EPA/620/R-94/004F
September 1998

ENVIRONMENTAL MONITORING AND ASSESSMENT PROGRAM-SURFACE WATERS:

FIELD OPERATIONS AND METHODS FOR MEASURING THE ECOLOGICAL CONDITION OF WADEABLE STREAMS

Edited by

James M. Lazorchak[1], Donald J. Klemm[1], and David V. Peck[2]

[1] U.S. Environmental Protection Agency
Ecosystems Research Branch
Ecological Exposure Research Division
National Exposure Research Laboratory
Cincinnati, OH 45268

[2] U.S. Environmental Protection Agency
Regional Ecology Branch
Western Ecology Division
National Health and Environmental Effects Research Laboratory
Corvallis, OR 97333

NATIONAL EXPOSURE RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

NATIONAL HEALTH AND ENVIRONMENTAL EFFECTS RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

SECTION 5
WATER CHEMISTRY

by
Alan T. Herlihy[1]

There are two components to collecting water chemistry information: Collecting samples of stream water to ship to the analytical laboratory, and obtaining *in situ* or streamside measurements of specific conductance, dissolved oxygen, and temperature. At each stream, teams fill one 4-L container and two 60 mL syringes with streamwater. These samples are stored in a cooler packed with plastic bags filled with ice and are shipped or driven to the analytical laboratory within 24 hours of collection (see Section 3). The primary purposes of the water samples and the field chemical measurements are to determine:

- Acid-base status
- Trophic condition (nutrient enrichment)
- Chemical Stressors
- Classification of water chemistry type.

Water from the 4-L bulk sample is used to measure the major cations and anions, nutrients, total iron and manganese, turbidity and color. The syringe samples are analyzed for pH, dissolved inorganic carbon, and monomeric aluminum species. Syringes are used to seal off the samples from the atmosphere because the pH, dissolved inorganic carbon (DIC), and aluminum concentrations will all change if the streamwater equilibrates with atmospheric CO_2. Overnight express mail for these samples is required because the syringe samples need to be analyzed, and the 4-L bulk sample needs to be stabilized (by filtration and/or acidification) within a short period of time (72 hours) after collection.

In situ and streamside measurements are made using field meters and recorded on standard data forms. Specific conductance (or conductivity) is a measure of the ability of the water to pass an electrical current which is related to the ionic strength of a solution. Dissolved oxygen (DO) is a measure of the amount of oxygen dissolved in solution. In

[1] Department of Fisheries and Wildlife, Oregon State University, c/o U.S. EPA, 200 SW 35th St., Corvallis, OR 97333

natural waters, minimal concentrations of oxygen are essential for survival of most aquatic organisms. Measures of DO and temperature are used to assess water quality and the potential for healthy aerobic organism populations. Most of the procedures outlined in this section are similar to the ones utilized by the EPA in streams for the National Surface Water Survey (Kaufmann et al., 1988) and have been adapted from the Survey's field operations handbook (U.S. EPA, 1989).

5.1 SAMPLE COLLECTION

Before leaving the base location, package the sample containers (one 4-L cubitainer and two 60 mL syringes) and the stream sample beaker to prevent contamination (see Section 3). Fill out a set of water chemistry sample labels as shown in Figure 5-1. Attach a completed label to the cubitainer and each syringe and cover with clear tape strips as described in Section 3. Make sure the syringe labels do not cover the volume gradations on the syringe. In the field, make sure that the labels all have the same sample ID number (barcode), and that the labels are securely attached.

The procedure to collect a water chemistry sample is described in Table 5-1. The sample is collected from the middle of the stream channel at the X-site, unless no water is present at that location (see Section 4). Throughout the sampling process, it is important to take precautions to avoid contaminating the sample. Rinse all sample containers three times with portions of stream water before filling them with the sample. Many of the streams have a very low ionic strength and can be contaminated quite easily by perspiration from hands, sneezing, smoking, insect repellent, or other chemicals used when collecting other types of samples. Thus, make sure that none of the water sample contacts your hands before going into the cubitainer. All of the chemical analyses conducted using the syringe samples are affected by equilibration with atmospheric carbon dioxide; thus, it is essential that no outside air contact the syringe samples during or after collection.

Record the information from the sample label on the Sample Collection Form as shown in Figure 5-2. Note any problems related to possible contamination in the comments section of the form.

5.2 FIELD MEASUREMENTS

Table 5-2 presents the procedures for obtaining field measurement data for the water chemistry indicator. The conductivity and dissolved oxygen meters are checked in

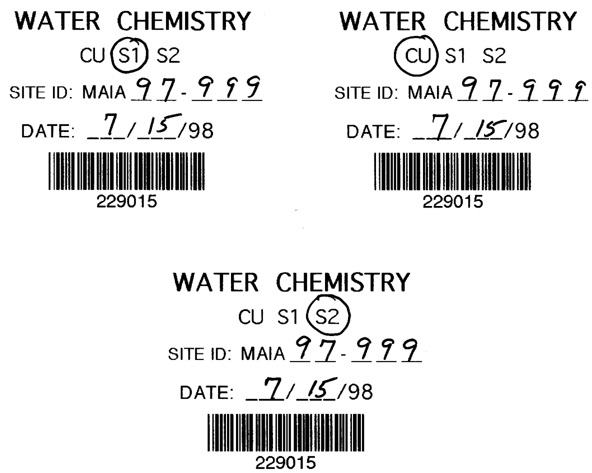

Figure 5-1. Completed sample labels for water chemistry.

the field using the same procedures as those used at a base location (Section 3). The quality control check sample solution (QCCS) is prepared according to directions presented in Section 3. The results of field checks of these meters, as well as the measured values for specific conductance, dissolved oxygen, and stream temperature, are recorded on the Field Measurement Form as shown in Figure 5-3.

5.3 EQUIPMENT AND SUPPLIES

A list of equipment and supplies required to collect samples and field data for the water chemistry indicator is presented in Figure 5-4. This checklist is similar to the checklist presented in Appendix A, which is used at the base location (Section 3) to ensure that all of the required equipment is brought to the stream. Use this checklist to ensure that equipment and supplies are organized and available at the stream site in order to conduct the activities efficiently.

5.4 LITERATURE CITED

Kaufmann, P., A. Herlihy, J. Elwood, M. Mitch, S. Overton, M. Sale, J. Messer, K. Reckhow, K. Cougan, D. Peck, J. Coe, A. Kinney, S. Christie, D. Brown, C. Hagley, and Y. Jager. 1988. *Chemical Characteristics of Streams in the Mid-Atlantic and Southeastern*

TABLE 5-1. SAMPLE COLLECTION PROCEDURES FOR WATER CHEMISTRY

Collect the water samples from the X-site in a flowing portion near the middle of the stream.

1. Rinse the 500 mL sample beaker three times with streamwater, Discard the rinse downstream.

2. Remove the cubitainer lid and expand the cubitainer by pulling out the sides. **NOTE: DO NOT BLOW into the cubitainers to expand them, this will cause contamination.**

3. Fill the beaker with streamwater and slowly pour 30-50 mL into the cubitainer. Cap the cubitainer and rotate it so that the water contacts all the surfaces. Discard the water downstream. Repeat the above rinsing procedure two more times.

4. Collect additional portions of streamwater with the beaker and pour them into the cubitainer. Let the weight of the water expand the cubitainer. The first two portions will have to be poured slowly as the cubitainer expands. Fill the cubitainer to its maximum volume. Rinse the cubitainer lid with streamwater. Eliminate any air space from the cubitainer, and cap it tightly. Make sure the cap is tightly sealed and not on at an angle.

5. Place the cubitainer in a cooler (on ice or streamwater) and shut the lid. If a cooler is not available, place the cubitainer in an opaque garbage bag and immerse it in the stream.

6. Submergie a 60-mL syringe halfway into the stream and withdraw a 15-20 mL aliquot. Pull the plunger to its maximum extension and shake the syringe so the water contacts all surfaces. Point the syringe downstream and discard the water by depressing the plunger. Repeat the rinsing procedure two more times.

7. Submerge the syringe into the stream again and **slowly** fill the syringe with a fresh sample. Try not to get any air bubbles in the syringe. If more than 1-2 tiny bubbles are present, discard the sample and draw another one.

8. Invert the syringe (tip pointing up), and cap it with a syringe valve. Tap the syringe lightly to detach any trapped air bubbles. With the valve open, expel the air bubbles and a small volume of water, leaving between 50 and 60 mL of sample in the syringe. Close the syringe valve. If any air bubbles were drawn into the syringe during this process, discard the sample and fill the syringe again (step 8).

9. Repeat Steps 6 through 8 with a second syringe. Place the syringes together in the cooler or in the streamwater with the cubitainer.

10. Record the barcode number (Sample ID) on the Sample Collection Form along with the pertinent stream information (stream name, ID, date, etc.). Note anything that could influence sample chemistry (heavy rain, potential contaminants) in the Comments section. If the sample was collected at the X-site, record an “X” in the “STATION COLLECTED” field. If you had to move to another part of the reach to collect the sample, place the letter of the nearest transect in the “STATION COLLECTED” field. Record more detailed reasons and/or information in the Comments section.

11. After carrying the samples out to the vehicles, place the cubitainer and syringes in a cooler and surround with 1 gallon self-sealing plastic bags filled with ice.

Reviewed by (initial): DP

SAMPLE COLLECTION FORM - STREAMS (continued)

SITE NAME: Mill Creek DATE: 7 / 15 / 97 VISIT: ☒1 ☐2

SITE ID: M A I A 9 7 - 9 9 9 TEAM ID (X): ☒1 ☐2 ☐3 ☐4 ☐5 ☐6 ☐7 ☐8

CHEMISTRY AND MICROBIAL WATER SAMPLE (Chem: 4-L Cubitainer and 2 Syringes, Micro: Glass Bottle)

	SAMPLE ID (BARCODE)	TRANSECT	FLAG	COMMENTS
CHEMISTRY	229015	X		
MICROBIAL				

SEDIMENT TOXICITY SAMPLES

SAMPLE ID (BARCODE)	FLAG	COMMENTS
229011		

FISH TISSUE SAMPLES - PRIMARY SAMPLE (min. 50g total wgt)

SAMPLE ID (BARCODE) → 229013

LINE	SPECIES CODE	COMMON NAME	NUMBER OF INDIVIDUALS	FLAG
P1	NOCOLE	Bluehead chub	16	F1

IS COMPOSITE SAMPLE COMPOSED OF INDIVIDUALS COLLECTED FROM THROUGHOUT REACH? (X) → ☒ YES ☐ NO

IF NO, EXPLAIN:

FISH TISSUE SAMPLES - SECONDARY SAMPLE (where available; 5 individuals)

SAMPLE ID (BARCODE) → 229012

LINE	SPECIES CODE	COMMON NAME	TOTAL LENGTH (MM)	FLAG
S1	CATOCO	White sucker	128	
S2	CATOCO	white sucker	125	
S3	CATOCO	white sucker	134	
S4	CATOCO	white sucker	128	
S5	CATOCO	white sucker	125	

IS COMPOSITE SAMPLE COMPOSED OF INDIVIDUALS COLLECTED FROM THROUGHOUT REACH? (X) → ☒ YES ☐ NO

IF NO, EXPLAIN:

LINE	COMMENT OR FLAG EXPLANATION FOR FISH TISSUE
P1	F1 = 16 individuals weighed 60 g.

Flag codes: K= Sample not collected; U= Suspect sample; F1, F2, etc.= misc. flag assigned by field crew. Explain all flags in Comments sections.

Rev. 06/02/97 (st__saco.97) SAMPLE COLLECTION FORM - STREAMS - 2

Figure 5-2. Sample Collection Form (page 2), showing data recorded for water chemistry samples.

TABLE 5-2. PROCEDURES FOR STREAMSIDE AND IN SITU CHEMISTRY MEASUREMENTS

Specific Conductance

1. Check the batteries and electronic functions (e.g., zero, “red line") of the conductivity meter (or a conductivity pen) as instructed by the operating manual.

2. Insert the probe into the “RINSE” container of the quality control check sample (QCCS) and swirl for 3 to 5 seconds. Transfer the probe to the "TEST" container of QCCS let stabilize for 20 seconds. Record the conductivity of the QCCS on the Field Measurement Form.

   If the measured conductivity is not within 10% or 10 :S/cm of theoretical value, repeat the measurement process. If the value is still unacceptable, flag the conductivity data on the Field Measurement Form.

3. Submerge the probe in and area of flowing water near the middle of the channel at the same location where the water chemistry sample is collected. Record the measured conductivity on the Field Measurement Form.

Dissolved Oxygen and Temperature

1. Inspect the probe for outward signs of fouling and for an intact membrane. Do not touch the electrodes inside the probe with any object. Always keep the probe moist by keeping it inside its calibration chamber.

2. Check the batteries and electronic functions of the meter as described in the operating manual. Record the results of these checks on the Field Measurement Form.

2. Calibrate the oxygen probe in water-saturated air as described in the operating manual. Allow at least 15 minutes for the probe to equilibrate before attempting to calibrate. Try to perform the calibration as close to stream temperature as possible (not air temperature) by using stream water to fill the calibration chamber prior to equilibration. For doing the elevation correction, the elevation of the sample site is given on the site Information sheet in the dossier for the site. Record the pertinent calibration information on the Field Measurement Form.

3. After the calibration, submerge the probe in midstream at mid-depth at the same location where the water chemistry sample is collected. Face the membrane of the probe upstream, and allow the probe to equilibrate. Record the measured DO and stream temperature on the Field Measurement Form. If the DO meter is not functioning, measure the stream temperature with a field thermometer and record the reading on the Field Measurement Form along with pertinent data flags and comments.

   NOTE: Older model dissolved oxygen probes require a continuous movement of water (0.3 to 0.5 m/s) across the probe to provide accurate measurements. If the velocity of the stream is appreciably less than that, jiggle the probe in the water as you are taking the measurement.

Reviewed by (initial): *[initials]*

FIELD MEASUREMENT FORM - STREAMS/RIVERS

SITE NAME: MILL CREEK DATE: 7 / 15 / 97 VISIT: ☒1 ☐2

SITE ID: MAIA97- 9 9 9 TEAM ID (X): ☒1 ☐2 ☐3 ☐4 ☐5 ☐6 ☐7 ☐8

WEATHER CONDITIONS (X)

CLOUD COVER	☒ < 5%	☐ 5-25%	☐ 25-50%	☐ 50-75%	☐ >75%
PRECIPITATION	☒ NONE	☐ LIGHT	☐ MODERATE	☐ HEAVY	
PREVIOUS PRECIPITATION (24 H)	☐ NONE	☒ LIGHT	☐ MODERATE	☐ HEAVY	
AIR TEMPERATURE XX	28 °C				

IN SITU MEASUREMENTS

STATION ID: E — Assume X-site unless marked

		FLAG	COMMENTS
QCCS COND µS/CM	72		
STREAM/RIVER COND µS/CM	500		
STREAM/RIVER DO MG/L	4.6		
STREAM/RIVER TEMP °C	20.0		

STREAM/RIVER METABOLISM DETERMINATION

INITIAL O_2 (MG/L)	INITIAL INCUBATION TEMP. (°C)	INCUBATION TIME (24-HR TIME) START (HH:MM)	INCUBATION TIME (24-HR TIME) FINISH (HH:MM)	DURATION OF INCUBATION (HH:MM)	FLAG	COMMENTS
4.9	20.0	11:35	2:40	3:05		

SAMPLE ID (BARCODE)	FINAL O_2 (MG/L)	FLAG	COMMENTS
999991	2.0		
999992	1.9		
999993	1.8		
999994	1.9		
999995	1.1		
BLANK	4.5		

OXYGEN METER CALIBRATION INFORMATION

MEMBRANE CHECK ☒ ELECTRONIC ZERO ☒ RED LINE: ☒

CALIBRATION CHAMBER TEMPERATURE:	27.9 °C	SATURATED O_2 @ TEMP.:	7.83 MG/L
STATION ELEVATION (FROM TOPO. MAP OR ALTIMETER):	1080 FT	ELEVATION CORRECTION FACTOR: ×	0.96
The calibration value is obtained by multiplying the saturated DO concentration times an elevation correction factor (obtained from the tables on the back of the YSI meter). Adjust the meter reading to the calibration value.		CALIBRATION VALUE:	7.52 MG/L
		COMMENTS:	

Flag Codes: K = no measurement or observation made; U= suspect measurement or observation; Q = unacceptable QC check associated with measurement; F1, F2, etc. = miscellaneous flags assigned by each field crew. Explain all flags in comments section.

Rev. 06/02/97 (strvfldm.97) FIELD MEASUREMENT FORM - STREAMS/RIVERS - 1

Figure 5-3. Field Measurement Form (page 1), showing data recorded for water chemistry.

EQUIPMENT AND SUPPLIES FOR WATER CHEMISTRY

QTY.	Item	
1	Dissolved oxygen/Temperature meter with probe	
1	DO repair kit containing additional membranes and probe filling solution	
1	Conductivity meter with probe	
1	500-mL plastic bottle of conductivity QCCS labeled “Rinse” (in plastic bag)	
1	500-mL plastic bottle of conductivity QCCS labeled “Test” (in plastic bag)	
1	500-mL plastic bottle of deionized water to store conductivity probe	
1	Field thermometer	
1	500 mL plastic beaker with handle (in clean plastic bag)	
1	4-L cubitainer with completed sample label attached (in clean plastic bag)	
2	60 mL plastic syringes (with Luer type tip) with completed sample labels attached	
1	Plastic container with snap-on lid to hold filled syringes	
2	Syringe valves (Mininert® with Luer type adapter, or equivalent, available from a chromatography supply company)	
1	Cooler with 4 to 6 plastic bags (1-gal) of ice OR a medium or large opaque garbage bag to store the water sample at streamside	
1	Sample Collection From	
1	Field Measurement Form	
	Soft-lead pencils for filling out field data forms	
	Fine-tipped indelible markers for filling out labels	
1 copy	Field operations and methods manual	
1 set	Laminated sheets of procedure tables and/or quick reference guides for water chemistry	

Figure 5-4. Checklist of equipment and supplies for water chemistry.

United States. Volume I: Population Descriptions and Physico-Chemical Relationships. EPA 600/3-88/021a. U.S. Environmental Protection Agency, Washington, D.C.

U.S. EPA. 1989. *Handbook of Methods for Acid Deposition Studies: Field Operations for Surface Water Chemistry*. EPA 600/4-89/020. U.S. Environmental Protection Agency, Office of Research and Development, Washington, D.C.