Data Integrity Work Group (DIWG) – Lab specific meeting

Wednesday, October 18, 2023

10:00AM-12:30PM

Meeting materials: link

Participants

Alexandra Fries (UMCES), Amber DeMarr (UMCES), August Goldfischer (CRC), Carl Friedrichs (VIMS), Chris Mason (USGS), Cindy Johnson (VADEQ), Clinton Leiby (PA DEP), Doug Chambers (USGS), Doug Moyer (USGS), Durga Ghosh (USGS), Ian McMullen (DNREC), Isabella Bertani (UMCES), Jaclyn Mantell (CBL), Jake Kilczewski (MDH), James Colgin (USGS), James Webber (USGS), Jay Armstrong (VA Division of Consolidated Laboratory Services), Jerry Frank (CBL), Kaylyn Gootman (EPA), Kevin Minga (ODU), Kim Blodnikar (UMCES), Lara Phillips (MDH), Lexis Carter (ODU), Mariah Smith (ODU), Pamela Higgins (PA DEP), Suzanne Doughten (ODU), Tammy Zimmerman (USGS) Tracee Cain (DNREC), Verónica Figueroa Negrón (UMCES), Meg Maddox (UMCES)

Actions/Next steps

- ✓ At next DIWG meeting members will discuss requirements for the sample comparison study when switching to a new instrument (how many samples should be required; specifically in the instance when most/all labs switch to the same instrument).

Minutes

10:00-10:05 Introductions & Announcements All

10:05-10:15 Updates: Monitoring, Field Audits, Blind Audits funding All

- Carl Friedrichs gave the update for VIMS. Betty Neikirk is doing the last data collection this week. VIMS will be taking the continuous monitoring stations out of the Rappahannock on November 1st-2nd.
- Suzanne Doughten gave the update for Old Dominion University (ODU). They have completed sampling through October for the mainstem.
- Doug Moyer gave the update for Virginia USGS - they are on target for all of their nontidal network sampling and encountered no issues.
- Cindy Johnson gave the update for VA DEQ – they have no issues and are on target for all monitoring.
- Lara Phillips gave the update for Maryland Department of Health (MDH) saying that there are no problems to address besides the Total Dissolved Phosphorous (TDP) issue they'll talk about later.
- Jerry Frank gave the update for Chesapeake Biological Laboratory saying things are fine and they've taken receipt of and had a new instrument installed. They had a new staff member Amber DeMarr join them in July.
- Doug Chambers gave the update for West Virginia USGS - things are going well.
- Tammy Zimmerman gave the update for Pennsylvania USGS. They had one problematic site in FY23, at their smallest site called Big Stream Run, which is less than 2 square miles of drainage area. They got only half the samples this year because flow is flashy and goes up and down in 5 hours or less. What they did to address the issue was to

purchase an ISCO refrigerated automated sampler, and they are planning to put it in next month to see if it helps. Other than that, they did well.

Field audits –

- Durga updated the group that she is still waiting on some funding from EPA. For the time being Durga is focusing more attention on the community science audits. There were two this summer, one for Arundel Rivers Federation and one for Anne Arundel Community College. Both audits went really well, and the groups were promoted to collecting Tier 3 data. Durga is also in conversation with the Potomac River Keeper for their bacterial data monitoring. They are trying to figure out how MDE wants to use the bacterial data because they don't have it in their integrated report.
- Kaylyn said that audits funding is at the top of their priority list.

Blind audits –

- Jerry Frank updated the group that he received a final extension and is currently finalizing the FY23 report, which will be complete and available by end of the month. For the next round, they had to restructure the contract, so they are switching to a calendar year basis. There won't be a fall round this time around; Jerry will send the first batch out in January and the second in July, with that year's combined report going out at the end of the calendar year. There was a need to restructure based on the funding of the project; it didn't have to do with the format of the program. That will stay the same as well as the format of data reporting.

10:15-11:15 Laboratory and Analysis Discussion All

Maryland Department of Health (MDH) showed a video explaining their issue with Total Dissolved Phosphorous (TDP) data anomalies. The video described the data anomalies, the investigation into the issue, and how they corrected the issue. In late 2022 and early 2023 they identified intermittent elevated results. The source of the problem was identified as the glass tubes. They started washing the digestion tubes using the Steris dishwasher including washing brand new tubes with a special acid wash and detergent. Some Total Dissolved Nitrogen (TDN) results were reported without TDP results. TDP results within the holding time were repeated after the wash step was repeated, and this fixed the issue. However, the scope of the problem was found to be larger. The TDP Standard Operating Procedure (SOP) was revised to include the washing step. In August MDH was notified by DNR of an issue with data discrepancies. Careful review and inspection identified specific stations and results to remove from the database.

Data trends analysis was not part of the review process which didn't allow them to see the full scope of the problem. In response to this issue, MDH Lab Nutrients Lead created a database for tracking sample trends. This adds another layer of quality control. Tracking these trends showed when the issue began and that it resolved once steps were taken to fix the issue. The SOP has been officially updated to be included in the QAPP. An MDH corrective action was also created.

<u>Discussion:</u>

Jerry Frank (CBL) thanked MDH for their transparency about the issue. Durga Ghosh (USGS) agreed and said this was very beneficial for the group. Many labs have control charts as part of

protocol, and it is a really valuable and a simple way of detecting errors. Lara Phillips (MDH) responded that they have control charts for their QCs, but they hadn't been tracking the sample results, but they had been tracking all of the nutrient results.

Jay Armstrong (DCLS) asked if the problem manifested in their blanks at all and Lara said they had sporadic elevation, but it wasn't consistent, so it was hard to see what was going on right away. Jay asked if the problem transferred to the analysis tubes. He said at DCLS they acid wash test tubes for low ranks tests like TDP and Total Dissolved Nitrogen (TDN) and do a similar cleaning to the digestion tubes before use. Lara answered that they hadn't noticed a problem with the Lachat tubes. She asked if Jay had any issues with tubes breaking when washing? Jay said they use plastic tubes from another manufacturer, so they don't have to worry about the pre-washing issue and safety issues of breaking and cutting someone.

Jay explained that DCLS buys those tubes from Skalar. The tubes fit the 60 position sample racks on the Lachat, the Seals and the Skalar. The wall thickness doesn't prevent them from being centered on the tube openings. They don't re-use the tubes; they concluded that the issues it can produce later weren't worth it. They do wash the tubes prior to use, so it's not really a time saving thing because they still wash them in 10% HCL.

Heather Wright (ODU) said that they use glass tubes in the Lachat, except for silicate they use plastic. The tubes are washed twice in 10% HCL, three times for ammonia, and then six times with reagent water before use. They do a digestion run with just the oxidizing reagent and water with new TDN digestion tubes prior to using them. They also acid rinse before dispensing samples.

Jay said they do the same thing with TDNP digestion tubes before their first use. They put them through a digestion cycle with the oxidizing agent in the equivalent volume of sample replaced with de-ionized (DI) water in order to digest any residues or anything else in those tubes and have it removed before using it for analysis. It sounds like the washing procedure in the dishwasher accomplishes same thing. Heather responded they don't have a dishwasher and don't have any issues.

Jay asked Lara to send him the brand of detergent Lara is using. Lara said she would.

New Flow Analyzers post- Lachat discussion

Jerry Frank said they've been using discrete analyzers for some time as well as segmented flow. They switched their Technicon AA2s out to new SEAL flow systems. Jerry asked if any of the people using Lachat have gone to discrete analyzers or to segmented flow. He asked if they are happy with their purchase and issues they are running into. He said that CBL had a really smooth transition with their first SEAL AA500. They brought their low-level cadmium energy reduced analysis to a SEAL and are in the process of bringing their lower-level Total Nitrogen (TN), Total Phosphorus (TP) analysis to SEAL as well, although that's been a little more complicated.

Lara Phillips said at MDH right now they have a FIA instrument and they validated it for low level nitrate nitrite. The results look good, but they have to run the test one at a time as opposed to the Lachat running multiple at a time, which isn't very efficient. It does run good results, though. The lab's feedback is that the software isn't as easy to use, however. They are having SEAL come in to demonstrate a discrete analyzer later.

Jerry asked which model MDH was using, and Lara said she didn't remember but can email him.

Jay said DCLS is running a SEAL 500 now for low level nitrite nitrate. They validated it and submitted all the studies, and the comparisons were good. It's taking some getting used to, however and there's a learning curve. The software is very powerful and overall, they are pleased. The mechanics, stability of baselines, and reproducibility of peaks is as good or better than the Lachat. They enjoy the ability of the automatic shutdown so it can run over night. They're using the cadmium coil for our nitrate set up. The cadmium coil uses a nitrogen bag, so there is no need to de-bubble. It doesn't destroy the copper coating going into the column. As someone who has used Lachat, Skalar and SEAL, Jay said he is pleased with it. In the DCLS lab they still use all 3 of those platforms. They had their first service for the SEAL 500 and learned a lot. The instrument seems pretty resilient. They're working on the data for moving Particulate Phosphorous (PP) over at the current time.

Suzanne Doughten commented that ODU got their first SEAL over the summer and just started using it. They had a couple questions. For PP, are you using a 1 normal HCL for the sampler wash? Jay said they are and asked if ODU does the PP extraction and run the extract straight, with no dilution? Suzanne said they use a [water] line on the instrument to do the dilution.

Jay said that DCLS didn't set up that way. They maintain doing the 10-milliliter extraction and 1 normal followed by dilution to 50 milliliters. They don't have the water line doing the dilution. The phosphorous colorimetric reaction – the acid concentration makes a difference in phosphate production. The reagent train being used needs to be able to handle whatever concentration of acid is introduced to it. Otherwise, it could reduce the color production or reduce the linear range. Jay said when DCLS got their instrument they sent what their PP method was going to be, with all the acid concentrations, to SEAL to make sure those acid concentrations would be acceptable with the chemistry they're using. It was, fortunately. The Lachat and SEAL have comparable results from the initial results. That's what would be expected with use of the same calibration method. They are just starting to validate this now, and the initial results are looking good. They're able to maintain the same range and same concentrations.

Suzanne said that ODU provided their methods to them [SEAL]. Jay said DCLS did the same and they came back to us saying that no changes were needed. They have good customer support.

Suzanne then asked the group, if everyone is going from Lachat to SEAL, does every lab have to do the 100-sample comparison study for each analysis?

Durga said that her initial response would be yes, but she'll need to about it. She said she thinks there are differences despite having the same instrument when considering the different labs that are using it. Durga would feel more comfortable if labs could run the samples but asked what the group thought about it from the lab perspective.

Suzanne responded that it's a lot of work and a lot of time for the data analyst.

Jay said that one of things they run into with parallel studies is that they've already purchased the instruments and they can't send them back once they get them. Depending on the analyte it is good data to have so if there is a concerning trend, it's possible to look back at the data and see if the parallel study showed something, which would provide some ideas on how to

normalize that going forward. But once an instrument is purchased, that is what it is. Jay added that when looking at the differences, a lot of the work that they do is down around or below reporting limits. It's necessary to be careful how you look at that data, what's significant and what isn't. Looking at the analytes, the simple nutrients which don't go through any digestion or prep, and the influence between the two instruments is more about what you pour in the tube than what you digested. Jay said he sees the value in the comparison studies but the number of samples in the comparison study is up for debate, and that would probably be up to a statistician.

Jay added that a lab doing several different conductivity ranges for their matrix probably want to look at the different conductivity ranges and make sure they are receiving similar results. For the tests where you digest things like particulate phosphorous, TDN, and TDP, those matrices become pretty similar once you do the digestion. The predominate matrix is an acid solution that's driving the results more than anything else. For TDN and TDP, once add the digestant is added to the samples, the digestant itself has a good amount of ionic strength to it, which somewhat normalizes the ionic strength of the solutions being analyzed.

Durga said she think it boils down to being able to run those samples concurrently, and identifying if there are any issues. She said she hear Jay when he said it's a done deal when you make the switch from one instrument to the other. At the same time, having the comparison sample information helps when looking at the data and figuring out later issues. Durga said it would be wise to run the samples and she thinks at least some number of samples is needed from all labs, but the number could be re-considered.

Lara said she thinks it's still a good idea to run a comparison study, and that it's useful.

Pam Higgins (PA DEP) thanked everyone who provided insight on the SEAL, which they are looking at to replace Lachat. As to 100 vs 50 samples question, for PA DEP, validation is according to their laboratory accreditation parameters from the New Jersey National Environmental Laboratory Accreditation Program (NELAP) laboratory. A lot of that involves revalidating with Method Detection Limits (MDLs), Reporting Limits, Precision Data and running Proficiency Testing. Pam asked if PA DEP validates a method according to their national accreditation standards, would that be acceptable as compared with running a large comparison study?

Durga responded she thinks it would be accepted. They had to consider this because the Chesapeake Bay Program doesn't require lab accreditation (CBP doesn't have the regulatory power to do so). However, CBP could ask (not require) the other labs to use those same procedures.

Kim Blodnikar (UMCES) commented her concern was when changing from a Lachat to a SEAL, there is a change from peak area to peak height. It will be important to make sure those two technologies go hand in hand. Kim said some sort of data comparison between Lachat and SEAL using Bay program data is needed, whether that's going through the NELAP certification steps, or just making sure split samples are comparable.

Durga said that this group should probably have a follow up discussion on this topic.

Suzanne said that the original comparison studies came from data analyst group, not the lab group. They all checked their MDLs and have method validation. But the actual comparison

studies came about when the data analysts requested it because of trends through the years and what they're doing with the data. They're more concerned about small differences between instruments.

Durga responded that from the perspective of looking at loads and trends, you want to know if you can compare data from the old instrument to data from the new instrument. She said she understands there are multiple layers here that need to be addressed from multiple perspectives.

Jerry said when this discussion took place in the past about establishing a policy for labs doing CBP work, no hundred pairs comparison was necessary for changing instrumentation that maintains the same technology, but it was necessary for switching to different technology, for example from segmented flow to discrete analyzers. Jerry's position was that going from segmented flow to segmented flow that would not require 100 pairs. CBL is an accredited lab, so they have a protocol to go through to bring any new instrument online. Jerry thinks that seems more than enough for new instrumentation with existing technology.

Jay commented that DCLS is accredited by the National Environmental Laboratories Accreditation Conference Institute (or the NELAC TNI) as well. The parallel studies that they do are above what's required by TNI for bringing up a reference method. When bringing up a reference method they do MDLs, determine Limit of Quantitation (LOQ), and do a limited precision and accuracy study. The requirements in the comparison study program are a little greater than what's required by TNI, but not prohibitive. When doing these parallel studies for filtered parameters like particulate carbon, phosphorus, and nitrogen, it's important to compare instruments. For instance, with PP you should be doing one extraction, and then comparing how that extract reads on two instruments. Otherwise, if you use two separate filter, you'd introduce filtration error. For phosphorus, carbon, nitrogen (PCN), a more logical way to look at how those instruments compare is to run a known homogenous material. If you do the combustion testing, there is little to no interference for carbon or nitrogen. If you were to compare homogenous materials, you get an idea of how those instruments compare. Jay said that to make any changes it would be necessary to look at what the Quality Assurance Project Plan (QAPP) says, and make sure that accredited labs wouldn't run into any issues following the QAPP.

Suzanne Doughten commented that in that document they did for Mary Ellen [Methods and Quality Assurance Manual, Chapter 2, method comparison table] with the labs there is something about comparison studies and requirements.

Jay said if changes are made, some type of addendum should be issued to the labs. But that's further down the line from now.

Durga said that she could go back and look but her thought process that for any change, labs need to run 100 samples. That was a general statement and the labs continued following that. This sort of a different question though: could we change the actual number of samples? Durga said the group should reach out to Elgin Perry if they decide to make a change. She said Jay brought up a good point in that labs want to follow what they're using for their lab's accreditation, and it would be difficult to have two different sets of protocols. For everyone to get on board and to treat all the labs similarly, let's see what lab protocol says for the lab accreditation and see if things can be streamlined. Durga said she would not make this exception for everything else but as was pointed out, once you purchase an instrument you can't go back on the instrument. For the question of do all labs need the 100 samples if they all

use the same instrument: amendments can probably be made but it should be the same for all labs. Now, let's see for labs who are accredited, let's streamline and say to other labs this is the minimum requirement we have. Durga emphasized this is a singular case and doesn't apply to future instrument changes.

Jake Kilczewski (MDH) asked, since MDH is deciding between the segmented flow and discrete analyzer from SEAL, and the salesperson is pushing them towards the discrete analyzer, what are the reasons that labs went with discrete analyzer vs segmented flow or vice versa? justification for doing so.

Jerry responded that he thinks CBL is the only lab using discrete analyzers. They have Thermofisher discrete analyzers and are not super familiar with the SEAL instruments yet. Some of the reasons they went to discrete analyzers include that the throughput is higher, the volume of reagent is lower, and it is easier to work on. Throughput was the main reason. Another reason is that for samples with a complicated matrix, you don't have to worry about it contaminating your entire system. CBL been using discrete analyzers for almost 20 years.

Jake asked if they had any issues getting reporting levels down.

Jerry said he would have to check but he thinks they saw some of their detection levels go down some. They were having to correct for salinity with phosphate in the past and they don't have to do that anymore. They do correct for salinity using ammonium, but they probably should've been doing that before. CBL has 3 discrete analyzers. Two Aquakem 250s (AQ250s) do 90% of the work. They have a Gallery as well which works like the other ones but the lamp is slightly different technology and the way in which the light is channeled to the detection chamber is different. They haven't been super happy with phosphorus; they haven't been able to get it as low as they like. They haven't been able to focus on method detection with gallery. Unfortunately, the AQ250s were discontinued. That's why they're looking at SEAL and Skalar as the most logical candidates for replacing either one of their current discrete analyzers.

Jake asked Jay if he could explain why he went the segmented flow route with the AA500.

Jay said they have multiple low platforms depending on what type of testing they're doing. They're fortunate to be able to segregate testing and develop the instruments to perform the narrow profile they want them to do. They don't have to switch out channels; their channels are dedicated. As far as comfort with a type of platform or technology, that plays into the decision because they are fortunate to have a group of analysts who have a lot of experience with these platforms. These abilities do transfer over to a new platform from Skalar to SEAL. The difference is in the software. As far as the AA500, before they purchased that instrument Jay did a bit of background and got references, and noticed those flow instruments were being used in labs doing oceanographic type work which made him confident it could do our work. They're not analyzing the heavy salinities that Jerry might be getting, they're a tributary laboratory. Instruments seem to be a good fit based on the matrices they were going to be doing. Going to discrete, they did have one, but not made by SEAL. It was made by a company Jay is not sure exists anymore. They set it up to do nitrate analysis for their drinking water work and they set it up using cadmium reduction. That was a challenge to keep the column efficiencies up. They were regenerating columns on a regular basis. Whether that was something with the instrument or with the lab, they never figured out.

Jay asked Jerry if his lab is running enzymatic reductions on their discrete analyzers. Jerry said yes they have been for 15 years with great success. They never used the cadmium column model.

Jay said he brought that up because Jake may want to talk to the salesperson about what they recommend for that setup and whether they recommend the enzymatic reduction. Jay remembers the nitrate was a little bit of a challenge.

Jerry offered that Jake and anyone else is welcome to come take a look at the CBL instruments any time.

Durga said going back to the comparison sample question, the group should get together again before making a decision. And the group should have a basic document with questions and what they're trying to address.

Questions submitted by labs:

- Who do labs use for nutrient PT studies?
    - DNREC, UMCES, MDH and DCLS responded that they use ERA.
- What instrument is each lab using for PC/PN?
    - DNREC, MDH, DCLS and CBL use the Exeter CE440.

Suzanne said ODU is asking because they're using the Thermoscientific CE Atlantic but it's getting old so they're looking at replacing. Suzanne asked if the labs were using an old or new instrument. Jake said MDH is using a very old instrument. Jay said DCLS purchased a new machine several years ago but they're very durable instruments and the instrument itself hasn't changed much since 1996/97. Both MDH and DCLS however are relying on one support person for the machine.

- Who do labs use for their thermometer calibration for their NIST traceable thermometer?

MDH uses Thermoworks calibration lab. They're A2LA and NIST accredited. DCLS uses Thermco and Traceable.

11:15-12:15 Decision Rules for Determining TP and TN Doug Moyer, James Colgin

Doug provided context for the agenda item.

There are a couple steps remaining. One is a Quality Assurance (QA) step. Once they pull the data, they want to go through and make sure there are no anomalies, and they meet our standards. They'll work with jurisdictions if there are QA issues, and potentially come back to labs if there is something that they need guidance from labs on.

The feedback sought today is evaluation and input on the decision tree. Do the labs agree with the order of preference on what they are using for total nitrogen and phosphorous that they calculated based on individual components?

<u>Discussion:</u>

Jay asked if they have started looking at the data for how the entries compare for some of the other things. The TN tree looks like the biggest one.

Doug said it is. James said he doesn't think they've been looking at comparisons between totals and sums of pieces but they could. They would rank any lab measured values over calculated pieces.

Doug said they can find the VA sites specific to Jay and go to other labs as well and say, where are there overlapping options for determining total nitrogen. They've looked at some of those and there are some times they compare well and other times there are differences between the two. They can show examples of paired analytes and how they differ or are similar in getting to TN.

Jay said they've been doing direct measure Total Kjeldahl Nitrogen (TKN) since 2003. Not sure if Doug and James matched up TKN and nitrate on those sites. When getting into the additive results the error associated with each other result is a hard thing to enumerate because there are so many things that go into that, from the collection in different bottles to adding preservatives for TKN. All of those steps can introduce error into the test. Jay said that is something to keep in mind if they are seeing anomalies in historical data.

Doug said that at some of the comprehensive sites, which are the River Input Monitoring (RIM) sites in VA, they still have both the whole water TN direct analysis and the per sulfate for some of the pieces. They would have TN, particulate and total dissolved nitrogen. Doug asked if Jay agrees.

Jay said yes and he looks at that relationship every time he approves a result for Doug.

Doug said for those sites there would be the option of going with the TN value or the sum of particulate nitrogen and TDN. They would go with the whole water TN direct derived over the sum of particulate N and TDN.

Jay said he did not disagree with that on the surface, but he will give it some more thought. Reviewing that type of work he does for Doug, he generally sees pretty good agreement between them. When he does those additions, and compares them, a lot of times the particulate nitrogen results are below their reporting level so he could be adding noise to the TDN. Those are considerations to make when looking at the two. He looks at them to make sure even if the PN is below the reporting level he is adding it to the TDN and comparing it to the TN. Treating it somewhat like a laboratory duplicate to see how close they are.

Doug said his offices are doing same thing. Doug asked for labs analyzing samples for the Nontidal Network, do you do the same thing or something different? And do you agree with the statement by Jay about choosing the whole over the sum of the parts?

Doug Chambers (USGS) said in West Virginia they were using a method that was determined to have some bias in complete digestion in some settings and not capturing all the nitrogen in the system. The recommendation was made to use a TDN analysis using alkaline per sulfate on a filtered sample and particulate nitrogen.

Doug Moyer said they did have some discussions about the bias of the method Doug Chambers just described. They found that across the different jurisdictions and labs there were mixed results. There was a difference in how West Virginia was applying the method.

Jay commented that they had Elgin look at the data and he came to some conclusions. There are some issues as solids loads increase. The bias was not that great. The only thing they were

doing that might've helped is when they pipette these samples, they use wide bore pipettes so they're not discriminating on particle size when they digest. If they saw discrepancies with higher solid samples they'd go back and mix that sample while they were pipetting it and that helped. They look at the addition of the results vs the whole because they get them out of the same sample for that type of study.

Doug Moyer said he remembers there were differences in that bias as indicated by NWQL. He said he can reach out to Elgin and see how to handle that and is that still ongoing. They have the comparisons that Mike Mallonee shows on the tidal side. He asked any other labs if they had thoughts on whole vs individual digestions (whole water TN vs particulate nitrogen, TDN determination)? James and Doug can look at the different paired results they have at each jurisdiction and linkages to different labs just to see how similar or different are the whole water vs the summed parts. There was a time when MD who was using NWQL for their RIM stations and VA who was using DCLS for their RIM stations, MD was focusing on parts particularly for nitrogen, and VA was using the total nitrogen summation to represent that. Since then, they try to be consistent across watershed. They'll need to find out NWQL's perspective moving forward. The next stop is probably total Kjeldahl. Doug asked the group if there is an overlapping period in lab analysis to the persulfate, if there is an overlap in any of the top two whole water vs any of the pieces, do you agree with putting the persulfate derived analytes above any of the total Kjeldahl nitrogen component summation?

Jay commented they run Kjeldahl for nitrogen for DEQ.

Kim said her personal opinion is that Kjeldahl is pretty obsolete at this point.

Doug said that this would be for any of their long-term sites with data going back to 1985 until the transition period and if there is any overlap. In those older stations they only have total Kjeldahl components, up to 1996, then they started to transition as other techniques replaced Kjeldahl approach. They've chosen to go with the per sulfate derived constituents over total Kjeldahl if there is an overlap. It would be good to pull some of those areas where there is an overlap and compare them. They do need to resolve for anything coming out of NWQL, they still believe there is a bias related to whole water analysis compared to summation of parts. May have to put parts over the whole water for any sites coming out of NWQL.

Jay said they are doing some work for a client where they actually have TKN and nitrate and nitrite (NO23) in the same service and they're able to look at them and how they compare. From what he's seen the TN and TKN whole and NO23 compare well. For the TKN since the TKN is organic nitrogen plus ammonia, so they're taking into account the ammonia and the other nitrate compounds are generally not going to exist undissolved so the filter portion should work right. Although this work it limited and with a freshwater matrix, they've seen good comparison and agreement between the TKN and NO23 in those samples (don't have statistics though).

James said about the non-detects, if one piece is a non-detect they're able to handle that statistically with their inputs through WRTDS. Doug added that they don't want to provide calculated values to WRTDS because of that censoring. If they have a value provided as a whole and one of the components was censored and when they sum it, the entire total nitrogen gets a censored value or less then – if they provide this to WRTDS when running estimation of concentration and loads, it treats the observation as somewhere between 0 and whatever the total concentration was. It's a pretty wide range that it tries to estimate for the censoring routine. What WRTDS has evolved to is best handled when it is provided the raw data and it takes care

of the summation. It uses interval censoring. So, if one of the components says a value was censored at 0.03 and there is a dissolved fraction that comes in at 1, WRTDS would say the true value is somewhere between 1 and 0.07. It allows for a tighter window to determine where the true value would lie. So the statistical package handles the calculations for total nitrogen.

Decision: Keep whole water derived phosphorus as primary and back up is particulate (no objections raised).

12:15-12:25 Community Science Monitoring Updates Alex Fries

Alex Fries (UMCES) said that Chesapeake Monitoring Cooperative (CMC) groups are working on Tier 2 (T2) benthic sample collection to fill the Chesapeake Basin-Wide Index of Biologic Integrity (Chessie BIBI) gaps. That will occur this October and November. CMC also has some T2 groups in MD that they're working with on updating to T3. They are continuing work on NFWF funded stream restoration monitoring project. They're working on something they're calling the CMC connector to better integrate T1 groups and volunteers. People who have some interest but may not know much about monitoring will be able to use this tool to find out where they can volunteer with the time they have. CMC is working on some report cards for Antietam, Conococheague and the Gunpowder Tributaries.

12:25-12:30 Topics for Next DI Meeting All

The next meeting will be in the winter, potentially in January 2024. Potential topics for the next Data Integrity Workgroup meeting are:

- Updating the method matrix
- Creating and updating an instrument inventory for labs
- Discussing the parallel sample requirements for comparison studies and coming to a decision on how many samples are required

12:30 Adjourn