Minnesota Pollution Control Agency

Biological Monitoring Program

WATER CHEMISTRY ASSESSMENT PROTOCOL FOR STREAM MONITORING SITES

I. PURPOSE

To describe the methods used by the Minnesota Pollution Control Agency's (MPCA) Biological Monitoring Program to collect water chemistry information at stream monitoring sites for the purpose of assessing water quality and developing biological criteria.

II. SCOPE/LIMITATIONS

This procedure applies to all integrated assessments of rivers and streams. An integrated assessment involves the collection of biological (fish and macroinvertebrate communities), physical habitat and chemical information to assess stream condition.

III. GENERAL INFORMATION

Sites may be selected for monitoring for a number of reasons including: 1) sites selected for condition monitoring as part of Intensive Watershed Monitoring (IWM), 2) sites randomly selected as part of the Environmental Monitoring and Assessment Program (EMAP), 3) sites selected for the development and calibration of biological criteria, and 4) sites selected for stressor identification. Although the reasons for monitoring a site vary, water chemistry assessment protocols outlined in this document apply to all stream monitoring sites unless otherwise noted.

IV. REQUIREMENTS

A. Qualifications of crew leaders: The crew leader must be a professional aquatic biologist with a minimum of a Bachelor of Science degree in aquatic biology or closely related specialization. He or she must have a minimum of six months field experience in physical habitat sampling methodology. Field crew leaders should also possess excellent map reading skills and a demonstrated proficiency in the use of a GPS (Global Positioning System) receiver and orienteering compass.

B. Qualifications of field technicians/interns: A field technician/intern must have at least one year of college education and coursework in environmental and/or biological science.

C. General qualifications: All personnel conducting this procedure must have the ability to perform rigorous physical activity. It is often necessary to wade through streams and/or wetlands, canoe, or hike for long distances to reach a sampling site.

V. RESPONSIBILITIES

A. Field crew leader: Implement the procedures outlined in the action steps and ensure that the data generated meets the standards and objectives of the Biological Monitoring Program.

B. Technicians/interns: Implement the procedures outlined in the action steps, including maintenance and stocking of equipment, data collection and recording.

VI. 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: Ten percent of sites sampled in any given year are resampled 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 technical personnel are following procedures in accordance with this SOP.

VII. TRAINING

A. All inexperienced personnel will receive instruction from a trainer designated by the program manager. Major revisions in this protocol require that all personnel be re-trained in the revised protocol by experienced personnel.

B. The field crew leader will provide instruction in the field and administer a field test to ensure personnel can execute this procedure.

VIII. ACTION STEPS

A. Equipment list: Verify that all necessary items are present before commencement of this procedure (Table 1).

B. Data collection method: The location and length of the sampling reach is determined during site reconnaissance (see SOP--"***Reconnaissance Procedures for Initial Visit to Stream Monitoring Sites***"). Sampling is conducted during daylight hours within the summer index period of mid-June through mid-September. Sampling should occur when streams are at or near base-flow. Water chemistry is sampled immediately prior to fish sampling.

One data sheet is required for the water chemistry assessment. One copy of the **Visit Summary** form is needed for each site. A copy of this form is attached. Guidelines for filling out the data sheet are described in the following pages.

C. Visit Summary Data Sheet

This data sheet contains location information, water chemistry data and channel characteristics of the station. Some of the data is derived from maps or from the other data sheets. Record the following information on this data sheet:

E.1. Visit Information

a) *Field Number* – Same as for **Station Features** data sheet.

b) *Date* – Same as for **Station Features** data sheet.

c) *Stream Name* – The name of the stream as shown on the most recent USGS 7.5" topographic map. Include all parts of the name (i.e. "North Branch", "Creek", "River", "Co. Ditch", etc.).

d) *Crew* – Same as for **Stream Features** data sheet.

e) *Visit Result and Reason* – The result of the sampling trip, typically as it pertains to biological assemblage collection. Check only one of the available choices. The "reason" is an explanation justifying the sampling event "result" chosen for the visit.

The *visit result* is "reportable" when sampling is conducted for the first time at a station and no problems are encountered that would render the data questionable. If subsequent sampling trips are made to the same station and no sampling problems occur, the *visit result* is considered a "replicate". The *visit result* is "non-reportable" when a sampling event is compromised due to technological error, insufficient effort, weather or

flow events, or the use of field methods not congruent to MPCA protocols. The *visit result* is "not sampled" when conditions at a monitoring site have changed since spring reconnaissance that prevent or dictate that a biological sampling event should no longer be conducted at the site.

The *visit result reason* provides additional information about the sampling conditions encountered at a site that explains the rationale for the selected *visit result*. The reason is "sufficient and representative sample" when no problems are encountered and >25 fish are sampled. The reason is "low sample size, (<25 fish)" when no problems have occurred but there are < 25 fish sampled. "Outside base flow, high" indicates that high stream flow conditions limited the ability to collect a representative sample. "Unsatisfactory taxis" refers to poor taxis due to equipment malfunctions or extremely high or low conductivity levels. Taxis, refers to the response of the organism to stimulus. As electro-fishing is the only means used to capture fish for MPCA biological surveys, it is essential to ascertain that the fish responded in the expected manner to the stimulus and that the equipment functioned effectively so that a representative sample was obtained. "Non-sampleable" reasons that could dictate a sampling event no longer be conducted at a monitoring site includes; insufficient flow, a definable channel is no longer present, or a recent beaver dam has impounded the site.

f) *GPS File Name* – The unique identifier of a rover file assigned by the GPS unit. If a GPS file is taken (to record the location of a sampling site), the unit will assign an eight-digit code consisting of a file prefix, date stamp, and time stamp that uniquely identifies that file. In most instances, it is not necessary to take a GPS file during the sampling visit because sampling sites are located and flagged during site reconnaissance. However, circumstances may occur that necessitate a file be taken during the sampling visit. These include but are not limited to: original reconnaissance file unreliable or inaccurate, flagging cannot be located, initial site location determined to be incorrect, and GPS file not obtained during initial site reconnaissance. If sampling and initial site reconnaissance are conducted at the same time, the GPS information should be recorded as part of the reconnaissance protocol. Consult the GPS user's manual and SOP--"***Reconnaissance Procedures for Initial Site Visit to Stream Monitoring Sites***" for additional guidance on GPS operation and protocol.

g) *GPS Coordinates* – The X and Y coordinates for the site in decimal degrees.

E.2. Field Water Chemistry: Water chemistry parameters should be sampled immediately prior to fish sampling. All water chemistry parameters are measured from the same general location at a representative stream cross-section within the sampling reach. Samples are taken at a point that is judged to represent the water quality of the total instantaneous flow at the cross-section. Avoid sampling areas that are poorly mixed, contain springs, or are upstream of or immediately adjacent to tributaries within the sampling reach. Water chemistry measurements and water samples are taken at an intermediate depth in the water column without disturbing substrate materials or collecting floating materials and constituents from the water surface. Refer to the manufacturer's owners manual for guidance concerning the calibration and operation of water quality meters.

a) *Time* – The time of day (24-hour clock) that field water chemistry parameters are measured.

b) *Air Temp* – The ambient air temperature (ºC) at the time of sampling, measure to the nearest degree with a dry thermometer.

c) *Water Temp* – The water temperature (ºC) of the station at the time of sampling, measure to the nearest tenth of a degree with a thermometer or water quality meter.

d) *HACH Meter #* – Indicate which meter was utilized during sampling.

e) *Conductivity* – Temperature compensated conductivity, or *specific conductance*, is the parameter actually being determined and is a measure of the ability of water to carry an electrical current. Consult your conductivity meter's manual for guidance measuring specific conductance (measured in mmhos/cm) compensated for temperature to 25 °C.

f) *pH* – A measure of the negative log of the hydrogen ion [H+] concentration in the water. Pure water has a pH of 7.00 and is considered neutral. Measure pH utilizing a temperature compensating pH meter.

g) *Dissolved Oxygen (DO)* – The amount of oxygen present in a water sample, expressed as milligrams of oxygen per liter of water (mg/L). Two water samples should be taken and measured for dissolved oxygen concentrations using a DO meter.

h) *% DO Saturation* – The relative proportion of oxygen that is dissolved in water compared to what the water can hold for a given temperature and altitude. Streams that have a dissolved oxygen saturation percent value of 80- 120% are considered to be excellent. Water that is super-saturated (>120%) may indicate conditions where excess nutrients are fueling the growth of plants and algae above normal which may cause diel oxygen swings that are a stress biological communities.

i) *Secchi Tube* – A measure of water clarity, an indicator of the water's ability to transmit light. Stream secchi serves as an indirect measure of the amount of dissolved and suspended materials present. Measure (nearest cm) with a secchi tube, a clear tube100 cm in length with a secchi disk on a string.

j) *Water Level* – An estimation of water level as it relates to summer base flow expectations. Check the appropriate category and measure the vertical distance (nearest 0.1 m) above or below the normal water line. In most streams, the "normal" water level can be determined with relative ease by observing channel characteristics.

k) *Precipitation* – Indicate current precipitation condition if present and comment regarding rainfall intensity in the comments section below. Information could provide insight to samples potentially collected during high flow situations.

E.3 Lab Water Chemistry: Water samples taken for laboratory analyses typically include total phosphorus (P), total suspended solids (TSS), total suspended volatile solids (TSVS), ammonia nitrogen (NH3+NH4), and nitrite-nitrate (NO2+NO3). Additional parameters may be measured in special circumstances. Samples taken for laboratory analyses are subject to the same general guidelines concerning sampling location and time as outlined above under field water chemistry.

Sterilized sample bottles are obtained from an accredited environmental laboratory (e.g. the Minnesota Department of Health (MDH) or A.W. Research Laboratories, etc.). Before collecting samples, record the date and field number on the container label with a waterproof pen or pencil. Collect a 250 ml nutrients sample and a one-liter general chemistry sample for laboratory analysis. The bottles should be lowered mouth down to an intermediate depth and then turned upstream to collect the sample; rinsing the sample bottle is not necessary. Immediately after sample collection, 5 ml of 10% sulfuric acid preservative solution is added to the nutrients sample. Both sample bottles must be stored at 4°C and shipped to an accredited water lab within minimum holding times. Note: Do not take water samples from biological sampling visits where more intensive water monitoring is already being conducted as part of IWM (e.g. 10X, WWTF).

a) *Chem. Sample ID* – Indicate field number and label recorded on sample jar.

b) *Collection Time (field sample)* – The time of day (24-hour clock) that water samples for laboratory analysis are collected.

c) *Chem. Sample ID (field duplicate)* – Indicate field number and label recorded on sample jar.

d) *Collection Time (field duplicate)* – A field duplicate is a second sample taken immediately following an initial sample in the same manner and location. Duplicate samples are taken at 10% of all sampling sites for quality assurance and control (QA/QC) purposes. If a duplicate water sample is taken, record the time (24 hour clock) here.

E.4 Tape-down Measurement: *(For convenience, a brief description of the protocol is included here; see the Protocol for Taking Tape-down Measurements for a more complete description).*

For 10x chemistry sites: Locate the reference mark used for previous tape-down measurements (a copy of this form should have been made during the first visit in May and handed to the lead biologist for the watershed). Conduct the tape-down measurement using the reference mark previously established for the 10x chemistry

location. If this information is not available, establish a temporary reference mark and describe the marks made (e.g., 3 black lines on US side of middle railing) and location of the reference marks (e.g., 30 feet from flat edge of cement railing on right bank) on the **Visit Summary** form.

For biological sites: Locate a surface above the water from which a tape-down measurement can be taken. For most streams, the tape-down measurement can be taken from a bridge or a culvert. If the bridge has a double or triple culvert, choose the culvert that appears to contain the thalweg (deeper water). Record the location from which the measurement was taken (e.g., upstream side, apex of culvert) on the **Visit Summary** form. Consider making a permanent mark with spray paint or a black Sharpie marker if at a double or triple culvert, or if the culvert is slanted. This will ensure that the macroinvertebrate crews will be able to make a comparable measurement in a future visit.

a) T*ape Down Length (reference to water height)* – Record the distance (1/100ths ft) between the reference mark and the top of water. If the water is choppy, record the distance from the reference mark to the crest (top) of the waves.

b) *Location and Description of Reference Mark* – Describe the location used for the tape-down measurement if not previously established. If applicable, describe the type of mark(s) made that will be used as the reference mark (tip of blue arrow, center of 3 black vertical lines, center of cross, etc.)

E.5 Channel Characteristics

a) *Transect Spacing* – Document the distance (m) that was used to space transects from one another (only applicable at stations where a quantitative physical habitat survey is conducted, see Quantitative Habitat SOP (**Transect** data sheet section)).

b) *Station Length* – The actual length (m) of the sampling reach as determined during the quantitative physical habitat assessment (Only applicable at stations where a quantitative physical habitat survey is conducted, see Quantitative Habitat SOP (**Stream Features** data sheet section). The station length should be recorded directly from the **Stream Features** data sheet, as measured from the start of the station to the upstream end of the reach, rounded to the nearest meter. This measurement of station length is considered more accurate than the measurement conducted during the initial site reconnaissance.

c) *Channel Condition* – The condition of the stream channel at the station, check the category that best describes the state of the stream channel:

Natural Channel: Stream channel has never been modified; channel morphology represents a natural condition and exhibits no obvious diversion or alteration of the channel.

Recent Channelization: Stream channel recently modified (usually within 2 years). Evidence of recent dredging/channel diversion activity is evident; e.g. unvegetated dredge spoil on bank(s).

Old Channelization: Stream channel has been modified in the past.

d) *Visual Condition* – Rate the general appearance, recreational suitability, and condition of the stream using ratings and codes included on the backside of the **Visit Summary** form. General descriptions for each category are as follows:

Appearance:

1A - Clear – crystal clear, transparent water.
1B - Tea-colored – transparent water, which has been colored by dissolved organic matter from upstream bogs or wetlands.
2 - Cloudy – not quite crystal clear; cloudy white, gray or light brown.
3 - Muddy – cloudy brown due to high sediment levels.
4 - Green – due to algae growth; indicative of excess nutrients released into the stream.
5 - Muddy and Green – a combination of cloudy brown from high sediment levels and green from algae.

Recreational Suitability:

1 - Beautiful, could not be better.
2 - Very minor aesthetic problems: excellent for body-contact recreation (swimming, wading, etc.).
3 - Body-contact recreation and aesthetic enjoyment slightly impaired.
4 - Recreation potential and level of enjoyment of the stream substantially reduced (would not swim but boating/canoeing is okay).
5 - Swimming and aesthetic enjoyment of the stream nearly impossible.

Stream condition:

The present water level in relation to the baseflow water level: **N** = Normal, **L** = Low, **Z** = No flow, **D** = Dry, **I** = Interstitial, **H** = High.

Description of water velocity: **SW** = Swift, **SL** = Slow, **MO** = Moderate.

Description of water clarity: **C** = Clear, **M** = Muddy, **O** = Other.

e) *Does the site appear to be low gradient?* – Using the conditions described within the check-boxes on the back of the **Visit Summary** form and other in-field observations, determine if the site appears to be low gradient. Characteristics of many low gradient sites include:

Flow velocity only slow, or slow and moderate.
Riffles absent or representing very low percentage of reach (typically <5%).
Dominated (>80%) by fines (silt, sand and detritus), coarse substrate uncommon (<10%).
Wetland vegetation (cattails, arum, water lily, etc) in channel and riparian zone.
It looks like a low gradient stream.

E.5. Comments/Notes: Record any additional information about the station in the space provided.

Table 1. Equipment List – This table identifies all equipment needed in the field in order to implement the sampling protocol as described.

Water Chemistry Sampling

Thermometer – for measuring air and water temperature

Multi – parameter meter – with the following three probes:

1. *Conductivity probe* – for measuring conductivity
2. *Dissolved oxygen probe* – for measuring dissolved oxygen
3. *pH probe* – for measuring pH

Transparency tube – for measuring stream water transparency

1-L plastic bottle – to collect general chemistry sample for lab analysis

250-ml plastic bottle – to collect nutrients sample for lab analysis

5-ml of 10% sulfuric acid – for preserving nutrients sample

Cooler and ice – for holding and preserving water samples

Tape Down Distance Measurement

Weighted measuring tape (in 1/10ths of feet) – for measuring distance between reference mark and water surface

Paint marker or can of spray paint (blue) – for indicating location of reference mark on bridge or culvert

Black Sharpie marker – alternate for making reference marks on bridge

Miscellaneous

Clipboard – to store forms and record data

Forms – for recording data

Pencil – for filling out forms

GPS – to locate and document sampling location (if necessary)

VISIT SUMMARY MPCA

VISIT INFORMATION ==========

Field Number:_____ Stream Name:_____

Date (mm/dd/yy):_____ Crew:_____

Visit Result and Reason (check one in appropriate column):

Reportable
- ☐ Reportable: Sufficient and representative sample
- ☐ Reportable: Low sample size (<25 fish)

Non-reportable
- ☐ Non-reportable: Unsatisfactory taxis
- ☐ Non-reportable: Outside base flow, high

Replicate
- ☐ Replicate: Sufficient and representative sample
- ☐ Replicate: Low sample size (<25 fish)

Not sampled
- ☐ Non-sampleable: Insufficient flow
- ☐ Non-sampleable: Beaver dam – too deep/wide
- ☐ Non-sampleable: No definable channel
- ☐ Non-sampleable: Other (explain in comments)

If **GPS** coordinates taken during site visit:

DS FileName:_____ **X** FileName:_____ **US** FileName:_____

DS Lat:_____ **X** Lat:_____ **US** Lat:_____

DS Lon:_____ **X** Lon:_____ **US** Lon:_____

FIELD WATER CHEMISTRY==========

Time (24 hr clock):_____ Water Temp. (°C):_____ Air Temp. (°C):_____

HACH Meter #:_____ Conductivity (umhos@25°C):_____ pH:_____

Dissolved Oxygen (DO)(mg/l):_____ %DO Saturation:_____ Secchi Tube:_____ /100cm

Water Level: ☐ Normal ☐ Below _____(m) ☐ Above _____(m)

Precipitation (if box(es) checked indicate intensity in comments) ☐ Currently raining ☐ Rain yesterday

LAB WATER CHEMISTRY ==========

Chem. Sample ID (field sample):_____ Chem. Sample ID (field duplicate):_____

Collection Time (field sample):_____ Collection Time (field duplicate):_____

TAPE DOWN DISTANCE MEASUREMENT ==========

Tape Down Length (100ths of ft):_____

Location/Description of Reference Mark (if made):_____

_____

CHANNEL CHARACTERISTICS==========

Transect Spacing (m):_____ Station Length (m):_____

Channel Condition (check appropriate box): ☐ Natural Channel ☐ Recent Channelization ☐ Old Channelization

Visual Condition (refer to the ratings and codes on the backside of this form):

Appearance:_____ Recreational Suitability:_____ Stream Condition:_____ / _____ / _____

Does the site appear to be low gradient? ☐ No ☐ Yes (use checkboxes on back to describe observations)

COMMENTS/NOTES:_____

_____

_____

_____

Visual Condition - Ratings and Codes

RATING	APPEARANCE DEFINITION
1A	Clear – crystal, clear transparent water
1B	Tea-colored – transparent water, which has been colored by dissolved organic matter from upstream bogs or wetlands
2	Cloudy – not quite crystal clear; cloudy white, gray or light brown
3	Muddy – cloudy brown due to high sediment levels
4	Green – due to algae growth; indicative of excess nutrients released into stream
5	Muddy AND Green – a combination of cloudy brown from high sediment levels and green from algae growth

RATING	RECREATIONAL SUITABILITY DEFINITION
1	Beautiful, could not be better
2	Very minor aesthetic problems: excellent for body-contact recreation
3	Body-contact recreation and aesthetic enjoyment slightly impaired
4	Recreation potential and level of enjoyment of the stream substantially reduced (would not swim but boating/canoeing is okay)
5	Swimming and aesthetic enjoyment of the stream nearly impossible

STREAM CONDITION: **N**=Normal, **L**=Low, **Z**= No Flow, **D**=Dry, **I**=Interstitial, **H**=High
SW=Swift, **SL**=Slow, **MO**=Moderate
C=Clear, **M**=Muddy, **O**=Other

Low Gradient Site Characteristics (check all that apply) (note any comments):

- ☐ Flow velocity only slow, or slow and moderate
- ☐ Riffles absent or representing very low percentage of reach (typically <5%)
- ☐ Dominated (>80%) by fines (silt, sand, detritus), coarse substrate uncommon (<10%)
- ☐ Wetland vegetation (cattails, arum, water lily, etc.) in channel or riparian zone
- ☐ It looks like a low gradient stream