Low Level Mercury Sample Collection / Analysis and Low Flow Sampling

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MWEA 2010
Lab Practices Seminar

June 15, 2010
• Bio-accumulation in food chain
OH YEAH?!!
WELL, I CAUGHT ONE
WITH A MERCURY LEVEL
THAT WAS THIS BIG!!!
Water Regulations

- **Great Lakes Water Quality Agreement 1987**

- **National Toxics Rule (40 CFR 131.36)**

## Mercury - Water Quality Criteria

<table>
<thead>
<tr>
<th>Criterion</th>
<th>NTR (ng/L)</th>
<th>Great Lakes (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freshwater Acute</td>
<td>2400</td>
<td>1440</td>
</tr>
<tr>
<td>Freshwater Chronic</td>
<td>12</td>
<td>770</td>
</tr>
<tr>
<td>Marine Acute</td>
<td>2100</td>
<td></td>
</tr>
<tr>
<td>Marine Chronic</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>Human Health</td>
<td>140</td>
<td>1.8</td>
</tr>
<tr>
<td>Wildlife</td>
<td></td>
<td>1.3</td>
</tr>
</tbody>
</table>

Source - US EPA Office of Water
Why is it hard to collect representative water samples for mercury?

• Regulatory limits are low
• Ambient water concentrations are low
• Test method is very sensitive to low concentrations
• Mercury is a common contaminant in solids
• Hard to prevent exposure to solid materials
Common Wastewater Results continued
<table>
<thead>
<tr>
<th>Method</th>
<th>Max. MDL</th>
<th>Actual MDL</th>
</tr>
</thead>
<tbody>
<tr>
<td>1631E</td>
<td>0.20 ng/L</td>
<td>0.11 ng/L</td>
</tr>
</tbody>
</table>
Where did it come from?

- **Manufacturing and natural processes**
  - industrial processes (e.g., Chlor-alkali plants)
  - volcano
- **Combustion**
  - fossil fuels (e.g., coal, oil)
  - municipal, medical, and hazardous waste incineration
- **Equipment**
  - thermometers
  - batteries
  - switching equipment
  - industrial control instruments
- **Additive**
  - paint
  - catalysts
  - turf products
  - explosives
<table>
<thead>
<tr>
<th><strong>Reagents</strong></th>
<th><strong>Environment</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>air - vapor/particulates</td>
</tr>
<tr>
<td>HCl</td>
<td>airborne dirt and dust</td>
</tr>
<tr>
<td>soap</td>
<td>water - particulates</td>
</tr>
<tr>
<td>solvents</td>
<td>settled or floating dirt and debris</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Field Personnel</strong></th>
<th><strong>Equipment</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>gloves</td>
<td>sample bottle</td>
</tr>
<tr>
<td>clothing</td>
<td>pump</td>
</tr>
<tr>
<td>dental work</td>
<td>tubing</td>
</tr>
<tr>
<td>skin</td>
<td>extension pole</td>
</tr>
<tr>
<td></td>
<td>dipper</td>
</tr>
<tr>
<td></td>
<td>filter</td>
</tr>
</tbody>
</table>
Sample Collection

- Methods 1669 & 1631
- Collection technique
- Cleanliness
- QC (equipment & field)
• Fluoropolymer or borosilicate glass bottle
• Double bagged bottle(s)
• **Dirty Hands**
  – operation of machinery, sampler preparation, outside bag handling
• **Clean Hands**
  – inside bag handling
  – sample bottle
  – sample transfer
Two-Person Clean Hands / Dirty Hands

- DH already opened outer bag
- CH opens inner bag
- CH handles bottles
1669 Collection Technique

- **US EPA Office of Water** video demonstrating “clean hands / dirty hands”
- **Direct manual surface sampling** (Sec. 8.2.5)
- **Grab sampling device** (8.2.6)
- **Depth sampling with jar** (8.2.7)
- **Continuous flow sampling with peristaltic pump** (8.2.8)
- **In-line sample filtration** (8.2.8.7)
- **Avoid exposure to rain (or snow)**

18 min. EPA video
1669 / 1631 Field & Equipment QC “Requirements”

- **Equipment blanks** (1669 Sec. 9.3)
  - bottle blanks
  - sampling equipment blanks - all equipment
- **Field blanks** (10% frequency) (1669 Sec. 9.4)
  - pretested water available from TestAmerica
- **Field duplicate** (10% frequency) (1669 Sec. 9.5)
- **MS/MSD** (1 pair per 10 site samples) (1631 Sec. 9.3)
- **Trip blank** (not in methods, available from TestAmerica)
- No metal / sample contact
- “Pretested” bottles, pump tubing, filters
- Equipment that contacts sample
  - manufactured clean
  - chemically cleaned
    - soaked in 5-10% HCl
    - rinsed with reagent water
  - double bagged
- Portable “glove box”
US EPA 1669 and 1631 Performance Based Methods

• 1669
  – Note: This document is intended as guidance only. Use of the terms "must," "may," and "should" are included to mean that EPA believes that these procedures must, may, or should be followed in order to produce the desired results when using this guidance. In addition, the guidance is intended to be performance-based, in that the use of less stringent procedures may be used so long as neither samples nor blanks are contaminated when following those modified procedures. Because the only way to measure the performance of the modified procedures is through the collection and analysis of uncontaminated blank samples in accordance with this guidance and the referenced methods, it is highly recommended that any modifications be thoroughly evaluated and demonstrated to be effective before field samples are collected.

• 1631
  – Note: This Method is performance based. The laboratory is permitted to omit steps or modify procedures provided that all performance requirements in this Method are met. The laboratory must not omit or modify any procedure defined by the term “shall” or “must” and must perform all quality control tests.
Illinois EPA Comparison of Sample Collection Techniques

Figure 6. CH/DH vs. Routine Illinois EPA Effluent Collection Method Study, Nov-Dec 2003

- Total Hg (ng/L)
- Facility Effluent

- GLWS: 1.3 ng/L
- HHS: 12 ng/L

Corr. Coeff. = 0.99
Mean RPD = 10.07%
Maximum RPD = 26.16%
Figure 10. Comparison of Three Collection Methods at AWQMN Stations

- CH/DH
- Single
- Routine

* Sample bottle broken during shipment

GLWS 1.3 ng/L
One - Person
Clean Hands / Dirty Hands

• Simple valve collection point
One - Person
Clean Hands / Dirty Hands

- Manhole collection point
- Use pump and tubing
Sample Collection Equipment

- **Pumps**
  - bladder
  - Peristaltic

- **Tubing**
  - Teflon
  - Teflon lined
  - flexible (for peristaltic pump)
Sample Collection using Bladder Pumps
Page 7 of 15
5. Bladder Pump: QED model MP-SP-4P (Sample Pro)

Sample Collection using Peristaltic Pumps
Page 10 of 15
4. Peristaltic Pump: Cole-Palmer or equiv., portable

- TestAmerica confirmation
  - non-corrosive
  - no measurable Hg contamination
Low-Flow Sampling Advantages

• **Improves sample quality**
  – sampling accuracy & precision

• **Minimizes**
  – drawdown, mixing & formation stress
  – isolates stagnant water

• **Represents**
  – naturally mobile contaminants,
  – not stagnant water
  – not mobilized contaminants
Lower flow improves sample quality

Low-flow purging and sampling controls turbidity and delivers higher quality samples
Reduced Purge Water Handling/Disposal

Purge volume is based on stabilization of indicator parameters measured during purging.

Traditional Purging

Low-Flow Purging
Effect on data accuracy and precision

Island County Landfill - Unfiltered Metals Concentrations - Well E2S

- Purged & sampled with bailers; high turbidity (>100 NTU)
- Purged with pump & sampled with bailers; varying turbidity (30-50 NTU)
- Low-flow sampling with dedicated bladder pumps
Low-Flow Sampling Limitations

- **Low-yield wells**
  - longer purging times
  - longer bottle filling

- **Very-low-yield wells**
  - not stabilize at all
  - practical lower limit is 50-100 mL/min.
Portable vs. Dedicated Sampling Systems

- **Short-term programs**
  - portable systems more economical
    - lower capital expense

- **Longer-term programs**
  - dedicated systems more economical
    - lower operating costs
• **Sample label on outer bag**

• **One sample**
  – 4 X 40 mL vials (8 X 40 mL for Sample/MS/MSD)
  – foam cube
  – double bags

• **No field preservation (28 day hold time)**
Lab Contamination Control

**Reagents**
- Water
- HCl
- KBr
- KBr0₃
- SnCl₂
- NH₂OH·HCl
- Ar

**Environment**
- Air - vapor/particulates
- Thermometer, manometer, barometer
- Bench top
- Ventilation hood

**Analyst**
- Gloves
- Lab coat
- Dental work

**Equipment**
- Sample bottle
- Autosampler vial
- Hoses & tubes
- Gas/liquid separator
- Gas supply line
- Pipet tips
Lab Receiving

- Unpack cooler
- Compare client label on outer bag to COC
- Inspect double bag for integrity
- Keep double bags intact
- Pass along to mercury area for preservation
Sample Preservation & Preparation

- Sample bags & vials opened
  - in mercury clean area

- Preserved ≤ 28 days of sample collection

- BrCl in HCl solution added
  - Stops biological activity
  - Oxidizes organic/inorganic mercury compounds

- Screening - instrument protection & dilution
1631 Summary

- **Reporting Limit**: 0.5 ng/L
- **BrCl** Oxidizer / Preservative
- **NH$_2$OH HCl** prereduction for excess BrCl
- **SnCl$_2$** reduction of Hg$^{2+}$ to Hg$^0$
- **Purge** Hg$^0$ from water with Ar
- **Trap** Hg$^0$ on Au coated sand
- **Thermally desorb** Hg$^0$ into Ar stream
- **Cold vapor atomic fluorescence spectrometer**
Automated Instrumentation

- Teledyne
- Tekran
- PS Analytical
- CETAC
- Nippon
- Brooks Rand
- SCP Science

Model RA-3320+Gold
Water and HCl Vapor Traps

Nafion Dryer

Counter-current gas flow design

Soda Lime Dryer
Gold Amalgamation

- 3 gold traps
  - “Clean” gas supply
  - 2 stage amalgamation
  - Gold coated sand
  - Gold dust
1631 Calibration

[Image of calibration software interface with data entries and graph]

**Protocol**

- **Line info**
- **Cal Curve**
- **Report**
- **Ctrl Chart**
- **Viewer**

**Data Table**

<table>
<thead>
<tr>
<th>S</th>
<th>Conc.</th>
<th>Calc.</th>
<th>Dev.</th>
<th>Mean</th>
<th>SD or %RSD</th>
<th>Rep 1</th>
<th>Rep 2</th>
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</table>
• 1 ng/L Hg
Low Level Mercury Area

- Limited access
- Non-metallic (or coated) fixtures
- Designated Separate Spaces for:
  - Incoming double bagged samples
  - Sample preservation / screening preparation
  - Sample storage
  - Known low level area
    - prep of bottles, reagents, field water
  - Standard preparation
  - Instrument with filtered air autosampler
• **Contamination control**
  – Blanks: field, tubing, bottle, reagent, instrument, sample prep, CCB

• **Gold and iodide**
  – MS/MSD recovery

• **Gold traps damaged by free halogens**
  – Initial calibration %RSD, low std %R
  – Mercury peak shape

• **Undigested organics**
  – MS/MSD recovery
  – CCV recovery
• **Low concentration work - RL 0.5 ng/L**
  – contamination control

• **Clean hands – dirty hands collection**
  – recommended by 1669 and 1631

• **Performance based modifications**
  – must still meet cleanliness requirements

• **One person clean techniques**
  – change gloves frequently / white shirt clean

• **Many ways to collect samples**
  – direct grab, extension pole, pump
• **Low Flow Sampling:**
  – More representative water samples

• **Shipping & Receiving:**
  – don’t contaminate

• **Sample preservation / preparation:**
  – clean designated spaces
  – contamination control training

• **Analysis (1631E):**
  – RL 0.5 ng/L, MDL ~ 0.1 ng/L
  – Instruments (7 providers)
• **National Environmental Monitoring Conference**
  – Tuesday, August 10, 2010
  – Washington D.C.
  – [www.nemc.us](http://www.nemc.us)

• **Session**
  – Historical Perspective – Bill Telliard
  – Sample Collection
  – Sample Preparation
  – Analysis and Instrumentation
  – Discussion Mercury Analysis Issues
Low-Flow Groundwater Sampling – An Update on Proper Application and Use

Dave Kaminski

- origins of traditional well purging
- correlation of drawdown & indicator parameter
- relationship between screen length & pump location
- advances in MicroPurge® low-flow sampling

Thursday, June 24, 2010 1:30 PM - 2:30 PM EDT
www.qedenv.com
Acknowledgments

Will Cordell, Joe Grant, Marc Haines

Mike Henebry
Field work side shows