

# Summary of Mercury Focuses

LMMB Project QA and Data Workgroups  
Peer Review Meeting

29-30 April 1999

Chicago, IL

# Quality Assurance Policy

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- QA program goal:
  - Assure that the quality of data derived from EDCAs is known (i.e., precision, bias, detectability, completeness, representativeness, and comparability) and meets the needs for which the data were intended.
- LMMB goals:
  - Develop the predictive ability to determine the environmental benefits of specific load reduction scenarios for toxic substances and the time required to realize those benefits
  - Improve our understanding of key environmental processes which govern the cycling and bioavailability of contaminants within relatively closed ecosystems

# Media for Mercury Focuses

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- MDLH - Open Lake
- MIAH - Atmospheric
- WWTH - Tributary
- LLSH - Sediment
- MNPH - Plankton
- MIFH - Fish

# Project Investigators for Each Mercury Focus

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- MDLH - *Robert Mason, Chesapeake Biological Laboratory*
- WWTH - *Jim Hurley, University of Wisconsin*
- MIAH - *Jerry Keeler and Matt Landis, University of Michigan*
- LLSH - *Ronald Rossmann, USEPA Large Lakes Research Station*
- MNPH - *Ed Nater, University of Minnesota*
- MIFH - *Jerome Nriagu, University of Michigan*

# Sample Collection Methods for MDLH and WWTH

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- Field sampling using strict trace metals protocols including pre-cleaned teflon bottles and equipment, sampling personnel outfitted in suits and gloves, and use of “clean hands/dirty hands” techniques

## *MDLH*

- Teflon-lined Go-Flo bottles attached to Kevlar line with non-metallic weight
- Aliquoted and filtered in clean room onboard ship
- Particulate samples collected onto 0.8  $\mu\text{m}$  quartz fiber filters

## *WWTH*

- Pumped through a teflon sample weight, teflon sampling tube, and C-flex pumphead tubing using a peristaltic pump
- Dissolved samples collected with in-line filtration
- Composite of upper and lower depths

# Sample Collection Method for MIAH

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- Particulate
  - Filter pack assembly containing 47mm glass fiber filter housed in sampling box with attached vacuum deployed 3m above ground
  - 10-30 lpm for 12-24 hours
- Precipitate
  - Collected on event basis May-October/weekly basis for remainder of sampling period
  - Automated sensor grid activated by precipitation - opens lid of borosilicate funnel/1L Teflon bottle assembly
- Vapor
  - Two traps in series; gold coated borosilicate glass bead trap in quartz tube (with glass fiber pre-filter) housed in sampling box 3m above ground and maintained at 93°C to prevent condensation

# Sample Collection Method for LLSH

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Trap  
Samples



Sediment Traps  
and Wet  
Sample Splitting

Ponar  
Samples



Ponar Grab  
Sampler

Sub-Core  
Samples



Retrieved using a  
10cm tube inserted  
into Box-Core  
collected with  
Soutar Corer

# Sample Collection Methods for MNPH and MIFH

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## MNPH

Phytoplankton

Phytovibe with  
10µm Nitex netting  
and 700mL PVC cup

Zooplankton

Standard Vertical  
Zooplankton Net  
Tows with PVC cup

## MIFH

Whole fish were  
collected, aged, composited,  
and homogenized

Homogenization completed using a  
40 qt vertical cutter mixer (VCM),  
12 qt Stephan Machinery vertical  
cutter (UM 12), or a high speed  
2 qt Robot Coupe (RSI241)

# Sample Analysis Method for MDLH and WWTH

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- Analytical techniques outlined in EPA's Method 1631: *Mercury in Water by Oxidation, Purge and Trap, and CVAFS*

# Sample Analysis Method for MIAH

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- Particulate
  - Extracted from filter with 1.6M nitric acid utilizing microwave digestion
  - Oxidation, Purge and Trap, and CVAFS
- Precipitate
  - Oxidation, Purge and Trap, and CVAFS
- Vapor
  - Thermally desorbed from gold-coated bead trap at 500°C and carried into CVAFS analyzer
  - Vapor phase/not total gaseous phase mercury

# Sample Analysis Methods for LLSH and MIFH

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## *LLSH*

- Sample Digestion with 10% nitric acid microwave digestion/ automated digestion with 50% Aqua Regia and Potassium Permanganate
- CVAAS (PS200 system)

## *MIFH*

- Concentrated nitric acid microwave digestion under high pressure and temperature
- Tekran CVAFS Mercury Analyzer Model 2500

# Sample Analysis Method for MNPH

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- Samples are freeze-dried.
- Samples are placed in a PFA Teflon digestion vessel with a 1:1 concentrated sulfuric and nitric acid mixture, and then placed in a 70°C hot water bath overnight.
- Oxidation, Purge and Trap, and CVAFS

# Challenges Unique to MDLH

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- Data included lab duplicates of field duplicates, which somehow had to be linked through SAMPIDs.
  - A suffix was added to the SAMPID in order to link the appropriate results.
- Information in Field Remark Codes was not always reflected in Analytical Remark Code and Exception to Method fields in lab file.
- Files were compared and adjusted to ensure same information was included.
- The REJ analytical remark code was inappropriately assigned in some instances.
  - Led to discussions and decisions regarding correct use of code.
  - Cases had to identified and resolved with the PI.

# Challenges Unique to LLSH

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- LLSH was one of the first focuses to be verified that included split and composite samples. Issues related to data reporting and processing the data through RDMQ had to be addressed.
- Sediment collection method codes were not a part of the database. Therefore, the QC Coordinator communicated with the PI to define unique codes and appropriate definitions in order that they could be added to the database.
- A “sample-specific” detection limit had not yet been defined. A new code was defined and added to the database.

# Challenges Unique to MNPH

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- Lab and field sample IDs did not correspond in the original data submission. The naming conventions used by the field and lab personnel were reviewed and the IDs were matched accordingly.
- The PI's assistant is no longer working on the project. Questions requiring his experience are time-consuming.
- Data included lab duplicates of field duplicates, which somehow had to be linked through SAMPIDs.
  - A suffix was added to the SAMPID in order to link the appropriate results.

# Challenges Unique to MIFH

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- Results were reported as an average of many results. In order to separate the results, lab notebooks were retrieved and the individual results entered into the data files.
- The original PI is no longer working on the project and therefore the current PI is relied on for his knowledge of the lab analyses that had been conducted.
- A new reporting standard was developed after the original submission of field data. The data had to be re-submitted according to the new standard, which is fairly complicated. Proper data reporting required extensive communication with the PI and is still in progress.

# Summary of QA Statistics - MDLH

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- Sensitivity
  - Daily Detection Limits
  - Mean: 0.063 ng/L
  - 8% of RFS samples below corresponding DDL
- Precision
  - System Precision
    - Particulate (>DDL): Mean RPD = 28% (n=16)
    - Total (<DDL): Mean RPD = 39% (n=1)
    - Total (>DDL): Mean RPD = 21% (n=13)
  - Analytical Precision
    - Particulate (<DDL): Mean RPD = 11% (n=1)
    - Particulate (>DDL): Mean RPD = 15% (n=47)
    - Total (<DDL): Mean RPD = 60% (n=3)
    - Total (>DDL): Mean RPD = 17% (n=68)

# Summary of QA Statistics - MDLH

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- Bias
  - System Bias: Could not be estimated with available QC data
  - Analytical Bias: Estimated through the preparation and analysis of laboratory performance check (LPC) samples
    - Mean LPC result = 1.1 ng, where 1.0 ng indicates 0% bias
- Variability due to Sampling and Analytical Measurement Uncertainty: Estimated using Bootstrap estimation procedure
  - Particulate: 28% of Variability due to Measurement Uncertainty
  - Total: 31% of Variability due to Measurement Uncertainty

# Summary of QA Statistics - MIAH

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- Sensitivity
  - System Detection Limit
    - Particulate: 1.0 pg/m<sup>3</sup>
    - Precipitate: 0.3 ng/L
    - Vapor: 0.2 ng/m<sup>3</sup>
  - All Particulate and Precipitate RFS results were above associated SDL; 1.53% of Vapor RFS results were below associated SDL
- Precision
  - System Precision
    - Particulate: Could not be estimated with available QC data
    - Precipitate: Mean RPD = 9.78% (n=33)
    - Vapor: Could not be estimated with available QC data
  - Analytical Precision
    - Could not be estimated with available QC data

# Summary of QA Statistics - MIAH

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- Bias
  - System Bias: Could not be estimated with available QC data
  - Analytical Bias: Estimated through the analysis of laboratory performance check (LPC) samples
    - Particulate: Mean LPC = -2.2%, where 0% indicates 0% bias
    - Precipitate: Mean LPC = 0.823%, where 0% indicates 0% bias
    - Vapor: Mean LPC = -1.51%, where 0% indicates 0% bias
- Variability due to Sampling and Analytical Measurement Uncertainty: Estimated using Bootstrap estimation procedure
  - Precipitate: 2.37% of Variability due to Measurement Uncertainty

# Summary of QA Statistics - WWTH

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- Sensitivity
  - Method Detection Limit = 0.1 ng/L
  - One RFS result was below the MDL
- Precision
  - System Precision
    - Dissolved (<5X MDL): Mean RPD = 45% (n=7)
    - Dissolved (>5X MDL): Mean RPD = 17% (n=34)
    - Total (<5X MDL): Mean RPD = 182% (n=1)
    - Total (>5X MDL): Mean RPD = 20% (n=46)
  - Analytical Precision
    - Dissolved (<5X MDL): Mean RPD = 14% (n=29)
    - Dissolved (>5X MDL): Mean RPD = 7.5% (n=338)
    - Total (<5X MDL): Mean RPD = 54% (n=1)
    - Total (>5X MDL): Mean RPD = 5.1% (n=381)

# Summary of QA Statistics - WWTH

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- Bias
  - System Bias: Could not be estimated with available QC data
  - Analytical Bias: Estimated through the preparation and analysis of laboratory spiked samples (LSFs)
    - Dissolved: Mean LSF recovery = 103%, where 100% indicates 0% bias
    - Total: Mean LSF recovery = 103%, where 100% indicates 0% bias
- Variability due to Sampling and Analytical Measurement  
Uncertainty: Estimated using Bootstrap estimation procedure
  - Dissolved: 13% of Variability due to Measurement Uncertainty
  - Total: 14% of Variability due to Measurement Uncertainty

# Summary of QA Statistics - LLSH

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- Sensitivity
  - Sample Specific Detection Limit (UDL)
  - Mean: 0.0070 mg/Kg
  - One RFS result was below associated UDL
- Precision
  - System Precision
    - Mean RPD = 38% (n=4)
    - Only four field duplicates were collected, field duplicates were not originally in the sampling plan
  - Analytical Precision
    - Mean RPD = 8.5% (n=30)

# Summary of QA Statistics - LLSH

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- Bias
  - System Bias: Could not be estimated with available QC data
  - Analytical Bias: Estimated through the preparation and analysis of standard reference materials (SRMs)
    - Mean SRM recovery = 92%, where 100% indicates 0% bias
- Variability due to Sampling and Analytical Measurement Uncertainty: Estimated using Bootstrap estimation procedure
  - 3.8% of Variability due to Measurement Uncertainty

# Summary of QA Statistics - MNPH

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- Sensitivity
  - Sample Specific Detection Limit (UDL)
  - Mean: 8.238 ng/g
  - One RFS result was below its associated UDL
- Precision
  - System Precision
    - Mean RPD = 19.83% (n=38)
  - Analytical Precision
    - Mean RPD = 11.15% (n=28)

# Summary of QA Statistics - MNPH

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- Bias
  - System Bias: Could not be estimated with available QC data
  - Analytical Bias: Estimated through the preparation and analysis of standard reference materials (SRMs) and laboratory spiked samples (LSFs)
    - Mean SRM result = 42.99 ng/g, where 44 ng/g would indicate 0% bias
    - Mean LSF recovery = 103.2%, where 100% indicates 0% bias
- Variability due to Sampling and Analytical Measurement Uncertainty: Estimated using Bootstrap estimation procedure
  - 13.36% of Variability due to Measurement Uncertainty

# Blank Results: MDLH

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|                      | Mean        | Minimum    | Maximum    | Standard Deviation |
|----------------------|-------------|------------|------------|--------------------|
| • FRB <sub>P</sub> : | -0.02 ng/L  | -0.32 ng/L | 0.099 ng/L | 0.13               |
| • RFS <sub>P</sub> : | 0.11 ng/L   | 0.027 ng/L | 0.30 ng/L  | 0.057              |
| • FRB <sub>T</sub> : | 0.0063 ng/L | -0.10 ng/L | 0.097 ng/L | 0.059              |
| • RFS <sub>T</sub> : | 0.32 ng/L   | 0.037 ng/L | 0.77 ng/L  | 0.12               |

FRB = Field Reagent Blank

# Blank Results: WWTH

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|                      | Mean      | Minimum    | Maximum   | Standard Deviation |
|----------------------|-----------|------------|-----------|--------------------|
| • FBT <sub>T</sub> : | 0.54 ng/L | 0.091 ng/L | 1.1 ng/L  | 0.32               |
| • FRB <sub>T</sub> : | 0.54 ng/L | 0.097 ng/L | 1.2 ng/L  | 0.33               |
| • RFS <sub>T</sub> : | 7.8 ng/L  | 0.54 ng/L  | 190 ng/L  | 13                 |
| • FFB <sub>D</sub> : | 0.51 ng/L | 0.12 ng/L  | 0.97 ng/L | 0.29               |
| • RFS <sub>D</sub> : | 1.8 ng/L  | 0.20 ng/L  | 40 ng/L   | 3.2                |

FBT = Field Tubing Blank

FRB = Field Reagent Blank

FFB = Field Filter Blank

# Blank Results: MIAH

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|                      | Mean                     | Minimum                 | Maximum                | Standard Deviation |
|----------------------|--------------------------|-------------------------|------------------------|--------------------|
| • FTB <sub>A</sub> : | 0.0654 ng/m <sup>3</sup> | 0.000 ng/m <sup>3</sup> | 1.74 ng/m <sup>3</sup> | 0.262              |
| • RFS <sub>A</sub> : | 2.49 ng/m <sup>3</sup>   | 1.16 ng/m <sup>3</sup>  | 22.2 ng/m <sup>3</sup> | 1.85               |
| • FTB <sub>D</sub> : | 11.3 pg/m <sup>3</sup>   | 0.000 pg/m <sup>3</sup> | 79.1 pg/m <sup>3</sup> | 17.7               |
| • RFS <sub>D</sub> : | 30.7 pg/m <sup>3</sup>   | 1.05 pg/m <sup>3</sup>  | 494 pg/m <sup>3</sup>  | 44.6               |

FTB = Field Trip Blank

A = Vapor

D = Particulate

# Blank Results: LLSH and MNPH

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## *LLSH*

|        | Mean         | Minimum       | Maximum      | Standard Deviation |
|--------|--------------|---------------|--------------|--------------------|
| • LRB: | 0.0029 mg/kg | 0.00023 mg/kg | 0.0084 mg/kg | 0.0020             |
| • RFS: | 0.68 mg/kg   | 0.002 mg/kg   | 27 mg/kg     | 2.3                |

## *MNPH*

|        | Mean       | Minimum    | Maximum    | Standard Deviation |
|--------|------------|------------|------------|--------------------|
| • LRB: | 0.06110 ng | 0.0000 ng  | 0.1000 ng  | 0.05020            |
| • RFS: | 44.73ng/g  | 10.90 ng/g | 376.3 ng/g | 38.65              |

LRB = Lab Reagent Blank

# Completeness of Mercury Data

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|      | % Invalid | % Flagged |
|------|-----------|-----------|
| MDLH | 0.4       | 38.4      |
| WWTH | 4.2       | 10.3      |
| MIAH | 0         | 0.8       |
| LLSH | 0         | 15.1      |
| MNPH | 0         | 83.4*     |

\* 72.3% of data were flagged EHT (Exceeded Holding Time)

# Representativeness and Comparability of Mercury Data

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- Representativeness
  - Estimates of precision using field duplicates can serve as an estimate
- Comparability
  - Assessed utilizing historical data sets
    - Some historical data sets may not be comparable because of the current use of clean techniques
    - The dynamic environment may result in data sets not being able to be compared

# Key Information to be Transferred to GLENDA for Future Use

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- Statistical assessments of the data
- Exception to method text
- Definitions of codes
- Flagging criteria
- Linking between samples and focuses