Analytical Methods & Quality Assurance Workgroup (AMQAW) Meeting
Wednesday, April 24, 2013
10:00 AM – 3:00 PM

Meeting materials:
http://www.chesapeakebay.net/S=0/calendar/event/19285/

MINUTES

Leadership	**Affiliation**	**Email**
Bruce Michael (Chair)	MD DNR	bmichael@dnr.state.md.us
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Participants	**Affiliation**	**Email**
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ACTION ITEMS:

- In collaboration with TMAW, AMQAW will work to design a plan to monitor ALL Bay segments as requested by the management board. (AMQAW)
- If AMQAW members are interested in participated in Automated Sampler Protocols Action Team, contact Mary Ellen Ley. (AMQAW)

- TSS and PCN method revisions authored by DCLS, will be brought to the group during next AMQAW meeting (DCLS representative)
- MD will now only send processed DI water samples to be analyzed by DHMH; will no longer send unprocessed banks to DHMH. (MD-DNR)
- Continue the discussion of a procedure for finalizing a total nitrogen method with the NTWG. Specifically field related issues. (Mary Ellen Ley, NTWG)
- Update USGS Reference Sample– Lab: CBL, Parameter: PO4 Low concentration, Result: 0.3393 (Lea Rubin)

Announcements (B. Michael, MDNR)

- Release of 2011 SAV Numbers (http://www.dnr.state.md.us/bay/sav/)
  - 2012 SAV numbers have been released
  - Decrease in Bay-wide SAV from 2009 by 48%
  - Acreage may be low, but high density provides rebound potential

- Decreased population of Maryland Blue Crabs in 2011 to 2012
- New Chesapeake Bay Report Card (http://ian.umces.edu/ecocheck/report-cards/chesapeake-bay/2012/)

Potential Monitoring Impacts related to Sequestration (B. Michael, MDNR)

Supplemental Materials: *CBP Monitoring Networks Funding and 2013 Shortfall*, *History of CBP Monitoring Network Funding*

- The Chesapeake Bay Program is waiting for more budget information from EPA Headquarters to determine potential impacts to the water quality monitoring programs.
- Funding reductions could potentially impact:
  - The number of mainstem cruises
  - The loss of one winter cruise
  - The processing of the physical parameters, without the collection of nutrient samples on one of two summer mainstem cruises per month

- Funding reductions currently projected to be 5-10%

- VA Funding impacts:
  - VA cut back on shallow water monitoring program
  - Half the funding from Bay Initiative grant from the General Assembly, was retracted (about $150K)
  - SAV program is in danger of reductions
  - Potentially postpone BIBI recalibration work ($54K project)

Enhanced Tidal Monitoring related to DO Criteria Assess (B. Michael, MDNR)

- Liza Hernandez, Coordinator of the Tidal Monitoring and Analysis Workgroup developed an Integrated Indicator to assess progress towards attainment of Water Quality Standards towards 2025 Goal of 60% delisted Bay segments.
    - If the monitoring information is not available to assess a Bay segment, it is listed as impaired under the Integrated Indicator.

- **ACTION:** In collaboration with TMAW, AMQAW will work to design a plan to monitor ALL Bay segments as requested by the management board. (AMQAW)

Reusing Bottles to Collect Chlorophyll Samples (S. Doughten, ODU)

- Currently: ODU is using new bottles for Chlorophyll a samples collected at each fixed station. They proposed using the same bottle for all chlorophyll a sample collections during a single cruise, to use a new one for every cruise.
- Purpose: To reduce the backup of bottles needing washing after each cruise
- ODU sees no difference in chlorophyll a value when looking at field blanks for comparison.
- QA officer sees no issue with switching to reusing bottles to collect chlorophyll a samples.

Progress on NTN Data Submittals (M. Mallonee, ICPRB/CBPO)

Supplemental Materials: *DUET Update Presentation (Presentation includes: Upload and QA check issues, Data submittals accepted into DUET, The NTN data timeline, and requirements for data uploads) Contact the data manager Mike Mallonee (mmallone@chesapeakebay.net) with questions.*

- The Tidal Water Quality Monitoring network is undergoing their first round of importing data into DUET.

- What differences do you foresee between submitting data for nontidal and tidal?
    - Submittal codes

Automated Samplers for Storm Event Collection (B. Michael, MDNR)

- VA is using automatic samplers for ancillary monitoring not included in the NTN, suggestions when using automated samplers:
    - When implementing an automated sampler, there are still man power needs such as:
        - Relating the auto-sampler to the cross-section of the segment
            - Sediment collection
            - Holding time – power to the automated sampler
    - Connect the auto sampler in-situ to a post, horizontally
    - Perform a comparison study of auto-sampler data to manually collected storm event samples over the full hydrological scale.

- Joel Blomquist mentioned preference for a Continuous Monitor as opposed to an automated sampler to sample for turbidity in order to correlate turbidity to other parameters.

- Thoughts from MD-DNR: Nutrient samples are collected same day, refrigerated automated samplers are not necessary, because the samples degrade over time, even when refrigerated.
    - Refrigeration needed for samples collected by automated samplers require a large car battery if no electric power is available, difficult to transport
        - Solar panel suggested
            - Site has dense shade cover, solar panel not compatible with physical conditions of site

- MD is considering automated sampling because with records of the high flow events (i.e. hydrological graph) captured, they are not collecting the top 3% of the hydrological graph.

- Are monitoring groups from the NTN collecting turbidity samples during storm events? If so, in-situ?
    - Yes, other NTN programs collect turbidity with YSI meters in-situ.
        - Due to USGS protocol; when possible to pair Turbidity and SSC data, publish regression curves
    - MD would need 4-6 turbidity probes to integrate turbidity sampling

- An Adhoc Team to address Automated Sampler protocols through the NTWG is forming; interested AMQAW members are invited to join.
    - First step is to develop a procedure for "how to establish equivalency" (i.e. manual composite sample vs. automated sampler)
    - **ACTION:** If AMQAW members are interested in participated in Automated Sampler Protocols Action Team, contact Mary Ellen Ley. (AMQAW)

Status of CBP Recommended Guidelines (M. Ley, USGS/CBPO)

- For Guidance please visit "projects and resources" tab of the AMQAW webpage
    - Changes to the guidelines since last meeting include:
        - Nancy Kaumeyer's DOC method was submitted, not yet reviewed or on the webpage.
        - Mary Ellen Ley is working on the Alkaline Persulfate Digestion method, to be discussed in detail at this meeting.
        - **ACTION:** TSS and PCN method revisions authored by DCLS, will be brought to the group during next AMQAW meeting (DCLS representative)

- Mary Ellen Ley emphasized the importance of collecting the appropriate number of blanks per water year.

- Question: Due to the guidelines, is it a required practice to send one blank per station per year to the Kentucky laboratory for SSC?
    - Answer: Yes
    - Currently, MD is not doing a paired blank with SSC samples

- Kristen Heyer preformed an analysis the accuracy in determining sediment concentration in the field due to field method (residual sediment when reusing the apparatus to filter samples)
    - Results: In method the filter apparatus is being reused. However, did not see sediment carrying over in the TSS or SSC samples.

- Unprocessed pad has a tendency to have a higher concentration than the processed pad; PC is the biggest culprit, possible contamination.

- What is the difference between the processed vs. unprocessed pads?
    - Answer: unprocessed pads are a blank for the DI water and the filtering system, processed includes the sample.

- What is the purpose of the un-processed pads being sent to DHMH for analysis?
    - Answer: Determine if there is a difference in concentration results between the processed and unprocessed pads.
    - **ACTION:** MD will now only send processed DI water samples to be analyzed by DHMH; will no longer send unprocessed banks to DHMH. (MD-DNR)
        - AMQAW participants determined that the TOC from the unprocessed pads are insignificant due to the magnitude of the sample.

- All constituents sampled in the field are being replicated.

Analysis of Total Nitrogen Using the Alkaline Persulfate Digestion

USGS Comparison Study Report and Recommendations (J. Blomquist, USGS, Charles Patton, USGS/NWQL)

J. Blomquist presented a comparison study assessing total nitrogen in surface-water samples – precision and bias of analytical and computational methods. He used Buffalo River sediment mixture and Montana soil samples to compare results of TN-A (Total nitrogen measured by alkaline persulfate digestion) and TKN (Total Kjeldahl N: ammonia plus organic N) methods for determining total nitrogen. Blomquist concluded that the alkaline persulfate digestion method has a negative bias, possibly due to some particulate nitrogen not being oxidized during digestion. The Kjeldahl method has a significant positive bias, more biased than the alkaline persulfate digestion method. With a laboratory and field studies comparison, the sample pattern is found.

Supplemental Material: J. Blomquist – USGS Comparison Study Presentation

Discussion and Questions

- What is the bias for the Chesapeake region data that we should assume from this analysis?
    - For most normal conditions during the period of study, on average, no strong bias observed.
    - Looking at the distribution of data over the United States map, a mean is listed in each area, and does not say what bias we are seeing for high flow samples, which would be of interest for the Bay Program.
    - Did not find patterns that would be predictors of bias. (i.e. land use)

- Did you look for seasonal trends in this study?
    - Seasonal differences were observed as related to high flow conditions and higher concentrations of suspended sediment.

- What was the method of comparing the TN methodologies?
    1) Analyzed duplicates and replicates of PN filters by high temp combustion oxidation method
    2) Compared to "TNC estimation procedure" – which stand for taking a filtered water sample, perform a TN-A method analysis and measure TDN (by TN-A) + PN (determined by high temperature Oxidation**)**. This calculation of TN was used as the unbiased measure of total nitrogen.
    3) The basis of comparison was looking at the TNC value compared to TN-A on a whole water sample or the few TKN on a whole water sample method.
        a. Noted: the TKN method can cause nitrate to yield ammonia

- Meeting participant asked if considerations were had for a comparison study method of taking a field sample, split into two equal volumes of water filtered, then analyzed by each method and comparing results for a simple comparison.
    - Challenges include: amount of PN may only contribute 5-10% of the TN to be measured. Using TNC estimation procedure for comparison eliminates the need to match the volumes when applying the two methods side-by-side.

Comparison of TN methods using Virginia RIM samples (Elgin Perry)

E. Perry presented a statistical evaluation of the total nitrogen (by alkaline persulfate digestion method) vs. the sum of TDN (through alkaline persulfate wet oxidation) + PN (through high temperature combustion). He evaluated the difference in the two methods spatially, seasonally and in association with suspended sediments. The results show negligible bias at very low TN, positive bias at moderately low TN with the bias becoming negative as TN increases.

Supplemental Material: *E. Perry – Comparison of TN methods*

Discussion and Questions:

- In C. Patton's work, total nitrogen concentrations greater than 750 mg/L is where the amount of bias starts to show up heavily. Data used by E. Perry (real data – from Mike Mallonee) rarely reaches a concentration above 700 mg/L. How often do concentration above 700 mg/L occur?
    - Above the 750 mg/L samples, Jay Armstrong has experience no difference between the results of the two methods.

- In Figure 7 of E. Perry – Comparison of TN methods the Loess regression of the TN difference against the TN mean with confidence intervals, Interval A (TN mean of 0.46 to 1.08) shows a positive bias and Interval B (TN mean of 1.40 to 1.88) shows a negative bias . If looking at the data points site specifically, it was suggested that Interval A may be solely influenced by two of the VA RIM sites: the Pamunkey River site and the Mattaponi River site.
    - A suggestion was made to expand the data set to include DEQ data based on a previous attempt to explain differences in methods in VA.

Techniques to improve accuracy of alkaline persulfate digested samples (Jay Armstrong, DCLS)

J. Armstrong discussed the mechanics of the total nitrogen laboratory methods. In the lab, Armstrong has the opportunity to compare multiple test results sourced from the same container. He found that when the sediment loads increased, reproducibility declined, TN was usually the culprit.

- One solution was with high sediment concentrations to use a stir plate to mix the solution while pipetting to get a representative sample.
- In DCLS lab, samples with concentrations above 2 mg/L gets re-digested at a dilution and re-analyzed from the start of the procedure.

Discussion and Questions:

- In SOP and validation report there is a note, when samples contain high amounts of suspended solids, use stir plate.
- At USGS lab, over 60% of samples have PN concentrations above 2 mg/L and no dilution in procedure at that concentration. USGS has a higher range selected due to higher concentration of PN in samples.
- AMQAW participant suggested that storm impacted samples could be a good comparison of all the labs methods dealing with high TN concentrations to determine if the differences are a lab issue or environmental issue (difference in type of bias experienced).

- Is there a certified reference material for TN to QA/QC labs?
    - Before sequestration, funding was available to develop a certified reference material, funding no longer available.

        - Cost estimate: $50K (analytical costs for certification, weighing, packaging)
            - To gather more interest (funding resources), gather another material such as a hormone or pesticide to increase the demand
        - Suggestion for material: NIST makes a certified dried sludge material 4.78% sludge sample for running N (but very high concentration, and not representative of suspended sediment)
    - Why is it important to have a certified sample, why not use a similar method to split sample?
        - Need an appropriate amount of suspended sediment.
        - Split samples would not investigate the question at hand of how accurate the different methods are at determining the true concentration of total nitrogen.

- Design a protocol to send high sediment samples to other labs with capabilities of performing both TN methods (TN by alkaline persulfate digestion and TDN by alkaline persulfate wet oxidation + PN by high temperature oxidation) 1-4 times a year.
- **ACTION:** Continue the discussion of a procedure for finalizing a total nitrogen method with the NTWG. Specifically field related issues. (Mary Ellen Ley, NTWG)

Interlaboratory Performance Studies

Coordinated Split Sample Results (Mike Mallonee, ICPRB/CBPO)

- Mainstem Split Sample Results – Results
- Tributary Split Sample Results – Results

Spring USGS Standard Reference Sample Results (Lea Rubin, CRC/CBPO)

- USGS Reference Sample Results – Results can be downloaded under "Related Files" click "L. Rubin – USGS Spring Reference Samples"
- **ACTION:** Update – CBL PO4 Low conc.= 0.3393 (Lea Rubin)

Blind Audit Update (Kathy Wood, CBL)

- Mary Ellen – I don't have anything down for this Blind Audit update, do you have anything to include here?

Next AMQAW Meeting

Location: CBL

Date: July 11, 2013