Metals Monitoring Workshop
Thursday September 25, 2014, 10:00 – 4:00
Archdale Building – Ground floor hearing room
512 N. Salisbury St., Raleigh, NC, 27640

AGENDA

10:00 – Welcome and Introductions

10:30 – Presentations

Triennial Review: Rules and Anticipated Timelines – *Connie Brower*
Proposed regulations for in-stream, hardness-dependent, acute and chronic metals standards, what the rules say, timeline, etc.

DWR's Metals Sampling Plan – *Steve Kroeger*
When, where and how to sample, site ranking, schedule for implementation, etc.

Dissolved Metals Field Sampling Techniques – *Tammy Hill & Carrie Ruhlman*
DWR techniques, approved methodology, clean techniques, equipment, SOPs, etc.

Metals Analytical Methods and Sampling Requirements – *Roy Byrd*
40 CFR, SM 200.7, 200.8 and 200.9, etc.

Potential Assessment Methodology for Metals – *Kathy Stecker*
Acute and chronic assessment options, timeline for implementing new assessment methodology, etc.

Q/A – *All DWR Reps*

12:00 – Lunch Break

12:30 – Q/A continued (if needed)

1:00 – Small group break-out (5 groups) – discuss the options

- Challenges
- Where to monitor
- How to monitor (acute, chronic, ambient, methods, etc.)
- What's affordable/doable

2:00 – Group round-table discussion, Q/A – reports from small groups

3:00 – Next steps, recommendations and ideas

4:00 – END

Note: Scheduled times are subject to change but workshop will begin promptly at 10:00 am and end no later than 4:00 pm.

Instream Metals Monitoring Workshop

For DWR Ambient and Coalition Programs

September 25, 2014

OBJECTIVES

* Clarify new metals monitoring requirements from Triennial Review
* Hear and answer any questions from Coalition Program participants on instream criteria and implementation
* Exchange ideas about implementation of instream dissolved metals monitoring across the State and across monitoring programs

The goal is not necessarily to agree, it's to gain a better understanding of all the options

Triennial Review
Ambient Monitoring Updates

Connie Brower

NC DENR: Division of Water Resources

Proposed Changes have distinct programmatic impacts:

- NPDES wastewater discharge limits and monitoring; stormwater monitoring
- *Instream (ambient) Monitoring*

Proposed Changes

NPDES Discharge Monitoring

- **Permit Limits -Equation based upon dissolved metals**
- **Dissolved criterion translated to Total Recoverable Permit Limit**
- **Permit Limits using median 8-digit HUC hardness /median of effluent hardness**
- **Implementation of Acute**
- **Implementation of Chronic**

Instream Monitoring

- **Equation based**
- **Dissolved Metal Measured**
  - **Filtration in the field**
- **Hardness sample collected**
- **Acute standards**
  - **2 samples within one hour**
- **Chronic standards**
  - **minimum of 4 samples (consecutive 4 days or 96 hour average)**

Laboratory Analysis

Water Quality Standards are **TOXICITY** based, not ***technology*** based.

- Standards **may be** below normal laboratory quantitation abilities
- Where the WQS is below the Practical Quantitation Limit (PQL), compliance is assumed when the data is reported as "below the PQL"
- Concerns about appropriate PQLs should be addressed to the NC Laboratory Certification program.

Ambient monitoring…..

Modifications to evaluate *instream* conditions ……

Instream Dissolved Metals

- DWR proposed dissolved metal water quality criterion (as equations)
- Collect instream **metal** sample(s)

  Filter in field *(per 40 CFR Part 136; Table II, Footnote 7)*

  (to capture the dissolved portion)
- Routine **metals analysis** by laboratory

Are all metals criterion in dissolved form?

- Arsenic – Total for human health protection
  Dissolved for aquatic life protection
- Chromium VI- Total
- Manganese (proposed for removal)
  Measured as Total (if retained)
- Mercury – Total
- Nickel – Total for water supply classified waters
  Dissolved for aquatic life protection
- Selenium- Total
- Silver - Total (chronic)

Instream Hardness-Dependent Metals

Equation-based instream standards are proposed

{1.101672-[*ln* hardness](0.041838)} · *e*^{0.7998[*ln* hardness]-4.4451}

So, to determine instream standard, measurement of the hardness is required.

What metals are “hardness-dependent”?

- Cadmium
- Chromium III
- Copper
- Lead
- Nickel
- Silver (acute)
- Zinc

Ambient Monitoring Process

- Collect instream sample(s) for metals analysis – filter in the field

  Routine **analysis** by laboratory
  = dissolved metal instream concentration(s)

- Collect instream sample for hardness- *NOT filtered*

  Lab reported hardness entered into equation(s) to *calculate* the sample-specific metal criterion

- Compare reported dissolved metal instream concentration to the ***sample-specific metal criterion*** to assess water quality

Aquatic Life: Acute

Acute standards include explicit collection requirements:

"Compliance with acute instream metals standards shall only be evaluated using an average of two or more samples collected within one hour."

Aquatic Life: Chronic

Chronic standards include explicit collection requirements:

"Compliance with chronic instream metals standards shall only be evaluated using averages of a minimum of four samples taken on consecutive days, or as a 96-hour average;"

Ambient Monitoring

Before

- Collect one sample
- Frequency determined by consultation w DWR
- Routine analysis by lab
- Lab results of instream sample compared to numeric criterion in rule

After

- Chronic: Collect 4 samples over 96 hours
- Acute: Collect at least two samples in one hour
- For appropriate metals, filter in the field
- Collect hardness sample
- Routine analysis by lab
- Hardness applied to equations = Instream criterion
- Lab results compared to calculated criterion

Projected Timeline

- *November 2014* — *EMC-Hearing Officer's Report of Proceedings*
  EMC approval request
- *Late 2014- early 2015* — *Rules Review Commission*
- *Early 2015* — *Formal State Adoption*
- *2015* — *Pkg to EPA for approval*

Contact Information

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919-807-6416

http://portal.ncdenr.org/web/wq/ps/csu/swtrirev

Water Quality Monitoring

Steven Kroeger

NC Division of Water Resources

Major Points - Monitoring for Dissolved Metals

- What question(s) are we trying to answer?
- Where do we sample?
- How do we assure legally and scientifically defensible data?
- Timeline

What Question(s) Are We Trying to Answer?

- General Question:

  Are water quality standards being met?

- Specific Question for 2018 303(d) list:

  If the 52 metal combinations are relisted by EPA, are they meeting water quality standards? **This is the DWR priority**

Where do we sample?

- We begin with the 52 water body combinations, if they are relisted by EPA
- Followed by where we have observed exceedances of the standards for metals (i.e., the 63 on 303(d) list, followed by the 120^{+} waters in Category 3 – “inconclusive”).

Legally Defensible

- Need to follow established quality control procedures
- Need to update SOPs and QAPPs

Scientifically Defensible

- How many samples are needed?
- What is the interval between samples?

Timeline

- Begin sampling in July 2015
- Complete sampling for priority sites by December 2016.

Contact Information

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Dissolved Metals Field Sampling Techniques

Tammy Hill & Carrie Ruhlman

DWR Water Sciences Section – Ecosystems Branch

Dissolved Metals

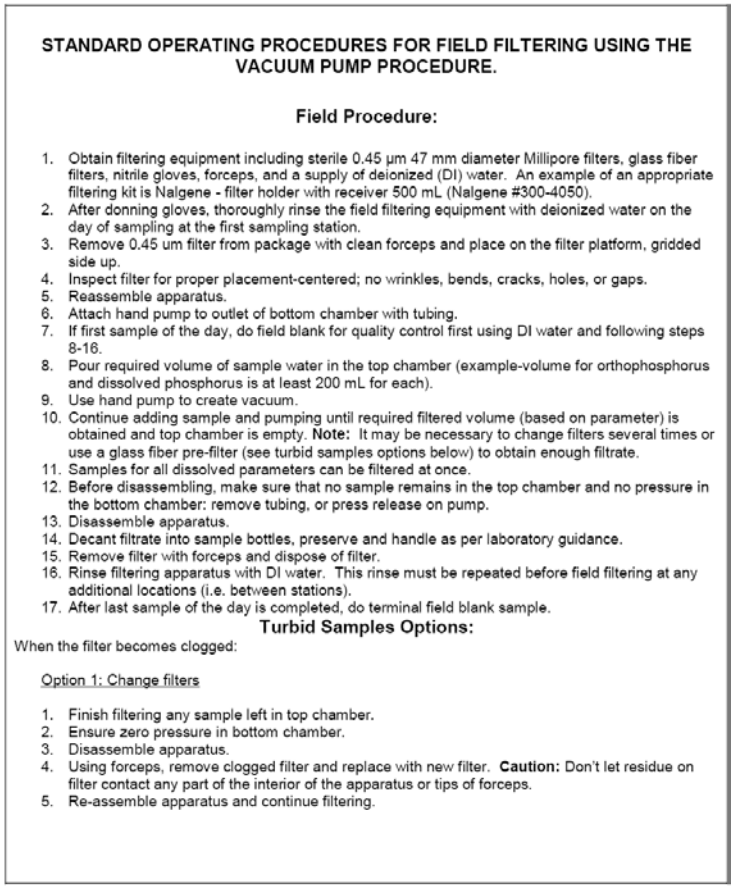
- Arsenic (aquatic life)
- Beryllium
- Cadmium
- Chromium III
- Chromium VI
- Copper
- Lead
- Nickel (aquatic life)
- Silver
- Zinc

Field Filtering For Dissolved Metals

- 40 CFR Part 136.3
  * Dissolved metals – those constituents which will pass through a 0.45 micron membrane filter
  * Metals except boron, chromium VI and mercury
  * Metals should be filtered immediately on-site before adding preservative for dissolved metals

DWR SOP for Field Filtering

- NC AMS QAPP Version 1.2 (Approved by EPA 3/28/14)
  - Appendix 6: SOP for Filtering in the Field



STANDARD OPERATING PROCEDURES FOR FIELD FILTERING USING THE VACUUM PUMP PROCEDURE.

Field Procedure:

1. Obtain filtering equipment including sterile 0.45 µm 47 mm diameter Millipore filters, glass fiber filters, nitrile gloves, forceps, and a supply of deionized (DI) water. An example of an appropriate filtering kit is Nalgene - filter holder with receiver 500 mL (Nalgene #300-4050).
2. After donning gloves, thoroughly rinse the field filtering equipment with deionized water on the day of sampling at the first sampling station.
3. Remove 0.45 um filter from package with clean forceps and place on the filter platform, gridded side up.
4. Inspect filter for proper placement-centered; no wrinkles, bends, cracks, holes, or gaps.
5. Reassemble apparatus.
6. Attach hand pump to outlet of bottom chamber with tubing.
7. If first sample of the day, do field blank for quality control first using DI water and following steps 8-16.
8. Pour required volume of sample water in the top chamber (example-volume for orthophosphorus and dissolved phosphorus is at least 200 mL for each).
9. Use hand pump to create vacuum.
10. Continue adding sample and pumping until required filtered volume (based on parameter) is obtained and top chamber is empty. **Note:** It may be necessary to change filters several times or use a glass fiber pre-filter (see turbid samples options below) to obtain enough filtrate.
11. Samples for all dissolved parameters can be filtered at once.
12. Before disassembling, make sure that no sample remains in the top chamber and no pressure in the bottom chamber: remove tubing, or press release on pump.
13. Disassemble apparatus.
14. Decant filtrate into sample bottles, preserve and handle as per laboratory guidance.
15. Remove filter with forceps and dispose of filter.
16. Rinse filtering apparatus with DI water. This rinse must be repeated before field filtering at any additional locations (i.e. between stations).
17. After last sample of the day is completed, do terminal field blank sample.

Turbid Samples Options:

When the filter becomes clogged:

Option 1: Change filters

1. Finish filtering any sample left in top chamber.
2. Ensure zero pressure in bottom chamber.
3. Disassemble apparatus.
4. Using forceps, remove clogged filter and replace with new filter. **Caution:** Don't let residue on filter contact any part of the interior of the apparatus or tips of forceps.
5. Re-assemble apparatus and continue filtering.

Filter Options (our experience)

Membrane Filters-
47 mm diameter

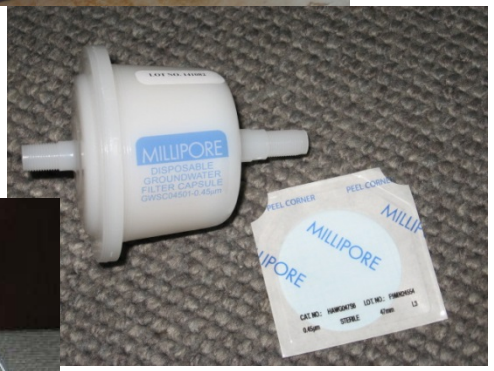
- Pros
  - Cost $0.30 per filter
  - Filtering Equipment Blanks- beginning & end of day only
- Cons
  - Small surface area
  - Easily clogged resulting in several filter changes
  - Slower filtering

Inline Capsule Filters-
600 cm^2

- Pros
  - Large surface area = one filter per sample
  - Faster filtering time
  - Reduce sample contamination potential due to numerous filter changes
- Cons
  - Cost- $17.87 per filter
  - Filter Blanks required per filter

Inline Capsule Filtering Method

- Supplies
  - Gloves - powder-free, nitrile or vinyl
  - Filtering apparatus - chamber, chamber cap, tubing adapter
  - Vacuum pump
  - Membrane filters/Inline capsule filters - 0.45 µm
  - Tubing
  - Ultrapure DI blank water
  - Clean 1L plastic bottles
  - Sample bottles, preservatives, tags & lab sheets

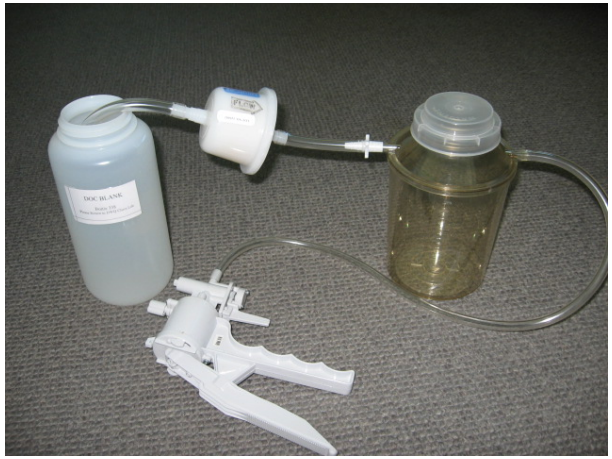


Field QC

- Filter Blank – 1 blank per filter
  * Preserve and handle like environmental samples

Additional QC:

Each lot of filters, tubing and Preservatives are lab tested for potential contamination



Environmental Sample

- Continue with same filter set-up from blank
- Filter 50 mL sample, discard
- Filter 300 - 500 mL for sample (*lab preference*)
- Preserve

* Discard used filter and tubing pieces
* Rinse filter apparatus with ultrapure DI water

Acute Sampling

- Unfiltered hardness sample (*1 minimum per acute event*)
- Two discrete environmental samples within 1 hour (15 min apart) = One Acute Sampling Event
- Each Discrete Sample
  * 1 capsule filter
  * 1 QC sample (filter blank)
  * 1 stream sample
- Per Acute Sampling Event
  * 2 capsule filters
  * 2 QC samples (filter blanks)
  * 2 stream samples

Chronic Sampling

- Unfiltered hardness Sample (*1 minimum per chronic event*)
- Four environmental samples on four consecutive days or within 96 hours = One chronic sampling event
- Each Discrete Sample
  * 1 capsule filter
  * 1 QC sample (Filter Blank)
  * 1 Stream Sample
- Per Chronic Sampling Event
  * 4 capsule filters
  * 4 QC samples (Filter Blanks)
  * 4 Stream Samples

Clean Sampling – EPA Method 1669

- DWR only uses this method (modified) for low-level mercury
- Sampling requires 2 people
- Sampling equipment must be properly cleaned, stored and transported
- Equipment preparation and laboratory analysis are conducted in Class 1000 clean room

Clean Filtering (Non-Hg samples)

- Laboratory cleaned and packaged sampling equipment and supplies
  - Bottles – sample and blank
  - Gloves
  - Filtering apparatus
  - Tubing
  - Storage bags
  - DI water
  - Glove bag

Clean-hands/ Dirty-hands

Environmental Sample

Sampling Options

Good Field Practices Vs. Clean Sampling

- Care taken to avoid sources of contamination
- QC samples
- Pros
  - Less staff time per sample
  - Lower cost
- Cons
  - Some potential for contamination

- Supplies prep & analysis in clean room; CH/DH methods
- QC samples
- Pros
  - Reduced potential for contamination
- Cons
  - Additional staff time
  - Higher cost

Metals Analytical Methods and Sampling Requirements

By

Roy W. Byrd
N.C. Division of Water Resources
Water Sciences Section

Introduction

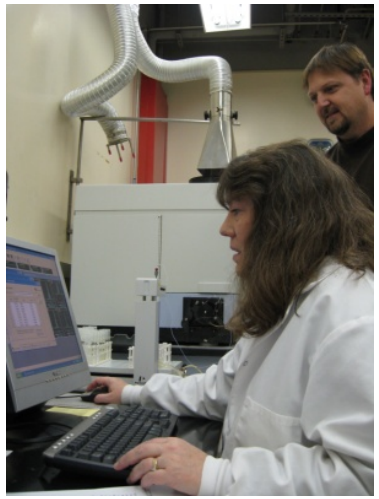
I am with the Division of Water Resources (DWR) Water Sciences Section located in Raleigh, NC.

We provide analytical laboratory support to the Department of Environment and Natural Resources (DENR) in the form of physical, chemical and microbiological analyses of stream, wastewater, coal ash waters, groundwater, soil, sediment and fish tissue samples.

The Water Sciences Section includes a certification program for wastewater/groundwater laboratories whose mission is to ensure the quality of monitoring analyses required by the state.

We also provide consultation and assistance to state, federal and local agencies, private laboratories and individuals in matters of analytical methodology and quality assurance.

Metals Unit staff analyzing samples.



Technology and Instrumentation Drives Method Development

First AA was PE 303 purchased in 1964.
It was one of the instruments I trained on.

1972
PE 403 AA (Pb 100 µg/L)
I started performing metals' analysis in 1977 using EPA *600\4-79-020 MCAW&W.

1979 – 1982
PE 5000 AA - HGA 500 furnace (Pb 10 µg/L)
Still using EPA 600\4-79-020 MCAW&W.

1986
1st ICP - Plasma II ICP
*Started using EPA Method 200.7, Rev 1.0

1995
1st axial view ICP (PE Optima 3000XL
*EPA Method 200.7, Rev 4.4 (Currently listed in CFR)

1999
1st ICPMS (PE Elan 6100) (Pb 10 µg/L)
*EPA Method 200.8, Rev 5.4 (Currently listed in CFR)

2004
1st dual view ICP (PE Optima 5300 DV ICP)
EPA Method 200.7, Rev 4.4 (Currently listed in CFR)

2005
2nd ICPMS (PE Elan Drc-e)
(Pb & Tl 2.0 µg/L)
EPA Method 200.8, Rev 5.4

2002
PE AAnalyst 800 THGA
*EPA Method 200.9 Rev. 2.2

2014
3rd ICPMS (NexION)
(Conducting MDL Studies)
EPA Method 200.8, Rev 5.4

EPA Methods Used by Water Science Section Chemistry Laboratory

Methods being presented are not new to the rules.

EPA Method 200.7, "DETERMINATION OF METALS AND TRACE ELEMENTS IN WATER AND WASTES BY INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRY", Rev 4.4

- Most widely used method for water, wastewater, and solid wastes for over 25 metals.
- Reporting level not as low as EPA Method 200.8 or EPA 200.9.
- Same Quality Control requirements as EPA 200.8 and EPA 200.9.
- New instruments have advance technological improvements that provide lower limits, interference correction and faster analysis.

EPA Method 200.8, "DETERMINATION OF TRACE ELEMENTS IN WATERS AND WASTES BY INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY", Rev. 5.4

- Provides the lowest reporting level for water, drinking water, wastewater, and solid wastes.
- Reporting levels equivalent or lower than EPA 200.9.
- Same Quality Control requirements as EPA 200.7 and EPA 200.9.
- Newer instruments have advance technology to improve interference corrections and provide lower limits.

EPA Method 200.9, "DETERMINATION OF TRACE ELEMENTS BY STABILIZED TEMPERATURE GRAPHITE FURNACE ATOMIC ABSORPTION", Rev. 2.2

- Provides reporting level equivalent or close to EPA Method 200.8 for water, drinking water, wastewater, and solid wastes.
- Same Quality Control requirements as EPA 200.8 and EPA 200.7.
- Disadvantage to using this method is it performs single element analysis.

Brief Overview of Method QC Requirements for EPA Method 200.8

Note: The following information on Quality Control can be found in Section 9.0 of all three methods.

- **Quality Control** – "Each laboratory using this method is required to operate a formal quality control (QC) program. The minimum requirements of this program consist of an initial demonstration of laboratory capability, and the periodic analysis of laboratory reagent blanks, fortified blanks and calibration solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data thus generated."

- **Initial Demonstration of Performance (mandatory)**
  - **Linear calibration ranges –** To ensure instrument calibration is linear.
  - **Quality control sample (QCS) –** To verify instrument calibration is accurate using a second source standard.
  - **Method detection limits (MDL) –** Use to help establish the laboratory reporting limits.

- **Assessing Laboratory Performance (mandatory)**
  - **Laboratory reagent blank (LRB) – "**LRB data is used to assess contamination from the laboratory environment and to characterize spectral background from the reagents used in sample processing."
  - **Laboratory fortified blank (LFB) – "**The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements." The LFB is a aliquot of the LRB that a known concentration of metals is added to. Mandatory recovery of 85 -115% is required by the method.

(Continue next slide)

Brief Overview of Method QC Requirements for EPA Method 200.8 (continued from slide 5)

- **Assessing Analyte Recovery and Data Quality** – "Each Sample homogeneity and the chemical nature of the sample matrix can affect analyte recovery and the quality of the data. Taking separate aliquots from the sample for replicate and fortified analyses can in some cases assess these effects."

- **Laboratory Fortified Sample Matrix (LFM) –**
  - An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results.
  - LFM or MS must go through the entire sample process and recovery must be between 70-130%.

- **Laboratory Duplicates (LD1 and LD2) –**
  - Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicates precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures."
  - The trend for duplicates is going to Matrix Spike Duplicates (MSD) and requiring a RPD (Relative Percent Difference) of around 20% or less depending on method. Low level mercury method 1631 RPD limit is 24% for Matrix Spike Duplicates.

- **Internal standards responses**
  - Use to monitor for changes from sample matrix or instrument during an analytical run. For example is a salt water samples will usually result in an unacceptable internal standard recovery due to change in sample viscosity.

Importance of LFM Recovery

Iodide Interference in Mercury Analysis Using EPA Method 245.1

- We analyzed a sample that had been spiked (LFM) and got 0% recovery from the spike. The analyst though the spike solution was left out, but further testing proved that was not the case and the recovery was still very close to 0%. A quick test using the sample as iodide added to starch was positive.
- Attempts to add more $SnCl_2$ to sample did not help, too much iodide in sample prevented the reduction of mercury to the vapor state for measurement.
- No result could be reported for this sample.
- This was a pretreatment sample taken close to medical facility which had the iodide in their waste.
- Solution was to move further down the line to sample for mercury in the waste.
- Iodide has the same effect on mercury determined by EPA Method 1631E.

Sampling Requirements

Routine Sampling for Metals and Mercury by EPA Method by 245.1

- Quality control starts with the sample container.
- The Metals Unit checks each lot of bottles for contamination by filling bottles with deionize water and acidifying to a pH < 2.0 with high purity HNO_3. Then container is left sitting for 24 hours before analyzing for metals.
- Next, consideration should be given to the type of data required, (i.e., dissolved or total recoverable
- For RAMS dissolved metals, we test the filters for contaminants prior to sampling event.
- A filter blank is collected in the field during the sampling event.
- Dissolved metals are filtered in the field and preserved with 1:1 HNO_3 to a pH of <2.0 after filtration with 0.45µ filter.
- Metal's sample that have been preserved with 1:1 HNO_3 to a pH <2.0 do not require thermal preservation with ice.

Sources for possible Contamination

- Sample containers
- Filter for dissolved metals
- Preservative, especially ampoules filled with 1:1 nitric acid
- Air borne contaminates at the sampling site, such as dust and rain

Sampling Requirements

Clean Sampling for Mercury by EPA Method by 1631E

- Low Level Mercury Analysis by EPA Method 1631 requires using clean techniques to avoid contamination in both the field and laboratory.
- The laboratory uses glass bottles and 5% of each lot must be tested for mercury contamination.
- Laboratory provides bottles and blank water in a cooler designated for low level mercury.
- Sampling kits are prepared in a Class 1000 clean room, shown in the next slide.
- Bottles are “double bagged’ before placing in the cooler and the cooler taped closed for shipping.
- Coolers returned with samples are not open in the receiving room but taken to the Metals Unit for unpacking.
- Two people unload the coolers by having one outside the clean room to remove inner sample bag and then hand to person in the clean room.

Data From Samples Analyzed By EPA 1631E

Below is the data for a sample taken from one of our RAMS station in Scotland County. Station number I093000, Joe's Creek at SR 1156 NR Laurel Hill, NC. The table shows the Quality Control limits required by Method 1631E and sampling requirements.

Notice that the analytical units are in ng/L (nanograms/Liter). Sample result of 2.85 ng/L will equal 0.00285 µg/L.

Sampling QC	Results	Method Requirement	Ongoing Precision and Recovery		
Method Blank	0.076 ng/L 0.066 ng/L 0.036 ng/L	Method Requirement is <0.5 ng/L for all 3 MD	QC	Results[3]	% Recovery[4] Method Limit = 71% to 125%
Field Blank	0.344 ng/L	"concentration equal to or greater than the ML" – Data not reported or data qualified.	MS[1]	12.8 ng/L	99.5 %
Sample Result	2.85 ng/L	DWR Laboratory Reporting Level (PQL) is 1.0 ng/L	MSD[2]	12.5 ng/L	96.5 %
			(Relative Percent Difference (RPD) Method Limit = 24%) RPD =		2.37 %
[1]MS – Matrix Spike. [2]MSD – Matrix Spike Duplicate [3]Spike concentration was 10 ng/L Hg and samples digested by UV.					

Class 1000 Clean Room

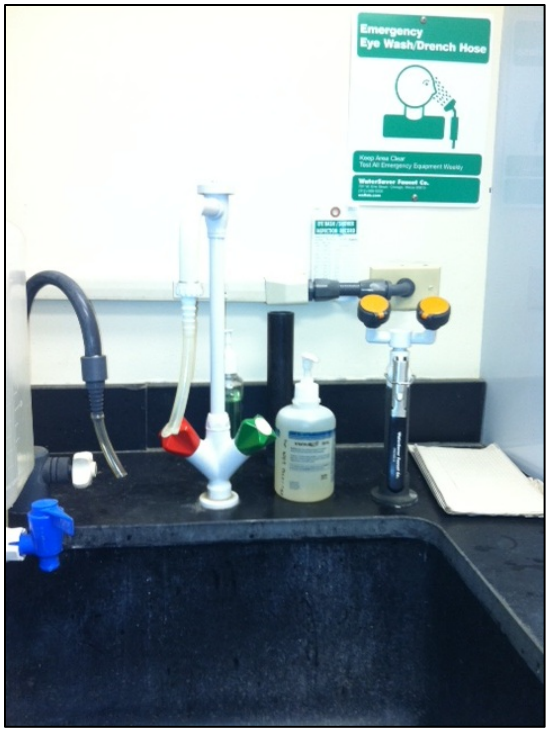
- Modular construction with polypropylene cabinets, clean benches and exhaust hood.
- It is actually constructed inside an existing laboratory room using soft walls. The HEPA filters are located in the ceiling grid.
- Our PQL for mercury is 1.00 ng/L.

Sample Preparation Room

Polypropylene hoods with acid storage below.

Polypropylene cabinets with **no metals parts**.

Sink fixtures with powered epoxy coating.



Questions and Contact Information

Contacts For Additional Information In This Presentation.

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Potential Assessment Methodology for Metals

Kathy Stecker

DWR Modeling & Assessment Branch

Outline

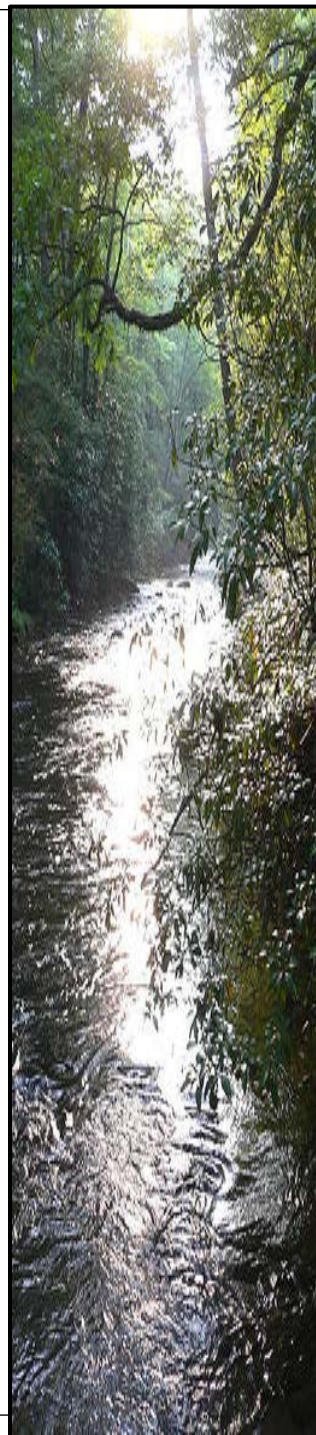
- 2014 303(d) list update
- Timeline for assessment
- Timeline for developing new methodology
- Origin of "not greater than 1 exceedance in 3 years"
- Acute and chronic assessment options

2014 303(d) List Update

- NC 303(d) list submitted to EPA for approval March 31
- EPA decision issued July 31
  - “>10%/90% confidence” approach not appropriate for metals
  - EPA intends to re-list 52 waterbody/pollutant combinations
  - EPA’s public comment period extended to October 14
- Until final decision, approved 2012 list remains in effect

Timeline for Assessment

- New dissolved metals criteria expected
- No dissolved metals data to assess for 2016
  - Data window closes December 31, 2014
- Begin to assess dissolved metals for **2018** 303(d) list
  - Data window 2012-2016
  - Can sample in 2015 and 2016



Timeline for Developing Methods

- No new metals assessment for 2016
- Public comment on 2018 methods
  - ~ July 2016
- Recommended 2018 methods to EMC for approval
  - ~ November 2016

Metals Assessment Options

1. >10% of all samples exceed, ≥ 10 samples
   - NC's approach for 2008, 2010, 2012

2. >10% of all samples exceed, ≥90% confidence, ≥ 10 samples
   - NC's approach for 2014
     - EPA does not concur

3. >1 exceedance in 3 years, chronic or acute

“>1 in 3”

- **Q:** Where does the “not greater than one exceedance in three years” assessment approach for toxics come from?

- **A:** EPA method for deriving criteria to protect aquatic life
  - Except where a locally important species is very sensitive, aquatic organisms should not be affected unacceptably if
    - The four-day average concentration (“chronic”) does not exceed more than once every three years, **and**
    - The one-hour average concentration (“acute”) does not exceed more than once every three years.

Number of Samples Needed

To de-list from current list, need <u>both</u> chronic <u>and</u> acute results

- "**10%**" or "**10/90**": ≥10 acute and chronic results
  - 60 samples +/-
    - e.g., (4 X 10 chronic) + (2 X 10 acute)
- "**1 in 3**": ≥ 2 acute and ≥ 2 chronic results
  - **8** samples +
    - e.g., 2 X 4 chronic, composed of 4 X 2 acute

Possible Sampling Strategy*

1 hour Day 1 + 1 hour Day 4

= **2 acute results and 1 chronic result**

*would require SOP change

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Metals Monitoring Workshop Evaluation SUMMARY

September 25, 2014

N= 12

1) What is your overall assessment of this workshop?

1- VERY BAD	2- BAD	3- JUST RIGHT	4- VERY HELPFUL
0	**0**	**4**	**7**

2) Please rate the presentations, using the scale above:

Triennial Review: Rules and Anticipated Timelines	**(8) 3's, (3) 4's**
DWR's Metals Sampling Plan	**(1) 2, (9) 3's, (2) 4's**
Dissolved Metals Field Sampling Techniques	**(9) 3's, (3) 4's**
Metals Analytical Methods and Sampling Requirements	**(1) 2, (8) 3's, (3) 4's**
Potential Assessment Methodology for Metals	**(10) 3's, (2) 4's**

3) Did the workshop provide the information you need to draw a path forward as your Coalition makes considerations and decisions on how to resume metals monitoring?

YES, CERTAINLY	YES, I THINK	NO	NO, NOT AT ALL
3	**8**	**1**	

Please clarify what additional information you need:

1. So many questions. Go slow and steady.

4) Do you feel that the objectives of this workshop (To gain a better understanding of all the options available for implementing dissolved metals monitoring in ambient monitoring programs) were met?

YES	NO
12	**0**

5) Is there anything you would like to suggest that would have made the workshop better?

1. Analysis of existing dissolved data.

2. Great job everyone! Off to a good start and a great discussion.

6) Please provide comments and suggestions (including activities, initiatives or follow-up you think would be useful prior to implementation of dissolved metals monitoring) (use the back of this form, if necessary).

1. Thanks.

2. Email minutes to participants.

3. Would like a workshop on how this affects NPDES permits.