship's officers and other PI's on board. The PI will monitor the sample collection and determine whether the samples have been collected "without obvious contamination." If the PI feels that the sample has been compromised, a redeployment with one of the other Go-Flo bottles will be the designated contingency.

Go-Flo bottles will be deployed from non-contaminating Kevlar line. Bottle messengers will be Teflon-coated and the line weight will be non-metallic and Teflon-coated, if possible. Due to the nature of the activity i.e. the attachment of the bottles requires the personnel to reach out over the guard rail, the personnel should be attached to a safety line. Also, personnel should wear a hard hat and steel cap boots to prevent injury. Go-Flo bottles will be removed from the polyethylene bags as close to deployment as feasible and will be returned to the polyethylene bags as soon as possible after retrieval. Bottles will be transported around the ship within bags and water will only be decanted within the clean room on board ship.

Figure 1. Map of Lake Michigan Mass Budget/Mass Balance Study



Inside the clean room, water will be decanted, as soon as possible, from the Go-Flo bottles into acid-cleaned Teflon bottles. Two liters of sample will be collected for total mercury analysis (and for methyl mercury analysis even though methyl mercury measurement is not part of the LMMB). Laboratory replicates will consist of subsamples of water taken from the same Go-Flo bottle or from the same Teflon sample bottle. Field replicates will consist of duplicate deployments at the same sampling location. To ascertain the field blank, MilliQ water of known concentration will be added to an empty Go-Flo and allowed to sit for a period comparable to the deployment time before being decanted from the bottle. This blank will represent, as near as possible, the blank associated will all sources of contamination from field collection to analysis. All samples will be collected in acid-cleaned Teflon bottles. Trace metal grade acids will be used in all cleaning and storage stages. Potential for contamination will be minimized by prepackaging sample bottles in double polyethylene bags. Bottles, and acidification acid will be analyzed for contamination before use.

Particulate samples will be collected onto quartz fiber filters, of nominally 0.8 μm pore size. Filters will be cleaned of mercury by heating in a muffle furnace for 12 hours at 600°C. After cooling in situ, filters will be removed and stored in a bagged acid-washed Teflon vial. Filters will be placed, under clean room conditions, within an in-line Teflon filter holder. Water will be pumped through the filter using a peristaltic pump. Tubing will be acid-cleaned Teflon, except for the small amount of tubing within the pump apparatus, which will be acid-cleaned silicone tubing. One or more liters of water will be pumped through the filter, the exact volume being recorded. The filter will be removed and placed in a clean Teflon vial placed in a polyethylene bag. Filters will be frozen as soon as possible after collection. Additional particulate collections will be stored for duplicates (and for methyl mercury analysis).

Appropriate QA/QC procedures will be adopted during field samples. The QC requirements are detailed in the previous section and details of QA related issues are in Appendix 1.

Samples will be stored frozen on board and will be shipped overnight to the University of Maryland by Federal express in particle-free plastic boxes soon after arrival in port. A maximum interval of two months is expected between sample collection and completion of analysis. However, samples have been successfully stored for six months by other investigators without loss (Hurley, pers. comm.). Thus, if a holding time of six months is exceeded and no evidence to support a longer interval is provided, the sample data will be qualified as estimated. Field labels are attached to the Go-Flo bottles are soon as possible after retrieval. This label will have an ID number that will be used as the primary control number for chain of custody. This ID number will be attached to the outer bag of the Teflon bottle etc. See chain of custody section below. The only calibration required is for the winch as the depth is determined from the "line out" record of the winch operator. The calibration of the winch is monitored by the ship personnel.

Teflon equipment will be cleaned in concentrated HNO_3 (ACS Reagent grade) for a week and rinsed with deionized water. Bottles will then be filled with 10% acid and will be kept for a week. After further MilliQ rinsing, bottles will be filled with 1% HCl and this dilute acid will remain in the bottles until samples are collected. Samples will be dispensed in the clean room into 2 L Teflon bottles as described above.

Appendix 1.

Field Sampling Protocols (from QAPjP)

1.0 Preparation of Sampling Bottles and Subsequent Collection of Mercury in Open Waters

This SOP is intended to provide a step by step procedure for the preparation of samplers and sample bottles necessary for the collection of contamination-free water samples from depth in open water environments, and for the collection methods to be employed in the sample collection.

1.1 Overview

Samples collected for mercury analysis form part of the LMMB study and the data will be used to constrain a mass balance for mercury in Lake Michigan. The samplers used in the collection of samples are specially designed Teflon-lined Go-Flo bottles, manufactured by General Oceanics. The bottles are able to be remotely triggered using a Teflon-coated metal "messenger" and thus can be used to collect samples at any pre-determined depth in the water column. The bottles are deployed attached to a non-metallic Kevlar line to ensure that the sampling apparatus does not lead to sample contamination. Procedures are designed to ensure that the Go-Flo bottles do not leach mercury into the sample water during deployment, recovery and before decanting of samples into specially prepared Teflon bottles. All bottles are kept in plastic bags when not in the clean room or in use to minimize contamination. Personnel handling the Go-Flo bottles need to wear plastic gloves and to avoid contact with the ball valves and internal parts of the Go-Flo bottles. All precaution is required if uncompromised samples are to be obtained. The Go-Flo bottles should never be placed directly on the deck or any hard surface otherwise foreign particles might be lodged in the plastic ball valves leading to subsequent contamination.

1.2 Go-Flo Bottle Preparation

Newly purchased Go-Flo bottles are first checked for obvious defects and the closing and opening mechanisms checked. The bottles are then rinsed and scrubbed, using a soft brush, with soapy water to remove any loose particles from inside or outside the bottle. The mechanism of the ball valves is removed and the bottle O-ring removed and washed. The components are then rinsed with deionized water. The bottle is then re-assembled. The bottles are then soaked in a weak 0.05% HCl solution for a week - this is done by placing the bottle in a plastic garbage pail that has been lined with a clean polyethylene bag. The ball valves are rotated periodically to ensure that all parts of the ball valve that could contact the sample water after the bottles are closed is cleaned. The bottle is then rinsed with MilliQ water and filled with water and allowed to stand for six hours with the balls in the closed position. A sample of the MilliQ water is taken for later comparison with the water concentration in the bottle after 6 hours of leaching. After six hours the water in the Go-Flo bottle is sampled and analyzed, along with the initial sample. Any significant increase in concentration (>15%) will suggest that the bottle is still contaminated and leaching mercury. If so, the bottle will be recleaned using the procedure above.

1.3 Teflon Bottle Preparation and Handling

All sample bottles used for sample collection are constructed of Teflon as this has been found to be the material that results in the least contamination of samples, after the bottles have been rigorously cleaned. New Teflon bottles are washed with soapy water, and then with acetone to remove any organic residues. The bottles are then leached with concentrated HNO_3 (ACS Reagent grade) for a week. After being rinsed with deionized water, bottles are then be filled with 10% acid and will be kept for a week. After further MilliQ rinsing, bottles will be filled with 1% HCl and this dilute acid will remain in the bottles until samples are collected. Bottles are hermetically sealed (i.e. the caps are wrenched tight using a wrench whose metal parts have been covered with several layers of plastic) at this point and stored and transported within two poly ziplock bags. The bottles are packed into a large poly bag and are typically transported in plastic coolers. On board, the coolers will be opened in the ante room of the clean room. When the bottles are removed from the coolers, the outer bag is removed and the bottle is taken into the clean room. Samples will be dispensed in the clean room from the Go-Flo bottles into the Teflon bottles as described below. Just prior to sample decanting, the Teflon bottles will be unbagged, emptied of their acid solution and rinsed with MilliQ water. Strict clean techniques will be used in the collection and decanting of samples, i.e. gloves are worn at all times and are changed whenever the personnel switch from handling "clean" and "dirty" things e.g. outer poly bags are considered dirty, inner bags clean; all things within the clean room are considered clean, otherwise they should not be inside.

1.4 Sample Collection

The samples are collected using a "hydrowire" deployment system, with Kevlar as the wire. The non-metallic weight, which is stored in a plastic bag in-between sampling events, is first attached to the end of the wire. The weight is lifted overboard by the winch operator and lowered until it is in the water. At least 10 m of wire should be extended prior to Go-flo bottle attachment. Prior to sampling, Go-Flo bottles should be moved to the ante room of the clean room, or a suitably clean environment closer to the deployment site, and placed in a container for easy access. The bottles are still bagged at this stage. The Go-Flo bottles are "pre-cocked" in the clean room. Details of the cocking methods are contained in the manual that is supplied with the Go-flo bottles. Briefly, the ball valve is rotated so that the string parts of the Go-Flo can be attached to the plunger mechanism. Throughout the whole cocking procedure, the Go-Flo should be either placed on a plastic covering on the floor or be hand-held. The pressure release valve is pulled out and the plastic balls on the string positioned around the valve. The "bungie cord" attached to the ball valve is then rotated back so that both the string and the cord are under tension. The cocking should be checked to ensure that it has been correctly cocked. Pushing the pressure release valve should cause the balls valves to move to the open position. Pressing the plunger should then release the string and result in the closure of the bottle. Recock the bottle after this check in a similar manner. The cocked bottle is then placed in poly bags and removed to the ante room and placed in the bottle container. The bottles are individually unbagged when required, and are carried by gloved personnel to the deployment site. The bottle is attached to the line by the person carrying the bottle with additional help, if required. The bottle is then lowered down into the water and slowly lowered to about 20 m. As the pressure release valve opens the Go-Flo underwater, a parcel of air is released to the surface. The bubbles are typically easily seen, and this is indicative that the bottle is open. If, on the rare occasion that bubbles are not seen, there is a concern that the bottle has not opened - this again is not the typical scenario - the bottle can be raised slowly so that personnel looking over the side of the ship can look and see if the bottle is open. This, of course, is only feasible in clear water as it is undesirable, from a contamination

standpoint, to bring the bottle to the surface. If the water is unclear or rough, it is better to just assume the bottle is open and accept the associated risk i.e. a redeployment. The weight of the retrieved bottle will be indicative of it being empty of filled with water. The bottle is lowered to the correct depth and then the messenger is attached to the line and released. The messenger will trigger the bottle and it can then be retrieved to the surface. Adequate time, based on the time required for the messenger to reach the bottle must be allowed before retrieval. When the bottle is retrieved to deck level, the person who attached the bottle will disengage it and carry it, without putting it down or touching the ship's parts to the box and replaced it in the plastic bags. The Go-Flo bottle is then taken into the cleanroom as soon as possible. The Go-Flo bottles can be deployed singularly or a string of bottles can be deployed at the same time, depending on the circumstance.

1.5 Sample Decanting and Labeling

The Go-Flo bottle is taken into the clean room and placed on the bench, on a plastic bag, in the upright position. Personnel should put on clean gloves at this point. The air release valve is opened and the sample is decanted into the rinsed and ready Teflon bottles. About 20 mL of water is decanted into the Teflon bottle, and the bottle rinsed. The sample is then decanted. As the samples will be frozen, the bottles should only be filled to the beginning of the neck to allow for the expansion of the water on freezing. If insufficient airspace is left, samples can leak or, if the bottle is very tightly sealed, the bottle can split. After filling, the bottle cap is immediately replaced and any additional samples taken. After all samples are taken, the caps of the Teflon bottles are wrenched tight using a plastic coated wrench. The bottles are then double-bagged, and taken to the freezer for storage. The information on station #, depth, collection date, Go-Flo #, and ID # will be entered into the data sheet.

Date
ID#
Station #
Depth (m)
Go-Flo #
Bottle #
Vol. (L)
As # H_2O Analy.
Hg-T Analy.
SHIPPED BY: Box # RECEIVED BY: Date:

Notes: 1) The ID # will consist of the date, station, and depth.

Field Sampling Using the Rosette Sampler

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May 1996

Field Sampling Using the Rosette Sampler

1.0 Rosette Sampler

The Rosette sampler is the primary sampling instrument for the collection of all Nutrient parameters, phytoplankton, chlorophyll a, phaeophytin a, and dissolved oxygen from the Biological Category, and temperature, total suspended solids, turbidity, specific conductance, and pH from the Physical Category.

A 12-bottle Rosette sampler system (Sea-Bird Electronics 32 Carousel Water Sampler) will be used to collect water samples. This equipment allows an operator to remotely actuate a sequence of up to 12 water sampling bottles. This system consists of a CTD (conductivity, temperature and depth sensor - Sea-Bird Electronics Model 9 Underwater Unit) attached at the bottom of the Rosette, an A-frame, 1000 feet of multi-conductor cable, a variable speed winch and Sea-Bird Electronics Model 11 Deck Unit with attached computer. The CTD measures water depth and temperature, which is graphically (CRT) displayed onboard the research vessel. The bottles can be closed in any predetermined order, remotely from the deck of the vessel while the array is submerged at the various sampling depths. The Rosette sampler is equipped with 8 L Niskin bottles.

The depth at which samples will be collected is detected by a pressure transducer on the CTD. To assure that the display parameters are set to include the entire water column, the Rosette winch operator obtains a depth sounding from the bridge and writes this on the Rosette form, then adjusts the computer program parameters controlling the depth range to be displayed (See "Instructions for use of the Sea-Bird 9/11+..."). The Rosette sampler will then be lowered to the bottom at between .5 and 1 meter/second, raised at least 5 meters after contacting the bottom. The operator will wait three minutes to allow the sampler to drift away from the disturbed area before the B-2 (2 meters up from the bottom) sample is taken. The Rosette sampler will be lowered to B-2 and the sample taken.

Additional time intervals of three minutes are allowed to elapse prior to taking the thermocline sample and the lower epilimnion sample. These intervals provide time for water equilibration within the Niskins.

The knees of the EBT temperature depth trace will be determined by trisecting the angle between the epilimnion and mesolimnion temperature traces (upper knee) and the angle between the mesolimnion and hypolimnion temperature traces (lower knee). The upper knee is the upper ⅓ angle intercept, the lower knee is the lower ⅓ angle intercept. The lower epilimnion sample is one meter above the upper knee. The upper hypolimnion sample is one meter below the lower knee.

2.0 Sequence of Sampling Events

The following is a brief summary of the sampling events. Some events may be done simultaneously and event order will be subject to conditions.

2.1 Visual and Physical Station Observations

Air temperature, wind speed, aesthetics, wind direction, depth, and wave height.

2.2 Rosette Sampling

Run Rosette/CTD down to define the temperature profile and determine the thermocline location during stratified situations. Examine the CTD profile. Select sampling depths according to depth selection. Trigger sample bottle at correct depths, while verifying the temperature profile Split Rosette Niskin samples into the required sample bottles/preservatives. A composite 20 m sample is taken for phytoplankton, chlorophyll a, pheophytin, and, when appropriate, primary productivity, by compositing Niskin samples at 1, 5, 10 and 20 meters.

3.0 Sample Integrity

Concentrations of chemicals in lake water are very dilute. A small amount of sample contamination can have a large effect on the results. Avoiding contamination is, therefore, a major quality control goal. Each Niskin sampling bottle shall be emptied into the sample bottles as soon as possible. All chemistry sample bottles shall be rinsed once with sample before filling. New 1 g polyethylene containers (PEC) will be used to hold the sample for the on board analyses and preparations.

One gallon polyethylene containers filled directly from Niskin sampling bottles are used for nutrients, pH, specific conductance, alkalinity and turbidity analyses. Samples for analysis of dissolved nutrients are taken from the 1 g containers and filtered into new 125 mL sample bottles.

Samples for chlorophyll *a* analysis are collected directly from Niskin sampling bottles into 300 mL brown polyethylene sampling bottles. Water to be used for primary productivity analysis taken directly from Niskin sampling bottles into 960 mL polyethylene bottles. These samples are composited into brown, 4 L polyethylene bottles.

To reduce contamination from atmospheric dust, empty bottles will be capped during preparation for sampling. Care should also be taken in the storage of bottles to reduce exposure to "dirty" environmental conditions. During sampling, each bottle is rinsed with sample water, emptied, and filled with sample water. The cap is replaced after addition of the preservative, or immediately on samples that require no preservative. Transfer of the samples from one container to another or manipulations of the sample are avoided as much as possible since each such action can result in contamination.

To reduce contamination and to control the volume of the preservatives, automatic pipettes or dispensers are used to dispense all preservatives. Prevention of inadvertent use of the wrong preservative is accomplished by the use of the same color tag on the sample bottle and preservative dispenser. Dissolved oxygen samples are "set up" immediately. This involves filling the bottle to overflowing, allowing overflowing to continue five seconds before adding, in series, the first two reagents, allowing the floc to settle, mixing and allowing floc to settle again. D.O. samples are then completed in the main laboratory.

4.0 Nutrient Sample Filtration

A number of samples must be filtered, after sample splitting. The following are brief summaries. Dissolved nutrient samples will be prepared by vacuum filtration (<7 psi) of an aliquot from the PEC for onboard analyses within an hour of sample collection. A 47 mm diameter 0.45 µm membrane filter (Sartorius) held in a polycarbonate filter holder (Gelman magnetic) with a polypropylene filter flask prewashed with 100 to 200 mL of demineralized water or sample water will be used. New 125 mL polyethylene sample bottles with linerless closures will be rinsed once with filtered sample prior to filling.

5.0 Instructions for Use of SeaBird 9/11+ and Rosette for Collection of Water Samples and Cast Information

The SeaBird 9/11+ is built to provide real time information on a number of water quality parameters as it moves through the water. The software used to run the instrument and collect data (Seasave) has been configured for generalized sampling conditions. Depending on the depth and expected values of the parameters, the configuration will likely require modifications.

The Dolch computer in the Rosette control room is loaded with the software to run the SeaBird 9/11+. After turning on the computer, go to the C:\SEA911 subdirectory. Enter the Seasave program by typing *Seasave*. The first screen that you see will give you choices on whether to Acquire Real Time Data or to Display Archived Data. Highlight the "Acquire..." option and press <*Enter*>. The next screen will require verification that the data will be written to disk, as well as the entry of a file name for the data to be acquired. After these are entered, highlight the "XY parameters to be plotted" and make sure that the ranges for depth, temp, etc. are appropriate for the station. After making any necessary changes, you exit from this screen by pressing <*Esc*>. At this point (or before) turn on the SeaBird deck unit. Press <*F10*> to begin acquiring data. Next you will see a header information screen. At a minimum, enter the station number. You may enter the position (latitude & longitude) information and any notes that you have about the station. After exiting this screen (by following the instructions on the screen), the program will delay slightly to initialize the rosette, and a graph will be displayed with function key menus on the top and bottom of the graph.

Remove the PAR sensor cover, remove the buffer bottle from the pH probe, and remove the Tygon tubing (GENTLY!) from the temperature probe. Deploy the SeaBird Rosette Keep the Rosette just under the surface of the water for one minute, then turn on the pump by entering <*Ctrl*><*F4*> Wait another minute and then begin the cast. If the altimeter is working, stop the Rosette 1-2 meters off the bottom. If it is not working, let the Rosette

touch bottom, then raise it to 5 meters off the bottom. Determine the sample depths and mark them on a data sheet. If the deepest sample will be below 5 meters off the bottom, wait two minutes before taking the sample. Otherwise begin sampling as the Rosette is raised. Bottles are fired by entering *<Ctrl><F3>*. A number will appear in the upper right hand of the screen when the bottle has fired. Continue taking samples until the Rosette reaches the surface. Take the surface sample, if required, then turn off the pump by entering *<Ctrl><F2>*. Exit the Seasave program by entering *<Ctrl><F1>*, and turn off the deck unit. Bring the Rosette onto the deck. Cover the PAR sensor, return the buffer bottle to the pH probe, return the Tygon tubing to the end of the temperature probe, and fill this with deionized water.

Exit completely from the Seasave program, until you see the C:\SEA911 prompt. Place a formatted disk in the A: drive of the Dolch. Enter "castproc *filename*", where *filename* is the file with the freshly gathered data. The data will be processed and copied to the A: disk. Take this disk into the wet lab and place it in the A: drive of the Compaq LTE Lite. From the Windows screen select the SeaBird icon, then the Seaplot icon. Once in Seaplot, make sure the file of interest is the one to be used by the program. Modify the parameter ranges to coincide with those of the station, and run Seaplot. This will graph the data for display.

Appendix A. Sample Log

U.S. EPA The R/V LAKE GUARDIAN 19____
STATION DATA SHEET - SEABIRD 9/11+ AND ROSETTE

DATE_____ GMT _____ LAKE_____ STATION _____

QA DEPTH: FIELD DUP(D) _____ LAB SPLIT(C)_____

SONAR (BRIDGE) DEPTH _____ AIR TEMP _____ SEA STATE_____

WEATHER _____

LATITUDE _____ LONGITUDE_____

SURFACE WATER TEMP. _____ SECCHI DEPTH _____

PERSONNEL: ROSETTE _____ NET_____ OTHER_____

Sample Number	Bottle Number	Depth Code	Use (S,D,I)	Depth	Profile Code

Standard Operating Procedure for the Sampling of Particulate-Phase and Dissolved-Phase Organic Carbon in Great Lakes Waters

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August 2, 1994

Standard Operating Procedure for the Sampling of Particulate-Phase and Dissolved-Phase Organic Carbon in Great Lakes Waters

1.0 Scope and Application

This Standard Operating Procedure describes the sampling of Great Lakes Waters for particulate-phase organic carbon (POC) and dissolved-phase organic carbon (DOC). Samples of lake water are collected and passed through a 0.7 µM pore-size glass fiber filter. POC is operationally defined as the mass of organic carbon retained on the filter per unit volume of water, and DOC is the material that passes through the filter.

2.0 Safety and Waste Handling

All applicable safety and waste handling rules are to be followed. These include the proper labeling and disposal of chemical wastes. Over-board discharges of chemical wastes are forbidden. Refer to the GLNPO Safety, Health, and Environmental Compliance Manual for specific rules.

3.0 Summary of Procedure

Great Lakes water samples are collected at pre-determined sampling stations and depths *via* either a submersible pump or Rosette sampler. The water is then filtered under vacuum through ashed 47 mm diameter glass fiber filters in an all-glass filtration apparatus. The samples are acidified during the filtration to remove inorganic carbonates. The POC is retained on the filter and frozen at -10 °C until analysis. The filtrate is collected and promptly analyzed for DOC in a ship-board laboratory.

4.0 Description of Apparatus

Water samples (typically 1-4 liters for open-lake locations) are collected from an over-board pump or Rosette sampler. Ashed glass fiber filters are supported in a commercially-available, all-glass, 350 mL vacuum filtration apparatus. Two filtration apparatuses are attached, side-by-side, to ring stands. Samples are filtered simultaneously in duplicate. Tygon tubing (3/8" ID) is used to connect the filtration flasks to an oil-less vacuum pump. The equipment needed are listed in Table 1.

5.0 Preparation of Filters and Reagents

5.1 Preparation of Filters

5.1.1 Filter preparation should take place as close to the start of the survey as possible.

5.1.2 Filters are to be handled only with stainless steel forceps. Filters that are mishandled after the ashing procedure (5.1.4) should be discarded.

5.1.3 47 mm diameter GF/F filters (0.7 µM pore-size) are placed individually in aluminum foil envelopes, dull side of foil facing inward, with three sides folded closed. The fourth side is left open to allow gases to escape from the envelope during ashing.

5.1.4 The filters are stacked in a muffle furnace and ashed for four hours at 450 °C.

5.1.5 Upon removal from the muffle furnace, the envelopes are sealed on the fourth side.

5.1.6 Fifty envelopes containing individual filters are placed into a Ziplock bag and the bag is labeled with the date and initials of the analyst who prepared the filters.

5.2 Preparation of Reagents

A solution of 0.2N HCL is prepared by transferring 17 mL of concentrated HCL (16.1N) to a 1000 mL volumetric flask and diluting to the mark with organic-free, distilled, deionized water (from now on referred to as organic-free water). Transfer the solution to a 1 L Teflon squeeze bottle.

6.0 Filtration Procedure

6.1 Using stainless steel forceps, place one 47 mm GF/F filter onto the fitted glass support of the sampling apparatus. Place the glass funnel on top of the filter and secure with the clamp. Label the Great Lake name, station number, sampling depth, and date onto the aluminum foil envelope.

6.2 Collect the lake water sub-samples from the submersible pump hose or Rosette sampler. Allow the overboard pump line to flush for 15-30 minutes. Collect the lake water into a 4 liter Cubitainer or four, 1 L Teflon bottles. Rinse the container(s) twice with approximately 1 liter of lake water before collecting the sample. If the lake water is to be collected from the Rosette, rinse the container(s) with only 200-300 mL of lake water to ensure there is enough remaining to establish a significant particulate load on the filter (see section 6.7).

6.3 Measure the volume of lake water to be filtered in a graduated cylinder, or mark four, 1 L Teflon bottles at the 1 liter level. Prior to filling, rinse the bottles, or cylinder, twice with approximately 100 mL of lake water.

6.4 Connect the vacuum pump to the filtration flask. Pour a measured volume of lake water into the glass filtration funnel. Turn on the vacuum pump. Maintain the vacuum between 5-10 inches of Hg during filtration.

6.5 After approximately 300 mL of lake water has been filtered, turn off the vacuum pump. Rinse the 200 mL DOC glass sample bottle several times with filtrate and collect approximately 150 mL of the filtrate. Label the Great Lake name, station number, sampling depth and date onto the DOC bottle. Collect the filtrate before step 6.6.

NOTE: Step 6.6 must be done before all the lake water is filtered to ensure that the distribution of the particles on the filter is not disturbed

6.6 Turn on the vacuum pump, and continue pouring lake water into the funnel until sufficient material has been collected (see section 6.7). Just before the last portion of the lake water has been filtered, squirt approximately 5 mL of 0.2N HCL solution into the funnel.

6.7 The volume of lake water required to produce a reliable POC measurement (i.e., an amount of material that is within the analytical instrument's linear range) will vary with lake station location, depth, and time of year. For open-lake, oligotrophic conditions, typically 2-4 liters will provide enough material. For near-shore locations, or meso-eutrophic and eutrophic conditions, lake water volumes in the range of 200-500 mL are typical. A filter that becomes visibly loaded with particles and a flow of water through the filter that drops significantly are evidence that sufficient particulate material has been collected.

6.8 After the lake water has been filtered, rinse the sides of the funnel with approximately 20 mL of organic-free water and filter this rinse. Turn off the vacuum pump.

6.9 Remove the funnel. Using stainless steel forceps, fold the filter in half and place back it into the labeled aluminum foil envelope. Place groups of foil envelopes in a labeled Ziplock bag and store at -10 °C. Record the Great Lake name, station number, sampling depth, volume filtered, analyst, date, and time of day on the POC/DOC Sampling Log Sheet.

6.10 Empty the remaining filtrate from the filtration flask.

6.11 Rinse the filtration funnel, fitted glass support, filtration flask, and the container(s) with organic-free water.

6.12 Re-assemble the filtration apparatus.

6.13 Place aluminum foil covers over the filtration funnels.

7.0 Quality Control

7.1 A duplicate sample will be filtered in parallel at least once during the sampling of each Great Lake.

7.2 A POC/DOC matrix blank will be collected, in duplicate, at the beginning of each survey of the Great Lakes, and at least once during the sampling of each Great Lake. A TSS matrix blank is collected by filtering 1 liter of organic-free water. A DOC matrix blank consists of the filtrate from a POC matrix blank. The matrix blanks are processed identically to Great Lakes water samples.

7.3 A POC field blank will be collected, in duplicate, at the beginning of each survey of the Great Lakes, and at least once during the sampling of each Great Lake. A POC field blank is prepared by taking a filter out of the foil envelope, placing it onto the fitted glass support of a clean filtration apparatus, wetting the filter with organic-free water and assembling the filtration apparatus. The apparatus is disassembled, and the filter is removed and processed in the same manner as a sample. There is no field blank for DOC.

7.4 Two trip blanks for POC will be processed after the survey has ended. This is done by placing two filters in their unopened foil envelopes into the Ziplock bag and processing these filters like samples. There is no DOC trip blank.

7.5 DOC samples are analyzed promptly, in a ship-board laboratory, during the course of a survey.

7.6 Because POC/DOC are parameters which are ancillary to the determination of hydrophobic organic contaminants (HOCs), the POC/DOC samples during an organics survey are taken simultaneous to the HOC samples. Therefore when a HOC matrix blank, field blank or duplicate sample is collected, a POC/DOC matrix blank, field blank or duplicate sample will also be collected.

Table 1: List of Filtration Equipment

Quantity	Equipment	Source or Equivalent
2	Oil-less Vacuum Pump	Schuco 5711-130
6	Teflon wash bottle	Cole-Parmer N-06052-60
2	350 ml, all-glass Filtration apparatus	Nucleopore
2	Stainless Steel Forceps	
2	Support/ring stand for filtration apparatus	

Miscellaneous (some quantities depend on number of samples)

- 47 mm GF/F filters (0.7 µM pore-size) — Whatman 1825-47
  Cubitainers
  Tygon tubing (3/8"ID)
- 200 ml glass bottles for DOC
- permanent markers
  Ziplock freezer bags
  Aluminum foil

Standard Operating Procedure for Chlorophyll-*a* Sampling Method: Field Procedure

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Standard Operating Procedure for Chlorophyll-*a* Sampling Method: Field Procedure

1.0 Scope and Application

This method is used to filter chlorophyll-*a* samples from the Great Lakes and Tributary streams.

2.0 Summary of Method

A representative lake water sample is collected from Niskin bottles from various depths and filtered by vacuum filtration in dim light. The filter is then placed in a screw cap culture tube in the dark. The tube is stored in the dark at sub-freezing temperatures and shipped to the laboratory for extraction and analysis.

3.0 Apparatus

Plastic filter funnel, Gelman
Vacuum system (3-4 psi)
GF/F filters, Whatman (47 mm)
16 X 100 mm screw cap culture tubes
Pasteur short disposable pipets
Rubber bulb
Plastic wash bottle, 500 mL
Plastic wash bottle, 500 mL, for $MgCO_3$
Filter forceps
Opaque sample bottles, 500 mL (Nalgene or equivalent)

4.0 Reagents

Saturated Magnesium Carbonate Solution Add 10 grams magnesium carbonate to 1000 mL of deionized water. The solution is settled for a minimum of 48 hours. Decant the clear solution into a new container for subsequent use. *Only the clear "powder free" solution is used during subsequent steps.*

5.0 Sample Handling and Preservation

The entire procedure should be carried out as much as is possible in subdued light (green) to prevent photodecomposition. The frozen samples should also be protected from light during storage for the same reason. During the filtration process, the samples are treated with $MgCO_3$ solution (section 4.1) to eliminate acid induced transformation of chlorophyll to it's degradation product, pheophytin. Samples are stored by station in aluminum foil and transported to a land-based laboratory in a cooler with dry ice. Analysis should be performed as soon as possible following sampling.

6.0 Field Procedure

6.1 Samples are provided in 500 mL opaque Nalgene bottles, labeled with the sample depth, *eg.* Surface, representing a surface sample, MI, representing the mid depth sample, or B-2, representing a bottom minus 2 meter sample.

6.2 Place filters, using forceps, textured side up. Assemble the filtration apparatus just prior to filtration.

6.3 Due to differing trophic levels among the Great Lakes, the volume of water filtered varies. For Lake Erie, 150 mLs of sample will be filtered. For Lakes Ontario, Huron, Michigan, and Superior, 250 mLs of sample will be filtered. After inverting the sample bottle several times to create a uniform mixture, carefully measure out the appropriate amount of sample using a graduated cylinder and pour contents into filtration funnel.

6.4 Turn on vacuum pressure on, not exceeding 3 psi.

Check Frequently During Filtration to Insure Pressure Does Not Go Above 3 PSI!!!

6.5 When approximately 10-50 mL of sample remains on the filter, add 10 drops of the $MgCO_3$ (section 4.1) solution using a disposable pipet. Thoroughly rinse the filter apparatus and graduated cylinder, using a squirt bottle, with deionized water. Turn off vacuum pressure as soon as the liquid disappears to prevent the breakage of cells.

6.6 Using the forceps, fold and remove the filter and carefully place it into the bottom portion of the prelabeled culture tube (see section 10) and close tightly. Lay all tubes flat and completely wrap in aluminum foil. Clearly label the Lake, station and date on masking tape and attach to above mentioned aluminum foil package. Immediately freeze. All the above procedures should be completed in subdued light.

7.0 Quality Control

The following controls are to be collected:

Control	Frequency
Lab Dupl.	Once/batch
Field Dupl.	Once/batch
Field Blk.	Once/batch

Field blanks (Field Blk) consist of water obtained from reverse osmosis and are filtered in the same method as described in the Procedure section. A laboratory duplicate (Lab Dupl.) results when a water sample, from the same sampling bottle, is filtered twice. A field duplicate (Field Dupl.), although sampled from the same depth, is contained in a separate bottle, marked "Fld Dup"

8.0 Waste Disposal

Follow all laboratory waste disposal guidelines regarding the disposal of $MgCO_3$ solutions.

9.0 Shipping

Once a lake has been completely sampled for chlorophyll or a batch of 35 samples has been completed, wrap all samples into one complete batch and clearly label with survey, lake and date. Pack tightly in a medium sized cooler and fill all spaces with enough dry ice to last 24 hours. Dry ice is considered a hazardous chemical by most shipping companies and has to be accompanied by authorizing paperwork. Once receipt at CRL, the samples should be immediately placed in the freezer.

10.0 Labeling

Sample identification information is provided on printed labels both prior to and during the survey. The labels are affixed to the side of the 16x100mm chlorophyll tube. The sample identification number is covered with clear tape in case the tube becomes wet.

Standard Operating Procedure for Primary Productivity Using ^{14}C: Field Procedure

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April 13, 1994

Standard Operating Procedure for Primary Productivity Using ^{14}C: Field Procedure

1.0 Scope and Application

This method is used to determine primary productivity and primary productivity parameters from Great Lakes waters.

2.0 Summary of Method

Samples of water, for which the productivity parameters are to be determined, are inoculated with a known quantity of bicarbonate substrate which is labeled with the radiotracer ^{14}C. Samples are incubated at various light intensities for two to four hours, after which the algal cells are separated from the water by filtration. Because the measured radioactivity of each filter will be proportional to the quantity of carbon fixed by the algae into organic material, the radioactivity of the filter containing the algal cells is determined by liquid scintillation counting. Calculation of the productivity parameter also require information about the total inorganic carbon available in the incubation vessel, the length of time of incubation, the chlorophyll content of the incubated sample and specific activity of the radiotracer.

3.0 Safety and Waste Handling

3.1 Safety

3.1.1 ^{14}C is classified as a low-level beta emitter. Wearing personnel protective laboratory gear (rubber apron, protective gloves and glasses) at all times when using with ^{14}C and in the primary productivity lab, can effectively prevent any exposure.

3.1.2 All spills of radioactive or suspected radioactive materials must be immediately reported to the person in charge of radiation safety and decontaminated immediately.

3.1.3 All radioactive samples and standards should be properly labeled with the isotope and activity indicated and properly stored in designated locations.

3.1.4 Use only labeled radioactive items, e.g. glassware, forceps, filtration apparatus. If returned to general use, all equipment must be properly decontaminated.

3.1.5 Use spill trays lined with absorbent paper for all analyses involving ^{14}C.

3.1.6 Since ^{14}C is an inhalation hazard, all innoculations need to be performed under a functional hood.

3.1.7 Under the Atomic Energy Act of 1954, a license is required designating the radioactive source, its use as applicable to the laboratories and conditions by which the licensed material should be used. The current license (#12-10243-01) expires on December 31, 2000.

3.2 Waste Handling

3.2.1 Liquid wastes cannot be poured down the drain in any circumstances. All radioactive liquid waste is contained within 5 gallon cubitainers, and when full, are wrapped up in heavy radioactive waste bags. The following information is clearly marked on the outside using radioactive waste placards: type of radioactive waste, approximate activity (millicuries) and waste volume.

3.2.2 To estimate activity for a complete label, keep accurate records as to the volume contained within each cubie. Multiply the number of milliliters by 0.0167 (assuming the BOD bottles contain 300 mL and the specific activity of 1 mL of ^{14}C is 5μCi: 5μCi/300 = 0.0167μCi/mL) to obtain an estimation of the activity in microcuries.

3.2.3 From each waste cubie take a 1.0 mL sample and put into a liquid scintillation vial. Add 20 mL of Ecoscint. Add 1 mL of phenylethylamine. Clearly label cap to match that of the cubie sampled. Put this vial with sample vials to be analyzed for actual activity at CRL.

3.2.4 The disposal of solid wastes and contaminated articles should be into designated containers and, under no circumstances, into ordinary trash receptacles.

4.0 Apparatus

Two Darkened carboys
Two large insulated coolers
Pipettor (MLA equivalent), 1.0 mL with disposable tip
Pipettor (MLA equivalent), 0.5 mL with disposable tip
Pipettor (MLA equivalent), 0.3 mL with disposable tip
100 mL graduated cylinder
Two incubators capable of achieving temperatures from 0-20°C
Cool white fluorescent lights, six per incubator (General Electric F24T12CWHO 800)
Filtration units, for 47μm, 0.45 diameter filters
Forceps
300 mL BOD bottles
Vacuum system with pressure regulator and waste container system
Brinkman Repippetor with 20 mL capacity
Shallow tray, smooth, non-absorbent surface
Irradiance meter with a remote sensor
Thermometer
Geiger Counter

5.0 Supplies

Liquid scintillation vials, 20 mL capacity
Membrane filters, 47 mm diameter, 0.45 μm pore size Sartorius cellulose acetate
Liquid scintillation cocktail, Ecoscint brand
HCL 0.5 N
Radiotracer-labeled substrate as $NaH^{14}CO_3$; working stock solution of 5μCi/mL
Phenylethylamine, CO_2-free

Absorbent bench paper, plastic backed
Decontaminant surfactant, Radiacwash or equivalent
Kimwipes
Paper towels
Pipette tips, Eppendorf large, medium
Masking tape
Waterproof marker

6.0 Sample Collection and Preparation

6.1 Using a Geiger counter, make an initial check of the laboratory to ensure no residual contamination is present from other assays.

6.2 Using a waterproof marker, numerically label the caps of the scintillation vials.

6.3 Obtain water samples from desired depths using a non-metallic water sampler such as Niskin water bottles. Record the water temperature of the sample using a thermometer.

6.3.1 When lake water temperatures are isothermal, the water sample is a composite or integrated sample, resulting in one set of incubated bottles.

6.3.2 When thermal stratification of lake water occurs in summer, samples are collected from both the hypolimnion and epilimnion. Representative hypolimnion samples are obtained from the M-3 depth. The epilimnion samples are designated from the integrated subsamples. The temperatures used for incubation (to 0.1 °C) should be the temperature determined from the M-3 and integrated samples.

6.4 Transfer the water sample from the collection bottle to a 4 L plastic, darkened bottle, marked "sample", taking care to avoid agitation or bubbles that could disrupt cells. A wash bottle labeled "wash" is also filled with any water left over in the rosette.

6.5 Immediately place the darkened bottle into a light-tight, insulated container to maintain constant temperature during transport to the on-board ship laboratory. During the summer, add freezer packs or ice to maintain the hypolimnion temperature.

6.6 Record the following information into field notebook; station number, depth, pH, alkalinity, temperature, date, sampling time and analyst identification.

7.0 Instrument Set-Up Procedure

7.1 Before introducing samples to the incubator, adjust the temperature control to that of the water from which the samples were taken. Confirm temperature setting with thermometer to the nearest 0.1 °C.

7.2 Before introducing samples for the first time into the incubator, determine the appropriate locations for two sets of incubation bottles at each of at least five light levels. Each shelf should allow approximately half the light through as the one above it, e.g. 300, 150, 75, 37, and 17 $\mu E\ M^{-2}sec^{-1}$. Perform this procedure with all other bottles in place and filled with water. Mark

on the shelf using tape where the bottles should be placed during subsequent incubation. Use grey screening material (e.g., window screen material commonly found in hardware stores) between shelves or bottles if needed to adjust irradiance to those suggested above.

8.0 Analytical Procedures

8.1 Field Operations

8.1.1 Sample collection and initial preparation, see Section 6.0.

8.1.2 In the laboratory, record in the logbook the following data: bottle number, station, depth, date, sampling time.

All of the Following Procedures Should Be Performed in Green Light

8.1.3 If possible, each darkened carboy (both rinse and sample water) should be filled to the top with lake water, about 4 L.

8.1.4 In the summer begin with the hypolimnion sample (see Section 6.3.2) first to avoid excess sample warming. Gently mix the water by inversion or rolling. Rinse each incubation bottle with sample lake water and empty into sink.

8.1.5 Place all incubation bottles onto absorbent paper-lined tray and carefully fill each of the 12 incubation bottles with sample water keeping agitation and bubbling to a minimum. Make sure to minimize the air space by filling the bottles up to the top with sample water. Cap each bottle using glass stopper and tilt bottle to remove excess water.

8.1.6 Remove 1.0 mL of $NaH^{14}CO_3$ stock solution using a pipettor. Remove the sample bottle stopper and *gently* inject the stock solution into the bottom half of the bottle. Immediately replace stopper and put a plastic cap over the top of the stopper to eliminate leakage. Only put a plastic cap over those sample bottles which have been inoculated!

8.1.7 Using a new pipette tip for each inoculation, repeat Step 8.1.6 until all 12 bottles have been inoculated. Discard the remaining 1 mL of stock solution into the liquid waste cubie and dispose of the empty vial in the solid waste receptacle.

8.1.8 Place each sample bottle on tape-marked areas (see Section 7.2) in the incubator. Use a spherical irradiance sensor, and measure the light intensity at each bottle location *with all other bottles in place*. Record readings into logbook.

8.1.9 Incubate the samples for two hours, recording the incubation starting time into the logbook. If conditions dictate, the incubation period can persist for up to four hours. However, to maintain consistency, attempt to keep the incubation period as close to two hours as possible

8.1.10 Remove the top two bottles receiving the highest light intensity (top shelf, nearest the lights). *Record the Time* when the samples were removed and incubator temperature into the logbook.

8.1.11 After gently mixing the sample by inversion, remove the cap, measure 100 mL in a graduated cylinder and filter through 47 mm Sartorius 45 µm pore cellulose acetate filter under 8 PSI (equal to 2.3 inches in mercury) vacuum. Sample volume to be filtered may be adjusted to conditions, i.e. reduce volume if high density of algae causes clogging of the filter.

8.1.12 Rinse the filter funnel thoroughly with distilled water.

8.1.13 Remove the filter from the funnel base by grasping the edge with forceps and rolling it into a loose cylinder, algae side inward. Set into a clean liquid scintillation vial and loosely cap.

8.1.14 Repeat Steps 8.1.10 through 8.1.13 until a sample from each incubation bottle has been filtered.

8.1.15 From one of the incubation bottles exposed to one of the three highest irradiances, filter a *second* duplicate sample. Record the bottle number of the sample and the duplicate onto the logbook.

8.1.16 Filter 100 mL deionized water through a filter and place it into a clean liquid scintillation vial to serve as a blank.

8.1.17 Into each liquid scintillation vial that contains a filter, inject 0.3 mL of 0.5 N HCL into the bottom. *Loosely* cap, and let sit for at least one hour.

8.1.18 After one hour, add 20 mL of liquid scintillation cocktail, Ecoscint brand or equivalent, into each vial that has received the acid treatment.

8.1.19 Cap each vial and gently shake it until all of the filter has been covered with cocktail and has sunk to the bottom of the vial.

8.1.20 Into two clean liquid scintillation vials, add 20 mL liquid scintillation cocktail plus 1 mL phenoethylamine (a CO_2 absorber).

8.1.21 Choose, at random, two incubation vessels and transfer 1.0 mL of each into a corresponding vial containing the cocktail and phenolethylamine (Section 8.1.20). These subsamples will be used to confirm the actual specific activity of the isotope in the incubation vessels. Record the bottle numbers into the logbook.

8.1.22 Make sure each vial cap is *tightly* secured and properly labeled. Store the vials for transport to CRL for scintillation counting.

8.2 Clean-up Procedures

8.2.1 Dispose of remaining sample in the sample bottles in the liquid waste cubie.

8.2.2 Soak incubation bottles in decontaminant surfactant for at least one hour. Rinse at least three times with tap water, until *absolutely no suds remain*. Using deionized water, rinse all bottles a final time and allow to air dry.

8.2.3 As needed, or once per day, wipe working areas with decontaminant wash. Wipe dry with paper towels.

8.2.4 Change absorbent bench paper if it becomes contaminated or ineffective because spills.

8.2.5 Dispose of potentially radioactive solid waste in specified receptacle.

8.2.6 At the end of the survey, after the lab has been completely cleaned, use filters moistened with distilled water to wipe 4 inch smears of all working surfaces. Put into a clean scintillation vial with 20 mL of Ecoscint and 1 mL of phenethylamine. Label cap with smear number and record location information into the logbook.

8.2.7 All solid and liquid waste is required to be labeled with estimated activity, volume and radioactive source. Prepare for transport to CRL by putting parafilm around the lid and covering liquid waste containers in radioactive waste bags. Tape solid waste boxes completely shut. The waste activity must be clearly seen from the outside of transport material and be accompanied by a Bill of Lading and a ^{14}C waste form (see Appendix 1).

9.0 Quality Control

Although a blank, duplicate and two total activity samples are completed for each depth, there is no on board analysis capabilities for reanalysis.

Appendix 1:
Radioactive Waste Form

Generating Waste Site_____

Radioisotope/Activity_____

Original Volume of above_____

Waste is properly packaged and labeled for transport: _____ Date___/___/___

Received at CRL in good condition and placed in Haz waste room: _____ Date___/___/___

_____ Date___/___/___
(CRL Safety Rep.)

AQUEOUS WASTE

CUBITAINER ID #	VOLUME mL	PRE-TRANSPORT	CRL: LIQUID SCINTILLATION SYSTEM		COMMENTS
		ESTIMATED TOTAL µCi	DPM/mL	ACTUAL TOTAL µCi	
AQUEOUS TOTAL					

DRY WASTE

BOX/BAG ID #	ESTIMATED µCi	COMMENTS
DRY TOTAL		

USGS Field Operation Plan: Tributary Monitoring

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Version 2.0

USGS Field Operation Plan:
Tributary Monitoring

Samples for organic analyses will consist of a composite sample obtained using USGS quarter-point sampling procedures. The stream will be visually divided into three equal flow areas using field data obtained during discharge calibration measurements. At the center of each flow area, water samples will be obtained at 0.2 and 0.8 times the depth. Water samples from each of the six sampling locations will be composited. Water for PCB, PAH, pesticide, and Atrazine analyses will be pumped by a submersible pump through a tee in the pump line. A peristaltic pump will draw water from the tee and pump water through the 293 mm, stainless steel, pentaplate filter holder. Two to five glass fiber filters will be used depending on the concentration of suspended material in the water column. The backpressure from the filter head shall not exceed 5 psi. Residual water will be evacuated from the filter head using the peristaltic pump. Filters from the pentaplate filter holders will be folded in quarters and wrapped in clean, acetone rinsed aluminum foil. The filtrate will be collected in clean, acetone-rinsed, 20 liter glass carboys. The filtrate will be processed through a large, 250 gram, XAD-2 resin column, at a flow rate between 500 and 1000 mL per minute. Water for DOC, POC, and conventional constituents will be obtained from an overflow line attached to the tee from the submersible pump tubing and composited from each of the six sampling locations into a polyethylene churn splitter. The churn splitter provides for efficient subsampling of the composite sample to provide the necessary samples required by the Wisconsin State Lab of Hygiene.

Preprinted, site-specific, laboratory request forms will have the date, time, and sequential sample number recorded for each sample. Filters, resin columns, and sample bottles will have an adhesive label attached which will identify the site, sample number, date and time of sampling. Processed samples will be kept in a chilled ice chest until refrigerated at the USGS. Samples and laboratory request forms will be delivered to the WSLH, chilled, in plastic coolers, by either the USGS or Federal Express. The WSLH will log the receipt of the samples into its Laboratory Information Management System (LIMS) database and sign the chain of custody on the laboratory request form.

The constituent list for which a contract laboratory will perform analyses is as follows:

Constituent	Field Requirement
Total Phosphorus Total Kjeldhal Nitrogen Total Ammonia Nitrogen Nitrate Nitrogen	250 mL nutrient bottle preserved with sulfuric acid to pH <2.0
Dissolved Reactive Phosphorus	60 mL, filtered/.45 µm membrane, chilled
Dissolved Chloride Dissolved Silica	60 mL, filtered/.45 µm membrane, chilled

Constituent Field Requirement (con't)

Total Alkalinity Total Suspended Solids Volatile Suspended Solids Conductivity pH	710 mL, no preservative chilled
***Dissolved*?????** Dissolved Calcium Dissolved Sodium Dissolved Potassium Hardness as $CaCO_3$	125 mL filtered/0.45 µ membrane filter in (250 mL) nutrient bottle (unacidified) (write "**ff**" on bottle cap)
Chlorophyll-a	200 to 1000 mL, filtered using 5.0 µm glass fiber filter retained in glass vial and chilled
Dissolved Organic Carbon Total Organic Carbon	25 to 50 mL filtered until filter clogs. Use syringe.

A variety of field parameters will be measured during the actual sample collection. A Hydrolab multiparameter meter will be used to measure temperature, conductivity, dissolved oxygen, and pH. A light extinction measurement will be made using standard Secchi disc equipment and techniques. Velocity and direction of flow will be recorded at each of the subsampling locations.

Field Operation

The procedure to be followed while obtaining water samples and field parameters will be as follows:

1. At each of the proposed sampling locations a cross section of the stream will be measured. The data will be used to subdivide the cross section into three approximately equal flow cells. The centroid of each of these cells will be identified on the field map.

2. The field crews will use visual reference points to position themselves on station during each sampling trip.

3. At each of the cell centroids water samples and Hydrolab parameters will be obtained at 0.2 and 0.8 times the total depth. Samples are to be taken during periods of downstream flow with the additional limitation that downstream flow must be established for a least ½ hour prior to sample initiation. Data from the AVM gaging stations or field determinations of velocity will be used to determine the proper sampling periods.

4. Water samples from each of the six centroid sampling locations will be composited in order to reduce analytical costs. Therefore the field crew will obtain 1/6 of the total required volume for organic and inorganic analyses at each of the subsampling locations. The flow rate through the 293 mm organics filter will be monitored to maintain an effective subsampling of the cross section. The 293 mm filters will be retained for particulate PCB analyses. The filtered sample will be stored in a 20 L glass carboys and transported to shore for soluble PCB extraction. Water samples for inorganic analyses will be taken from a tee in tubing between the peristaltic pump and the 293 mm filter holder. A 47 mm stainless steel filter holder will be used for dissolved inorganic constituent sample collection. The filtrate will be processed through a large, 250 g, XAD-2 resin column, at a flow rate between 500 and 1000 mL per minute.

5. Secchi disk observations will be taken at the cell centroid locations for each cross section.

6. Velocity and flow direction will be recorded at each of the subsampling locations.

7. Preprinted adhesive labels shall be affixed to each sample container which will be delivered to the analytical laboratory. Sample log forms will be completed and included with the sample containers. An itemized list will be included with each shipment of samples to the labs. A copy of the memo should be noted with the date received and returned to the USGS to preserve a chain of custody for the samples. Samples delivered to contract laboratories which will be hand carried must have drop-off date and time recorded in the Sample Log.

Trace Metal and Mercury Sampling Methods for Lake Michigan Tributaries

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Revision 2

Trace Metal and Mercury Sampling Methods for Lake Michigan Tributaries

1.0 Bottle Labeling and Supply Sorting

Prior to boat deployment, all sample bottles must be selected, labeled, and sorted into a cooler for easy access during sampling. Consult the master sampling plan, and/or specific instructions for a given sampling trip to determine what samples should be obtained. Remove the requisite number of Teflon Sampling Bottles from each of the Trace Metal and Mercury Bottle storage containers. With a black Sharpie label the outer bag with the site code, date, and type of sample (unfiltered, filtered, replicate, blank, spike, etc.). Record this same information on the Field Data Sheet, which is to be consulted during the sampling process to prevent mixup of sample bottles and bags. A sample bottle label can be affixed to the outer bag *after* sampling is completed. Remove a 1000 mL poly bottle from the storage bag and using a black Sharpie label it as a SPM/DOC Trace Metal Composite, and with site code.

The following sampling supplies should also be placed into the cooler for transport:

1. Calyx Filters
2. Pump Head Tubing
3. Trace Metal Acidification Kit
4. Mercury Acidification Supplies (Acid and Vials)
5. Bagged Wrench

The 1 gallon tubing rinse container must be filled ⅔ full with 2% HNO_3 from the 20 L carboy and then placed into the egg crate for use on the boat.

2.0 Boat Deployment and Anchoring

The Boston Whaler must always be transported with cover intact. Periodically wash cover in a manual car wash to prevent build-up of contaminants.

The inside surfaces of the Boston Whaler should have been rinsed after completion of previous sampling (see clean-up), if not, rinse them now before loading and launching.

Position equipment containers into the Boston Whaler in a manner which will minimize reorganization out on the river. Review equipment checklist to verify that all necessary supplies have been loaded. Prior to launching, all required (consult sample bottle manifest) sample bottles should be organized and labeled (see above).

Anchor Boston Whaler at sampling site (above centroid of river) using two anchors, bow and stern. The bow anchor line is threaded through metal eye and tied-off on port cleat. Transport anchors, especially bow anchor, in plastic bags. Upon completion of sampling, thoroughly wash anchors with river water before bringing on-board, and place directly into plastic bags to avoid muddying up the boat.

3.0 Set-Up

Steps 3.1-3.3 may be performed without clean suits.

3.1 Equipment Organization

Position tubs, and other sampling equipment in appropriate locations in boat.

3.2 Boom Installation

Hook fiberglass cleat adaptor into place on bow cleat. Remove plastic protective bags (place in bag container) from bow sampling boom and put boom in place by resting in fiberglass cleat adaptor, hooking straight end under bungie cord, and securing boom in fiberglass cleat by tieing with an arm-length glove.

3.3 Sampling Platform Pump Installation

Wrap a large PE bag over the starboard gunnels of the boat. Hook the plexiglass sampling platform over the gunnels on top of the plastic bag. Insert the canopy frame into the sampling platform. Place a plastic bag over the canopy frame, and secure with split tubing clamps. Attach power cord to Geo-pump, wrap pump with an arm-length glove, and set into sampling platform. Run power cord to stern of boat and attach to pump battery.

4.0 Sampling

Clean Suits and Gloves Must Be Worn For All The Following Steps.

4.1 Lowering Tubing Line

Open plastic cartons containing sampling line and kevlar support rope. Tie kevlar rope to loop of Teflon string attached to sampling-line weight. (The end of the rope is two feet above sampling intake). Slowly and carefully begin removing lower end of sampling line (i.e. Teflon weight end) from plastic bag (use extreme caution to avoid kinking and contamination), insert weight through receptacle on end of boom and lower into river to first depth (0.2 x River Depth). Secure kevlar support rope onto starboard plastic cleat. Keep remainder of sampling line tubing in plastic bag until pump head tubing is attached.

Note: Rope is marked in one foot increments - beginning six inches from the end. Use the six inches to tie off to Teflon string. The distance from sampling ports to top of Teflon string is two feet. A double line is marked every five feet, and a triple line is marked every 10 feet.

To drop the sampling line to the lower depth, the kevlar rope is un-cleated, and both rope and Teflon sampling line slowly let out to (0.8 x River Depth). It is usually necessary to uncouple Sampling Line from pump-head tubing before lowering line. Clean-hands uncouples and re-couples sampling line from pump-head tubing.

4.2 Geo-Pump Loading and Sample Line Connection

Load pump-head tubing into Geo-Pump using clean protocol. {Gloved dirty hands opens pump head clamp lever and holds outer bag of pump-head tubing, while gloved clean hands removes inner bag and loop of tubing. Clean hands inserts closed tubing loop into pump head and dirty hands closes clamp lever making sure that tubing is properly positioned. Dirty hands makes sure that Teflon Tubing Adaptor Fitting (TTAF) and plexiglass clamp ring (PCR) are ready. At this point dirty hands re-gloves, and retrieves open end of sampling line from storage bag, while clean hands opens pump head tubing loop. Dirty hands gives clean hands sampling line who inserts it into pump head tubing. Dirty hands collects TTAF bag and opens outer bag, while clean hands opens inner bag and removes TTAF and tightly inserts it into the long end of the pump head tubing. The TTAF bags should be kept in the sample transport cooler during sampling (inner bag is always kept inside dirty outer bag. Dirty hands, with new gloves, collects PCR from storage bag, removes PCR, and holds it while clean hands inserts TTAF into PCR. Dirty hands then inserts assembly into groove in sampling platform. The PCR bag should also be kept in the cooler during sampling to minimize contamination and prevent it from being blown away.

4.3 Sample Collection

Place the appropriate sample bottles into the plastic sample organizing container using the following protocol. The outer bags should have been previously labeled with site and sample type information. The outer bags are removed using clean techniques and sample bottles with inner bag are placed in the organizing container. Dirty hands (with new gloves) retrieves appropriate double bagged Teflon sample bottle and opens outer bag. Clean hands (with new gloves) pulls inner-bag out of outer bag and places single-bagged bottles in the organizing container. Outer bags are stowed in the sample transport cooler, out of the wind.

The typical sampling sequence will be:

[1] 250 mL Unfiltered sample for Trace Metals
[2] 500 mL Unfiltered sample for Mercury
[3] 125 mL Unfiltered sample for Methyl Mercury (see Note)
[4] 1000 mL Unfiltered sample for SPM and DOC
[5] 250 mL Filtered sample for Trace Metals
[6] 500 mL Filtered sample for Mercury
[7] 125 mL Filtered sample for Methyl Mercury (see Note)

Filling each bottle ½ full.

Note: For Methyl Mercury; Sheboygan, Manistique, Pere Marquette, and Grand rivers only.

This sequence will be repeated at the lower depth (except that filtered samples will be collected first) to fill the remaining ½ of bottle and then samples are acidified, and double-bagged.

4.3.1 Upper Depth

4.3.1.1 Unfiltered Sample Collection

Dirty hands starts Geo-pump and adjusts to moderately high speed to flush lines (Verify that water flow is correct, through platform hole, and not splashing sides). Sampling lines are flushed for a minimum of five minutes before unfiltered samples are collected.

Sample Bottle Handling: Clean hands (with new gloves) pulls appropriate bottle out of inner-bag leaving inner-bag in organizing container.

Trace Metal Sample Collection: Teflon bottles are supplied empty and dry. Clean hands reaches under water stream and partially (⅛) fills bottle. The bottle is loosely capped and gently shaken to rinse. This process is repeated for a total of three bottle rinses. On the fourth collection the bottle is filled ½ full. *Do Not Touch Bottle Mouth To TTAF Or Any Other Surface.* Clean hands then returns sample bottle to inner-bag in organizing container. The bags do not have to be sealed at this point. Dirty hands removes and replaces organizing container lid during sampling.

Mercury Sample Collection: Teflon bottles are supplied filled with dilute HCl. Clean hands dumps acid into waste container. *Do Not Touch Bottle Mouth To Waste Container Or Any Other Surface.* Clean hands reaches under water stream and partially (⅛) fills bottle. The bottle is loosely capped and gently shaken to rinse. This process is repeated for a total of four bottle rinses. On the fifth collection the bottle is filled ½ full. Clean hands then returns sample bottle to inner-bag in organizing container. The bags do not have to be sealed at this point.

SPM - Carbon Sample Collection: One-Liter polyethylene bottles are supplied empty and dry. Clean hands reaches under water stream and partially fills bottle. The bottle is loosely capped and gently shaken to rinse. This process is repeated for a total of three bottle rinses. On the fourth collection the bottle is filled ½ full. Clean hands re-gloves after handling the poly bottle.

4.3.1.2 Filtered Sample Collection

After all unfiltered samples are obtained from the upper depth, dirty hands reduces pump speed and then shuts off pump. Dirty hands re-gloves, retrieves a bagged Calex filter, and opens outer bag. Clean hands opens inner bag, removes filter capsule, opens vents, and drains off storage MQ into river (The filter bags may be discarded - the filter capsule is a disposable, single-site use, item). Dirty hands removes PCL/TTAF assembly from sampling platform, and clean hands uncouples TTAF and screws filter capsule onto TTAF. Clean hands inserts filter capsule into support on sampling platform. Dirty hands starts Geo-pump and adjusts to moderate speed to flush capsule (Verify that water flow is correct, through platform hole, and not splashing sides). The filter capsule is flushed for five minutes or approx. 3 L before filtered samples are collected. At this point Filtered Trace Metal samples and Filtered Mercury samples are collected in an

identical manner to Unfiltered samples as described above. To minimize the potential for filter clogging, dirty hands shuts off pump after each rinse or sample has been obtained. Upon completion of Filtered sample collection from the upper depth, clean hands un-couples Teflon sampling line from pump-head tubing and dirty hands lowers tubing to 0.8 depth. When at depth, the sample tubing line is then reattached to the pump-head tubing using the clean technique.

4.3.2 Lower Depth

The collection process is identical to that described above for Upper Depth, except that obviously ½ full bottles are not rinsed and filtered samples are collected first. The protocol for flushing and equilibration of sampling line and filter is similar to Upper Depth, except that here one is flushing the line and filter as a unit. Flushing as a unit for five minutes should not present a problem except under conditions of very high suspended solids levels. If during Upper Depth sampling or early stages of Lower Depth flushing, significant reduction of sample flow rate through the filter is noted, do the following to minimize filter clogging. Uncouple filter capsule from the TTAF and flush the sample tubing line for the full five minutes. While tubing is flushing, drain the river water from the capsule filter. After tubing is flushed, connect to drained filter and flush filter for 90 seconds. Clean techniques must be followed. Bottles are filled to near capacity, leaving space for preservation acid. After each sample bottle is filled, and before re-bagging, preservation acid is added to the sample.

4.4 Acidification

4.4.1 Trace Metal Sample Acidification (250 mL Sample Bottles)

Acid (50% Ultrex HNO_3) is supplied pre-measured in small Teflon Vials, one for each sample. Acid transfer to the sample must be quantitative. Dirty hands (with new gloves) retrieves the bag containing acid vials and opens it. Clean hands reaches in and removes a vial. Dirty hands wrenches open the vial while clean hands holds it. Clean hands then removes vial cap and pours acid into sample bottle which should be available and loosely capped on work surface. Used acid vials are re-capped and placed into a designated Zip-bag, to be returned to Water Chemistry Lab along with metal samples. Note the acid batch number on the field data sheet. The acidified sample is ready to be double-bagged using clean-hands protocol after the cap is wrenched tight. Clean hands holds bottle tightly while dirty-hands takes a double-bagged channel-lock pliers to cap. Clean-hands twists bottle to secure cap. Place new bags on the wrench before use at each site, and during a sampling period if the bags appear worn.

4.4.2 Mercury Sample Acidification (500 mL Sample Bottles)

Acid (50% HCl) is supplied in a 250 mL double-bagged Teflon bottle. Also supplied is a Teflon measuring vial into which acid is poured to measure out 10 mL aliquots. Before starting the acidification process, verify that the samples to be acidified are organized on the clean work surface, and that their bottle caps are loose. Dirty-hands retrieves acid bottle and opens outer bag. Clean hands opens inner bag and removes Teflon acid bottle, setting it on plastic covered work surface. Dirty-hands retrieves Teflon measuring vial and opens outer bag. Clean hands opens inner bag and removes vial. Temporarily place acid

and vial bags (inner bag inside outer bag) in the sample organization box. Clean hands pours acid into the vial up to the etched line and then quickly pours contained volume into the sample bottle. *Do not let acid measuring vial touch lip of sample bottle.* Clean-hands - dirty-hands procedures are then used to wrench shut and double-bag sample bottles, and to double bag acid bottle and measuring vial.

Do not acidify 125 mL methyl Hg bottles.

Verify that Everything Has Been Recorded and that Bags are Labeled.

5.0 Clean-up

5.1 Tubing-Line and Weight

Upon completion of lower depth sampling, the sampling line and support line are retrieved by slowly pulling on the Kevlar line (Dirty-hands person) while the clean-hands person coils the tubing into the storage bag. The sample line tubing should be un-coupled from the pump-tubing before retrieval so that the river water drains out. Untie the support line and seal in storage box. The weight and tubing must be flushed with dilute acid to prevent cross-contamination and to prevent contaminant build-up. A dilute acid solution is supplied in a 1 gallon PE bottle. Before inserting the tubing weight into the acid bottle, wipe the top outer surfaces of the weight with a clean-room wiper. Insert the tubing weight into the acid bottle, connect the free end of the sampling line to the pump-head tubing, and flush at moderate-high pump speed. Pump until all of the acid solution has flushed through the tubing, and then continue pumping until a majority of the tubing has been pumped dry (you may have to lift the tubing weight out of the acid jar to ensure that the tubing pumps dry). Remove the weight from the acid bottle, place in a *new* plastic bag, and wipe the top outer surfaces with a new clean room wiper. Recoil the tubing, tie with an arm length glove, and place in plastic bag. Store in dedicated storage container. Tubing will be periodically resupplied from the Water Chemistry Lab.

5.2 Sampling Platform

Calex filter is discarded.
Rinse PCL and TTAF with MQ, double-bag using clean techniques, and place in tubing storage container. (The TTAF fittings should be periodically returned to Madison along with samples for more rigorous cleaning).
Canopy bag is discarded.
Platform is rinsed with MQ and wiped with clean-room wipers.
Canopy frame and platform are bagged and placed in rubbermaid container.

5.3 Boom

Bagged in two large PE bags.
Fiberglass cleat adaptor is bagged and stored in supplies container.

5.4 Anchors and Anchor Line

Any sediment on anchors or line is washed off in the river before bringing into the boat. When anchor is clean, remove from water and place directly into a plastic bag.

5.5 Boat Rinsing

The inside surfaces of the boat must be rinsed with water after sampling is completed. If simple flushing with water is not sufficient to remove grime, then use the supplied brush to loosen dirt.

6.0 Additional Trace Metal (Non-Hg) QC Procedures

6.1 Trip Bottle Blank

With every batch of bottles a field bottle blank is created. The bottle blank is a 250 mL Teflon bottle, prepared identically to the sample bottles, except that before double-bagging it is filled with MQ water in the lab. This bottle travels to the field along with the sample bottles (In the field keep this bottle in the QC sample container). The bottle blank is to be acidified in the field with the same pre-measured acid vials as supplied for the samples. Soon after receipt of a batch of samples bottles, include the associated bottle blank with the set of sample bottles that are taken out in the boat. Handle the bottle/sample using clean techniques, and acidify in an identical manner as described for actual samples. Send bottle blank immediately back to Madison along with samples from that site.

6.2 Analyte Spiking

At a frequency of approximately 10% (see master sampling schedule), duplicate un-filtered and filtered river water samples, as well as a MQ water blank will be spiked with an acidified solution of the analytes of concern. The MQ water blank for spike addition (Blank Spike) and spiking solutions are kept in the QC sample container. The large 6 mL vials are used for the *un-filtered* river water, and the small 3 mL vials are used for the *filtered* river water and *MQ blank*. These vials contain sufficient acid to properly stabilize the sample - Do Not Acidify Again with Normal Acid Vials. The spike addition must be quantitative. The procedure is to simply collect sequential duplicate un-filtered and filtered samples in the standard 250 mL Teflon bottles using clean protocols (i.e. fill an additional 250 mL bottle for the un-filtered spike and an additional 250 mL Teflon bottle for the filtered spike *at the same time* you are collecting normal filtered and un-filtered samples. Composite 0.2 and 0.8 as usual). It is important for the duplicate samples to be as similar as possible These samples along with the Blank Spike MQ bottle are then acidified in the boat using clean techniques with the spiked acid solution in place of the normal acid. Send the three spiked samples back to Madison along with other samples from that site.

7.0 Field Blanking Procedure

Field blanking is performed to estimate the level of metal contamination from the sample tubing line, filter cartridge, and general handling of the sampling apparatus. In addition these blanks are used as field diagnostic tools, and to generate method detection limits.

The field blank kit consists of the following gear:

1 5000 mL Teflon bottle filled with Milli-Q water.
1 3000 mL Teflon bottle filled with Milli-Q water.
3 250 mL Teflon bottles for trace metal samples.
3 500 mL Teflon bottles for mercury samples.
Short length (3 ft) of Teflon Tubing.
Zip-lock bags for 5 L bottle caps.
Plastic bags.

Blank collection will follow the sequence:

Source Water.
Filter Blank.
Tubing Blank.

Please perform the blanking procedure *before* beginning normal sampling.

Trace Metal Clean Procedures Must be Followed.

[1] Label three sets (250 mL trace metal, 500 mL mercury) of bottles as follows:

Source Water Filter Blank Tubing Blank
Record bottle numbers and type on field data sheets.

[2] Set up filtration platform as usual. Install a new section of pump head tubing in peri-pump. Attach TTAF and lock in PCL. Uncouple tubing weight from sample line.

[3] Remove Teflon cap/insert from 5 L bottle, place caps in zip-lock bag. Insert short length of Teflon tubing into bottle and connect other end to pump head tubing in peri-pump. Place a plastic bag over 5 L bottle to isolate during blanking procedure.

[4] Flush approx. 500 mL of blank water through pump head tubing. Collect Source Water samples as per protocol, with appropriate number of rinses. Conserve water! Shut off peri-pump when not collecting samples or flushing.

[5] Remove Teflon tubing from 5 L bottle and place into 3 L bottle (Rinse MQ). Connect a filter cartridge to TTAF and lock into holder. Flush approx. 1500 mL of Rinse MQ through filter cartridge. Place tubing back into 5 L blank water bottle and collect Filter Blank samples as per protocol.

[6] Remove filter cartridge (save for later use). Uncouple short Teflon line - rebag. Insert one end of sampling line into 3 L bottle, connect other end to peri-pump. Flush approx. 1500 mL of Rinse MQ through line. Place sample tubing line into 5 L blank water bottle and collect Tubing Blank samples as per protocol.

[7] Acidify samples as per protocol.

[8] Cap 3 L and 5 L bottle. Place samples bottles, 3 and 5 L bottles, short Teflon tubing in Blank Kit Cooler and return to Water Chemistry in Madison.

[9] Re-couple tubing weight to sample line (Fasten Securely).

8.0 Equipment List

[1] Plastic bow boom packaged in two large PE bags.
[2] Fiberglass boom cleat adaptor.
[3] Rubbermaid carton for plastic bags.
[4] Rubbermaid carton containing plexiglass sampling platform and canopy.
[5] Geo-pump and power cord.
[6] Deep-discharge battery in plexiglass case for running peri-pump.
[7] Rubbermaid container with kevlar support line (50 feet - marked in increments of one foot).
[8] Rubbermaid container with Teflon sampling line, Teflon sampling weight.
[9] Plastic container with insert to secure and organize sample bottles.
[10] Sampling Supplies.

a. Teflon sample bottles
b. Pump-head tubing (Double-bagged)
c. Teflon fitting for end of sampling line (TTAF)
d. Plexiglass clamp ring (PCR)
e. Calex Filter capsules
f. Acidification supplies
g. Double-bagged channel-locks
h. Arm-length gloves
i. Wrist-length gloves

[11] Dilute acid solution in 1 gallon container.

Electric Motor
Motor Battery
Oars
Two Plastic Coated Anchors with poly- line

Trace Metal Field Quality Assurance Plan Summary - 1994 and 1995

Sample Type	QAPjP Frequency	1994 Accomp.	1995 Goal	1995 # Samples	Comments
Field Replicates	15-20%	25 (13.7%) U 21 (11.5%) F	15% U 15% F	40 U 40 F	
Analyte Spike Sample Matrix	10%	18 (9.8%) U 18 (9.8%) F	10% U 10% F	27 U 27 F	
Analyte Spike Blank Matrix	5%	21 (4.7%)	2.5%	15	one every other bottle batch (20)
Field Bottle Blank	5%	23 (5.1%)	5%	30	one every bottle batch (20)
Filter Blank	2.5%	5 (1.1%)	2%	12	four per team
Tubing Blank	2.5%	5 (1.1%)	2%	12	four per team
Lab Bottle Blank	5%	28 (6.2%)	5%	30	one every bottle batch (20)

Replicate and spike percentages given as a percent of site visits (183 in 1994).
Blank percentages are expressed as a percent of non-blank samples (449 in 1994).

1995 QA samples based on 271 site visits (Jan- Nov) and 596 non-blank samples.

Trace Metal Field Quality Assurance Plan Summary - 1995

Site	Replicates				Spikes				Large Me-Hg Bottle Site Count
	Spring Runoff	Summer Event	Baseflow	Σ	Spring Runoff	Summer Event	Baseflow	Σ	
Manistique	1	0	1	2	1	0	1	2	
Menominee	1	2	1	4	1	0	1	2	
Fox	1	2	1	4	1	1	1	3	
Sheboygan	1	2	2	5	1	0	1	2	
Milwaukee	1	2	2	5	1	1	1	3	
Grand Cal.	1	0	1	2	1	0	1	2	
St. Joseph	1	1	2	4	1	1	1	3	
Kalamazoo	1	2	2	5	1	1	1	3	
Grand	1	2	2	5	1	1	1	3	
Muskegon	1	0	1	2	1	0	1	2	
P. Marquette	1	0	1	2	1	0	1	2	
Σ	11	13	15	40	11	5	11	27	

1. Replicates and Spikes are obtained from both Unfiltered and Filtered Samples. Hg samples are not spiked in the field.

2. Field Bottle Blanks are sent with each batch of 20 bottles and should be acidified as soon as possible and returned to lab.

3. Field Spike Blanks are sent with every other batch of 20 bottles and should be spiked when performing a sample spike.

4. The Blanking Kit (Filter and Tubing Blanks) will be rotated between field teams, and must be performed as soon as possible in order that each team can obtain four method blanks over the study year.

5. One 250 mL Teflon MeHg bottle must be substituted for one of the unfiltered or filtered 125 mL MeHg bottles every 5th site visit. Site visits can be recorded in MeHg site count column.

Trace Metal Sample Treatment Summary

Sample Type	Bottle Size	Treatment
Routine Field Sample		
-Unfiltered	250 mL	contents (3 mL) of one *acidification* vial
-Filtered	250 mL	contents (3 mL) of one *acidification* vial
Field Bottle Blank		
-milli-Q	250 mL	contents (3 mL) of one *acidification* vial
Field Sample Spike		
-Unfiltered	250 mL	contents (3 mL) of one *large spiking* vial
-Filtered	250 mL	contents (2 mL) of one *small spiking* vial
Field Blank Spike		
-milli-Q	250 mL	contents (2 mL) of one *small spiking* vial
Blank Kit		
-Feed Water	250 mL	contents (3 mL) of one *acidification* vial
-Filter Blank	250 mL	contents (3 mL) of one *acidification* vial
-Line Blank	250 mL	contents (3 mL) of one *acidification* vial

Field Acidification vials are packaged in zip-lock bags labeled Field Acidification Solution, Lot #FS95##. All vials are the large 6 mL capacity.

Field Spiking vials are packaged in zip-lock bags labeled as follows:

a. Unfiltered (or Total) Sample Spiking Solution, Lot #SPU95##. All vials are the large 6 mL capacity.

b. Filtered Sample Spiking Solution, Lot #SPF95##. All vials are the small 3 mL capacity. Both the Unfiltered and Filtered Spiking Solutions contain sufficient acid to stabilize the samples. *Do not* use an acidification vial in addition to spiking solution. Please do not interchange spiking solutions - they are designed for a specific matrix.

Field Bottle Blanks should be acidified in the boat in a manner identical to routine field samples, and returned to the lab within two to three weeks of receipt.

Field Blank Spikes should be spiked at the same time as sample spikes. If you have scheduled a sample spike and a blank spike bottle exists - spike it. Return to lab as soon as possible.

Field Sampling QA Final Project (1994-1995) Accounting

Blank Accounting

Source	QC Sample Type	Number of Samples	Percent of Non-Blank Samples (891)
Teflon Sample Bottle (prep. and sample storage)	Lab Bottle Blanks	56	6.3
Sample Bottle Handling in Field and Acidification	Field Bottle Blanks	54	6.1
Acidification Acid	Acid Batch Qualifier	14	Each Acid Batch
Filter	Dedicated Lab Study	----	----
Filter/Pump-Head Tubing and Filtering in Field	Field Filter Blanks	13	1.5
Pump-Head Tubing	Dedicated Lab Study	----	----
Field Sample Tubing	Field Tubing Blanks	13	1.5

	Number of Samples	Percent of Site Visits (356)
Recovery		
Field Analyte Spike (Blank Matrix)	41	4.6
Field Analyte Spike (Filtered Sample Matrix)	42	11.8
Field Analyte Spike (Unfiltered Sample Matrix)	42	11.8
Field Surrogate Spike (four rare metals in Sample)	1081	100
Precision		
Field Replicates (Filtered Sample Matrix)	46	12.9
Field Replicates (Unfiltered Sample Matrix)	50	14.0
Accuracy		
Interlab Studies (Prepared Samples)	3 studies	
Interlab Studies (Ambient Samples)	2 studies	

ICP-MS Batch Analysis QA Outline
15-18 Samples per Batch

Sample Type	Frequency
ICP-MS Qualification	
-Blank Levels	Before each sample batch
-Stability	Before each sample batch
-Sensitivity	Before each sample batch
-Resolution	Before each sample batch
-Interference Check	Once per week
Blanks Levels During Run	
Calibration Blank	One per batch
Check Blanks	Four per batch
Memory Check	One per batch
Recovery	
Lab Analyte Spike, Blank Matrix	One per batch
Lab Analyte Spike, Sample Matrix	Two per batch
Internal Standards, 3-metals	All samples
Precision	
Replicate Sample Acquisitions	Four per sample
Lab Sample Replicates (within batch)	Two per batch
Lab Sample Replicates (different batch)	20%
Accuracy	
Standard Reference Material (SLRS-3)	Three per batch
Laboratory Control Sample (Trib Matrix)	One per batch

Volume 1

Chapter 3: Sediment

Standard Operating Procedure for Collection of Sediment Samples

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1991

Standard Operating Procedure for Collection of Sediment Samples

1.0 Scope and Application

The application of this sampling procedure is for the collection of sediment cores, using a box corer, for the analysis of radionuclides to provide estimates of the sedimentation rate and mixing depth for the GLNPO Lake Michigan Mass Balance Study.

2.0 Summary of Procedure

Before any box cores are taken, test grabs, using a ponar, will be taken to determine the suitability of the sediment for coring. If coring is possible, then the box corer will be deployed. Once the box coring is completed and box core is back onboard the ship, then four 10 cm (ID) plastic tubes will be inserted by hand into the Master box core, thereby creating 4 subcores (A-D). Each of the subcores will be sectioned and these subsamples stored for future analysis.

3.0 List of Equipment

Item	Quantity
Modified box corer (Soutar corer)	1
Box corer extraction rigging	1
Set of critical spare parts for box corer and extraction rigging	1
Hydraulic extruding stand for 4" diameter subcores	1
Set of core sectioning gear	1
125 mL Polyethylene bottles/ pre-labeled and tared	as needed
Ponar grab sampler	2
Winch for Ponar deployment	1
10 cm/4" diameter subcore butyrate tubes	12
vacuum-extractor caps	2
Portable vacuum pumps with tygon tubing	2

4.0 Sampling Procedure

4.1 Test grabs, using a Ponar grab sampler, will be taken to determine the suitability of the sediment for coring. If three grabs return without a sample, then the site will be vacated. If the Ponar grabs are obtained but coring is not feasible, then surface samples from the grabs will be obtained. If coring is possible then box coring will be undertaken as long as there appears to be a limited risk of damage to the box core.

4.2 Once the box core has been retrieved and is back on the ship's deck, then the core is examined for acceptability. This examination is done by using the viewing window on the front side of the box core. If the core is unacceptable, then the contents of the box core will be released and the box corer redeployed.

4.3 Acceptable box cores are sub-cored by carefully inserting a 10 cm diameter butyrate tube into the core. Distortion of the sediment during the tube insertion is minimized by the application of a partial vacuum to the tube top. By continuous manual adjustment of the vacuum as the core is inserted, the interface within the tube remains in alignment with the interface of the surrounding sediment in the box core.

4.4 Sediments within the tube are hydraulically extruded and sectioned onboard the ship. Extrusion is done by the application of water pressure from the ship's hose line to a rubber stopper inserted into the base of the core tube. Fine control of water flow allows slow movement of the core upward into a separate short section of tube (the collar) placed in-line with the core tube top. The collar is scribed in cm intervals so as to define the amount of core section to be displaced laterally into an aluminum receiving tray.

4.5 Sub-core taken for the analysis of radionuclides will be sectioned with plastic utensils.

4.6 Sub-core samples are stored in conformity with EPA QA/OC requirements.

4.7 A back-up core is taken in case of unexpected problems in analyzing the first core or if an interest in analysis of additional material develops.

4.8 Core lengths are expected not to exceed 50 cm in length and should more than cover the entire post-settlement history of deposition.

4.9 A detailed record of the sediment characteristics, as a function of depth, as well as a notation of any unusual properties (i.e. large wood chips) will be entered in the sampling log. An example of the sampling log form is shown in Figure 1.

5.0 Sample Custody

After the sectioning of each core, the Co-PI's will verify that all the samples are accounted for and that they are transferred to proper storage. After sampling has been completed and the samples transported to the lab, the CO-PI's will again verify that all samples have properly transferred and stored. The location of all samples is noted in the sample log.

6.0 Sample Labeling and Logs

Prior to each sampling event a complete set of sample bottle labels will be prepared. The number and type of these labels will depend on the length of the sediment core recovered and the estimated sedimentation rate. An example of a typical label is seen in Figure 2.

Lake Michigan Mass Balance and EMAP Study Sediment Sampling Log

Station No_____ Core No_____

Date_____ Time_____

Latitude_____ Longitude_____

Section	Description	Section	Description
0 - 1		29 - 30	
1 - 2		31 32	
2 - 3		32 33	
3 - 4		33 - 34	
4 - 5		34 - 35	
5 - 6		35 - 36	
6 - 7		36 - 37	
7 - 8		37 38	
8 - 9		38 - 39	
9 - 10		39 - 40	
10 - 11		40 - 41	
.	.	.	.
28 - 29		59 - 60	

Sectioned by_____ Recorded by_____

Samples Checked by_____ Received & Checked by_____

Samples Stored at_____ Date_____

Figure 1. Sediment Sampling Log

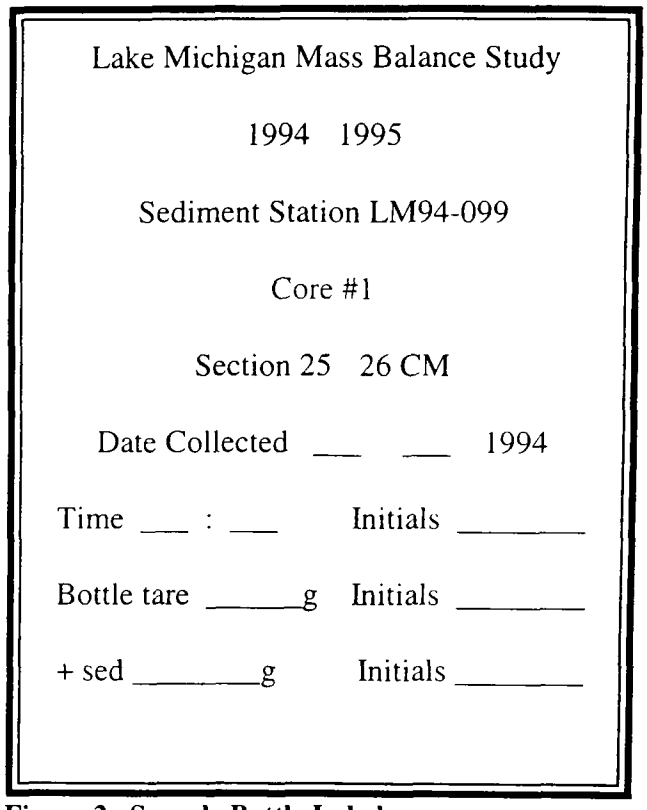

Figure 2. Sample Bottle Label

Trap Sample Splitting (wet):

Use of Sediment Traps for the Measurement of Particle and Associated Contaminant Fluxes

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Trap Sample Splitting (wet): Use of Sediment Traps for the Measurement of Particle and Associated Contaminant Fluxes

Flux is equal to the mass collected divided by the length of collection and the trap cross section. In order to calculate fluxes from the trapped material a reliable measurement of the total weight is required. In previous studies we had always split sediment trap samples after they were freeze dried and weighed. Pat VanHoof, who will be analyzing these samples for PCBs and other trace organic contaminants, wants to extract all of her samples while they are still wet. In splitting the sample while wet, it is necessary to be able to estimate the total weight of the sample from some fraction of that material.

Thus it was necessary to buy or develop a wet sample splitting procedure. A wet splitter for trap samples, designed at Woods Hole, is commercially available for $6-7000 and it splits samples into four or eight subsamples. This was both too expensive and fractionated the samples too much; we would need to recombine to get our two fractions requiring considerable container cleaning, etc. as excess overhead.

After further literature and catalog searches we purchased an all stainless steel dry sediment sample micro-splitter (Model SP-241x; Gilson Co. Inc., PO Box 677, Worthington, OH, 43085-0677). This device has a reservoir of approximately 80 mL into which the sample is poured. A bottom vent is then opened and the sample pours into 30 evenly spaced (1 mm) slots. The even numbered slots empty into a stainless steel tray on the left and the odd numbered slots empty on the right. We then tested this device for our wet sample splitting requirements and came up with satisfactory results, described below.

Sample Matrices: We examined four samples. The objective was to determine the precision of splitting and the ratio of the two samples. The four samples were:

1. Distilled water (DDW)

2. Distilled water (55 mL) + chloroform (6 mL); our standard trap poison solution

3. Ground Lake Michigan sediment in # 2

4. A sediment trap sample from Lake Michigan near LMMB station 6; 5m above bottom from a 100m deep station.

Five replicates of each matrix were made. The samples were poured into the splitter and the left and right trays weighed for matrices 1 and 2. For matrices 3 and 4, the left and right trays were emptied into preweighed beakers which were dried at 90°C then weighed. The data are presented in Table 1.

Table 1. Sample Splitting Data

	Total Dry Wt (g)	Wt (left) (g)	Wt (Right) (g)	Fract left	Fract Rt
DDW		33.4473	31.4184	0.516	0.484
DDW		32.5575	30.962	0.513	0.487
DDW		32.9653	30.9628	0.516	0.484
DDW		32.2945	29.296	0.524	0.476
DDW		31.7108	29.3542	0.519	0.481
DDW(55):CHCl3(6)		31.6683	33.0099	0.490	0.510
DDW(55):CHCl3(6)		30.2318	31.3103	0.491	0.509
DDW(55):CHCl3(6)		31.2056	31.5524	0.497	0.503
DDW(55):CHCl3(6)		30.8368	31.6704	0.493	0.507
DDW(55):CHCl3(6)		31.0031	33.3368	0.482	0.518
Grnd Sed in DDW(55):CHCl3(6); DRY	0.5639	0.2779	0.286	0.493	0.507
Grnd Sed in DDW(55):CHCl3(6); DRY	1.387	0.6952	0.6918	0.501	0.499
Grnd Sed in DDW(55):CHCl3(6); DRY	2.9349	1.5035	1.4314	0.512	0.488
Grnd Sed in DDW(55):CHCl3(6); DRY	3.9479	1.9049	2.043	0.483	0.517
Grnd Sed in DDW(55):CHCl3(6); DRY	5.1343	2.5843	2.55	0.503	0.497
Trap from 5m AB @ 100 m sta.; DRY	0.4434	0.2224	0.221	0.502	0.498
Trap from 5m AB @ 100 m sta.; DRY	0.7476	0.367	0.3806	0.491	0.509
Trap from 5m AB @ 100 m sta.; DRY	1.2745	0.6423	0.6322	0.504	0.496
Trap from 5m AB @ 100 m sta.; DRY	1.3124	0.648	0.6644	0.494	0.506
Trap from 5m AB @ 100 m sta.; DRY	2.2998	1.1689	1.1309	0.508	0.492

Excellent replication was obtained in the tests (Table 2). Matrices 3 and 4, with sediment or trap materials, were split into two equal portions without bias. In other studies we have determined that replicate traps placed side by side have a coefficient of variation (100*sd/mean) of a little less than 10%. The splitting errors appear substantially smaller and will not degrade our interpretation of the data.

Table 2. Accuracy and precision of sample splitting (n=5; all mixtures)

Mixture	Left Side Fraction	Right Side Fraction	P (paired t)
DDW	0.518 ± 0.004	0.483 ± 0.004	
DDW + CHCl3	0.491 ± 0.005	0.509 ± 0.005	
Ground sediment	0.501 ± 0.001	0.499 ± 0.001	0.92
Ground sediment Org C	6.68 ± 0.01	6.62 ± 0.02	0.56
Trap	0.500 ± 0.006	0.500 ± 0.006	0.93

Our standard splitting procedure will be:

1. Allow the 60 mL trap bottles to settle for approximately 24 hours in refrigeration.
2. Pour off approximately 25 mL of the overlying water into a pre-cleaned beaker.
3. Pour the remaining trap sample through a 700 µm screen into the splitter reservoir.
4. Split by opening the bottom valve.
5. Rinse with the water from #2.
6. Further rinse (if needed) with pre-extracted DDW.
7. Pour left tray back into trap sample bottle for freeze drying.
8. Pour right side into pre-cleaned glass jar for PCB, etc.
9. Transfer >700 µm materials to precleaned, preweighed scintillation vial.
10. Rinse screen and splitter under faucet, then with pre-extracted DDW.

Volume 1

Chapter 4: Plankton

Standard Operating Procedure for Sampling Lake Michigan Lower Pelagic Foodchain for PCBs, Nonachlor, and Mercury

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Revision 1

Standard Operating Procedure for Sampling Lake Michigan Lower Pelagic Foodchain for PCBs, Nonachlor and Mercury

1.0 Zooplankton Sampling (>102 μm net, >500 μm net)

1.1 Equipment and Materials

- Zooplankton net, 1 m diameter, 4 m long, 102 μm mesh Nitex netting
- Zooplankton net, 1 m diameter, 4 m long, 500 um mesh Nitex netting
- PVC sample cups, 1000 mL volume, with 102 or 500 μm mesh
- Winch
- 5 lb weight
- Lake water hose
- 4 L glass bottle
- 1 L glass bottle
- Poly pro funnel, 20 cm diameter
- 102 μm Nitex netting, 18" x 18", supported by poly pro large mesh strainer
- Stainless steel kitchen strainer stainless spatula
- Rectangular baking pan
- Glass Qorpak 9 or 16 oz wide mouth jars
- Spray bottle for filtered lake water
- 500 mL PFA teflon jar
- PFA teflon spatula
- Nalgene polycarbonate disposable analytical filter unit, 0.45 μm, 100 mL
- 60 mL PFA teflon jar
- 30 mL PFA teflon vial
- 10 mL autopipetter and disposable poly pro tips
- Shurco vacuum pump
- Nylon forceps

1.2 Preparation of materials and equipment

1.2.1 Net: wash by hosing down with lake water between stations and between casts.

1.2.2 Collection materials: rinse dewatering netting and strainer between uses with nanopure water.

1.2.3 Organics (PCBs and nonachlor): Qorpak jars are ashed at 450°C for minimum of 4 hours before use.

1.2.4 Mercury

1.2.4.1 All teflonware is acid-washed in concentrated nitric acid and rinsed with nanopure water and either dried under dust-free conditions or stored filled with 1% (v/v) HCl. It is stored in acid-washed polypro bags, double bagged.

1.2.4.2. All polypro and nylon is washed in 1.0 M nitric acid and rinsed in nano-pure water, and dried under dust free conditions.

1.2.4.3. Filtration units are used as received from vendor (come sealed).

1.3 Collection Procedure

1.3.1 Sample locations: pre-selected by GLNPO and LMMBS. Sites include three Biota Zones (Stations 110, 140, 180, 240, 280, 310, 340, and 380), two Master Stations (Stations 18 and 47), and Station 5 off of Chicago for organics and mercury. The order of sample collection is 47, 180, 140, 110, 280, 240, 18, 380, 340, 310, 5. All other Master Stations (8) are sampled for mercury analyses only, when possible.

1.3.2 Depth of tow: Vertical tows from near the bottom to surface (depth depends on water depth, time of day, and sea conditions) are done under standard net tow procedures from port side A-frame winch with the assistance of ship's crew. Net is attached to winch and safety line is attached to one of net cables. Cup safety line is attached to net rim.

1.3.3 Number of tows: is dependent on mass collected per tow. Several grams of wet weight of material are required for organics and mercury analyses; a few hundreds of mg of material are needed for mercury analyses only. Approximately 4-6 tows are typically needed for organics, 1-2 tows are needed for mercury only.

1.3.4 Isolating sample

1.3.4.1 Net is brought to just above the surface and lake water hose is used to wash down sides of net from outside so that material adhering to inside of net collects in bottom cup.

1.3.4.2 The cup is removed from the net and poured into the glass bottle (4 L bottle for 102 μm net, 1 L bottle for 500 μm net) via the funnel. Cup is rinsed and rinsate added to bottle. If another tow is required, the procedure is repeated.

1.3.5 Dewatering 102 μm sample: Contents of 4 L bottle are poured into netting held by strainer. Dewatered material is removed by spatula to appropriate container for either organics or mercury (see below).

1.3.6 Dewatering 500 μm sample: Contents of 1 L bottle are poured through stainless stell strainer, or into rectangular pan. Using forceps, sample is segregated into species-specific groups as much as possible. For instance, mysis are picked out with tweezers and removed to sample jar. Remainder of sample is removed to jar with spatula.

1.3.7 Apportionment of sample for organics and mercury analyses: Approximately 5% of the sample is reserved for mercury analysis. Only a minor fraction is required due to the difference in detection limits between PCBs and mercury. The aliquot for mercury is either taken directly from the bottle to the 500 mL PFA teflon jar by pouring prior to dewatering (if sample is highly concentrated), or after dewatering (if sample is not highly concentrated). The remainder of the sample is transferred by spatula to the Qorpak jar for organics analysis.

1.3.8 Sample Processing and Handling

1.3.8.1 Mercury: Sample is isolated for analysis by filtration.

1.3.8.1.1 A mass determination is necessary to know the amount of sample being analyzed. This is accomplished by homogenizing sample by swirling container. A 10, 20, or 30 mL subsample is removed by pipet to a 30 mL PFA teflon vial and frozen for later dehydration and mass determination by standard gravimetric procedures.

1.3.8.1.2 Prior to sample filtration the filter is leached with 10 mL of 1% HCl. A known volume (10-100 mL) of sample suspension is filtered through the disposable analytical filtration unit. The filter is removed, placed in 60 mL PFA teflon jar, labeled according to labeling procedure (see Sampling QAPjP), double bagged, and frozen for transport and storage. If dewatered sample is used, it is resuspended in nanopure water and handled as above.

1.3.8.2 Organics: Dewatered sample is frozen in bulk.

Material in Qorpak jar is labeled according to labeling procedure (see Sampling QAPjP) and frozen for transport and storage. All appropriate tracking information is recorded in field notebooks. This includes the label i.d., the number of tows, the depth of the tow, and any species identification that has been made from microscopic analysis.

2.0 Phytoplankton Sampling (102 > P > 10 μm)

2.1 Equipment and Materials

- Phytovibe with 10 μm Nitex netting and 700 mL PVC cup
- Lake water hose
- Two submersible pumping systems attached to nylon- 11 hose
- 102 μm Nitex net cover
- 500 mL PFA teflon jar
- PFA teflon spatula
- Nalgene polycarbonate disposable analytical filter unit, 0.8 μm, 100 mL
- 60 mL PFA teflon jar
- 30 mL PFA teflon vial
- 10 mL autopipetter and disposable poly pro tips
- Shurco vacuum pump
- Nylon forceps
- 1 L glass jar with graduated markings
- 10 mL glass graduated pipets
- Pipet bulb
- 47 mm glass Millipore filtration apparatus (2)
- 47 mm plastic magnetic Nalgene filtration apparatus (2)

- Stainless forceps
- 47 mm polycarbonate Nuclepore filters, pre-weighed
- 47 mm GF/F glass fiber filters, ashed
- Plastic petri dishes
- Aluminum foil, ashed
- 125 mm ceramic Buchner funnel
- 125 mm GF/F glass fiber filters, ashed

2.2. Preparation of Materials and Equipment

2.2.1 Phytovibe: is washed down with lake water between uses. If necessary, remove the 102 μm net cover from the end of the hoses and clean thoroughly with lake water, and replace. Cups are rinsed thoroughly with lake water. If flow through net during collection is restricted, net is removed between stations from phytovibe support and washed in the washing machine.

2.2.2 Organics

2.2.2.1 All glassware is wrapped in foil and ashed. All ashed materials are combusted at 450°C for a minimum of 4 hours.

2.2.2.2 Nuclepore filters are preweighed on a Satorius analytical balance in the laboratory, and individually stored in petri dishes for transport to and from the field.

2.2.2.3 The 47 mm GF/F glass fiber filters are wrapped in foil in packages of 9 and ashed. The 125 GF/F filters are individually wrapped in foil and ashed.

2.2.3 Mercury

2.2.3.1 All teflonware is acid-washed in concentrated nitric acid and rinsed with nano-pure water and either dried under dust-free conditions or stored filled with 1% HCl. It is stored in acid-washed polypro bags, and double bagged.

2.2.3.2 All prolypro and nylon is washed in 1.0 M nitric acid and rinsed in nano-pure water, and dried under dust free conditions.

2.2.3.3 Filtration units are used as received from vendor (come sealed).

2.3 Collection Procedure

2.3.1 Sample Locations: pre-selected by GLNPO and LMMBS. Sites include three Biota Zones (Stations 110, 140, 180, 240, 280, 310, 340, and 380), two Master Stations (Stations 18 and 47), and Station 5 off of Chicago for organics and mercury. The order of sample collection is 47, 180, 140, 110, 280, 240, 18, 380, 340, 310, 5. All other Master Stations (8) are sampled for mercury when possible.

2.3.2 Depth the collection (pumping) depth is chosen based on an interpretation of the temperature, fluorescence, and BA profiles from the SeaBird. The objective is to choose a depth that maximizes the occurrence (and hence collection) of Phytoplankton that are being grazed. This generally will be mid-epilimnion, or at the subthermocline chlorophyll maximum in stratified conditions.

2.3.3 Phytovibe operation

2.3.3.1 Once the ship is at anchor following the SeaBird and Rosette operations and with clearance from the Chief Scientist, pumps are placed at the sampling depth.

2.3.3.2 The outflow end is covered with a bag of 102 μm Nitex netting to remove large particles and secured with a hose clamp. The lines are flushed for a minimum of 15 minutes.

2.3.3.3 After flushing, the outflows are directed into the phytovibe, the vibrating motors turned on, and the pumps are allowed to pump for the duration of the time on station, or until sufficient mass (several grams of wet weight material for organics and mercury; several hundred mg material for mercury) is collected. Pumping rate is approximately 20-30 L/min. The netting at the end of the hose must be checked frequently to check for plugging. It is cleaned and/or replaced as necessary. The phytopvibes should be covered with a tarp if it is raining or if insects appear to be fouling the sample. Eight to ten hours of pumping time may be necessary. At several points during the pumping lake water should be used to rinse the sides of the net down by spraying the outside of the net.

2.3.4 Sample isolation: lake water is used to wash the material adhering to the net surface down into the cup by rinsing the outside of the net. When all the water has drained to below the top of the cup, the cup is removed to the extraction lab.

2.3.5 Apportionment of sample for organics and mercury analyses:
Approximately 5-10% of the sample is reserved for mercury analysis. Only a minor fraction is required due to the difference in detection limits between PCBs and mercury. The aliquot for mercury is taken directly from the cup to the 500 mL PFA teflon jar by pouring. This split is not quantitative, as the mass of sample analyzed for organics and mercury is determined separately for the different analyses. The remainder of the sample is transferred to the 1 L glass bottle for organics analysis.

2.3.6 Sample Processing and Handling

2.3.6.1 Mercury: Sample is isolated for analysis by filtration.

2.3.6.1.1 A mass determination is necessary to know the amount of sample being analyzed. This is accomplished by homogenizing sample by swirling the container. A 10, 20, 30 mL subsample is removed by pipet to a 30 mL PFA teflon vial and frozen for later dehydration and mass determination by standard gravimetric procedures.

2.3.6.1.2 Prior to sample filtration the filter is leached with IO mL of 1 % HCl. A known volume (10- 100 mL) of sample suspension is filtered through the disposable analytical filtration unit. The filter is removed, placed in 60 mL PFA teflon jar, labeled according to labeling procedure, double bagged, and frozen for transport and storage.

2.3.6.2 Organics: The sample is diluted to a known volume, subsampled for mass and carbon determinations, and collected on a filter for analysis.

2.3.6.2.1 Subsampling: This is accomplished by diluting the sample in the 1 L bottle to a known volume with filtered lake water.

2.3.6.2.1.1 Dry mass: A known volume (1 - 2 mL) is removed in duplicate by pipet for filtering through a pre-weighed 1.0 μm 47 mm Nuclepore filter for dry mass determination by standard gravimetric procedures. The filter reservoir is rinsed with a small amount of nanopure water, and the filter folded in quarters and placed back in the petri dish for transport and storage. All volumes and pertinent information is recorded in the Mass field notebook and master file. This includes: filter i.d. number, tare weight in mg (previously recorded in notebook in lab), sample label i.d., volume of sample filtered.

2.3.6.2.1.2 Organic Carbon: A known volume (1 2 mL) is removed in duplicate by pipet for filtering through an ashed 47 mm. GF/F filter for particulate organic carbon (POC) determination. The filter reservoir is rinsed with a small amount of nanopure water. The filter is folded in half, wrapped in ashed foil, labeled, and the wrapped filters placed in labeled ziplock bags which are frozen for transport and storage. All pertinent information is recorded in the POC field notebook and master file. This includes: sample label i.d., and volume filtered.

2.3.6.2.2 Processing: The remainder of the sample is filtered through a 125 mm GF/F glass fiber filter in a Buchner funnel to isolate the Phytoplankton from suspension. The filter is placed in the Buchner funnel, wetted with nanopure water, and vacuum applied. The bottle contents are then carefully poured in. The bottle is rinsed twice with filtered lake water and the rinsate passed through the filter. The filter is folded in quarters, wrapped in ashed foil, labeled (see Sampling QAPjP) placed in labeled ziplock bag, and frozen for transport and storage. If any residual

sample is on the inner rim of the Buchner funnel, the rim is wiped with a wetted kimwipe, and the kimwipe added to the foil package within the ziplock. This is analyzed along with the filter. Pertinent information to be recorded includes: sample label i.d., approximately time the phytovibe was turned on and off, depth of the water that was sampled, volume the organic sample was diluted to, volumes of subsamples removed for mass and carbon determinations.

3.0 Detrital Fraction Sampling (Organic Analytes Only)

3.1 Materials and Equipment

- 293 mm stainless filtration apparatus
- 280 mm stainless stacked filtration apparatus
- Peristaltic pumps .
- ½" od polyethylene tubing
- 293 mm GF/F glass fiber filters, ashed
- 280 mm 102 μm nitex netting
- 280 mm 10 μm nitex netting
- Teflon wash bottle with nanopure water
- Teflon wash bottle with methanol
- Large kimwipes
- Large stainless steel forceps (2)
- Ziplock bags

3.2 Preparation of Materials and Equipment

3.2.1 The filtration apparati are wiped clean with a kimwipe wetted with methanol, and rinsed with nanopure water between samples.

3.2.2 Nitex netting is rinsed with nanopure water.

3.3 Collection Procedure

3.3.1 An ashed 293 mm GF/F glass fiber filter is placed on the filter holder with forceps and wetted with nanopure water. The top of the filter head is replaced and secured.

3.3.2 The 10 μm nitex net is placed on a stainless steel screen support on the bottom-most layer of the stacked filter system, the next stage is added, and the 100 μm net is placed on the stainless steel screen support. The top of the system is then added and secured. The system is slowly filled with nanopure water from the bottom (reverse direction from sample collection) so that undue pressure from the incoming sample does not rupture or break the seal of the 10 μm net. The system is charged by attaching the outflow hose from the bottom of the filtration system to the outflow of the nanopure water.

3.3.3 The polyethylene tubing is replaced at the beginning of the sampling cruise (prior to Station 47), after the first Biota Zone (after Station 110), and after the end of the third Biota Zone (Station 310). This is to prevent contamination from a more contaminated site to a less contaminated site by desorption of the target analytes from the tubing.

3.3.4 The submersible pump is placed at the appropriate sample collection depth (see 2.0 Phytoplankton Sampling, above) and the lines are flushed (up to the peristaltic pump) for approximately 30 minutes. The pump and plumbing from the pump to the extraction lab are provided by the ship. The plumbing within the extraction lab is provided by the University of Minnesota.

3.3.5 The water flow is as follows: water is drawn by submersible pump through nylon- 11 line to the deck of the ship and flows to the outer door of the extraction lab. A T in the line allows for some of the water to be drawn into the lab, with the remainder returned to the lake. Water is drawn by peristaltic pump through polyethylene tubing from the T, delivered to the top of the stacked filtration apparatus, and the outflow from the apparatus is drawn by a second head of the same peristaltic pump and delivered to the top of the 293 mm filter head. The outflow is collected in teflon lined stainless steel kettles for dissolved contaminant extraction, or discharged overboard. Water must be pumped to and from the stacked filtration apparatus to minimize pressure on the 10 μm nitex layer.

3.3.6 The pumps are turned on, and the time recorded in the field notebook. The pump setting should be approximately 4. Air is removed from the system by holding the outflow closed with a finger and opening the pressure release valve at the top of the 293 mm filter head until water comes out. The flow rate of the water through the glass fiber filter is determined at the beginning, and every hour until filtering ends, unless a filter is changed in which case the flow rate is determined a minimum of at the beginning of the filtering and at the end just prior to changing the filter. Flow rate is determined by collecting exactly 1 L of water in a polypropylene graduated cylinder and noting the time on a stopwatch. The flow rate should be 4-5 L/min. When time permits duplicate flow rate measurements should be taken at any given time point. The setting should not require adjustments during a cruise. If changes are made, flow rate must be determined at the time of change and the time the setting was changed must be recorded to determine the volume of water processed with sufficient accuracy.

3.3.7 When pressure on the 293 filter head exceeds 5-6 psi, the glass fiber filter should be changed. This is to prevent significant lysis of cells in the detrital fraction. To change a filter, the peristaltic pump is stopped and the time recorded. The outflow from the stacked filtration apparatus is disconnected from the peristaltic pump and directed to waste, and the pumps turned on to remove water from the 293 mm filter head (i.e. air is being pumped through the 293 mm filter head). The peristaltic pump is turned off, and the filter head is dissassembled, the filter is folded in quarters using the large forceps, and wrapped in ashed foil. It is labeled, placed in a ziplock bag, and frozen for transport and storage. All filters for one sample are stored together in one ziplock bag. The order of the filter is indicated on the individual filter label. All filters will be analyzed together as one sample. The filter head is wiped clean with a kimwipe wetted with nanopure water, and a new filter installed as described above. The outflow from the stacked filtration apparatus is reconnected to the peristaltic pump, and the pumps restarted. The time of restart is noted, and flow rate determined.

3.3.8 When sufficient mass of the detrital fraction has been collected (approximately 1000 L of water, or 4 x 293 mm filters) the peristaltic pump is turned off and the time noted. The 293 mm filter is removed as described above. The stacked filtration apparatus is dissassembled, and the netting removed, washed thoroughly in nanopure water, and examined for rips or -holes before being replaced for the next sample. Total water volume for this sample is calculated as:

*volume = [(rate, L/min) * (min)] - (volume of subsamnples removed for filtering, L)*

3.3.9 Subsampling

3.3.9.1 Dry Mass: A known volume (150-250 mL) is removed through the valve in the water stream on the 293 mm filter head just prior to the 293 mm filter. Water is filtered through a pre-weighed 0.4 μm 47 mm Nuclepore filter for dry mass determination by standard gravimetric procedures. The filter reservoir is rinsed with a small amount of nanopure water, and the filter folded in quarters and placed back in the petri dish for transport and storage. All mass determinations are done in duplicate. All volumes and pertinent information is recorded in the Mass field notebook and master file. This includes: filter i.d. number, tare weight in mg (previously recorded in notebook in lab), sample label i.d., and volume of sample filtered, and volume removed for filtering.

3.3.9.2 Organic Carbon: A known volume (1.5 - 2 L) is removed by dispensing from the valve in the water stream on the 293 nim filter head just prior to the 293 mm filter. Water is filtered through a 47 mm GF/F filter for particulate organic carbon (POC) determination. The filter reservoir is rinsed with a small amount of nanopure water. The filter is folded in half, wrapped in ashed foil, labeled, and the wrapped filters placed in labeled ziplock bags which are frozen for transport and storage. All POC filtrations are done in duplicate. All pertinent information is recorded in the POC field notebook and master file. This includes: sample label i.d., volume filtered, and volume removed for filtering.

4.0 Transport and Storage

4.1 Sample Packing: All frozen samples are removed from the ship's freezers and immediately packed in coolers with frozen blue ice just prior to transport. XAD-2 columns are stored in refrigerators at 4 C. They are also packed in coolers and kept cold with blue ice during transport. Coolers are taped shut to prevent inadvertent opening during transport.

4.2 Sample transport: Samples are transported in coolers by University of Minnesota personnel. Samples will remain either directly in the custody of the personnel performing transport, or in the possession of commercial air carriers if the personnel travel by air.

4.3 Sample Logging: All samples are logged out of ship's storage at the time they are packed into coolers, and again at arrival at the PIs' laboratories at the University of Minnesota as they are placed into storage. Sample logs will note sample number, date of each sample transfer, initials of personnel responsible for custody during each stage of transport, and final storage location of each sample in the PIs' laboratories. Examples of tracking forms are shown in Figures 1 and 2.

4.4 Sample Custody: The sample log indicates the personnel responsible for sample custody during transport. Samples will remain in the custody of ship's personnel while in storage onboard ship, the University of Minnesota personnel during transport, and their respective PI once checked into the PI's laboratory.

4.5 Sample Storage in the Laboratory: Labeled samples will be stored in freezers or refrigerators located in the PI's laboratories. All labs are locked except when in use.

CRUISE:

	Sample i.d.	date/initials from ship	to UMN	date extracted	date cleaned	date GC-ECD	date NCI	date baselines	date final quant.
1									
2									
3									
4									
5									
6									
7									
8									
9									
10									
11									
12									
13									
14									
15									
16									
17									
18									
19									
20									
21									
22									
23									
24									
25									
26									
27									
28									
29									
30									

Sample id:
Date collected:
Time collected:
Initials of individual collecting sample:
Time of storage:
Date of removal from storage:
Initials of transport personnel:
Date of arrival at laboratory:
Location of storage:
Date of processing
    Digestion:
    Denydration:
Date of analysis
    Hg measurement:
    Weighing:
Standard curve identifier:

Figure 2. Example tracking form for Hg

5.0 Dissolved Fraction Sampling (Organic Analytes Only)

5.1 Materials and Equipment

- 75 L teflon lined stainless steel kettles with stainless steel lids (2)
- Small peristaltic pump
- Teflon and tygon tubing, 3/8 " id
- Glass columns, 3x30 cm, packed with cleaned XAD-2 resin
- Wash bottle with methanol
- Wash bottle with nanopure water
- Kimwipes
- Strap wrench
- 100 mL polycarbonate bottle

5.2 Preparation of Material and Equipment

5.2.1 XAD-2 resin: The resin is pre-cleaned in the laboratory by sequential Sohxlet extraction, and packed in individual extraction columns for transport to and from the field. It is cleaned in large batch quantities by extracting for 24 hours with methanol, followed by 24 hours with acetone, followed by 24 hours with hexane, followed by 24 hours with dichloromethane. It is then extracted with the same solvents in reverse order for 4 hours each, and then washed thoroughly with nanopure water. It is stored in amber bottles under water until the columns are packed.

5.2.2 Resin Columns: The glass columns are ashed at 450°C for a minimum of 4 hours. A teflon end cap with outflow hole is placed on one end, and a plug of ashed glass wool is added. The outflow is blocked, and resin in nanopure water is poured into the top of the column through a funnel. The water is allowed to drain from the outflow as necessary to allow the resin to settle and to reduce the volume of water in the column, while never allowing the level of the water to fall below the resin. The columns are filled to approximately 2/3 their capacity (approximately 150 mL resin and water), a glass wool plug added to secure the resin in place, and the columns are topped with nanopure water and end caps secured on either end. The columns are wrapped in foil, wrapped in bubblewrap, and stored in a cooler for transport and storage.

5.2.2 Stainless steel kettles: The kettles are wiped thoroughly with kimwipes and methanol, followed by a thorough rinse with nanopure water. The lids are taped on to prevent contamination before use.

5.2.3 The polycarbonate bottles are for dissolved organic carbon samples. They are washed with soap and water, rinsed with tap water followed by nanopure water, soaked in 2% nitric acid for 24 hours, rinsed with nanopure water, soaked for 4 hours with nanopure water, and filled with nanopure water until use.

5.3 Sample Collection

5.3.1 The outflow from the 293 mm filter is directed to the kettles. The foil is removed from two XAD columns. The endcap of the outflow end of each of the XAD columns is replaced with an endcap with a quick-connect fitting to teflon tubing which flows to the small peristaltic pump. The column and tubing are wiped a kimwipe wetted with methanol, followed by a wipe using nanopure water. The inflow endcap is replaced with an endcap with a hole, any air is relieved with nanopure water, and using a finger to hold this closed the column is immersed in the water and the finger released. The peristaltic pump is started at the same time, and the time noted. A setting of about 3 should produce the desired flow rate of 300 mL/min. The outflow of the peristaltic pump is directed overboard.

5.3.2 Flow rates are determined at the beginning, at 30 minutes, at 60 minutes, and then hourly until the extraction is complete. Flow rate is determined by filling a 250 mL graduated cylinder and noting the time with a stopwatch. The outflows from each column are both monitored. Time of measurement, and flow rate, are recorded in the XAD field notebook. Total volume in L is a volume-weighted sum of minutes pumped times the flow rate for that time period in L/minute. A minimum of 200 L is extracted; 300 L is desirable. Thus several volumes of the kettles are processed. Particulate filtering must occur long enough to allow for the generation of a sufficient volume of water to complete the dissolved phase extraction.

5.3.3 When sufficient volumes of water have been passed through the resin, the peristaltic pump is turned off and the time recorded. The resin column endcaps are replaced with the storage endcaps, the sample is labeled, the foil and bubblepack are replaced, and the columns are placed in the refrigerator until transit back to the laboratory.

5.3.4 Subsamples: Samples for the measurement of dissolved organic carbon are collected from the XAD inflow. A 100 mL polycarbonate bottle is rinsed with the sample water, filled approximately halfway, labeled, and frozen for transport and storage.

Sampling Procedure for Collection of Benthic Invertebrates for Contaminant Analysis

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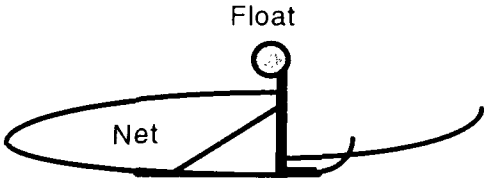
May 1996

Sampling Procedure for Collection of Benthic Invertebrates for Contaminant Analysis

1.0 Benthic Sled Tow

The benthic sled is used to collect benthic invertebrates for contaminant analysis. The sled is fabricated of mild steel and consists of a rectangular frame, to which a net is attached, welded to two runners which slide along the bottom as the sled is towed. A small float is attached to the top of the frame to maintain upright orientation as the sled is deployed. The net has a rectangular opening of dimensions? and a mesh size?

The net should be clean from previous deployment and sample removal. If it is not, clean it using lakewater supplied by a submersible pump.



2.0 Deployment and Collection

The sled is deployed from the stern of the ship from a cable running through a pulley (sheave) on the main A-frame and to the main stern winch. The sled is first attached to the cable on the fantail, with the A-frame in its forwardmost position. The center section of stern guardrail is removed for deployment. After the net is ready, the winch operator lifts the sled from the deck as the A-frame is extended over the water. The pilot is apprised of the progress in deployment over two-way radio. The pilot maintains a steady course with a speed of 2 - 3 knots. This is accomplished by clutching the propellers in and out. The winch operator lowers the sled into the water, preferably during a period of glide, rather than with the propellers engaged, and continues paying out wire. If a tension meter is used, if is often possible to determine when the sled reaches the bottom by an increase in load displayed on the meter's readout. The winch operator continues to pay out cable to a length of between two and three times the depth of the water column. The tow is most often timed from the contact of the sled with the bottom. Tows may be of variable length, but are generally between 10 and 20 minutes long. At completion of the tow, the winch operator retrieves the sled. When the sled is visible at the surface, retrieval is slowed. As the sled is pulled from the water, the A-frame is brought back over the deck. The sled is lowered to the deck.

The benthos collected during the tow will be at the cod end of the net. These are removed with clean utensils (e.g., spatulas, clean spoons, etc.) with the aid of water from squirt bottles or hoses supplied with lakewater. They are placed into a clean pan for later processing. After transfer of the contents of the net to the pan, it is taken to the laboratory where the organisms of interest are picked from the collection using clean forceps. Other techniques may be used to separate taxa within the collection, including stirring, dilution with clean water, etc.

Standard Operating Procedure for Phytoplankton Sample Collection and Preservation

Grace Analytical Lab
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April 13, 1994

Standard Operating Procedure for Phytoplankton Sample Collection and Preservation

1.0 Scope and Application

This Standard Operating Procedure describes the sampling and preservation of phytoplankton samples taken for the GLNPO open water Great Lakes surveys.

2.0 Summary of Method

Phytoplankton samples are created from a composite of water samples taken at discrete depths (surface, 5M, 10M, and 20M) with the rosette. Aliquots from each depth are combined, and approximately 1 L of the composite sample is preserved with Lugol's Solution for analysis at the CRL.

3.0 Safety and Waste Handling

Preservation of the phytoplankton samples with Lugol's solution must take place in a hood, and gloves and safety glasses should be worn.

4.0 Equipment and Supplies

960 mL plastic sample bottle
1 gallon cubitainer
Repipetter with 10 mL delivery capability
Distilled or super Q H_2O
Glacial Acetic Acid
I_2
KI
Hotplate
1L Flask
Opaque 1L container
Magnetic Stirring Bar
Glass funnel

5.0 Reagents

5.1 Lugol's Solution: Prepare at least one week prior to survey

5.1.1 Using a Mettler balance or equivalent, measure 100 g KI and 50 g of I_2. Cover the I_2 reagent with tinfoil as it is light sensitive and will evaporate.

5.1.2 Combine 900 mL Super Q H_2O and dry chemicals in a large flask. This should be performed in a fume hood.

5.1.3 Add a magnetic stir bar and place on hotplate equipped with stirring action.

5.1.4 Warm slightly while stirring to facilitate dissolution of the dry chemicals. *Do Not Boil!*

5.1.5 In about an hour, once the solution is completely dissolved, pour into an opaque container using a glass funnel. Add 100 mL Glacial Acetic Acid to container and cap tightly. Invert several times to mix solution.

5.1.6 Label container with date, contents, and pH (usually around 2.4).

6.0 Sample Collection and Preservation

Note: Steps 6.1-6.4 are generally done by the ship contractor or EPA personnel. GLAS contract personnel will conduct this task when requested.

6.1 Remove 1 L of water from each of the Niskin bottles on the rosette from 20M, 10M, 5M and 1M, and add them to a 1 gallon cubitainer. This is the composite sample.

6.2 Mix the sample by gently turning the cubitainer over several times.

6.3 Pour approximately 1 L of the sample into the plastic sample bottle which has been labeled with station, sample number and survey.

6.4 In the Biology lab add Lugol's solution (5.1) to make the concentration 1%. If the sample nearly fills the entire sample container, add 10 mL of Lugol's solution to the sample. If less sample has been added to the container, adjust the volume of Lugol's solution that is added to achieve a 1% preservative concentration.

6.5 Samples must be stored in the dark and under refrigeration. Store the sample in the area designated by the sample coordinator.

Standard Operating Procedure for Zooplankton Sample Collection and Preservation

Grace Analytical Lab
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April 13, 1994

Standard Operating Procedure for Zooplankton Sample Collection and Preservation

1.0 Scope and Application

This standard operating procedure describes the sampling operations and the preservation methods for open lake zooplankton samples taken for the GLNPO Great Lakes surveys.

2.0 Summary of Method

Samples are taken using a plankton tow net that is maneuvered using a winch on the starboard side of the rear work area of the R.V Lake Guardian. The tow net, with a screened sample bucket attached to the end, is lowered to the desired depth, and raised at a constant, slow speed to collect the sample. Once the net is lifted out of the water, it is rinsed from the outside to free organisms from the side of the net, and to concentrate them into the sample bucket. The sample is transferred to a sample container, the organisms are narcotized and preserved. The samples are brought back to the CRL for analysis.

3.0 Safety and Waste Handling

Formaldehyde is a known carcinogen. During the preservation of samples, the formalin should be dispensed under a hood, using gloves and safety glasses.

4.0 Equipment and Supplies

Plankton tow net 64 μm pore size (#25).
Tow net sample bucket with a 61 μm pore size metal screen.
Flowmeter
Weights 10-20 lbs.
Safety line for sample bucket
Lines for attaching weights
Garden hose with attached water source
Spray bottle
Soda water (Club soda)
Formalin (37% formaldehyde)
500 mL piastic sample bottles
Repipettor with 10 mL delivery capability
Graduated cylinder 50 - 100 mL capacity
Waterproof notebook
CDT

5.0 Sample Depth

Sample tows are generally taken from a depth of 20 meters from the water surface (integrated sample). In waters which are shallower than 20 meters, (Western basin of L. Erie) samples (B-1 sample) are collected from 1 meter above the bottom to the surface. In cases such as this, only a B-1 sample will be taken. At Master stations, duplicate tows are taken

Note: During each survey season, when calm weather permits, the flowmeter should be calibrated by repeatedly lowering it to 20 meters in very calm seas, and recording the reading. This is performed using just the flowmeter with the accompanying support ring (no net). This should be repeated 20 times. The mean value of these 20 readings divided by the depth will be used to calculate filtering efficiency for sample tows.

Note: If a CDT instrument is being used on the tow line, real depth will be used for sampling instead of line length. In this case, the distance from the depth meter on the CDT to the rim of the plankton net (about 1 meter) must be measured and that distance will taken into account when reading the CDT depth. Subtract this distance from the sample depth, and have the winch operator stop the winch when the CDT indicates the corrected depth.

6.0 Sampling Procedure

6.1 Once on station, obtain the bottom depth from the rosette information provided in the wet lab.

6.2 Convert the bottom depth into meters by means of a conversion table, or 3.281 ft = 1 M.

6.3 Screw on the sample bucket so that it becomes snug. Do not over tighten. Attach the net to the winch line. Attach the safety line from the winch cable to the net ring.

6.4 Open the hatch on the flowmeter and reset all the dials to zero.

6.5 Inform the winch operator the depth of the sample to be taken.

6.6 Have the winch operator lower the net to the desired depth. The zero point for the depth on the winch is when the top of the net is at the water surface. Make sure that the tow line is as vertical as possible. If the angle exceeds 30°, repeat the tow using the CTD, and if needed, contact the bridge to have the ship re-positioned.

Note: If weather conditions continually produce drifting net tows, inform the EPA Chief Scientist.

6.7 The net should be raised at a constant speed until the rim is above the water. Refer to the factory calibration for each flowmeter as each one has an optimal speed at which it functions most efficiently. Currently, the winch speed used for flowmeter #3478 is on setting "8" and corresponds to approximately 0.60 m/s. It is very important to complete each zooplankton tow using this setting. When the flowmeter or winch is eventually replaced, a new speed will have to be determined.

6.8 Do not interrupt the tow by stopping and starting the which while the net is being raised to the surface. If this occurs, repeat the tow.

6.9 Rinse the net down gently with the garden hose from the outside to wash all of the organisms off of the side of the net. Detach the sample bucket. Rinse the screening and the sides of the bucket with the spray bottle or very gently with the garden hose to collect all of the sample into the 500 mL sample container which has been appropriately labeled. Double check the labels on the bottles to make sure that the caps and bottle labels match, and that the sample is going into the appropriate bottle.

6.10 Record the date, station, flowmeter reading, depth of tow, and angle of tow into the waterproof notebook while on deck.

6.11 In the biology lab, pour 20 mL of soda water into the sample to narcotize the organisms. Let sit for 30 minutes. Adjust the volume of the sample, using distilled water, to accommodate 20 mL of formalin solution. Once the formalin has been added, the container should be nearly full. If the container is *too* full to add the correct amount of formalin, allow the sample to sit for at least 1 hour after addition of the soda water. Using a pipette covered with netting, draw off enough solution in the top portion of the sample to accommodate the formalin. Store the sample in the area designated by the sample coordinator.

6.12 Transfer the recorded information taken during the sampling process from the field notebook to the *Zooplankton Field Collection Sheet* in the biology lab on the ship immediately after the sample is put into the cooler. The following information should be entered on each sheet: Lake, Survey, Date, Flowmeter #. The following information should be entered for each sample taken: Station, Sample type (INT, B-1), Angle, Meter start, Meter reading end, Station depth.

Volume 1

Chapter 5: Fish

Fish Processing Method

Standard Operating Procedure SOP No. HC 523A.SOP

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May 13, 1996

Version 1.0

Fish Processing Method

The following aging, compositing, and grinding method was used for fish collected for the Lake Michigan Mass Balance Study.

Fish were collected for the Lake Michigan Mass Balance study during the spring, summer, and fall of 1994, and spring and fall of 1995 from Sturgeon Bay, Port Washington, and Saugatuck on Lake Michigan. Information on the species, and number of fish caught is shown in Table 1. Coho shown in Table 1 were collected along varying locations each season (depending on migration) in 1994 and in 1995 collection occurred only during the spring and fall.

Table 1. Species, Seasons, and Number of Fish Collected for the Lake Michigan Mass Balance Study.

Biota Sampled	Spring 94	Summer 94	Fall 94	Spring 95	Fall 95
lake trout 2-4 yr	25	25	25	25	25
lake trout 5-7 yr	25	25	25	25	25
lake trout 8-10 yr	25	25	25	25	25
coho hatchery	25			25	
coho 1 + jacks			25		25
coho 2 + adults	25	25	25	25	25
chubs 0 - 2 yr	25	25	25	25	25
chubs 4+ yr	25	25	25	25	25
alewife 60-120 mm	25	25	25	25	25
alewife »120 mm	25	25	25	25	25
smelt »100 mm	25	25	25	25	25
sculpin slimy	25	25	25	25	25
sculpin deepwater	25	25	25	25	25

Note: Lake trout were composited by age rather than length.

The same number of fish (except coho) shown in the table were repeated at Saugatuck, Port Washington, and Sturgeon Bay. The number of coho sampled was according to the table and taken across various sites each season depending on their migration location (see QA plan for Holey & Elloit, USFWS, Greenbay, WI).

1.0 Fish Processing Method

The following sample preparation procedure was originally developed for the International Joint Commission (I.J.C.) Surveillance Program. The sites, species, sizes and seasons collected and composites were modified for the Mass Balance Study.

2.0 Collection

Whole fish were collected from Lake Michigan (intact, with all body fluids and no incisions, except lake trout, which had stomachs removed), wrapped in aluminum foil, placed in 4 mil thick polyethylene bags after collection, tagged, and frozen as soon as possible on board the vessel. The information on the tag included species, size, date, location of collection and labeled for the Lake Michigan Mass Balance Study. Fish were transported to NBS/GLSC in coolers and stored frozen at about -20°C.

3.0 Aging

Prior to homogenization lake trout were first aged. To age the fish, the head of each whole fish was checked for the presence of a coded wire tag (CWT) and clipped fins to age the fish. If a CWT was detected, (CWTs are only a few mm long) with a special metal detector the first two or three cm of the fish snout was cut off and checked again with the detector to see if it contained the CWT. If not the next few cm of the snout was cut off and checked with the detector. The cut off section of the snout containing the CWT was cut in half and the half containing the CWT was cut in half again. This procedure was repeated until the tag was found or the remaining piece was less than a gram. At this point the tissue containing the CWT was placed in 10 mL solution of 15-30% NaOH for digestion. After a few hours the CWT was removed from the solution of NaOH using a small suitable teflon coated magnet and placed under a microscope. Using 5 or 10 magnification on the scope, the series of marks on the CWT were recorded. The sequence of these markings was decoded using an instruction sheet which made it possible to determine the date the fish was hatched along with other information. This date was subtracted from the date collected to determine age.

Scales were also taken from each lake trout and the fin clips were recorded. Lake trout that contained no CWT were aged by a combination of reading annual rings on the scales and fin clips. Because of the uncertainty of aging lake trout over seven years old from the scale, these age results were compared to fish in stocking records that would have the same combinations of fin clips and resulting age was base on the stocking data. If the age determined from the scale and fin clips did not match the age by the scale method we would substitute the aged lake trout in question with one of the extra lake trout collected. In cases where there were no extra fish (rare) and the age by scales and fin clips in Lake Michigan stocking records were more than two years apart the fin clips records from other Great Lakes were checked for a better match. It has been determined from tagging records that a few lake trout migrate to Lake Michigan from other Great Lakes.

4.0 Homogenization

Fish were removed from the freezer at the GLSC and allowed to thaw slowly over an 8 to 12 hour period in their sealed bags (generally overnight). Prior to homogenization, glass jars (4 oz) that were used to store subsamples were prepared by first washing in a dishwasher, then rinsed (in sequence) with in HNO3, Millipore-filtered water, and acetone.

The contents of the polyethylene bag (fish and fluids) were weighed and recorded in the grinding log. For each species, location, and season sampled (Table 1) about 75 fish (covering three sizes or age for lake trout) were composited into about 15 samples and then ground. For a given year, site, and season lakes trout were sorted into composite samples. Depending on the number of fish in an age group available, each composite contained 2-5 fish (five when available) of the same age. Other species of the fish were sorted into five fish composite samples according to year, location, species, and size range. Each composite is put into an aluminum pan which had been cleaned with detergent and water and rinsed with deionized water. The fish were measured (millimeters) on a measuring board that was washed with detergent/water, and rinsed with distilled water. Each fish was weighed to the nearest gram and length measured to the nearest mm. The measuring board, balance, and scalpel were cleaned between each group. Homogenization equipment was washed with detergent/water, rinsed with millipore water, and then with acetone (alcohol for plastic pieces) before each sample was ground. Each composite sample was homogenized (except lake trout which were homogenized individually) and a fixed weight was sub-sampled from each lake trout for the composite and then the resulting sample was re-homogenized. Large fish such as adult lake trout and coho were homogenized using a high speed 40 qt. Hobart vertical cutter Mixer (VCM). Medium size fish were homogenized with a 12 qt. Stephan Machinery vertical cutter (UM 12) and small fish with a high speed two quart Robot Coupe (RSI241). When the large and medium size vertical cutters were used for homogenization about 1000 g of subsamples was taken and re-homogenized using the Robot Coupe cutter which obtained a finer consistency. From the final homogenized tissue about 80 g was added to each of three (depending on the amount of homogenized tissue) 4 oz jars, the lids (lined with acetone rinse aluminum foil) were screwed on, and then each jar was labeled with the identification number and the grams of tissue. The jars were boxed and then placed into the freezer (approx. -20° C) until analyzed.

Quality Assurance Project Plan for Lake Trout and Forage Fish Sampling for Diet Analysis and/or Contaminant Analysis

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Version 1.0

Quality Assurance Project Plan for Lake Trout and Forage Fish Sampling for Diet Analysis and/or Contaminant Analysis

1.0 Project Description

1.1 Introduction

The Great Lakes National Program Office (GLNPO) of the U.S. EPA has initiated a Mass Balance Study for selected toxic contaminants in Lake Michigan. The Mass balance effort will be part of a "Lake Michigan Enhanced Monitoring Program" which includes tributary and atmospheric load monitoring, source inventories, and fate and effects evaluations. In general, the primary goal of this enhanced monitoring program is to develop a sound, scientific base of information to guide future toxic load reduction efforts at the Federal, State and local levels.

A modeling team will construct a mass budget and mass balance model for a limited group of contaminants which are present in Lake Michigan at concentrations which pose a risk to aquatic and terrestrial organisms (including humans) within the ecosystem. Components to the mass balance model will be designed to predict contaminant concentrations in the water column and target fish species over a two-year period, relative to loadings. Predictions of contaminant levels in three species of fish will be calculated as final output of the model. The target fish species include:

Lake trout (*Salvelinus namaycush*)
Coho salmon (*Oncoryhynchus kisutch*)
Bloater chub (*Coregonus hoyi*)

The calibration of the food web model(s) for these target species requires data on contaminant concentrations and fluxes (diet) not only in these species, but also in the supporting trophic levels. The contaminant burden of each prey species varies based on feeding patterns at lower trophic levels. The concentration of contaminants in lake trout and bloater chubs will depend on what prey items they choose to consume. The diet information for lake trout sampled by this project will enable the modelers to quantify the movement of contaminants from their source, through the food web, and ultimately the body burden in lake trout.

The basic design and data requirements for the fish samples have been outlined in Tables 5 and 6 and in Appendix 4 of Lake Michigan Mass Budget/Mass Balance (LMMB) work plan of October 14, 1993. This project addresses a subset of the work objectives for lake trout and bloater chubs, two of the target species described in the LMMB work plan, and for the five principal forage species also described in that work plan, including bloater chub, alewife, smelt, slimy sculpin, and deepwater sculpin, which are consumed by lake trout and coho salmon.

The specific objectives are to:

1. Collect representative samples of lake trout, bloater chubs, alewives, smelt, slimy sculpins, and deepwater sculpins for contaminant analysis.
2. Describe the diet of lake trout in Lake Michigan from May through October 1994.
3. Review past published and unpublished information on the diet of lake trout in Lake Michigan and report on the comparability of the data collected in 1994 to past data.

1.2 Experimental Design

Because of spatial and temporal variations in feeding habits and/or distributions of lake trout, bloater chub, and the other four forage species we will collect them in spring, summer, and fall from each of three Biota Sampling Sites identified in the LMMB work plan of October 1994; these include (1) the northwestern region near Sturgeon Bay, WI, (2) the southeastern region near Saugatuck, MI, and (3) the central Midlake Reef region east of Port Washington, WI (Fig. 1). The bloater chub was identified as both a target species and a forage species for trout and salmon in the LMMB work plan of October 1994. The sampling regimes in Table 1.0 will be followed at each of the three Biota Sites in spring (May to early June), summer (July to early August), and fall (October to early November):

The staff on this project will have the advantage of making all of its targeted fish collections for contaminants and diet analyses from the R/V Cisco which is assigned to the NBS' Lake Michigan Project in the Section of Resource Assessment and Fish Community Dynamics at the GLSC and is stationed at the Saugatuck Vessel Base. The most difficult part will be obtaining all of the specified age and size groups of lake trout and forage fish at all locations and in all seasons, because of vagaries partly associated with changes in weather, stocking densities and locations of the trout reared in Federal Hatcheries, and natural variations and trends in abundance of forage fish. Sampling on the Sheyboygan or Midlake Reef, more than 30 miles offshore of the nearest port (Port Washington), poses the most difficult physical problem because a round trip takes six hours or longer and there is no protection from sudden storms.

1.2.1 Contaminant Sampling

Because of the cost of the analytical chemistry, the total number of lake trout listed in the LMMB Work Plan for contaminant analysis has been reduced from 450 to 225 per season: i.e., 75 per Biota Site (Table 1.0) times three sites. These samples will be packaged as required for contaminant analysis, frozen, and delivered to the GLSC Laboratory of NBS in Ann Arbor.

1.2.2 Diet Sampling

The LMMB Work Plan did not have a sample size objective for describing the diet of lake trout. However, based on recent diet variations observed in coho salmon, Holey and Elliott (1994) estimated that at least 100 salmon per season per region would be necessary to provide a reasonable analysis of the variation. Although past work has shown that higher percentages of lake trout than salmon are found with food in their stomachs, 75 lake trout in addition to those collected for contaminant analysis will be collected per Biota Site per season (Table 1.0). Published information on the diet of Lake Michigan lake trout will also be reviewed to complement and aid in interpretation of that which will be collected in the present study in 1994.

Both critical and noncritical parameter measurements for the evaluation of contaminants and diet of lake trout and contaminants of bloater chub are summarized in Table 1.1.

Table 1.0. Sample size objectives for the collection of lake trout, bloater chub, and four other forage species in Lake Michigan by season, age or size group, and pending analysis.

Biotic group	Age or size	Number collected for			Total samples
		Contaminants and diet	Contaminants only	Diet only	
Lake trout	2-4 yr	25		25	50
	5-7 yr	25		25	50
	8-10 yr	25		25	50
Bloater chub	0-2 yr		25		25
	4+ yr		25		25
Alewife	60-120 mm		25		25
	>120 mm		25		25
Smelt	>100 mm		25		25
Slimy sculpin			25		25
Deepwater sculpin			25		25
Total fish		75	175	75	325

Table 1.1. Summary of critical and non-critical parameter measurements for the evaluation of contaminants and diet of lake trout, and contaminants of bloater chub.

Parameter	Sampling Instrument	Sampling Method	Analytical Instrument	Analytical Method	Reporting Units	LOD
Location (critical)	GPS, Loran, Port Location	SOP-1	NA	NA	biota sites	southeast, central and northwest
Sample Date (critical)	none	NA	NA	NA	mo / day / yr xx / xx / xx	day
Lake Trout length (critical)	measuring board ruler	NA	NA	NA	mm	1 mm
Lake Trout weight (critical)	spring or electronic balance	SOP-1	NA	NA	Kg	0.1 Kg
Lake Trout age (critical)	knife and envelope	SOP-1 and Bowen 1983	bi-noc scale projector	SOP-2, 3	years	1 year
Diet Species of Lake Trout (critical)	NA	SOP-1	NA	SOP-2	total number	Species - fish & common invertebrates. Order for less common invertebrates
Diet Item length (critical)	NA	NA	ruler	SOP-2	mm	1 mm
Diet Item weight (critical)	NA	NA	spring or electronic balance	SOP-2	grams	0.1 gram
Bloater age (critical)	NA	SOP-1	scale projector microscope	SOP-2	years	1 year
Sample Depth (non-critical)	echo sounder	operating instructions	NA	NA	meters	0.1 meters
Time of Sample (non-critical)	clock	NA	NA	NA	HH:MM	minutes
Water Temp. when sampled (non-critical)	electronic BT	NA	NA	NA	degrees C	1 degree C

2.0 Project Organization and Responsibilities

Paul Bertram
EPA Project Officer
Biota Co-Chair

John Gannon
NBS
Biota Co-Chair

Lou Blume
EPA QA Manager

Edward Brown
NBS
Project Manager

Gary Eck
NBS
Field Manager

Ralph Stedman
Randall Owens
NBS
Alternate Field
Managers

George Boyce
Tim Desorcie
NBS
Field Sampling
Analysis

2.1 GLNPO Project Officer and Biota Co-Chair

The GLNPO Project Officer is the Agency official who initiates the grant, evaluates the proposal, and is the technical representative for EPA. The Project officer is responsible for:

Budgeting
Program planning, scheduling, and prioritization
Developing project objectives and data quality objectives
Ensuring that project meet GLNPO missions
Technical guidance
Program and data reviews including audits
Data quality
Final deliverables

2.2 GLNPO QA Manager

The GLNPO QA Manager (QAM) is responsible for ensuring that each project funded by EPA satisfies the Agency's requirements for QA programs. The QAM is responsible for:

Offering guidance on QA techniques
Evaluating QA Project Plans (QAPjPs) and approving QAPjPs for the Agency
Assisting in the coordination of audits

2.3 NBS Biota Co-Chair

The Biota Co-Chair from NBS works in partnership with the GLNPO QA Project Leader to implement the Biota portion of the Lake Michigan Mass Balance Project. Duties are:

Program planning, scheduling, and prioritization
Developing project objectives and data quality objectives
Ensuring that project meets GLNPO missions

2.4 NBS Project Manager

The Project Manager is the NBS official who initiated the proposal to perform the lake trout and forage fish sampling portions of the LMMB project and is responsible for:

Developing the sampling plan for lake trout and forage fish collections
Administration of the lake trout and forage fish segment of the Biota objectives
Overall supervision of field work
Ensures QA objectives are met
Technical supervision
Final deliverables
Data quality assessment

2.5 NBS Field Manager

The Field Manager is the NBS position that will provide daily supervision of the field collection activities and achievement of the QA objectives. This position is responsible for:

Collecting field data
Directly supervise the field crew activities
Reviews progress toward QA objectives
Develops and implements sampling and analytical procedures
Prepares reports and deliverables
Trains field crews on sampling and analytical procedures
Data quality assessments and audits for lab and field segments

2.6 Field Sampling and Analysis Personnel

These positions are responsible for the majority of the field sampling and lab identification. They will receive training and guidance from the Project and Field Managers, who will also audit their work to ensure QA objectives are met.

At a minimum, Field Sampling and Analytical Personnel have or, if future hires, will have Bachelors Degrees in biological science, natural resources, or related fields, or appropriate relevant experience. Project and Field Managers who will provide job-specific training all hold Masters Degrees in natural resources or fishery science and have 15 years or more of experience in fishery research, ecology, and management on the Great Lakes.

3.0 Quality Assurance Objectives

As outlined in the Lake Michigan Mass Budget/Mass balance Work Plan, the proposed model output should be within a factor of two of the observed concentrations in the water column and target fish. It is also estimated that the required level of model accuracy can be achieved if loadings and contaminant mass in significant environmental compartment are determined to within ±20 to 30% of the actual value.

3.1 Objectives

1) Within each season and regional biota site, collect as representative samples of lake trout and forage fish as possible so as to minimize the spatial and temporal population uncertainty (Sp) to the extent possible (given the sample size that can be collected with the financial, logistic, and biological constraints of this project).

2) To collect, package, and transport each sample, and to record, summarize, and report each physical measurement with a level of recision, accuracy, deductibility, and completeness that will ensure the Measurement.

Uncertainty (Sm) will be nominal compared to Sp and therefore not affect the interpretation of the results.

The level of population uncertainty can not be determined prior. That the contaminant levels in the lake trout and forage fish collected will be within ±20 to 30% of the actual population values is a function of sample size and the collection procedures. The sample size for contaminants has been established by the LMMB Work Plan and subsequent modifications. The designed collection procedures described here attempt to make the most of the sample size target.

Variability in the diet of Lake Michigan lake trout can be great, especially when examined from a lakewide perspective encompassing large scale spatial and temporal gradients. The desired sample size for determining diet is to a large degree constrained by the difficulty of collecting these fish. Presently lake trout abundance and therefor catch is very low off Saugatuck, a biota site, and some other areas in the southern basin because of changes in interagency stocking protocols (Lake Michigan Lake Trout Technical Committee 1985). Alewife abundance is also low throughout the Lake and they are no longer the dominant forage species that they were in the 1960s and early 1970s (Eck and Wells 1987).

3.2 Measurement Quality Objectives

Measurement quality objectives are designed to control various phases of the measurement process and to ensure that total measurement uncertainty is within ranges prescribed by the DQOs. The MQOs can be defined in terms of data quality attributes; precision, accuracy, completeness, delectability, representativeness, and comparability. The first four can be defined in quantitative terms, while the latter two are qualitative.

Precision. A measure of mutual agreement among multiple measurements of the same property, usually under prescribed similar conditions. Precision will be evaluated through auditing of data collection activities to determine whether activities are performed in a consistent manner, and by established protocol.

Accuracy. The degree of agreement between a measurement (or an average of measurements of the same thing), and the amount actually present.

Completeness. For this QAPJP, completeness is the measure of the number of valid samples obtained compared to the amount that is needed to meet the DQOS. The completeness goal is 90%.

Detectability. The determination of the low-range critical value of a characteristic that a method-specific procedure can reliably discern or is necessary to meet program objectives.

Representativeness. Expresses the degree to which data accurately and precisely represent characteristic of a population, parameter variations at a sampling point, a proceed condition, or an environmental condition.

Comparability. Expresses the confidence with which one data set can be compared to another.

3.3 Field MQOs

The following information describes the procedures used to control and assess measurement uncertainty occurring during the field sampling. Field parameters in this section will include location, lake trout length, lake trout weight, and lake trout age and forage fish lengths, weights and ages. Since these measurements are straightforward, the measurement quality evaluations will be simple remeasurements.

The majority of the uncertainties occurring in the field can be alleviated by the development of detailed standard operating procedures (SOPs), an adequate training program at appropriate frequency, and a field audit program. SOPs have been developed and training has occurred. Field audits will be implemented during the course of the program implementation.

3.4 Precision

Another term for precision is repeatability. Repeatability in the field is very important to precision, as well as data comparability. Repeatability is controlled by the development of detailed SOPs and adequate training in those SOPS. Field precision will be checked by remeasuring 5% of the samples. Remeasurements must be within the acceptance criteria as stated in Table 3.0. Field precision can also be evaluated through the implementation of field technical systems audits. These audits will be used to evaluate the adherence to the SOPS. Audits are discussed in Section 8.0.

3.5 Accuracy

As stated earlier, accuracy is based on the differences between an estimate derived from data and the true value of the parameter being estimated. For the field measurements, with the exception of location, the true value is dependent on the calibration of the instrument (ruler or scale). Following calibration procedures and precision requirements will provide an indication of accuracy. Following SOPs as written should reduce contamination as much as possible. Accuracy is also based on training. Therefore, during audits the trainer will remeasure 5% of the samples to determine accuracy. If accuracy requirements are not met, the trainer will review the methods with the sampler until agreement is reached

3.6 Detectability

Detectability in this study is a function of how accurate and repeatable the measuring instruments can be maintained. Rulers or tape measurements, unless broken, will be considered accurate. Therefore, delectability of lake trout length is a function of following the SOPS. Similarly, scales, if calibrated properly, should reflect an accurate weight unless various conditions (wind or rain) create a situation where an accurate weight (within detectable limits) cannot be met. The SOPs will discuss ways to measure samples within the delectability requirements.

3.7 Completeness

Completeness for the field is defined as the successful collection of all viable samples in the appropriate time frame. A viable sample would be defined as any single sample whose integrity has not been effected during the collection process and would therefore not be flagged with a field qualifier. In some cases the sampler has no control on the integrity (e.g., samples remaining in the sun too long) while in other cases the sampler might effect the integrity (e.g., contaminating a sample through improper handling).

In any case, the DQOs are based on the evaluation of a statistically relevant number of samples which are affected by all errors occurring in the field and laboratory. Therefore, the overall goal is a completeness of 90%. The completeness objective for the measurement phase is 100%. As with the other data quality attributes, completeness can be controlled through the adherence to the SOPs in order to minimize contamination and sampling errors.

3.8 Representativeness

Representativeness, with respect to the overall program objectives, is a function of the statistical sampling design and how well this design estimates the measurement parameters to this project. Variation in lake trout diet is expected seasonally but also from year-to-year, depending on the abundance of prey and environmental factors that might affect feeding behavior. Since the sampling period for this project is only one year, the review of past lake trout diet data will assist in determining how representative the 1994 diet of lake trout is to the yearly variation that can be expected.

3.9 Comparability

Comparability will be maintained by the adherence to the SOPs. Adherence to these SOPs by all samplers will allow for comparability of data among sites and throughout the project. Evaluation of comparability occurs through the implementation of the training program and the field technical systems audits.

Measurement quality objectives for the parameters that will be used to evaluate lake trout diet in this project are summarized in Table 3.0.

Table 3.0. Measurement quality objectives for parameters for the evaluation of lake trout diet.

Parameters	Sample Type	Frequency	Acceptance; Other Corrective Action
Location			The accuracy required is to regions of the lake.
Lake Trout Length			
Precision	Remeasurement	5 %	1 cm of original measurement - recalibrate instrument and remeasure sample to compare to closest.
Accuracy	Independent remeasurement	5 %	1 cm of original measurement - review protocols and remeasure another sample.
Completeness		NA	90 %
Lake Trout Weight			
Precision	Remeasurement	5 %	0.1 Kg of original measurement - recalibrate instrument and remeasure sample to compare to closest.
Accuracy	Independent remeasurement	5 %	0.1 Kg of original measurement - review protocols and remeasure another sample.
Completeness		NA	100 % for lake trout collected for contaminant analysis. 0 % for lake trout collected only for diet analysis.
Lake Trout Age			
Precision	Coded-wire tag	100 %	Confirmation with scale aging.
	Re-age, inspection	5 %	Direct match with original.
Accuracy	Independent Re-age, inspection	5 %	Direct match with original.
Completeness		NA	
Diet Species of Lake Trout			
Precision	Re-identify, inspection	5 %	95 % identification, precision will be maintained through training and periodic audits to verity accuracy of identification of prey items.
Accuracy	Re-identify, inspection	5 %	95 % identification, to determine accuracy, samples will be re-identified and compared to reference samples.
Completeness		NA	

Table 3.0. Measurement quality objectives for parameters for the evaluation of lake trout diet. (Cont'd)

Parameters	Sample Type	Frequency	Acceptance; Other Corrective Action
Diet Item Length			
Precision	Remeasurement	5 %	2 mm of original measurement - recalibrate instrument, remeasure sample and compare to closest.
Accuracy	Independent remeasurement	5 %	2 mm of original measurement - review protocols and remeasure another sample.
Completeness		NA	90 %
Diet Item Weight			
Precision	Remeasurement	5 %	0.1 g of original measurement - recalibrate instrument, remeasure sample and compare to closest.
Accuracy	Independent remeasurement	5 %	0.1 g of original measurement - review protocols and remeasure another sample.

4.0 Site Selection and Sampling Procedures

Lake trout and five forage species, bloater chub, alewife, smelt, slimy sculpin, and deepwater sculpin, will be sampled from the NBS's R/V Cisco in spring, summer, and fall at each of the three Biota Sites identified in the Lake Michigan Mass Budget/Mass Balance Work Plan. The precise locations will depend on the differential seasonal distributions of the six species at each site.

4.1 Sampling Procedures and Sample Custody

Each entire fishing operation or cruise in each season will be permanently documented in considerable detail in the Captain's Log and in the Section of Resource Assessment and Fish Community Dynamics' Research Vessel Catch Information System (RVCAT). An overview of this system is given in Appendix 4.

Fishing operation data (e.g., location, gear, total catch and effort by species) and biological data and measurements on individual fish are now entered directly into a laptop computer aboard the vessel. This has eliminated the need for much of the hand recording on a detailed set of field data forms that was done in the past. Each lake trout or other predator species, for example, is uniquely identified by an individual I. D. Number, while the catch from which it came is identified by a unique Serial Number. The data entry screens used aboard the vessel are shown in Appendix 5.

Samples of individual fish and composite samples of several or more fish will be labeled with tags bearing the information shown in Appendix 6. Any temporary or permanent change in the custody of these samples will be recorded on the Chain of Custody Record shown as Appendix 7. Any detected changes in the quality of these samples which might compromise their intended use(s) will be indicated by an appropriate FLAG (See list in Section 10) in the Chain of Custody Record, and corrective action to prevent it happening again will be taken by the Field Manager and reported to the Project Manager who will take additional reinforcing action if warranted. In either

case, emphasis will be placed in identifying the cause and whether it resulted from an inherent system or procedural problem or from negligence. Training to correct the situation will be provided by the Managers if appropriate. A separate set of Custody records will be filed with each of the Projects or Sections at the GLSC of NBS in Ann Arbor that played a significant role in collection and or temporary or final custody of the given samples.

4.2 Contaminant Sampling

All of the lake trout and forage species (identified above) to be used in contaminant analysis will be collected from the NBS's R/V Cisco, using gradedmesh gill nets to obtain the trout and a standard 12 meter bottom trawl to obtain the forage fish. The field sample preparation procedures are described in SOP 1. An NBS biologist will be on board during all of the fishing operations to insure proper handling of the samples. Immediately after they are processed, packaged, and labeled (Appendix 6), all samples of lake trout and forage fish will be frozen in a chest freezer aboard the vessel. If freezer capacity is exhausted, the fish will be held on ice for up to about eight hours so that they can be frozen and stored temporarily at a shore facility or transported frozen in coolers to either the Saugatuck Vessel Base of NBS for temporary storage in chest freezers or directly to the GLSC in Ann Arbor, Michigan for storage in a walkin freezer. All samples will be transported in an NBS vehicle. Custody forms will be used for transfer of samples between authorized individuals, showing the dates(s) when frozen and subsequently delivered, and the receiving location/facility. The number of samples and the range of I.D. numbers, if individual fish, will also be recorded on the Chain of Custody form. A set of Custody records will be filed with the Lake Michigan Project at the GLSC of NBS in Ann Arbor; a duplicate set of records will be filed as backup in another appropriate location at the GLSC.

4.3 Diet Analysis

Stomachs for lake trout diet analysis will be removed with their contents intact from the fish being processed and packaged above in accordance with SOP 1 (Appendix 1). The stomachs will be frozen individually, labeled (Appendix 6), stored, transported, and transferred as described under contaminant sampling of the whole fish above. Diet analysis will take place in the laboratory at GLSC in Ann Arbor after field work is completed.

All members of the Lake Michigan Project at GLSC including the Project Manager for this segment of NBS's LMMB Projects, Edward Brown, the Field Manager, Gary Eck, alternate Field Managers, Ralph Stedman and Randall Owens, and Biological Technicians, Tim Desorcie and George Boyce, will participate in part or all of the field sampling in various capacities. These and other qualified staff whose services may become available later will collect and label all field samples.

5.0 Analytical Procedures and Calibration

Analytical procedures will generally follow those outlined in Bowen 1983, Elliott 1994, Miller and Holey 1992, and others. Details of the various analytical procedures that will be used in the field and laboratory are contained in SOPs 1 and 2 in (Appendices 1 and 2). Measurements of length and weight are the basic analytical procedures to be conducted for this project. Lengths of lake trout and their diet items will be measured to the nearest mm with a measuring board or ruler. Weight will be measured to the nearest 0.1 Kg for lake trout and 0.1 gram (g) for their diet items. Tables of calibration equipment, technique, and frequency are also given in SOPs 1 and 2 for the respective field and laboratory operations. Lake trout will be aged by reading coded-wire tags (see SOP-3 Appendix 3).

6.0 Data Reduction, Validation, and Reporting

The main responsibility for data reduction, validation, and reporting will be shared by Edward Brown and Gary Eck with assistance from other qualified staff. Following is a description of the step by step procedure used to reduce the raw diet data into summary statistics, verify those statistics, and report them as products that describe the diet of lake trout in the manner required for this project.

6.1 Overview and Summary of Method

The raw data as entered and described in SOP 2 (Appendix 2) will be reduced so that the average diet of all lake trout within a given stratum (age-region season) can be reported. Diet will be reported for both lake trout that are sampled for contaminants, and for those that are sampled for diet alone (Table 1.0). The primary descriptive statistic calculated and reported will be the percent that each prey type contributes to the average wet weight of all prey found in the stomachs. The range and frequency distribution of individual weight values and percent weight values from which the average values are calculated will indicate the variance associated with these data. The range and distribution of site specific and biological variables will characterize the lake trout sample within each major stratum. Length distributions of prey fish in the diet will describe the characteristics of each species found in the stomachs of lake trout.

Data collected and results reported during other diet studies of Lake Michigan lake trout will be reviewed to provide a reference framework with which to help evaluate the representativeness of the diet information collected during this project.

It is assumed that the sampling design will provide samples of lake trout that are representative, especially in regard to diet, of all trout available to the sampling gear in each of the three age strata, at each of the three sampling sites, and in each of the three seasons. The samples combined across age strata would not be representative of all fish available to the gear in those strata combined, however, unless the samples in each stratum were first weighted by the relative abundance at the sampling sites of fish in those age intervals.

6.2 Reduction Procedures

The following procedures will be discussed:

- testing between samples
- combining or averaging samples, etc.

Using the database developed in SOP 2 (Appendix 2), calculate the percent that each prey type contributes to the average wet weight of all prey found in the stomach as follows.

Within each stratum (age, region, season), group lake trout and their associated data by general location (port) and date-specific groups.

For each of the location-date specific groups, calculate the average weight (0.1g) per stomach, and percent (0.1%) of the total weight, for each prey category. Also calculate the percent (1%) of the stomachs found empty or void of prey. Omit data flagged as outliers from these and subsequent calculations.

Use Wilcoxon-Mann Whitney two sample tests and Chi-square tests of independence to determine if and where significant differences in the diet exist between the location-date groups.

If significant differences between groups exist, compute a grand average of all location-date specific average weight values. Then calculate the percent that these average prey weights are of the total grand average weight of all prey combined.

If no significant differences between groups exist, combine data for all lake trout sampled within that strata, recalculate average weights, and then calculate the percent that these average prey weights are of the total average weight of all prey combined.

For each stratum, calculate the range and the frequency distribution of individual weight values and percent weight values for each prey species. If necessary, adjust the weight value intervals to reflect fresh weights using conversion formula determined in SOP 2.4.3.

For each stratum, calculate the range and the frequency distribution of prey lengths for each prey fish species. If necessary, adjust the lengths to reflect fresh lengths using conversion formula determined in SOP 2.4.3.

For each stratum, calculate the range and frequency distribution of site specific and biological variables (lake trout length, weight, sex, time, water depth, capture depth, temperature, where captured etc.).

Maintain updated/backed up independent copies of the reduced data (hard drive, disk, and hard copy printout) in the same manner as is done for the raw database (SOP 2.4.4) for the duration of the project.

6.3 Validation Procedures

Verification of the raw database is described in SOP 2.4.4. Validation of reductions/calculations is divided into two procedures: validation of correctness, and validation of representativeness.

6.4 Validation of Correctness

Reductions/calculations result from manipulations of the database by a personal computer using a set sequence of commands and formula (a program). This ensures that all reductions/calculations are consistent and not subject to random error. Verify that the values resulting from the reduction/calculation procedures are correct by reproducing by hand the process carried out by the computer for a randomly selected portion of the database.

6.5 Validation of Representativeness

To determine if the results of the reductions/calculations of this data set are representative of the diet of lake trout in Lake Michigan for this year and for other years in recent history, data collected and results reported during other diet studies of Lake Michigan lake trout will be summarized and compared to the results produced from this database.

6.6 Reporting Procedures

The average size and variability of lake trout and the size, variability, and contribution of the diet taxa to the total diet within age-season-region strata will be reported (Table 6.1), based on reduction of the raw data as detailed above. The raw data itself will be permanently archived in RVCAT computer files at the NBS GLSC. Copies of all files are held separately at the NOAA Great Lakes Environmental Research Laboratory for backup protection against fire, vandalism, and computer failure.

Table 6.1. Reported statistics associated with each biotic element.

Biotic element	Strata	Measurement	Statistic
Lake trout	age, season, region	length, weight	mean, standard error, range, sample size
Lake trout diet	age, season, region, diet taxon	number, wet weight, length	mean, frequency of occurrence, percent by weight of all prey, standard error, range, sample size

This information together with QA findings will be reported to the GLNPO, PO, QAM, and Biota Group.

7.0 Internal Quality Control Checks

Quality assurance for this project will be achieved primarily through specific training both prior to sampling and during the sampling season. Several persons on the GLSC staff are experienced in diet sampling (Eck and Wells 1983, Gary Eck, and Edward Brown, Cruise Reports of the R/V Cisco on file at GLSC of NBS, Ann Arbor), and will provide training on procedures before the sampling begins and while it is in progress. Less experienced field staff will work with experienced staff until such time that the quality of their work justifies them working independently. The quality of field staff work will be checked by the Field Manager or Project Manager sampling at least once or twice during each sampling cruise throughout the duration of the project. Additional checks will be made whenever needed.

Measurements of length and weight required for this project are straight forward, and their variation will be a function of the ruler or weight scale used rather than the person taking the measurements. Measuring boards or rulers will be examined prior to field work to ensure that the error between them is less than ±2 mm. As indicated in Table 1.1, the readability of the weight scales used is 0.1 g for small fish and diet items measured in g, and 50 grams for most lake trout which are much larger and therefore measured in Kg.

In the field, the Project and Field Manager will make independent measurements and Field Sampling Analysts will make remeasurements as detailed in SOP 1 (Appendix 1) for at least 5% of the samples from each season/region stratum. Similarly, in the lab, the Field Manager will make independent measurements and Field Sampling Analysts will make remeasurements as detailed in SOP 2 (Appendix 2) for at least 5% of the samples from each season/region stratum. The resulting data will be recorded on separate Field and Lab Data Sheets, as described in SOPs 1 and 2, and identified as QC Audits. Using these data and data from original measurements, precision, accuracy, and completeness will be calculated for all parameters identified in Table 3.0.

During the diet analysis of lake trout stomach contents in the lab, examples of each species of prey fish and taxonomic group of invertebrate consumed by the trout will be preserved in glass jars with 5% formalin for reference in identification. Examples should cover the range in stages of digestion of the different sizes of prey observed. These specimens will aid in documenting the methods of identification and quantification used in the stomach contents analysis. Each sample will be labeled as to its source (Sample 1. D. No.), taxonomic identification, and measurement values (i.e. length and weight, etc.).

In addition, identification criteria will be developed during training when no good ones exist.

8.0 Performance and Systems Audits

Specific audits will not be conducted as part of this sampling project. Procedures required for the project are straight forward and uncomplicated. The duration of the project is also short enough that at least one or two checks per field trip and per month in the laboratory on performance of the field and lab staff will serve as audit checks for the project. The number of staff involved in this project will be small, therefore, the ability to control the quality of the project will not require elaborate auditing procedures. Quality control audits at each stage of the field sampling and analysis will be conducted by the Project Manager, the Field Manager, or the EPA QA Manager. The auditing will focus mainly on the precision, accuracy, and completeness of the parameter measurements identified in Table 3.0 as well as on the proper handling and processing of the contaminant and diet samples. The auditing will involve remeasurement and independent measurement procedures listed in Table 3.0 and discussed as to frequency in Section 8.0, and observation of the sampling/processing operation and the condition of the samples. Audit reports will be kept on file at the GLSC of NBS and available for review at any time. Moreover, EPA may audit at any time.

Inadequacies in sampling procedures or the quality of the data collected will immediately be addressed immediately by the Project Manager or Field Manager when discovered. All previous and current data collected by the person when the inadequacies were first discovered will be reviewed for accuracy. Additional training and supervision will then be provided until the quality of work is adequate. In addition, an audit form for this project will be developed.

9.0 Calculation of Data Quality Indicators

This QA Plan has defined the DQOs and MQOs (Section 3.0). This section describes the statistical assessment procedures that are applied to the data and the general assessment of the data quality accomplishments.

9.1 Precision

The precision will be evaluated by performing duplicate analyses. Various types of duplicate samples are described in Section 3.0. Precision will be assessed by relative percent difference (RPD).

Relative Percent Difference (RPD)

$$RPD = \frac{(X_1 - X_2) * 100}{(X_1 + X_2)/2}$$

Relative standard deviation (RSO) may be used when aggregating data.

Relative Standard Division (RSD)

$$RSD = (s/\bar{y}) * 100$$

Where: s = *standard deviation*
$\bar{y}$ = *mean of replicate analyses*

Standard deviation is defined as follows:

$$s = \sqrt{\sum_{n-1}^{n} \frac{(y_1 - \bar{y})^2}{(n-1)}}$$

Where: y_i = *measured value of the i the replicate*
$\bar{y}$ = *mean of replicate analyses*
n = *number of replicates*

9.2 Accuracy

Accuracy will be based upon expert remeasurements of a percentage of samples.

Accuracy will be evaluated by determining whether the measurements are within the acceptance limits. Deviations beyond the acceptance criteria could be justification for retraining technicians.

Bias can be estimated from the theoretical "true" value of the expert measurement. "System" bias for the study may be calculated from individual samples and is defined:

$$Bias = \frac{\sum (Y_{ik} - R_i)}{n}$$

Where: Y_{ik} = *the average observed value for the i the audit sample and k observations.*
R_i = *is the theoretical reference value*
n = *the number of reference samples used in the assessment*

9.3 Completeness

Completeness for most measurements should be 90%. Completeness is defined:

$$Completeness = \frac{V}{n} \times 100$$

Where: V = *number of samples judged valid*
n = *total number of measurements necessary to achieve project objectives*

The 90% goal means that the objectives of the survey can be met, even if 10% of the samples are deemed to be invalid. An invalid sample is defined by a number of combination of flags associated with the sample. This value will be reported on an annual basis.

9.4 Representativeness

Based upon the objectives, the three seasonal collections (spring, summer, fall) represent different lake trout diet conditions. In order to determine whether a change is statistically significant, the samples must be representative of the population, and the samples must be collected and analyzed in a consistent manner.

Representativeness will be evaluated through variance estimates of routine sample in comparison to previous years estimates if the latter are available. These estimates would be performed at within-site and between-site levels, as appropriate. Analysis of variance (ANOVA) will be used to determine whether variances are significantly different.

9.5 Comparability

Comparability is very similar to representativeness in that comparability is ensured through the use of similar sampling and analytical techniques. Comparability will be assessed through the evaluation of precision and accuracy measurements and technical systems audits.

10.0 Corrective Action

The possible corrective actions that can be anticipated in advance have been covered and discussed in Table 3.0 and in Sections 7.0 and 8.0. If any nonroutine corrective action is required it will be initiated and implemented by the Project Manager, Edward Brown, or by the Field Manager (Gary Eck, Ralph Stedman, or Randall Owens) as appropriate. Such action will be documented in audit reports, through data flags listed in Table 10.0 or yet to be developed, in revisions of the QA Plan if methods must be changed, and in the final report.

Table 10.0. List of data flags.

LAC	Laboratory accident	There was an accident in the laboratory that either destroyed the sample or rendered it not suitable for analysis.
FAC	Field accident	There was an accident in the field that either destroyed the sample or rendered it not suitable for analysis.
ISP	Improper sample preservation	Due to improper preservation of the sample, it was rendered not suitable for analysis.
CON	Consensus	Consensus to report a range of ages.
UNK	Unknown sex	In the case of species, indicates undetermined sex.
EER	Entry error	The recorded value is known to be incorrect but the correct value cannot be determined to enter a cortecton.
OTL	Data point outlier	When a series of data are plotted and anaylzed, this point is obviously not within the normal distribution of data, and eliminated from further analysis.

11.0 Quality Control Reports to Management

A progress report outlining the achievement of the Quality Assurance Objectives will be provided to the Program Manager, the QA Manager, and the Project Co-coordinators at the end of the project. The Project Manager will be notified immediately, however, if substantive changes are made to the QAPJP The Quality Control Report will include a summary of the results of audits that were conducted, data quality assessment, and the corrective actions that were taken. In short, the degree to which the targeted precision, accuracy, and completeness goals were met will be indicated in the Final Report.

12.0 References

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12.4 Elliott, Robert F. 1993. Feeding habits of chinook salmon in eastern Lake Michigan. M.S. Thesis, Michigan State University, Lansing, MI, 108 pp.

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12.6 Lake Michigan Lake Trout Technical Committee. 1985. A draft lakewide management plan for lake trout rehabilitation in Lake Michigan. Minutes of Lake Michigan Committee, Great Lakes Fishery Commission, 1985 Annual Meeting, Ann Arbor, Michigan, March 1985.

12.7 Miller, Michael A. and Holey, Mark E. 1992. Diets of lake trout inhabiting nearshore and offshore Lake Michigan environments. J. Great Lakes Res. 18(1.): 51-60.

12.8 Nielson, L.A. and Johnson, D.L. eds. 1983. Fisheries Techniques. American Fisheries Society, Bethesda, MD. 468 pp.

Appendix 1.

SOP-1:
Sampling Lake Trout and Forage Fish for Contaminant Analysis and for Diet Analysis of the Trout

1.0 SAMPLING LAKE TROUT AND FORAGE FISH FOR CONTAMINANT ANALYSIS AND FOR DIET ANALYSIS OF THE TROUT

This SOP provides the step by step procedure for collecting, measuring, preserving, and transporting Lake Trout and forage fish and stomach contents removed from lake trout for the Enhanced Monitoring Program Lake Michigan Mass Balance Study.

1.1 Overview

Lake trout and forage fish samples will be collected at the three Biota Sites identified in the Lake Michigan Mass Balance Work Plan of October 14, 1993. These samples will be used to measure contaminant concentrations in the fish tissue of PCBs, Mercury, and trans-nonachlor and to examine the diet of the trout by evaluating their stomach contents. The following critical and noncritical information associated with the samples will be recorded:

Critical	Noncritical
1. Location	1. Gear
2. Date of sample	2. Sampling depth
3. Sample length	3. Time sampled
4. Sample weight	4. Water temperature
5. Fin clip (Or absence of clip)	

The lake trout and forage fish samples to be collected for contaminant analysis are of primary importance and therefore must be prepared and preserved as soon after collection as possible for transport to the laboratory for analysis. During the field processing, stomachs will be removed from the lake trout and preserved for diet analysis in the laboratory.

1.1.1 Summary of Method

Lake trout will be sampled with graded-mesh gill and forage fish with trawls fished from the NBS's R/V Cisco on the bottom at each of the three Biota Sites in spring, summer, and fall. The numbers of fish specified in the LMMB Work Plan together with the extracted stomachs of the trout will be transported frozen to the GLSC laboratory of NBS in Ann Arbor, Michigan for contaminants and diet analyses. Individual lake trout will be aged at GLSC from coded wire tags inserted in their snouts and indicated by adipose fin clip or from other fin clips or scales. Bloater chubs, one of the three target species, will be aged from scales.

1.2 Safety

In any field operation, emphasis must be placed on safety. Samplers must be aware of the potential safety hazards to which they are subjected. Follow all safety protocols and equipment guidelines, and be prepared for emergency situations. The sampler is primarily responsible for his/her safety from potential hazards.

1.3 Equipment check and calibration

The following is a list of all needed equipment and consumables.

1.3.1 Equipment

Serviceable Equipment

Fishing vessel equipped with
- -Locational instruments (GPS, Loran, Radar)
- -Sampling gear (gill nets, bottom and midwater trawls)
- -Electronic BT

Ice chests and bagged ice
Measuring board (mm markings required)
Plastic buckets (3- and 5-gallon)
Spring scale (1-10 Kg; Kg markings required)
Beam balance scale (0.1 to ? g; g markings required)
Calibrating weight
Dissecting pan (contaminant fish sampling only)
Dissecting knives
Thermometer (contaminant fish sampling only)
Lap-top computer

Consumable Equipment

Dissecting gloves (contaminant fish sampling only)
Aluminum foil (contaminant fish sampling only)
Plastic fish storage bags (contaminant fish sampling only)
Whirl-pac bags
Sample labels (contaminant fish sampling only)
Marking tools (pencils & permanent markers)
Fish scale envelopes
Cleaning sponge and brush
Rubber gloves for
- -preserving fish
- -handling fish

1.3.2 Calibration and Standardization

Equipment necessary for calibration and the required frequency can be found in Table 1.

Table 1. Equipment necessary for calibration and the required frequency.

Instrument	Calibration technique	Frequency	Acceptance criteria
Thermometer	Ice bath and boiling water	1/year	+/- 2 degrees C
Locational device	Calibration to a standard of known Lat and Long	per trip	+/- 0.25 Km
Measuring Board	Check against second device	1/year	+/- 2mm
Scale	Check against standard S class weights; 1,5,10,25 kgs	daily	+/- 0.1 kg

1.4 Procedures

1.4.1 Collection of Contaminant Samples

Contaminant samples will be collected onboard the NBS's R/V Cisco, using gill nets for lake trout and trawls for forage fish. Because age of fish will only be roughly approximated in the field based on length, the Field Manager should oversample as necessary to help insure that the specified sample sizes are met for both contaminants and diet analyses (Table 1.0).

1.4.1.1 Daily location, weather, and fishing operation data are routinely recorded by the Vessel Captain in the Ship's Log. Detailed information on location, gear, fishing effort, catch (total number and weight by species), length frequencies of selected species, predator-prey data including size and stomach contents of selected species such as lake trout, etc, were formerly recorded on a detailed set of field forms, but are now entered directly into a lap-top computer for later transferral to the GLSC's RVCAT data base. (See RVCAT overview in Appendix 4 and Data Entry Screens in Appendix 5 of the QAPP). Surface to bottom water temperature profiles are taken with an electronic BT when each gear is set and are later downloaded in table format.

1.4.1.2 For each lake trout collected and each composite sample of each forate species, record the following site and sample indentification data on two I.D. Labels, and on a whirl-pac bag (see Appendix 6 of the QAPP Planfor data required on label). Note: The recorded data will include: Sampling objective (contaminant, diet, audit), Date, Lake, Location (including Biota Site & Port), Serial No., Species, Sample I.D. No., Age/Size Group, Field Qualifier Flag, Collector's Name, and Preservative.

1.4.1.3 For all lake trout sampled determine and record the following in the field or in the laboratory of GLSC if indicated otherwise.

-Maximum Total Length (mouth closed and caudal fin dorso-ventrally compressed) to nearest mm using the measuring board.
-Total Weight (to the nearest 0.1 Kg. using the spring balance) of fish taken for diet only; fish for both contaminant and diet analyses will be weighed in the GLSC laboratory.
-Fin clips will be recorded in the field for diet samples only; fish for both contaminants and diet will have clips recorded in the laboratory.

1.4.1.4 For each lake trout referred to in Section 1.3 that is 600 mm and longer remove at least five scales (from just above the lateral line and below the posterior insertion of the dorsal fin) with a clean knife when fin clips are recorded and place the scales in a scale envelope. Label the envelope.

1.4.1.5 Line the examination tray with aluminum foil and place a lake trout in the tray. Make a 3-5 inch incision with a clean knife in the belly of the fish. Pull out and remove the stomach (anterior esophagus to pyloric sphincter) and all its contents. The spleen and any other organs or excess flesh that may be attached to the stomach should be placed back inside the fish. If the stomach appears empty, open it to verify that it is completely void. Indicate so in the predator-prey file in the Lap-Top Computer. Void stomachs need not be kept. Pack the whirl-pac bag with the stomach and its contents and preserve them in the chest freezer.

1.4.1.6 Wrap each lake trout completely with the foil lining the examination tray and attach one I.D. label to the foil, while being careful to retain all body fluids within the foil. Place wrapped fish in a 4 mil polyethylene (Arcan Manufacturing, Plainwell, MI), seal the bag and attach the other I.D. label.

1.4.1.7 Place the bagged fish in Vessel's chest freezer for preservation, or in a cooler and pack with ice until it can be transferred to another freezer.

1.4.1.8 Thoroughly clean and rinse all equipment that comes in contact with sampled fish between sampling individual fish.

1.4.1.9 Keep all samples in your possession in their preserved state (frozen or on ice) until they have been delivered to the GLSC laboratory of NBS in Ann Arbor where subsequent analysis will be conducted. Transport only in NBS approved vehicles. Initiate a Chain of Custody form showing date of delivery and state of preservation, etc. (See a copy of the form in Appendix 7 of the QAPP) Flags if appropriate should be included in the Remarks or Comments columns of the Custody form.

1.4.1.10 Wrap Forage Fish including the Bloater Chub, which is categorized as both a target and forage species in the LMMB PLAN, in the aggregate in aluminum foil. Make no incisions in these fish. Then place them in the polyethylene bags in the aggregate by species and age/size groups specified in the PLAN. Label each bag inside and out with the information shown in Appendix 6 of the QAPP, except for Sample No. which is applicable only for individual predator species (e.g. lake trout), and preserve them in the chest freezer or a cooler with ice. Keep these samples in possession in accordance with instructions for lake trout in 1.4.1.9 above.

1.4.1.11 Within the constraints of the demarcation of forage fish for diet sampling into the age and size groups specified in the LMMB Plan of October 14, 1993, special care must be taken to assure that these fish are representative by size (and hence age) of all fish caught of the various categories being sampled.

1.4.1.12 When the trawl catch is small, the entire catch is retained and sorted by species on the sorting table in the bow of the R/V Cisco. When the catch is large, however, it is first randomly subsampled in the stern of the boat after running it into plastic fish boxes that hold about 50 lbs. each. The randomization is accomplished by running the fish box or boxes back over a 5 gallon bucket or buckets while fish are slowly "pouring" from the box. The subsample in the buckets is sorted into species in the lab, and each species is counted and weighed. The numbers and weight of the individual species in the total trawl catch are estimated from the total weight of the trawl catch and the proportions (weights and numbers) of the individual species in the subsample.

1.4.1.13 A sample of the catch of fish in each diet group will then be obtained by first mixing and spreading all fish in a given group on the sorting table. All fish on a section of the table will then be retained for the diet sample. This procedure is intended to avoid the inevitable bias that occurs when the sorter picks fish individually from the catch.

1.4.1.14 Because the age of bloater chubs will not be known in the field, a length cut-off based on sampling in recent years will be used to obtain an approximate separation by age into the specified age categories for chubs of 0-2 years and 4 + years of age.

1.4.1.15 As for lake trout as described in 1.4.1.9 above, keep all field samples of forage fish for contaminant analysis in your possession in their preserved state (frozen or on ice) until they have been delivered to the GLSC laboratory of NBS in Ann Arbor where the analysis will be conducted. Transport only in NBS approved vehicles. Initiate a Chain of Custody form showing date of delivery and state of preservation, etc. (See copy of the form in Appendix 7 of the QAPP). Flags if appropriate should be included in the Remarks or Comments columns of the Custody Form.

Appendix 2.

SOP-2:
Lab Analysis of Lake Trout Stomachs and Data Entry

2.0 LAB ANALYSIS OF LAKE TROUT STOMACHS AND DATA ENTRY

This SOP is intended to provide a step by step procedure for examining and quantifying the contents of the stomachs sampled, and then entering all data on the computer as part of determining the diet of lake trout for the Enhance Monitoring Program Lake Michigan Mass Balance Study.

2.1 Overview

2.1.1 Summary of method

2.2 Safety

In any laboratory operation, emphasis must be placed on safety. Personnel must be aware of the potential safety hazards to which they are subjected. Follow all safety protocols and equipment guidelines, and be prepared for emergency situations. Each person is primarily responsible for his/her safety from potential hazards.

2.3 Equipment Check and Calibration Check

Check to insure that all equipment and supplies are available in required amounts. The following is a list of all needed equipment and consumables.

2.3.1 Equipment

Serviceable Equipment

Fume hood
Rinse water supply and rinsing bath
Rinse tray
Dissecting tray and tools (scalpel, forceps, scissors)
Dissecting microscope
Electronic balance and calibration weights
Plastic ruler (mm divisions)
Glass specimen jars
Scale press
Scale projector/reader
Computer & printer (with hard drive, disk drive, and necessary software)

Consumable Equipment/Supplies

Formalin (5%)
Rubber gloves
Impression acetate
Paper toweling
Plastic bags (2-5)
Reporting sheets and marking devices

2.3.2 Calibration and Standardization

Equipment necessary for calibration and the required frequency can be found in Table 2.1.

Table 2.1 Equipment necessary for calibration and required frequency

Instrument	**Calibration technique**	**Frequency**	**Accepted criteria**
Plastic ruler	Check against second device	Start-End/ season	+/- 1 mm
Electronic balance	Use calibration weight (300 g) and slope adjust	Daily	+/- 0.1 g
Computer	Virus scan	Every boot-up	No viruses

2.4 Procedures

The following procedures will be discussed:

Sample preparation
Identification and quantification of prey items
-Numeration and estimation (for invertebrates)
-Length measurement and
-Weight measurement and estimation
Archiving representative samples
Mounting and aging scales
Data recording
Verifying data
Determining conversion data and developing formula

2.4.1 Analysis of Stomach Contents

Proceed with the following steps in a well ventilated (fume hood operating if necessary) area intended for such work. Wear rubber gloves when handling preserved prey items. Have equipment set up, calibrated, and ready for use, and start with and maintain a clean work area.

2.4.1.1 Identify each prey fish to species, assign it a percent digested state, and measure (nearest mm) and weigh (nearest 0.1 g) it. Record data as indicated on the lab data sheet. Measure length to the level of precision allowed by the amount of fish remaining. Order of priority is: 1) maximum total length, 2) standard length, 3) vertebral column length, 4) length of a multiple of 5 vertebrae (preferably near the caudal region). For those fish or parts of fish that cannot be positively identified, record as unidentified remains.

2.4.1.2 Identify and group invertebrates into appropriate taxa and weigh (nearest 0.1 g) each taxon as a group. Either count all individuals in a group or estimate the total number based on weight (at least 0.5 g or 25 individuals) of a known number representative of the group. Record data as indicated on a lab data sheet.

2.4.1.3 Repackage stomach contents in their whirl-pac bag and freeze. To facilitate sample retrieval and verification under quality control, store groups (10-25) of the whirl-pool bags containing the individual samples from similar locations and dates together in clear plastic bags in freezer storage.

2.4.1.4 Make several photo copies of each completed Lab Data Sheet and file at separate designated locations.

2.4.2 Aging Lake Trout and Bloater Chubs from Scales

The methods for preparing scales for aging fish and for verifying age are adequately described in Fisheries Techniques (Nielson and Johnson 1983) and in the published literature. The following highlight the procedure.

2.4.2.1 Make an impression of at least 5 lake trout scales from each scale envelope on an acetate slide and return the scales and slide to the envelope after checking the slide for clarity and detail.

2.4.2.2 Age each fish by counting annuli observed on a clear impression of one of the scales viewed on a scale projector. Record the age in years using the convention that a fish is age O in the year hatched and becomes one on January 1st of each subsequent year of life.

2.4.2.3 Follow the same procedure for bloater chubs. However, if detail needed for aging is incomplete, the scales may be placed between glass slides, cleared with water, and read direct with the scale projector.

2.4.2.4 At least 5% of the fish should be reaged by the original person making the determination and by a second person. Assign and record final age on the envelope based on consensus reached by both of these individuals or by the majority if a third independent reader is necessary. A length at age frequency distribution based on known-age lake trout as determined from coded-wire tags may be used to locate possible outliers for reaging, but allowance must be made for previously observed differences in growth rate between Biota Sites (e.g. growth has been slower on the Midlake Reef)

2.4.3 Standard Measurements for Developing Conversion Equations

To allow reconstruction of total prey length and weight from partial length measures, and to allow the conversion of total length and weight of preserved prey to length and weight of fresh prey (or vice-versa), the following procedures will be followed.

2.4.3.1 For up to 50 intact individuals representing all sizes of each prey fish species (5 per 1/10 of size range encountered from preserved stomachs), measure total length and weight, and then dissect the fish and measure (nearest mm) the standard length, the vertebral column length, and the length of 5 vertebrae from the posterior and anterior regions of the vertebral column; also count the total number of vertebrae. Record these measures on a separate lab data sheet and identify as Standard Measures.

2.4.3.2 When in the field, the Project Field Manager will conduct independent measurements of enough stomach contents (steps 2.4.1.2 and 2.4.1.2 of SOP 2) so that at least 50 prey fish representing all sizes and digested states be identified and measured prior to preservation for later lab analysis. These data will be recorded on a lab data sheet identified as Standard Measurements.

2.4.3.3 Enter all data from Standard Measurements Data Sheets into prescribed fields of the appropriate data base.

2.4.3.4 Develop the following conversion equations with associated errors for each prey species:

Vertebrae length to vertebral column length and total length
Vertebral column length to standard length and total length
Standard length to total length
Total length to wet weight
Preserved total length to fresh total length
Preserved wet weight to fresh wet weight

2.4.3.5 Compare to similar equations developed from other studies to determine validity.

2.4.4 Data Entry and Verification

2.4.4.1 Maintain three independent copies of the data (on hard drive, on disk, and hard copy printout) in different locations and update/backup each on a daily basis when altered.

2.4.4.2 Record all data generated in the laboratory on lake trout diet and age on special Lab Data Sheets that will be designed for that purpose. Record complementary observations and qualitative data in a Lab Log Book. On a daily basis if practical, enter these data from the data sheets into the RVCAT data base from which it can be accessed and analyzed with the aid of personal computers.

2.4.4.3 Using equations determined in 2.4.3:

-Calculate missing total length measures from partial length measures and add to the database.

-If entered data are from both fresh and preserved prey, transform one and add to the database so that a consistent measure is entered for all.

2.4.4.4 Identify and correct inaccuracies in data recording and entry, and identify outliers as follows:

1) Plot data variables, identify peripheral values, and cross-reference with original data records. Example plots include:

-Predator length vs weight
-predator length vs date
-Prey length vs date
-prey length vs weight (by length type)

2) Query all data fields for values above and below expected values and cross-reference with original data records.

3) Visually compare and verify each computer record with field and lab records on original data sheets.

4) Resolve with the data collector any possible errors in recording.

5) Flag as an outlier any data that after completing the above, still appears to be outside the range of expected values.

Appendix 3.

SOP-3, Coded Wire Tags (CWT)

STANDARD OPERATING PROCEDURE (Modified from Lake Ontario SOP)

Lake Michigan

Purpose:
Use of a coded wire tag (CWT) injected into the snout for marking hatchery-reared lake trout stocked into Lake Michigan began in earnest in 1985. Lake trout marked with CWTs have also been stocked into Lakes Erie, Huron, and Ontario. Chinook salmon have been marked with CWTs and stocked into Lakes Michigan and Ontario. Evaluation of the returns from fish injected with CWTs provides information about growth, movement, and mortality of populations of hatchery-reared fish released to the lakes.

Marking Convention:
The Great Lakes Fishery Commission has reserved the adipose fin clip, as a single clip, for lake trout that receive a CWT. For fish that do not receive a CWT the adipose fin may be clipped in combination with another fin. Sometimes hatchery personnel fail to clip the adipose fin or clip some other fin of fish that are injected with a CWT. In addition, a dorsal, pectoral, or pelvic fin may be injured, malformed, or congenitally missing. Thus, a few fish with no clip or a mark other than an adipose clip may have a CWT in their snout. An electronic wand used to detect and signal the presence of metal in the snouts of fish may be used either in the field or in the laboratory to help verify the presence of CWTs in individual fish.

Field Procedure:
Record total length (mm), weight (g), fin clips, sex, maturity, sea lamprey wounds and scars, and stomach contents using the computer or standard field data entry form.

If there is a possibility that a fish has been marked with a CWT, cut off the snout behind the eye sockets, and place the snout in a compartmented polypropylene box. Each box should have a unique number engraved on the lid and front, and each compartment should be permanently numbered. Record the box and compartment numbers on the field data form in the space provided.

If the snout is too large for the compartment, or if no compartmented box is available, place the snout in a jar or plastic bag (one snout per container). Record the sample, serial number and fish number on a waterproof label and place the label in the bag or jar and securely close the top.

Freeze the collection of snouts. In the special circumstance that a fish identified as containing a CWT is also a fish required for contaminant analysis, the fish is left intact and handled according to the contaminant analysis protocol in force. The CWT is extracted later at the laboratory under joint responsibility of Lake Michigan and Contaminant Monitoring personnel.

Laboratory Procedure:
Prepare a solution of sodium hydroxide (effective concentration of 15%). Warning - Sodium hydroxide is caustic and should be handled with extreme care. When preparing the solution, laboratory gloves, lab coat and eye protection should be worn. Sodium hydroxide solution is to be slowly added and stirred into the water, NOT the reverse; that is, water is NOT to be added to the solution. Remember that a highly exothermic reaction results from adding sodium hydroxide to water so be careful about the integrity of the

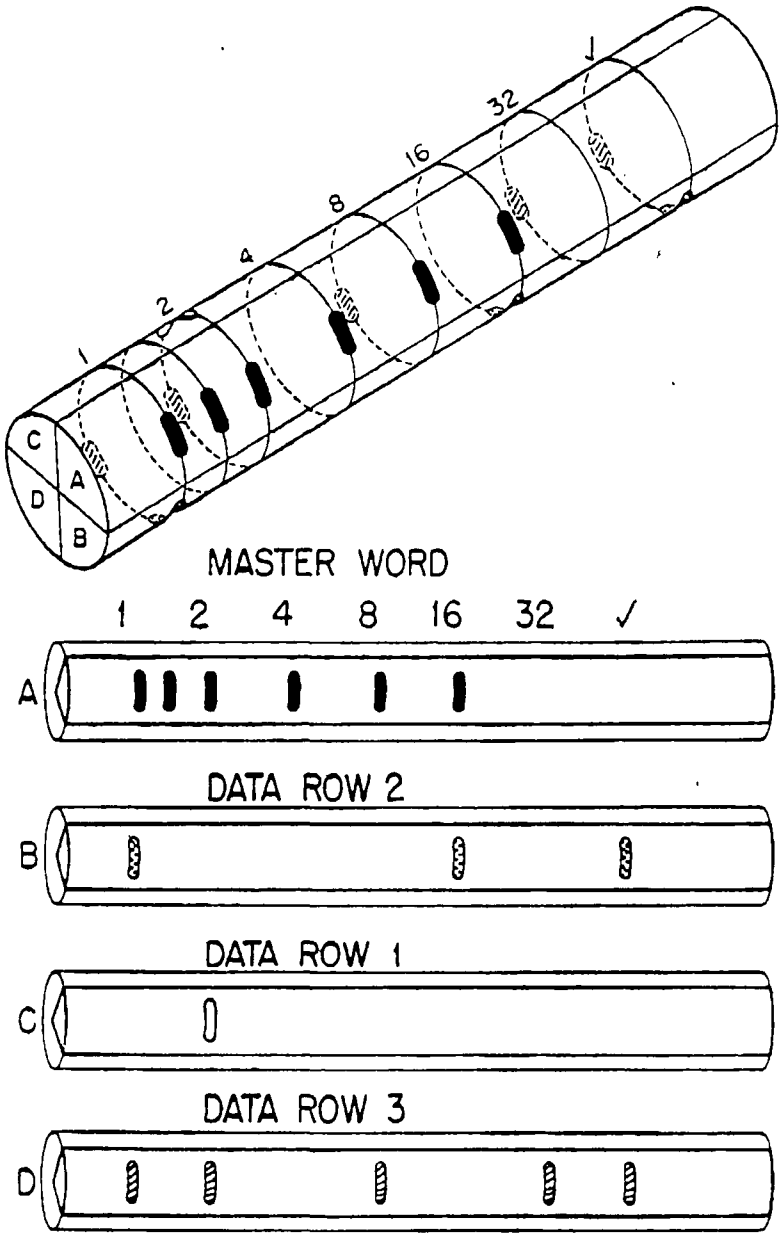
containers used to carry the solution. Refer to the Material Safety Data Sheet (MSDS) in the Laboratory Safety Manual. Cover each snout with the sodium hydroxide solution and let stand until the flesh is liquified (usually overnight). Remove the CWT from the solution with a magnetic stirring rod. Rinse the stirring bar/CWT in vinegar and then in water and transfer the CWT to a magnetic pencil.

Using a tag-reading jig and a binocular microscope, decipher the code. A procedure provided by the tag manufacturer for deciphering the CWT code is attached.

Record the six-digit code in the space provided on the field data form. Affix the CWT to the field data form adjacent to the code using a double strip of clear adhesive tape.

A second reading by an independent observer without reference to the code recorded on first reading is required. If the two readings do not agree, another reading by each of the observers should resolve the disagreement.

BINARY CODED MICRO-TAG



BINARY CODED TAG FORMAT

Data is carried on binary coded wire tags in six binary-digit words, or numbers. Consider the number 1066. It might similarly be called a four decimal-digit word, and can be written in columns as follows:

1000s	100s	10s	1s
1	0	6	6

Said another way, it means the sum of 1 thousand, no hundreds, six tens, and six ones.

Binary-digit words, or numbers, can be written in columns in the same way:

32s	16s	8s	4s	2s	1s
1	1	0	1	0	1

The binary number 110101 thus means the sum of 1 thirty two, 1 sixteen, O eights, 1 four, 0 twos, and 1 one, or 110101 binary = 53 decimal.

The binary coded wire tag material is marked with four six-digit binary words written lengthwise on the wire, 90° apart around its circumference. Three of these words carry the data, and following them is a seventh digit in each row which is used as an error check as explained below. The fourth word is known as the master word and is always the same. Its purpose is to mark the beginning of the data words and to identify the direction in which they are to be read.

The information is carried by notches on the wire spaced .0048" apart. Notches are read as binary 1; no notch is read as binary 0. At the standard length .042", this means that there are at least 8 visible mark positions on a tag. The logic in the coding system is such that tags as short as .030" guarantee unambiguous data recovery. (A similar, but not identical, scheme is used to mark "half-length" or .020" tags. Reading instructions for half-length tags are available request.)

The data format on a coded wire tag is keyed to the seven-bit word which we call the master word. This word, always the same, is unusual in that it contains an extra, in-between, mark, i.e., the word looks like

00111M.

The half-interval mark between the first and second normal marks is instantly apparent. Every tag bears this word, although it may start and end in different places, e.g., 11M001, as a result of the random nature of the cutting process.

To read a coded wire tag, find the master word and orient the tag horizontally so that the master word reads in the correct direction, 00111M. Then the remaining data are to be read according to the following conventions:

1. The column labels for the data words are derived from the master word:

0	0	1	1	1	1	1	1	MASTER
Ck	32	16	8	4	2		1	COLUMN IDENTIFICATION

2. With the master word on top of the wire and running in the proper direction, rotate the tag on its axis so that the master word moves up. As the three data words come into view, they are, in order:

    1. DATA WORD 1
    2. AGENCY CODE
    3. DATA WORD 2

If one were to imagine the surface of the tag unrolled as if it were a sheet or paper, it would look like this:

Check	32s	16s	8s	4s	2s	1s	COLUMN IDENTIFICATION
0	0	1	1	1	1 1	1	MASTER WORD
1	1	0	1	1	0	1	DATA 1 = DECIMAL 45
1	0	0	1	1	1	1	AGENCY = DECIMAL 15
0	1	1	0	0	1	0	DATA 2 = DECIMAL 50

The convention adopted for the seventh column, the check bit, is that the sum of the notches in each of the three data rows must always be odd. This provides a check against coding errors in the data. For example, if the required number was

101101 (six bit word),

there are four binary ones, or notches; the sum is, therefore, even; and the check bit must also be a one. The data would appear on the tag wire as

1101101.

If the data were to be

010110,

the checked data would appear on the tag wire as

0010110

since the data word already has an odd number of bits, and the check bit must be zero.

The information on each of the four sides of the tag wire is repeated continuously every seven spaces. Since tags are cut off every 8.5 spaces, actual tags may be cut at any point in the word. An example of a tag cut between the 4s and the 8s columns follows:

4s	2s	1s	Ck	32s	16s	8s	COLUMN IDENTIFICATION
1	1 1	1	0	0	1	1	MASTER
1	0	1	1	1	0	1	DATA 1 = DECIMAL 45
1	1	1	1	0	0	1	AGENCY = DECIMAL 15
0	1	0	0	1	1	0	DATA 2 = DECIMAL 50

APPENDIX 4.

Research Vessel Catch Information System (RVCAT)

Introduction

RVCAT - System Overview

This is an overview of the information system used by the Resource Assessment Section of the National Fisheries Center - Great Lakes. The system will be referred to simply as RVCAT (Research Vessel Catch Information System). It is a living and growing system pulling raw data from the Great Lakes and producing information of use to the Lakes Community. The purpose of RVCAT is to provide clear, consistent and easy access to research vessel data for vessel biologists.

Research vessel data was first collected on Lake Superior in 1953 and each year since the vessel base was established in 1957. Data was collected from Lake Michigan in 1954, 1955 and annually since 1960. Collections were made in 1956, 1969 and regularly beginning in 1972 on Lake Huron. The Lake Erie Vessel base was established in 1959 with collections made as well in 1957 and 1958. The Lake Ontario station was begun in 1977 with vessel operations beginning in 1978.

The intended computer hardware platform for RVCAT is any system which supports Statistical Analysis System (SAS Institute, Cary, NC) and ORACLE (ORACLE Corp., Belmont, CA) software. Currently, RVCAT is implemented an a Data General MV series mini-computer and IBM-PC compatible micro-computers. One goal of RVCAT is to be transportable to diverse computing environments, so that it is not limited by hardware or software which becomes out of date, or of differing capacities.

ORACLE is used for all basic data management and reporting functions, and SAS is used for statistical analysis. Other software may be used as well for specialized needs.

RVCAT is implemented and maintained jointly by Vessel Biologists of Resource Assessment and Biometrics and Computer Services staff. The system has been partitioned into 12 compartments. A list of Responsible People and their suggested assignments is included elsewhere in this manual.

RVCAT Background

The RVCAT system began in 1972 as a collection of miscellaneous batch programs written for the IBM 1130. As the need arose for specific reports, new programs were added. Several users took part in designing these reports and the new data record formats needed to enter data into the system. Data were originally stored on punched cards.

In 1976, the laboratory gained access to the University of Michigan MTS computing system, as a remote batch station.

Programs and data files were gradually transferred to that system and backed on magnetic tapes. Edit programs were written to provide greater control over data accuracy.

Over the years, it became necessary to change record formats, and programs had to be modified in various ways to accommodate changing needs. In 1978, the entire data base was rewritten in the new format.

Then, in 1984, it was decided that the programs should be rewritten to be interactive, giving users various options in the way data was to be organized and tabulated. At the same time, data retrieval programs were written to allow users to retrieve subsets of data from the original master files, and routines were developed to permit users to run the various programs associated with the data. This system was called RVCAT I.

In the spring of 1985, Viking Forms Management software was purchased for IBM-XTs to replace key-to-card data entry with key-to-disk data entry.

In the fall of 1985, a Data General MV4000 mini-computer was purchased to replace the 1130 system, and it became necessary to transfer programs and data to a new operating system. Data files were converted from the tape format used by MTS to a form acceptable by the Data General, and transferred to the new system. At the same time, various report format changes were decided upon, and the need for more flexibility in running the programs was recognized. To meet these needs, the system called RVCAT II was developed, and became operational in September, 1986.

In January, 1988, a committee was formed to completely review and revise RVCAT. A relational database management system (ORACLE) was identified which would permit the development of a system which would be compatible between the field stations and the Center. It was projected that ORACLE could provide DBMS needs and Statistical Analysis System (SAS) could provide statistical support. Automated data entry on the research vessels was proposed including digital measuring devices.

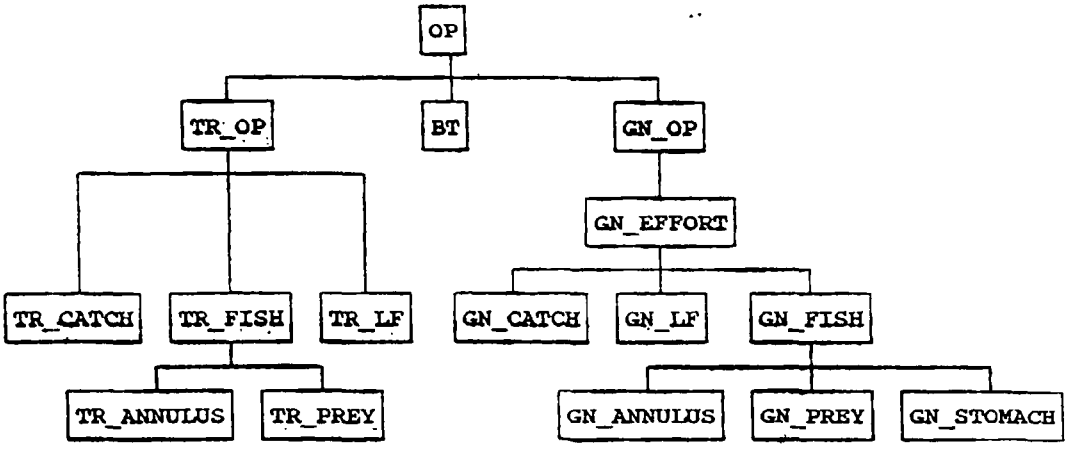
In the fall of 1988, ORACLE was purchased as part of a GCMS purchase and installed on the mini-computer, The process of designing database tables was completed in the spring of 1989. At that point, the process of loading existing data into the database was begun.

In the fall of 1989, 80386 micro-computers and ORACLE were purchased for the field stations. The field stations were then nearly identical in computing capability with the Center.

By March, 1990, data tables were designed, loading of card image data into the tables was progressing, and a prototype data selection and reporting system was demonstrated.

In June 1990, proposals were circulated specifying how a more comprehensive approach to implementing the RVCAT system might be handled. In July, manuals and starter systems were circulated to the field stations. The starter system included table definitions, a data entry form, a data selection system, and trawl length frequency report linked to the selection system.

Data Tables (Hierarchical)



Lookup Tables (alphabetical - no schema)

Data Selection Tables (hierarchical)

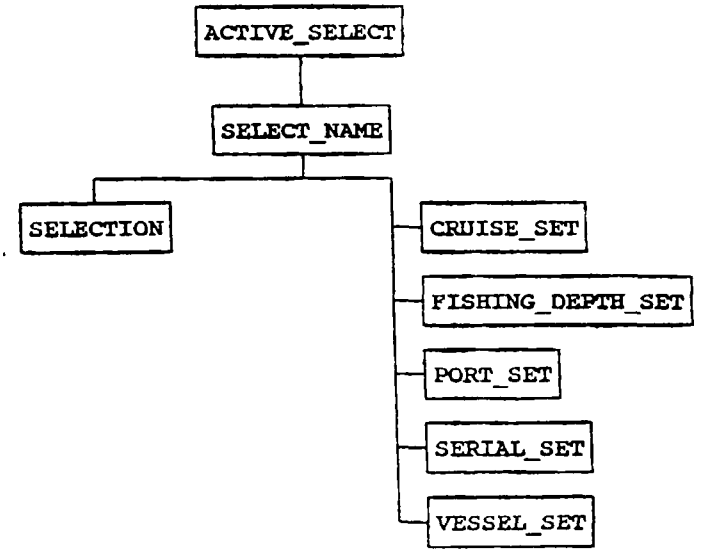


Table Definitions

This document defines the Research Vessel Catch Information System tables. It is divided into these sections:

Naming Conventions
Abbreviations
Table Schemas
Data Table Definitions
Lookup Table Definitions
Selection Table Definitions
Report Table Definitions

Naming Conventions

Table names are in capital letters and column names are in lower case. Next to each table name is the table pneumonic used in report specifications. There are four groups of tables: Data, Lookup, Selection, and Report. Tables are listed in hierarchical or alphabetical order. Listed below each table name are: the column number (used for report definitions), column name, the data type and size, and the primary key - not null designator. The primary key (pk) is a column or group of non-superfluous columns that insure the uniqueness of rows within a table. Columns designated primary key are assumed not null unless otherwise specified.

1. Table names are unique.
2. Column names are unique within a table.
3. Names are descriptive and meaningful.
4. Names will be displayed on terminals and hardcopy.
5. Users will be familiar with and will use names to communicate with the system.
6. Names are brief, using whole names where possible.
7. Names are consistent between tables.

Abbreviations

acro	acronym
ave	average
bt	bathy thermograph slide number
cu	chub management unit
cwt	coded wire tag
dc	diameter at capture
gn	gillnet
id	identification number (system assigned key)
lf	length frequency
lw	length weight
n	number or frequency
nn	not null
op	operation
pk	primary key
sci	scientific
sd	statistical district
sta	station
temp	temperature
tr	trawl
wfu	whitefish management unit

Table Descriptions

This document describes the system of tables as defined in the document "Table Definitions" The model captures the spirit of the method described in "Relational Database Design" The model minimizes redundancy (it is impossible to eliminate redundancy), update anomalies are eliminated, and it has a high degree of maintenance-resistance (the model will stand the test of time, will be widely accepted, and will require few alterations other than additions). Non-loss data reduction has been achieved. Goals of the design process are simplicity, use-ability, and efficiency.

A data model is a collection of constructs, operators and integrity rules which together support a dynamic representation of real-world objects and events, The only construct in a relational model is the table. Operators are add, change, delete, select, project, join, group, and so forth. Integrity rules include no null, primary key and no duplicate; and serve to maintain order and consistency in the database.

The scope of this document is construct and integrity. Beyond the scope of this document are operators which are used by data entry and report tools for input and output, and values that can be calculated from table values.

Many of the tables composing this model are lookup tables, They have one numeric column containing the code, and one or two columns containing the description(s). These tables are largely static in the content. They are used for system integrity and to provide labels when output is generated.

The remaining tables are those which will contain the actual Research Vessel data. They will continue to grow in content as data are collected and entered. Each table models a particular kind of data, and is related to the other tables in a clear and consistent fashion. These tables are related to each other hierarchically, that is, there is one master table, and a number of dependent tables, The master table is called OP (operation). Most of the subordinant table names begin with either GN (gillnet), or TR (trawl). Another subordinate table is BT which contains temperature profile data.

All data stored in the tables is represented the same as in the ASCII (card image) data sets with the following exceptions:

> Port is stored as the combination of lake code and port code. For example, Saugatuck (24) in Lake Michigan (2) is stored as 224. This convention will keep port codes unique throughout the system.
>
> Likewise grid is stored as the combination of lake code and grid number. For example, grid 721 in Lake Ontario (6) is stored as 60721. This convention will keep grid codes unique throughout the system.
>
> Depths are stored in meters rather than fathoms or feet. Precision is to the nearest decimeter. This is a consistent simple way of storing depth that will accomodate the needs of all five lakes. Although meters is the only accepted unit in the scientific literature, depth measurements can be displayed in any unit desired through a simple conversion factor.

The following is a description of each data base table starting with OP and working down the hierarchy.

OP

Table OP (operation) contains a log of Research Vessel operations. Each row represents a deployment of a sampling device by a research vessel. The primary key is composed of year, vessel, serial, and sample_type. Column op_id represents the primary key, is system (arbitrarily) assigned, and is a key to each operation throughout the system. Information includes time, location, conditions, and target organism(s). Examples of distinct operations are: trawl tow, gillnet set, gillnet lift, remote operated vehicle (ROV) transect, hydroacoustic transect, and plankton tow. A separate op row is created even when two operations are done simultaneously (Note: This does not necessarily imply more than one Vessel Operations Form.).

GN_OP

Table GN_OP (gillnet operation) contains information about each whole gillnet deployed by a research vessel. There will be one row in GN_OP for each gillnet set row in OP. The primary key is column op_id.

TR_OP

Table TR_OP (trawl operation) contains information about each trawl tow. There will be one row in TR_OP for each trawl-set row in OP. The primary key column is op_id.

GN_EFFORT

Table GN_EFFORT (gillnet effort) contains information about each panel of a whole gillnet. Each panel is represented as a row in GN_EFFORT. The primary key is composed of columns op_id, mesh-size, and net_material. Column gn_effort_id is system assigned, is representative of the primary key, and is used to relate rows in GN_CATCH, GN_LF, and GN_FISH to a panel of net. GN_EFFORT is in a many to one (M:1) relationship with OP Notice that a particular gillnet-set row in OP will key directly to one row in GN_OP and many rows in GN_EFFORT. Information includes fishing depth, mesh size, length, and material composition of the panel.

GN_CATCH and TR_CATCH

These tables represent the gross catch of each unit of gillnet or trawl effort. They are identical in structure except for the system assigned key. GN_CATCH is subordinate to GN_EFFORT linked through gn_effort_id and TR_CATCH is subordinate to TR_OP linked through op_id. The primary key for GN_CATCH is composed of the columns gn_effort_id, species, and life_stage. The primary key for TR_CATCH is op_id, species, and life_stage. Information includes fish species, life stage, and total number and weight.

GN_LF and TR_LF

These tables will contain length frequency data and are keyed through gn_effort_id and op_id to related units of effort. Each row models a number of a species of fish at a particular length. The primary key for GN_LF is gn_effort_id, species, and length. The primary key for TR_LF is op_id, species, and length.

GN_FISH and TR_FISH

Individual fish are modeled in these tables. Rows are keyed through gn_effort_id or op_id to related units of effort. Information includes fish species, length, weight, sex, maturity, age, diameter at capture of age structure, fin clip, cwt number, scar and wound information. These tables are a combination of the historical Length Weight, Scale, and Predator Prey data. **There is no primary key for these tables!** TR_fish_id and gn_fish_id are system assigned and key to subordinate information which includes annulus and prey data.

GN_PREY and TR_PREY

These tables are identical in structure to GN_LF and TR_LF except that rows are subordinate to a predator in GN_FISH or TR_FISH rather than a unit of effort. Rows are keyed to individual predators through gn_fish_id and tr_fish_id. The primary key is composed of columns gn_fish_id, species, and length for GN_FISH, and tr_fish_id, species, and length for TR_FISH.

GN_ANNULUS and TR_ANNULUS

The annulus tables model individual annulus measurements. Rows are keyed to individual fish through gn_fish_id and tr_fish_id. Each row includes the annulus number, age_struct, and size. The primary key is composed of gn_fish_id, age_struct, and annulus for GN_ANNULUS and tr_fish_id, age_struct, and annulus for TR_ANNULUS.

BT

Each row in BT represents a temperature at a depth for a particular operation and bt cast. The primary key is composed of op_id, bt, and depth. As many depths as desired may be stored for each profile.

LIFE_SIZE

Each row in LIFE_SIZE represents a range of cut off lengths for the life_stage of a species of fish for a lake and year. It documents this information within the database, and is used to segregate length frequency data during report generation. The primary key is composed of year, lake, species and life_stage.

```
SQL> describe op
 Name                           Null?    Type
 ------------------------------ -------- ----
 OP_ID                          NOT NULL NUMBER(6)
 YEAR                           NOT NULL NUMBER(4)
 VESSEL                         NOT NULL NUMBER(2)
 SERIAL                         NOT NULL NUMBER(4)
 SAMPLE_TYPE                    NOT NULL NUMBER(2)
 TARGET                                  NUMBER(3)
 LAKE                           NOT NULL NUMBER(2)
 PORT                           NOT NULL NUMBER(6)
 CRUISE                         NOT NULL NUMBER(2)
 OP_DATE                        NOT NULL DATE
 TIME                           NOT NULL NUMBER(4)
 GRID                                    NUMBER(5)
 BEG_X                                   NUMBER(7,2)
 BEG_Y                                   NUMBER(7,2)
 END_X                                   NUMBER(7,2)
 END_Y                                   NUMBER(7,2)
 LATITUDE                                NUMBER(4)
 LONGITUDE                               NUMBER(5)
 AVE_DEPTH                               NUMBER(5,1)
 BEG_DEPTH                               NUMBER(5,1)
 END_DEPTH                               NUMBER(5,1)
 BEG_BT                                  NUMBER(3)
 END_BT                                  NUMBER(3)
 TEMP_METHOD                             NUMBER(1)
 SURF_TEMP                               NUMBER(3,1)
 SECCHI                                  NUMBER(4,1)
 WEATHER                                 NUMBER(1)
 WIND_SPEED                              NUMBER(2)
 SEA_CONDITION                           NUMBER(1)
 BOTTOM                                  NUMBER(2)
 VESSEL_DIRECTION                        NUMBER(1)
 WIND_DIRECTION                          NUMBER(1)
 BEG_LORAN                               NUMBER(7,1)
 END_LORAN                               NUMBER(7,1)
 COMPLETE                                NUMBER(1)
 REMARK                                  CHAR(80)
 BEG_BT_ID                               NUMBER(6)
 END_BT_ID                               NUMBER(6)

SQL> describe op_target
 Name                           Null?    Type
 ------------------------------ -------- ----
 OP_ID                          NOT NULL NUMBER(6)
 TARGET                         NOT NULL NUMBER(3)

SQL> describe bt
 Name                           Null?    Type
 ------------------------------ -------- ----
 OP_ID                          NOT NULL NUMBER(6)
 BT                             NOT NULL NUMBER(2)
 DEPTH                          NOT NULL NUMBER(5,1)
 TEMP                           NOT NULL NUMBER(3,1)

SQL> describe ebt
 Name                           Null?    Type
 ------------------------------ -------- ----
 BT_ID                          NOT NULL NUMBER(6)
 DEPTH                          NOT NULL NUMBER(4,1)
 TEMP                           NOT NULL NUMBER(3,1)
 LIGHT                                   NUMBER(6,2)

SQL> describe gn_op
 Name                           Null?    Type
 ------------------------------ -------- ----
 OP_ID                          NOT NULL NUMBER(6)
 SET_TIME                                NUMBER(4)
 LIFT_TIME                      NOT NULL NUMBER(4)
 NIGHTS_OUT                     NOT NULL NUMBER(2)
 TYPE_SET                       NOT NULL NUMBER(1)
```

```
FISHING_TEMP_SET                          NUMBER(3,1)
GRID                                      NUMBER(5)
FISHING_TEMP_LIFT                         NUMBER(3,1)

SQL> describe gn_effort
 Name                           Null?    Type
 ------------------------------ -------- ----
 GN_EFFORT_ID                   NOT NULL NUMBER(6)
 OP_ID                          NOT NULL NUMBER(6)
 MESH_SIZE                      NOT NULL NUMBER(2)
 NET_MATERIAL                   NOT NULL NUMBER(1)
 BEG_DEPTH                               NUMBER(5,1)
 END_DEPTH                               NUMBER(5,1)
 NET_LENGTH                     NOT NULL NUMBER(4)

SQL> describe gn_catch
 Name                           Null?    Type
 ------------------------------ -------- ----
 GN_EFFORT_ID                   NOT NULL NUMBER(6)
 SPECIES                        NOT NULL NUMBER(3)
 LIFE_STAGE                              NUMBER(1)
 N                              NOT NULL NUMBER(6)
 WEIGHT                                  NUMBER(6)
 LF_N                                    NUMBER(3)

SQL> describe gn_lf
 Name                           Null?    Type
 ------------------------------ -------- ----
 GN_EFFORT_ID                   NOT NULL NUMBER(6)
 SPECIES                        NOT NULL NUMBER(3)
 LENGTH                         NOT NULL NUMBER(4)
 N                              NOT NULL NUMBER(4)
 LIFE_STAGE                              NUMBER(1)

SQL> describe gn_fish
 Name                           Null?    Type
 ------------------------------ -------- ----
 GN_FISH_ID                     NOT NULL NUMBER(6)
 GN_EFFORT_ID                   NOT NULL NUMBER(6)
 SAMPLE                                  NUMBER(4)
 SPECIES                        NOT NULL NUMBER(3)
 LENGTH                         NOT NULL NUMBER(4)
 WEIGHT                                  NUMBER(5)
 SEX                                     NUMBER(1)
 MATURITY                                NUMBER(1)
 AGE                                     NUMBER(2)
 AGE_STRUCT                              NUMBER(2)
 DC                                      NUMBER(4)
 FIN_CLIP                                NUMBER(2)
 TAG                                     NUMBER(1)
 CWT                                     NUMBER(6)
 STOMACH                                 NUMBER(1)
 A1                                      NUMBER(1)
 A2                                      NUMBER(1)
 A3                                      NUMBER(1)
 A4                                      NUMBER(1)
 B1                                      NUMBER(1)
 B2                                      NUMBER(1)
 B3                                      NUMBER(1)
 B4                                      NUMBER(1)
 SCAR                                    NUMBER(1)
 WOUND                                   NUMBER(1)

 SQL> describe gn_annulus
 Name                           Null?    Type
 ------------------------------ -------- ----
 GN_FISH_ID                     NOT NULL NUMBER(6)
 AGE_STRUCT                     NOT NULL NUMBER(2)
 ANNULUS                        NOT NULL NUMBER(2)
 DIAMETER                       NOT NULL NUMBER(4)

 SQL> describe gn_prey
```

```
Name                           Null?    Type
------------------------------ -------- ----
GN_FISH_ID                     NOT NULL NUMBER(6)
SPECIES                        NOT NULL NUMBER(3)
LENGTH                                  NUMBER(4)
N                                       NUMBER(3)

SQL> describe gn_stomach
Name                           Null?    Type
------------------------------ -------- ----
GN_FISH_ID                     NOT NULL NUMBER(6)
SPECIES                        NOT NULL NUMBER(3)
N                                       NUMBER(2)
AVE_LENGTH                              NUMBER(4)
WEIGHT                                  NUMBER(6,2)
VOLUME                                  NUMBER(4)

SQL> describe tr_op
Name                           Null?    Type
------------------------------ -------- ----
OP_ID                          NOT NULL NUMBER(6)
SET_TIME                                NUMBER(4)
TOW_TIME                       NOT NULL NUMBER(3,1)
SPEED                          NOT NULL NUMBER(5,1)
SPEED_UNIT                     NOT NULL NUMBER(1)
TYPE_SET                       NOT NULL NUMBER(1)
FISHING_TEMP                            NUMBER(3,1)
FISHING_DEPTH                           NUMBER(5,1)
MESH_SIZE                      NOT NULL NUMBER(2)
TR_DESIGN                      NOT NULL NUMBER(2)
GRID                                    NUMBER(5)

SQL> describe tr_catch
Name                           Null?    Type
------------------------------ -------- ----
OP_ID                          NOT NULL NUMBER(6)
LIFE_STAGE                              NUMBER(1)
SPECIES                        NOT NULL NUMBER(3)
N                              NOT NULL NUMBER(6)
WEIGHT                                  NUMBER(7)
LF_N                                    NUMBER(4)

SQL> describe bucket
Name                           Null?    Type
------------------------------ -------- ----
OP_ID                          NOT NULL NUMBER(6)
WEIGHT                         NOT NULL NUMBER(7)

SQL> describe tr_sub
Name                           Null?    Type
------------------------------ -------- ----
OP_ID                          NOT NULL NUMBER(6)
LIFE_STAGE                              NUMBER(1)
SPECIES                        NOT NULL NUMBER(4)
MM_N                                    NUMBER(4)
LF_N                                    NUMBER(3)
SUB_WEIGHT                              NUMBER(6)

SQL> describe tr_lf
Name                           Null?    Type
------------------------------ -------- ----
OP_ID                          NOT NULL NUMBER(6)
SPECIES                        NOT NULL NUMBER(3)
LENGTH                         NOT NULL NUMBER(4)
N                              NOT NULL NUMBER(4)
LIFE_STAGE                              NUMBER(1)

SQL> describe tr_l
Name                           Null?    Type
------------------------------ -------- ----
OP_ID                          NOT NULL NUMBER(6)
LIFE_STAGE                              NUMBER(1)
```

```
SPECIES                                   NUMBER(1)
LENGTH                                    NUMBER(1)

SQL> describe tr_fish
 Name                                     Null?    Type
 ---------------------------------------- -------- ----
 TR_FISH_ID                               NOT NULL NUMBER(6)
 OP_ID                                    NOT NULL NUMBER(6)
 SAMPLE                                            NUMBER(4)
 SPECIES                                  NOT NULL NUMBER(3)
 LENGTH                                   NOT NULL NUMBER(4)
 WEIGHT                                            NUMBER(5)
 SEX                                               NUMBER(1)
 MATURITY                                          NUMBER(1)
 AGE                                               NUMBER(2)
 AGE_STRUCT                                        NUMBER(2)
 DC                                                NUMBER(4)
 FIN_CLIP                                          NUMBER(2)
 TAG                                               NUMBER(1)
 CWT                                               NUMBER(6)
 STOMACH                                           NUMBER(1)
 A1                                                NUMBER(1)
 A2                                                NUMBER(1)
 A3                                                NUMBER(1)
 A4                                                NUMBER(1)
 B1                                                NUMBER(1)
 B2                                                NUMBER(1)
 B3                                                NUMBER(1)
 B4                                                NUMBER(1)
 SCAR                                              NUMBER(1)
 WOUND                                             NUMBER(1)
 LF                                                NUMBER(1)

SQL> describe tr_annulus
 Name                                     Null?    Type
 ---------------------------------------- -------- ----
 TR_FISH_ID                               NOT NULL NUMBER(6)
 AGE_STRUCT                               NOT NULL NUMBER(2)
 ANNULUS                                  NOT NULL NUMBER(2)
 DIAMETER                                 NOT NULL NUMBER(4)

SQL> describe tr_prey
 Name                                     Null?    Type
 ---------------------------------------- -------- ----
 TR_FISH_ID                               NOT NULL NUMBER(6)
 SPECIES                                  NOT NULL NUMBER(4)
 LENGTH                                            NUMBER(4)
 N                                                 NUMBER(3)

SQL> spool off
```

```
SQL>
SQL> select * from age_struct order by age_struct;

AGE_STRUCT AGE_STRUCT
---------- ----------
         1 Scale
         2 Otolith
         3 Operculum
         4 CWT
         5 Fin Clip
         6 Spine
         7 Fin Ray
         8 Vertebra

8 records selected.

SQL> select * from bottom order by bottom;

    BOTTOM BOTTOM_NAME
---------- ---------------
         1 Bedrock
         2 Rubble
         3 Coarse gravel
         4 Fine gravel
         5 Sand
         6 Silt
         7 Clay
         8 Marl
         9 Mud
        10 Organic debris
        11 Mud & Gravel
        12 Gravel & Clay
        13 Sand & Clay
        14 Sand & Silt
        15 Sand & Gravel
        16 Sand & Mud
        17 Silt & Clay
        18 Mud & Silt
        19 Mud & Clay
        20 Other (remarks)
        99 N/D

21 records selected.

SQL> select * from direction order by direction;

 DIRECTION DIREC
---------- -----
         0 V
         1 NE
         2 E
         3 SE
         4 S
         5 SW
         6 W
         7 NW
         8 N
         9 N/D

10 records selected.

SQL> select * from fin_clip order by fin_clip;

  FIN_CLIP FIN_CLIP_A FIN_CLIP_NAME
---------- ---------- --------------------------------
         0 NC         No clip
         1 AD         Adipose
         2 ADLV       Adipose-left ventral
         3 ADRV       Adipose-right ventral
         4 ADLVRV     Adipose-left ventral-right ventral
         5 ADLP       Adipose-left pectoral
         6 ADRP       Adipose-right pectoral
```

```
         7 ADLM        Adipose-left maxillary
         8 LPRM        Left pectoral-right maxillary
         9 RPRM        Right pectoral-right maxillary
        10 LV          Left ventral
        11 RV          Right ventral
        12 BV LVRV     Left ventral-right ventral
        13 LP          Left pectoral
        14 RP          Right pectoral
        15 BP LPRP     Left pectoral-right pectoral
        16 LPLV        Left pectoral-left ventral
        17 RVLP LPRV   Left pectoral-right ventral
        18 RPLV        Right pectoral-left ventral
        19 D           Dorsal
        20 DLV         Dorsal-left ventral
        21 DRV         Dorsal-right ventral
        22 DBV DRVLV   Dorsal-right ventral-left ventral
        23 DLP         Dorsal-left pectoral
        24 DRP         Dorsal-right pectoral
        25 UNK         Origin unknown
        26 RM          Right maxillary
        27 LM          Left maxillary
        28 RPRV        Right pectoral-right ventral
        29 ADBP
        30 DAD         Adipose-dorsal
        31 LPLM        Left pectoral-left maxillary
        99 No Code

33 records selected.

SQL> select * from food order by food;

      FOOD FOOD_NAME
---------- --------------------
         0 MT
         1 Pont
         2 Mysis
         3 Clams
         4 UFR
         5 Leech
         6 Insects
         7 Fish Eggs
         8 Snails
         9 Vegetable
        10 Caddis
        11 UIR
        12 Isopods
        13 Midge Larvae
        14 Microdriles
        15 Crayfish
        16 Megadriles
        17 Bythotrephes
        18 Spherids
        19 Zooplankton
       106 Alewife
       108 gizzard shad
       109 Smelt
       127 burbot
       129 Threespine Stickleba
       130 Ninespine Sticklebac
       131 Trout Perch
       200 Coregonids
       204 Bloater
       216 chub
       301 Chinook
       307 Lake Trout
       706 Johnny Darter
       801 yellow perch
       900 Sculpins
       902 Slimy Sculpin
       904 Deepwater Sculpin
      1001 Acroperus harp
      1002 Alona
```

FOOD	FOOD_NAME
1003	Bosmina longir
1004	Calanoid copep
1005	Ceriodaphnia
1006	Copepod nauplı
1007	Chydorus sphaer
1008	Cyclopoid copep
1009	Diacyclops thom
1010	Cyclops varic
1011	Acanthocyclops v
1012	Daphnia
1013	Daphnia galeata
1014	Daphnia pulex
1015	Diaphanosoma
1016	Epischura lacus
1017	Eucyclops agil
1018	Eurycercus lam
1019	Graptoleberis
1020	Harpacticoida
1021	Macrocyclops
1022	Mesocyclop edax
1023	Ophryoxus
1024	Pleuroxus
1025	Polyphemus
1026	Scapholeberis
1027	Simocephalus
1028	Skistodiaptomus
1029	Tropocycl pras
1030	Acarina
1031	Angulus
1032	Bryozoan statbl
1033	Ceratium (Prot)
1034	Ceratopogonid
1035	Chaoborus punct
1036	Chiron. larvae
1037	Collembola
1038	Ergasilus
1039	Hydra
1040	Nematoda
1041	Oligochaeta
1042	Ostracoda
1043	Diaporeia affin
1044	Tardigrade
1045	Kellicottia
1046	All Other Rotifers
1047	Mayfly
1048	Cyclopoid adult
1049	Alonella
1050	Terr. Insect
1051	Diptera (larv.)
1052	Ectocyclops
1053	Trichoptera
1054	Odonata nyaph
1055	Chiron. pupae
1056	Corixidae
1057	Paracyclops
1058	Holopedium
1059	Turbellaria
1060	Leptodiap. sicilis
1061	Limnocalanus
1062	Ilyocryptus
1063	Asplanchna
1064	Macrothrix
1065	Chiron. eggs
1066	Sida
1067	Leptodiap. ash
1068	Leptodiap. oin
1069	Mysis relicta
1070	Bythotrephes ce
1071	Ceratopog. pupa

```
      1072 Daphnia retrocu
      1073 Eurytemora affi
      1074 Eubosmina coreg
      1075 Leptodora kindt
      1076 Daphnia catawba
      1077 Daphnia parvula

      FOOD FOOD_NAME
---------- --------------------
      1078 Daphnia pulicaria
      1079 Daphnia schodleri
      1080 Latona setifera
      1081 Leptodiaptomous
      1082 Cyclopoida
      1083 Eucyclops
      1084 Diaptomidae
      1085 Adult calanoid
      1086 Senecella
      1087 Leptodiapt. sicilcid

124 records selected.

SQL> select * from lake order by lake;

      LAKE LAKE_NAME
---------- ---------------
         1 Superior
         2 Michigan
         3 Huron
         4 St. Clair
         5 Erie
         6 Ontario
         7 Oshe
         8 St. Clair River
         9 Detroit River
        10 St. Marys River
        11 Anchor Bay
        99 Other

12 records selected.

SQL> select * from life_stage order by life_stage;

LIFE_STAGE LIFE_STAGE_NAME
---------- --------------------------------------------------
         0 Young of Year
         1 Yearling
         2 Beyond second year (age-group II and older)
         3 Subsample
         4 Subsample
         5 Subsample
         6 Life Stage Not Recorded
         7 Adult
         8 Less than 7 inches
         9 Greater than 7 inches

10 records selected.

SQL> select * from maturity order by maturity;

  MATURITY MATURITY_NAME
---------- ---------------
         0 Unknown
         1 Immature
         2 Mature
         3 Gravid
         4 Ripe
         5 Partly spent
         6 Spent
         7 Abnormal
         8 Unrecorded
```

```
9 records selected.

SQL> select * from mesh_size order by mesh_size;

 MESH_SIZE MESH_SIZE_NAME
---------- --------------
         0 0 0
         1 0 1/8
         2 0 2/8
         3 0 3/8
         4 0 4/8
         5 0 5/8
         6 0 6/8
         7 0 7/8
        10 1 0
        11 1 1/8
        12 1 2/8
        13 1 3/8
        14 1 4/8
        15 1 5/8
        16 1 6/8
        17 1 7/8
        20 2 0
        21 2 1/8
        22 2 2/8
        23 2 3/8
        24 2 4/8
        25 2 5/8
        26 2 6/8
        27 2 7/8
        30 3 0
        31 3 1/8
        32 3 2/8
        33 3 3/8
        34 3 4/8
        35 3 5/8
        36 3 6/8
        37 3 7/8
        40 4 0
        41 4 1/8
        42 4 2/8
        43 4 3/8
        44 4 4/8
        45 4 5/8
        46 4 6/8
        47 4 7/8
        50 5 0
        51 5 1/8
        52 5 2/8
        53 5 3/8
        54 5 4/8
        55 5 5/8
        56 5 6/8
        57 5 7/8
        60 6 0
        61 6 1/8
        62 6 2/8
        63 6 3/8
        64 6 4/8
        65 6 5/8
        66 6 6/8
        67 6 7/8
        70 7 0

 MESH_SIZE MESH_SIZE_NAME
---------- --------------
        71 7 1/8
        72 7 2/8
        73 7 3/8
        74 7 4/8
        75 7 5/8
        76 7 6/8
```

```
       77 7 7/8

64 records selected.

SQL> select * from net_material order by net_material;

NET_MATERIAL NET_MATERIAL_NA
------------ ---------------
           1 Nylon
           2 Cotton
           3 Linen
           4 Monofilament

SQL> select * from port order by port;

      PORT PORT_NAME
---------- ------------------------
       102 Sault Ste. Marie Mich.
       104 Whitefish Bay
       106 Grand Marais
       108 Munising
       110 Shelter Bay
       112 Marquette
       114 Stannard Rock
       116 Big Bay
       118 Huron Bay
       120 L'Anse
       122 Portage Entry
       124 Grand Traverse Bay
       126 Bete Gris Bay
       128 Copper Hr.-Eagle Hr.
       130 Upper Entry
       132 Portage Lake
       134 Ontonagon
       136 Black River
       138 Chequamegon Bay
       140 Apostle Islands
       142 Cornucopia-Port Wing
       144 Superior-Duluth
       146 Two Harbors
       148 Taconite Harbor
       150 Grand Marias (Minn.)
       152 Pigeon Bay
       154 Washington Harbor
       156 Siskiwit Bay
       158 Rock Harbor
       160 North Channel
       162 Thunder Bay
       164 Black Bay
       166 Nipigon Bay
       168 Rossport
       170 Jackfish
       172 Heron Bay-Marathon
       174 Superior Shoal
       176 Otter Head
       178 Michipicoten Is.
       180 Caribou Is.
       182 Michipicoten Hr.
       184 Gargantua Hr.
       186 Montreal R.
       188 Batchawana Bay
       202 St. James
       203 Cross Village
       204 Charlevoix
       205 Little Traverse Bay
       206 Grand Traverse Bay
       207 Northern Refuge
       208 Leland
       209 Fox Islands and reef area
       210 Frankfort
       211 Point Betsie
       212 Manistee
```

PORT	PORT_NAME
214	Ludington
216	Pentwater

PORT	PORT_NAME
218	White Lake
220	Muskegon
222	Grand Haven
223	Port Sheldon
224	Saugatuck-Holland
226	South Haven, Palisades
228	Benton Hr.-St. Joe, Cook
229	New Buffalo
230	Michigan City
231	Gary, Indiana
232	Chicago
234	Waukegan
235	Highland Park
236	Racine-Kenosha
238	Milwaukee
240	Port Washington
241	Milwaukee Reef
242	Sheboygan
244	Manitowoc-Two Rivers
246	Kewaunee-Algoma
248	Sturgeon Bay
249	Baily's Harbor
250	Washington Island
252	Fairport
254	Manistique
256	Naubinway, Epoufette
257	North Shore
258	Simmons Reef
259	White Shoals
270	Washington Isles
272	Gills Rock
274	Sturgeon Bay
276	Suamico
278	Oconto
280	Marinette, Menominee
282	Cedar River
284	Escanaba
286	Little Bay De Noc
288	Big Bay De Noc
290	Fairport
302	Mackinac-St. Ignace
303	Six-Fathom Bank
304	Cheboygan
305	Hammond Bay
306	Rogers City
307	Presque Isle, Rockport
308	Alpena-Thunder Bay
309	Yankee Reef
310	Harrisville, Oscoda
311	Au Sable Point
312	Tawas City
314	Bay City
316	Bay Port
318	Port Austin
320	Harbor Beach
322	Port Sanilac
324	Lexington, Port Huron

PORT	PORT_NAME
325	St. Clair River
326	Goderich
328	Kincardine
330	Southampton
332	Pike Bay
334	Tobermory
336	South Baymouth

PORT	PORT_NAME
338	South Bay
340	Burnt Island
342	Detour
344	Cedarville
346	Refuge
350	Tobermory
352	Lionhead
354	Owen Sound
356	Meaford, Collingwood
358	Victoria Harbor
360	Parry Sound
362	Britt
364	Killarney
380	Manotoaning Bay
382	Little Current
384	Spanish
386	Blind River
388	Thessalon
390	St. Marys River
401	Clinton River
402	United States
403	Anchor Bay
404	Canada
405	Thames River
415	Pine Creek
502	Pts.-Mouillee-Amherstburg
504	Monroe
506	Toledo
508	Bono_Eod Bay
510	Port Clinton
512	Bass Island
513	Sash Harbor
514	Sandusky
515	Cedar Point
516	Sandusky-Huron
518	Vermilion-Loraine
520	Cleveland
522	Fairport
524	Ashtabulas
526	Conneaut
528	Erie
530	Barcelona
532	Dunkirk
534	Buffalo
536	Port Colborne
538	Port Maitland
539	Nanticoke
540	Port Dover
542	Long Point
544	Port Burwell
545	Lakeview
546	Port Stanley-Pt. Talbot
548	Erieau
550	Wheatley
552	Pt. Pelee-Pelee Island
554	Leamington-Kingsville
556	Colchester
602	Youngstown
603	Wilson
604	Olcott
605	Thirty Mile Pt.
606	Oak Orchard
607	Hamlin
608	Rochester
609	Smoky Pt.
610	Pultneyville
611	Sodus
612	Fairhaven
613	Oswego

```
       614 Mexico Bay
       615 Southwick
       616 Gallo-Stoney Islands
       618 Henderson Bay
       620 Black River Bay
       622 Chaumont Bay
       623 Cape Vincent
       624 St. Lawrence River
       626 Amherst
       628 North Channel
       630 Adolphus Reach
       632 Bay of Quinte
       634 Prince Edward Bay
       635 Prince Edward Point
       636 Wellington
       638 Lakeport
       640 Port Hope-Cobourg
       642 Oshawa-Pt. Whitney
       644 Toronto
       645 Port Credit
       646 Hamilton
       648 Jordan Harbor
       650 Niagara-on-the-Lake
       844 Marine City
      9980 unknown source
      9981 non-Great Lakes samples
      9982 round robin samples
      9984 reference material sample
      9990 laboratory samples
      9994 Great Lake sample no port
      9996 matrix sample unspiked
      9997 matrix sample spiked
      9998 check samples

223 records selected.

SQL> select * from sample_type order by sample_type;

SAMPLE_TYPE SAMPLE_TYPE_NAME
----------- --------------------
          1 Trawl
          2 Gillnet Set
          3 Gillnet Lift
          4 Gillnet Set and Lift
          5 Hydroacoustics
          6 ROV
          7 Zooplankton
          8 Bongo Net Fry Tow
          9 Ponar Dredge
         10 Water Chemistry
         11 Trap Net
         12 Temperature Only
         13 Light Trap Set
         14 Light Trap Lift

14 records selected.

SQL> select * from sea_condition order by sea_condition;

SEA_CONDITION SEA_CONDIT
------------- ----------
            0 0 ft.
            1 < 1 ft.
            2 1 - 2 ft.
            3 2 - 4 ft.
            4 4   6 ft.
            5 6 - 8 ft.
            6 8+ ft.
            9 N/D

8 records selected.
```

```
SQL> select * from sex order by sex;

       SEX SEX_NAME
---------- --------------
         0 Unknown
         1 Male
         2 Female
         3 Hermaphrodite

SQL> select * from sop order by sop;

       SOP SOP_NAME
---------- ----------------------------------------
         0 Standard Operating Procedures

SQL> select * from species order by species;

   SPECIES COMMON_NAME                                SCI_NAME
---------- ---------------------------------------- ----------------------------------------
         0 No fish caught
         1 Chestnut lamprey                         Ichthyomyzon castaneus
         2 Northern brook lamprey                   Ichthyomyzon fossor
         3 Silver lamprey                           Ichthyomyzon unicuspis
         4 American brook lamprey                   Lampetra lamottei
         5 Sea lamprey                              Petromyzon marinus
       101 Lake sturgeon                            Acipenser fulvescens
       102 Paddlefish                               Polyodon spathula
       103 Spotted gar                              Lepisosteus oculatus
       104 Longnose gar                             Lepisosteus osseus
       105 Bowfin                                   Amia calva
       106 Alewife                                  Alosa pseudoharengus
       107 American shad                            Alosa sapidissima
       108 Gizzard shad                             Dorosoma cepedianum
       109 Rainbow smelt                            Osmerus mordax
       110 Mooneye                                  Hiodon tergisus
       111 Central mudminnow                        Umbra limi
       112 Grass pickerel                           Esox americanus vermiculatus
       113 Northern pike                            Esox lucius
       114 Muskellunge                              Esox masquinongy
       115 White catfish                            Ictalurus catus
       116 Black bullhead                           Ictalurus melas
       117 Yellow bullhead                          Ictalurus natalis
       118 Brown bullhead                           Ictalurus nebulosus
       119 Channel catfish                          Ictalurus punctatus
       120 Stonecat                                 Noturus flavus
       121 Tadpole madtom                           Noturus gyrinus
       122 Brindled madtom                          Noturus miurus
       123 Flathead catfish                         Pylodictus olivaris
       124 American eel                             Anguilla rostrata
       125 Banded killifish                         Fundulus diaphanus
       126 Mosquitofish                             Gambusia affinis
       127 Burbot                                   Lota lota
       128 Brook stickleback                        Eucalia inconstans
       129 Threespine stickleback                   Gasterosteus aculeatus
       130 Ninespine stickleback                    Pungitius pungitius
       131 Trout-perch                              Percopsis omiscomaycus
       132 White perch                              Morone americanus
       133 White bass                               Morone chrysops
       134 Freshwater drum                          Aplodinotus grunniens
       135 Shortnose sturgeon                       Acipenser brevirostrum
       136 Pallid sturgeon                          Scaphirhynchus
       137 Shovelnose sturgeon                      Scaphirhynchus platorynchus
       138 Gar
       139 Alligator gar                            Lepisosteus spatula
       140 Shortnose gar                            Lepisosteus platostomus
       142 Ohio shad                                Olosa ohiensis
       143 Skipjack herring                         Alosa chrysochloris
       146 Goldeye                                  Hiodon alosoides
       150 Blue catfish                             Ictalurus furcatus
       151 Bullheads
       160 Muskellunge x Northern Pike Hybrid
       170 Brook silverside                         Labidesthes sicculus
```

SPECIES	COMMON_NAME	SCI_NAME
190	White perch/White bass (hybrid)	
200	Whitefishes	
201	Longjaw cisco (rare)	Coregonus (Leucichthys) alpenae
202	Cisco (lake herring)	Coregonus (Leucichthys) artedi
203	Lake whitefish	Coregonus clupeaformis
204	Bloater	Coregonus (Leucichthys) hoyi
205	Deepwater cisco (extinct)	Coregonus (Leucichthys) johannae
206	Kiyi	Coregonus (Leucichthys) kiyi
207	Blackfin cisco (rare or extinct)	Coregonus (Leucichthys) nigripinnis
208	Shortnose cisco	Coregonus (Leucichthys) reighardi
209	L. Superior shortnose	Coregonus (Leucichthys) reighardi dymondi
210	Shortjaw cisco (rare)	Coregonus (Leucichthys) zenithicus
211	Pygmy whitefish	Prosopium coulteri
212	Round whitefish	Prosopium cylindraceum
213	Unidentified chubs	
214	Chubs (large)	
215	Chubs (small)	
216	Chubs	
217	Unidentified coregonid	
300	Trouts and graylings	
301	Chinook salmon	Oncorhynchus tshawytscha
302	Cutthroat trout	Salmo clarki
303	Rainbow trout (Steelhead)	Salmo gairdneri
304	Atlantic salmon	Salmo salar
305	Brown trout	Salmo trutta
306	Brook trout	Salvelinus fontinalis
307	Lake trout	Salvelinus namaycush
308	Siscowet (fat trout)	Salvelinus namaycush siscowet
309	Artic grayling	Thymallus arcticus
310	Coho salmon	Oncorhynchus kisutch
311	Kokanee	Oncorhynchus nerka
312	Humper lake trout	
313	Halfbreed lake trout	
314	Splake (brook trout x lake trout)	
315	Released lake trout (commercial) MDNR use	
316	Pink salmon	Oncorhynchus gorbuscha
317	Native lake trout	
400	Suckers	
401	Goldfish	Carassius auratus
402	Carp	Cyprinus carpio
403	Quillback	Carpiodes cyprinus
404	Longnose sucker	Catostomus catostomus
405	White sucker	Catostomus commersoni
406	Lake chubsucker	Erimyzon sucetta
407	Northern hogsucker	Hypentelium nigricans
408	Bigmouth buffalo	Ictiobus cyprinellus
409	Spotted sucker	Minytrema melanops
410	Silver redhorse	Moxostoma anisurum
411	Black redhorse	Moxostoma duquesnei
412	Golden redhorse	Moxostoma erythrurum
413	Northern redhorse	Moxostoma macrolepidotum
414	Greater redhorse	Moxostoma valenciennesi
415	Unidentified redhorse	
416	Goldfish x carp hybrid	
417	River redhorse	Moxostoma carinatum
418	Shorthead Redhorse	Moxostoma breviceps
423	River carpsucker	Carpiodes carpio
424	Highfin carpsucker	Carpiodes velifer
425	Plains carpsucker	Carpiodes forbesi
429	Blue sucker	Cycleptus elongatus
435	Smallmouth buffalo	Ictiobus bubalus
436	Black buffalo	Ictiobus niger
500	Minnows	
501	Silver chub	Hybopsis storeriana
502	Golden shiner	Notemigonus crysoleucas
503	Pugnose shiner	Notropis anogenus

```
       504 Emerald shiner                          Notropis atherinoides
       505 Common shiner                           Notropis cornutus
       506 Blackchin shiner                        Notropis heterodon
       507 Blacknose shiner                        Notropis heterolepis
       508 Spottail shiner                         Notropis hudsonius
       509 Spotfin shiner                          Notropis spilopterus
       510 Sand shiner                             Notropis stramineus
       511 Mimic shiner                            Notropis volucellus
       512 Pugnose minnow                          Opsopoeodus emiliae
       513 Bluntnose minnow                        Pimephales notatus
       514 Fathead minnow                          Pimephales promelas
       515 Longnose dace                           Rhinichthys cataractae
       516 Unidentified minnows
       517 Stoneroller                             Campostoma anomalum
       518 Creek chub                              Semotilus atromaculatus
       519 Lake chub                               Hybopsis plumbea
       520 Sturgeon chub                           Hybopsis gelida
       521 Fallfish                                Semotilus corporalis
       522 Silver minnow                           Hybognathus nuchalis
       523 Cutlips minnow                          Exoglossum maxillingua
       524 Bridle shiner                           Notropis bifrenatus
       525 Striped shiner
       526 Horneyhead chub
       527 Redfin shiner                           Notropis umbratilis cyanocephalus
       528 Silver shiner
       600 Sunfish and bass
       601 Rockbass                                Ambloplites rupestris
       602 Warmouth                                Chaenobryttus gulosus
       603 Green sunfish                           Lepomis cyanellus
       604 Pumpkinseed                             Lepomis gibbosus
       605 Bluegill                                Lepomis macrochirus
       606 Longear sunfish                         Lepomis megalotis
       607 Smallmouth bass                         Micropterus dolomieui
       608 Largemouth bass                         Micropterus salmoides
       609 White crappie                           Pomoxis annularis
       610 Black crappie                           Pomoxis nigromaculatus
       611 Crappies                                Pomoxis spp.
       612 Orange spotted sunfish                  Lepomis humilis
       700 Darters
       701 Eastern sand darter                     Ammocrypta pellucida
       702 Greenside darter                        Etheostoma blennioides
       703 Iowa darter                             Etheostoma exile
       704 Fantail darter                          Etheostoma flabellare
       705 Least darter                            Etheostoma microperca
       706 Johnny darter                           Etheostoma nigrum
       707 Logperch                                Percina caprodes
       708 Channel darter                          Percina copelandi
       709 Blackside darter                        Percina maculata
       710 River darter                            Percina shumardi
       711 Unidentified darters
       800 Yellow perch and pikeperch
       801 Yellow perch                            Perca flavescens

  SPECIES COMMON_NAME                              SCI_NAME
--------- ---------------------------------------- ----------------------------------------
       802 Sauger                                  Stizostedion canadense
       803 Walleye                                 Stizostedion vitreum vitreum
       804 Blue pike (rare or extinct)             Stizostedion vitreum glaucum
       805 Ruffe                                   Gymnocephalus cernuus
       900 Sculpin
       901 Mottled sculpin                         Cottus bairdi
       902 Slimy sculpin                           Cottus cognatus
       903 Spoonhead sculpin                       Cottus ricei
       904 Deepwater sculpin                       Myoxocephalus thompsoni
       950 zebra_mussel                            dreissena_polymorpha
       999 Miscellaneous or unidentified species

182 records selected.

SQL> select * from speed_unit order by speed_unit;

SPEED_UNIT SPE
```

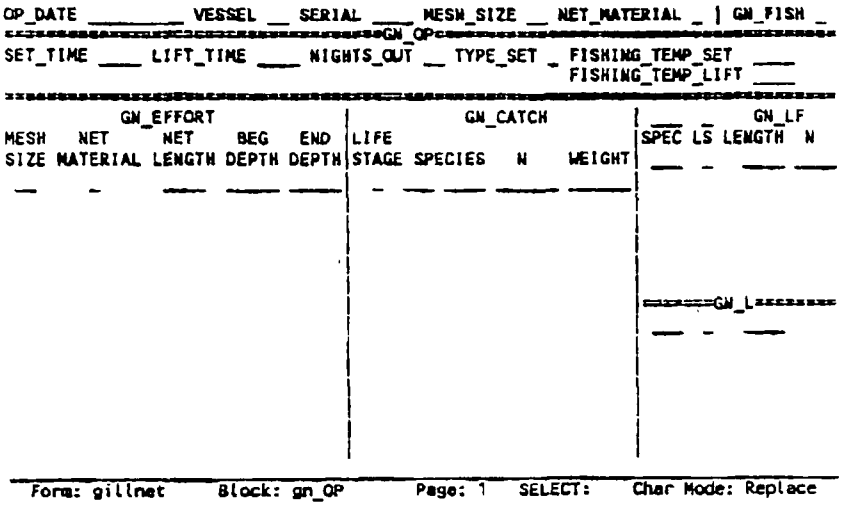
```
---------- ---
         1 MPH
         2 RPM

SQL> select * from stomach order by stomach;

   STOMACH STOMACH_NA
---------- ----------
           Not Taken
         0 Empty
         1 LF
         2 Volume

SQL> select * from target order by target;

    TARGET TARGET_NAME
---------- ----------------------------------------
         0 System Wide Targets
         1 Fall Forage Assessment
         2 Spring Forage Assessment
         3 Yellow Perch Assessment
         4 Lake Whitefish Assessment
         5 Ciscoes Assessment
         6 Lake Trout Assessment
         7 Lake Trout - Refuge
        20 Gear Mensuration
        99 Operation Aborted
       100 Lake Superior Specific Targets
       200 Lake Michigan Specific Targets
       201 Burbot Refuge
       202 Chinook - IDNR
       203 Bythotrephes - Lehman
       210 Fall Acoustic/Midwater Trawl Stdy
       211 Spring Acoustic/Midwater Trawl Study
       212 Summer Acoustic/Midwater Trawl Survey
       300 Lake Huron Specific Targets
       301 Down Bank Trawling,AuSable Pt.,'78
       302 21M WTR, Fall
       303 21M WTR, Spring
       304 National Pesticide Monitoring Prog.
       305 FF - 47' MTR
       306 Lake Trout CWT, Outside Sources
       307 Juv. LT, Down Bank, '83 thru '86
       308 FF - 54' MTR
       309 Lake Whitefish Recruitment
       310 Cisco Lamprey Wounding
       311 IJC Lake Trout & Smelt Collections
       315 Summer Forage Assessment
       326 FF - Goderich, Ontario
       327 SF - Goderich, Ontario
       399 Replicate Tows
       500 Lake Erie Specific Targets
       600 Lake Ontario Specific Targets

36 records selected.

SQL> select * from temp_method order by temp_method;

TEMP_METHOD TEMP_METHOD
----------- -----------
          0 Other
          1 Bucket
          2 Injection
          3 Rev. Therm.
          4 Thermograph
          5 BT
          6 Elctrnc-YSI
          9 Unknown

8 records selected.

SQL> select * from tr_design order by tr_design;
```

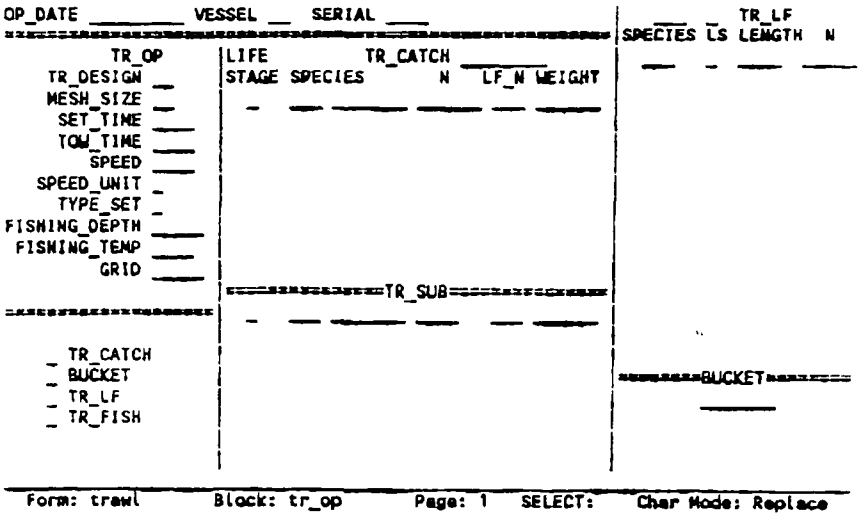
```
TR_DESIGN TR_DESIGN_NAME
--------- ------------------------
        1 K-3a; 52' balloon 7' wing
        4 39' Trawl
       16 K-1; 52' (Cod end: 1/2 in
       21 47' Midwater
       22 54' Headrope midwater
       23 70' Wing trawl
       24 60' Highrise bottom trawl
       25 39' Roller Trawl
       26 18' Bottom trawl
       27 3 meter naturalist trawl
       28 4' Beam trawl
       29 8' Tucker trawl
       30 20' NR Trawl (Steelhead)
       31 89' NR Midwater
       32 20' NR Midwater old
       33 25' NR Midwater new
       34 16' Rockhopper
       35 26' SB Bottom
       36 20'NR long (Steelhead)

19 records selected.

SQL> select * from type_set order by type_set;

  TYPE_SET TYPE_SET_NAME
---------- ------------------------
         1 Bottom across contour
         2 Bottom along contour
         3 Oblique
         4 Surface
         5 Midwater

SQL> select * from vessel order by vessel;

    VESSEL VESSEL_NAME
---------- --------------------------------------------------
         1 Siscowet
         2 Cisco
         3 Musky II
         4 Kaho
         5 Buffalo
         6 Hiodon
         7 Judy
         8 Mooneye
         9 Daphnia
        10 Madtom and little Boston Whaler (Hammond Bay)
        11 Greyling
        12 21 ft. Boston Whaler 'Outrage' (Ann Arbor)
        14 17 ft. outboard at Saug.
        15 Seth Green
        16 Bowfin
        17 Steelhead (State owned)
        18 22' Boston Whaler 'Outrage (Pike) (Sandusky)
        20 Togue
        31 Chambers Bros.
        45 A. E. Clifford
        90 Lady Hilma
        99 Coaster

22 records selected.

SQL> select * from weather order by weather;

   WEATHER WEATHER_NAME
---------- ----------------------------------------
         0 Clear (no clouds at any level)
         1 Partly cloudy (scattered or broken)
         2 Continuous layer(s) of cloud(s)
         3 Sandstorm, duststorm or blowing snow
```

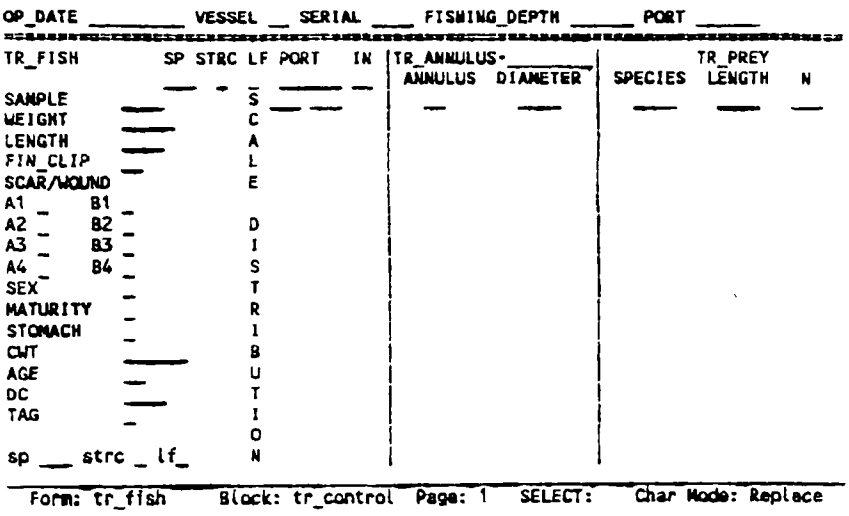
```
          4 Fog, thick dust, or haze
          5 Drizzle
          6 Rain
          7 Snow, sleet, hail
          8 Storm
          9 M/D

10 records selected.

SQL> spool off
```

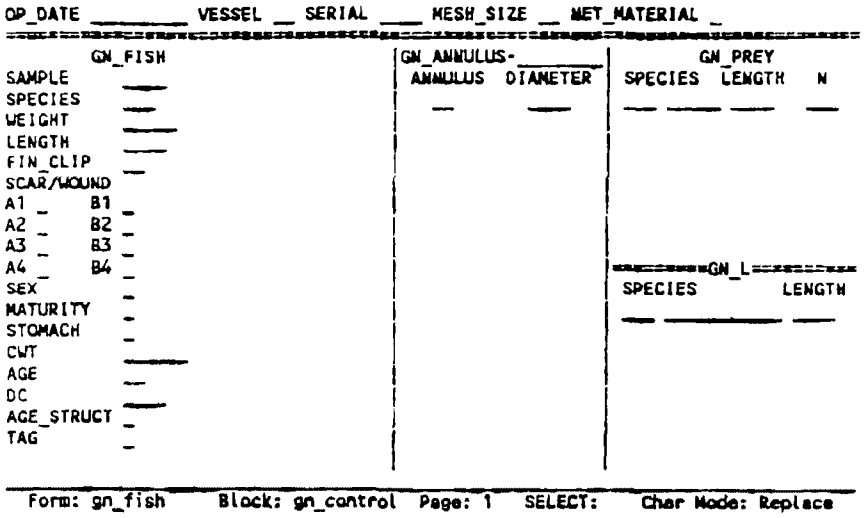
Appendix 5.

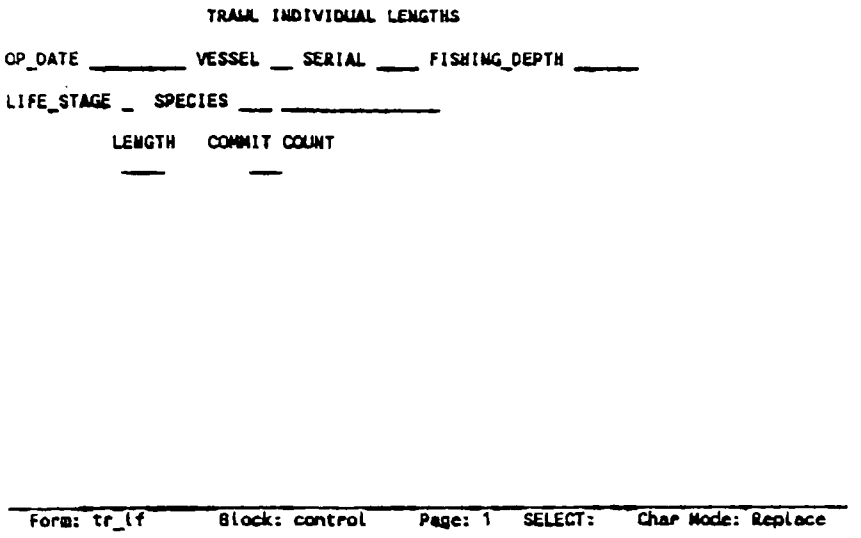
Research Vessel Data Entry Screens Used Under RVCAT




OP_DATE _____ VESSEL __ SERIAL ____
TR_OP
TR_DESIGN __
MESH_SIZE __
SET_TIME ____
TOW_TIME ____
SPEED ____
SPEED_UNIT _
TYPE_SET _
FISHING_DEPTH ____
FISHING_TEMP ____
GRID ____
LIFE STAGE
TR_CATCH
SPECIES N LF_N WEIGHT
TR_SUB
_ TR_CATCH
_ BUCKET
_ TR_LF
_ TR_FISH
SPECIES LS
TR_LF
LENGTH N
BUCKET
Form: trawl
Block: tr_op
Page: 1
SELECT:
Char Mode: Replace


OP_DATE _____ VESSEL __ SERIAL ____ FISHING_DEPTH _____ PORT _____
TR_FISH
SP STRC LF PORT IN
SAMPLE
WEIGHT
LENGTH
FIN_CLIP
SCAR/WOUND
A1 _ B1 _
A2 _ B2 _
A3 _ B3 _
A4 _ B4 _
SEX
MATURITY
STOMACH
CWT
AGE
DC
TAG
sp ___ strc _ lf_
SCLIENT
TR_ANNULUS
ANNULUS DIAMETER
TR_PREY
SPECIES LENGTH N
Form: tr_fish Block: tr_control Page: 1 SELECT: Char Mode: Replace


OP_DATE _____ VESSEL __ SERIAL ____ MESH_SIZE __ NET_MATERIAL _
GN_FISH
SAMPLE
SPECIES
WEIGHT
LENGTH
FIN_CLIP
SCAR/WOUND
A1 _ B1
A2 _ B2
A3 _ B3
A4 _ B4
SEX
MATURITY
STOMACH
CWT
AGE
DC
AGE_STRUCT
TAG
GN_ANNULUS-
ANNULUS DIAMETER
GN_PREY
SPECIES LENGTH N
GN_L
SPECIES LENGTH
Form: gn_fish Block: gn_control Page: 1 SELECT: Char Mode: Replace


TRAWL INDIVIDUAL LENGTHS
OP_DATE _____ VESSEL __ SERIAL ___ FISHING_DEPTH _____
LIFE_STAGE _ SPECIES ___ _____
LENGTH
COMMIT COUNT
Form: tr_lf
Block: control
Page: 1
SELECT:
Char Mode: Replace

Appendix 6.

Label Information Recorded on Fish Sample Tags
Sample Label

NATIONAL BIOLOGICAL SURVEY
Great Lakes Science Center
1451 Green Road
Ann Arbor, MI 48105-2899

Sample Description and Objective_____

_____

Date_____

Lake_____

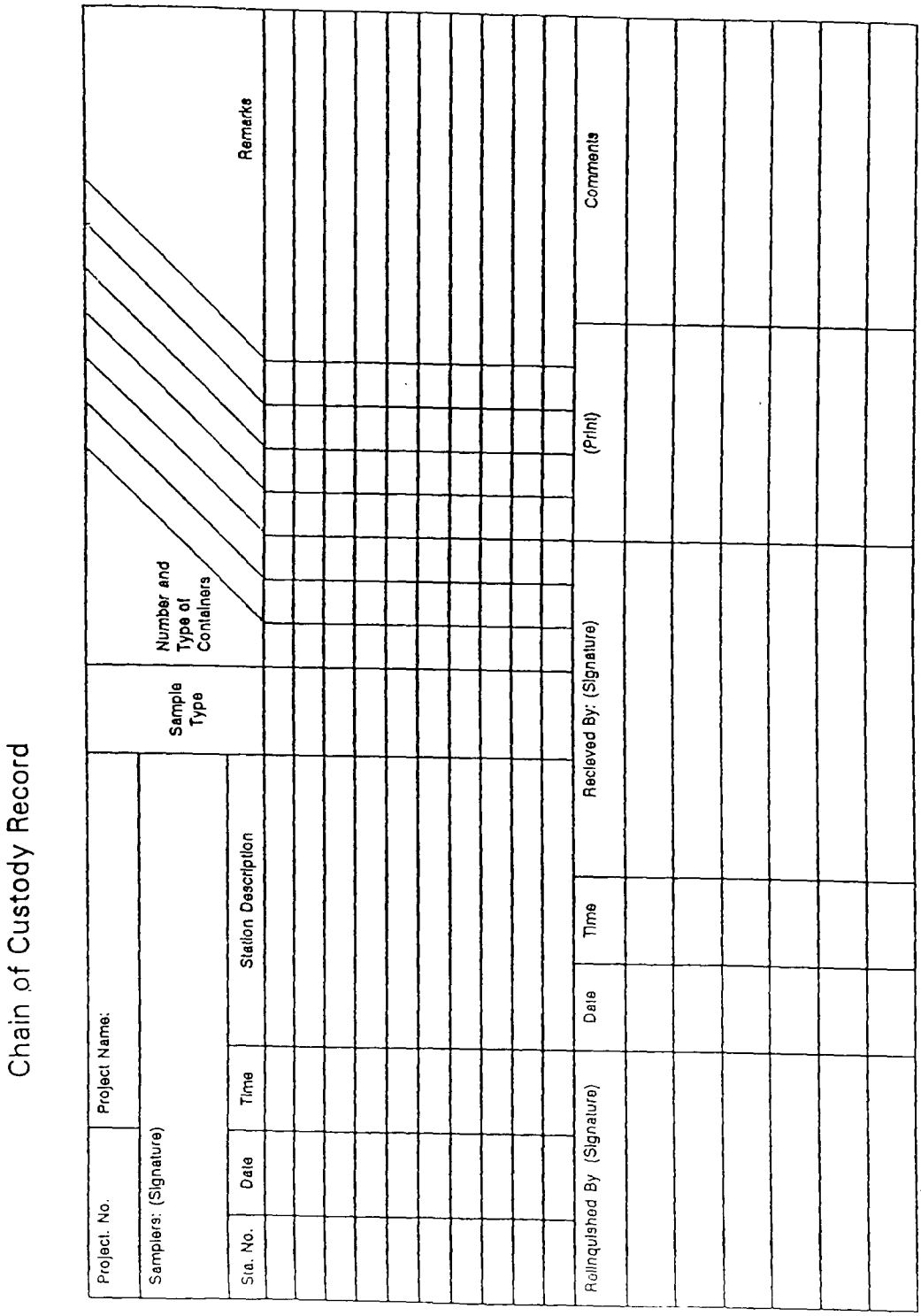
Location_____

Serial No._____

Species_____

Sample No._____

Appendix 7.
Chain of Custody Record Form



Resource Assessment, Lake Michigan Project 1994.

Quality Assurance Project Plan for Coho Sampling for Contaminant and Diet Analysis

Biota Work Group

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U.S. Fish & Wildlife Service
Fishery Resources Office
1015 Challenger Court
Green Bay, WI 54311

April 1994

Quality Assurance Project Plan for Coho Sampling for Contaminant and Diet Analysis

1.0 Introduction and Project Description

1.1 Overview

The Great Lakes National Program Office (GLNPO) of the US EPA has initiated a Mass Balance Study for selected toxic contaminants in Lake Michigan. The mass balance effort will be part of a "Lake Michigan Enhanced Monitoring Program" which includes tributary and atmospheric load monitoring, source inventories, and fate and effects evaluations. In general, the primary goal of this enhanced monitoring program is to develop a sound, scientific base of information to guide future toxic load reduction efforts at the Federal, State and local levels.

A modeling team will construct a mass budget/mass balance model for a limited group of contaminants which are present in Lake Michigan at concentrations which pose a risk to aquatic and terrestrial organisms (including humans) within the ecosystem. Components to the mass balance model will be designed to predict contaminant concentrations in the water column and target fish species over a two year period, relative to loadings. Predictions of contaminant levels in three species of fish will be calculated as final output of the model. The target fish species include:

Lake trout (*Salvelinus namaycush*)
Coho salmon (*Oncorhynchus kisutch*)
Bloater chub (*Coregonus hoyi*)

The calibration of the food web model(s) for these target species requires data on contaminant concentrations and fluxes (diet) not only in these species, but also in the supporting trophic levels. The contaminant burden of each prey species varies based on feeding patterns at lower trophic levels. The concentration of contaminants in coho salmon will depend on what prey items they choose to consume. The diet information for coho salmon sampled by this project will enable the modelers to quantify the movement of contaminants from their source, through the food web, and ultimately the body burden in coho salmon.

The basic design and data requirements for the fish samples have been outlined in Tables 5 and 6 and in Appendix 4 of the Lake Michigan Mass Budget/Mass Balance (LMMB) work plan of October 14, 1993. This project addresses a subset of the work objectives for coho salmon, one of the target species described in the LMMB work plan.

The specific objectives are to:

1) Describe the diet of coho salmon in Lake Michigan from April-October 1994.
2) Collect representative samples of coho salmon from spring, summer, and fall in 1994 for the purpose of conducting contaminant analysis.
3) Review past published and unpublished information on the diet of coho salmon in Lake Michigan and report on the comparability of the data collected in 1994 to past data.

1.2 Experimental Design

Spatial and temporal variations in coho salmon feeding habits and movement will require fish to be collected in spring, summer, and fall and from both the east and west shore of Lake Michigan. Based on coho migration patterns, spring samples will be collected primarily from the southern region of the lake, summer samples from the central region, and fall samples from the north central region of the lake near the egg collection facilities (Table 1.0). The 1993 year class (age 1.1) of coho will be sampled during the entire sampling period (Table 1.0). The 1994 year class will be sampled while in the hatchery (age 1.0) and once in the fall (Table 1.0). The hatchery sample will quantify the amount of contaminants the coho acquired, if any, from the hatchery before they enter the lake and began feeding on natural foods.

Table 1.0. Sample Size Objectives for the Collection of Coho Salmon in Lake Michigan by Season and Location

Season	Location	Age	Contaminants	Diet	Total
Spring (April to mid-June)					
	Hatcheries	1.0	25	0	25
	East Shore (Indiana to Benton Harbor, MI)	1.1	25	75	100
	West Shore (Illinois waters)	1.1	25	75	100
Summer (mid-June to mid-August)					
	East Shore (Benton Harbor to Ludington, MI)	1.1	25	75	100
	West Shore (Kenosha to Sheboygan, WI)	1.1	25	75	100
Fall (mid-August to October)					
	East Shore	1.0	25	75	100
	(Ludington to Frankfort, MI)	1.1	25	75	100
	West Shore	1.0	25	75	100
	(Sheboygan to Kewaunee, WI)	1.1	25	75	100
Total			225	600	825

The most difficult part of this project will be the collection of the necessary samples of coho salmon. Netting techniques to capture salmon in the open water of the Great Lakes is difficult, expensive, and not widely practiced. For salmon, angling is the most appropriate method for addressing the specific needs of this project. Coho salmon collected for contaminant analysis will be obtained by contracting sport charter anglers from the areas sampled (Table 1.0). As necessary and available, samples from assessment netting or creel surveys by state or other research agencies will be used. Standard biological and site specific information (length, weight, age, sex, location, and season) will be recorded for all coho collected.

1.3 Contaminant Sampling

The total number of coho required for contaminant analysis outlined in the LMMB work plan was been modified from 450 to 225 (Table 1.0). Samples will be packaged as required for contaminant analysis, frozen, and delivered to the NBS Great Lakes Research Center. To make these collections as representative as possible, samples will be taken throughout each season to the extent possible. Salmon for contaminant analysis will be collected primarily by contracted charter fishermen.

1.4 Diet Sampling

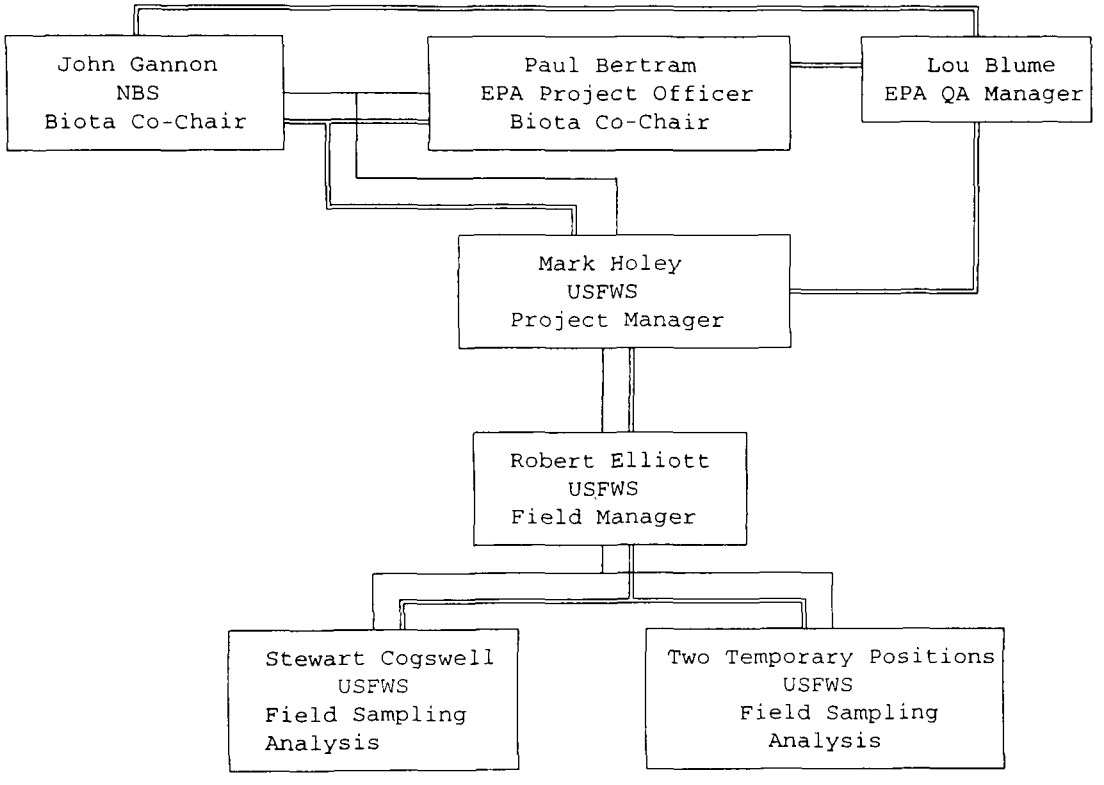
The LMMB work plan did not have a sample size objective for describing the diet. Based on recent diet work describing variation typically observed in the diets of salmon from Lake Michigan (Elliott 1993), we estimate the sample size goal should be at least 100 fish per season per region (Table 1.0). To account for as much of the spatial and temporal variation as possible, sampling effort will be distributed throughout each season in the regions of the lake where the fish are commonly found. To achieve the 100 fish per season per region goal, 75 fish (per season per region) in addition to the salmon collected for contaminant analysis will have to be collected. Diet samples will be collected from contracting charter fishermen and from sampling sport angler catches at boat ramps (see section 4.0 for description of methods).

Historical data describing coho diet will be analyzed and summarized to complement the information collected from those coho sampled in 1994 and 1995. This will serve to put the 1994-95 diet information in perspective and minimize the dangers of having to assume that the diet of a relatively small number of fish collected in 1994-95 is representative of typical years.

Table 1.1 Summary of Critical and Non-Critical Parameter Measurements for the Evaluation of Coho Salmon Diet.

Parameter	Sampling Instrument	Sampling Method	Analytical Instrument	Analytical Method	Reporting Units	LOD
Location (critical)	GPS, Loran, Port Location	SOP-1	NA	NA	Lake Regions	Basin-East, West-North, Central, Southern
Sampie Date (critical)	None	NA	NA	NA	mo/day/yr xx/xx/xx	day
Coho length (critical)	measuring board ruler	NA	NA	NA	mm	1 mm
Coho weight (critical)	spring or electronic balance	SOP-1	NA	NA	Kg	0.1 Kg
Coho age (critical)	Knife and envelope	SOP-1 and Bowen 1983	scale projector	SOP-2	years	1 year
Diet Species (critical)	NA	SOP-1	NA	SOP-2	total number	Species-fish & Common invertebrates Order for less common invertebrates
Diet item Length (critical)	NA	NA	ruler	SOP-2	mm	1 mm
Diet item Weight (critical)	NA	NA	ruler or electronic balance	SOP-2	grams	0.1 gram
Sample Depth (non-critical)	echo sounder	operating instructions	NA	NA	meters	0.1 meters
Time of Sample (non-critical)	clock	NA	NA	NA	HH:MM	minutes
Water Temperature when sampled (non-critical)	thermometer	NA	NA	NA	degrees C	1 °C

2.0 Project Organization and Responsibilities



— Project communication
= QA communication

2.1 GLNPO Project Officer and Biota Co-Chair

The GLNPO Project Officer is the Agency official who initiates the grant, evaluates the proposal, is the technical representative for EPA, and is also co-chair of the Biota workgroup for the Lake Michigan Mass Balance Program. The Project Officer is responsible for:

Budgeting
Program planning, scheduling, and prioritization
Developing project objectives and data quality objectives
Ensuring that project meet GLNPO missions
Technical guidance
Program and data reviews including audits
Data quality
Final deliverables

2.2 GLNPO QA Manager

The GLNPO QA Manager (QAM) is responsible for ensuring that each project funded by EPA satisfies the Agency's requirements for QA programs. The QAM is responsible for:

Offering guidance on QA techniques
Evaluating QA Project Plans (QAPjPs) and approving QAPjPs for the Agency
Assisting in the coordination of audits

2.3 NBS Biota Co-Chair

The Biota Co-Chair from NBS works in partnership with the GLNPO QA Project Leader to implement the Biota portion of the Lake Michigan Mass Balance Project. Duties are:

Program planning, scheduling, and prioritization
Developing project objectives and data quality objectives
Ensuring that project meets GLNPO missions

2.4 USFWS Project Manager

The Project Manager is the USFWS official who initiated the proposal to perform the coho sampling portion of the LMMB project and is responsible for:

Developing the sampling plan for coho collection
Administration of the coho segment of the Biota objectives
Overall supervision of field work
Ensures QA objectives are met
Technical supervision
Final deliverables
Data Quality Assessment

2.5 USFWS Field Manager

The Field Manager is the USFWS position that will provide daily supervision of the field collection activities and achievement of the QA objectives. This position is responsible for:

Collecting field data
Directly supervise the field crew activities
Reviews progress toward QA objectives
Develops and implements sampling and analytical procedures
Prepares reports and deliverables
Trains field crews on sampling and analytical procedures
Technical systems audits for field and laboratory activities
Data quality assessments for lab and field segments

2.6 Field Sampling and Analysis Personnel

These positions are responsible for the majority of the field sampling and lab ID. They will receiving training and guidance from the Project and Field Managers, who will also audit their work to ensure QA objectives are met. These positions will be temporary positions hired at a GS-5 fishery biologist level. Minimum requirements for a GS-5 are six college credits of fishery related courses and 12 credits of related natural resources or animal science related courses or appropriate experience.

3.0 Quality Assurance Objectives

As outlined in the Lake Michigan Mass Budget/Mass Balance Work Plan, the proposed model output should be within a factor of two of the observed concentrations in the water column and target fish. It is also estimated that the required level of model accuracy can be achieved if loadings and contaminant mass in significant environmental compartments are determined to within +/- 20 to 30 percent of the actual value.

Objectives:

1) Within each season/region strata, collect as representative a sample of coho salmon as possible so as to minimize the spatial and temporal population uncertainty (Sp^2) to the extent possible (given the sample size that can be collected with the financial, logistic, and biological constraints of this project).

2) To collect, package, and transport each sample, and to record, summarize, and report each physical measurement with a level of precision, accuracy, detectability, and completeness that will ensure that Measurement Uncertainty (Sm^2) will be nominal compared to Sp^2 and therefor not affect the interpretation of the results.

The level of population uncertainty can not be determined priori. That the contaminant levels in the coho collected will be within +/- 20 to 30 percent of the actual population values is a function of sample size and the collection procedures. The sample size for contaminants has been established by the LMMB Work Plan and subsequent modifications. The designed collection procedures described here attempt to make the most of the sample size target.

Variability in the diet of Lake Michigan salmon can be great, especially when examined from a lakewide perspective encompassing large scale spatial and temporal gradients. The desired sample size for determining diet is to a large degree constrained by the difficulty of collection of these fish. Presently coho abundance in Lake Michigan and therefor catch is very low.

3.1 Measurement Quality Objectives

Measurement quality objectives (MQOs) are designed to control various phases of the measurement process and to ensure that total measurement uncertainty is within ranges prescribed by the DQOs. The MQOs can be defined in terms of data quality attributes; precision, accuracy, completeness, detectability, representativeness, and comparability. The first four can be defined in a quantitative terms, while the later two are qualitative. MQOs are listed in table 3.0.

Precision: A measure of mutual agreement among multiple measurements of the same property, usually under prescribed similar conditions. Precision will be evaluated through auditing of data collection activities to determine whether activities are performed in a consistent manner, and by established protocol.

Accuracy: The degree of agreement between a measurement (or an average of measurements of the same thing), and the amount actually present.

Completeness: For this QAPjP, completeness is the measure of the number of valid samples obtained compared to the amount that is needed to meet the DQOs. The completeness goal is 90%.

Detectability: The determination of the low-range critical value of a characteristic that a method-specific procedure can reliably discern or is necessary to meet program objectives.

Representativeness: Express the degree to which data accurately and precisely represent characteristics of a population, parameter variations at a sampling point, a process condition, or an environmental condition.

Comparability: Express the confidence with which one data set can be compared to another.

3.2 Field MQOs

The following information describes the procedures used to control and assess measurement uncertainty occurring during the field sampling. Field parameters in this section will include location, coho length, coho weight, and coho age. Since these measurements are straightforward, the measurement quality evaluations will be simple remeasurements.

The majority of the uncertainties occurring in the field can be alleviated by the development detailed standard operating procedures (SOPs), an adequate training program at appropriate frequency, and a field audit program. SOPs have been developed (appendices A and B) and training has occurred. Field audits will be implemented during the course of the program implementation.

3.3 Precision

Another term for precision is repeatability. Repeatability in the field is very important to precision, as well as data comparability. Repeatability is controlled by the development of detailed SOPs and adequate training in those SOPs. Field precision will be checked by remeasuring 5% of the samples. Remeasurements must be within the acceptance criteria as stated in Table 3.1. Field precision can also be evaluated through the implementation of field technical systems audits. These audits will be used to evaluate the adherence to the SOPs. Audits are discussed in section 8.

3.4 Accuracy

As stated earlier, accuracy is based on the difference between an estimate, derived from data, and the true value of the parameter being estimated. For the field measurements, with the exception of location, the true value is dependent on the calibration of the instrument (ruler or scale).

Following calibration procedures and precision requirements will provide an indication of accuracy. Following SOPs as written should reduce contamination as much as possible. Accuracy is also based on training. Therefore, during audits the trainer will remeasure 5% of the samples to determine accuracy. If accuracy requirements are not met, the trainer will review the methods with the sampler until agreement is reached.

3.5 Detectability

Detectability in this study is a function of how accurate and repeatable the measuring instruments can be maintained. Rulers or tape measurements, unless broken, will be considered accurate. Therefore, detectability of coho length is a function of following the SOPs. Similarly, scales, if calibrated properly, should reflect an accurate weight unless various conditions (wind or rain) create a situation where an accurate weight (within detectable limits) cannot be met. The SOPs will discuss ways to measure samples within the detectability requirements.

3.6 Completeness

Completeness for the field is defined as the successful collection of all viable samples in the appropriate time frame. A viable sample would be defined as any single sample whose integrity has not been effected during the collection process and would therefor not be flagged with a field qualifier. In some cases, the sampler has no control on the integrity (e.g., samples remaining in the sun too long) while in other cases the sampler might effect the integrity (e.g., contaminating a sample through improper handling).

In any case, the DQOs are based on the evaluation of a statistically relevant number of samples which are effected by all errors occurring in the field and laboratory. Therefore, the overall goal is a completeness of 90%. The completeness objective for the measurement phase is 100%. As with the other data quality attributes, completeness can be controlled through the adherence to the SOPs in order to minimize contamination and sampling errors.

3.7 Representativeness

Representativeness, with respect to the overall program objectives is a function of the statistical sampling design and how well this design estimates the measurement parameters to this project. Variation in coho diet is expected seasonally but also from year-to-year, depending on the abundance of prey and environmental factors that might affect feeding behavior. Since the sampling period for this project is only one year, the review of past coho diet data will assist in determining how representative the 1994 diet of coho salmon is to the yearly variation that can be expected.

3.8 Comparability

Comparability will be maintained by the adherence of the SOPs. Adherence of these SOPs by all samplers will allow for comparability of data among sites and throughout the project. Evaluation of comparability occurs through the implementation of the training program and the field technical systems audit.

Table 3.0. Measurement Quality Objectives for Parameters for the Evaluation of Coho Salmon Diet

Parameters	Sample Type	Frequency	Acceptance; Other Corrective Action
Location			The accuracy required is to regions of the lake.
Coho Length Precision	Remeasurement	5%	1 cm of original measurement - recalibrate instrument and remeasure sample to compare to closest.
Accuracy	Independent remeasurement	5%	1 cm of original measurement - review protocols and remeasure another sample
Completeness		NA	90%
Coho Weight Precision	Remeasurement	5%	0.1 Kg of the original measurement - recalibrate instrument and remeasure sample to compare to closest.
Accuracy	Independent remeasurement	5%	0.1 Kg of original measurement - review protocols and remeasure another sample
Completeness		NA	100% for salmon collected for contaminant analysis 0% for salmon collected only for diet analysis
Coho Age Precision	Length Frequency	100%	Confirmation with scale aging
	Re-age, inspection	5%	Direct match with original
Accuracy	Independent Re-age, inspection	5%	Direct match with original
Completeness		NA	
Diet Species Precision	Re-identify, inspection	5%	95% identification, precision will be maintained through training and periodic audits to verify accuracy of identification of prey items
Accuracy	Re-identify, inspection	5%	95% identification, to determine accuracy, samples will be re-identified and compared to reference samples.
Completeness		NA	

Table 3.0. Measurement Quality Objectives for Parameters for the Evaluation of Coho Salmon Diet

Parameters	Sample Type	Frequency	Acceptance; Other Corrective Action
Diet Item Length			
Precision	Remeasurement	5%	+/- 2 mm of original measurement - recalibrate instrument, remeasure sample and compare to closest
Accuracy	Independent remeasurement	5%	+/- 2 mm of original measurement - review protocols and remeasure another sample
Completeness		NA	90%
Diet Item Weight			
Precision	Remeasurement	5%	0.1 g of the original measurement - recalibrate instrument and remeasure sample to compare to closest
Accuracy	Independent Remeasurement	5%	0.1 g of the original measurement - review protocols and remeasure another sample
Completeness		NA	90%

4.0 Site Selection and Sampling Procedures

A site-specific sampling plan for coho salmon is not available prior to the sample period since it depends on the migration patterns of the salmon and how that pattern is affected by environmental factors. In each of the three seasonal periods (spring, summer, and fall), we will sample coho where ever they happen to be in their migration pattern. The exact location of our sampling will also be determined by the location the anglers who caught the fish chose to fish on any given day. Table 1.0 outlines the anticipated sampling regions by season.

4.1 Sampling Procedures and Sample Custody

Detailed sampling procedures can be found in Appendix A. Method summaries are presented in this section.

4.2 Contaminant Sampling

We plan on collecting all the coho salmon used in contaminant analysis from contracted sport charter anglers or on board USFWS vessels. The field sample preparation procedures will follow the SOP guidelines. A Service biologist will be onboard during all the fishing to insure proper handling of the samples. After capture, the stomach of a coho salmon will be removed in such a way that all body fluids will be captured in the aluminum foil that the fish will be frozen in for analysis. After the fish has been put in the storage bag and labeled, it will be kept on ice until it can be frozen within 24 hours after capture. The samples will be transported frozen in a cooler to the Green Bay Fishery Resources Office where they will logged and placed in a chest freezer until delivery to the Great Lakes Center in Ann Arbor, MI. All samples will be delivered by Service vehicle. Each transfer to a new location will be recorded on the sample collection sheets (Appendix C) and each sample will be labeled individually and recorded on a summary data sheet.

4.3 Diet Analysis

Diet samples may be collected from contracted sport charter anglers, sport anglers, or from assessment activities of the USFWS. Each fish sampled only for diet will have the stomach removed as soon after it was caught as possible. The stomach will be placed in individually numbered whirl-pac bags, preserved with 10-15% formalin, recorded on a summary data sheet, and stored in a sealable five gallon plastic bucket. Diet samples will be transported to the GBFRO for analysis. Chain-of custody procedures for transported samples will be the same as those mentioned above.

The GBFRO is a small developing office and all staff will be involved in the sampling in some way. Those individuals include, Mark Holey, Robert Elliott, Stewart Cogswell, Pat Bouchard, and Bruce Peffers. These biologists will collect all field samples and prepare the field labeling of the samples. Each sample will be clearly identified with date, location, species, length, weight, and sampling gear (see attached table example).

5.0 Analytical Procedures and Calibration

Analytical procedures will follow those outlined in Bowen 1083, Elliott 1994, and Miller and Holey 1992. Standard Operating Procedures for the laboratory activities are included in the *SOP for Lab Analysis of Coho Salmon Stomachs and Data Entry.*

6.0 Data Reduction, Validation, and Reporting

The responsibility for data reduction, validation, and reporting will be shared between Mark Holey and Robert Elliott. This section is intended to describe the step by step procedure used to reduce the raw diet data into summary statistics, verify those statistics, and report them as products that describe the diet of coho salmon in the manner required for this project.

6.1 Overview and Summary of Method

The raw data as entered and described in SOP-2 will be reduced so that the average diet of all coho within a given strata (age-region-season) can be reported. Diet will be reported for both coho that were sampled for contaminants, and for all coho sampled during this project. The primary descriptive statistic calculated and reported will be the percent that each prey type contributes to the average wet weight of all prey found in the stomach. The range and frequency distribution individual weight values and percent weight values from which the average values are calculated will indicate the variance associated with these data. The range and distribution of site specific and biological variables will characterize the coho sample within each major strata. Length distributions of prey fish in the diet will describe the characteristics of each species found in the stomachs of coho.

Data collected and results reported during other diet studies of Lake Michigan coho will be summarized to provide a framework with which to ascertain how valid and representative the diet information collected during this project is.

It is assumed that the sampling design will provide a sample of coho having characteristics (including diet) that are representative of all coho available for capture by anglers, and that collected samples will be representative of the entire strata. Therefore, although variables such as date, general location, depth, time, temperature, sex, exact location, and gear etc. will vary within a strata, determining their effect on diet will not be necessary for this project.

6.2 Reduction Procedures

Methods of data analysis will generally follow those outlined in the Lake Michigan Technical Committee's document entitled "Conducting Diet Studies Of Lake Michigan Piscivores, A Protocol" (Elliott et. al 1996).

In brief, using the database developed in SOP-2, calculate the percent that each prey type contributes to the average wet weight of all prey found in the stomachs of coho salmon as follows.

Within each strata (age, region, season), group coho and their associated data by general location (port) and date specific groups. This will generally result in groups of data that will describe the diet on a weekly basis in each region of the lake.

For each of the location-date specific groups, calculate the average weight (0.1g) per stomach, and percent (0.1%) of the total weight, for each prey category. Also calculate the percent (1%) of the stomachs found empty or void of prey. Omit data flagged as outliers from these and subsequent calculations.

Compute a grand average of all location-date specific average weight values. Then calculate the percent that these average prey weights are of the total grand average weight of all prey combined.

For each strata, calculate the range and the frequency distribution of individual weight values and percent weight values for each prey species. If necessary, adjust the weight value intervals to reflect fresh weights using conversion formula determined in SOP 2.4.3.

For each strata, calculate the range and the frequency distribution of prey lengths for each prey fish species. If necessary, adjust the lengths to reflect fresh lengths using conversion formula determined in SOP 2.4.3.

For each strata, calculate the range and frequency distribution of site specific and biological variables (coho length, weight, sex; time, water depth, capture depth, temperature, where captured etc).

Maintain updated/backed up independent copies of the reduced data (hard drive, disk, and hard copy printout) in the same manner as is done for the raw database (SOP 2.4.4) for the duration of the project.

6.3 Validation Procedures

Verification of the raw database is described in SOP 2.4.4. Validation of reductions/calculations is divided into two procedures: validation of correctness, and validation of representativeness.

6.4 Validation of Correctness

Reductions/Calculations result from manipulations of the database by a personal computer using a set sequence of commands and formula (a program). This ensures that all reductions/calculations are consistent and not subject to random error. Verify that the values resulting from the reduction/calculation procedures are correct by reproducing by hand the process carried out by the computer for a randomly selected portion of the database.

6.5 Validation of Representativeness

To determine if the results of the reductions/calculations of this data set are representative of the diet of coho in Lake Michigan for this year and for other years in recent history, data collected and results reported during other diet studies of Lake Michigan coho will be summarized and compared to the results produced from this database.

6.6 Reporting Procedures

For each strata, report graphically and/or in table form the following:

The percent that each prey type contributes to the average wet weight of all prey found in the stomach.

The range and frequency distribution individual weight values and percent weight values from which the average values are calculated.

The range and distribution of site specific and biological variables.

Length distributions of prey fish in the diet will describe the characteristics of each species found in the stomachs of coho.

Summarize the results of data collected and results reported during other diet studies of Lake Michigan coho and contrast and compared to the results produced from this database.

Raw data in paper and electronic medium, and copies of the reports generated from the data will be stored at the GBFRO for a minimum period of five years.

7.0 Internal Quality Control Checks

Quality assurance for this project will be achieved primarily through specific training both prior to sampling and during the sampling season. Several persons on the GBFRO staff are experienced in diet sampling (Miller and Holey 1993, Elliott 1994), and will provide training sessions on procedures in the SOPs and parameter measurement requirements in Table 1.1 before the sampling begins and while in progress. Field staff will work in pairs with experienced staff until such a time that the quality of their work justify them working independently. The quality of field staff work will be checked periodically throughout the project duration, roughly once or twice per month. The field staff hired will be required to have completed six credits of fishery related college course work and 12 credits of related natural resources or animal science courses, or have appropriate equivalent work experience.

Measurements of length and weight required for this project are straight forward, and their variation will be a function of the ruler or weight scale used than the person taking the measurement. The rulers or measuring boards will be examined prior to the field season to ensure the error between them is less than +/- 2 mm. The weight scales used for this project will be standardized against standard weights at the beginning of the project and compared to each other throughout the sampling period. The readability of the scales used is 0.1 g for small fish and prey types measured in g, and 50 grams for large fish measured in Kg.

8.0 Performance and Systems Audits

Specific Audits will not be conducted as part of this sampling project. Procedures required for this project are straight forward and not complicated. The duration of the project is also short enough that the periodic checks on performance of the field and lab staff will serve as audit checks for this project. The amount of staff involved in this project will be few, therefor, the ability to control the quality of the project will not require elaborate auditing procedures. Quality control audits at each stage of the field sampling and analysis will be conducted by the Project Manager, the Field Manager, or the EPA QA Manager. Audit reports will be kept on file at the GBFRO and available for review at any time.

Inadequacies in sampling procedures or the quality of the data collected will be addressed immediately by the Project Manager or Field Manager when discovered. All previous and current data collected by the person when the inadequacies will be review for accuracy. Additional training and supervision will be provided until the quality of work is appropriate.

9.0 Calculation of Data Quality Indicators

This QA Plan has defined the DQOs and MQOs (Section 3). This section describes the statistical assessment procedures that are applied to the data and the general assessment of the data quality accomplishments.

9.1 Precision

The precision will be evaluated by performing duplicate analyses. Various types of duplicate samples are described in Section 3. Precision will be assessed by relative percent difference (RPD)

9.2 Relative Percent Difference (RPD)

$$RPD = \frac{(X_1 - X_2) * 100}{(X_1 + X_2)/2}$$

Relative standard deviation (RSD) may be used when aggregating data.

9.3 Relative Standard Deviation (RSD)

$$RSD = (s/\bar{y}) \times 100$$

Where: s = *standard deviation*
y = *mean of replicate analyses*

Standard deviation is defined as follows:

$$s = \sqrt{\sum_{n=1}^{n} \frac{(y_i - \bar{y})^2}{(n-1)}}$$

Where: y_i = *measured value of the I the replicate*
y = *mean of replicate analyses*
n = *number of replicates*

9.4 Accuracy

Accuracy will be based upon expert remeasurements of a percentage of samples.

Accuracy will be evaluated by determining whether the measurements are within the acceptance limits. Deviations beyond the acceptance criteria could be justification for retraining technicians.

Bias can be estimated from the theoretical "true" value of the expert measurement. "System" bias for the study may be calculated from individual samples and is defined:

$$Bias = \frac{\sum (Y_{ik} - R_i)}{n}$$

Where: Y_{ik} = *the average observed value for the ith audit sample and k observations.*
R_i = *is the theoretical reference value*
n = *the number of reference samples used in the assessment*

9.5 Completeness

Completeness for most measurements should be 90%. Completeness is defined:

$$Completeness = \frac{V}{n} \times 100$$

Where: V = *number of samples judged valid*
n = *total number of measurements necessary to achieve project objectives*

The 90% goal means that the objectives of the survey can be met, even if 10% of the samples are deemed to be invalid. An invalid sample is defined by a number or combination of flags associated with the sample. This value will be reported on a annual basis.

9.6 Representativeness

Based upon the objectives, the three seasonal collections (spring, summer, fall) represent different coho diet conditions. In order to determine whether a change is statistically significant, the samples must be representative of the population, and the samples must be collected and analyzed in a consistent manner.

Representativeness will be evaluated through variance estimates of routine sample in comparison to previous years estimates. These estimates can be performed at within-site and between-site levels. Analysis of variance (ANOVA) will be used to determine whether variances are significantly different.

9.7 Comparability

Comparability is very similar to representativeness in that comparability is ensured through the use of similar sampling and analytical techniques. Comparability will be assessed through the evaluation of precision and accuracy measurements and technical systems audits.

10.0 Corrective Action

Corrective actions are discussed in Table 1.1, the internal quality control section (7.0), SOPs, and in the performance and systems audit section (8.0). The Project Manager and the Field Manager will initiate corrective actions. Corrective actions will be documented in audit reports, through data flags, and revisions to the QA plan if methods are changed.

Table 10.0 List of Data flags

LAC	laboratory accident	There was an accident in the laboratory that either destroyed the sample or rendered it not suitable for analysis.
FAC	field accident	There was an accident in the field that either destroyed the sample or rendered it not suitable for analysis.
ISP	improper sample preservation	Due to improper preservation of the sample, it was rendered not suitable for analysis.
AVG	average value	Average value-used to report a range of values.
UNK	unknown sex	In the case of species, indicates undetermined sex.
EER	entry error	The recorded value is known to be incorrect but the correct value cannot be determined to enter a correction.
OTL	data point outlier	When a series of data are plotted and analyzed, this point is obviously not within the normal distribution of the data, and eliminated from further analysis.

11.0 Quality Control Reports to Management

A progress report outlining the achievement of the Quality Assurance Objectives will be provided to the Program Manager at the end of the project. The Project Manager will be notified immediately, however, if substantive changes are made to the QAPjP. The Quality control report will include a summary of the results of audits that were conducted, data quality assessment, and the corrective actions that were taken. Quality control reports will be provided to the Project Officer and QA Manager at EPA-GLNPO and the Biota Work Group.

12.0 References

12.1 Auer, N. A. 1982. Identification of larval fishes of the Great Lakes basin with emphasis on the Lake Michigan drainage. 744 pp. Spec. Publ. 82-3, Great Lakes Fishery Commission, Ann Arbor, MI.

12.2 Bowen, S. H. 1983. Quantitative description of the diet, p. 325-336. In *Nielson, L. A. and Johnson, D. L. (eds.) Fisheries Techniques.* American Fisheries Society, Bethesda, MD. 468 pp.

12.3 Becker, G. C. 1983. Fishes of Wisconsin. 1052 pp. University of Wisconsin Press, Madison, WI.

12.4 Elliott, R. F 1993. Feeding habits of chinook salmon in eastern Lake Michigan. M.S. Thesis, Michigan State University, Lansing, MI, 108 pp.

12.5 Elliott, R. F and eight other authors. 1986. Conducting diet studies of Lake Michigan piscivores, a protocol. U.S. Fish and Wildlife Service, Green Bay fisheries Resources Office, Report No. 96-2.

12.6 Miller, M. A. and M. E. Holey. 1992. Diets of lake trout inhabiting nearshore and offshore Lake Michigan environments. J. Great Lakes Res. 18(1):51-60.

12.7 Nielson, L. A. and Johnson D. L. eds. 1983. Fisheries Techniques. American Fisheries Society, Bethesda, MD. 468 pp.

12.8 Scott, W. B. and E. J. Crossman. 1973. Freshwater fishes of Canada. Bulletin 184. Fish. Res. Board Can. 966 p.

Appendix A. Standard Operating Procedure for Sampling Coho Salmon

This SOP is intended to provide a step by step procedure for collecting measuring, preserving and transporting Coho salmon and stomach contents from coho salmon for the Enhanced Monitoring Program Lake Michigan Mass Balance.

1.0 Overview

Coho salmon samples will be collected at various region within Lake Michigan in order to measure contaminant concentrations in the fish tissue of PCBs, Mercury, and trans-nonachlor and to examine the diet of the salmon by evaluating the stomach contents. Specific details of the study are documented in the Lake Michigan Mass Balance work plan and in the QA project plan. Critical and non-critical associated information, as follows, will be recorded:

Critical	Non-critical
Location	Fin clip
Date of sample	Sex
Sample length	Stomach fullness
Sample weight	Sample depth
Age	Water temperature
Physical characteristics	
Capture Time	
Sample Time	
Preservation Time	

Two techniques will be used to collect samples: contaminant sampling and diet sampling. Of primary importance is the collection of fish samples for contaminant analysis which must be collected, prepared, and preserved as soon as possible for transport to the laboratory for analysis. These samples will be collected by USFWS personnel while on a chartered fishing vessel. Therefore, there is a good chance that both critical and non-critical measurements will be taken. Locational accuracy will also be much improved. Diet sampling will involve the collection of samples after they arrive from various fishing vessels and sport fisherman. Due to various types of locational equipment (some fisherman may not have sophisticated equipment), locational accuracy may be low and non-critical measurements may not be collected. However, critical measurements will occur when fish are collected and the same techniques will be used as those aboard the fishing vessel.

1.1 Summary of Method

Samplers will visit the ports (weekly/daily) in the regions mentioned in the Sampling QAPjP to check for catches. Boats will be chartered as frequently as necessary in order to collect the minimum number of samples (25) for contaminant analysis is each region within the specified time frame. The following sampling activities will take place and are discussed in detail in the order listed.

1) Collection of sample
2) Size measurement
3) Scale collection
4) Stomach removal/preservation
5) Data reporting
6) Sample labeling
7) Sample preservation and storage
8) Waste disposal and clean-up
9) Sample shipment

1.2 Safety

In any field operation, emphasis must be place on safety. Samplers must be aware of the potential safety hazards to which they are subjected. Follow all safety protocols and equipment guidelines, and be prepared for emergency situations. The sampler is responsible for his/her safety from potential hazards.

1.3 Equipment check and calibration

Check to make sure all equipment and supplies are available in required amounts. The following is a list of all needed equipment and consumables.

1.3.1 Serviceable Equipment

Fishing vessel equipped with navigational instruments and appropriate sampling gear to catch coho salmon.
Ice chests, including appropriate amount of ice or freeze packs
5-gallon plastic bucket (diet sampling only)
Measuring board (mm markings required)
Spring or electronic scale (1-10 Kg, 0.1 Kg markings required)
Calibrating weight
Dissecting pan
Dissecting knives
Thermometer

1.3.2 Consumable Equipment

Dissecting gloves for preserving and handling fish
Aluminum foil
Fish storage bag
Whirl-pac bags
Formalin (10-15% and full strength for mixing)
Sample labels
Reporting sheet
Marking equipment
Scale envelopes
Cleaning sponge and brush

1.3.3 Calibration and Standardization

Equipment necessary for calibration and the required frequency can be found in table 1.

Table 1. Equipment Calibration and Required Frequency

Instrument	Calibration Technique	Frequency	Acceptance Criteria
Thermometer	Ice bath and boiling water	1/year	+/- 2 degrees
Locational Device	Calibration to a standard of known Lat and Long	per trip	+/- .25 Km
Measuring Board	Check against second device	1/year	+/- 2 mm
Scale	Check against a standard S class weights 1, 5, 10, 25 kgs.	daily	+/- .1 kg

2.0 Procedures

2.1 Collection Of Contaminant Samples

Contaminant samples will be collected on-board a chartered or USFWS owned vessel using angling equipment.

2.1.1 Throughout each season, contract charter operators to fish for coho salmon in areas where coho are currently or are most likely to be caught. Verify that chartered vessels will have on-board adequate instrumentation and gear to catch fish and establish the location, time, and depth of capture. Samples of age 1.0 coho before they are stocked into the lake will be sampled at the state fish hatcheries where they are reared.

2.1.2 For each coho salmon captured, record all site and sample identification data specified on the Field Data Sheet, on two I.D. Labels, and on a whirl-pac bag (see attached examples).

Note: Data recorded will include: Objective (contaminant, diet, audit) Gear, Lake, Region, Nearest Port, Lat/Long or Statistical Grid, Species, Date, I.D. number, Lake Depth/Capture Depth, Water Temperature, Time Of Capture/Time Of Sampling, Field Qualifier Flag, Collectors Name.

Immediately after capture:

2.1.3 Determine and record:

Maximum Total Length (mouth closed and caudal fin dorso-ventrally compressed to nearest mm) using the measuring board.

Total Weight (0.1 kg) using the spring or electronic balance. For the hatchery sample, weigh fish with an electronic balance to the nearest 0.1 g.

2.1.4 Remove at least five scales (from just above the lateral line and below the posterior insertion of the dorsal fin) with a clean knife and place in the scale envelope. Record on the label the fish length, weight if taken, date, location sampled, and sample number.

2.1.5 Line the examination tray or measuring board with foil and place the coho on the board or in the tray. Make a 3-5 inch incision with a clean knife in the belly of the fish. Determine and record the sex and physical characteristics. Pull out and remove the stomach (anterior esophagus to pyloric sphincter) and all its contents. The spleen and any other organs that may be attached to the stomach should be removed and left inside the fish. Make a small slit in the stomach to allow preservative to enter, and place in the whirl-pac bag. If the stomach appears empty, open the stomach completely to verify that it is completely void. Indicate so on the field data sheet. Void stomachs do not need to be kept. Pack the whirl-pac bag with stomach contents on ice until you return to port where they can be safely preserved (see 2.1.9).

2.1.6 Maintaining all body fluids within the foil, wrap the coho completely with the foil lining the measuring board and attach one I.D. label to the foil. Place wrapped fish in a 4 mil polyethylene bag, seal the bag and attach the other I.D. label.

2.1.7 Place the bagged fish in a cooler and pack with ice until it can be transferred to a freezer and frozen. Verify that the samples were frozen within 24 hours by recording the date and time when the fish was captured, sampled, and placed in the freezer.

2.1.8 Clean/rinse all equipment thoroughly that comes in contact with sampled fish between sampling each fish.

2.1.9 After returning to port, preserve the stomach contents in the whirl-pac bag with at least 2X their volume of 10% formalin. Seal the bag and place in the sealable 5 gallon bucket. When handling formalin, wear rubber gloves, keep away from fish, food, and other people, stay in a well ventilated area, and thoroughly rinse with water any object or surface that comes in contact with the formalin.

2.1.10 Keep all samples in your possession and in their preserved state (on ice, frozen, in formalin etc.) until they have been delivered to the laboratory where the subsequent analysis will occur. For foil-wrapped coho, this is the NBS-Great Lakes Center in Ann Arbor. For preserved stomachs and all Field Data Sheets, this is the FWS Green Bay FRO. Transport only in FWS approved vehicles. With each transfer between locations, record the date and sample ID number to verify sample integrity.

2.1.11 Contaminant samples will be composited by the GBFRO. Samples for contaminant analysis will be taken throughout each season sampled. The five fish composites will be prepared after each season has been sampled. Each season is roughly eight weeks long (56 days). Composites will be combine as similar as fish as possible based on size, location of capture, and when possible, sex in consultation with the LMMB modelers.

2.2 Collection of Diet Samples

In addition to diet samples (stomachs) collected from coho sampled for contaminant analysis, diet samples will be collected at port from various fishing vessels.

2.2.1 As soon as anglers/operators return to shore, obtain permission to examine and sample their catch. Permanent cleaning stations located near boat launches and marinas provide ideal locations for this sampling. To ensure that as representative a sample as possible is collected, sample from as many boats as possible over all hours of the day, and sample all coho creeled by anglers aboard an individual boat.

2.2.2 For all fish sampled, record all site and sample identification data specified on the Field Data Sheet, and on a whirl-pac bag (see attached examples).

Note: Data recorded will include: Objective (contaminant, diet, audit) Gear, Lake, Region, Nearest Port, Lat/Long or Statistical Grid, Species, Date, I.D. number, Lake Depth/Capture Depth, Water Temperature, Time Of Capture/Time Of Sampling, Field Qualifier Flag, Collectors Name.

As soon as possible after capture:

2.2.3 Determine and record:

Maximum Total Length (mouth closed and caudal fin dorso-ventrally compressed to nearest mm) using the measuring board. Flex fish several times if rigor mortis has set in so that fish lays flat on the board.

Total Weight (0.1 kg) using the spring or electronic balance (when time permits).

2.2.4 Remove at least five scales (from just above the lateral line and below the posterior insertion of the dorsal fin) with a clean knife and place in the scale envelope.

2.2.5 Make a 3-5 inch incision in the belly of the fish. Determine and record the sex and the clinical condition of the fish. Pull out and remove the stomach (anterior esophagus to pyloric sphincter) and all its contents. Return the fish to the angler/operator. Make a small slit in the stomach to allow preservative to enter, and place in the whirl-pac bag. If the stomach appears empty, open the stomach completely to verify that it is completely void. Indicate so on the field data sheet. Void stomachs do not need to be kept.

Temporarily place the whirl-pac bag with stomach contents on ice until they can be safely preserved (see 2.2.7). Stomachs from hatchery sampled fish will not be taken.

Note: Step 2.2.5 may be done after the fish has been filiated if the angler/operator prefers to clean the fish before the stomach is removed.

2.2.6 Preserve the contents in the whirl-pac bag with at least 2X their volume of 10% formalin. Seal the bag and place in the sealable 5 gallon bucket. When handling formalin, wear rubber gloves, keep away from fish, food, and other people, stay in a well ventilated area, and thoroughly rinse water any object or surface that comes in contact with the formalin. If extra personnel are available, preservation can be done as soon as the stomach contents are removed. If not, wait until all fish have been worked up, packed, and stored.

2.2.7 Keep all samples and data sheets in your possession until they have been delivered to the FWS Green Bay FRO. Transport only in FWS approved vehicles. Upon return to the GBFRO, make photocopies of the original Field Data Sheets to be kept on file at a location other than where the original data sheets are filed. With each transfer between locations, record the date and sample ID number to verify sample integrity.

Appendix B. Standard Operating Procedure for Lab Analysis of Coho Salmon Stomachs and Data Entry

This SOP is intended to provide a step by step procedure for examining and quantifying the contents of the stomachs sampled, and then entering all data on the computer as part of determining the diet of coho salmon for the Enhanced Monitoring Program Lake Michigan Mass Balance Study.

1.0 Overview

Contents of stomachs collected from Lake Michigan coho salmon will be identified, enumerated, and weighed. Data will be recorded on data sheets and entered into a computer data base.

Summary of Method

Stomachs will be rinsed to free excess formalin and allow for safe handling of the sample. Fish found in the stomachs will be identified to species, assigned a percent digested state, measured and weighed. Invertebrates will be identified into the appropriate taxon and weighed as a group. The age of the fish will be determined by a length frequency analysis and a subsample will be verified through scale aging. Reconstruction of the prey length will also be used to determine reconstructed weight. The data will be entered into database (FoxPro) and spreadsheet (Lotus) software, verified, and summary reports created.

2.0 Safety

In any lab operation, emphasis must be place on safety. Samplers must be aware of the potential safety hazards to which they are subjected. Follow all safety protocols and equipment guidelines, and be prepared for emergency situations. The sampler is responsible for his/her safety from potential hazards.

3.0 Equipment Check and Calibration

Check to make sure all equipment and supplies are available in required amounts. The following is a list of all needed equipment and consumables.

3.1 Equipment

Serviceable Equipment

Fume Hood
Rinse Water Supply and rinsing bath
Rinse Tray
Dissecting Tray and Tools (scalpel, forceps, scissors)
Dissecting Microscope
Electronic Balance and calibration weights
Plastic Ruler (mm divisions)

Glass Specimen Jars
Scale Press
Scale Projector/Reader
Computer & Printer (with hard drive, disk drive, and necessary software)

Consumable Equipment/Supplies

Weighing trays
Formalin (5%)
Rubber Gloves
Impression Acetate
Paper Toweling
Plastic Bags (2-5 gal)
Reporting Sheets and Marking devices

3.2 Calibration and Standardization

Equipment necessary for calibration and the required frequency can be found in Table 1.

Table 1. Equipment Necessary for Calibration and Required Frequency.

Instrument	Calibration Technique	Frequency	Accepted Criteria
Plastic Ruler	Check against second device	Start-end/season	±1 mm
Electronic Balance	Use calibration weight methods as prescribed by scale manufacturer	Daily	±0.1 g
Computer	Virus scan	Every boot-up	No viruses

4.0 Procedures

The following procedures will be discussed:

Sample preparation
Identification and quantification of prey items
Numeration and estimation (for invertebrates)
Length measurement and
Weight measurement and estimation
Archiving representative samples
Mounting and ageing scales
Data Recording
Data Entry
Verifying Data
Determining conversion data and developing formula

4.1 Analysis of Stomach Contents

Proceed with the following steps in a well ventilated (fume hood operating if necessary) area intended for work of this nature. Wear rubber gloves when handling preserved prey items, have equipment set up, calibrated and ready for use, and start with and maintain a clean work area.

4.1.1 Open whirl-pac bag, pour contents into rinsing container with 365 micron mesh screen, flush with rinse water until contents are free of excess formalin, remove from rinse container and allow to drip free of excess water.

4.1.2 For each prey fish, identify to species, assign an estimated percent digested state, measure (nearest mm) and weigh (nearest 0.1 g for large items and 0.02 g for small prey items). For identification of fish, Becker (1983), Scott and Crossman (1973), Auer (1982), and Elliott et al. (1996) will be used as reference material. In addition, during the training period we will develop our own reference specimens for identification purposes. Record data as indicated on the lab data sheet (see attached). Measure length to level of precision allowed depending on how much of the fish is remaining. Order of priority is: 1) maximum total length, 2) standard length, 3) vertebral column length, and 4) length of as many vertebrae as possible. For those fish or parts of fish that can not be positively identified, record as unidentified.

4.1.3 For invertebrates, group into appropriate taxon and weigh (nearest 0.02 g). Either count directly or estimate indirectly the total number based on weight (at least 0.5 g or 25 individuals) of a known number representative of the group. Determine an average length and digested state for each taxon group. Record data as indicated on the lab data sheet.

4.1.4 If the identification of a prey item is uncertain, the item will be examined by a second identifier and compared to the reference collection of diet items prepared for training. If an agreement on the identification can not be reached, the prey item shall be recorded as unidentifiable.

4.1.5 Throughout the stomach analysis, set aside and preserve in glass jars with 5% formalin, examples of each species of prey fish and taxonomic group of invertebrate. Examples should represent the range of both digested conditions and sizes of prey observed and be able to document the methods of identification and quantification used in this analysis. Label saved samples as to their source (sample I.D. number), their identification.

4.1.6 Package contents back into whirl-pac bag and preserve. To facilitate easy retrieval of samples for quality control verification, package samples from similar locations and dates together (groups of 10-25) into clear plastic bags. Maintain the reference collection for identification until the final project report is accepted by EPA.

4.1.7 Make photocopies of each completed Lab Data Sheet and file at designated separate locations.

4.2 Aging Coho Scales

The method aging fish by length frequencies or scales, and verifying age is adequately described in fisheries Techniques (Nielson and Johnson 1983). The following highlights the procedure to use.

4.2.1 Prepare a length frequency histogram by 10 mm increments of all the coho samples for each season sampled. Only two year classes of coho will be in the lake at any one time, therefore separation of age by length should be obvious. Based on the length of each sample, assign an age based on the age/length frequency histogram developed. To verify the ages determined from the length frequency analysis, especially if ages overlap in length, scales will be aged.

4.2.2 Remove scales from the envelope and clean them in a solution of 5% Clorox in water with brush or wooden stick.

4.2.3 Place cleaned scales on the glass plate of a microfiche reader, add a few drops of water, and cover with a glass slide. Examine all scales to determine which scale exhibits the most representative growth pattern of the available scales. Age that scale by counting annuli observed. Record the age using the European method (stream years lake years) on the scale envelope along with the readers initials.

4.2.4 To verify, re-age those fish that would have different ages assigned using the two methods. Also, re-age enough additional fish that have sizes nearest the size division indicated by the length frequency analysis so that at least 5% of all fish are re-aged. Re-aging is to be done by both the individual who originally aged the fish and a second individual who has not yet aged that fish, both using the same methods as in Section 4.2.2. Assign and record final age on the envelope based on consensus reached by both individuals or by the majority if a third independent reader is necessary.

4.3 Standard Measurements for Developing Conversion Equations

To allow reconstruction of total prey length and weight from partial length measures, and to allow the conversion of total length and weight of preserved prey to length and weight of fresh prey (or visa-versa), the following procedures will be followed.

4.3.1 For up to 50 intact individuals representing all sizes of each prey fish species (5 per 1/10 of size range encountered from preserved stomachs), measure total length and weight, dissect the fish and measure (nearest mm) the standard length, the vertebral column length, the length of as many vertebrae as possible, and count the total number of vertebrae. Record these measures on a lab data sheet identified as Standard Measures.

4.3.2 When in the field, the Project Field Manager will conduct independent measurements of enough stomach contents (Section 4.1) so that representing all sizes and digested states will be identified and measured prior to preservation for later lab analysis. Data will be recorded on a lab data sheet identified as Standard Measures.

4.3.3 Enter all data from Standard Measurements Data Sheets into database in prescribed fields.

4.3.4 Develop the following conversion equations with associated errors for each prey species:

Vertebrae length to vertebral column length and total length
Vertebral column length to standard length and total length
Standard length to total length
Total length to wet weight
Preserved total length to fresh total length
Preserved wet weight to fresh wet weight

4.3.5 Compare to similar equations developed from other studies to determine validity.

4.4 Data Entry and Verification

4.4.1 Maintain three independent copies of the data (on hard drive, on disk, and hard copy printout) in different locations and update/backup each on a daily basis when altered.

4.4.2 Enter all data from Field and Lab Data Sheets into database in prescribed fields.

4.4.3 Using equations determined in 4.3, calculate missing total length measures from partial length measures and add to the database.

4.4.4 Identify and correct inaccuracies in data recording and entry, and identify outliers as follows:

Plot data variables, identify peripheral values, and cross-reference with original data records. Example plots include:

Predator length vs. weight	Predator length vs. date (by age)
Prey length vs. date	Prey length vs. weight (by length type)

Query all data fields for values above and below expected values and cross-reference with original data records.

Visually compare and verify each computer record with field and lab records on original data sheets.

Resolve with the data collector any possible errors in recording.

Identify data points as an outlier, that after completing the above, still appears to be outside the range of expected values.

LAKE MICHIGAN MASS BUDGET/MASS BALANCE PROJECT
Coho Salmon Contaminant Sample

SEASON	REGION	AGE	
SP SU FA	WE - S C N	0 1 2	LENGTH (mm)
			WEIGHT (kg)
			SEX (M,F)

DATE:
(YEAR - MONTH - DAY) FISH # COLLECTOR I.D.

__ - __ - __ - __ - __

For sample collection information contact: USFWS Green Bay Fishery Resources Office
Mark Holey - Project Leader ph: 414-433-3803

LAKE MICHIGAN MASS BUDGET/MASS BALANCE PROJECT
Coho Salmon Contaminant Sample
SEASON REGION AGE
SP SU FA WE - S C N 0 1 2 LENGTH (mm)
WEIGHT (kg)
SEX (M,F)
DATE:
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LAKE	SEASON	REGION	OBJECTIVE	GEAR
MI	SP SU FA	W I S C N		

Date _____

Page ___ of ___

YEAR	MONTH	DAY	FISH #'s	COLLECTOR I.D.	LOCATION	CONDITIONS
DATE -	-	-	-	-		

USFWS
Green Bay FRO
Field Data Sheet

FISH #	SPECIES	WEIGHT ( )	LENGTH ( )	CUP	Scales Head	SEX	STOMACH	CLINICAL-CONDITION-SCARS	LOCATION: (Grid, Lat/Long)	CAPTURE DEPTH,DOWN,TEMP	TIMES: CAPTURE	SAMPLE	FREEZE	FLAG

Transfer DATE and TIME History: GBFRO Freezer: _____/_____ NBS LAB: _____/_____ Sheet Copied: _____ Data Entered: _____

USFWS, Green Bay FRO, Lab Data Sheett

OBJECTIVE: ______________________________

Sheet Copied: _____ Data Entered: _____

LAKE: MI

REGION: W I S C N

DATE: YEAR ____ - MONTH ____ - DAY ____ - FISH #'s ____ - COLLECTOR I.D. ____

LOCATION ____

PRESERVED STATE ____

Date __________

Page ___ of ___

FISH #	SPECIES	D. STATE	WEIGHT (0.1 gr)	LENGTHS (mm): Total (TL)	Standard (SL)	Vertebral (VL)	# vert/VL	Ant. # vert/l	Post. # vert/l	??: # vert/l	INITLS	DATE	FLAG

State of Wisconsin
Department of Natural Resources

Form 4100-145

CHAIN OF CUSTODY RECORD
7-87

Author(s)	Title/Work Station	Telephone No. (include area code)
Property Owner	Property Address	Telephone No. (include area code)

Split Samples: Offered? ☐ Yes ☐ No (Check One)
Accepted? ☐ Yes ☐ No (Check One) Accepted By: _____
Signature

Field ID No.	Date	Time	Sample Type		Station Location Sample Description	Lab ID Number	No. of Containers	Comments
			Comp	Grab				

I hereby certify that I received, properly handled, and disposed of these samples as noted below:

Relinquished By (Signature)	Date/Time	Received by: (Signature)

Disposition of Unused Portion of Sample

Audit Finding

Audit Title: _____ Audit #: _____ Finding #:_____

Finding:

Discussion:

Audit Finding
Response Form

Audit Title: _____ Audit #: _____ Finding #:_____

_____

Finding:

Cause of the problem:

Actions taken or planned for correction:

Responsibilities and timetable for the above actions:

Prepared by: _____ Date: _____

_____

Reviewed by: _____ Date: _____

Remarks: