WATER CHEMISTRY ASSESSMENT PROTOCOL FOR DEPRESSIONAL WETLAND MONITORING SITES

I. PURPOSE

To describe and document the standard operating procedure (SOP) used by the Minnesota Pollution Control Agency's (MPCA) Biological Monitoring Program to collect water chemistry information at depressional wetland monitoring sites for the purpose of assessing water quality and developing biological assessment criteria.

II. SCOPE/LIMITATIONS

The following SOP applies to all depressional wetland monitoring sites for which an integrated assessment of water quality is to be conducted. An integrated depressional wetland assessment involves the collection of biological (macroinvertebrate and plant) and chemical data to assess wetland condition. The MPCA defines depressional wetlands as wetlands that occur within a shallow depression in the landscape that are not directly associated with streams (i.e., riparian wetland) or lakes (i.e., fringing wetland); have a semi-permanent to permanent flooding regime (i.e., not temporarily flooded wetland or vernal pool); and have predominantly emergent marsh to shallow open water (aquatic) vegetation types (Eggers and Reed 1997). This combination of water regime and vegetation communities corresponds to U.S. Fish and Wildlife Service (US FWS) Circular 39 wetland types 3, 4, and 5 (Shaw and Fredine 1956).

The protocols included here only describe those used by MPCA biologists to collect wetland water samples and measure water chemistry parameters in the field. This document does not include any of the analytical procedures utilized by the Minnesota Department of Health (MDH) Environmental Laboratory, the laboratory which analyzes the MPCA wetland water samples. For more information about their analytical procedures see the MDH Environmental Laboratory Handbook (MDH 2007).

III. GENERAL INFORMATION

Sites may be selected for a number of reasons including: 1) sites randomly selected for ambient condition monitoring, 2) sites selected for the development and calibration of biological criteria, 3) sites selected to evaluate a suspected source of pollution, and 4) sites selected for wetland trend assessment. Although the reasons for monitoring a site may vary, the water chemistry sampling protocol described in this document applies to all MPCA wetland monitoring sites unless otherwise noted.

IV. PERSONNEL REQUIREMENTS

A. Field Crew Leader: The field crew leader must be a professional aquatic biologist with a good knowledge of wetland ecology. He or she must have a minimum of a Bachelor of Science degree in aquatic biology or a closely related field; and have a minimum of six months field experience in environmental monitoring. Field crew leaders should also be

proficient with map reading and orienteering, using both Global Positioning System (GPS) and compass.

B. Field Assistant/Intern: The field assistant/intern must have at least one year of college education and an interest in aquatic biology. Coursework in environmental, natural resource, and/or biological science is preferred.

C. General Qualifications: All personnel conducting this procedure must have the ability to perform rigorous physical activity in an outdoor setting and be capable of carrying up to 50 lbs. of sampling equipment.

V. RESPONSIBILITIES

A. Field Crew Leader: The field crew leader is responsible for implementing the action steps of the procedure and ensuring that the data generated meets the standards and objectives of the Biological Monitoring Program and the MPCA. In addition, the field crew leader is responsible for planning sampling activities and ensuring that MPCA policies and protocols are followed during all sampling activities.

B. Field Assistant/Intern: The field assistant/intern is responsible for implementing the action steps of the procedure; including the maintenance, stocking, and storage of sampling equipment, data collection, and data recording.

VI. TRAINING

All inexperienced personnel will receive instruction from a trainer designated by the program manager. Major revisions in this protocol require that all personnel that apply this procedure on behalf of the MPCA be re-trained in the revised protocol by experienced personnel. The field crew leader will provide additional instruction to the field assistant/intern and will be responsible for monitoring the performance of the field assistant/intern throughout the field season.

VII. ACTION STEPS

A. Equipment Check: Before heading into the field confirm that all equipment necessary to complete this procedure is present and in proper working condition (Table 1).

B. Field Sampling: The wetland water sampling techniques employed by the MPCA measure the chemical and physical properties of the water column within or just beyond the emergent vegetation zone of the wetland. Where to collect water samples within a wetland is important for insuring valid comparisons across all of the wetland sites. Both chemical (e.g. dissolved oxygen) and physical (e.g. temperature, turbidity) properties of the water column can vary greatly within a wetland depending on factors such as sampling date and time, vegetative structure and water depth. Assuring that similar areas are sampled across all of the wetland sites will reduce the contribution of within site variability as much as possible, allowing between site variability to become the major component explaining any observed inter-site differences.

Table 1. Equipment needed to complete the MPCA wetland water chemistry SOP.

Equipment	Purpose	Operation Check
Sample Bottles:		
MDH 125 ml General (plastic)	-Collect water for chloride and sulfate measurement	-Sufficient quantity for sampling all sites (1/site) -Clean labels attached -Expiration date
MDH 250 ml Nutrient (plastic)	-Collect water for Kjeldahl nitrogen, nitrate + nitrite, total phosphorus, and total organic carbon measurement	-Sufficient quantity for sampling all sites (1/site) -Clean labels attached -Expiration date
5 ml 10% H_2SO_4 Preservative vial for nutrient samples	-Preserve nutrient samples	-Sufficient quantity for sampling all sites (1/site) -Verify adequate volume (e.g., no empty containers)
Other equipment:		
Multi-probe meter	-Measure pH, specific conductivity, water temperature, and dissolved oxygen in the field	-Proper calibration -Calibration standards present -Associated charger, batteries, and operating manual present
Color Wheel	-Measure water color in the field	-Deionized water for reference standard -Associated instructions present
Transparency Tubes (60 & 100 cm)	-Measure water clarity in the field	-Release valves work properly
Cooler with Ice	-Short term preservation of water chemistry samples	-Adequate supply of ice
Cell Phone	-Communication	-Associated chargers present
Site Files and Maps	-Site location information	
GPS Unit	-Record sampling location coordinates	-Associated charger, batteries, and operating manual present
Paper Data Sheets & Clipboard	-Record water chemistry field parameters	-Only pertains to invert sampling crew
Handheld Data Recorder	-Record water chemistry field parameters	-Only pertains to plant sampling crew
Pencils	-Record data	
Fine Point Permanent Marker	-Label water sample bottles	
MDH Lab Sheets	-Request analyses for grab samples	
Chest Waders	-Keep sampling crew dry	-Waders and wading boots -Materials to repair waders
Raingear	-Keep sampling crew dry	

The MPCA wetland biological monitoring program collects water samples and measures water column characteristics just beyond the emergent vegetation as this zone transitions to open water or a zone of different vegetative structure (e.g., floating or submergent) within each wetland (Figure 1). If such an area can not be accessed (e.g., too deep) or does not exist (e.g., entire wetland is emergent vegetation) then the water samples should be collected from a pocket of open water/floating or submerged vegetation within the emergent zone (Figure 2). For instances where no emergent vegetation is present either naturally or due to anthropogenic influences, water samples should be collected in the near shore area closest to where either the invertebrates or plants are being sampled. The zone water samples are collected from should be recorded on either the Wetland Invertebrate Visit Form (see Appendix A) or in the handheld data recorder (plant crew). A more detailed description of the zone where the sample was collected should be included if the sample could not be collected from just beyond the emergent vegetation zone (e.g., primary sampling area).

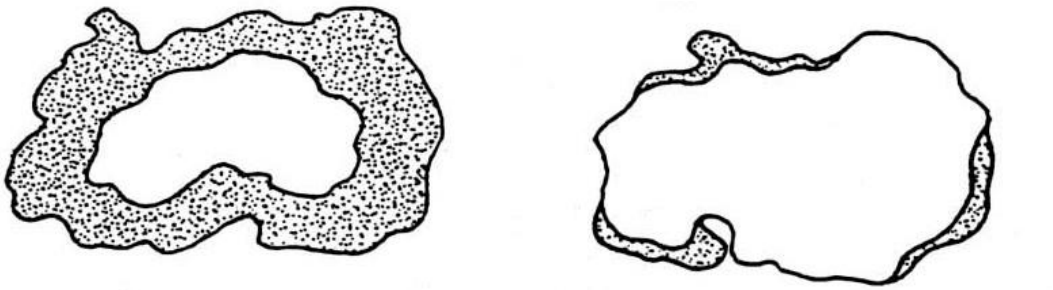


Figure 1. Wetlands with fringe of emergent vegetation (stippled area). White areas indicate open water, including floating and submerged plants. Sample water chemistry along margin of emergent vegetation as it transitions to open water, floating vegetation, or submerged vegetation. Figure adapted from Golet (1976).

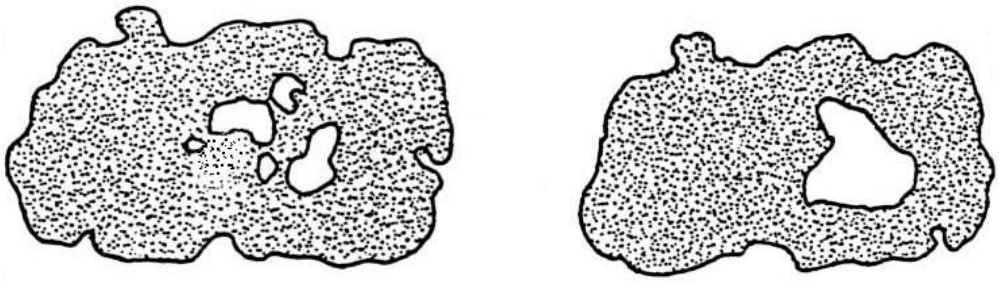


Figure 2. Wetlands with emergent vegetation (stippled area) throughout majority of wetland. White areas indicate open water, including floating and submerged plants. Sample water chemistry within pockets of open water, floating vegetation, or submerged vegetation. Figure adapted from Golet (1976).

Sufficient water sample volume should be collected in appropriate sample bottles to analyze all parameters included in Table 2. The 125 ml general chemistry sample bottle has enough

volume to analyze for the following: chloride and sulfate. The 250 ml nutrient bottle has enough volume for the following analyses: Kjeldahl nitrogen, nitrate + nitrite, total phosphorus, and total organic carbon (TOC).

Table 2. Wetland water chemistry sample parameters with sample container type, preservation, holding times, and MDH analysis codes.

Parameter	Units	Sample Collection	Sample Bottle	Preservation	Holding Time	MDH Analysis Code
Dissolved O_2	mg/L	Measured in the field w/ multiprobe meter	na	None	na	na
Temperature	^oC	Measured in the field w/ multiprobe meter	na	None	na	na
Specific Conductivity	µS/cm	Measured in the field w/ multiprobe meter	na	None	na	na
pH		Measured in the field w/ multiprobe meter	na	None	na	na
Transparency	cm	Measured in the field w/ transparency tube	na	None	na	na
Color	PCU	Measured in the field w/ color wheel	na	None	na	na
Total Phosphorus	mg/L	Composite grab sample at just below the surface	250 ml nutrient	10% H_2S0_4 4 °C	28-days	59
Total Kjeldahl Nitrogen	mg/L	Composite grab sample at just below the surface	250 ml nutrient	10% H_2S0_4 4 °C	28-days	68
Total Nitrate + Nitrite-N	mg/L	Composite grab sample at just below the surface	250 ml nutrient	10% H_2S0_4 4 °C	28-days	69
TOC	mg/L	Composite grab sample at just below the surface	250 ml nutrient	10% H_2S0_4 4 °C	28-days	98
Total Chloride	mg/L	Composite grab sample at just below the surface	125 ml general	4 °C	28-days	23
Total Dissolved Sulfate	mg/L	Composite grab sample at just below the surface	125 ml general	4 °C	28-days	293

B.1.Label Bottles: Sample bottles are difficult to label after being immersed in water, therefore, bottles should be labeled prior to sample collection. Using a fine point permanent marker clearly print the site (e.g.‘03Redw064’), sample ID# (e.g., 064), and date on the sample bottle label. When multiple samples are collected from a wetland, the site and sample IDs must be modified in order to distinguish these replicate samples. A single letter code will be added to the site name (e.g. ‘03Redw064A’) and sample ID# (e.g., 064A), indicating which replicate each sample represents. The letter ‘A’ represents replicate number one (= ‘Reportable’), ‘B’ represents replicate number two, and so on. These replicate identifiers are important because they link the water chemistry data to the biological data collected from the same location within the wetland.

B.2.Collect Water Samples: Once the location for sample collection has been established and the bottles have been properly labeled, water samples should be collected prior to any other sampling activities (e.g., invert, plant, or probe measurements) in the area. (*Note: MDH does not recommend pre-rinsing their bottles with sample water before collection of the sample*).

With sample bottle caps in place carefully wade to the location where water sampling is to occur. Holding the bottle downwind with its opening facing the downwind direction, remove the cap and immerse the bottle with the opening facing down into clear water outside of any area of wetland bottom disturbance (roil) to collect the sample from approximately 10 – 20 cm below the water surface. Take one integrated sample through the water column at this depth, moving the bottle horizontally with the neck tilted up slightly (to allow it to fill) until it is filled to its shoulder. *(Note: This technique is intended to create artificial flow into the bottle and thus reduce contamination from hands and the outside surface of the bottle).* Replace the cap and take a few steps into another area to collect the other grab sample, repeating the steps above. Both bottles, 125 ml general and 250 ml nutrient, should only be filled in areas where the bottom sediments have not been disturbed. In wetlands with dense duckweed or filamentous algae at the water surface use one hand to gently make a clearing for both bottle immersion as well as removal (i.e., after sample has been collected).

B.3.Preserve Water Samples: When both sample bottles are filled, add preservative to the nutrient bottle and mix thoroughly by inverting several times. Though not required it is recommended that sample bottles be placed in re-sealable plastic bags (e.g., ziplock ©) in order to keep sample bottles collected from one site together and also to help maintain label integrity in the cooler. Place all sample bottles in a cooler packed with ice as soon as possible. Keep samples on ice until delivery to MPCA Field Operations Center where they are then stored in a refrigerator prior to their delivery to the MDH Environmental Laboratory (601 Robert Street North, St. Paul, MN).

MDH lab sheets must accompany any samples sent to the Environmental Laboratory for analysis. Under the 'Lab Information' section the following fields should be filled out: **Project ID**, **Project Station ID** (= 'site' on sample bottle), **Date**, **Time**, **Sample Depth**, **Site ID** (= 'ID#' on sample bottle), **Analysis Group No.** ('10' selects all of the MDH analysis codes listed in Table 2), and **QA** (only filled out when sample represents a field duplicate). (*Note: MDH has a 10 character limit on Project Station ID and a 6 character limit on Site ID)* Recording the **Date** and **Time** each sample was collected on the lab sheet is vital in case the **Project Station ID** and/or **Site ID** is incorrectly transcribed at MDH. In such cases, the **Date** and **Time** may be the only manner in which the sample can be properly identified on the MDH data report. Prior to each monitoring season, a lab sheet template will be provided to each sampler to illustrate the pertinent information that needs to be included on the lab sheets that season. Upon delivery of samples to the Field Operations Center, fill out the 'Chain of Custody' section on the back of page one of the MDH Stream/Lake Lab Sheet.

B.4.Measure Field Parameters: In addition to the water samples that are collected and then analyzed in the laboratory, the MPCA measures a number of parameters in the field using a multi-probe meter. With this instrument the following parameters are measured: pH, specific conductivity, dissolved oxygen, and water temperature. Place the sensors at an approximate depth of 10 - 20 cm below the water surface in an area where bottom sediments have not been disturbed. Allow adequate time for the readings to stabilize before recording or logging the data. Once stabilized, either immediately record measurements onto a datasheet (e.g., Appendix A) or log data and transcribe onto a datasheet once back on land. Also record the time at which the measurements were made.

Use the transparency tubes to measure the clarity of the water column according to protocols adapted from their use in streams (see Appendix B). Measure water color using the color test kit according to the manufacturer's instruction manual. (*Note: Reduction of the sample volume will be necessary if the initial reading is out of range; see 'High Range' method*) Immediately record readings onto datasheet or into handheld data recorder.

C. Decontamination: Prior to leaving the wetland, rinse waders and all field equipment to prevent spread of exotic and invasive species. Once back at the vehicle, if necessary, rinse further with clean water supply. For more detailed information on this procedure see *Decontamination* SOP.

D. Data and Equipment Maintenance: Immediately after each day of field sampling, the following actions must be taken to insure sample integrity and maintain sampling equipment for further use:

D.1. Multi-Probe Meter Assessment and Maintenance: Recharge or replace batteries in multi-probe as necessary. Download and/or transcribe any data from the probe that was not previously done so in the field. In general, probes should be calibrated weekly prior to leaving the Field Operations Center. Periodically calibration may be required during a sampling excursion if the probe is having problems stabilizing or if readings are suspect. Each time a probe is calibrated an entry should be made into its calibration log book that includes the date, time, personnel, probe type, reference standard, and pre-calibration values.

D.2.Miscellaneous: Dry and repair waders as necessary. Acquire fresh ice for cooler when the equivalent of one 5 lb bag of ice remains. Charge batteries in cell phone and handheld data recorder as necessary.

VIII. QUALITY ASSURANCE AND QUALITY CONTROL

Compliance with this procedure will be maintained through annual internal reviews. Technical personnel will conduct periodic self-checks by comparing their results with other trained personnel. Calibration and maintenance of equipment will be conducted according to the guidelines specified in the manufacturer's manuals.

In addition to adhering to the specific requirements of this sampling protocol and any supplementary site specific procedures, the minimum QA/QC requirements for this activity are as follows:

A. Control of deviations: Deviation shall be sufficiently documented to allow repetition of the activity as performed.

B. QC samples: Replicate samples or resampling efforts will be collected from at least ten percent of sites sampled in any given year as a means of determining sampling error and temporal variability.

C. Verification: The field crew leader will conduct periodic reviews of field personnel to ensure that the procedures detailed in this SOP are being followed.

IX. LITERATURE CITED

Eggers, S.D. and D.M. Reed. 1997. Wetland Plants and Plant Communities of Minnesota and Wisconsin. 2nd edition. U.S. Army Corps of Engineers, St. Paul District, St. Paul, MN.

Golet, F.C. 1976. Wildlife wetland evaluation model. pp. 13-34 *In* J.S. Larson [ed.], Models for assessment of freshwater wetlands. University of Massachusetts Water Resources Research Center, Publication No. 32, Amherst, MA.

Minnesota Department of Health (MDH). 2007. Environmental Laboratory Handbook. Environmental Laboratory Section, Public Health Laboratory Division, Minnesota Department of Health, St. Paul, MN.
http://www.health.state.mn.us/divs/phl/environmental/handbook/internet/envhandbook.html

Shaw, S.P., and C.G. Fredine. 1956. Wetlands of the United States. U.S. Fish and Wildlife Service, Circular 39.

APPENDIX A

MPCA Wetland Monitoring Program

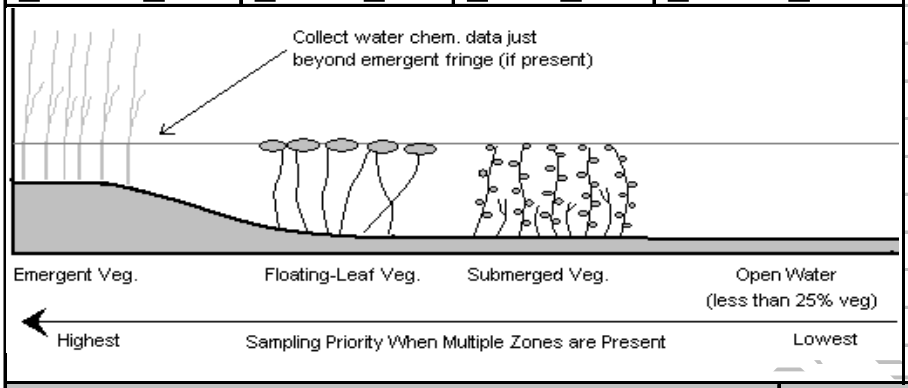
WETLAND INVERTEBRATE VISIT FORM

Wetland Name:		**Date:**	☐ **Reportable (A)** ☐ **Replicate**
Field Number:	**County:**	**Crew:**	**Replicate Identifier:** **B C D E**

COORDINATES	**LATITUDE**	**LONGITUDE**
Field GPS:	____ ° ____ ' ____ . ____ "	____ ° ____ ' ____ . ____ "

Indicate Relative Sampling Locations (using zones in diagram)

Emergent	**Floating**	**Submergent**	**Open Water**
☐ DN ☐Chem	☐ DN ☐Chem	☐ DN ☐Chem	☐ DN ☐Chem



NOTES/COMMENTS

OTHER BIOLOGICAL OBSERVATIONS

Taxa	**Present?**	**Abundance**		
Fish	☐	One	Few	Many
Fathead Minnow	☐	One	Few	Many
Stickleback	☐	One	Few	Many
Central Mudminnow	☐	One	Few	Many
Carp	☐	One	Few	Many
Bullhead	☐	One	Few	Many
Redbelly Dace	☐	One	Few	Many
Other _____	☐	One	Few	Many
Frog (seen or heard in wetland)	☐	One	Few	Many
Tadpoles	☐	One	Few	Many
Adults: _____	☐	One	Few	Many
Northern Leopard	☐	One	Few	Many
Green	☐	One	Few	Many
Other _____	☐	One	Few	Many
Salamander	☐	One	Few	Many
Juvenile: _____	☐	One	Few	Many
Adults: _____	☐	One	Few	Many
Birds (seen or heard in wetland)	☐	One	Few	Many
Red-Winged Blackbird	☐	One	Few	Many
Yellow Headed Blackbird	☐	One	Few	Many
Mallard	☐	One	Few	Many
Wood Duck	☐	One	Few	Many
Canada Goose	☐	One	Few	Many
Sora	☐	One	Few	Many
Great Blue Heron	☐	One	Few	Many
Others _____	☐	One	Few	Many

DIPNET SAMPLE

☐ **D-net Sample Taken** **TIME:**

D-net taken by: **DATE:** ____ / ____ / ____

TEMP:

Number of D-nets Taken: _____

D-net Sample #	**~ Depth (m)**	**#Jars**
1	_____	_____
2	_____	_____

SAMPLE SITE INFORMATION

Wetland Bottom: Firm Soft Mucky Help!!

Comments:

Aquatic Vegetation:

Submergent: None Sparse Moderate Dense

Emergent: None Sparse Moderate Dense

Floating: None Sparse Moderate Dense

Filament. Algae: None Sparse Moderate Dense

Shoreline Vegetation:

Grassy Shrubs Wooded Other

Comments:

Weather: Sunny Partly-Cloudy Overcast Windy Calm Rainy

PHOTOGRAPHIC DOCUMENTATION

Looking left from sampling location: #

Looking opposite shore from sampling location: #

Looking right from sampling location: #

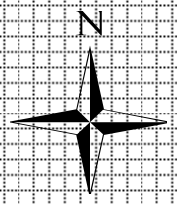
Best Overall View of Wetland: #

WATER CHEMISTRY

DEPARTMENT OF HEALTH SAMPLES	FIELD MEASUREMENTS
☐ **125 ml General**	☐ **pH ------**
☐ **250 ml Nutrient**	☐ **Specific Conductivity ---**
☐ **Preserved with H_2SO_4**	☐ **Water Temp ---** **^{o}C**
WATER CHEM. SAMPLING NOTES	☐ **Dissolved Oxygen ---** **mg/L**
	% Saturation ---
	time of measurement____ : ____ : ____
	☐ **T-tube reading ---**
	60-cm tube **100-cm tube**
	symbol: **cm** **symbol:** **cm**
	screw: **cm** **screw:** **cm**
	☐ **Color Wheel ----** **PCU**

SKETCH OF WETLAND

Include roads/trails used to access site, most convenient parking, location of sampling, any other relevant info.



APPENDIX B. Measuring Wetland Water Clarity with Transparency Tubes

Note: Do not wear sunglasses while taking measurements, as this affects the accuracy of your reading. Start with 60-cm tube and go to 100-cm tube if needed (see step#3).

ACTION STEPS

1. Collect water sample in tube or if needed use a 1 or 2 L General bottle to fill tube. When collecting with tube, hold hand over open end to keep entire volume of water within the tube when you raise the tube above the water surface. Use of bottle to fill tube may be required when shallow depths preclude the collection of a clean sample with the tube.
   - Collect sample where sediments have not been stirred up.
   - Avoid collecting algae, duckweed, or any other material in the tube.

2. Take tube readings in open conditions. Avoid direct sunlight by turning your back to the sun if necessary.
   - Take reading on shore or in shallow water so that bottom of 100-cm tube is not submerged.

3. While looking down into tube, open the valve at the bottom and slowly release water until you can JUST begin to make out the black and white symbol on the bottom of the tube. Record this depth.
   - If the symbol is visible when the 60-cm tube is full, begin again at step #1 with 100-cm tube.
   - If the symbol is visible when the 100-cm tube is full, record ">100" on the data sheet for the symbol depth. Steps 4 & 5 not necessary.

4. Slowly release more water until the screw in the middle of the black and white symbol is visible. Record this depth.
   - When using 100-cm tube, if clarity drops below 60-cm, take a transparency reading with both tubes.

5. Calculate the average of the two depths taken in steps 3 and 4. This last step can be done during data entry.