MINUTES
Data Integrity Work Group (DIWG)

Virtual Meeting

Monday, September 30, 2024
1:00PM-3:00PM
Meeting materials link
This meeting was recorded for internal use only to assure the accuracy of meeting notes.

Participants:
Amber DeMarr (UMCES), August Goldfischer (CRC), Carl Friedrichs (VIMS), Cindy Johnson (VA DEQ), Clinton Leiby (PA DEP), Doug Chambers (USGS), Durga Ghosh (USGS), Elgin Perry (independent statistician), Emily Young (ICPRB), Heather Wright (ODU), Ian McMullen (DNREC), Jaclyn Mantell (NASL), Jake Kilczewski (MDH), Jay Armstrong (DCLS), Jerry Frank (CBL), Kelly Krock (EPA), Kevin Minga (ODU), Kim Blodnikar (CBL), Kristen Heyer (MD DNR), Lara Phillips (MDH), Lexis Carter (ODU), Mariah Smith (ODU), Meg Maddox (UMCES), Meighan Wisswell (VA DEQ), Mike Mallonee (ICPRB), Nianhing Chen (UMCES), Peter Tango (USGS), Phil Alsher (PA DEP), Rajya Lakshmi Mogilineedi (PA DEP, Samira Azemati (MDH), Sidney Anderson (UMCES), Suzanne Doughten (ODU), Tracee Cain (DNREC), Tyler Shenk (SRBC), Verónica Figueroa Negrón (CBL)

Next steps/action items:

- ✓ Carl Friedrichs and Dave Parrish will share an update on their use of remote sensing to assess water clarity at the next DIWG meeting.
- ✓ Peter Tango and Durga Ghosh will talk before the next Nontidal Network Workgroup meeting about potential next steps to re-examine and potentially qualify data that could be impacted by the bottle bias that Doug Chambers discussed.
- ✓ Durga Ghosh will follow up with Doug Chambers and Peter Tango about potential for a summer intern project to work on identification of other potentially affected sites in the watershed.
- ✓ Jerry Frank will share a timetable for the Blind Audit samples.

1:00 PM **Introductions, Announcements**
Monitoring, Laboratory and Community Science updates
Updates on SEAL Instrument Switch

Cindy Johnson introduced herself as the Chair of the DIWG and the Chesapeake Bay Grant monitoring coordinator and gave the update for VA DEQ. VA DEQ is on schedule for collecting samples. The additional rain in the southwestern part of the state has caused a lot of flooding,

and there were tornadoes. The Division of Consolidated Laboratory Services (DCLS) seems to be keeping up with their samples.

Carl Friedrichs (VIMS) introduced himself. Carl is a professor at VIMS and Associate Director of the Chesapeake Bay National Estuarine Research Reserve (CBNERR). He is a Principal Investigator on the tidal estuarine water shallow water modeling (funded by VA DEQ and EPA). They've continued to do standard water quality assessment DataFlow cruises focusing on the York River and Mobjack Bay each month since March. They've also doing proof of concept cruises in the York that use drones or satellites to guide DataFlow sampling. This doesn't take data that's used presently for assessment but they're working on a proof of concept and have done 3 of these so far. Dave Parrish will provide an update on their use of remote sensing to assess water clarity at the October 9th Criteria Assessment Protocol Workgroup meeting.

There are 3 year-round continual monitoring fixed stations in the Rappahannock supported by VA DEQ and EPA and they will be adding 3 more year-round con-mon fixed stations in the James as part of FY25 contract. They have another dozen or so year-round con-mons in VA waters that they pool as part of the VA Estuarine Coastal Observing System (VECOS) hosted at VIMS.

Durga Ghosh asked if Dave and Carl could share the update on their use of remote sensing at the next Data Integrity Meeting, and Carl said they could do this. Durga introduced herself as the Quality Assurance Coordinator for the Chesapeake Bay Program. She works for USGS at the MD-DE-DC Water Science Center, and coordinates the DIWG.

Doug Chambers introduced himself as a biologist with USGS VA-WV Water Science Center and provided the update for West Virginia. Doug is the Center's water quality specialist and project chief for the WV portion of the nontidal monitoring program. Things are going well in WV. They had a significant drought until the last few days, when they've been able to get storm samples in the last part of the water year.

Suzanne Doughten introduced herself and Heather Wright, who are with Old Dominion University (ODU), and provided the update for ODU. They collected summer cruises twice a month. They just did September despite the bad weather and got all the stations. They had one cruise this summer with extremely low DO; they actually had no oxygen in some of the stations. All the samples are being analyzed on time and they anticipate going out in October. For their instrumentation switch they provided all the data to Mike Lane but he hasn't produced a report yet. They haven't yet switched over TDN and TDP, they're still working on that method, but all the other parameters have been switched over to the SEAL instrument.

Ian McMullen (DNREC) said DNREC has been switching to the SEAL for most of their analyses. Tracee Cain (DNREC) introduced herself as the assistant Quality Manager at DNREC. She shared that DNREC moved a lot of their nutrients from an Astoria Pacific Flow Analyzer over to a SEAL flow analyzer. They have a three channel. One channel is dedicated to ammonia, another channel is for orthophosphorous, and the other is dedicated to nitrate/nitrite, and it also does

nitrite as well. They're quite pleased with the SEAL. They've noticed better consistency. Tracee shared that all the planning from SEAL on the front end helped – when they installed the machine they had the methods ready to go. During the install they ran a PT and got great results. DNREC just got the purchase order approved to move total phosphorous and total nitrogen over from the Lachat to another SEAL three channel flow analyzer. That should get delivered at the end of the year and be installed.

Durga said she might reach out to Tracee with additional questions.

Lara Phillips, inorganics supervisor at Maryland Department of Health (MDH) provided an update for MDH. She said that MDH is still working on instrumentation procurements. She shared that their long time employee in the lab will be retiring at the end of October so there will be a job posting soon. August said to share the job opening with them when it is posted to share in the Bay Brief newsletter.

Jerry Frank provided the update for Chesapeake Biological Laboratory (CBL). They have some new instrumentation they're working with but haven't brought fully online. CBL didn't make any major switches, just upgraded discrete analyzers, but they're not fully online yet.

Kelly Krock (EPA Region 3) introduced herself. Kelly is in the science division field services branch and quality assurance officer and biologist who does stream sampling.

Kristen Heyer introduced herself and provided the update for Maryland. Kristen manages the water quality monitoring field office for MD DNR. That office participates in both tidal and nontidal monitoring so they collect mainstem and tributary samples. MD had a bit of trouble with the mainstem research vessel - the boat engine broke in February. VIMS helpfully loaned their boat to assist with sampling. MD completed their September sampling last week. It was challenging due to the bad weather but they were able to get the VIMS boat for a few days and then complete the rest of the sampling on MD's small boat. MD DNR also recently deployed continuous monitors in the Choptank. That work is in conjunction with the DO arrays that NOAA deployed in the Choptank. MD will work with NOAA to see how the data matches up between the continuous monitoring sonds and NOAA's arrays. MD DNR is also sampling in Fishing Bay in conjunction with MDE. They have a vertical profiler and two continuous monitors there. In the National Estuarine Research Reserve they have 5 stations in MD they monitor. They also do the NTN sampling for routine and storm samples. They'll probably come up short a few samples this year.

Nianhing Chen introduced himself and provided an update for UMCES Horn Point. He works with Meg Maddox at UMCES Horn Point analytical services. They bought a new SEAL autoanalyzer last year and have been working on it. They're ready for next steps. Right now they only work with the dissolved parameters, not TDN, TDP or particulate.

Phil Alsher and Rajya Lakshmi Mogilineedi were attending the call as quality assurance chemists with PA DEP Bureau of Laboratories.

Tyler Shenk introduced himself and shared updates for the Susquehanna River Basin Coalition. They haven't had enough rain to get storm flows (despite not seeing the sun much recently).

1:20 PM Blind Audits Update – *Jerry Frank (CBL)*

Jerry said the samples will be coming out soon – by the end of October at the latest. The contracting for the Blind Audits project was moved outside the contract CBL typically has with the CBP through MD DNR to a third party. It was the first time UMCES had to negotiate a contract with that third party and was a bit cumbersome. That's worked out now and samples should be coming soon. Due to the delays the second round of sample shipments (usually there are two per fiscal year) will come quickly after the first round. Jerry will share a time table for that soon.

Durga said to let her know if CBP can help with any contract related concerns.

1:30 PM Coordinated Split Sample Program – *Mike Mallonee (ICPRB)*

The May 2024 sample has been added to the last presentation. There were no questions or issues raised.

Mainstem split sample
Tributary split sample

1:40 PM Update/presentation on potential bias in the SSC analysis for NTN stations in karst watersheds – *Doug Chambers (USGS)*

Summary:
The nontidal network sites in West Virginia are in the Eastern panhandle, with all 10 sites in the Potomac River basin. It is a diverse set of sites from less than 10 square miles to over 3,000 square miles. The sites vary in physiography and are mostly in the valley and ridge physiographic province but with portions in the Blue Ridge and Appalachian Plateau provinces as well. Sampling started in 2005 and grew to the current 10 sites by mid-2012. Sites vary in water quality characteristics as well as in size and physiography. There's some variability in suspended sediment concentration, and a significant difference in nutrient state is indicated in nitrate concentration and dissolved material as indicated by specific conductance.

In late 2016 the USGS Kentucky sediment lab notified us there would be an additional charge for using 500ml disposable bottles that had been in use since the beginning of sampling. This charge was to cover the additional effort in retrieving suspended sediment due to the bottle's narrow mouth. They recommend a 1 Liter reusable bottle instead. The WV nontidal sites adopted the reusable bottle to avoid the extra charge. After the switch they started to receive suspended sediment results and for most sites there was no significant difference. However, Mill Creek had a significant difference in suspended sediment concentrations associated with

bottle type. After the bottle switch there was a positive shift in the suspended sediment and turbidity relationship almost exclusively in the samples decanted from the reusable bottles.

This pattern of a positive bias in the suspended sediment turbidity relationship associated with bottle type was also reflected in 2 other sites for a total of 3 of the WV nontidal sites: Mill Creek at Bunker Hill, Opequon Creek near Martinsburg, and Rocky Marsh Run. No other site reflected this pattern even though the bottle change had been implemented at all sites at the same time. The most obvious difference among sites was geology. Significant portions of valley and ridge physiographic provinces are underlain by carbonate rock aquifers and Karst terrain. The three sites with the bottle type associated sediment bias they drain basins dominated by karst landscapes. These three sites differ significantly; the streams carry more dissolved materials derived from the soluble carbonate landscapes that dominate their watersheds.

To address this issue, Doug implemented a program collecting replicate samples for each sediment bottle. The main sample in a reusable bottle, and the replicate in a disposable bottle. They collected bottle type replicates for all types of samples; environmental samples, blanks, and even replicates of replicates. Doug talked to the lab about possible sources of variability that may have been overlooked but did not receive valuable feedback. Doug kept up with the replicate samples and a year or two down the line Sam Miller, USGS hydrologist, asked why might these sites have high sediment at low turbidity? The suspended sediment – turbidity relationships were biased high for sediment at the low end of turbidity. Sam looked at his sites in comparison and found common patterns. All of these sites were in the Great Valley, an area of extensive Karst terrain. Sam noted samples with suspended sediment concentrations exceeding 100 mg/L while having turbidity values of less than 10 fmu. In Sam's models he found higher specific conductance associated with greater uncertainty in suspended sediment – turbidity models. There was increased uncertainty in the WV dataset in data co-occurring with the bottle change. Sam examined the suspended sediment – turbidity relationships in the Midwest and found high biased patterns in many areas underlain by carbonate geology. This strengthened the hypothesis that elevated solids could contribute to high bias in suspended sediment concentration analysis. With these multiple lines of evidence Doug re-engaged the lab in this issue.

The lab paid closer attention to samples from Karst sites and saw the re-usable bottle types almost always had higher suspended sediment concentrations. One explanation suggested it was the small mouth of the single use bottle that precluded the efficient use of the spatula to harvest sediment from the bottles. But if this were the case an increase in sediment would be seen in all 10 WV sites, not just those in Karst terrain. At this point, while Doug realized may be an issue with the re-usable bottles, the lab had only used their standard 1 pint glass bottles for their lab blanks. With the possibility of bottle type being the source of bottles, the lab processed a series of blanks using glass bottles, the recyclable plastic bottle Doug used previously, and the 4 common types of reusable bottles: 500 mL, 1 L Isco bottle, 1 L sampler bottle and a 3 L bottle. Reused plastics, particularly the 1 L sampler bottle performed somewhat poorly in blanks.

How could high dissolved solids be contributing to high bias in sediment? Precipitation dissolved materials. Why this occurs in re-usable plastic bottles and not single use plastic in glass? Possible factors include condition and residue. Plastic is more susceptible to abrasions, gauges and other damage from harvesting sediment with spatulas or cleaning with brushes. These scrapes may serve as nucleation sites for precipitation of dissolved material. Residue left in the bottle from either cleaning or environmental residue not removed from cleaning can contribute to high bias. Residual material may also serve as nucleation sites for previously dissolved constituents. Glass is less susceptible to wear and scratches. Glass surfaces are more readily cleaned. Single use plastics are not cleaned, therefore not damaged or having a possibility of residue build-up. The final factor could be holding time. The lab is conducting an experiment to analyze the influence of organics such as algae or biofilms, and initial analysis demonstrate that organic constituents are not a contributor to bias. However a study of holding time and precipitation of dissolved inorganics has not been conducted to date.

Doug concluded by sharing key takeaways: High bias in SSC has been observed for sites with high dissolved solids (as measured by specific conductance), and is not isolated to one lab. Findings have been shared with the USGS Sediment Labs Workgroup. Kentucky Sediment Lab incorporated new procedures: Specific Conductance (SpCond) measurements for all samples; additional rinses for samples with SpCond > 500 µS/cm; acid rinsing of all sample bottles during cleaning. Plastic sample bottles should be routinely replaced, or glass bottles used. Karst Terranes are present throughout the Chesapeake Bay Watershed and many NTN sampled watersheds contain karst terrains, therefore careful examinations of SSC:Turbidity are needed and field staff should pay close attention to conditions of reusable sample vessels.

Discussion:

Elgin Perry: Is it a separate turbidity measure for a single use bottle and a reused bottle or are they both being paired against a single turbidity measurement?

Doug Chambers: They're both being paired against a single turbidity measurement. Those are collected as a median value of a cross section of 10 measurements taken across the width of a stream.

Elgin Perry: You had a hypothesis that one possible explanation for the additional SSC in the reusable bottles was that dissolved constituents were precipitating onto microparticles of plastic, and that would raise the SSC. I was wondering, it seems like that would also lower the specific conductance, did you look for that?

Doug Chambers: Specific conductance was measured in the field. It wasn't necessarily only microplastics in the bottle, but maybe irregularities in the surface of the bottles – places where an irregular surface was exposed to the sample. We did not examine specific conductance comparing the measures in the field to that measured at time of analysis by the lab. They only started implementing a specific conductance measurement in the lab after identifying the problem so we have a fairly small data set for that. We'll take a closer look at that data but we have a pretty good idea there is bias between the bottle types.

Elgin: I agree, the evidence for bias is very strong. I was just curious about explanations for what's causing it, that would make the argument stronger and make remediation even more possible.

Doug: The step function in our suspended sediment just for three sites stood out to me. It was more than merely the change in bottles; it was the change in bottles plus another factor.

Durga: Really neat study and very thorough. Thank you for initiating and catching this. You mentioned the time frame; the lab is now taking measures to remediate the issues. What is that time frame up until you stopped seeing it? Or are we still not sure if the remedial measures the lab is taking are adequate?

Doug: We're seeing in the reused bottles that some of their remedies are showing some level of efficacy. I have instructed my field crews to shift to using glass bottles which are more readily cleaned and don't show the level of bias and perform well in blank studies. They're a little harder to deal with in the field but produce better data.

Durga: You mentioned this isn't restricted to the sites in WV and VA. Do you have a sense of whether we could be implementing this across the watershed? Has there been a consensus among the nontidal groups?

Doug: This has been presented to the Nontidal Network Workgroup. There's a mix in that group of those using plastic single use vessels or glass. I don't think there's been any guidance issued on that. I think most of our project chiefs will take the information that's been presented and apply it in an appropriate manner.

Mike Mallonee: Do you think at some point it will be necessary to go back and qualify the data for any of these sites?

Doug: What I've done recently is I replaced data that was submitted to the CBP using the re-used bottles. I have taken the data from the single use bottle that did not exhibit bias and replaced that data for those three sites. The data currently in the database is the "low bias" data (what we perceive to be the more correct data).

Durga: Should this be done for other sites as well? Should we be revisiting all the post-2012 data, and not just for WV?

Doug: That would have to be re-examined on a site-by-site basis using the history of what sample vessels were used. I think that would be a prudent step.

Durga: Peter, do you think we should address this – either the NTN or DIWG group?

Peter: I'm willing to follow up further on that. I'll catch you between now and the next NTN meeting.

Carl Friedrichs: I was thinking about how we might see if there's ever an issue in places that had other contributions to conductivity. In our estuaries conductivity is almost always dominated by the mixture of salinity from the marine and of the estuary. I was wondering if there might be other proxies that might help identify water where there might be a lot of dissolved calcium carbonate. That's not something in water quality circles we look for often, but we do measure pH a lot. Maybe that could be a flag to worry about situations (if the pH is high) because dissolved materials from karst topography tends to have quite high pH.

Doug: If you're looking for other contributors you can consider pH, specific conductance, solubility indices.

Carl: I was thinking if pH levels were low enough in our estuarine observations (and we don't want them too low) – maybe you'd have to have a pretty high pH if you have that much calcium carbonate that could precipitate to such high levels of suspended sediment concentrations.

Doug: All these sites, compared to the rest of the network, have fairly high pHs, depending on where you are in the diel cycle, ranging up above 9.

Elgin: You focused on the suspended sediment issue. I assume you must have checked, once you observed there was a special combination of the karst background and reusable bottle, did you look at other parameters to see if they also had a bias?

Doug: I tried to look as broadly as possible within what's in the data we had available. I didn't settle on karst being the cause right away. As I looked at what data I had those were the things that stood out. There were differences in pH, specific conductance. These sites have our highest base flow contribution – how much of stream flow is actually from groundwater. Such as Rocky Marsh Run at Scrabble – we've done hydrograph separations. Depending on which model is used it's up to 98% base flow. Based on the information I had, the carbonate rock aquifers karst terrain was the explanation that best fit the anomaly we saw in the suspended sediment data.

Elgin: I agree you've done a great job of narrowing down the situation. What I am wondering about is would this special combination lead to bias in other water quality parameters?

Doug: Those three sites had differing nutrient statuses as reflected by nitrate. That's all tied into the karst terrain and what you see in the ground water vs surface water. Most of the nutrients, particularly nitrogen, in flux in the system, is coming from ground water. They have a common source but I don't believe them to be one biasing the other.

Elgin: It's not related to the sample bottle, just to the geology?

Doug: Yes. And the geology is what's influencing what's going on in the sample bottle with sediment.

Durga: Peter/ Doug- would identification of other potentially affected sites in the watershed make for a summer intern project? If so, please let me know, we can part fund it from northeast regional office. I'll follow up with you.

Cindy: Who is using what kind of containers to collect SSC? At DEQ we're not using re-usables for TSS or SSC, but we're using cubitainers for single use. I don't know what the Richmond office is using.

Doug: Depends which lab they're sending it to. Samples that are going to DCLS (for River Input Monitoring sites and Nontidal) are going in a cubitainer. Anything going to the Kentucky Sediment Lab is going in a glass pipe bottle. I will check on that on a project by project basis.

Kristen Heyer: Maryland uses all 500 ml reusable bottles and has since the beginning of NTN.

3:00 PM Adjourn