NOS Meeting Minutes – NADP 2023 Spring Meeting, Madison, WI, May 1-5, 12023

NOS Agenda (Session I)

Wednesday May 3, 2023: 01:30-5:00 PM CDT

1:30 PM Welcome, Logistics, Introductions (Tim Sharac)

1:40 PM Sample/Supply Updates (Amy Mager)

1:45 PM Network Analytical and QA Reports 5

2:00 PM NTN (Katie Blaydes)

2:15 PM AMoN (Nicole Miller)

2:25 PM MDN (Christa Dahman)

2:35 PM MLN (Christa Dahman)

2:45 PM AMNet (Wyatt Sherlock)

3:00 PM Break

3:15 PM EEMS Field Survey Update (Eric Hebert)

3:40 PM Updating spot report questions (Eric Hebert)

3:50 PM Site Liaison/NED Update (Richard Tanabe)

4:05 PM Site Support Hub Demonstration (Richard Tanabe)

4:10 PM Virtual surveys (Richard Tanabe)

4:20 PM NTN New Bags (Nichole Miller)

4:30 PM Data Updates and Improvements (Zac Najacht)

4:40 PM Event Recorders, Dry Exposure, and QR coding (Dana Grabowski)

NOS Agenda (Session II)

Thursday May 4, 2023: 08:30-10:30 AM CDT

8:30 AM Automation of lab processes (David Gay)

8:35 AM Use of the NTN to assess the impact on the environment of the East Palestine train derailment (David Gay)

8:40 AM Redesign of the Hg-collector sample train for MDN (David Gay)

8:45 AM MDN 2-week sampling preliminary results (Christa Dahman)

8:55 AM USGS External Precipitation Chemistry QA Project Update (Noel Deyette)

9:20 AM USGS Telemetry Upgrades and Integration (Mike McHale)

9:30 AM Break

9:45 AM Summary and demo of 5-year NTN sample frozen/refrigeration study dashboard (Nichole Miller)

10:00 AM NOS Succession Plan (Winston Luke)

10:05 AM Spring Meeting 2024 (Michael McHale)

10:10 AM Final Discussion/Questions/Wrap-up (Tim Sharac)

Motion to approve 2022 Fall NOS Minutes -Tim Sharac, Second by Richard Tanabe; Motion Passed

Sample and Supply Processing Updates - Amy Mager

Overview of Sample and Supply Processing Tasks

Receive/Login/Data Entry – samples for all networks (NTN, AMoN, MDN, MLN)

Receive/Clean/Ship sampling supplies for all networks

Collect supply QC

Contamination coding/pH/Conductivity/filter NTN samples

Store sample archive, process and ship special studies samples

Team (Colin Kelly, Cami Ritonia, Anita Peterson, Renee Klann, Kat McKinnon, students Li and Ella) works closely with Field Operations (NED/Site Support)

- Receives ~ 1600 samples/month in 2022 (1081 NTN, 228 AMoN sample sets (including duplicates, travel blanks, etc.), 342 MDN, 268 MLN individual bin samples – for 2022 season)
- Staffing Updates since Fall 2022

Prompted by Amy Mager's becoming Lab Director of Environmental Survey Programs (Soil and Forage Analysis, PFAS Research Lab) – in addition to NADP duties

Zac Najacht is Sample & Data Processing Supervisor – Amy's old position

Sample and Supply receiving/shipping

Data review/reporting

Dana Grabowski, Field Operations Supervisor (new position)

Site Support Hub oversight (site comms, site issues, equipment issues into one location) NED operations

Next steps to help Zac and Dana with their data review responsibilities by

Process improvements/gain efficiencies

Use sample receiving staff for preliminary steps

Association of Public Health Laboratories (APHL) interns and fellows at no cost to program – data scientist and engineering students sought

Supply Updates since Fall 2022

Instituted NTN Supply Survey 1 year ago

Query NTN operators prior to shipping supplies to them – ascertain what is on-hand already, which is allowing lab to ship only what is needed

Conserves supply stock at lab

Avoids build up of supplies at sites

Recent change: Building in an extra 2 weeks of supplies to each box (gives a little extra room for mistakes, delays, etc.)

NTN Sampling BAGS

New gusseted style bag (Degage Corp.) - Began sending to sites in mid-March, 2023 Easier for Operators; Positive feedback so far

MDN Sample Bottles (PET vs. PETG led to MUCH more...)

During COVID MDN switched to PET (PETG unavailable); prompted a PET vs. PETG study Discovered a contamination issue with the lot of PETG bottles in rotation; immediately stopped sending bottles

Further studies of the lot revealed box by box contamination; so many potentially OK BUT were confronted with supply chain issues, so had to leave the bottles in rotation – some bottles good, others not.

So, tracked bottles by ID and lot number

Prompted a closer look at analytical results/data

Samples received from September '22 through January '23 were impacted

Has led to improved QC procedures; track bottles by box & lot now, testing more boxes Still planning to do a PET vs. PETG study

Currently using a validated PETG lot that will last over 1 year

General Items

Supply Chain - things have been good since the Fall meeting (knock on wood....)
Streamlining supplies/inventory tracking, ordering and shipping
Still ordering more in bulk vs. standing orders (avoid supply chain glitches)

Shipping Updates (Since Fall 2022)

Higher Shipping Rates - due to loss of UPS contract campus-wide - WLSH working with UPS Rep to get better contract in place campus wide; problems using FedEx so stick with UPS.

Focus on shipping improvements/efficiencies

Use smaller boxes when we can; dimensions matter!

MDN – send multiple weeks of supplies in one cooler to reduce MDN shipping costs Bag sampling for MDN?

Sample Receiving/Processing Updates

Developing closer connection between Sample Receiving and Field Operations Site Support Hub

One place for tracking equipment issues, equipment requests, operator communications

Built in automation

Trouble Ticket button in data entry now links directly to Site Support Hub instead of going to separate system

pH/Conductivity/Filtering

Planning to move these processes to Ag Drive (analytical group)

These steps are the first steps in the analytical process, better fit in analytical group
The move allows Henry Mall to focus on receiving/shipping/field ops/data review and
improvements in these areas

Discussion

Doug Burns – can pH be done in automated fashion?

Amy Mager – We will continue as manual probe method (for now). Testing and comparison between manual and automated methods needed

NTN Update - Katie Blaydes

 Lots of turnover in lab and PO staff starting in 2021 - Introduction of current analytical and sample receiving/NED teams

Lab Space

Acquired new bench space in existing lab

Better continuity of operations and overall flow in the lab

pH, conductivity, & filtering operations moving back to Ag Drive in June:

Will house all analytical and filtering operations

Samples will be received at Henry Mall for receiving/contamination coding, then transported to Ag Drive

Instrumentation

In 2020, HACH announced discontinuation of Lachat QuikChem

Used for ammonium, orthophosphate, total N and P

Support continues through 2025

After 5 years, support dependent on parts availability

Next steps - replace? Keep running?

Purchase parts now and stockpile?

Other options – FIAlab or Skalar instruments?

ICP for cation analysis; only 1 in-house

ICP main board was corrupted in January

Agilent experiencing an engineer shortage

ICP was down for 11 business days; we were able to meet sample hold times

Working on a contingency plan

Inorganic metals group utilizes ICP-OES instrumentation

Validate method on their instrument

Quality Assurance

Occurrences since Fall 2022 meeting – any deviation outside of SOPs are logged/noted

11/2022 – IC software issues

12/2022 - Issue with 2016 NTN NH4 data

2/2023 – ICP down for 2 weeks

2/2023 – conductivity calibration not recorded

2/2023 - Expired SO4 stock used

3/2023 – USGS PT sample leaked during shipment

3/2023 – Failing PO4 & NH4 QC Standards

Supply QC

Check for contamination of bottles, lids, buckets, bags, filters

Low failure rates overall - with exception of Ca2+ on syringe filters (12 were tested, 3 failed)

Lab QC Standards (April 2022-April 2023) –within runs; 37,742 were run within analytical runs –

only a handful of exceedances (<1%)

Other Items

PT standards 2022: ECCC, WMO, USGS; Some slight biases but overall good results

Research

Over-acidification of Total N and P samples during collection in field Bring pH values back up? To eliminate bias in FIA measurements – updates in Fall 2023

Discussion

Noel Deyette – why do you think you are seeing pH exceedances in the QC standards? I observe similar results – any changes to calibration standards?

Katie – Target value of standards changes a bit – but exceedances are typically a problem of carryover; when we re-run the set, they pass

Noel – how often do you change pH probes? Any records of this?

Katie deferred to Amy and Nichole – will have to review logs to verify, but implemented stirring and rinsing protocols to alleviate carryover

AMoN Update - Nichole Miller

• Changes in AMoN

Changed procedure for glass jar blanks (containing passive samplers) – use two small citric acid filters in shipping bags containing passives – to adsorb NH3 - instead of ½ of a large one

AMoN Method Detection Limits (MDLs)

2023 Network MDL 0.084 mg NH4+/L 2023 Lab MDL – 0.014 mg NH4+/L Both in line with previous results/years

Supply QC Results

0 exceedances in 2022 for 2 week hood blanks, Core & prep blanks, sonicator & method blanks 10 exceedances of 0.011-0.023 mg/L NH4 for Jar blanks - 10 mL MQ water in jar upright in hood overnight)

Changed procedure for jar blanks to deploying a prepped sampler in jar in bag at least overnight

- 0 exceedances after that

Field QC Results

Travel Blanks (each site gets minimum of 3 TBs on annual basis)

In 2022: 396 valid travel blanks, median 0.0389 mg/L NH4; only one over criteria at 0.21 mg/L Historical Travel Blank Results from 7/2018 to 10/2022

Mean: 0.038 mg NH4+/L, Median: 0.035, Max: 0.257, Number valid TBs: 2455

Number invalid TBs (QR Code C): 12 (0.5%)

Overall decrease in TB values since 2007

Duplicates (3 duplicates per site in a year)

293 valid duplicate sets for 2022, 82% RPD < 10% of duplicates, 89% RPD < 20% of duplicates, only 10% of the duplicates were over 20% RPD

• Analytical QC (from bench runs)

Blanks – run every 10 samples; only one elevated batch – problem identified/rectified Low Standard (0.05 mg NH4+/L) – all within control limits

Midlevel Standard (0.75 mg NH4+/L) – one batch elevated but below control limit, all slightly elevated above expected, but all within limits

Research Initiatives

Starting up Tom Butler's Watershed Study again - first samplers were deployed April 25th, 2023 Currently 5 sites (TB01, TB03, TB04, TB08, TB10)

Possibility of adding more sites on two other lakes

Alpha sampler testing and development

MDN/MLN Update - Christa Dahman

Mercury Staff

Chris Lepley primary analyst (90% NADP)

Kirsten Widmayer backup analyst (20% NADP)

Christa Dahman, Supervisor, backup analyst, data review (35% NADP)

Major Changes

5/1/2022: End MeHg aliquoting/compositing from THg samples; Study showed high THg

bias after removing aliquots for MeHg; most samples have very low or

no MeHg

5/25/22: Changed extraction solution for MeHg distillation or litterfall from dilute HCl to

KCI/H2SO4/CuSO4

Recoveries affected – lab reevaluated the method and reached our to Jake

Ogorek (USGS) for advice. Adopted USGS's method

• Occurrence Management Reports

11/1/22: MeHg Dilution Calculation Error (LIMS) – no samples were re-reported

11/7/22: MDN PET bottle lot #1335499 contaminated (1/2 the lot affected) –lot removed

from use, working now on flagging the affected data

11/8/22: MDN acid preservative failure one lot exceeded criteria. A new lot was

prepared and passed.

2/13/23: Analyst Demonstration of Capability (DOC) not current; expired DOC,

immediately completed upon discovery. No effect on data quality

Supply QC

MDN supply quality checks are:

Acid preservative (every lot) - only one lot rejected

Sample Train blanks (1 per week) – no failures

Bottle blanks (every lot) – noted previous contamination (see Amy's presentation

MLN Supply checks

Collector netting blanks (every lot) – no failures

Bag blanks (every lot) - no failures

• Analytical QC Failures

Most failures can be corrected and samples reported w/o any qualifiers

From April 2022 to present:

4 MDN THg samples reported with a "q" note (fails QC at first analysis, original QC no longer available at later reanalysis)

16 MDN MeHg samples reported with a "q" note (failing QC, insufficient sample volume available for reanalysis)

No MLN failures

• Method Detection Limits

MDN THg reviewed using ongoing controls – no update needed (MDL 0.2 ng/L, LoQ 0.5 ng/L) MLN THg was evaluated as an initial MDL study due to insufficient ongoing data (MDL: 3.33 mg/g. LoQ 6.67 ng/g)

MLN MeHg was evaluated as an initial MDL study – a new variation of the method was used (USGS KCI/H2SP4) (MDL 0.050 ng/g, LoQ 0.15 mg/g)

Proficiency Test Results – all look good (ECCC, USGS SRS)

MLN Analytical Updates

2021-2022 litterfall analysis complete, reports drafted. A LIMS data upload and report function had to be built from scratch, causing delays.

2022-2023 samples are being dried – will be composited/ground in the coming weeks

AMNet Update – Richard Tanabe

• Site Update

Currently 10 active sites
OH02 is currently inactive (down > 1 year), may switch to new location
Mexico City site starting soon

Data Review

Received all data for 2022, review nearly complete Sent request for Q1 2023 data

• Updating data ingest process, software changes

An idea: Move towards automatic data retrieval

DropBox® would be an option

Starting to gauge interest from site operators/sponsors

Data would come in automatically → operator does not have to send emails

Quicker data comes in → quicker data can be reviewed

• Site Audits

EEMS trained in Madison (with Mark Olson) to learn audit process in 2022 Also trained with Winston Luke and Paul Kelley (NOAA)

Performed 2022 site audits at MD99, HI00 and NY98

Working with EEMS to get additional sites done this year

Missed 2-3 years due to Covid, want to deploy EEMS quickly to catch up.

Elaboration by Eric Hebert - EEMS

NY98 – EEMS repaired the instrument (was inop), managed one injection –results looked good.

MD99, HI00 sites ok

Discussion

David Schmeltz - How many surplus Tekran systems are collecting dust in the warehouse?

RT – Quite a few. Not all are running, but we shipped two to Rodolfo Sosa, one to Guey-Rong Sheu. We are keeping one 2537X in reserve, but goal is to get other 2537A/Bs running to ship out if needed

DS – Is there any reason we can't support Vietnam National University's request for a Tekran system?

RT – from an equipment perspective we can, but Vietnam would need to join AMNet and pay the network fee.

DS – do we need a motion?

Mike McHale – It sounds like Vietnam National University doesn't have the funds yet to pay the network fees, correct?

RT – They are trying to come up with the money.

MM – So you're saying that if VNU pays the network fee we will ship a full speciation system?

Doug Burns - will PO cover shipping?

RT – no, VNU will cover shipping

Greg Wetherbee – Why not ship the equipment at their cost but do not provide data services until they pay the AMNet fee? This way VNU will get instrument set up, learn how to run it, etc. It would allow them to get started – as an outreach effort?

Eric Prestbo – The PO will never get the network fee if we ship prior to their paying

Motion – The program office will make a Tekran mercury speciation system available to Vietnam National University, with the understanding that the university must join AMNet and pay the associated network fees. Shipping costs will be borne by the Vietnam National University, and the equipment will not be shipped until the network fee is paid.

Moved by Mike McHale, Eric Prestbo second: Motion passes

2023 Site Survey Program Report - Eric Hebert

<u>Sites Surveyed in 2022</u>
 113 collectors, 101 locations
 92 NTN collectors (55 ACM, 37 NCON)

21 MDN collectors (9 ACM, 12 NCON

101 Rain gages – 65 ETI, 36 Otts (various models)

Visited sites across continental US, Virgin Islands, PR, Alaska Site Sites visited every 4 years (prior to 2019 it was 3 years) Current EPA contract ends August 13 2023, will visit additional sites if win the new contract

Rain Gages

As found accuracy – excellent in general (Response vs challenge precip amount (weight): slope 0.9997, intercept = 0.0014, R2 = 1)

3 gages did not pass; under-reported the weight/simulated precip

We work up to a 20 inch precip challenge – start with a weight equivalent to $\frac{1}{2}$ " precip, add 5 more weights to get to 20 inches simulated precip

We start by emptying the gage bucket (tare weight = 0), then add weights

But operators do not empty collectors every time – incremental increases to precip are added to a (semi) full gage, not empty - the challenge test does not really represent conditions in the field – we are really interested in looking at small incremental weight changes on a significant weight imposed by a (full) gage

• New Rain Gage Challenge Test

Work with PO to determine the average (85% confidence) baseline precipitation depth for each type of gage in the network. This data would be determined from cumulative raw bucket depth.

Work with PO to determine average 15-minute ppt report value at three confidence intervals

(50%, 85%, 95%). This would be the weight difference that the gage is actually measuring in a 15-minute period. Hopefully this would give us a few values to test that cover low to high ppt events

Continue to test gages as we have been to confirm linearity up to (or past) the average baseline determined in step 1

Add one or two weights that represent the average ppt report values.

This would be the Real Earth Simulated Precipitation Event Test "RESPECT"

Look at egage Accuracy Slope Since 2014

Slight negative trend but very small – how do the loads cells perform as they age?

Sensor tests

ACM - Some new sensors were refurbished at the NED with updated electronics – should track the new sensors to see if they activate at warmer temp or in line with older sensors Max temperature tests- - should get to 50 60C in ten minutes; 3 failed (WY06, AZ03, WY99) NCON collector surveyed and adjusted – tighten ~50% of collector arms (poor lid seal) By contrast, ACM collectors provide a better lid seal overall

Thies sensors – some activate with fewer than the "5 passes" of the hand through the sensing beam. 5 passes used as a standard – if activates sooner – will it open/close more often? Contamination? Higher precip volumes? What is an acceptable range of passes to open collector?

Field Photos

Continued problems with field maintenance, training, equipment condition – as usual Battery corrosion, etc. – battery AND sensor terminals/connectors can corrode Some rusty/dirty ACM sensors

Loose collector lids (NCON typically) – NTN and MDN -evaporation, contamination Dirty dry side buckets

Dirty, ripped lid liners, dirty collector lids - these are training issues.

MDN Thistle tubes – the WSLH was supposed to send tubes that match the bottles so the tube doesn't fall to the bottom of the bottle, and to get a better seal between the bulb and bottle opening to prevent evaporation and contamination.

If a site operator gets a thistle tube that is too long, etc., what should he do if he has no others?

Richard Tanabe - I thought we removed all the bad thistle tubes from the network. Operator should leave existing bottle on, call 800 number and PO will ship new equipment.

Eric Hebert continues presentation:

Need training for operator, along with guidance to operators about emptying rain gauges, etc.

We are not correcting ongoing problems. Training? Rewards system to get operators to comply?

Removed final Belfort gauge from MS19/MS98

• News – EEMS is:

Installing GOES/Cell data transmission for USGS Replacing internal CR800 Li batteries Replacing PDA and SC115 with Android Updating Ott and Campbell firmware and programs

Building replacement ACM collector sensors using Thies sensor

Building CR1000X Bluetooth adaptors

AMNet – for further discussion

Now replacing ETI sensors without shipping the shell – can replace in field

If contract is renewed we can change the way we photograph sites using a phone app – will give you direction of photo orientation. Upload directly from phones – rather than using a digital camera

Discussion

Winston Luke – I've always been concerned about metadata we cannot capture in the field – are lids loose? Lid liners in poor shape? Consider mandating tightening collector arms annually? Also maybe start sending our lid liners on a regular basis, rather than when requested?

Eric Hebert – This may be a training issue. Site operators can come and go without our knowledge

Tim Sharac – maybe we send lid liners for overdue sites, whether requested or not?

EH – there is a procedure to adjust collector arms – not simple, must adjust lid carefully after tightening arms to prevent motor burnout. Maybe implement remote annual survey, as had been discussed?

TS – Spring cleaning of the sites – send photos every year?

Greg Wetherbee - The (MDN) thistle tubes and bottles are all the same size, correct? Does this mean that ALL of the MDN collectors are not sealed correctly?

Richard Tanabe – No. All thistle tubes are hand blown to our specs, but can vary. There might be tubes out there that need to be replaced.

Cari Furiness – Eric, on balance, given issues with NCON lid seals and loosening screws, do you have an opinion on preference of using NCONs or ACMs, perhaps modified with Thies sensors?

EH – Good question. There is a cost benefit - NCON is generally much better, easier and cheaper to maintain. But it is not suited for solar power sites (sensor needs continuous power) – we can work on this, maybe switch from 24V to 12 V operation. The ACMS work well, but more \$ to operate. Each has pros/cons. I think NCONs are just fine, you just have to do the maintenance on them, annually if needed (arms).

RT – The NCONs produced now have the DC voltage option - eliminate the need for an inverter

EH – So now it's a question of the Thies sensor power and spline on the motorbox

Doug Burns – do you think NCON can modify older collectors with the new DC voltage option?

RT - I think they can, but CapMoN bought NCONs when NADP did, and we ere able to do it. It's doable. Not too expensive

Mike McHale – to get back to Tim's point – I love the idea of sending a Spring cleaning reminder to have operators look at their equipment. Send a reminder annually.

TS – do the lid liners have dates on them when you send them?

RT – yes they do. In terms of reminders – we put memos for winterizing and summarizing the gages., etc. Operators don't read them. Likely even listserv emails would not be read. In theory it's great, and we have made progress with ascertaining NTN inventories before we send supplies. Anita has been diligent in contacting them, and they do respond.

GW - How about assessing a \$200 surcharge to a site sponsoring agency for every site that does not send proof of annual spring cleaning? We use the funds to purchase replacement equipment for the NED. Actually, it should be fall cleaning to rid the collectors of nests etc.

TS – Is there an EEMS newsletter showing site deficiencies?

RT – We don't want to show the bad, show only the good of NADP

TS – Maybe include sample photos of ideal conditions, and note "as found" violations in the spot reports to illustrate and identify the problems?

Alexander Nyhus - I agree with you Greg... I think it is good to have direct tactful criticism as soon as practical, especially if they are paying for the analysis. Shaming them publicly would not be a good idea. More reminders annually for all operators or check-lists?

Kulbir Banwait - How about having site operators recording sampler condition on the Sample History Form. CAPMoN has a spot for it — when lid cover was wipe-cleaned/changed/ etc.

GW – Tim, are you suggesting showing these pictures online?

TS – No as an email to site sponsors and whoever receives the spot reports – a tight distribution list. These are common, ongoing problems – try to correct them. Do you have ideas on walking the fine line between constructive criticism and shaming?

GW – It is hard to stay on top of all problems at the sites – but it is incumbent on site sponsoring agencies to communicate with their operators- we all need to work on this. It is a constant battle.

Teresa Burlingame (NEON) – This was an eye-opening talk. One thing that has improved morale and data quality – annual training sessions. Better employee participation, morale, etc. NEON has preventive maintenance procedures for the sites, based on NADP's documentation protocols. A part of data collection is a review of the operability of sensor itself – can you implement this?

RT – There is a block on collector and gage operation on the field form, where issues can be reported. Are the people collecting your samples NEON employees?

TB - Yes. NEON staff and seasonal staff

RT – This is a big difference. NADP has a wide variety of operators, funding agencies, etc. – we have less/variable participation from our operators.

GW – we used to offer in person training when we had more \$.

Zac Najacht – Richard, you have put together some online/virtual modules on specific topics in in the past?

RT – Yes, and the modules are available online. The material is sent to new operators via a link

Anita Peterson – A suggestion about Spring cleaning – make it fun? A carrot instead of a stick. Propose a scavenger hunt - a list of activities to perform – look at screws, collector arms, etc. The operator takes pictures after issues have been fixed/remedied. The PO will send something fun to the operator. Mandatory fun?

Kristi Morris – We are all so used to required training – no stick, but call it required – have the operators call in for X number of training hours annually?

RT – Challenge is to identify the operator. We are often not notified of site operator changes.

TS – Keep a Scavenger hunt Excel Spreadsheet? Green boxes denote compliance per site – collector lids, lid seals, etc. Track these over the years via Excel to get a visual indication of how sites are responding or maintaining – identify recurring deficiencies. It's In the best interest of the networks if all the operational pieces are working together. Prize for compliance

Maria Jones – Who gets to review the pictures of dirty collectors, full gages, etc.? Does anyone review those to notify the operator?

RT – if the question is if this is on the spot reports, then the PO should be following up but we don't see pics until they are uploaded to the EPA website and we download them.

MJ – OK, so when EEMS finds problems they should report it at once – this would be the easiest way to do it. Send email to RT on the findings

RT – Yes, we can work that in, will address in my talk coming up on the Site Support Hub.

EH – We will have a discussion with RT and TS about changing how the spot report looks and what/how questions we ask and how to tweak them, and incorporate changes discussed in the fall meeting (e.g., siting criteria) - if we win the next EPA contract hopefully the database will be redesigned to be more effective and communicate the info you need.

TS – For the spot report questions - the difference between "yes" and "no" responses is ambiguous.

EH – Yes, the questions are not written consistently so that a Yes response is always good – we will rephrase the questions for clarity – no double negatives, etc. - to make questions and responses to them more logical and consistent.

NADP Site Liaison/NED Report - Richard Tanabe

- Changes to the 1-800 number (January 2023)
 - If a site Operator calls it rings Richard's cell and desk phone, then goes to voicemail if no answer, and an email is sent to Richard's address and the NADP SLH account Incorporating the ned@slh.wisc.edu has been useful for reducing the amount of email in personal accounts, as well as keeping others up to date of site issues
- <u>EEMS and PO</u>
 Continuing with monthly PO/EEMS meeting to review the next months site surveys; USGS and

Wood invited to monthly calls

Dana and Richard are continually in communication with EEMS staff as issues arise

Dana and RT have Access to EEMS outlook calendar to see travel schedule, site visits to use

EEMS proximity to sites to provide additional parts for vans

Priority: Quicker response to action items in Site Survey spot reports

Operator Training

Fell off the table last year – staff changes, RT's additional duties arose

Priority to restart virtual training sessions in 2023

Format is brief presentation of a particular topic followed by a Q&A session – typically 50 operators out of 340 sites attend

Sessions are recorded and made available on the website

Continue with live Zoom sessions – will re-address old topics to reach new operators

Communication with sites: monthly memos, listserv, website, 1-800, email

Should we be looking at other options to broaden our communication?

Discord – Online platform for networking

Another option for mobile device/app generation

Network Equipment Depot

Primarily shipping NTN/MDN ACM motorboxes – NCON rarely need them Sensors – primarily for ACMs, some Thies sensors on NCONs The last Belfort gauge (MS19) was removed in 2022 – none remaining in network NED still has some supplies available – can ship to operators for special studies/use

Improving Operator Resources

Need to Improve our operator troubleshooting documentation

Creating simple one-page PDF emailed to operators for issues identified by precipitation data review - full gages, blocked sensors, power ... Site Support Hub feature

Develop surveys for specific checks, i.e. event recorder issues

Improve website resources – we have SOPs, etc., but troubleshooting tips, etc. can be added to reduce calls to the 800 number

Use of AI to add voiceover to existing training videos and future videos (Come to EOS)

• Severe Weather Notifications - increasing threats of extreme weather

Equipment is at risk of being underwater at certain sites (e.g., FL05 is 3m and FL11 is 2 m) Ideally equipment should be moved to higher ground/storage. Not easy...

Who's responsibility to ask the operators to assess their situations and make these site decisions? PO staff, operating agency rep, funding agency rep?

For Hurricane Ian (2022), RT sent an email to predicted impacted operators in FL/GA, suggest emptying rain gauges, but operator safety was stressed as top priority.

Success - no equipment damage at the FL sites

Not just hurricanes: ACM Motorbox requests 2/8/2022 due to earlier ice/snow storm activity Automate these notifications? Possibly

Continue to monitor, send emails to operators/sponsors/funders and let them respond?

Site operators in coastal regions in the SE/Gulf states would be able to pull equipment out a day or two ahead of any storms, but is it their priority?

Site Support Hub (SSH)

Came out of PO review finding - Develop a process to effectively gather data on network problems from all sources of information, make available in centralized location for all to address the issue.

Background: Site information was logged in multiple places making it difficult to keep track: individual email, 1-800, field forms, trouble ticket system, etc.

Data weren't always shared/made available to all who needed the information, especially if an issue was resolved.

Developed with Google Sheets, widely available through UW accounts

PO Review completed 10/6/2022 - SSH active 10/18/2022, initial training done that week.

Continually evolves to meet team needs

Hub has a dashboard - Topic (e.g, Collector, Gage issues, etc.), Description of problem, total # of issues, # open/unresolved

Can identify all open issues assigned to an individual to resolve, or at a given site, etc.

Open issues, site histories, trouble tickets, etc. sample lag, etc.

Key Features of SSH

Assign an issue to staff member, with auto email pulling information from columns. Issues identified by 1-800, email, trouble ticket

Send email to site operator notifying of issue, attaches troubleshooting PDF if available. Issues identified from precip review.

Added auto fill (lookup), enter Site ID - SSH fills in collector/gage type, operator.

Continually improving

Replaced old Trouble Ticket app from U of I (PO Review recommendation) Integrating Sample Receiving team functionality, Trouble Tickets, Sample Lag reports Richard Demonstrated the SSH functionality at length

Virtual Site Survey Revisited

EEMS is currently every 4 years for site surveys ~25% of network sites/yr

How does the PO keep sites engaged and aware of their site?

Ideally, something that can be done on site from phone - photos of lid seal, seal condition, etc., add to site record – send back to PO as part of survey response

For sites with no internet available – hardcopy print out?

Frequency: 1 yr? 2? Seasonally? Sites on EEMS schedule? - to notify EEMS what to expect/repair

What to Focus on?

Site (N,E,S,W) and equipment photos, Vegetation height around collector(s) and rain gage, objects within 5m, new activities near site (within 100m, 500m, 20km)

Pictures – PO can provide examples of what we want - send to operator a photo of ideal condition (good lid seal, intact lid pads, clean dry side bucket, etc., and ask operators to send a photo of their site; ideally the two should match

With the right photo, we can learn a lot about the site conditions.

Collector photos, Rain gage photos, Lid pad conditions and seal with bucket/funnel, Objects nearby, Dry side bucket condition, etc.

Focus on items that may be directly impacting sample quality, less on items that don't change as frequently

Finalize questions, keep it concise

Need Guidance:

How frequent?

Which sites?

What should the feedback be to site?

Discussion

Kristi Morris – Commented on excellence of the site support hub, question about how NPS equipment held up out west in winter (deep snowpack)

Richard Tanabe - We went through a lot of ACM motorboxes, particularly in CO. Can track this in future.

Bag Study Update - Nichole Miller

Recap of past studies with new lot of Degage bags (9/2022)

Good blank levels

Spike Tests with FMDLs & FR50 - Good recovery w/FR50, Lower recoveries in FMDL trials – esp. K+, NO3-, NH4+, PO42-

Spike FMDLs with Na2So4 – still poor results

Dilute FR50s in gradient fashion, look at bottle stability for NO3- and NH4+; stability still decreases w/decreasing concentration

Most Recent Study Design

Focused only on NH4 and NO3 at different concentrations and combinations

Used NH₄Cl and KNO₃ stock solutions - 250 mL of solution, 5 different packets of bags, room temperature, with a lid for 7 days − two controls in 60 mL bottles

Recoveries 95-107% - original problem was with FMDL solution stability, not bag

Next Steps

These bags are currently out in the field for use – no issues reported

Based on all of the studies, it seems the issue is with the FMDL solution stability

Discussion on reworking the solution – change the acid used? Currently using nitric – stability?

This solution is used as an in run QC check that is not required to pass in our protocol – it is made at low levels for each platform

NADP Data Review and Reporting - Zac Najacht

NADP Data Overview

Precip Data Review (Dana) - Daily effort, 1-week turnaround

Precipitation data - precip totals, collector exposure, optical sensor activity, gage voltage processed and reviewed weekly.

Correct Data, remove false precip data

Network Preliminary Data Review

AMoN data review (Zac)

MLN data reviewed manually (Hg Lab & Zac/Dana) - 2021 data done, reports ready AMNet data reviewed independently (Wyatt)

NTN & MDN - reviewed precip data brought into Data Review programs

Field/analytical data reviewed for all samples received in a specific month

Automated error flags, notes codes

Manual notes codes/lab qualifiers added* - trying to move to automation

Quality Rating (QR) Code (A, B or C)

Final visual checks

Reports are generated and sent

Zac demonstrated data review example – After review and prelim reports sent out, the data are published to the website

Network Site Updates since Fall 2022

#Sites: 255 NTN, 82 MDN (+1), 92 AMoN (-1), 11 AMNet, 24 MLN

Since 2018: NTN peaked at 262 in 2018, AMoN at 115 in 2021 and 2022, MDN at 91 in 2019,

AMNet at 18 in 2019 and 2020

• Data Review and Reporting – Preliminary Report Turnaround time

We are not at our 90 day goal – NTN was 160 (up from 139 in 2022), AMoN 86 days (down from 117 days in 2022), MDN 147 days (up from 105 days in 2022) – turnaround was even shorter in 2021

Steps implemented moving forward

New roles & transitions

Working with sample receiving team, supplies/shipping, and data team Dana now working with site support team; still doing data review Weekly meetings (data, program development, site support & QA) – ONGOING

Data Management Advisory Group (DMAG)

Added two new members

Mark Kuether & Zac are now co-chairs

Continue to improve data stream from preliminary lab data review to final data processing to website

Data focus is on 2022 data for annual summaries/maps

Continue to increase efficiencies and respond to external audit findings

• Improvements/upgrades made to data review programs & processes

Examine preliminary data review and Program Office (PO) processing/publishing (what) & roles (who)

Continuous upgrades to sample processing & data review programs

Increasing automation, reducing mouse clicks, less copy & paste

Lab qualifiers program developed (automated comments & notes codes)

NADP Site Support Hub (track communications, site issues, actions, timelines).

Better communication = better site operation = better data

Using statistical program(s) to prescreen data sets – POTENTIAL

Filter out some samples that are definitely valid (QR=A) or invalid (QR=C) Focus on middle range (QR=B)

• Branched vs linear data review approach – ONGOING/ADVANCING

Incorporating more staff into data review – get away from linear data review to improve efficiency

Break review process into smaller pieces, better divide tasks to run concurrently

Discussion

Ryan McCammon - Does anyone check the data transfer from the FORF to the online entry form?

Zac – yes, the first data entry is performed by one individual – a different person enters the data on the second data entry step and the two reported forms are compared for discrepancies.

Collector Event Recorders - Dana Grabowski

Background

Concern – sample validity when collector exposure time was unknown and not being recorded Samples considered valid unless operator told us there were issues with the collector The approach at the end of Spring 2022 NOS was to correct the reason for the missing event recorder data rather than add additional coding to samples

Approach

Event Recorder (ER) Qualtrics Surveys – sent to operators directly

Step by step guide to troubleshoot ER at the motorbox and at the datalogger.

Survey completed online with ability to attach pictures, results automatically sent back to PO

ACM/ETS surveys sent in December 2022

NCON/ETL – surveys sent in January 2023

Development and utilization of Site Support Hub to track, update and resolve issues Communicating with EEMS before Site Audits

Reaching out to sites individually

Types of Issues

Motorbox/blown fuse (rare)

Datalogger program(rare)

ER cable issues (main reason for failure)

Incorrect wiring at motorbox or data logger (main reason for failure)

GOES telemetry issue (rare)

Where are we Now?

Of 59 sites where no collector event recorder signal was received, 30 resolved, 21 in progress PO is providing EEMS with supplies for building ER cables and replacing if necessary in the field Updated the ETI's default CR1000X program to not comment out collector code Of sites resolved/repaired, none should have been invalidated due to excessive dry exposure Continue to utilize Site Support Hub

Discussion

Greg Wetherbee – When did you implement the surveys? We (USGS) are dealing with a lot of ER issues now...

Dana Grabowski - ACM in December 2022, NCON in January – none developed for Ott gauges

GW – So the ER issues on my list are current and should be remedied?

DG - I believe so

Mike McHale – this is a ton of work that has been done, while continuing to run samples. Greatly appreciated – you have done a great job!

NOS 2 - May 4, 2023

Automation of Lab Processes – David Gay

• <u>Identified the most time consuming lab processes – Sample Filtering, pH measurement</u>

Grew out of discussions with Richard and Martin

Investigated faster, cheaper, more consistent methods

Identified the Skalar SP2000 fluid handler (robot) as a possibility

Can Automatically filter our sample volume (analytical is done with filtered sample

Auto pH measurement (using a standard probe)

We should be able to control/tailor much of how this measurement is made

Auto conductivity measuring

Auto fill the vial for IC, ICP, and FIA

Filter and autofill our archive sample

Move all of this data into our LIMS system

Process

The NTN sample receiving team opens the boxes and arrange samples and FORF as usual, and move the samples down the hall

One Technologist would:

Tell the robot what rack numbers for IC/ICP/FIA are (each has to be identified)

Put racks in correct position on the robot and in the appropriate orientation

Pull a sample bottle off the cart, open the top, and place it on the robot

Scan the sheet/QR Code identifying bottle and sample by site and week

The robot:

Pulls in sample, rinses all of the tubing

Pulls in 12 ml of sample and filters it. Filtered water is added to IC, ICP, and FIA vials Begins the pH sample test (in original bottle); we have full control over duration

of test, how small of variance we wish to have, etc.

Completes and records pH value

Repeats the same for the specific conductance measurement

Filters 60 ml of sample and places it into the archive bottle

While robot is processing the first sample, the technologist:

Types in the FORF (digitizes it, first data entry)

Computer reads the FORF back to check the input (second data entry – confirmatory)

Can then make any corrections needed

Archive label is printed at station, and gets affixed to the archive bottle

Any special sample requests for that location

Sample Completion Time 10-12 minutes - 48 samples per day, 240 per week

Results:

All vials ready to go on FIA, ICP, and IC (just put the rack onto the instrument

Archive sample done

Double data entry complete

Advantages

Saves time for analyst - no removing sample from filtered bottle and setting up analytical trays Less chance of misidentifying sample

pH and conductivity are measured consistently

Work taking 9 tech-days currently is reduced to 4 tech-days

analysts do less work; no sample set up

Archive sample is filled

FORF is digitized

Can also automate standards processing

Video demonstration of Skalar Instruments SP2000 (fluid handler) Cost ~\$60,000

Discussion

Doug Burns – it will take some time for precip samples to converge on a pH value – must tweak the drift criteria to promote convergence on a value – tricky

Martin Shafer – We do have a choice of pH electrodes optimized for low-conductivity samples, but it will be a challenge initially

Catherine (?) – We process a lot of low volume samples: WD samples are 14-27 mls – they get pH, conductivity measured, and then syringe filtered. WI are 4-13 mls – no pH or Cond, but syringe filtered – Would the Skalar be able to accommodate that or would we have to filter by hand?

David Gay – I suggest to start that we avoid low-volume samples and do them manually, but we should be able to identify WI/WD samples for special sampling in the Skalar

Catherine – Can we accommodate special studies? Special vials and equipment, volume set-asides?

DG – Again, we would do by hand to start, but eventually have the Skalar do it

Catherine – We now collect NTN samples in 1 L bottles, but looks like the Skalar uses smaller vials? Would we have to pour the sample into smaller vials?

DG – You can use the line reader and 1L bottle and put it directly on the sample tray; ultimately we could go to even a 250 ml sample and program the robot to sample from those.

Colin Kelly - Wouldn't the sample have to be logged in (have an ascension number before it can be queued up for operation by the robot? if not how is the data, sample linked?

DG – The incoming sample bottle will have a UPC code, so we know what sample goes into the bottle before hand

Mark Kuether (?) – How much is annual maintenance cost – lots of moving parts to this instrument?

DG – The software is maintained thru engineers in Boston – I'm sure there is a maintenance cost, but do not know how much. Field engineers are close by – Al Yates is nearby and could probably do mechanical repairs. But all software changes done remotely and uploaded. Set up cost includes software setup and trial shakedown, plus training for the users/operators

Mike McHale - In terms of calibration standard (new vs old) – how long would you expect to be double analyzing to compare results from manual vs auto?

DG – Maybe 3 months?

MS – Hard to say, but 3 months is probably a fair estimate

DG – Skalar said they would run samples we submit and send results back to us for comparison with ours, but there will be learning and QC issues to implement this.

Zac Najacht – I've had experience with automated systems – we should consider the time it takes if there is a mechanical problem – need to have backup manual protocols on line to fill in.

DG – I see the Skalar in room 135 where the manual tests are done now, so we can easily transition back to manual if there are problems. Technology now is much improved, so expect few problems

Mike McHale – Consider sending sample to Skalar and have them assign the right pH probe to the system for optimal results. What probe(s) do we need to use?

MS – We have a lot of experience with this but can certainly ask Skalar to start with this.

??? - Do you plan to have the Skalar in Henry Mall, when we're moving Analytics to Ag Drive

DG – I will leave it to you and Amy, but I think of it done in HM but will be your call

Colin Kelly - There was discussion about moving pH/conductivity to the Ag Drive location, will this machine fit on the bench space there?

DG – Yes, there is bench space there.

Observations of the East Palestine Ohio Train Accident Feb 3, 2023 - David Gay

• <u>Summary</u>

Friday 3rd February 2023 - a 150-car freight train (Norfolk Southern) derailed outside of East Palestine, Ohio (pop 5,000)

38 cars thrown off the track ~20 were listed as containing hazardous materials

Evacuation orders were issued to all households within a two-mile radius

Feb 8th - Emergency Services breached five of the derailed cars (increasing pressure – explosion hazard) to conduct a controlled burn of ~250,000 gallons of liquid vinyl chloride - released into a trough and ignited, creating a large plume above East Palestine.

Public health concerns over chemical release from derailment and fire, and controlled burn Chemicals of concern:

Vinyl Chloride - precursor to PVC, one of the most ubiquitous plastics

Butyl acrylate – used in production of automotive coatings, paints, plastics and resins.

Ethylhexyl acrylate - also in modern paints and plastics

Local fire departments used fire fighting foam (think PFAS) – confirmed by DG

~ 3 weeks after the accident, Katie mentioned some odd pH values showing up at sites.

Many NTN sites surround the accident site.

Meteorology

Within 24 hours after wreck & initial fire:

Some rain in the area - Buffalo and Western NY, stationary front, overrunning situation Upper air: westerly, towards ESE a bit, surface air moving north at the beginning Rain in NY, Maine, Quebec

Occluded front in NY, PA

During controlled burn (2/8)

Rain in West Virginia and Virginia, rain all along PA to Maine

Upper air west to east, surface air moving N to S

Precip totals (Feb 4 -14)

Heavy in south VA and NC

Precip throughout the accident area

Heavy precip MI, WI, IN

HYSPLIT forward trajectories – Air moved to NE (NY and New England) and also to S-SE (VA, etc.) Compared Historic observations at sites E of Mississippi river: CI- in all winter weeks since 2014 Calculated means, medians, quartiles

Typical Results

NY01:

A week before accident – Cl- values were in center of wintertime distribution

First week after accident – Cl much higher than the norm

2 weeks after - CI- back to normal levels

pH a week before accident – in line with historical distribution (a little higher)

1 week after, pH is very HIGH (6.6) not low as would expect with HCl release – Why?

2 weeks after – pH is still high but reduced

Similar results at VT99 and VA13

Percentile ranks, week of accident:

pH among highest to NE of crash – PA into upstate NY/New England, but lower precip amounts

Also high in WI-MI

Cl- percentiles – 90th + percentile ranks from PA east to NY- New England, also MI, WI due to low pressure system sweeping CCW and washing out - same for Na, K, Ca

SO4=, NO3-, NH4+ elevated in these regions, but not to the same extent

2nd week after accident:

High pH gone from MI and WI, high pH moved to E seaboard

Cl- elevated as well

Many NY sites high after accident – again, lower precip amounts here, so concentrations were high

But even sites with high precip levels elevated as well

Summary

High pH, Cl, Na, Ca, K, some others observed in a large area where some were the highest values measured since 2014, primarily in NY through Maine, but also into VA

Not a lot of observations in PA (little rain)

Not so extreme for NO3-, SO4=

But not just chloride and pH

Consistent with winds and meteorology – low pressure system dropped pollutants/deposited in WI and MI

pH and ion concentrations were not dangerous, but very high relative to normal Impacts go into the second week, more easterly and southeasterly from the accident So, widespread effects beyond just the immediate area of the accident

Discussion

Doug Burns – Do you have a hypothesis about alkaline signal?

Martin Shafer – We need to know more about fire fighting agents – but K salts are commonly used - alkaline; would increase pH and produce high K if aerosolized.

DB – I think the fires may have been so intense that it was volatilizing mineral matter from ground beneath crash site (limestone soils etc.) – a contributing factor?

(Unknown speaker) Because of the unusual chemical soup, how do we know that there were not analytical artifacts and matrix complexities, confusing the instrumentation?

Katie Blaydes – IC traces did not show organic acids.

Colleen Flanagan-Pritz - Any mercury data?

David Gay - I did not look at this, but I can.

Rodolfo Sosa – Have you looked at correlating info from other networks?

DG – We could do this, with CASTNET, etc. - So far I have just looked at NADP data

Chris Rogers – We see impacts in our (CASTNET) data as well.

Jason O'Brien - CAPMoN has several sites in southern Ontario (daily precip.) and we'll look into the impact on our samples.

DG – Need to look at PFAS samples as well – the cleanup plan was to dispose of contaminated soils in landfills in other states. Houston, TX refused due to suspected PFAS contamination.

MS – Some PFAS monitoring sites are in the path of the plume and we can check.

Greg Wetherbee - Were those forward or back trajectories?

DG – Forward.

Colin Kelly - Does the Radiological Chemistry department at Ag Drive still take weekly radiation readings? If they do, I wonder if there is any correlation with that data as well.

Amy Mager (?) - There is rooftop sampling at Ag drive, but not clear on details. We can check.

Jason O'Brien - CAPMoN has several sites in southern Ontario (daily precip.), and we'll look into the impact on our samples.

MDN Bag Sampling - David Gay

Idea of bag sampling for MDN – we use bags for NTN, seem to be working well. Going to bags in MDN will reduce costs, avoid glassware cleaning, etc. - just need a different bag shape.

DG demonstrated the design of a bag, made from a (homemade) custom-sealed plastic bag, with a funnel shape on top, a replacement "thistle tube" in middle to reduce evaporation, and a "blood bag" at the bottom.

"Thistle tube" restriction reduces evaporation. We can add acid to the bag.

Eric Prestbo has suggested using solid Br salts instead of acid.

DG installed the bag over the opening of the NCON sampler "chimney" to demonstrate. Lightweight, no glassware needed, no plastic sample bottles – could save lots of \$ in shipping and labor. Degage should be able to make it for us at low cost. Bag would be PET or Teflon

Discussion

Mike Bell – Are there volume issues with large rain events? Would bag pull off sampler?

DG – I tested with the equivalent of ~ 5 " rain – think we can handle 15" in a week. Can support the bottom of the bag with a base if needed. Will also have to deal with the bag in the lab as well.

Martin Shafer - With the right bag you can brominate in the bag and not decant the sample into a bottle.

DG – Yes, everything is done in the bag. We can build a clamping contraption to close the bag, or have the site seal them, or seal them at the lab. There are engineering solutions....

Eric Hebert – We heat the MDN collectors to prevent glass breakage. - Will that pose a problem? Can we turn them off, so the bag doesn't melt?

DG- we only need the heaters to melt snow but don't need a heater to keep glass warm. Not a problem.

Mike McHale – Maybe fold the bag over and zip tie it closed?

DG – Yes, we can design a holder to hold bag upright and keep it /clip it closed/open.

Richard Tanabe – NCON and ACM collectors should have overflow containers (buckets) already – These will need to be acidified as well – maybe with a high concentration acid/low volume mist, or > solid Br compounds?

Gregory Wetherbee – I would be more concerned about low-volume weeks. We are sampling fewer low-volume weeks in NTN due to bags. There would be fewer data points with bags, but that should not deter us from using them. Just a thought.

Alexander Nyhus - The N-CON heater is not that hot. Holder is like Kwik Trip grab coffee box.

DG – good idea – Will keep the bag upright?

GW - Skip the laboratory evaluation of sample stability, and move directly to co-located sampling in the field to compare the standard and bag methods.

Anita Peterson (?) - Might be hard for short operators to get a bag tightly over the NCON collector lid – will they need a ladder?

DG - Need a collar or lid to keep the bag tight against the collector. Need a clip to the top of the bag? Seal at site? Seal at the WSLH? Should be engineering solutions here.

RT – I wouldn't use a band clamp . The bag will fit over the chimney with a fairly snug fit. (NCON and ACM).

MDN Biweekly Sampling – Christa Dahman

Background

Multi-week sampling proposed as cost- and effort-saving measure

Make MDN a more accessible network for prospective site sponsors, grow/maintain network.

Initial testing performed in 2021: Stability of spiked mercury over several weeks. Study

demonstrated that subsampling was not a viable approach. Mercury interacts with the surface of the containers, causing low bias in the solution. Despite this, loss of mercury to air was not suspected.

Introducing multiple controls to a collector environment and retrieving them over time is logistically challenging/impossible.

At 2022 Spring Meeting, discussed collocated collections of one and two week samples.

Testing

WI06 – UW Arboretum: Weekly/Biweekly Collocated, data compared by summing volumes and masses of mercury in the two weekly samples for the equivalent biweekly interval. 7/22-1/23.

WI31 – Devil's Lake: Weekly Collocated, normal weekly collections on both sides used to compare typical variability (1/22-7/22).

Results

Sample volume: weekly vs bi-weekly Sign test p-value 0.1460

Median biweekly WI06/06WI precip volume: differences not statistically different from zero median RPD -1.5%, Biweekly > weekly

THg concentrations: weekly vs bi-weekly Sign test p-value 0.387

Median biweekly WI06/06WI concentration difference not statistically different from zero median RPD +1.5%, weekly>Biweekly

• <u>Summary</u>

WI06 samples collected 7/2022 – 1/2023, WI31 from 1/2022 and 7/2022 Volume and concentration differences are comparable to typical collocated samples No significant evaporation with extended deployment Likely representative of temperate/Midwest sites Feedback? More information? Ready for prime time?

Discussion

Doug Burns - Did NEON do weekly vs biweekly study?

Teresa Burlingame - We only have done biweekly samples so far – and not for Hg concentrations, but can look at co-located MDN/NTN and NEON?

Greg Wetherbee – Great results –can cut MDN costs in half. ½ bottles, ½ analyses.

Tim Sharac - We should move the tests west to a more arid environment, and to areas with higher precip volumes – to push the limits of the 2-week sampling.

Christa Dahman – We will need dual collectors

Richard Tanabe – There are no dual collectors in the West – we can lend from our stock.

Mike McHale – Need to talk next steps - what do we need to do to implement? Co-locate a site out west – how to push this forward?

Martin Shafer – At high precip volumes, pH of collected samples might not have been appropriate – might be an issue with long deployments – something to consider.

CD – At max volume samples were pH ~3, brominated within 28 days, as required by EPA 1631. Not sure if it makes a difference or not? There were a few high-volume samples but never exceeded capacity of bottle.

Alexander Nyhus - I could run a weekly and biweekly sample for you, at Devil's Lake for testing.

CD – Testing was done at Devil's Lake - thanks for offer but not sure it will provide much additional info

USGS Precipitation Chemistry QA Project for NADP NTN and MDN 2022 Results - Greg Wetherbee and Noel Deyette

• Changes to the USGS project in 2022

WSLH is now preparing and shipping the Field Audit and System Blank samples to sites.

Noel is preparing and shipping the Interlaboratory-Comparison Program samples in the USGS NY Water Science Center.

Hg Interlaboratory-Comparison Program samples are being shipped quarterly – a leftover cost savings from the COVID era.

MDN Results

Positive analytical bias \sim 0.375 ng Hg /L indicated for HAL: Sign test p-value 0.2632 HAL variability \sim 220% higher than overall among labs

Hg Network Max Contamination ~ 0.102 ng / sample (slight uptick, but similar to recent results) Max probable effect on deposition 0.442 ug Hg m-2 yr-1

NTN Results

Positive, statistically significant analytical bias Ca, NH4, and H+ in the CAL - not of practical importance.

Negative, statistically significant analytical bias indicated for K, Cl-, SO4 for CAL, but not of practical importance.

CAL variability is lower than overall among labs, < 5.5% Relative Standard Deviation among replicates for all analytes indicates excellent precision

Field Audit samples show sustained increases in Network Maximum Contamination Levels that spiked in 2021.

Field Audit samples indicate decrease in H+-ion loss, but positive analytical bias for H+ is back again

WSLH performed well for RSD of replicate samples – typically of the order of 1% or less, with the exception of H+ (5.5%)

Co-located sites – OH09/09OH and NE99/99NE (for QR A or B only)

NE99 had higher variability on analyte concentrations — due to higher variability in catch efficiency and sample volume — sensor differences? Lid pad seal problems?

Publications

2019 -20 USGS SIR QA Report received USGS Director's approval

Submitted to Denver Pubs Unit Feb. 2022

Recommend publishing as NADP QA Report for 2021–2022 report

USGS Open-File report on reactive N deposition at Rocky Flats NWR (CO86)

Approved! In preparation at Denver Pubs Unit.

Paper on Fort Collins, CO urban deposition was planned for FY22, but no time to work on this.

Discussion

Doug Burns – Positive bias in Hg is consistent and concerning - any explanation or thoughts?

Martin Shafer – It was more the variability – any ideas why?

Christa Dahman – This is news to me. I don't [know] but could hazard a couple of guesses. I will look at the sample reports.

Noel Deyette – The issue was the variability in the standards. The bias in reported concentration was not alarming, but the variability of the HAL results was 220% of the other labs.

DB – Is the side by side collector comparison worthwhile? Continue?

MS – It provides a measure of the overall variability in the whole network.

DB – I thought it might be telling you something about the individual collector issues, but I guess that is part of the network operations functions.

ND – Most of the time the historical co-located results have been close, maybe the NE99 infrastructure is aging and should be checked?

Update – Telemetry Upgrades at USGS Sites – Mike McHale

We had 8 sites with telemetry, now 14 – satellite transmitters and cell modems (preferred, 2-way Communications/uploads)

Use satellite telemetry where there is no cell coverage – harder to install and set up

Planning on more deployments next year – USGS will keep NADP updated. Goal is to install at all sites

5 Year Preservation Study – Nichole Miller

Background

This study was set up to determine sample stability by refrigeration versus freezing.

It spans over a five year time frame – starting in 2019.

Data is pulled annually from the analytical runs and compared to Year 0.

Long term archive samples are currently stored in a refrigerator (4°C).

Fixed and forever sites are currently stored in a freezer (-20°C).

It is believed that at ISWS, only the fixed and forever sites were frozen – not positive if they were frozen immediately or at the end of the year that they were received.

Study Setup

112 higher volume NTN samples were saved in the refrigerator for ~2 weeks after the working NTN samples were filtered.

All refrigerated samples were filtered on day one and then all frozen samples were filtered on day two. Each sample has refrigerated and frozen pair, for each year of study.

6 bottles were filtered for refrigeration and 5 bottles for freezing following normal protocol.

The frozen and refrigerated samples have a different LIMS ID to prevent analytical mix-ups.

The first set of refrigerated samples were analyzed immediately (Year 0).

Samples are run roughly the same time every year and data is uploaded to LIMS.

True value = first refrigerated year zero sample for each site – calculate averages on all 112.

Samples - difference in analyte concentrations between TV and prior years refrigerated and frozen.

Largest differences noted in conductivity and pH.

Observations

Year 2 sulfate and nitrate have a negative bias compared to other years.

More drastic loss of NH₄ for refrigerated samples.

Conductivity shows a negative bias for refrigerated and a positive bias for frozen.

pH shows a loss across all samples.

Next Steps

Next year will be the last data set processed (April 2024).

There is a plan to possibly have a UW student run in depth statistics on the full data set.

We will discuss if there is an advantage or disadvantage to either freezing or refrigerating the long term archive samples.

Discussion

Amy Mager – Great summary! To clarify – We are currently saving 5 years of archived samples (those with enough volume) –all for 5 years; at end of year 5 we get rid of oldest set of samples. Forever sites – save every sample we have ever collected from these WI06, NH02, IL11, etc. – frozen. Fixed sites – we save one sample month from these 12 sites – also frozen.

John Walker – This is interesting work – It would be interesting to look at when you see large differences in NH4+, do you see bias in NO3- that goes in the other direction? – This might inform the mechanism responsible.

Nichole Miller - Yes, a good idea thanks. To reiterate – all fixes and forever samples are filtered as well.

NOS Succession Plan – Winston Luke

Discussion

Tim Sharac - We will be looking for a new NOS Secretary this Fall.

Winston Luke – Retirement is looming although no decisions have been made yet. I have agreed to be acting NOS Secretary this year but we should have another plan in place.

Mike McHale – I have someone in mind for NOS Secretary in the Fall.

TS – Serving as NOS Secretary/Vice Chair/Chair is an interesting process - you get to run this meeting, and there are a lot of helpers here, and NADP is a great collection of people.

Spring Meeting 2024 - Mike McHale

Meeting will be in Madison, maybe not this space (\$) – we may find another building to host the meeting. Madison works well, and is easier on the PO staff.

Final Discussion – Tim Sharac

Discussion

Winston Luke – We might want to entertain a motion to form an ad-hoc committee within NOS to advance plans and maintain progress on operator engagement/training issues, to get a handle on hidden operational details that may affect data quality.

Tim Sharac – Similar to Siting Criteria WG - a small collection of people?

WL - yes

TS – A good idea. EEMS is excellent at what they do but sometimes the maintenance messages to operators is not getting through, or operators are not hearing the messages or acting upon them – clean the collectors, lids, dry side buckets, etc. Maybe make it a scavenger hunt to find the loose nuts on the collector arms, look at and clean lid pads, etc.

Those interested in participating – Eric Hebert, Richard Tanabe, Winston Luke, Noel Deyette, Tim Sharac. Martin Shafer, others?

TS – The program has seen dramatic improvements in sample and data QA once the samples are received at the WSLH, but we need to concentrate on external drivers at the point of sample collection.

Mike McHale – I want to move the biweekly MDN collection effort forward – Greg Wetherbee and I will reach out to move this plan forward – next steps, etc. If anyone is interested in helping, please reach out to MM or GW.

Eric Hebert – We need to test the (MDN) bag sampling idea as well – see if that saves us enough \$ before going to biweekly collection.

Kristi Morris – I would like to offer up an NPS site in the West for biweekly sampling

David Gay – Are you thinking that every site goes to 2-week collection, or on a site-by-site basis? Regarding keeping sites running well – historically it fell to the Coordinator to call the site funder to correct site ops problems. I can restart this.

MM – Not sure if we go biweekly at each site, but logistically challenging if different sites are following different protocols – might lead to serious complications.

Greg Wetherbee – It will also affect data analysis – less robust trend analyses with less data. Initial results regarding the tests are great. If we get the same annual (deposition) numbers, and that is our objective, great. If we want trends, however, we loose statistical power. But there are tradeoffs. If biweekly collection can keep some sites in the network, maybe we consider it and decide on a site by site basis. It might also attract new MDN site sponsors. I think it would be too bad if we do 2-week sampling across the board, but funding issues may compel us to do so. We need to test in the field.

WL – Cost savings are driving this – we should do a budget analysis? If switching to bags saves enough \$ we keep weekly sampling. But a budget analysis for each proposed change will help us here.

MM – I'm looking at trends with MDN data now. it will be easy to look at impacts on trends at sites with 10+ years of data if we drop out every other week's data and perform the trend analysis with $\frac{1}{2}$ the number of samples per site.

Martin Shafer – The spatial distribution of results depends on the number of valid samples per site – if you lose one or two you may lose ability to perform geospatial analysis.

MM – David Gay, do you want to put a motion forward to test the MDN bags?

Richard Tanabe – It may be a bit early for a motion. There are two steps to this process. The PO needs to continue to explore bag sampling options for MDN and analyze impacts on costs, SOPs, etc. I would rather go back to the PO and come up with a plan for bag sampling – find a supplier, how to accommodate NCON and ACM collectors, explore the heater issue with NCON, etc. Once we figure these issues out, we can come back with a motion to proceed.

DG – Need to consider logistics and lab issues as well.

Eric Hebert – I wouldn't make a decision to go biweekly until we explore the bag issue to save money.

End of Discussion

Motion to Adjourn – moved by Tim Sharac, second Ryan McCammon. Motion passed.