

Standard Operating Procedure #6: Field Measurements and Water Sample Collection

Version 1.3 (2021)

In Water Quality Monitoring Protocol for Inland Lakes: Great Lakes Inventory and Monitoring Network

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Revision History Log

The following table lists all edits and amendments to this document since the original publication date. Information entered in the log must be complete and concise. Users of this standard operating procedure will promptly notify the project manager and/or the Great Lakes Network (GLKN) data manager about recommended and required changes. The project manager must review and incorporate all changes, complete the revision history log, and change the date and version number on the title page and in the header of the document file. For complete instructions, please refer to Revising the Protocol, SOP #13.

Previous Version #	Revision Date	Author (with title and affiliation)	Location in Document and Concise Description of Revision	Reason for Change	New Version #
1.0	2/18/2010	Richard Damstra, David VanderMeulen, Joan Elias, GLKN	Clarified some verbiage throughout, made changes to field sequence, field gear checklist, added optical DO probe info, equipment blank procedures, and data backup procedures.	To clarify protocol and bring field procedures and protocol into agreement, based on new equipment and staff field experience.	1.1
1.1	5/01/2015	David VanderMeulen, GLKN	Updated the NPS contact author, added information about continuous monitoring, added information about thermal arrays, referenced the Aquarius database, fixed a handful of grammatical errors throughout	To clarify and update SOP based on changes that have occurred since Version 1.1 was published in 2010	1.2
1.2	3/2021	Alexander Egan, Aquatic Ecologist, GLKN	Minor text changes; modified Secchi disk method to require two readings instead of one due to somewhat regular inaccurate readings occurring in the field when measuring the marked line; replaced the field form with a modified version that improves spacing and clarity for field staff.	To clarify and update SOP based on changes that have occurred since Version 1.2 was published in 2015	1.3
Add rows as needed for each change or set of changes tied to an updated version number					

Acknowledgements

Combinations of existing protocols were used to develop this standard operating procedure for measuring the required water quality field parameters for the Great Lakes Network (GLKN). We consulted protocols written for the EPA, USGS, an online curriculum for monitoring water quality, this and other NPS networks, NPS internal documents, and the NPS–WRD website. We wish to acknowledge these sources and thank them for the valuable contribution that they have made to this document.

6.0 Introduction

Field measurements should represent, as closely as possible, the natural condition of the surface water at the time of sampling. Experience with and knowledge of the sampling equipment and the collection, storage, and processing of water samples for subsequent laboratory analyses are critical for collecting data of high quality. To ensure consistent, high-quality data, always:

- Make field measurements only with calibrated instruments that have been error-checked.
- Maintain a permanent log book for each field instrument for recording calibrations and repairs. Review the log book before leaving for the field. This book should also be used for recording results of pre-and post-calibration checks as well as housing copies of results from alternate measurement sensitivity (AMS) checks, if applicable.
- Test each instrument (meters and sensors) before leaving for the field. Become familiar with new instruments and new measurement techniques before collecting data.
- Have backup instruments readily available and in good working condition, whenever possible.
- Follow quality assurance/quality control procedures in SOP #12. Such protocols are mandatory for every data collection effort and include practicing good field procedures and implementing quality-control checks. Make field measurements in a manner to minimize artifacts that can bias the result. Check field-measurement precision and accuracy (variability and bias).

6.0.1 Core Suite of Water Quality Variables

The core field variables are temperature, specific conductance, pH, water level, and dissolved oxygen, all of which are mandated by the National Park Service Water Resources Division (NPS-WRD). To this mandated suite, GLKN has added a measure of water clarity. Depth profiles of temperature, specific conductance, pH, and dissolved oxygen will be measured at each sampling station using a multiparameter instrument (multiprobe). Continuous water temperature profile data will be collected from a subset of inland lakes across four parks (Isle Royale and Voyageurs national parks, and Pictured Rocks and Sleeping Bear Dunes national lakeshores) that contain a significant number of inland lakes. Water level will be measured at benchmark stations with an eye or laser level and a surveyor's rod (described in detail in SOP #4). Water clarity will be measured with a transparency tube or Secchi disk. The expected ranges and resolutions required of multiprobes are listed in Table 1, and the methods for taking field measurements are described in Section 6.4.

6.0.2 Advanced Suite of Water Quality Variables

The advanced suite variables consist of total phosphorus, total nitrogen, nitrate+nitrite-nitrogen, ammonia-nitrogen, sulfate, chloride, magnesium, calcium, potassium, sodium, dissolved silica, dissolved organic carbon, alkalinity, and total chlorophyll-*a*. The methods for collecting water samples for these variables are described in Section 6.5. These water quality variables were chosen to monitor effects of the likely stressors on the resource, including land use change and atmospheric deposition. Other variables symptomatic of contamination (e.g., DDT and PCBs) are addressed in GLKN's protocol for monitoring bioaccumulative contaminants (Route et al. 2009).

6.1 Equipment and Supplies

6.1.1 Instrument Specifications

Toward low bias and high precision of water quality data for this protocol, Table 1 lists typical field sensor performance specifications that should be expected from monitoring equipment for this protocol. Multiparameter sensor instruments (or multiprobes), while expensive, are convenient and commonly used in water quality monitoring. A multiprobe instrument should be selected based on the observable range for each variable. However, an additional investment in a back-up set of less expensive individual sensors will help ensure the development of a long-term data set, should the multiprobe not be working properly.

Table 1. Typical sensor performance specifications^a for field instruments (Penoyer 2003).

Sensor	Expected Range	Reporting Resolution ^b	Estimated Bias ^c
Temperature	-5°C to 45°C	0.01°C	±0.15°C
Specific Conductivity (SC25)	0 to 2000 µS/cm	1 µS/cm (range dependent)	±0.5% of reading + 1 µS/cm
pH	1 to 14 units	0.01 unit	±0.2 units
Dissolved Oxygen (Concentration)	0 to 50 mg/L	0.01 mg/L	0 to 20 mg/L ±0.2 mg/L; 20 to 50 mg/L ±0.6 mg/L
Dissolved Oxygen (% saturation)	0%–200%	0.1%	ca. ±2 %
Turbidity	---	---	---
Depth - Z (pressure sensor)	0–>100 m	0.1 m	ca. 0.1 m

^a In the case of field probes, accuracy is typically a best-case maximum deviation from known correct values (typically based on comparisons with known NIST certified reference materials or standards).

True accuracy is a combination of high precision and low bias (see Irwin 2004 for more details).

^b Resolution/sensitivity is a data quality indicator related to detection limits but typically handled differently for field probes than for laboratory parameters. For more information, see Irwin (2004).

^c Estimated bias specifications reflect the uncertainty in measurement of the instrument and sensor in combination only, and not other factors that can affect accuracy, such as environmental variables or the ability of field personnel to calibrate and operate the instrument using proper protocols.

Instrument-specific estimations of the range of uncertainty for each variable must be calculated for use in the interpretation of data. Therefore, documentation will be maintained regarding the ability of each multiprobe to meet the data quality objectives of this project; blank forms are included in SOP #12. The completed forms for each multiprobe will be maintained along with the calibration and maintenance logs for the multiprobe.

Details on estimating instrument sensitivity are included in SOP #12, Quality Assurance/Quality Control. Because field equipment is likely to change during the course of this long-term monitoring project, QA/QC procedures must be followed on documenting cumulative bias (SOP #12).

6.1.2 Additional Equipment, Supplies, Forms

Refer to the checklist of supplies and equipment needed for field sampling (Table 2) prior to each sampling trip. Keep on hand all necessary forms, calibration logbooks, field logbooks, field data sheets, procedural manuals, and equipment instructional manuals.

Table 2. Checklist of field equipment and supplies required for monitoring water quality.

✓	Equipment and Supplies
☐	Field notebook, pencils, and pen (waterproof ink)
☐	New field forms on waterproof paper
☐	Up-to-date field folders containing recent data sheets for field comparison (copies only; never take originals in the field)
☐	Multiparameter instrument (calibrated), calibration standards, check solutions, data logger
☐	Long and short cables for multiprobe instrument(s)
☐	Equipment for thermal arrays (temperature sensors, lines, buoys, anchor, data logger, etc.)
☐	Calibration logbook for each instrument
☐	All maintenance parts and calibration standards for field instruments
☐	Backup instruments in case of electronic failure of multiprobe (for example: YSI 85 [T-DO-SC25] or equivalent, YSI 200 [T-DO], Hannah Dist3 [SC25], armored NIST certified thermometer [°C], portable pH meter)
☐	Transparency tube
☐	Secchi disk and metered line (marked at 0.5 m intervals)
☐	Sounding weight(s)
☐	Surveyor's rod and level
☐	Water samplers: Integrating tube, Van Dorn type sampler
☐	Compositing jug and other bottles, including brown or amber bottles for chlorophyll-a
☐	Sonde with barometric pressure sensor, weather radio barometer, or other way to obtain barometric pressure
☐	Pocket calculator (waterproof, if possible)
☐	Extra batteries for all field equipment (multiparameter probe, calculator, GPS, etc.)
☐	Rain gear
☐	First aid kit
☐	Personal flotation device(s)
☐	Field trip itinerary
☐	Cellular phone and/or park radio
☐	Digital camera with extra flash cards and battery
☐	Map(s) of station location, preferably at different scales
☐	Global positioning system (GPS) with extra batteries
☐	Deionized or distilled water for field rinsing

Copy field data sheets on waterproof paper. See the attachments for blank data sheets. The instruction manuals for each instrument should be copied and the originals placed in a secure file and kept in the office. Specific sections of the manual that might be important to have in the field should be copied onto waterproof paper and remain in the field kit. Include copies of a datalogger software manual.

6.2 Overview of Field Work

6.2.1 Sequence of Activities During Field Work Day

1. Review field gear checklist.
2. Create a new field form for each monitoring station, printed on waterproof paper.
3. Prepare sample bottles and labels in advance and place in a cooler.
4. Conduct daily calibration of appropriate meters and probes.
5. Inspect vehicles at the beginning of every field day, including all safety and directional lights, oil, gasoline, tire air pressure levels.
6. Inspect boat; ensure all safety gear is on board.
7. Drive to boat landing or portage boat into lake to be sampled. Load boat with sampling gear, launch boat, and navigate to monitoring site. Set up a clean work space on the boat for sampling.
8. Refer to description of monitoring station location, directions, maps, and photo to verify correct location. Verify coordinates on GPS unit.
9. Measure field water quality variables per Section 6.4 and collect samples per Section 6.5.
10. Be sure that all samples are correctly labeled and preserved on ice.
11. Locate benchmark and record measurements of water level as detailed in SOP #4.
12. Verify that field form is completely filled out, and initial the form.
13. If sampling from more than one monitoring station in a day, follow procedures for decontamination of equipment per SOP #5, and go back to step 6, above.
14. Upon return to shore, inspect boat, trailer, and all equipment that has come into contact with the water for invasive species.
15. Return to office or field station.
16. Process samples according to SOP #7. Refrigerate or freeze samples, as required and package samples for sending to contract analytical laboratory.

17. Clean sampling equipment per SOP #7. Rinse sensors with deionized water and perform calibration re-checks, as detailed in SOP #12. This can be done upon returning to home base. Perform decontamination of the probe or other instruments as detailed in SOP #5.
18. As soon as possible after returning from the field, review both hardcopy and electronic data; offload electronic data onto computer; review laboratory data as it is received.
19. At the end of the field season, enter or import all field and laboratory data into NPSTORET or Aquarius databases.

6.2.2 Recording Field Information Upon Arrival at Monitoring Site

Consistent methods are important to long-term data quality. In actuality, the ideal conditions are not always met in the field or in the lab and changes in staff occur. Therefore, documentation of procedures, site conditions, laboratory analysis, and reasons for deviations of any kind is important. Personnel are encouraged to write down more than they feel may be necessary in the moment, as the future interpretation of their data will depend on the written record and not the memory of an individual. Waterproof field forms (copy available in the attachments) should be prepared ahead of time labeled with the project and station IDs. Sampling stations will be identified by park and water body name according to GLKN guidance. Information on the sampling station and park will comply with NPSTORET and Aquarius database requirements. Field sampling forms are used to record the physical and chemical water quality variables measured at the time of sample collection. In addition to recording the field variables, any samples collected for laboratory analyses must be so indicated. Documentation should include calibration data for each instrument, field conditions at the time of sample collection, visual observations, and other information that might prove useful in interpreting these data in the future.

While at each monitoring site, the information recorded on field sampling forms should include:

- Date
- Time of arrival
- Names of field team members
- GPS coordinates, to verify location
- Current weather (air temperature and wind speed) and relevant notes about recent weather (storms or drought), including days since last significant precipitation
- Observations of water quality conditions (see below)
- Multiparameter meter (model/serial no.), calibration date, and field measurements of core suite variables
- List of sample IDs and collection times for advanced suite variables or quality assurance samples
- Whether any samples were not collected, and reason
- Quality assurance/quality control procedures followed
- Water level measurement
- Any other required metadata for NPSTORET data entry

- Any additional non-routine monitoring (e.g., collection of dragonfly larvae for mercury analysis) by GLKN or park staff, or park partners
- Time of departure

All entries should be made clearly. If an incorrect entry is made, a single heavy line should be drawn through the incorrect entry and the correction made. All corrections should be initialed and dated. The completed field forms will be maintained in chronological order by station, copied into project binders and the originals maintained on file indefinitely. Field data are reviewed annually by GLKN personnel (see SOP #8, Data Entry and Management, for details).

Upon arrival at the monitoring station, record visual observations of water quality conditions that will be useful in interpreting water quality data.

- Water appearance—General observations on water may include color, unusual amount of suspended matter, debris, or foam.
- Biological activity—Excessive macrophyte, phytoplankton, or periphyton growth. The observation of water color and excessive algal growth is important in explaining high chlorophyll-*a* values. Other observations to note include types of fish, birds, or spawning fish.
- Unusual odors—Examples include hydrogen sulfide, mustiness, sewage, petroleum, chemicals, or chlorine.
- Watershed activities—Activities or events that are impacting water quality; for example, forest fires, road construction, timber harvest, shoreline mowing, beaver activity, or livestock watering.

6.2.3 Preventing Contamination

Field technicians should be aware of and record potential sources of contamination at each field site. Decontaminate field sampling equipment according to SOP #5 for minimizing the risk of spreading invasive species. Clean field and laboratory equipment according to SOP #7 to avoid contamination of analytes to be measured. Do not allow sample water to touch hands; do not touch insides of sampling equipment, containers, or laboratory bottles.

6.2.4 Using Disposable Gloves

Wearing disposable gloves is strongly recommended when handling acid preservatives. Check manufacturer's chemical resistance information to be sure gloves are appropriate for compounds to which they will be exposed. Common glove types include those made of vinyl, latex, and nitrile; nitrile is in standard use for USGS sampling work because of its resistance to most of the chemicals to which it typically will be exposed for the length of exposure (usually < 15 minutes). Field personnel are cautioned that direct contact with materials such as latex or nitrile can cause severe allergic reactions in some individuals and should be monitored.

Physical properties to consider when selecting disposable gloves are glove length, slip protection, puncture resistance, heat and flame resistance, cold protection and comfort. These factors can vary between manufacturers. Gloves should be inspected visually for defects. Check for tears, punctures

and other flaws that can prevent the glove from being an effective shield. After putting the gloves on, rinse them with water while gently rubbing hands together to remove any surface residue before handling sampling equipment.

6.2.5 Bottle Preparation – Types and Sizes of Bottles

For each monitoring station, select the bottles appropriate for each analyte and label them with Station ID, sample date, and analyte code according to the requirements of the contact analytical laboratory. Store pre-labeled bottles in a dry box or in separate bags for each station.

6.3 Field Measurement Procedures

6.3.1 Where and When to Measure Field Variables

The deepest part of the lake is the preferred sampling site for both discrete and continuous (temperature array) monitoring. If the morphometry is not known, sample at the estimated geographic center unless there is another basis for selecting the site. Upon visiting a site that has been visited before, a GPS should be used to locate the sample site. If a GPS is not available, use a compass and known landmarks to triangulate the sample site. A depth finder can also be used to verify that the deepest part of the lake is being sampled.

Discrete routine monitoring will occur three times throughout the open-water season, typically from May through October, with more narrowly-defined sampling windows depending on a park's latitude. All three sampling periods should occur when lakes are stratified. It is extremely difficult to predict either spring or fall turnover, although the spring period immediately follows ice-out. Fall turnover, in the sense of a period when the temperature is uniform, and more importantly, when DO is uniformly 100% saturated, is much less predictable. It also occurs at a more dangerous time of year to be on the water (November to December). May through October will provide ample sampling dates to be able to fully characterize the major period of plant growth, oxygen depletion, water clarity, temperature change, maximum public use, and the variable periods of algal nuisance blooms.

Sampling should be conducted during mid-day, from 10:00 AM to 3:00 PM, when possible. Water samples and Secchi depth readings are typically collected during mid-day to reduce variability in the data due to the differences in daylight, and to a lesser extent, temperature (Carlson and Simpson 1996). Mid-day is usually the peak period of algal photosynthesis, which can have dramatic effects on DO, transparency, and dissolved inorganic phosphorus (phosphate) and dissolved inorganic nitrogen (nitrite+nitrate+ammonium) throughout a 24 hr cycle.

Continuous water temperature profile data will be collected from a subset of inland lakes, at the same location where discrete routine monitoring takes place. At these lakes sensors will record water temperature at 1-hour intervals, year round, from the surface to bottom at 1-meter intervals. In a typical season the thermal arrays are serviced and data are downloaded during the first and last rounds of planned discrete monitoring. In some cases field logistics (e.g., timing) might dictate that arrays are serviced outside of discrete routine monitoring events (see SOP #14).

For all sampling, it is critical to avoid sampling water showing evidence of oil, gasoline or anything else from the boat motor. It is best to turn off the engine and set the anchor, although this may not be possible or advisable in bad weather or with a balky engine. The engine is commonly located in the stern of the boat; therefore, the anchor should be secured near the prow of the boat, such that strong winds will rotate the stern to the downwind. After setting anchor, allow surface water to clear of disturbances. Collect samples on the upwind side of the boat, to minimize contamination and disturbance. Avoid surfactants, floating debris, and turbid aeration during sample collection. Discard rinse water or excess sampling water on the downwind side of the boat.

6.3.2 Stabilization of Sensor Probe Readings

Before making field measurements, properly calibrated sensors must be allowed to equilibrate to the condition of the water being monitored. Sensors have equilibrated adequately when instrument readings have stabilized, that is, when the variability among measurements does not exceed an established criterion. The criteria for stabilized field readings were defined by O’Ney (2005) for a set of three or more sequential measurements (Table 3). Although the criteria used by the Greater Yellowstone Network (O’Ney 2005) differ from those used in the upper Midwest by the NRRI-UMD group (WOW 2004), the differences are small in comparison to the true range of variability one might expect in the field and with aging instrument sensors. The natural variability inherent in surface water or ground water at the time of sampling generally falls within these stability criteria and reflects the accuracy that should be attainable with a calibrated instrument. In the case of field probes, accuracy is typically a best-case maximum deviation from known correct values (typically based on comparisons with known NIST certified reference materials or standards). True accuracy is a combination of high precision and low bias (see Irwin 2006, 2004 for more details).

Dissolved oxygen typically requires the greatest amount of time to stabilize. For dissolved oxygen sensors that utilize a membrane, differences in polarigraphic sensor membrane thicknesses, age, and rates of oxygen consumption increase the variability of the equilibration time. The longest equilibration times will typically occur where dissolved oxygen exhibits a steep gradient (change in DO concentration >5 mg/L) or very low oxidic levels (DO concentration <3 mg/L). Depending on the site characteristics and the specific oxygen sensor, 3 to 5 minutes may be required for complete equilibration. This time far exceeds what is needed for the other variables, which typically stabilize in less than 60 seconds. Observers should only note instrument DO readings after the stabilization criteria in Table 3 are met, and then record readings for all variables at once.

Table 3. Recommended instrument stabilization criteria for recording field measurements.

Standard Direct Field Measurement	Stabilization Criteria (O’Ney 2005)	Stabilization Criteria <i>In situ</i> Multisensors (WOW 2005)
Temperature:		
Thermistor Thermometer	$\pm 0.2^{\circ}\text{C}$	$\pm 0.2^{\circ}\text{C}$
Liquid-in-glass Thermometer	$\pm 0.5^{\circ}\text{C}$	(5%)

Standard Direct Field Measurement	Stabilization Criteria (O'Ney 2005)	Stabilization Criteria <i>In situ</i> Multisensors (WOW 2005)
Specific Conductivity (SC25)		
When $\leq 100 \mu\text{S/cm}$	$\pm 5\%$	$< 5 \mu\text{S/cm}$
When $> 100 \mu\text{S/cm}$	$\pm 3\%$	(10%)
pH: Meter displays to 0.01	± 0.1 unit	± 0.2 unit (10%)
Dissolved oxygen:		
Amperometric (same as polarigraphic) method	± 0.3 mg/L $\pm 2\%$	± 0.5 mg/L (10%)

6.3.3 Outline of Discrete Water Profile Measurements

Acquiring high quality results requires the use of consistent measurement methods. Adhere to the following guidelines:

1. Depths < 20 m: Measure T, DO, pH, and SC25 surface to bottom at 1 m intervals.
2. Depths > 20 m: Decrease measurements to 2 m intervals down to 30 m and to as much as 5 m increments for greater depths.
3. Wait for the DO value to stabilize first, record the value, then read the other parameters. Because DO takes the longest to stabilize this assures all parameters have equilibrated. See section 6.4.4 for further details. Stabilization of the DO value will typically take anywhere from 30 seconds to several minutes, depending on the gradient from the previous depth and the age and type of oxygen sensor. Extra time should be allowed for equilibration when values are below approximately 3 mg/L. If the sonde does not have a stirring mechanism, jiggle the cable gently approximately once per second.
4. Enter all data on field forms.
5. Quality Assurance (QA): At a minimum, replicate one of every 10 sets of measurements (e.g., at 1 m, 10 m, etc.). The replicate should be taken immediately following the original reading. Values should agree within $\pm 10\%$ or the detection limits listed in Table 3, whichever is larger.
6. Additional QA: At least once per field day, when a multiprobe is used to record water quality parameters, record 7 sets of measurements at the same depth after all parameters have stabilized. The readings should be taken immediately after one another in quick succession. These readings will be used to calculate the alternative measurement sensitivity (AMS) of each sensor on the multiprobe, which provides a way to track long-term sensor accuracy.

Instrument problems or failure

- If water quality sensor measurements are not representative of field conditions based on previous data or limnological knowledge, re-calibrate and try again.

- If readings seem reasonable, proceed. If not, first check the troubleshooting guide in the instrument manual. If problem persists, collect as much data as possible using back-up hand held instruments, if available. Using the Van Dorn bottle, collect a sample from 2.5, 5, 7.5, and 10 m, and then at 5 m intervals to the bottom, and record values obtained by dipping the sensors into the top of the sampler. In the case of measuring DO, jiggle the probe without causing bubbles to form in low DO hypolimnetic samples. If, after approximately 2 min, the value continues to decrease, increase the rate of swirling or jiggling to see if it will stabilize; if it is increasing after 2 minutes, you may be agitating the water enough to be causing an aeration artifact near the surface. If too much time elapses and the temperature of the water sample has increased by more than 1°C, collect a fresh sample.

6.3.4 Detailed Description and Troubleshooting Hints for Field Variables

Because temperature, DO, and other water quality variables are important determinants of biotic habitats, it is important that observers write down values on field forms and think about their ecological meaning, even if a data logger is recording the measurements. The hard copy also serves as backup in case there is an electronic failure.

6.3.4.1 Temperature

Temperature (T) is measured in units of degrees Celsius (°C) and recorded to the nearest degree or tenth of a degree as warranted by instrument.

1. If a cabled thermistor is not available, the high specific heat of water allows a temperature profile to be obtained by bringing deep samples to the surface with a water sampler and immediately measuring temperature with a hand-held thermometer or thermistor. Anything immersed into the water sampler potentially contaminates that particular sample; a separate sample must be collected for water chemistry.
2. The upper few centimeters of soft sediments are often several tenths of a degree warmer than the overlying water. The rise in temperature can be an indication that the probe is submersed into the sediments. If this happens, be sure to vigorously shake the instrument in shallow water with high DO to clean it before re-taking measurements. Check intermediate depth values, and if these values do not meet QA criteria, pull the instrument to the surface and clean it.

6.3.4.2 Specific Conductivity

Specific conductivity (SC) is the ability of water to conduct an electrical current for a unit length and unit cross-section at a certain temperature, measured in units of microsiemens per centimeter ($\mu\text{S}/\text{cm}$), and recorded to the nearest $\mu\text{S}/\text{cm}$. Commonly used in water quality monitoring, SC is a general measure of the number of ions dissolved in the water. It is important to be aware of the difference between SC (specific conductivity at the ambient temperature of the sensor) and SC25 (an abbreviation for specific conductivity temperature compensated to 25°C). This difference becomes very important in profiling stratified lakes where the hypolimnion is cold with respect to the epilimnion. In such cases, the typical increase in ions with depth, as estimated by SC25, would be substantially offset by the corresponding decrease in SC due to decreasing temperature. The

difference between SC and SC25 can confound analyses of seasonal patterns of dissolved ions since water temperatures vary throughout the year. The SC25 can be used to monitor seasonal changes in total dissolved salts (TDS) such as a spring flush of road salt, which is why the temperature compensation is so important. Many instruments will display SC in addition to SC25. In the event that an uncompensated sensor must be used (older instruments and most pocket conductivity meters are not temperature-compensated), the value of SC25 can be calculated from SC and temperature values (see # 3 below). The value of SC should be recorded on the field form even when SC25 will be calculated.

1. A common physical problem in using a specific conductance probe (or meter) is entrapment of air in the conductivity probe chambers. Its presence is indicated by unstable specific conductance values fluctuating up to ± 100 $\mu\text{S}/\text{cm}$. This problem is much more prevalent in turbulent stream waters and can be minimized by slowly and carefully placing the probe vertically into the water and when completely submerged, quickly moving it back and forth through the water to release any air bubbles. An SC probe with an open flow design does not trap air.
2. Is the value real or is the instrument out of calibration? Having specific conductance standards in the field can help verify values that fall outside the expected range. For example, the expected specific conductivity is around 200 and the reading is 1500. A known standard can be put in the instrument storage cup to determine if the instrument is reading correctly or is out of calibration.
3. SC25 values can be calculated from uncompensated SC values via a temperature-compensation formula. For example, for YSI probes, use:

$$SC_{25} = \frac{SC_m}{1 + 0.0191(t_m - 25)}$$

Where, SC_{25} = corrected conductivity value adjusted to 25°C,

SC_m = measured conductivity before correction, and

t_m = water temperature at time of SC_m measurement.

Contact the instrument vendor for the appropriate formula.

6.3.4.3 Hydrogen Ion Activity (pH)

Commonly used in water quality monitoring, pH is a measure of the acidity of water, measured in standard pH units (SU), and recorded to the nearest 0.1 pH unit. The pH scale is from 1 to 14: neutral water is pH 7, acidic waters have pH <7, and alkaline waters have pH >7.

- Is the value real or is the instrument out of calibration? Having pH standards in the field can help verify values that fall outside the expected range. For example, the expected pH is around 7.0 and the reading is 9.5. A known standard can be put in the instrument storage cup to determine if the instrument is reading correctly or out of calibration.

- As with dissolved oxygen, a pH probe can take longer to equilibrate when the gradient from the previous measurement is large (>1.0 pH SU).
- Low ionic strength waters with SC25 <50 $\mu\text{S}/\text{cm}$ can cause pH measurement stability problems with some probes, necessitating use of low ionic strength probes. Probes will often calibrate fine in strong ionic strength buffers but will not read accurately in lower ionic strength surface waters. If you suspect this is the case, use a sensor that is designed for low ionic strength waters.
- Because the pH scale is logarithmic, field values may first have to be converted to hydrogen ion activity (i.e., concentration) values, averaged, and re-transformed to pH standard units prior to conducting statistical analysis. To compute a mean pH for a group of data:
 - Convert each pH value to hydrogen-ion activity, using the equation: Hydrogen Activity = $10^{-\text{pH}}$.
 - Calculate the mean of the activity values by adding the values and dividing the sum by the total number of values.
 - Convert the calculated mean activity back to pH units, using the equation, $\text{pH} = -\log_{10}$ (mean hydrogen activity).

6.3.4.4 Dissolved Oxygen

Dissolved oxygen (DO): units of mg/L record value to nearest 0.1 mg/L unless otherwise justified; percent saturation (% DO) record value to nearest %; also temperature compensated to 25°C.

- Be aware that if a water sample has a strong rotten egg smell (H_2S gas) it must have a DO of zero. This is one way to check your meter. You can use the measured offset value to correct your higher DO values. Do not report negative DO values in the final database although it is important to report them on the field data sheet. Do the correction afterwards but note on the field sheet the depth at which you could smell sulfide gas. Avoid touching the bottom, if possible, as the membrane may become fouled.
- Equilibration time is critical; the steeper the DO gradient, the longer the equilibration time. It may take >5 minutes when DO drops abruptly to near zero.
- The DO probes with membranes (Clark cell) actually consume oxygen in the immediate vicinity around the membrane as they work; measurements therefore require moving water using either a built-in stirrer (typical in multiparameter sondes and BOD probes) or moving the cable up and down (e.g., 6" each side of the desired depth) during the measurement. Optical sensors do not consume oxygen and hence do not require moving water.
- Accuracy of an optical DO probe can be compromised if it is covered with a residue that inhibits or increases oxygen reaching the sensor surface. Algae on the sensor surface may increase DO measurements, while oils or sediments may lower them. If measurements seem suspect, or if the instrument was used in contaminated water, the sensing surface should be cleaned with a soft brush and a mild detergent.
- If the electronic DO meter is not functioning properly, DO can be measured by Winkler titration (Clesceri et al. 1998). A variety of field kits are convenient and cost effective, including Lamotte, Hach, and others.

6.3.4.5 Clarity

Measurement of Secchi disk transparency has historically been the most common means of measuring water clarity due to its simplicity. It is a qualitative evaluation of the transparency of water to light based on the reflection of light from the surface of the Secchi disk and is a function of the absorption characteristics both of the water and its dissolved and particulate matter. To get an accurate measure of Secchi depth, the disk must hang vertically from the side of the boat. The transparency tube, which uses the same principle as a Secchi disk, is recommended when the Secchi disk can be seen on the lake bottom or when the disk does not hang vertically due to a current or an unstable boat.

6.3.4.5.1 Secchi Depth:

1. Measure Secchi depth using a 20 cm (8 in diameter) black and white Secchi disk from the shaded side of the boat. Do not wear sunglasses while viewing the Secchi disk.
2. Measurements should be made as near to midday as possible (10 AM to 3 PM; sunny and calm is optimal). Visit each lake as close to the same time of day as previous visits in order to minimize diurnal variation.
3. Try to lower the disk in the shade of the boat and make sure that the line is hanging vertically. In strong currents or choppy waves, it may be helpful to tape a rock or weight to the bottom of the disk.
4. Slowly lower the disk into the water until it disappears and note the depth.
5. Lower the disk a little farther, then slowly raise it until the disk reappears and note the depth again.
6. Average the two readings and record the value. Record the Secchi observer on the data sheet (see #8 below).
7. Record the conditions present when the Secchi measurement was made, with 1 being excellent (sunny clear skies, calm water), 2 being moderate (some clouds, small waves), or 3 being poor (dark skies, very choppy water, or currents that make it extremely difficult to read).
8. Quality Assurance (QA): Secchi readings should be replicated each time they are taken, ideally by different observers, because inaccurate measurements of the marked line are somewhat common. This additional step should only take a few extra minutes. The crew should not reveal their value until all are finished and then all values should be recorded and compared. Values should agree within $\pm 10\%$ for Secchi measurements < 5 m and ± 0.5 m for greater values. Record the mean of all values that are within the agreement range and record this final value on the data sheet.

6.3.4.5.2 Transparency Tube:

1. Measure transparency tube clarity using a 120 cm tube if the Secchi is visible on the bottom of a lake or wetland pond. For all shallow (<2 m) lakes and ponds, measure clarity with a transparency tube even if Secchi measurements can be made on occasion because clear water times can occur, when Secchi depth cannot be measured.
2. The tube should be set on a white towel background, shaded by your body, and read without sunglasses.
3. Water should be dispensed from a carboy that was used for integrating water samples (see below) rather than dipped from the water body. The carboy must be well shaken prior to filling the tube to minimize artifacts due to settling of sand and larger silt particles. Allow air bubbles to disappear before making the final measurement.
4. While slowly releasing water from the bottom of the tube via its valve, note and record the depth at which the mini-Secchi first becomes visible. Discard the remaining water and repeat the measurement with a second subsample from the carboy.
5. Several attempts to read the clarity may be necessary because of overshooting the endpoint, so collect plenty of water for this analysis. A standard 120 cm × 4.5 cm outside diameter tube requires approximately 1.5 L to fill it, so dedicate at least 4 L of water for this measurement.
6. During clear water periods, the tube may not be long enough for a measurement. In such cases, the value should be recorded as >120 cm. If it appears to be barely visible, this fact should be recorded to distinguish it from a measurement where it is clearly visible.
7. Quality Assurance (QA): At a minimum, replicate transparency tube readings at every tenth site. As for the Secchi reading, because of the apparent ease of this measurement yet its potential difficulty in less than ideal conditions, all field crew members should take this measurement at each site for at least the first round of sampling. Crew members should not reveal their values until all are finished and then all values should be recorded and compared. Values should agree within 10%. This acceptance criterion is subject to change as more data from various volunteer monitoring programs become available (such as the Minnesota Citizen Stream Monitoring Program (<http://www.pca.state.mn.us/water/csmp.html>)).

Maintenance notes and other precautions:

1. The rubber stopper (with attached Secchi) can be dislodged easily. Tape the stopper with black vinyl electrical tape and carry an extra stopper-Secchi.
2. Clean the transparency tube periodically with mild dish soap and a soft cloth.
3. Although water from the tube may be saved for turbidity and TSS measurements, do not save it for nutrient or other pollutant analyses because the tubes are not cleaned according to certified protocols.

4. Subsampling and settling issues are important, as particles settle quickly. A stopper for the top of the tube is useful to allow for resuspension during the measurement if rapid settling occurs.
5. Dissolved color due to organic matter (humic and fulvic acids, usually from bogs and conifer needles) can confound comparisons of transparency tube data between lakes. Also, lakes with similar concentrations of suspended sediments can have different transparency because smaller particles scatter more light.
6. A transparency reading taken from one tube cannot be compared with a reading taken from another tube made by a different manufacturer if the dimensions are different.

6.3.5 Measuring Water Level

Water level will be measured relative to a benchmark or reference mark. GLKN will always install markers above water level, but extreme water level fluctuations could submerge a marker that was originally well above the ordinary high-water mark. In some cases, benchmarks may have been installed by other agencies, and may not be above current water level. Water levels that are below the reference marker will be recorded as negative numbers; levels above the marker will be positive.

A single person can measure water level above a reference mark by placing a measuring device, such as a meter stick, on the marker and reading the water level directly on the device. Two people are required to measure water level when the reference marker is above the current water level. One person holds a stadia rod at the water's edge, while the second person uses an eye level or laser level at the benchmark to view the stadia rod.

Detailed instructions for installing reference markers and measuring water levels can be found in SOP #4, Measuring Water Level.

6.4 Water Sample Collection

A tube sampler collects and integrates a column of water into a single sample. If the top end is capped, all or most of the water will remain in the tube as it is raised. The main advantage over using a surface dip (often called a grab sample), is that a larger stratum of water in the epilimnion is represented by the sample, reducing the effect of high chlorophyll concentrations from concentrated scums on the seasonal mean. Bottom water, and on occasion other depths, will be sampled using a Van Dorn or Niskin type remote-closing water bottle. Although less durable, a transparent acrylic bottle allows the crew to ensure that near bottom water samples do not contain suspended bottom sediment before pouring the (contaminated) water into the sample bottles. Precautions will be taken to check with the manufacturer regarding the potential for nutrient or other contamination from the sampler. Before its first use, the sampler will be cleaned thoroughly by rinsing three times with hot tap water, rinsing three times with 0.1 N HCl, and finally, rinsing three times with deionized water.

6.4.1 Integrated Sampling Tube

1. Rinse compositing jug 3 times before sampling. Increase surface water flushing to 6 rinses if the compositing jug previously contained water that was contaminated with sediment or water deemed to have much higher nutrient levels.
2. Remove both stoppers from integrated sampler. Rinse the integrated sampler in lake water 3 times (lower to 2 m, raise, lower again, etc. for 3 rinses).
3. Collect sample by lowering sampler into water column (if water depth will allow it). If the site is too shallow for the 2 m sampler, then use one of the following methods:
 - a. collect sample by using the integrated sampler on an angle instead of vertically,
 - b. fill jug with 0.5 m deep water using the Van Dorn sampler,
 - c. or fill jug via surface grab.

Secure the top stopper, raise the sampler vertically, and immediately drain it into the rinsed compositing jug. The sampler will start releasing its water as soon as it clears the water surface. Two or three integrated samplers of water will be needed to fill a 6 L jug. Fill the jug at least 75% full to ensure adequate water for all analyses; if a transparency tube measurement will be done, an entire jug is needed. Extra water simply reduces variance associated with the site.

4. Once water is collected, immediately begin dispensing it into appropriate analyte bottles or keep jug cold and dark until processing in the park lab or home base at the end of the day (details below).

6.4.2 Discrete Depth Sampling

During the mid-summer sampling when the lake is thermally stratified, defined as a gradient of $\geq 1^{\circ}\text{C}/\text{m}$ or DO levels $\leq 2 \text{ mgO}_2/\text{L}$, collect two separate samples.

Collect surface water with the 0–2 m integrated tube sampler as above; collect bottom water with Van Dorn sampler from approximately 0.5 to 1 m above the lake bottom. Because the hypolimnetic water will be used for nutrient analyses only, a smaller container (1 or 2 L) may be used for storage and transport to the sample processing site. Do not collect bottom water from lakes that are not thermally stratified, as evidenced by temperature (and oxygen) profile data recorded with a multiprobe.

6.4.3 Distributing Sample Water from the Compositing Jugs

- Always ensure composite water is well mixed prior to dispensing it to any other containers.
- Rinse bottles and caps for chlorophyll-*a* with lake water three times, prior to filling. Uncap and re-cap bottles below water surface to avoid surface scum or debris.
- Fill dark plastic bottle for chlorophyll-*a* (at least 1 L); keep cold and dark until filtering at the end of the day.

If the water sample is processed on-site, follow the instructions below, in addition to those in SOP #7.

Integrated 0–2 m Water

1. Rinse caps and bottles with composite water three times, using approximately 50 mL for each rinse, prior to filling. Shake out excess water.
2. Cap and re-agitate composite jug and then dispense water into previously labeled appropriate bottles. Be careful not to overfill bottles pre-loaded with acid. Fill nutrient bottle to the bottom of the neck of the bottle – this will prevent the bottle from breaking when the water expands as it freezes.
3. Use remaining water for transparency tube measurement if specified. If insufficient water is left, collect additional water until there is enough for replicate measurements.

Bottom Water

- *From compositing jug*—Rinse the bottle caps and bottles in composite water as for surface water.
- *From Van Dorn*—Carefully stand the Van Dorn bottle on the side of the boat or on a seat, crack the top slightly to start the flow, rinse and dump 3 aliquots before filling the bottles to their necks. If there is not enough water in the Van Dorn to fill all the bottles, start over and either be more cautious with draining the sampler or use the compositing jug after rinsing, as above. Two Van Dorn samples may be pooled. Cap loosely and agitate the jug before dispensing water into the plastic bottles for raw and filtered nutrients (probably the only analyses to be done for bottom water).

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 carboy with surface water.

6.4.4 Sample Handling While in the Field

Store water samples in cooler with ice until return to home base for further processing.

In bad weather on lakes with a single sampling station or with a small boat it will be more convenient and safer to sample the bottom water first, collect the surface sample after the profiling is done, and then return to shore to pour the subsamples from a full compositing jug.

6.4.5 Quality Assurance of Field Duplicates

Collect a field duplicate every 10 samples. Label the duplicate analysis bottles with the code appropriate for the duplicate, using the same date and time of sampling. Indicate on the data field form which site or lake is the duplicate. Treat the duplicate as a regular sample for all phases of

collection, processing, and analysis. The duplicate should be a split sample, taken from the same composite jug. See section 6.6.3.2, below, for more details.

6.5 Departing From the Monitoring Site

Before leaving the monitoring site, all field forms and sample labels must be reviewed for legibility, accuracy, and completeness. Any changes in procedure due to field condition must be explained in the comments section. Make sure the information is complete on all forms. Record the departure time on the field form. After reviewing each form, initial the upper right corner of each page of the form. Document any photos taken by including the photo number and roll number or digital camera photo number on the field form.

6.6 Quality Assurance/Quality Control (QA/QC)

QA/QC basically refers to all those things good investigators do to make sure their measurements are right-on (accurate; the absolute true value), reproducible (precise; consistent), and include good estimates of uncertainty. It specifically involves following established rules in the field and lab to assure everyone that the sample is representative of the site; free from outside contamination by the sample collector, and that it has been analyzed following standard QA/QC methods. See SOP #12, Quality Assurance/Quality Control, for more details.

6.6.1 Calibration of Field Instrument Sensors

Calibration schedules overlap but differ from sampling schedules, so calibration methods are listed here as a separate procedural step. Instrument calibration is an essential part of quality assurance. Table 4 summarizes the ideal calibration frequency and minimum acceptance criteria for some of the most commonly collected water quality parameters. The reality of logistical constraints at back country sites may preclude calibration and checks of calibration at the ideal frequency. This SOP provides only generic guidelines for equipment use and maintenance. A wide variety of field instruments is 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.

Table 4. Ideal calibration frequency and acceptance criteria.

Parameter	USEPA Method	Minimum Calibration Frequency and QC Checks	Acceptance Criteria	Corrective Actions
Temperature	170.1	Annually, 2-point check with NIST thermometer	± 1.0 °C	Re-test with a different thermometer; repeat measurement.

Parameter	USEPA Method	Minimum Calibration Frequency and QC Checks	Acceptance Criteria	Corrective Actions
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%	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	Re-test; check low battery indicator; use different standards; repeat measurement; don't move cords or cause friction/static
		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	
		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

Parameter	USEPA Method	Minimum Calibration Frequency and QC Checks	Acceptance Criteria	Corrective Actions
Depth	--	Daily, prior to field mobilization, check at the field site. Check annually against commercially purchased brass sash chain labeled every 0.5 m to ensure that it reads zero at the surface and varies <0.3 m for depths <10 m and no more than 2% for greater depths.	±0.1 m	Retest, check low battery indicator; repeat measurement; use with accurately calibrated line
Transparency tube	--	Transparency tubes have a 100 or 120 cm scale; ensure tube is clean	±1.0 cm for transparency tube	
Marked lines (e.g., Secchi, Van Dorn)	--	Check markings annually against brass sash chain. If lines are heated (for decontamination) check prior to each round of sampling.	±1%, 0–10 m ±2%, >10 m	Re-mark line.

6.6.1.1 Instrument Calibration and Maintenance Logbooks

Calibration and maintenance logs for multi-parameter sondes and all back-up sensor probes will be maintained and will document the frequency of calibration, maintenance, and calibration checks. See the attachments for a blank calibration log form. Keep calibration logs with each instrument during the sampling season. Logs will later be archived at the network office in Ashland, Wisconsin. A new log will be started for each field season. Each instrument will 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

6.6.1.2 Handling of Calibration Standard Solutions

Store all calibration standards in a temperature-controlled environment. Standards should be dated upon receipt and upon opening. Commercially-purchased calibration standards come with an expiration date that must be observed. Ensure that calibration standards are not used beyond expiration dates.

Properly dispose of all waste materials. Used calibration solutions, in general, may be rinsed down a sink with water after consideration of the wastewater treatment system available to that sink. Safety data sheets (SDS) that are sent with manufacturer purchased calibration solutions should be kept on file. These documents describe the flammability, toxicity, and other safety hazards of reagents. Some reagents may include constituents that are toxic to aquatic life. These should not be rinsed down a sink in any large quantities in primitive areas where the ultimate destination of wastewater is the aquatic environment. Instead, these reagents should be collected in a properly-marked leak-proof container for disposal in an adequate treatment system.

6.6.1.3 Temperature

Temperature is typically not adjustable on an electronic sensor but should be cross-compared to a National Institute of Standards and Technology (NIST) traceable thermometer at the beginning of each field season, as follows:

- Compare against a NIST-certified or NIST-traceable thermometer at a broad range of temperatures, for example 0°C to 40°C;
- The sensor should read within $\pm 1.0^\circ\text{C}$ of the NIST thermometer;
- Typically you cannot adjust the instrument to calibrate it but check the manual. It is a good idea to check the instrument at 0°C in slurry of ice-water if a calibrated (NIST) thermometer is not available since electronic and non-electronic temperature sensors are typically linear over the likely range of field temperatures.

An armored glass thermometer that has been referenced to the NIST standard should be taken into the field for air temperature and surface water temperature measurements and for checks of the electronic sensor.

6.6.1.4 Specific Conductivity

Specific conductivity (SC25) will be calibrated using a KCl solution as specified by the instrument manual. Stock calibration solutions can be purchased commercially, prepared by a water quality contract lab, or made in an academic or agency lab. If the KCl solution is prepared by an academic or agency lab, it should be cross checked by an external certified lab. Set the instrument to record temperature-compensated SC (SC25) rather than SC.

Because the typical modern SC25 sensor is linear to <3% over the range from approximately 20 to 10,000 $\mu\text{S}/\text{cm}$, a single point calibration is typically sufficient. A typical standard is 1000 or 1413

μS/cm. Pre-mobilization error checks of this sensor using 10, 100, 1413, and 10,000 uS/cm standards may be used to establish sensor error over the range of most interest in freshwater work.

6.6.1.5 pH

The pH is calibrated using the standard two buffer technique, using either pH 4 and pH 7, or pH 7 and pH 10, depending on the expected field values. Calibrate the probe according to the manufacturer's recommendations, usually starting with pH 7 buffer followed by the second buffer. If a water body is classified as low acid neutralizing capacity (ANC) acid-sensitive (i.e., ANC approximately 100 ueq/L or lower), it should also be checked against a low ionic strength buffer (LISB) with pH approximately 4, as per protocols from the National Acid Precipitation Assessment Program (NAPAP 1990). A low ionic strength pH combination electrode may be necessary to acquire this extra level of sensitivity if stabilized pH measurements are not achieved with standard pH sensors. Prior to each round of sampling, check the calibration with a third standard with a pH value between those used for calibration.

6.6.1.6 Dissolved Oxygen

Two types of dissolved oxygen (DO) sensors are typically utilized: Clark cell and optical. A Clark cell (membrane) sensor is air-calibrated, while an optical DO sensor is calibrated in 100% saturated tap water. For a Clark cell, it is assumed that the dry sensor will read 100% saturation in an enclosed airspace with enough water in the bottom of the container to saturate the air with water vapor. For optical DO sensors, the sensor window must be submerged in 100% DO saturated water, which is obtained by agitating tap water in a container for one minute and then decanting it into the calibration chamber until the DO sensor is completely covered with water.

A Clark cell should be checked for bubbles under the surface of the membrane. If bubbles are observed, change the electrolyte solution and replace the membrane. An optical DO sensor's surface should be observed to make certain that no air bubbles are clinging to it. The calibration chamber can be tapped gently to dislodge any bubbles.

Temperature affects DO saturation, as does the air pressure, which varies with elevation and ambient weather. Both sensors require a known barometric pressure (BP), obtained by the multiprobe itself (if equipped with a BP sensor) or from another source. Acceptable sources for BP are from another instrument, such as a calibrated barometer, or a third-party source, such as the local weather bureau or airport. Typically, one can assume the barometric pressure to vary with elevation. As a result, the instrument should be re-calibrated at each site if the elevation has changed more than 50 feet.

6.6.1.7 Depth

The length measurement of brass Secchi chains, transparency tubes, and depth sounders usually require little calibration after purchase and an initial check for accuracy. Compare all depth cables to each other and ensure they are synchronized. A brass Secchi chain can be used to calibrate other cables and lines. The use of a brass chain is particularly important because this single tool is likely to provide consistent long-term data. Nylon and certain braided weave ropes and cords can stretch as much as 20% and may vary depending upon wetness, load, and age. Lines may also shrink, as when they are soaked in hot water to avoid spread of exotic species.

Electronic depth sensors, or pressure transducers, are based on pressure differences and need to be set to zero at the water surface initially. Perform this zero check at every station; however, verify the depth measurement with labels on the actual instrument cable.

A useful and widely-used labeling system for coding depths is:

1. 5 m increments: Wrap vinyl tape of a specified color at 5 m increments and add an extra wrap every 5 m. Therefore, there is a single wrap at 5 m: two wraps at 10 m separated by approx.. 0.5 cm with 10 m lying exactly between the wraps; three wraps at 15 m with the 15 m depth located at the middle of the second wrap, and so on. A permanent marking pen should be used to write the actual depth on the tape.
2. 0–10 m depth: Use a second color to make wraps at 1 m intervals to best define shallow water columns.
3. 10–20 m depth: Use the second color, or new third color, to wrap at 2 m intervals.
4. >20 m: Mark the line at 2.5 m intervals or continue with 2 m intervals.

6.6.1.8 Post-Field Calibration Checks

Post-field calibration checks must be performed after each use of the instrument and before any instrument maintenance. 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. After making measurements at the last station, fill the sampling cup with ambient water (not deionized or tap water). Repeat the initial calibration procedures performed before the sampling trip. Record post-field calibration values in the calibration logbook (generally on the same page with the initial calibration for that sampling trip). Deviation beyond the manufacturer's specifications is cause for concern and should be addressed before the next sampling date.

Do not adjust the instrument (using calibration controls) during the post-calibration check.
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The purpose of the post-calibration is to determine if the instrument has 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.

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 for more details on QA/QC). 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 5. Post-calibration check error limits.

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

6.6.1.9 Sensor Maintenance and Storage

Most multiparameter sondes should be stored with a small amount of water in the storage cup. Refer to the manufacturer's manual for tips on cleaning the probes and housing, routine maintenance procedures, and proper storage procedures.

6.6.2 Calculation of Field Instrument Performance Criteria

Performance of field instruments must be checked in several ways, as detailed in the QA/QC procedures of SOP #12. Formulae for calculating instrument sensitivity, instrument precision, instrument bias, and cumulative bias are found in SOP #12.

Documentation of these performance criteria include estimation of the limits of detection of the multiprobe, the relative percent difference of duplicates, measurement of reference solutions, and estimates of change due to change in methods or instrumentation.

6.6.3 Quality Assurance/Quality Control Samples

Quality control samples are commonly used in documenting quality control associated with the collection of samples in the field. Field blanks and duplicates are routinely incorporated into a monitoring program without a good understanding of their function. The purpose of these samples is to validate the precision and accuracy of laboratory data, and to determine the adequacy of preservation techniques, equipment cleaning and preparation, and sampling procedures. Field 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 (alter its true value or concentration).

6.6.3.1 Equipment Blanks

Blanks are an integral part of quality control (QC) and are required for all sampling activities. Their creation should be noted in the field log book. Blanks establish that there is no sample contamination from the containers during custody, transportation, and or pre-analysis preparation either in the field or in the laboratory. Blanks establish the level of constituents introduced into a sample by the equipment used for sampling, preservatives, and/or containers. We will conduct equipment blanks prior to each field season and occasionally during the field season between field sites to ensure field rinsing is adequate.

Collect an equipment blank prior to the field season as follows:

1. Clean all equipment used to collect, store, and process water samples (e.g., integrating sampler, compositing jug, filtering apparatus) according to SOP #7.
2. Rinse the equipment used to collect and store water samples (integrating sampler and compositing jug) with laboratory reagent grade water three times and discard.
3. 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.

Another source of systematic error is sample cross contamination from field sampling equipment used to handle a multiple number of samples. The integrated sampler and compositing jugs are to be rinsed in the field three times at each site prior to taking a sample. Either piece of equipment may be a source of cross contamination. Collect periodic equipment blanks as follows:

1. In between sample sites, rinse the equipment used to transfer water samples (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. This type of blank is a check for cross contamination between sampling sites and control for bias introduced by cross contamination.

Other types of blanks will be used as needed: 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; or bottle blanks, any time sample collection bottles are of uncertain quality or cleanliness or from a source not previously used.

6.6.3.2 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 and duplicate analyses may be made in the field: 1) as a form of field quality control; 2) to measure or quantify the homogeneity of the sample, the stability and representativeness of a sample site, the sample collection method(s) and/or the technician's technique.

Duplicates are analyzed in the laboratory for the same parameters as the monitoring sample to which they apply. Laboratory duplicates which exceed QA/QC standards for the parameter are retested. Analytical results of duplicate samples will, theoretically, be the same. Realistically, results may differ due to the non-homogeneity of the sample source, and sampling and analytical errors. Duplicate samples also document the technique and ability of the technician and analyst to produce representative water quality data.

The laboratory analytical report must show test results for the duplicates, blanks and spikes, the method and the results for summary quality control statistics calculations. Copies of these reports are a permanent part of the site file.

Duplicates will ideally be splits of homogeneous samples to estimate measurement precision in the context of repeatability unless otherwise documented and justified. If enough sample water cannot be collected in the compositing container to facilitate a split sample, then duplicate samples will be co-located.

Duplicate field samples must be collected every sampling trip for each type of sample collected and the results must have a Relative Percent Difference (RPD) less than or equal to the guidelines in Table 6. Required field parameter measurements can be duplicated to estimate the precision of the equipment. Every tenth measurement may be duplicated, and the results of both measurements recorded and evaluated as RPD. The result can be compared with the stated precision of the instrument.

Table 6. Frequency, acceptable range, and corrective actions for duplicate samples.

Type of Duplicate	Frequency	Acceptable Range for Precision	Corrective Action
Field duplicates (samples)	Minimum of 1 per trip per parameter or 10% of all samples per parameter per day	Chlorophyll-a, TSS and nutrients $\pm 30\%$ RPD; all other parameters $\pm 15\%$ RPD	Audit field personnel and verify sample collection procedure; resample; reanalyze; revise SOP; audit and train field personnel; project manager determines whether associated data is usable
Field duplicates (multi-probes)	Minimum of 1 per trip per parameter or 10% of all samples per parameter per day	All parameters $\pm 10\%$ RPD	Re-calibrate instrument; replace batteries; perform instrument field check with different standards; repair or replace instrument; notify management; audit and train field personnel; project manager determines whether associated data is usable

6.6.4 Summary of Quality Assurance/Quality Control Field Procedures

Quality assurance protocols are means to ensure data collected are as representative of the natural environment as possible. Quality assurance procedures are required in all data collection efforts as part of this monitoring protocol. Many of the key elements of quality assurance have been included in the SOPs where appropriate, as well as detailed in SOP #12. A summary of important QA/QC procedures follows. Table 7 lists additional requirements for QA/QC methods and documentation.

- Field staff must be trained by personnel experienced in the protocol. Training will include classroom time as well as field and lab components. Details of the training are given in the Standard Operating Procedure #2: Training and Safety.

- Use calibrated instruments for all field measurements. Test and/or calibrate the instruments before leaving for the field. Each field instrument must have a permanent log book for recording calibrations and repairs. Review the log book before leaving for the field.
- All manually recorded field measurement data will be collected on field forms; data that are automatically recorded will be captured electronically and the equipment used will be documented on field forms. Hard and electronic copies will be made as soon as possible after surveys and kept at a separate location as backup.

Table 7. Summary of QA/QC documentation and sampling methods.

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

- Complete records will be maintained for each sampling station and all supporting metadata will be recorded appropriately (field forms or electronically).
- Make field measurements in a manner that minimizes bias of results.
- Check field-measurement precision and accuracy. Follow the procedures in SOP #12.

- Collect 10% duplicate water samples; conduct duplicate measurements of field parameters at approximately 10%.
- Create field blanks prior to the beginning of each field season and periodically throughout the season.

6.6.5 Corrective Responsive Action

The project manager, in consultation with experienced professionals, will be responsible for taking corrective responsive action in the case in which QA/QC is not followed or in the case of an unexpected event. Responsive action is often needed in the event of broken sample bottles, missing data, errors on field sheets, changes due to field conditions, problematic analyses and other events that do not fall within the standard operating procedures. A “Memo-to-file” will be used to document any decisions or corrections that are made. This memo will include the date, name of author, site or sample referred to, a description of the problem or error and a statement describing the decision made or action taken. The memo will be archived with the appropriate site data and files.

6.7 Data and Records Management

- Hand-written field sheets with core suite profiles should be reviewed for completeness immediately upon returning to the shore. Make photocopies as soon as possible and file them appropriately. Download and back up data from data loggers as soon as possible.
- 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.
- Schedule and perform regular data transfer and backup. Data will be protected from loss or damage by daily backup, when possible, or on a feasible schedule approved by the project leader and the data manager. Ideally, raw and electronic data are backed up off-site as soon as a sampling trip is completed.
- Record and verify observed or measured data values. Complete paper forms and enter or import data into NPSTORET and/or other electronic databases.
- A ‘Memo-to-file’ will be used to document any decisions or corrections that are made. This memo will include the date, name of author, site or sample referred to, a description of the problem or error, and a statement describing the decision made or action taken. The memo will be archived with the appropriate site data and files.
- Data validation, the process by which data are proven or disproved to be accurate, involves the review of the results of all measurements, samples, and QC samples. Sample data should be flagged if the analyte was detected in a blank at a concentration similar to that in the sample; flagged data contain much more uncertainty than unflagged data. Some investigation into the sampling method may be needed if flagged data are a continual occurrence.
- Refer to SOP #8 for more details regarding data entry and management.

6.8 Literature Cited

- Carlson, R. E., and J. Simpson. 1996. A coordinator's guide to volunteer lake monitoring methods. North American Lake Management Society (www.nalms.org). Available at http://dipin.kent.edu/Sampling_Procedures.htm.
- Clesceri, L. S., A. E. Greenberg, and A. D. Eaton (editors). 1998. Standard methods for the examination of water and wastewater (20th edition). American Public Health Association, Washington, D.C.
- Irwin, R. 2006. Draft Part B lite (Just the Basics) QA/QC review checklist for aquatic vital sign monitoring protocols and SOPs. National Park Service, Water Resources Division. Fort Collins, Colorado. Available at www.nature.nps.gov/water/Vital_Signs_Guidance/Guidance_Documents/part_b_lite_05_2005.pdf.
- Irwin, R. 2004. Vital signs long-term aquatic monitoring projects, planning process steps: Part B, issues to consider and then document in a detailed study plan that includes a quality assurance project plan (QAPP) and monitoring "protocols" (including standard operating procedures), January 2004 draft. Available at <http://science.nature.nps.gov/im/monitor/protocols/wqPartB.doc>.
- NAPAP (National Acid Precipitation Assessment Program). 1990. Acid deposition: State of science and technology, Volume II aquatic processes and effects. National Acid Precipitation Assessment Program, Office of the Director, Washington, DC.
- O'Ney, S. E. 2005. Standard operating procedure #5: Procedure for collection of required field parameters, version 1.0. Appendix E in Regulatory water quality monitoring protocol, version 1.0. National Park Service, Greater Yellowstone Network, Bozeman, Montana.
- Penoyer, P. 2003. Vital signs long-term aquatic monitoring projects: Part C, draft guidance on WRD required and other field parameter measurements, general monitoring methods and some design considerations in preparation of a detailed study plan. Aug. 6, 2003. Draft. Available at <http://science.nature.nps.gov/im/monitor/protocols/wqPartC.doc>.
- Route, B., W. Bowerman, and K. Kozie. 2009. Protocol for monitoring environmental contaminants in bald eagles, version 1.2: Great Lakes Inventory and Monitoring Network. Natural Resource Report NPS/GLKN/NRR—2009/092. National Park Service, Fort Collins, Colorado.
- WOW (Water on the Web). 2004. Water on the Web—Monitoring Minnesota lakes on the internet and training water science technicians for the future: A national on-line curriculum using advanced technologies and real-time data. University of Minnesota—Duluth, Duluth, Minnesota. Available at <http://waterontheweb.org>.

Attachments

- Field Data Sheet
- Multiprobe Calibration Log
- Eureka Manta Maintenance Log
- Multiprobe Calibration/Maintenance Log

GREAT LAKES NETWORK - WATER QUALITY MONITORING						Initials _____																																																																						
Park _____ Site Code _____			Date _____ Start time _____ End time _____																																																																									
Location Name _____			Secchi (m) 1st _____ 2nd _____ Ave. _____																																																																									
UTM/LatLong _____			Secchi reading cond.: excellent 1 moderate 2 poor 3 on bottom 4																																																																									
NAD _____ Zone*: 15N 16N WP# _____			Transparency Tube (cm) 1st _____ 2nd _____ Ave. _____																																																																									
Personnel _____			Water color (visual, in composite jug) _____																																																																									
Instrument(s) _____ Cal Date _____			Water sample type: I-tube Grab Van Dorn Other _____																																																																									
Model/Model# _____			VanDorn depth (m) _____ Wave Height (cm - in [circle one]) _____																																																																									
FIELD CALIBRATION: Elevation (MSL, ft or m?) _____			Zmax (m) sonde: _____, sounder: _____, other _____																																																																									
Barometric Pressure (_____ in Hg) (25.4mm/in) = _____ mm Hg			DO Cal (% sat.) Start _____ Finish _____																																																																									
B= Bottom, Q=QA/QC																																																																												
Water Level Measurement																																																																												
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(SACN only) TSS _____																																																																												
Other (diatoms, Hg, contaminants, etc.) _____																																																																												
Current Weather Observations - fill in blanks or circle code																																																																												
Wind Dir. (as °)	Air Temp (°C or °F?)	Wind Condition	Code	Past 48 hours																																																																								
		Smoke rises vertically	0	Cloud cover, Rainfall & Wind																																																																								
		Smoke drifts, leaves rustle	1																																																																									
		Wind felt on face	2																																																																									
		Flag extended, leaves move	3																																																																									
		Dust, sm. branches move	4																																																																									
		Small trees begin to sway	5																																																																									
		Large branches move, wires	6																																																																									
		whistle, umbrellas hard to control																																																																										
		Beyond 6, you shouldn't be out in a boat																																																																										
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* UTM 83 zones: 15N = APIS, MISS, SACN, VOYA; 16N = GRPO, INDU, ISRO, PIRI, SLBE																																																																												

Figure A1. The water quality monitoring field data sheet (front).

Water Quality Monitoring Protocol for Inland Lakes

Eureka Manta Multiprobe Calibration

Personnel

Date

DO Membrane Changed

Multiprobe

Date

pH Reference Electrolyte Changed

Time

Date

	Calibration Standard (True Value)	Pre- Calibration Reading	Calibration Reading	Calibration Check	Pre- or Post- Field?
Battery Voltage					
Depth	0				
SpCond ($\mu\text{S}/\text{cm}$)	Air (0)				
SpCond ($\mu\text{S}/\text{cm}$)	value				
	Lot#				
SpCond ($\mu\text{S}/\text{cm}$)	value				
	Lot#				
SpCond ($\mu\text{S}/\text{cm}$)	value				
	Lot#				
Temperature					
pH	7				
	Lot#				
pH	10				
	Lot#				
pH	4				
	Lot#				
pH	Lot#				
Baro Pressure					
DO% Saturation					
DO (mg/L)					

Eureka Manta Maintenance Log

Record maintenance performed, date, and person conducting maintenance

Date & Personnel	DO Probe	pH probe	EC25 probe	Temperature	Depth Sensor