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| <i>Title:</i> NEON Field Protocol: Surface Water Dissolved Gas Sampling in Streams and Lakes | <i>Author:</i> Keli Goodman | <i>Date:</i> 10/04/2013 |
| <i>NEON Doc. #:</i> NEON.DOC.001199  |                             | <i>Revision:</i> A      |

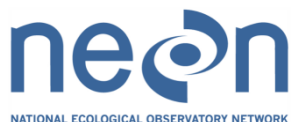
## NEON FIELD PROTOCOL: SURFACE WATER DISSOLVED GAS SAMPLING IN STREAMS AND LAKES

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See Configuration Management System for Approval History



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### Change Record

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## 1 DESCRIPTION

### 1.1 Purpose

The primary purpose of this document is to provide a change-controlled version of Observatory protocols and procedures. This document provides the content for training and field-based materials for NEON staff and contractors. Documentation of content changes (i.e. changes in particular tasks or safety practices) will occur via this change-controlled document, not through field manuals or training materials.

This document is a detailed description of the field data collection, relevant pre- and post-field tasks, and safety issues as they relate to this procedure and protocol.

### 1.2 Scope

This document relates the tasks for a specific field sampling or laboratory processing activity and directly associated activities and safety practices. This document does not describe:

- General safety practices
- Site-specific safety practices
- General equipment maintenance

It does identify procedure-specific safety hazards and associated safety requirements such as safe handling of small mammals or safe use of required chemicals and reagents.

### 1.3 Acknowledgements

The field protocol used by NEON for collecting surface water dissolved gas samples in small, wadeable streams, non-wadeable streams and lakes broadly follows the requirements set forth by Lotic Intersite Nitrogen eXperiment (LINX), the Environmental Protection Agency, the laboratories of Dr. Stephen Hamilton, Michigan State University, and the USGS Lake Monitoring Field Manual by Nevers & Whitman (2007).

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## 2 RELATED DOCUMENTS AND ACRONYMS

### 2.1 Applicable Documents

Applicable documents contain information that shall be applied in the current document. Examples are higher-level requirements documents, standards, rules and regulations.

|         |                 |   |
|---------|-----------------|---|
| AD [01] | NEON.DOC.004300 | EHS Safety Policy and Program Manual              |
| AD [02] | NEON.DOC.004316 | Operations Field Safety and Security Plan         |
| AD [03] | NEON.DOC.000724 | Domain Chemical Hygiene Plan and Biosafety Manual |
| AD [04] | NEON.DOC.001155 | NEON Training Plan                                |
| AD [05] | NEON.DOC.050005 | Field Operations Job Instruction Training Plan    |

### 2.2 Reference Documents

Reference documents contain information complementing, explaining, detailing, or otherwise supporting the information included in the current document.

|         |                  |  |
|---------|------------------|--|
| RD [01] | NEON.DOC.000008  | NEON Acronym List  |
| RD [02] | NEON.DOC.000243  | NEON Glossary of Terms                                   |
| RD [03] | NEON.DOC.005003  | NEON Scientific Data Products Catalog                    |
| RD [04] | NEON.DOC.014051  | Field Audit Plan   |
| RD [05] | NEON.DOC.001152  | NEON Aquatic Sample Strategy document                    |
| RD [06] | NEON.DOC.000824  | Data and Data Product Quality Assurance and Control Plan |
| RD [07] | NEON.DOC.001154  | NEON Aquatic Decontamination Protocol                    |
| RD [08] | NEON.DOC.000694  | Surface Water Chemistry Sampling in Wadeable Streams     |
| RD [09] | NEON.DOC.00 1190 | Lake and Non-Wadeable Stream Water Chemistry             |

### 2.3 Acronyms

|      |                                 |
|------|---------------------------------|
| mL   | milliliter                      |
| P&P  | Procedure and Protocol          |
| USGS | United States Geological Survey |

### 2.4 Verb Convention

“Shall” is used whenever a statement expresses a convention that is binding. The verbs “should” and “may” express non-mandatory provisions. “Will” is used to express a declaration of purpose on the part of the design activity.

### 2.5 Definitions

A **protocol** is a formal summary description of a procedure and its related rationale, and includes information on knowledge and resources needed to implement the procedure. A procedure is a set of prescribed actions that must take place to achieve a certain result, and can also be called a method. It differs from a science design in that science designs provide a more complete description of the

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rationale for selecting specific protocols. It differs from a training manual in that training manuals provide materials in support of skills acquisition in the topic areas including information on how to best train staff rather than detailing only the steps of the procedure.

Ambient – the conditions of the surrounding environment, such as the temperature of a stream where a sample was collected.

Headspace – A gaseous space above a closed liquid sample.

Supersaturation – A solution that contains a vapor of a compound that has a higher (partial) pressure than the vapor pressure of that compound.

Stratification - The thermal stratification of lakes refers to a change in the temperature at different depths in the lake that results from the change in water's density with temperature

Thalweg – Deepest part of the stream channel.

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### 3 BACKGROUND AND OBJECTIVES

#### 3.1 Background

The following protocol outlines field sampling of surface water dissolved gas chemistry in aquatic environments. The movement of dissolved gases in water (e.g., diffusing, dissolving and reacting) is governed by the partial pressure of the gas, not the concentration. Gases move from zones of high to low pressure until equilibrium is reached. The dissolution of gases in water is a function of the solubility of the gas, which is dependent on the temperature and salinity of the medium. The distribution and partial pressure of dissolved gases in water at any point in time are dependent on physical (e.g., evaporation, evasion and advection), chemical (e.g., binding, pH), and biological (e.g., heterotrophic and autotrophic metabolism, methanogenesis, denitrification) processes and reactions occurring within the water body and across the sediment-water and water-atmosphere interfaces. The rates of these processes and reactions will govern if a system is undersaturated or supersaturated in dissolved gases relative to the atmosphere, which can fluctuate both daily and seasonally. In lakes, stratification can limit the exchange and movement of dissolved gases between the hypolimnion and epilimnion, further influencing the chemical speciation of gases (i.e., CO<sub>2</sub> and CH<sub>4</sub>).

Although less attention is given to dissolved gases than dissolved nutrients, environmental changes such as the release of greenhouse gases and ozone degradation have led to increased measurements of dissolved gases in aquatic environments. Additionally, concerns over the effect of increased CO<sub>2</sub> on fish populations (i.e., elevated CO<sub>2</sub> can decrease metabolic efficiencies) have spurred the interest in measuring dissolved gas in aquatic environments (Danley et al. 2005). Stream dissolved chemistry may provides scientists, managers and decision makers with valuable information to consider potential water quality responses to natural and anthropogenic changes. Supersaturation and undersaturation of pCO<sub>2</sub> in freshwaters may result from nutrient loading, point and non-point pollution sources, and groundwater inputs. By assessing the degree of saturation of pCO<sub>2</sub> over time, annual net CO<sub>2</sub> balances may be inferred for the system and may provide insight about how changes in the surrounding landscape may influence stream function and structure. For example, how do increased nitrogen inputs influence stream denitrification? How are increases in CO<sub>2</sub> affecting the biological communities?

#### 3.2 NEON Science Requirements

This protocol fulfills Observatory science requirements that reside in NEON’s Dynamic Object-Oriented Requirements System (DOORS). Copies of approved science requirements have been exported from DOORS and are available in NEON’s document repository, or upon request.

#### 3.3 NEON Data Products.

Execution of this protocol procures samples and/or generates raw data satisfying NEON Observatory scientific requirements. These data and samples are used to create NEON data products, which are documented in the NEON Scientific Data Products Catalog (RD[03]), available on the NEON website.



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## 4 PROTOCOL

The following protocol describes the collection, processing, storage and shipping of dissolved gas samples from aquatic environments, both for lakes and streams. In streams, samples are collected in the deepest part of the channel (A.K.A. thalweg, the line of least resistance to water flow), where it is assumed that the stream channel is well mixed. The sampling location is located away from, or upstream of, any major local disturbances and other areas where NEON sampling activities commonly occur. In streams with a shallow water column, technicians must be cautious not to disturb the benthic sediments when sampling. In lakes, samples are collected along a depth profile at the deepest point of the lake near the buoy. The vertical location of samples to be taken in lakes depends upon lake depth and stratification. For shallow (<5m) non-stratified lakes, one sample is taken from 0.5 m below the surface of the water. For shallow stratified lakes, two samples are taken: one from 0.5 m below the surface of the water and one 1 m above the sediment-water interface. For deep stratified lakes (>5 m), up to three samples are taken: one from 0.5 m below the surface of the water, one below the base of the thermocline and one 1 m from the sediment- water interface.

Disruption of the sediments by walking or by sampling too close to the stream and lake bottom can contaminate samples. Thus, always sample upstream from wading activity and minimize the suspension of sediments when sampling. If sediments are disrupted, wait until the area has cleared before sampling. Due to the diel variability in partial pressure of dissolved gases, samples should be consistently taken at the same time of day.

## 5 QUALITY ASSURANCE AND CONTROL

The procedures associated with this protocol will be audited according to the Field Audit Plan (RD[04]). Additional quality assurance will be performed on data collected via these procedures according to the NEON Data and Data Product Quality Assurance and Control Plan (RD[06]).

To ensure sample quality, dissolved gas samples should be collected upstream of any solute injection work occurring on the same day as sampling, as well as upstream and upwind of any fieldwork disrupting the stream or lake bottom (e.g., morphology mapping, invertebrate collection, macrophyte collection, etc.). When sampling ambient air, collectors must take care not to contaminate samples. Thus, the collector should sample by holding the syringe into the wind and away from humans or any other sources of carbon or nitrogen gas.

Properly evacuated vials will suck gas from the syringe into the vial. If a gas vial is improperly evacuated, resample and use another evacuated gas vial. Label all improperly evacuated vials as such and return to the gas lab with samples. While properly evacuated gas vials will suck in some sample, the collector must push as much gas into the gas vial as possible by pushing on the syringe plunger. Always hold the syringe upright when transferring gas from the syringe to the gas vial to avoid transferring liquid to the gas vial.

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When unexpected field conditions require deviations from this protocol, the following field implementation guidance must be followed to ensure quality standards are met:

If the water chemistry sampling location is too shallow to obtain a sample, sample upstream in a flowing section of the stream (always sample in the thalweg, if possible) and note this change in field sheet. If no flow exists, sample in a nearby pool where the water is deep enough to obtain a clean, sediment free sample, and note this change in the field sheet. For lakes, also record new GPS position and total depth of the water column sampled from (Appendix A). Be sure to note this on the field sheet as a “non-flowing sample.” If the stream is entirely dry or frozen solid, note that on the field sheet. If the stream is ice-covered, but is still flowing, the ice should be broken so the stream can be sampled (following a few minute period to allow the water to clear). Always make note of any weather or stream conditions that could influence chemistry, including but not limited to wind, activities in the surrounding watershed, prior flood or rain events, ice, and changes in sampling locations (Appendix A).

If the lake is frozen only superficially and safe to walk on (minimum of 15 cm thickness) make a hole in the ice and proceed with sampling. The thickness of the ice shall be tested on the nearshore environment prior walking on the lake, by drilling a hole in the ice and measuring the ice thickness and consistency.

Samples should be processed as soon as possible. If necessary, stream water may be collected in a 60 mL syringe, submerged in a container of streamwater to reduce gas loss, and processed within 4 hours at a base camp or Domain Lab (i.e., if weather dictates that need to get out of the field immediately and stream discharge is increasing). Sample collection time, processing station and processing time must be recorded on the Dissolved Gas Sampling Data Sheet.

### 5.1 Decision Tree

- 1) Has there been any sampling in the past hour that has potentially affected the sampling location?
  - a) If YES, go to 2.
  - b) If NO, continue sampling.
- 2) Did any of the previous work stir up sediments or add chemical constituents to the stream/lake (i.e., gas additions)?
  - a) If Yes:
    - i) Allow the water to clear and disturbance to pass
    - ii) Sample upstream/upwind of the disturbance
  - b) If NO, continue sampling.

## 6 SAFETY

Personnel working at a NEON site must be compliant with safe fieldwork practices as outlined in the Operations Field Safety and Security Plan (AD[02]) and EHS Safety Policy and Program Manual (AD[01]). Additional safety issues associated with this field procedure are outlined below. The Field Operations Manager and the Lead Field Technician have primary authority to stop work activities based on unsafe field conditions; however, all employees have the responsibility and right to stop their work in unsafe conditions.

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Activities in streams should only be performed when flow conditions are safe. Do not attempt to wade a stream where velocity x depth is  $\geq 10 \text{ ft}^2/\text{s}$  ( $0.93 \text{ m}^2/\text{s}$ ) (AD[01]). When working around ice, use caution and good judgment to carefully evaluate site conditions including ice strength. Do not continue if the risk is too great.

## 7 PERSONNEL REQUIREMENTS

We estimate sampling and shipping requires 1-2 technicians for 1-2 hours each sampling day plus travel to and from the site.

## 8 TRAINING REQUIREMENTS

All technicians must complete required safety training as defined in the NEON Training Plan (AD[04]). Additionally technicians complete protocol specific training for safety and implementation of protocol as required in Field Operations Job Instruction Training Plan (AD[05]). Personnel are to be trained in wading stream dissolved gas measurements and safe working practices for stream fieldwork.

## 9 FIELD STANDARD OPERATING PROCEDURE

### 9.1 Sampling Frequency and Timing

Sample timing is provided annually by Science Operations (RD[05]).

#### 9.1.1 Criteria for Determining Sampling Dates

Dissolved gas chemistry sampling occurs in conjunction with water chemistry (RD[08] and RD[09]) sampling 26 times per year in wadeable and non-wadeable streams/rivers (approximately every other week) and 12 times per year in lakes. The timing of sampling allows researchers to assess aquatic biogeochemical cycles, and therefore timing depends on the dominant driver(s) of nutrient flux and cycling within each system. Timing of sampling is site-specific and determined by rules developed using historical discharge for streams and environmental data for both streams and lakes (RD[05]). For example, streams with little or no flow during the summer dry-season or streams that are frozen during the winter are sampled more intensively during other periods that have more flow. Systems that have a snowmelt-dominated or storm-dominated flow regime are sampled more intensively during elevated flows (i.e., time periods when the majority of the nutrients are moving through the system), and sampled sporadically during times of baseflow (RD[05]). Stream systems that are heavily influenced winter rains are more heavily sampled in the winter. Samples in lakes will be taken approximately monthly, with several samples being taken to capture major events such as ice-off, major storm, turnover and stratification. Samples should always be taken at the same time of day (i.e., 2 hours following sunrise +/- 1hr) in both lakes and streams in order to minimize errors incurred by natural diel variations in dissolved gases.

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### 9.1.2 Sampling Frequency

Dissolved gas sampling occurs 26 times per year (approximately every other week) in wadeable and non-wadeable streams/ rivers and 12 times per year in lakes at each NEON location.

### 9.1.3 Sampling Timing Parameters

Other than event based sampling, chemistry samples should be collected on Tuesday to coincide with other national chemistry sampling efforts (RD[05]).

## 9.2 Equipment and Materials

**Table 1.** Equipment and Consumables for Dissolved Gas Sampling Preparation

| Maximo Item No. | Item Description                                 | Quantity | Habitat-Specific | Special Handling |
|-----------------|--|----------|------------------|------------------|
|                 | 12 mL evacuated gas vial(s); evacuated <50 mTorr | 2        |                  |                  |
|                 | Dissolved gas label(s)                           | 2        |                  |                  |
|                 | Permanent markers                                | 1        |                  |                  |

**Table 2.** Equipment and Consumables for Dissolved Gas Sampling in Wadeable Streams, Non-Wadeable Streams and Lakes

| Maximo Item No. | Item Description  | Quantity | Habitat-Specific | Special Handling |
|-----------------|---|----------|------------------|------------------|
|                 | 12 mL evacuated gas vial with rubber septa, pre-labeled | 2*       |                  |                  |
|                 | 60 mL syringe, polyethylene                             | 2*       |                  |                  |
|                 | 50 mL polypropelene centrifuge tubes                    | 2*       |                  |                  |
|                 | 2-way male Luer-lock stopcock, polycarbonate            | 2*       |                  |                  |
|                 | Needles, 27 G ½ inch                                    | 2*       |                  | Yes              |
|                 | Sharps container  | 1        |                  |                  |
|                 | Field thermometer                                       | 1        |                  |                  |
|                 | Storage container for field storage and transport       | 1        |                  |                  |

\* Always take extra to the field.

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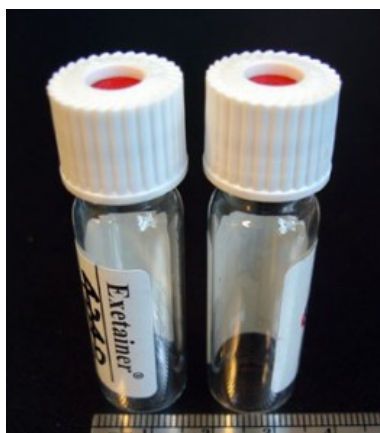


Figure 1. Image of a gas vial with septum lid. Image from <http://isotopes.forestry.ubc.ca>

Table 3. Additional Equipment and Consumables for Dissolved Gas Sampling in Lakes and Non-Wadeables.

| Maximo Item No. | Item Description                    | Quantity | Habitat-Specific | Special Handling |
|-----------------|-------------------------------------|----------|------------------|------------------|
|                 | Boat and oars                       | 1        |                  |                  |
|                 | Safety kit                          | 1        |                  |                  |
|                 | Kemmerer sampler                    | 1        |                  |                  |
|                 | Tubing with flow control hose clamp | 1        |                  |                  |
|                 | GPS                                 | 1        |                  |                  |
|                 | First Aid Kit                       | 1        |                  |                  |
|                 | Waders or boots                     | 2        |                  |                  |
|                 | Personal Flotation Devices          | 2        |                  |                  |

### 9.3 Preparation

- 1) Check the water dissolved gas field sampling kit to make sure all supplies are packed.
- 2) **Labels are waterproof but should be filled out before getting wet to ensure ink will stick to the labels.**
- 3) Attach pre-printed labels (Figure 2) to gas vials (Figure 1). Use a **Sharpie** to fill out labels (Figure 2) before going into the field. Sample ID should be labeled as 1, 2, 3, etc., restarting the numbering for each station ID and sample date.

Station Name: Arikaree River, CO

Station ID: D10 ARIK Sample ID: \_\_\_\_\_

Date and Time: \_\_\_\_\_

Gas Type: CO<sub>2</sub> CH<sub>4</sub> N<sub>2</sub>O




Figure 2. NEON dissolved gas chemistry labels.

- 4) Determine the depths for sampling lakes according to the data downloaded from the real-time data on the website or using the latest profiling data available acquired by the buoy. Look at the

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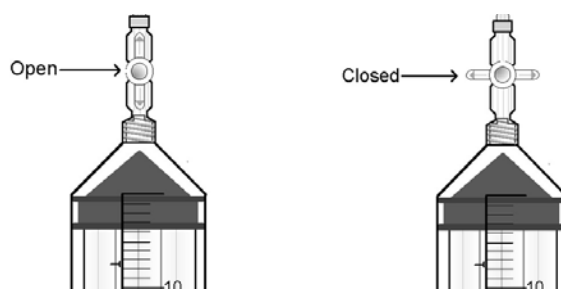
temperature profile and determine if and where stratification occurs and how many samples will be taken.

- a) For shallow (<5 m) non-stratified lakes, one sample will be taken from 0.5 m below the surface of the water.
  - b) For shallow stratified lakes, two samples will be taken: one from 0.5 m below the surface of the water and one at the mid-point of the hypolimnion.
  - c) For deep stratified lakes (>5 m) where a deep hypolimnion is present, up to three samples will be taken: one from 0.5 m below the surface of the water, and one sample each at 30 and 60% depth of the hypolimnion.
- 5) Dissolved gas sampling in streams will be completed in same location as surface water chemistry (RD[08]), upstream of any stream disruption and in a flowing area of the stream, if possible.

#### 9.4 Sample Collection in the Field

**NOTE: Be cautious when sampling. Items can easily fall into the water while bending to sample.**

- 1) Rinse the collection syringe and stopcock twice with the stream/lake water.
  - a) Place the syringe tip (with 2-way stopcock attached and turned to open; Figure 3) into the stream or lake so that the water is sampled ~10 cm under the surface.



**Figure 3.** Example of a syringe with a 2-way Luer lock stopcock in the “Open” and “Closed” positions.

- b) Pull in ~20-30 mL of water and remove syringe from stream or lake.
  - c) Roll the water around the syringe and plunger tip to collect air bubbles.
  - d) Turn syringe tip-upward and tap the sides of the syringe to release any trapped air bubbles. Tap hard to remove air bubbles. Removing small air bubbles may not be possible.
  - e) Holding the syringe upright, expel the air.
  - f) Repeat steps i-iv if large (>2 mm) air bubbles persist.
- 2) Collect sample.
- a) Wadeable Streams:
    - i) ALWAYS sample in the THALWEG (the deepest location in the stream cross-section) and 5-10 centimeters below the surface (to avoid sampling floating material or surface film). If the usual location is too shallow select another location within the stream reach that is deep enough, preferably in the thalweg. Personnel can step into the stream, but must approach the sampling location from downstream. Be sure to take samples upstream from the standing location of the personnel.

- ii) Place the syringe tip back into the water so that it is ~10 cm below the surface, and expel the remaining water into the stream, leaving approximately 1 mL in the syringe, which will help reduce the collection of air bubbles when sampling.
- iii) **SLOWLY** pull the plunger to draw a water sample until the syringe is completely full with the plunger at the 60 mL mark (Figure 4). 60 mL is more than needed, but collecting more will make the processing step easier. **Be careful not to entrain any air bubbles. If large air bubbles are captured in the syringe, resample.**

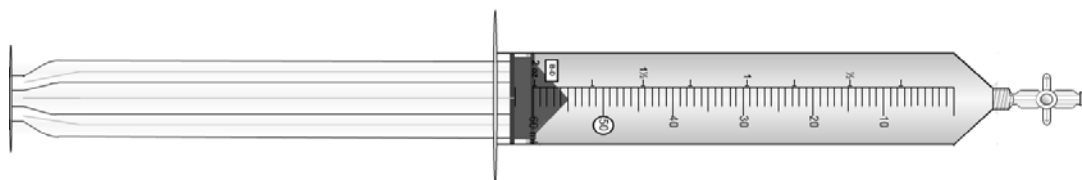
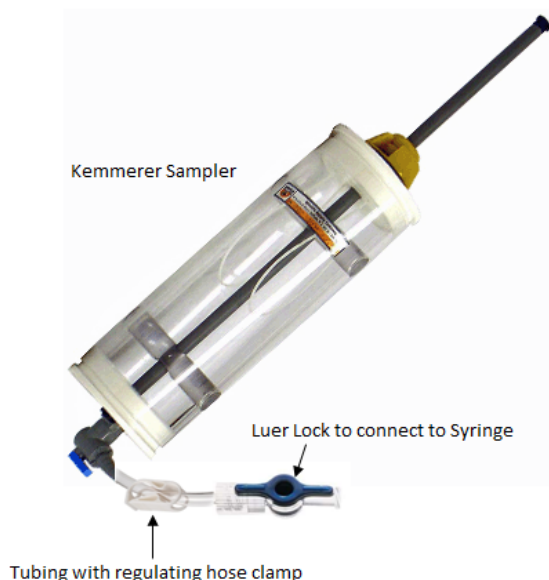


Figure 4. A full 60 mL syringe with a closed 2-way stopcock.

- iv) **BEFORE** removing the syringe from the stream, immediately turn the 2-way stopcock to the closed position (Figures 3, 4).
  - v) Place the syringe in a storage container (i.e., small cooler, pitcher or bucket) of streamwater at ambient stream temperature to help maintain temperature prior to processing and to avoid degassing.
  - vi) Proceed to Step 3, Sample Processing.
- b) Non-Wadeable Streams and Lakes:
- i) Move to the sampling location.
  - ii) Note the GPS position on the field sheet.
  - iii) Open and secure the Kemmerer bottle.
  - iv) Gently lower the bottle to the desired depth (based on the center of the sampler) and release the messenger. Give the rope a slight tug to ensure the sampler has shut properly.
  - v) Gently bring the Kemmerer back to the surface and ensure the sampler is tightly closed. Should the sampler not be properly closed, discard the sample and take another.
  - vi) Attach the tubing with the flow control hose clamp to the spigot of the Kemmerer (Figure 5).
  - vii) Open the spigot valve and then the hose clamp on the tubing and allow some water to pour out in order to flush the tubing.
  - viii) Attach the other end of the tubing with the female Luer-lock fitting to the Luer-lock stopcock (Figure 5).
  - ix) Rotate the stopcock valve so that the sample syringe is "Open."
  - x) Rinse the syringe by slowly filling the syringe to 30 mL with water and then 30 mL with air, shake vigorously for 30 seconds and discard the sample.
  - xi) **SLOWLY** pull the plunger to draw a water sample until the syringe is completely full, the plunger at the 60 mL mark (Figure 4). 60 mL is more than needed, but collecting more will make the processing step easier. **Be careful not to entrain any air bubbles. If large air bubbles are captured in the syringe, resample.**

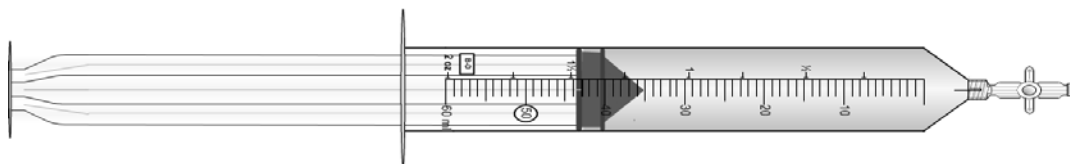
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- xii) Place the syringe in a small cooler, pitcher or bucket of lake water at ambient water temperature to help maintain temperature prior to processing and to avoid degassing.
- xiii) Proceed to Step 3, Sample Processing.



**Figure 5.** Example of tubing attachment with hose clamp and Luer-Lock to Kemmerer spigot.

- 3) Process Stream and Lake Dissolved Gas Sample within 3-4 hours of sample collection:
  - a) Record the Date (YYYYMMDD) and the time of day (use military time and record the time zone, indicating standard or daylight (Ex. 13:46 MST)) that each sample was collected from the stream or lake on the bottle labels (Figure 2), the General Field Sampling Data Sheet and the Dissolved Gas Data Sheet (Appendix B). You DO NOT need to complete a second General Field Sampling Datasheet unless dissolved gas samples are collected on a different date than the water chemistry samples.
  - b) Point the sample syringe UPWARD and tap syringe to move any small air bubbles to the top of the syringe. With syringe still pointing up, push the plunger to the 40 mL mark to expel entrapped gas and excess sample (Figure 6).



**Figure 6.** A syringe with 40 mL of sample water.

- c) Add 20 mLs of ambient air to the sample syringe:
  - i) Hold syringe at ~1.5 m above ground and at a full arms length from the body. Point syringe into the wind and away from contamination (e.g., human breath).



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- ii) Draw in 20 mLs of ambient air. Rotate stopcock to close syringe (Figure 3).
- d) The sample syringe should be filled to the 60 mL mark with 40 mL of sample water and 20 mL of ambient air headspace (Figure 7). Ensure stopcock is closed.

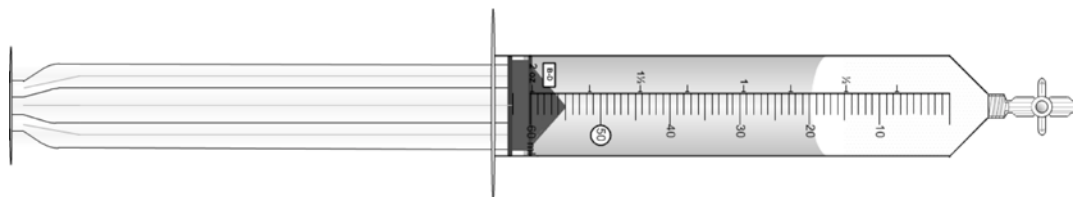


Figure 7. A syringe with 40 mL of water and 20 mL of ambient air.

- e) **Immediately** after adding 20 mLs of air to sample syringe, collect an ambient air sample using an empty syringe. This will be used to determine atmospheric gas concentrations, which will be used to correct the dissolved gas concentrations via subtraction:
  - i) Hold syringe into the wind and away from contamination (e.g., human breath).
  - ii) Draw in 60 mLs of air and expel to flush the syringe and ensure no previous gas build-up.
  - iii) Draw in at least 20 mLs of ambient air.
  - iv) Rotate stopcock to close syringe (Figure 3).
- f) Shake the sample syringe for the full 5 minutes so that the dissolved gases in the sample water come to equilibrium with the ambient air in the headspace. **NOTE: it is important to be consistent and shake the syringe for a minimum of 5 minutes since this affects the amount of dissolved gas released into the headspace.** Hold the syringe where the plunger enters the syringe. Avoid holding the syringe at the sample water, as this will increase the sample water temperature. Avoid holding the syringe in direct sunlight.
- g) **Record** the temperature of the sample storage water (the water in the bucket) for each sample ID.
- h) **Record** the sample type (i.e., sample water (S) or ambient air (A), volume of sample water and gas in the syringe on the Dissolved Gas Data Sheet (Appendix B). This should be done **immediately before gas transfer**. Be sure the labels on the gas vials match the sample ID's and type on the data sheet.
- i) Transfer dissolved gases to an evacuated gas vial (Figure 8).
  - i) Attach the needle to the 2-way stopcock on the syringes.
  - ii) With stopcock 'open' and syringe held upright, expel a few milliliters of the syringe headspace gas to flush the needle.
  - iii) Insert the needle through the rubber septum of the gas vial (Figure 8) and push gas into the vial. Properly evacuated vials will automatically suck in some gas. Be sure to push as much gas into the vial as possible until gas vial is over-pressurized (i.e., inject more gas than the volume of the gas vial). If vial is not properly evacuated, re-do the sampling and processing (Step 1) using the extra, evacuated gas vials.

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- iv) Continue to push gas into the vial while removing the needle from the vial septum as quickly as possible. Do this before turning off the stopcock because turning the stopcock to the closed position can cause some air to be drawn back into the syringe.
- v) Turn stopcock off.
- vi) Ensure sample labels are completed, as appropriate.
- vii) **Record** the volume of gas injected into the gas vial (**read the syringe to determine volume of gas injected**) on the Dissolved Gas Data Sheet (Appendix A).
- viii) Repeat step i for all Sample ID's.
- j) Discard needles into a sharps container with a lid.



**Figure 8.** Transfer of dissolved gases to an evacuated gas vial.

- k) Store gas vial by submersing in water filled centrifuge tubes without air bubbles.
- l) Return to the Domain Support Facility for sample storage and/or shipping. Samples can be stored at room temperature for a couple weeks. Store samples upside down if large bubbles in centrifuge tube occur or refill underwater. Ship gas samples to the gas analysis lab monthly.

### 9.5 Sample Shipping

- 1) Ship samples to the Dissolved Gas Laboratory following processing.
  - a) Place centrifuge tubes in box lined with a trash bag.
  - b) Include the completed laboratory form.
  - c) Ship to appropriate address.

### 9.6 Data Handling

- 1) Information from the General Field Sampling Data Sheet should be entered into excel file named 'DXX\_Dissolved Gas Data Sheet'.

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- 2) All photos, data and notes shall be uploaded and transcribed into the database within 7 days of sampling.

### 9.7 Refreshing the Sampling Kit

- 1) Restock the sampling kit with new evacuated dissolved gas sampling vial (with new labels attached), centrifuge tubes, needles, etc. Refer to equipment list, Section 10.3.1
- 2) Syringes will eventually begin to wear as the rubber of the plunger wears. Replace syringes when they become noticeably harder to draw in water.

### 9.8 Equipment Maintenance, Cleaning and Storage

- 1) Ensure all equipment is properly decontaminated (see RD[07]) and dry prior to storage.

## 10 REFERENCES

- Butman, D. and P.A. Raymond. 2011. Significant efflux of carbon dioxide from streams and rivers in the United States. *Nature Geoscience* 4, 839-842. Doi:10.1038/ngeo1294
- Danley, M.L., P.B. Kenney, P.M. Mazik, R. Kiser, J.A. Hankins. 2005. Effects of Carbon Dioxide Exposure on Intensively Cultured Rainbow Trout *Oncorhynchus mykiss*: Physiological Responses and Fillet Attributes. *Journal of the World Aquaculture Society* 36(3), 249-261. DOI: 10.1111/j.1749-7345.2005.tb00329.x.
- Hamilton, S.K., and N.E. Ostrom. 2007. Measurement of the stable isotope ratio of dissolved N<sub>2</sub> in <sup>15</sup>N tracer experiments. *Limnology and Oceanography: Methods* 5, 233-240.
- Nevers, M.B., and R.L. Whitman. 2007. Lake Monitoring Field Manual. USGS Lake Michigan Ecological Research Station.

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## Appendix A **FIELD DATA SHEETS**

The following field data sheets serve as a backup procedure for times when electronic data collection devices (PDA) are not available.

|   |                      |                  |
|---|----------------------|------------------|
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### General Field Sampling Data Sheet

Domain ID: \_\_\_\_\_ Site ID: \_\_\_\_\_ Date (YYYYMMDD): \_\_\_\_\_

Collectors' Name(s): \_\_\_\_\_ Team Lead: \_\_\_\_\_

Arrival Time (ex. 13:26 MST): \_\_\_\_\_ Departure Time: \_\_\_\_\_

**\*Be sure to include the time zone and standard or daylight savings time, e.g., MST**

Initial stage (m): \_\_\_\_\_ End stage (m): \_\_\_\_\_

**Weather**

Wind: Calm Breezy Windy Gusty

Sky: Clear Partly Cloudy (25, 50, 75%) Overcast

Precipitation: None Mist/Fog Light Rain Rain Heavy Rain Sleet Snow

Previous rain event within 48 hours (Y/N): \_\_\_\_\_

Evidence of previous rain event:

Air Temperature (F): <30 30s 40s 50s 60s 70s 80s 90s >100

Water Color/Clarity: Clear Blue Green Brown Gray

Riparian Phenology: no leaves breaking buds leaves increasing leaf size

colored leaves falling leaves

**General Comments/Flow conditions:**

**Post Field Work Observations (Check and comment if observed in channel):**

Algae \_\_\_\_\_ Woody Debris \_\_\_\_\_

Macrophytes \_\_\_\_\_ Oils/Surface Films \_\_\_\_\_

Leaf Litter \_\_\_\_\_ Trash \_\_\_\_\_

Other \_\_\_\_\_

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Appendix B **DISSOLVED GAS SAMPLING DATA SHEET**

| Domain | Site ID | Sample ID | Sample Type (sample water (S) or air (A)) | Sample Processing Location (Field or Domain Lab) | Date (YYYYMMDD) | Time (13:26 MST) | Temp (°C) | Hypolimnion (1) or epilimnion (2) | Littoral (1) or Pelagic (2) | Volume of sample water in syringe (ml) | Volume of sample gas in syringe (ml) | Gas volume injected to gas vial (ml) | Notes |
|--------|---------|-----------|---|--|-----------------|------------------|-----------|-----------------------------------|-----------------------------|--|--------------------------------------|--------------------------------------|-------|
|        |         |           |   |  |                 |                  |           |                                   |                             |  |                                      |                                      |       |
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