Lake RMN Protocol Document.
Water Chemistry (12/28/2022)

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Why collect water chemistry data?

Water chemistry data provide information on trophic status and water quality, and allow for tracking of potential stressors (e.g., nutrients, conductivity, sulfate). For the lake RMN, recommended parameters include measures of nutrients, transparency/water clarity and general water quality.

1 Level of effort

The RMN framework allows for different levels of effort (LOE) to maximize participation. Table 1 contains the LOE matrix for the highest priority water chemistry parameters, which include Total Phosphorus (TP), chlorophyll-a (chl-a) and Dissolved Organic Carbon (DOC) (listed in order of highest to lowest priority). Table 2 lists the lower priority parameters. If unable to collect the full set of indicators in Table 2, select the options that best fit your priorities, and work towards participating at a higher level as resources permit (phased approaches are common, in which RMN partners add more parameters and potentially sites as you gain experience and build capacity). Appendix A describes rationale for collecting each recommended parameter.

Water samples are collected from the exact same location each time (typically the deepest point in the lake, with some exceptions). At a minimum, one set of water grab samples should be collected from the top 0-2 meters during July 24 to August 7, with the intent of coordinating the timing of at least one set of regional measurements. While efforts should be made to sample during this time period whenever possible, situations may arise where people need to monitor during the week before or after. Those data will still be used but will be flagged. The July 24-August 7 time period is when lake temperatures are typically warmest and chlorophyll-a tends to reach its annual maximum. This is also a time when the lake is likely to be stratified (if it stratifies at all) and dissolved oxygen is likely lowest in the hypolimnion. Many lake monitoring programs typically sample around this time.

The minimum level of effort (once per year) has limited value for trend detection, but it is useful for setting a baseline against which future changes can be measured. More frequent sampling is recommended, at least for the two highest priority nutrient parameters – TP and chlorophyll-a, as described in Table 1.

Table 1. Recommended level of effort for the highest priority parameters for the RMNs (ordered from highest to lowest priority). Appendix A describes the rationale for collecting each parameter.

Highest priority	Field method	Minimum	Target	Better
Total phosphorus	SURFACE. Integrated grab sample from top 0-2m. BOTTOM (0.5-1m) sample if lake is stratified	1x/year (July 24-Aug 7)*	SURFACE. spring turnover + 3X/year during summer (15 July – 15 Sept); one of the 3 visits should occur during July 24-Aug 7. BOTTOM. 1x/year (July 24-Aug 7)	The more frequent the measurements, the higher the likelihood of detecting trends over shorter time periods and the higher the probability of correctly detecting subtle trends
Chlorophyll-a	SURFACE. Integrated grab sample from top 0-2m into 2-L container; filter on shore; keep frozen until processed	1x/year (July 24-Aug 7)*	3X/year during summer (15 July – 15 Sept); one of the 3 visits should occur during July 24-Aug 7	
Dissolved organic carbon (DOC)	SURFACE. Integrated grab sample from top 0-2m. BOTTOM (0.5-1m) sample if lake is stratified	1x/year (July 24-Aug 7)*		

*While efforts should be made to sample during this time period whenever possible, situations may arise where people need to monitor during the week before or after. Those data will still be used but will be flagged.

Table 2. Recommended level of effort for the lower priority parameters for the RMNs, which are **surface samples (integrated grab sample from top 0-2m 1x/year) collected once per year (July 24-August 7, ± 1 week). After the first two years, if the parameters in gray shading are similar across years, they are collected once every 3-5 years.** Appendix A describes rationale for collection of each recommended parameter. If unable to collect the full set, select the options that best fit your priorities, and work towards participating at a higher level as resources permit.

Group	Parameter	Notes
Nutrients – Nitrogen*	Total Nitrogen (TN)	Inorganic + organic nitrogen (equals [NO2 + NO3] + NH3 + organic N)
	Total Kjeldahl Nitrogen (TKN)	Organic N + ammonia (NH3)
	Nitrate and nitrite (NO3 + NO2)	Inorganic forms of nitrogen
	Ammonia (NH3)	Inorganic form of nitrogen
Transparency/ water clarity	Colored dissolved organic matter (CDOM)	Ideally collected at a time when there is clear sky satellite overpass (Landsat 8 data or Sentinel 2A & B) - for more information, see Appendix B
	True Color	
	Apparent Color	
	Total suspended solids (TSS)	
	Turbidity	Can be measured with a (calibrated) field meter
General water quality	Specific conductivity	
	pH	
	Water temperature	
	Dissolved oxygen (DO)	
	Alkalinity	Most RMN partners can use the CaCO3 method, but some lakes require the laboratory gran-plot method (alkalinity/ANC) because they have ANC values near or below 0 ueq/L and the standard “as CaCO3” method is not sensitive enough down to that level
Major anions	Chloride (Cl)	Significant decadal trends in lake salinization have been identified in North America, which threatens lake water quality (Dugan et al. 2017). For stratified lakes where road salt is used, consider collecting a bottom sample as well (0.5 to 1-m above bottom)
	Sulfate (SO4)	Collect 1x/yr for the first two years, then, if results are similar across years, collect once every 3-5 years
Major cations	Calcium (Ca)	
	Magnesium (Mg)	
	Sodium (Na)	
	Potassium (K)	
Other	Dissolved silica (SiO2)	

*To reduce analytical costs, you could monitor TKN and NO3+NO2, and then derive TN from those data using this formula TN = TKN + [NO3 + NO2].

2 Protocols

If you already have existing EPA-approved Standard Operating Procedures (SOPs) and/or Quality Assurance Project Plans (QAPPs) for many if not all of the recommended water chemistry samples, keep collecting data in accordance with your approved methods. If you do not have existing SOPs or QAPPs for all of the parameters, or are starting from scratch, this document will provide you with an overview of the basics (workflow, methods, equipment and resource needs, etc.). Your RMN regional lead can also provide resources that will help you develop your own approved sampling plans (for example, the Great Lakes Inventory and Monitoring Network has an excellent, comprehensive document with much if not all of the information you would need – see Elias et al. 2015). To find out who your regional lead is, contact Britta Bierwagen (Bierwagen.Britta@epa.gov).

All field staff should receive training on these protocols.

Pre-trip preparations

- Review protocols
- Make sure you have necessary permissions to access the lake and perform monitoring activities
- Obtain guidance from the designated laboratory regarding appropriate bottle labelling, sample preservation, holding times and Chain of Custody (COC) procedures.
- Prepare equipment
    - Use a trip-specific checklist of equipment and supplies
    - Confirm that the number of bottles and preservative necessary to collect all regular and duplicate samples are packed.
    - Lessen the chances of contamination by keeping your sample bottles in zip lock bags and a clean cooler
    - Calibrate multi-probe meters in accordance with manufacturer specifications.
- Prepare lake monitoring data sheets with the specific site/date information relevant to the sampling event
- Label bottles (to the extent possible; this can be done en route to the site as well)
- If working in lakes with invasive species infestations, bring decontamination materials

Travel to sampling site

- Go to the predetermined sample location(s) via GPS (in our case, the deep point in the lake)
- Stop the boat and lower the anchor; ensure the boat is not drifting.
    - For all sampling, it is critical to avoid sampling water showing evidence of oil, gasoline or anything else from the boat. It is best to kill the engine and set the anchor, however we understand this may not be possible in bad weather or with a balky engine.
- Verify depth of sampling location to confirm that the correct location is being sampled

Take field meter measurements for a water column profile (where applicable)

- The field meter should be properly-calibrated and maintained in accordance with an approved SOP or QAPP and/or manufacturer specifications
- Record temperature, specific conductance, DO and pH measurements at appropriate depths. Before recording measurements, wait until the numbers stabilize to ensure that the sensors have equilibrated to the condition of the water being monitored
    - If you already have an EPA-approved SOP or QAPP with protocols for taking vertical profile measurements, follow your existing protocols

- If you do not have existing guidance, use the EPA National Lake Assessment (NLA) protocols (USEPA 2017), which call for sampling at the following depths:

  - <u>Lakes with a maximum depth ≤ 3 m</u>
    - Just below surface
    - 0.5-m intervals
    - 0.5-m from bottom

  - <u>Lakes with a maximum depth 3-20 m</u>
    - Just below surface
    - Every 1-m ending at 0.5-m from bottom

  - <u>Lakes with a maximum depth (>20 m)</u>
    - Just below surface
    - Every 1-m up to 20-m
    - Then every 2-m ending at 0.5-m from bottom, with this exception -
      - Within the metalimnion, take measurements at least every 1 meter.

Take surface water grab samples

FIRST - before collecting, take steps to avoid possible sources of contamination.

- Do not handle any food, drink, sunscreen, or insect repellant until after samples have been collected, or implement measures to reduce contamination by such chemicals, if applied, such as washing, wearing long gloves, etc.
- Wear (clean) gloves when collecting the sample
- Keep the sample bottles clean by keeping them in a plastic bag in a clean cooler for the trip.
- Do not touch the inner surfaces or mouths of the jars, or the covers.
- Make sure the integrated sampler is clean[1]
- Avoid obtaining sample(s) in areas where there is an oil sheen or debris floating on the water's surface, near the motor or other sources of contamination or disturbance

SAMPLE COLLECTION

- Aim to be consistent with this general guidance (EPA NLA 2017)
  - Prepare sample bottles in accordance with laboratory instructions (which varies across parameters)
    - Some bottles and caps should be rinsed 3x with lake water (as an example, this is done with the 2-L brown bottle for chl-a). Uncap and re-cap bottles below water surface to avoid surface scum or debris.
    - Other bottles should not be rinsed (e.g., some are pre-preserved with H_2S0_4))
  - Use an integrated sampler to collect a composite water sample from the top 2 meters of the water column
    - Remove stoppers from the integrated sampler (note: some samplers have rubber stoppers at the top and bottom; others have a rubber stopper at the top and a valve or ball at the bottom; either is acceptable)

[1] Training videos on how to use, clean and maintain integrated samplers are available. For example https://www.rmbel.info/lakes/lake-training-videos/

- Clean the sampler - lower sampler vertically into the water, insert stopper on the upper end of sampler, remove from water and release stopper. Repeat this process two more times to complete rinsing.
- Collect the samples on the opposite side of the boat. Lower the un-stoppered integrated sampler into the water column until the top is at the water surface. Be sure that sampling personnel keep hands on the outside of the tube and stopper only to avoid contamination.
- Place the stopper in the top of the tube.
- Slowly raise the tube so the lower opening is just below the water surface, keeping it vertical
- As the tube breaks the surface, either quickly cap the bottom or close the valve, or allow contents to pour into a clean, plastic container that you'll use to composite multiple samples (some people use 4-liter beakers with pour spouts but there are no special requirements for the composite container). Again, ensure that sampling personnel do not touch the inside of the bottle or cap.
- Repeat as needed until you collect sufficient water for all of your samples. Then composite/mix the water and dispense it into the appropriate containers.
    - When emptying the sampler, place containers in the shaded area of the boat to avoid exposing them to direct sunlight when dispensed

What if the lake is less than two meters deep (and you can't fully submerge the sampler)?

If you already have an EPA-approved SOP or QAPP for collecting water grab samples in shallow lakes, follow your existing protocols. If you do not have existing guidance, take a hand-collected sample instead.

- Wear (clean) gloves
- Prepare sample bottles in accordance with laboratory instructions (which varies across parameters; e.g., with some, you should rinse 3x with lake water)
- Tip the bottle upside down and lower it into the water column, pointing away from the boat. Be sure not to touch the inside of the bottle and cap.
- Invert the bottle and allow it to fill.
- Bring the bottle to the surface, taking care to avoid any surface scum/material.
- Cap and invert the bottle.

Take bottom water grab samples (optional)

If the lake is stratified, collection of bottom samples (depth = 1 m above bottom) for TP, DOC and chloride (where road salt is used) are encouraged (1x between July 24 and August 7).

If you already have an EPA-approved SOP or QAPP for collecting bottom samples, follow your existing protocols. If you do not have existing guidance, here are basic guidelines:

- The integrated sampler can only be used at the surface so a different type of water sampler is needed for depth samples. Many programs use Kemmerer or Van Dorn samplers (see Section 4).
- Lower the sampler until it is 1 m above bottom and collect the sample (be careful not to stir up bottom sediments)
- Pay special attention to the appearance (visual color and turbidity) and smell (rotten egg gas, H2S) of the water. If there is any evidence suggesting that bottom sediments were stirred up and captured by the sampler, re-do the collection taking care to vigorously clean the sampler and compositing container with surface water

Processing samples
Some processing is done on the boat, some on the shoreline and some in the laboratory. If you already have an EPA-approved SOP or QAPP for sample collection and preservation, follow your existing protocols. If you do not have approved methods, we cannot offer universal guidance because instructions vary depending on the parameter, laboratory, etc. but here is some basic guidance –

- When dispensing water from the composite container to the appropriate bottles, make sure the composite water is well-mixed
- Don't overfill the bottles. You may need to add preservative later, or may need to freeze the sample (and if overfilled, the bottle will break when the water expands as it freezes)
- The chl-a filtration is typically done on shore. If you have existing EPA-approved protocols, use those. Otherwise use the NLA 2017 protocols (see Appendix D).
- Ensure preservative is added to appropriate sample bottles. If you add preservative, use caution. Protective gloves are recommended. Immediately rinse hands in water if acid is spilled.
- For some parameters, you need to purge all air before sealing the bottle (in which case, make sure no air bubbles remain).
- Double check bottle labeling. Ensure that all identification is correct and easily readable. Sample containers should be labeled in indelible ink with, at a minimum, the station name, date and time of collection, and preservation method, if applicable. We recommend covering the labels with clear tape.
- Make sure field forms and COCs are complete.
- Prepare samples for shipment
    - Follow laboratory specifications
    - Ensure all bottle caps are tightly sealed and that all bottles are packed securely to avoid breakage.
    - If ice is needed, ensure an adequate amount of ice to account for shipment or delivery time (if ice is appropriate)

3 Quality Assurance/Quality Control (QA/QC)

QA/QC is a critical component of monitoring, as it ensures data quality objectives are being met. Table 3 contains a list of procedures and documentation that are typically included as part of water chemistry QA/QC to help ensure that data remain consistent and comparable over time.

The three subsections below contain QA/QC protocols for field meters, water grab samples and laboratory performance. These come from SOPs # 6 and #12 in the Great Lakes Inventory and Monitoring Network (GLKN) Water Quality Monitoring Protocol for Inland Lakes (Elias et al. 2015). If you already have an EPA-approved SOP or QAPP that meet these minimum requirements, continue following your approved protocols. Oversight and compliance is left up to participants.

Table 3. Summary of QA/QC documentation and sampling methods (source: Elias et al. 2015, SOP #6).

Procedure	Description/reason
Instrument calibration logs	Each instrument must have a log in the form of a permanently bound logbook. Calibration schedule must be observed, using fresh calibration standards.
Project binder	Containing: checklist of QA/QC reminders, copies of decontamination, sample collection and processing SOPs, copies of equipment calibration and troubleshooting instructions, ASR and COC forms, blank field forms.
Site binders	Containing: GPS coordinates for verification of correct sampling location, table of previous field measurements to compare with new measurements
Field forms	Field forms are the only written record of field measurements, so copies are placed in site binders and originals must be kept on file indefinitely.
Field instrument methods	Require consistent measurement methods and detection limits
Sample preservation and minimum holding time	Water quality variable concentrations are maintained as close to sampling conditions as possible.
Chain-of-custody	A chain-of-custody includes not only the form, but all references to the sample in any form, document or log book which allow tracing the sample back to its collection, and documents the possession of the samples from the time they were collected until the sample analytical results are received.
Laboratory methods	Require consistent analytical methods and detection limits

3.1 Field meters

QA/QC protocols for field meters should meet the minimum requirements described below. Source: Elias et al. 2015 (SOP #6). Oversight and compliance is left up to participants.

Disclaimer: these protocols provide only generic guidelines for equipment use and maintenance. A wide variety of meters are available; such instruments are continuously being updated or replaced using newer technology. Keep equipment manufacturers' maintenance and calibration instructions for all instruments for reference purposes. Field personnel must be familiar with the instructions provided by manufacturers. Contact manufacturers for answers to technical questions.

Use calibrated instruments for all field measurements. Meters should be calibrated each sample date for all parameters relevant to each meter. At a minimum, this includes dissolved oxygen (check the

barometric pressure at the nearest weather station). Calibration solutions should be used for conductivity and pH. Refer to your meter's operations manual.

Each instrument should have a logbook for recording all maintenance and calibration information, including:

- serial number, date received, manufacturer's contact information, especially technical service representatives
- service records, dates of probe replacements
- maintenance records, for example, whenever the following general maintenance occurs: DO membrane replacement, pH reference probe junction and filling solution, probe cleanings, sonde (the sensor housing) replacement, impellor replacement or cleaning, etc.
- calibration dates and calibration data
- any problems with sensors
- pre-mobilization, post-calibration checks performed on individual sensor probes

Instrument calibration (before use) is an essential part of quality assurance. Table 4 summarizes the target calibration frequency and minimum acceptance criteria for pH, conductivity, water temperature and DO.

Post-field calibration checks should be performed after each use of the instrument and before any instrument maintenance. The purpose of the post-calibration is to determine if the instrument held calibration during the day of sampling. Compare the post-calibration values to the expected values for the standards. This will ensure that the field measurements for the day can be reported with confidence. The difference between the post-calibration value and expected standard value can be used to indicate both calibration precision and instrument performance.

The sooner this procedure is performed, the more representative the results will be for assessing performance during the preceding field measurements. Calibration and post-calibration should be no more than 24 hours apart. When sampling daily, the second day's calibration can serve as the first day's post-field calibration check. Take the same care used in performing the initial calibration by rinsing the sensors and waiting for sensors to stabilize.

If post-calibration values (Table 5) fall outside the error limits for DO, pH, and specific conductance, data collected do not meet quality assurance (QA) standards and should be flagged appropriately (see SOP #12 in Elias et al. 2015 for more details). Measurements may be repeated with a different or back-up instrument. If post-calibration measurements do not consistently fall within the error limits after in-house trouble shooting, the instrument should be returned to the manufacturer for maintenance.

Table 4. Calibration frequencies and acceptance criteria for field instruments. Source: Elias et al. 2015

Parameter	USEPA Method	Minimum Calibration Frequency and QC checks	Acceptance Criteria	Corrective Actions
Temperature	170.1	Annually, 2-point check with NIST thermometer	±1.0ºC	Re-test with a different thermometer; repeat measurement
Specific Conductance (SC25)	120.1	Daily, prior to field mobilization; calibration check prior to each round of sampling; 10% of the readings taken each day must be duplicated or a minimum of 1 reading if fewer than 10 samples are read.	±5% RPD 10%	Re-test; check low battery indicator; use a different meter; use different standards; repeat measurement
pH	150.1	Daily, prior to field mobilization (two buffers should be selected that bracket the anticipated pH of the water body to be sampled)	±0.05 pH unit	
		Calibration check w/ third buffer prior to each round of sampling; check with low ionic strength buffer in addition, if conductivity is <50 µS/cm	±0.1 pH unit	Re-test; check low battery indicator; use different standards; repeat measurement; don't move cords or cause friction/static
		10% of the readings taken each day must be duplicated or a minimum of 1 reading if fewer than 10 samples are read.	RPD 10%	
Dissolved Oxygen	360.1	Daily, prior to field mobilization; check at the field site if elevation or barometric pressure changed since calibration	0.2 mg/L concentration or ±10% saturation	Re-enter altitude; re-test; check low battery indicator; check membrane for wrinkles, tears or air bubbles; replace membrane; use a different meter; repeat measurement; allow more time for stabilization

Table 5. Post-calibration check error limits (source: Elias et al. 2015)

Parameter	Value
Temperature	±1°C, annual calibration check
Specific Conductance	±5%
pH	±0.1 standard units
Dissolved Oxygen	±0.2 mg/L, ± 10% saturation

3.2 QA/QC Samples

QA/QC protocols for quality control samples should meet the minimum requirements described below. Source: Elias et al. 2015 (SOP #6). Oversight and compliance is left up to participants.

Equipment/field blanks and sampling duplicates should be collected at a rate of 10% (i.e., for every 10 regular samples, collect at least one blank or duplicate sample).

Equipment/Field blanks
Blanks are used to measure and quantify the amount of contamination from extraneous sources (preservatives, sample bottles, sample handling, automatic samplers, etc.) that might compromise the integrity of a sample – e.g., the integrated sampler and compositing jugs are potential sources of cross contamination between sampling sites.

Follow your laboratory's guidance. Typical protocols are as follows:

1. Between sample sites, rinse the integrating sampler and compositing jug with laboratory reagent grade water three times and discard.
2. Fill the integrating sampler with a fourth aliquot of laboratory reagent grade water and handle and process this aliquot as if it were a lake sample to be analyzed.

This sample is labeled as an equipment blank and information kept on a datasheet describing the source of the blank. Results for all parameters should be non-detect.

Other types of blanks can be used as needed. Examples include -

- Field sampling conditions or ambient blanks, if there is any reason to suspect that ambient air pollution has the potential to contaminate water quality samples
- Preservative blanks, if there is any reason to suspect that a preservative may be contaminated
- Bottle blanks, any time sample collection bottles are of uncertain quality or cleanliness or from a source not previously used.

Sampling duplicates
The purpose of a duplicate sample is to estimate the inherent variability of a procedure, technique, characteristic or contaminant. Duplicate samples are collected: 1) as a form of field or laboratory quality control; 2) to measure or quantify the homogeneity of the sampled system, the stability and representativeness of a sample site, the sample collection method(s) and/or the technician's technique. Duplicate samples also document the technique and ability of the technician and analyst to produce representative water quality data.

Follow your laboratory's guidance for whatever parameters you are doing duplicates on (and collect two samples using those methods instead of one). Label appropriately. Laboratory duplicates (not field duplicates) which exceed QA/QC standards for the parameter are retested.

The laboratory analytical report should show test results for the duplicates and the method and the results for summary quality control statistics calculations. Copies of these reports should be retained as a permanent part of the site file.

3.3 Laboratory performance

Source: Ledder et al. 2015 (SOP #12). Oversight and compliance is left up to participants.

We recommend that you use only laboratories with NELAC certification or at least certification by the state programs that also use the laboratory. Appendix E contains a checklist that can be used when selecting contract laboratories and documenting their compliance with QA/QC expectations. The chosen contract laboratories should prove their capability annually through participation in blind quality control checks and other methods prescribed by the states in which they receive certification and/or federal programs in which they participate. Keep copies of certifications for each analyte and/or method along with QAPPs for each laboratory contracted for the duration of this monitoring effort.

The laboratories should flag samples that are past defined target holding times, as well as samples that are damaged during the shipping process. The lab should evaluate flagged samples to determine if either impacts sample integrity or any potential end uses of the data.

Most laboratories routinely recalculate MDLs, MLs, and QC sample control limits using repeated measurement of standard samples or multiple percent recoveries on a quarterly or annual basis. Request and maintain copies of this information for the relevant analytical methods.

Performance measures include:

- Data Completeness
- Sensitivity
- Precision
    - Target: a maximum of 10% relative percent difference (RPD) for all lab parameters except chlorophyll-a and nutrients, for which the maximum RPD is 30%.
- Bias
    - Target: a maximum of 15% RPD for all parameters, or state-credible data defaults, whichever is more stringent

For more detailed information on laboratory performance criteria, see SOP #12 in Elias et al. 2015, and for recommendations on keeping data records consistent and comparable over time, see Appendix F.

4 Equipment

Tables 6 and 7 contain information on basic equipment needs and costs for in-situ monitoring with field meters and water grab samples. This assumes you have access to a boat and anchor, a GPS unit for locating the sampling location and safety gear.

4.1 Field meters

Prices vary widely depending on which platform you select and which probes you use (Table 6). YSI and Hydrolab are commonly used (but this is not an endorsement). Initial purchase cost for a sonde with conductivity, temperature, DO and pH sensors cost around $10K, depending on how many probes and what features you choose. In addition, if you use the probe frequently throughout the ice free season, expect to spend $500-1000 for annual maintenance and repairs. In addition, you will need to purchase

certified calibration standards. Costs will vary depending on how often you calibrate your meter of use (one RMN partner estimates a cost of around $25 per calibration for pH and conductivity). To calibrate the temperature probe, you will need a NIST-calibrated thermometer. For DO, people typically have a lab barometer (which runs about $200) and deionized water.

Table 6. The cost and features of multi-probe meters varies widely. Here are some basic specs and estimated costs (1/31/2019).

Item	Description	Estimated Costs[1]
Field meter	Sonde with 100-m depth, 4 sensor ports	$4,950
	Conductivity/temperature sensor	$890
	pH sensor	$560
	Optical DO sensor	$1,960
	10-m field cable	$610
	Handheld display	$2,700
	Wheeled carrying case	$395
Annual calibration costs	pH solutions (4,7,10)	$15 per calibration
	Conductivity solutions	$7.65 per calibration
	Temperature	See below[2]
	DO	See below[3]
Annual Maintenance	Sometimes probes break	$500-1000

[1]as of 1/31/2019
[2]Need to purchase NIST-calibrated thermometer, and get it checked annually
[3]Need to purchase lab barometer. Some people purchase a water deionizer as well.

4.2 Water sampling

Prices vary widely depending on which analytes you are sampling, number of samples, what type of water sampler you use, what type of filtration system you use, what laboratory you use (in-house vs. outside), etc. (Table 7). At a minimum, surface water samples should be collected at RMN lakes. If you use the EPA NLA protocols, you can construct your own 2-m integrated PVC tube sampler for about $20 (Figure 1). This sampler is used in the EPA NLA surveys and is based on a design by the Minnesota Pollution Control Agency (MPCA). Pre-made integrated samplers can also be purchased online for about $50. Bottom samplers (like Kemmerers and Van Dorns) are more complicated (and expensive) since they need a line and messenger to trigger closure of the container at the appropriate depth. The bottom samplers should be clear plastic so that field crews can see whether the samples contain suspended bottom sediment when they are raised.

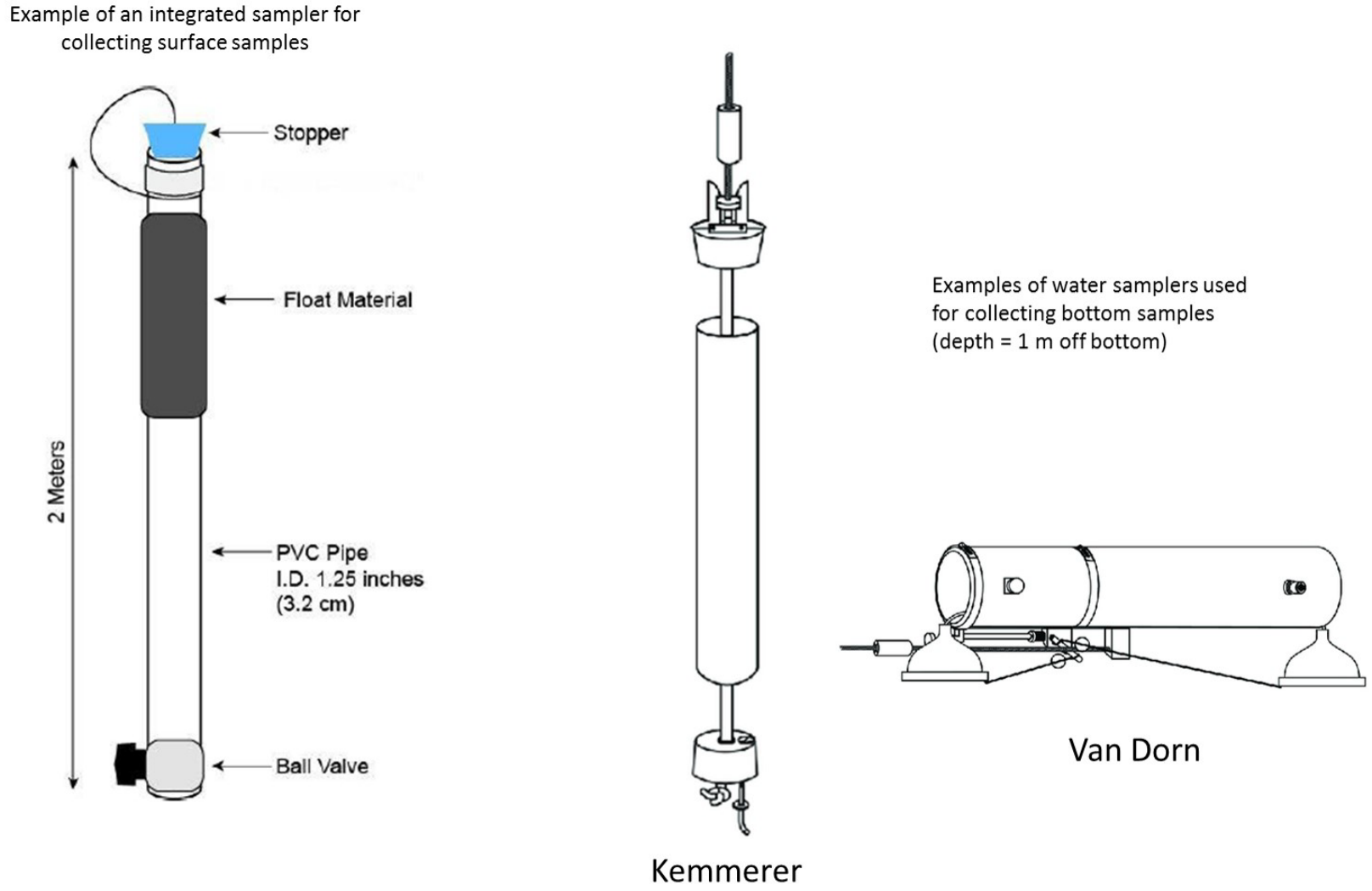

Figure 1. Example of a vertical integrated sampler (left) for collecting surface samples, and bottom samplers (two options are Kemmerer and Van Dorn samplers). The integrated sampler is a PVC tube 6.6 feet (2 meters) long with an inside diameter of 1.24 inches (3.2 centimeters) fitted with a stopper plug on one end and a valve or stopper plug on the other.

Table 7. Basic lake monitoring field work items and estimated costs (1/31/2019).

Item	Description	Estimated Costs*
Surface water sampler	2-m integrated sampler	homemade $20
		pre-made $50
Composite/ mixing container	Varies (e.g., some use a 2-L container, others use a 4L beaker with a spout). It is up to the user.	$10
Sample bottles	Number and type (plastic, glass) vary widely	Cost varies
Cooler		$50
Preservatives	varies depending on the analyte (some take nitric acid, others sulfuric acid, others need to stay cool - 4°C)	Cost varies
Ice	Usually 1-2 bags/sampling trip	$5
Other misc	Sharpies, clear tape, electrical tape, plastic gloves, zip lock bags	$20
Bottom water sampler (e.g., Kemmerer, Van Dorn)	Water sampler, messenger and line. Clear plastic*. Size depends on your needs (1.2 liter usually works)	Cost varies ($250-$800+)
	Spare parts kit	varies
	Carrying case	$100
Filters	0.45 µm for laboratory filtrations (e.g., DOC)	unsure
Laboratory analysis	Varies widely depending on the analyte and lab	in our inventory, costs ranged from $8-$129 per analyte
Chlorophyll-a	2-L amber plastic collection bottle	$15
	0.7 µm GF/F glass fiber filter	Pack of 100 for $45 (Cynmar)
	Centrifuge tube (50 mL, screw top)	Pack of 25 for $30 (cheaper if you make larger bulk order)
	Filter forceps (flat blade)	$12 Fisher
	Filtration chamber (with filter holder)	Magnetic filter funnel 300 ml $375
	Filtration flask (with silicone stopper and adapter)	1 Liter, #8 stopper $47 Fisher
	Filtration pump (hand vacuum)	$320 Fisher
	Graduated cylinder (250 mL)	Polypropylene $18
	Squirt bottle (1 L Nalgene) – de-ionized (DI)	$45 pack of 2 Fisher
	Foil squares	$8 Fisher
	DI water	Varies (depends on whether you have a water deionizer or need to purchase it)

*Clear plastic allows the crew to ensure that bottom water samples do not contain suspended bottom sediment

5 Field forms/records

Forms for recording RMN water chemistry field work should include:

- Lake name and site identification code
- Sample date, time
- GPS coordinates, to verify location
- Names of field team members
- Field meter (model), calibration date, and field measurements of core suite variables
- Samples taken for laboratory analysis (sample identification number, collection times, etc.)
- Confirm sample preservation
- Amount of water filtered for the chl-a sample
- Whether quality control samples were collected
- Any additional notes or observations pertinent to a particular sample and/or the sampling event
    - Whether any samples were *not* collected, and reason
    - Weather (air temperature and wind speed) and relevant notes about recent weather (storms or drought)
- Time of departure

Ensure that field forms, field notebooks, and other hardcopy records are secure, organized, and available for viewing, reproduction, or transfer upon request and/or at the end of each field season.

6 Data management

The goal is to upload the water chemistry data to the Water Quality Portal/Water Quality Exchange (WQX), where it can be accessed by other regional partners. There are three options for uploading water chemistry data into WQX:

- Option 1: Standard web-based application (WQX Web) that uses Microsoft Excel spreadsheets.
- Option 2: Create a custom submission application using WQX XML schema through Exchange Network Nodes or Node Clients
- Option 3: via a third-party system such as The Ambient Water Quality Monitoring System (AWQMS).

Instructions are available online: https://www.epa.gov/waterdata/water-quality-data-wqx.

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Appendix A

Table A1. Recommended list of 'core' parameters for Phase One of the RMNs. The highest priority parameters within each group are in bold text.

Group	Parameter	Rationale
Nutrients	**Total Phosphorus (TP)**	Indicators of nutrient enrichment and trophic status; key regulators of phytoplankton and aquatic macrophyte growth.
	Chlorophyll-a	
	Nitrate and nitrite (NO3-NO2)	
	Total Kjeldahl Nitrogen (TKN)	
	Total Nitrogen (TN)	
	Ammonia-N (NH3-N)	
Transparency/ water clarity	**Dissolved organic carbon (DOC)**	Integrates multiple responses in lake and catchment processes. Affects light and heat penetration to sub-surface layers, which in turn affects water clarity, lake productivity, chemical reactions and lake mixing patterns.
	Colored dissolved organic matter (CDOM)	Used to help characterize the quantity and composition of dissolved organic matter in natural waters. Remote sensing labs use CDOM to calibrate algorithms that allow for tracking of widespread patterns in water clarity.
	True Color	Provides information about the water body (e.g., nutrient load, algal growth, and water quality) and the surrounding landscape. True color = color with the turbidity removed (usually by filtration). Apparent color = with turbidity.
	Apparent Color	
	Turbidity	Provides information on non-algal suspended sediment loading (e.g., from agricultural and urban runoff, shoreline erosion), which affects light penetration, which is an important regulator of rate of primary production and plant species composition.
	Total suspended solids (TSS)	

Table A1 continued…

Group	Parameter	Rationale
General water quality	**Specific conductivity**	Important indicator of polluted runoff that may contain excess nutrients, organic matter, pathogenic microbes, heavy metals, and organic contaminants
	pH	Determines the solubility and biological availability of chemical constituents such as nutrients (phosphorus, nitrogen, and carbon) and heavy metals (e.g., lead, copper, cadmium)
	Water temperature	Directly affects individual species and ecosystem-level processes, water chemistry, suitability for human use and lake mixing patterns
	Dissolved oxygen (DO)	Needed to sustain most aquatic life and is critical for supporting cold water fisheries.
	Alkalinity, Total (CaCO3)	Directly estimates the majority of the buffering capacity of the water and is used to estimate sensitivity to acid precipitation
Major anions	**Chloride (Cl)**	Good indicator of wastewater plumes as well as inputs and accumulation of road salt. It may be used as a tracer, as it moves through soil without significant absorption or adsorption. Can also affect lake mixing patterns. Significant decadal trends in lake salinization have been identified in North America, which threatens lake water quality (Dugan et al. 2017).
	Sulfate (SO4)	Important for assessing acid deposition effects. Also a critical parameter for understanding and modeling mercury cycling.
Major cations	**Calcium (Ca)**	The anions and cations influence the lake's ability to assimilate pollutants (e.g., acidification) and maintain nutrients in solution. For example, high Ca+2 and Mg+2 directly reduce the bioavailability and toxicity of many heavy metals, and indirectly affect mercury cycling (e.g., Horne and Goldman 1994, Driscoll et al. 1994, Driscoll et al. 1995).
	Magnesium (Mg)	
	Sodium (Na)	
	Potassium (K)	
Other	Dissolved Silica	Essential micronutrient for microorganisms and diatom algae; used to form shells and other protective structures

Nutrients

Phosphorus, nitrogen and chlorophyll-a are commonly-measured indicators of nutrient enrichment and trophic status. Collection of all three is encouraged. If only one can be collected, total phosphorus (TP) is the top priority, followed in order by chlorophyll-a and nitrogen.

Phosphorus. Total phosphorus (TP) is the top priority due to its association with algal blooms[2]. Also, a recent analysis of TP data from USEPA's National Aquatic Resource Surveys showed patterns of increasing TP in streams and lakes nationwide, including oligotrophic lakes in relatively undisturbed catchments (Stoddard et al. 2016). The recommended target for the RMNs is to collect a TP sample from the top 0-2 meters 4x/year (spring turnover[3] + 3X during summer (15 July – 15 September), with one of the three visits occurring during the July 24 – August 7 time period). If the lake is thermally stratified, to better understand internal loading (phosphorus sources from inside the lake), collection of one bottom TP sample (depth = 1 m above bottom) during July 24 – August 7 time period is also recommended. Some programs collect TP more frequently than this (e.g., monthly), which further improves trend detection times and increases the probability of correctly identifying subtle trends (Figure A1).

In addition to TP, some entities collect other measures of phosphorus like PO4-3 as P, orthophosphate, or reactive P. This document only contains guidance for TP. If you are interested in obtaining protocols for these other phosphorus parameters, contact Britta Bierwagen (Bierwagen.Britta@epa.gov) with your request and she will put word out to the other RMN partners.

[2] Algal blooms often result from high concentrations of nutrients— phosphorus in particular—being released from sediment at the bottom of lakes.

[3] Why spring turnover? Bioavailable forms of phosphorus and nitrogen (dissolved phosphate, nitrate, and ammonium) are typically highest in the spring due to snowmelt runoff and the mixing of accumulated nutrients from the bottom during spring turnover. Concentrations typically decrease in the epilimnion during summer stratification, as nutrients are taken up by algae and eventually transported to the hypolimnion when the algae die and settle out. When stratified, any input of nutrients into the upper lake water may trigger a bloom of algae (Elias et al. 2015).

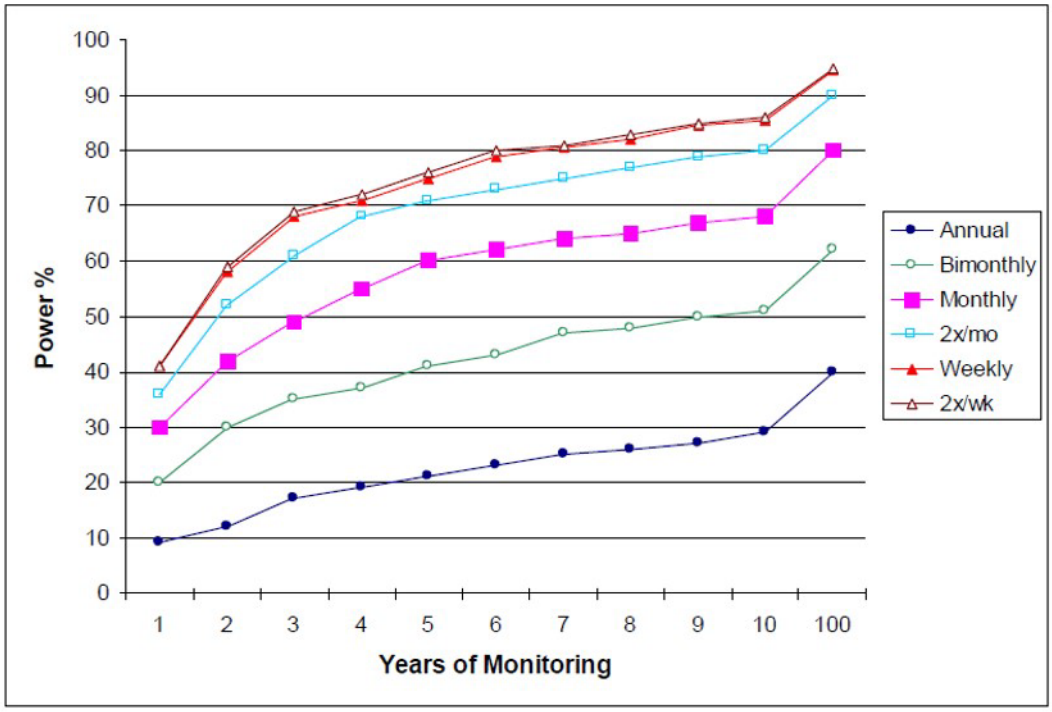

Figure A2. Trend analysis of long-term monitoring of TP in summer based on VT data (Smeltzer et al. 1989). Power is the likelihood or probability of correctly detecting an outcome of a given size; for example, 80% power means that there is an 80% probability that an outcome of a given size is correctly detected. Power analyses are well-suited for experimental design because one can experiment with different settings, such as power (e.g., 80% or higher), sample size (e.g., 25 vs. 50), and effect size (0.5, 1 or 2%), to get a sense of how long it will take to detect a change of a given size at a certain level of confidence.

Chlorophyll-a (chl-a). The RMN target is to collect chl-a from the top 0-2 meters[4] 3x during summer (15 July – 15 Sept), with one of the 3 visits occurring during the July 24 – August 7 time period (which is when temperatures are typically warmest and chl-a concentrations are typically highest). Some programs collect chl-a more frequently than this, which improves the likelihood of detecting trends over shorter time periods.

In addition to chl-a, some entities collect pheophytin a. Pheophytin is a natural degradation product of chlorophyll and has an absorption peak in the same spectral region as chlorophyll a. The chl-a concentration is corrected for pheophytin. This document does not contain guidance for pheophytin but if you are interested in learning more about it, contact Britta Bierwagen (Bierwagen.Britta@epa.gov) and she can request pheophytin protocols from other RMN partners.

[4]Some people have found that on calm, sunny days, algae can sink deeper than the top 2 meters. To address this, one of the RMN partners with a chlorophyll fluorometer has offered to collect information on how deep the chl-a go. Once we get more information on this, we will re-evaluate the RMN chl-a protocols. Also, some recent studies in northern lakes have documented high chl-a concentrations under the ice during the winter, which also warrants further evaluation.

Nitrogen. Nitrogen is the lowest priority RMN nutrient parameter but its collection (at least 1x/year) is highly encouraged when possible. Many RMN partners collect nitrogen but measure it in different forms. At this time, here are the recommended RMN parameters for nitrogen in order of highest preference first:

- Total Nitrogen (TN) = [NO2 + NO3] + NH3 + organic N; this is inorganic + organic nitrogen
- Total Kjeldahl Nitrogen (TKN) = organic N + ammonia (NH3)
- Nitrate and nitrite (NO3 + NO2) (these are inorganic forms of nitrogen)
- Ammonia (NH3) (this is an inorganic form of nitrogen)

To reduce analytical costs, you could monitor TKN and NO3+NO2, and then derive TN from those data using this formula TN = TKN + [NO3 + NO2].

RMN partners also collect different forms of ammonia (e.g., Ammonium-N [NH4-N]) or Ammonia - N (NH3 + NH4) or Ammonia-N (NH3-N)). Ammonia's aquatic toxicity is principally due to the un-ionized form, NH3 and most water quality standards (WQS) are based on Ammonia-N (NH3-N). Thus, NH3 is the form we recommend for the RMNs. For more information on ammonia toxicity, see the literature review by Levit (2010).

It is also worth noting that some entities collect Dissolved Inorganic Nitrogen (DIN) during extreme algal blooms to evaluate whether the algal growth is limited by nitrogen. This document does not contain guidance for DIN but if you are interested in learning more about it, contact Britta Bierwagen (Bierwagen.Britta@epa.gov) and she can request DIN protocols from the other RMN partners,

Transparency/water clarity

Measures of transparency and water clarity are also high priority indicators at RMN lakes. Transparency affects light and heat penetration to sub-surface layers, which in turn affects water clarity, lake productivity, chemical reactions and lake mixing patterns (Read and Rose 2013, Schmid et al. 2014, Rose et al. 2016).

Dissolved Organic Carbon (DOC) is a top priority parameter at RMN lakes. It integrates multiple responses in lake and catchment processes (Adrian et al. 2009) and is associated with long-term browning trends in inland lakes (Williamson et al. 2015). If possible, a DOC sample from the top 0-2 meters should be collected 1x/year between July 24 and August 7. To better understand the effects of ultraviolet (UV) radiation on DOC, collection of a bottom DOC sample (depth = 1 m above bottom) is encouraged as well (but this is lower priority than the top layer sample). Some programs collect DOC more frequently than 1x/year, which improves trend detection times and increases the probability of correctly identifying subtle trends.

Colored Dissolved Organic Matter (CDOM) is a high priority parameter. Brezonik et al. (2019) found that Secchi depth (SD), which many lake programs use as a primary metric for assessing trophic state, is affected by CDOM in moderately to highly colored lakes in Minnesota. Thus, it is important for programs that rely on SD in regions with large landscape sources of CDOM to better understand the effects of CDOM on SD. The CDOM sampling and processing methods are described in Appendix B. Samples are analyzed with spectrophotometers. CDOM is used to help characterize the quantity and composition of dissolved organic matter in natural waters. Remote sensing labs use CDOM measurements to calibrate

algorithms that allow for tracking of widespread patterns in water clarity (vs. being limited to the small subset of sampled lakes alone). If you are planning to collect CDOM, consider contacting Jacques Finlay at the University of Minnesota (jfinlay@umn.edu). His lab may be able to process your CDOM samples for free if you cover the shipping costs. Moreover, having at least one year of CDOM samples processed at a common laboratory would reduce potential sources of variability and allow for establishment of a baseline that could be tracked over time across sites.

Another technique for obtaining CDOM data is currently being piloted (RMN partners are encouraged to participate). It involves taking photos while doing Secchi Depth measurements, and then inferring CDOM from the photos. Appendix C contains instructions on the protocols. For more information, contact Patrick Brezonik (brezonik@umn.edu).

Other lower priority parameters include true and apparent **color**[5], which have more limited applications than DOC and CDOM but still provide useful information. If historic color data are available for RMN lakes, continue collecting those data in accordance with your existing protocols. At a minimum, perform a visual assessment for color when taking Secchi depth measurements, using the following four categories (which are in keeping with Minnesota DNR's protocols):

- **Clear**: Clear, blue water with a low amount of particles or dissolved, colored materials that reflect light. The deeper the water, the darker blue it may appear.
- **Green**: Green water caused by suspended particles of living material such as suspended algae.
- **Stained**: Brown or red stained clear water that may look like iced tea which results from dissolved organic matter.
- **Sediment**: Muddy or cloudy brown water due to high sediment levels; often resembles chocolate milk.

Monitoring turbidity and total suspended solids (TSS) is encouraged as well, as they affect light penetration. High readings could indicate stressors from agricultural and urban runoff and/or shoreline erosion. Turbidity may be measured with a multi-probe meter (assuming the meter is calibrated and maintained in accordance with manufacturer specifications). However, interpret these results with caution (based on feedback from RMN partners, the accuracy of the probe measurements is sometimes questionable).

Text Box # 1. Can CDOM be used as a proxy for DOC?
The relationship between DOC and CDOM varies across lakes (Griffin et al. 2018) so we encourage collection of both DOC and CDOM, at least until the relationship at each lake has been established.

General water quality

Lake monitors often measure specific conductivity, pH, water temperature and dissolved oxygen with field meters when they do vertical profile measurements at the deep point in the lake (for more information, see the Vertical Profile protocols document). This method is acceptable at RMN lakes, assuming the meter is calibrated and maintained in accordance with manufacturer specifications. Specific conductivity and pH can be analyzed in the lab as well (optional, if resources permit). Total

[5]True color = color with the turbidity removed (usually by filtration). Apparent color includes turbidity.

alkalinity ($CaCO_3$) is also a high priority indicator; is serves as a measure of the buffering capacity of the water and as an estimate of the lake's sensitivity to acid precipitation.

Major anions/major cations/other

Major cations (calcium, magnesium, potassium, sodium) and major anions (chloride, sulfate) are lower priority yet important to collect if resources permit. They influence the lake's ability to assimilate pollutants (e.g., acidification) and maintain nutrients in solution. They can also be important determinants of habitat suitability for invasive plants and animals like zebra mussels (which have minimum calcium requirements). RMN protocols call for sampling them 1x/year for the first two years. If there is little variability between years and resources are limited, the frequency can be shifted to 1x every 3 to 5 years.

Another recommended 'core' measure is dissolved silica, which is an essential micronutrient for microorganisms and diatom algae. Organisms use it to form shells and other protective structures.

Appendix B

CDOM water sampling

Updated May 12, 2019

Expanding CDOM data in the Lake Regional Monitoring Network

As part of ongoing work on remote sensing of water quality at the University of Minnesota, we are interested in partnering with Lake RMN to increase data on colored dissolved organic matter (CDOM) from lakes across the Upper Midwest. Our work is currently focused on Minnesota, Wisconsin, and Michigan, but while we are most interested in data from those states, we are willing to analyze samples for CDOM collected by RMN in 2019. For more information on our ongoing work, including interactive browsers of lake clarity and CDOM for Minnesota, please see our website: https://rs.umn.edu/water

Increased availability of CDOM data will assist with validation of remote sensing models, and allow them to be adjusted and improved in the future as needed. We encourage you to collect CDOM or color data as part of routine monitoring to help characterize the quantity and composition of dissolved organic matter in regional lakes. For remote sensing purposes, we generally use absorption at 440 nm (a_{440}), but measuring full absorption scans from 200-800 nm can provide a great deal of useful information on the quantity and composition of organic matter in natural waters.

Samples that are collected within a few days of a clear sky satellite overpass are useful but not essential. CDOM is relatively stable over the course of the summer for most lake types, so coordinating sampling with satellite overpasses is not essential. If you happen to notice a particularly cloudless and haze-free day and have some flexibility in your schedule, sampling within a few days of such conditions would maximize chances of concurrent satellite imagery. (Remote sensing of chlorophyll-*a* does require close timing between satellites and on the ground sampling however).

New satellites launched over the past few years have resulted in imagery being collected every two to three days at northern temperate latitudes. For those interested, we currently use USGS' Landsat 8 data and the European Space Agency's Sentinel 2A & B data. Acquisition calendars can be found on the USGS site for Landsat or by downloading KML files for Sentinel. Sentinel collects data every 5 days, but owing to overlap between scenes at higher latitudes, the Upper Midwest regularly has imagery every 2-3 days. Imagery is often posted publicly within 24 hours - Amazon Web Services is an easy way to browse available imagery. We can also supply calendars of satellite acquisition for specific regions at anyone's request.

We are happy to work with groups who would like to use CDOM analyses in their own work, but lack access to spectrophotometers to conduct their own analyses. Please contact Jacques Finlay (contact below), to arrange sample analyses. We can analyze water samples for CDOM, and would be happy to discuss other opportunities for collaboration. For questions about remote sensing and historical datasets, please feel free to contact Claire Griffin (contact below)
Thanks very much for your consideration!

Claire Griffin
Postdoctoral Associate
griffin.claireg@gmail.com
University of Virginia

Jacques Finlay
Professor
jfinlay@umn.edu
University of Minnesota

Abridged CDOM Sample Collection and Processing Protocol

Equipment needed for CDOM collection and processing

1 HDPE or polycarbonate bottle, at least 250 mL for sample collection
1 40 mL glass amber vial per site
Filtration equipment: variable based on what's available. Filtration through either capsule filter with 0.45 µm nominal pore size or GF/F filter with 0.7 µm nominal pore size acceptable. If using other type of filtering, please check with Claire or other member of UMN Remote Sensing team.

Collection and processing

1. Sample collection
    a. Use a HDPE or polycarbonate bottle for water collection. Avoid sampling in areas that are downstream of the boat, stirred sediments, etc.
        i. Rinse bottle 3 times by filling ~1/3 full and loosely capping the bottle. Shake vigorously, then dump the water downstream of the sampling site.
        ii. Fill collection bottle to shoulder and keep cool until filtering.
2. Sample processing
    Filter with standard methods used for other dissolved constituents as part of your project. GFF filters are fine; always rinse filters with sample water before filling CDOM bottle. Detailed filtration protocols can be provided on request.
3. Sample storage
    Keep cool and out of direct light until analyses. Do NOT freeze the sample. No other preservation is necessary. Analyses are ideally performed within ~1 week of collection if possible, but since CDOM is relatively stable, hold times of up to two weeks are OK as long as samples are kept cold and dark.
4. Sample analysis
    a. We would strongly encourage using a UV-Visible spectrophotometer for color/CDOM analysis, rather than a Pt-Co scale. If you only have the Pt-Co method available, please contact Jacques or Shelly and we can arrange to analyze CDOM at the University of Minnesota.
    b. For remote sensing purposes, absorption at 440 nm is commonly used as a measurement of CDOM. However, additional information on organic matter composition can be gained by measuring absorbance from 200-800 nm, if possible. Specific UV absorbance, for instance, is a common proxy for aromaticity that normalizes absorbance at 254 nm by DOC concentrations. If possible, full scans provide additional information that benefit both the larger goals of the LRMN and our own project on remote sensing.

Shipping samples to the University of Minnesota

Samples should be tightly packed so that bottles do not touch each other or anything hard (foam mailing pouches or paper towels work well) and do no move in the cooler.

Please include a sample list with ID's and email a spreadsheet to Jacques Finlay.

Please note on the outside of the shipping container to "Keep Cold. Do Not Freeze." Because samples are not delivered directly to our lab, our office staff will know to put the packages directly in a cold room.

If possible, ship early in the week, Wednesday at the very latest. We have had issues with delayed delivery in the past and this can create problems if delivery is re-scheduled for the weekend.

For more information, please contact Jacques Finlay (jfinlay@umn.edu)

Appendix C

Measuring CDOM from Secchi disk photos

Protocol for smartphone Secchi disk photos to measure CDOM

1. **Weather/measurement conditions**. Photos should be taken on a sunny day between ~ 10:30 AM and 3:00 PM. Overcast conditions also are acceptable, but days with partial clouds, especially large cumulus clouds, should be avoided. Best photos are taken under calm or near-calm conditions. Some small wavelet activity may be unavoidable, but photos should not be taken under wavy and rough conditions.

2. **Smartphone settings**. Common brands and models of smartphones can be used. Cameras should be set to default conditions for picture taking (i.e., no special effects), and cameras with an HDR (high density color) setting should have that turned off. Cameras that can produce raw images should be put in that mode, but only some newer cameras have this option. Otherwise, photos should be saved as jpgs, which is the default way most smartphones save photos.

3. **Secchi disk and photo orientation**. For photos that are useful to estimate CDOM levels, it is important that photos be taken in a consistent manner. Please follow these directions:

   a. The boat should be positioned in approximately a SN or NS direction (rather than EW).
   b. Secchi disk should be held as close to 1.0 ft depth in the water as possible, as far from the side of the boat as can be safely achieved, and out of the shadow of the boat itself.
   c. The smartphone should be held parallel to the water surface about 1 ft above the surface, directly above the Secchi disk, and as close as possible to a S-N direction, facing away from the sun, which in the Northern Hemisphere is always (near midday) to our south. We strongly recommend the use of selfie sticks to avoid possibilities of phones falling into the water. We are **not responsible** for any loss of phones by volunteers.

4. **Photo taking**. Snap one or two images of the Secchi disk and check the images to make sure that you have clearly captured one of the white quadrants of the disk (if you are using a black and white disk); if not, try again. Next, hold the Secchi disk just above the water surface and take a photo of it (again using the selfie stick) with the smartphone oriented as before (to the north, away from the sun, parallel to the disk surface and ~ 1 ft above it.

5. **Sample collection**. Collect a water sample for CDOM analysis using the procedure and bottle described in your protocol.

6. **Photo and data submission**. Send your photos to Patrick Brezonik at brezonik@umn.edu by conventional email. Attach the photo files to the message (rather than including them within the message). In the text of the message, please provide information on the make and model of smartphone used for the photos, the date and time of photo collection, name and location of the lake, if possible, the person who took the photos, and any other information you deem pertinent. If you took more than one photo of the submerged Secchi disk, include all of them as attachments to your message unless you conclude that some photos are of poor quality (e.g., because of wave activity or because camera placement resulted in not getting a good image of the white part of the disk). Receipt of the photos will be acknowledged as quickly as possible.

Appendix D

Filtering the Chlorophyll-a sample

Chlorophyll-a sample will be filtered on shore after completing site. This guidance is based on the NLA 2017 protocols.

Procedures for Processing the Chlorophyll-*a* Samples

The procedure for processing the chlorophyll-*a* sample is presented below. Whenever possible, sample processing should be done in subdued light, out of direct sunlight.

1. Place a glass fiber filter in the filter holder apparatus with the grid side down. Do not handle the filter with bare hands; use clean forceps.

2. Shake the chlorophyll-*a* sample collection bottle to homogenize the sample, measure and pour 250 mL of water into the filter holder using the graduated cylinder, replace the cap of the filter holder, and pump the sample through the filter. Take care not to exceed 7 inches of Hg (approximately 3.4 psi) in the vacuum gauge on the filtration pump. If 250 mL of lake water will not pass through the filter, discard the filter, rinse the apparatus with DI water, and repeat the procedures using a new filter and 100 mL of lake water. NOTE: If the water is green or turbid, use a smaller volume to start.

3. Observe the filter for visible color. If no visible color is present, repeat step 3 until color is visible on the filter or until a maximum of 2,000 mL have been filtered.

4. Once visible color is present and/or 2,000 mL of lake water has been filtered, record the actual sample volume filtered on the Index Sample Collection form and on the sample label. Rinse the graduated cylinder and upper portion of the filtration apparatus thoroughly with DI water to include any remaining cells adhering to the sides and pump through the filter. Monitor the level of water in the lower chamber to ensure that it does not contact the filter or flow into the pump.

5. Disconnect the upper portion of the filter apparatus from the lower portion. Remove the filter from the holder with clean forceps. Avoid touching the colored portion of the filter. Fold the filter in half, with the colored side folded in on itself.

6. Place the folded filter into a 50 mL screw-top centrifuge tube and replace the cap. Tighten the cap as tightly as possible. The cap will seal tightly after an additional ¼ turn past the point at which initial resistance is met. Failure to tighten the lid completely could allow water to infiltrate into the sample and may compromise its integrity. Seal the cap of the centrifuge tube with plastic electrical tape

7. Record the sample volume filtered on a chlorophyll-*a* label and attach it to the centrifuge tube. Ensure that all written information is complete and legible. Cover with a strip of clear tape. Double check that the “total volume of water filtered” on the **Index Sample Collection** form matches the total volume recorded on the sample label.

8. Wrap the tube in aluminum foil and place in a zip top bag. Place the completed outer label on the outside of the bag. Place this bag on ice in a cooler.

9. Remove the filter holder silicone stopper and adapter from the filtration flask. Pour off water from the bottom chamber.

10. Rinse filter chamber components thoroughly with DI water.

11. Retain the filter chamber, including the graduated cylinder, silicone plug, adapter, and the pad that sits under the filter. Rinse these items with DI water between sites. Thoroughly rinse the graduated cylinder, cups, the brown sample collection bottle and cap with tap water and store for next sample event.

Appendix E

Contract Laboratory Checklist

Source: Ledder et al. 2015 (SOP #12). Oversight and compliance is left up to participants.

Contract Laboratory Checklist

Laboratory:

Address:

Contact person:

_____ Received QAPP

_____ Received copy of certifications

_____ Received a list of analytical methods used

_____ Define the limits of detection and limit of quantitation calculation method
(can lab report as MDL and ML if currently calculated as LOD and LOQ?)

_____ Received a copy of latest MDL/ML/control limits calculations for relevant methods

_____ MDL/ML as listed meet project needs
(list any analyte for which the ML requirement is not met – discuss options with lab)

_____ Received successful interlaboratory participation documentation

_____ Sample handling log in and COC are documented in the QAPP

_____ Equipment maintenance and calibration procedures are documented in the QAPP

_____ Internal QA/QC documented in QAPP

Control limits calculations are made by what method
(QC includes blanks, duplicates, spikes, reference standards and LCS)

Calibration curves cover level of analytical interest
(QC includes ICV and ICB, and CCV and CCB)

Reporting data flags used include

Attach all copies

Reviewed by _____ Date _____

Appendix F

Keeping data records consistent and comparable over time

Keeping data records consistent and comparable over time

The ability to use water chemistry data to reveal long-term trends requires consistent analytical methods and detection limits. It is very important to keep the data records consistent and comparable over time. Even within the same organization this can be challenging. For example, field equipment and contract laboratories are likely to change during the course of this long-term monitoring project.

Recommendations for keeping long-term records consistent and comparable:

- Collect data in accordance with field and lab protocols in EPA-approved SOPs or QAPPs
- Consider using only laboratories with NELAC certification or at least certification by the state programs that also use the laboratory (for information on laboratory performance criteria, see Section 3.4.3)
- Create a table like Table F1 (from NJ DEP's 2017 QAPP) to track samples and changes that might contribute to variability. A table like this also facilitates comparisons of field and lab protocols across entities. Update the table as needed (and retain the older versions as documentation of what has changed over time). Try to stick to the original plan to the best of your ability.
- Perform side-by-side sampling or analyses during times of transition (e.g., when personnel or equipment are changing) (see Ledder et al. 2015, SOP #12 Section 12.8.5, which is summarized in text box #2)
- Keep documentation of field crews, procedures, site conditions, laboratory analyses, and reasons for deviations of any kind. Write down more than you feel may be necessary as the future interpretation of the data will depend on the written record and not the memory of an individual

If opportunities arise to process samples at common regional laboratories, we encourage this so that we can get a better sense of differences across sites and entities. However, this should not come at the expense of your long-term records. In these situations (at least initially, until relationships have been established) – collect two sets of samples (side by side); analyze one set in accordance with your normal protocols; send the other to the common regional lab; and then compare results.

Table F1. Example laboratory records (source: NJ DEP 2017)

Parameter	Laboratory	Lab Number	Method	Method ID Context	Lower Reporting Limit	units	Method Detection Limit	units	Upper Reporting Limit (MPN/100 ml)	units	Holding Time	Preservative
Nitrite + Nitrate, as N	NJ DEPARTMENT OF HEALTH - 11036	11036	4500-NO3(F)	APHA	0.012	mg/l	0.0038	mg/l			28 days	pH<2, Ice to 4ºC
Total Kjeldahl Nitrogen	NJ DEPARTMENT OF HEALTH - 11036	11036	351.2	USEPA	0.1	mg/l	0.055	mg/l			28 days	pH<2, Ice to 4ºC
Ammonia as N	NJ DEPARTMENT OF HEALTH - 11036	11036	4500-NH3(H)	APHA	0.01	mg/l	0.0038	mg/l			28 days	pH<2, Ice to 4ºC
Phosphorus, Total	NJ DEPARTMENT OF HEALTH - 11036	11036	365.1	USEPA	0.01	mg/l	0.0047	mg/l			28 days	pH<2, Ice to 4ºC
Orthophosphate as P	NJ DEPARTMENT OF HEALTH - 11036	11036	365.1	USEPA	0.005	mg/l	0.0016	mg/l			48 hours	Ice to <4 ºC
Total Alkalinity	NJ DEPARTMENT OF HEALTH - 11036	11005	2320-B	APHA	1	mg/l	1	mg/l			14 days	Ice to <4 ºC
Hardness, Total	NJ DEPARTMENT OF HEALTH - 11036	11036	200.7(W)	APHA	0.662	mg/l	0.069	mg/l			14 days	Ice to <4 ºC
Chlorophyll a	NJDEP - ENVIRONMENTAL MONITORING LABORATORY - 11896	11896	445	USEPA	*	ug/l	*	ug/l			24 hours	Ice to <4 ºC
Microcystins	NJDEP - ENVIRONMENTAL MONITORING LABORATORY - 11896	11896	546	USEPA	0.1	ug/l	0.1	ug/l			24 hours	Ice to <4 ºC
Cylindrospermposin	NJDEP - ENVIRONMENTAL MONITORING LABORATORY - 11896	11896	ELISA	ABRAXIS	0.04	ug/l	0.04	ug/l			24 hours	Ice to <4 ºC
Antatoxin-A	NJDEP - ENVIRONMENTAL MONITORING LABORATORY - 11896	11896	ELISA	ABRAXIS	0.1	ug/l	0.1	ug/l			24 hours	Ice to <4 ºC

* To be determined when spectrophotometer is calibrated

Text Box # 2. Changing Methods and Documenting Cumulative Bias (source: Elias et al. 2015)

Cumulative bias can become significant over time even though changes in methods are small. To reduce bias, when a change occurs, when feasible, perform side-by-side field measurements (seven times is a good target) and compare results. For example, if there is a scheduled change in staff, both the new staff member and old staff member should perform side-by-side field measurements several times during training when possible. Similarly, when a field or laboratory method is changed, a new probe is put into use, or a new lab is used, side-by-side sampling should be performed whenever possible and results compared. Data from these comparisons can be used to calculate statistics such as percent difference and fraction of change (see SOP #12 Section 12.8.5 in Elias et al. 2015). Having this information may allow new values to be normalized to the old method values, and documents any bias.