

RiverNET Community Water QUALITY Monitoring Protocols

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Yellowstone Ecological Research Center December 2019 [DRAFT]



YERC 2018 field crew leader Ryan Cornwall collecting a water quality grab sample in the Upper



Yellowstone River

INTRODUCTION

These protocols describe water quality sampling and analysis techniques developed by the Yellowstone Ecological Research Center (YERC) for the *RiverNET* Community Science Program. Among *RiverNET*'s initial goals were to develop a suite of user-friendly, low-cost, fast-turnaround tools and techniques to empower local communities to have an active role in monitoring water quality and quantity. In addition to fostering local participation, the program aims to increase the spatial and temporal resolution of water quality and quantity data at the watershed scale in order to (a) establish current baselines and annual/seasonal trends across important main stem and tributary sites, and (b) identify deviations from those trends that could indicate a water quality impairment event, prompting a focused investigation with additional sampling, community organization, and other responses. As soon as it has passed quality assurance/quality control review, all *RiverNET* data is made publicly available on an online download and visualization platform at www.yellowstoneresearch.org/rivernet, so that local communities can use and act on them in a timely manner.

RiverNET began in 2010 as a collaborative project between YERC and the University of Montana as part of a National Science Foundation-funded EPSCoR proposal, with products including concepts used in the dissertation work of Dr. Brian Hand and the 2018 article he published in Frontiers in Ecology and the Environment, A social-ecological perspective for riverscape management in the Columbia River Basin. In 2017, those concepts were applied to the Upper Yellowstone Watershed during YERC's Envision Yellowstone conference, a strategic planning meeting of thought-leaders from the private technology sector aimed at identifying the most pressing conservation issues in the Greater Yellowstone Ecosystem as well as solutions using the best available science and technology. The following two summers (2018 and 2019), YERC piloted RiverNET in the Upper Yellowstone Watershed in collaboration with local partners including the Park County Environmental Council, Montana Trout Unlimited, Upper Yellowstone Watershed Group, and Angler's West Fly Fishing Outfitters, with support and participation from numerous other local residents, K-12 students, fishing guides, landowners, and businesses.

Upon completion of the pilot program and in fulfillment of *RiverNET*'s long-term goals, it now seeks to ensure that (a) all protocols and procedures involved in project design, sample collection, analysis, data management, and data interpretation, can be managed by local community organizations with minimal scientific training, and (b) the program is capable of being scaled and transferred to other watersheds beyond the Upper Yellowstone, so that other communities and watersheds can benefit from the work as well as join *RiverNET*'s online data access and visualization network.

How to use these protocols:



All content here was originally sourced from manufacturer Methods and Material Safety Data Sheet, and from established field procedure manuals cited in **Section X** (References). YERC staff amalgamated these sources to maximize efficiency of mass sampling efforts, to provide a single source for all procedures with step-by-step instructions developed over the two-year pilot phase, and to include YERC's standard safety protocols for all field and lab operations. It is applied to the *RiverNET* program in the Upper Yellowstone Watershed, but can serve as a template for any other watershed or community water monitoring program, using the Yellowstone-specific site locations, parameters, and procedures as example placeholders.

To establish new sites in a different watershed, recreate the table described in **Section II.C** (Site Selection/Site Establishment) and displayed in **Appendix B** (*RiverNET* Site Location Database). To modify existing parameters or add new parameters, obtain the manufacturer Methods and the Material and Safety Data Sheets for all chemicals used in the analyses, add them to the reference section, update the table in **Section V.A** (In-House Sample Analysis/Hach Method Details), and update the step-by-step instructions for sample analysis (**Section V.C**), chemical disposal (**Section VI.D**), and lab safety and first aid (**Sections IX.B, IX.C**) following the same format, as necessary. Also update the *RiverNET* Upper Yellowstone Sampling & Analysis Plan (**Appendix A**), the *RiverNET* Water Quality Field Datasheets (**Appendix C**), and the *RiverNET* Water Quality Analysis Database (**Appendix D**, described in **Section VII.A** (Data Management/Data Entry)) with the new site locations and parameters. Most other content (e.g., equipment, sample collection and handling, equipment cleaning, data management, quality control, field safety) should be transferable as is with minimal changes.

This content can be used in whole or in part by any other community water monitoring program. However, for other programs to be included in the *RiverNET* network, they must follow these protocols exactly, or with modifications approved by YERC program managers. To be included in *RiverNET*, contact YERC or your participating community watershed organizer responsible for local outreach and coordination, prepare and send the metadata in your Site Location Database and your revised Sampling & Analysis Plan, and we will coordinate with you on Data Entry so that your data is included on the *RiverNET* online platform. We welcome and encourage participation from other organizations in other watersheds, and will provide technical assistance to get you started.

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Suggested Citation:

Cross PR, Howie MG, Crabtree RL. 2019. *RiverNET* Community Water QUALITY Monitoring Protocols. Yellowstone Ecological Research Center, Bozeman MT.

Available at: www.yellowstoneresearch.org/rivernet

I. <u>EQUIPMENT</u>(* = consumable)

A. Sample Collection -- All/Routine Sampling

- Carrying Tote
- 750 mL HDPE jars + lids (n = 30), labeled with a unique ID number
- YERC Coolers (blue; n = 3)
- *Cube Ice (21 lbs @ 7lbs/cooler) in 6 Ziploc® gallon freezer bags
- *Latex Gloves
- Watch
- Fully Charged Smartphone (i.e., GPS, camera)
- _□ Thermometer
- _D pH Meter
- Extra Batteries
- Protocols
- *Clipboard: Data Sheets, Pens, Maps
- Waders, Wading Boots, Wading Belt
- Personal clothing (+ extra dry layers) and equipment



First Aid Kit, Emergency Vehicle Tools, etc.

B. Sample Collection -- Energy Labs Duplicate Sampling

- Everything listed in Section A above, plus:
- *Energy Labs Sample Collection Kits (n = 18)
- Energy Labs Coolers (red, each w/ temperature blank bottle; n = 3)
- *Cube Ice (60 lbs @ 20lbs/cooler) in 12 Ziploc® gallon freezer bags)
- *1 extra Ziploc® bag for garbage
- *Paper Towels (for drying sample jars)
- *60 mL syringes (n = 15)
- *25 mm diam/45 um pore size Syringe Filters (n = 30)
- *DI Water
- _n Protocols
- *Energy Labs Chain of Custody Form
- *Energy Labs Custody Seals
- *Energy Labs Shipping Labels
- *YERC Review for Completeness Form
- *Packing Tape (n = 2 full rolls)

C. Sample Analysis

- A clean, clear workspace
- Computer with access to database (optional)
- *Latex Gloves
- PPE (Goggles, Face Masks, Long Sleeve/Full Toe)
- Hach DR900 Colorimeters (n = 2)
- 16mm Well Adaptor for DR900 (n = 2)
- Hach DRB200 Reactor (double block)
- Black Pipette TenSette
- Glass Pipette Tip, 1.0-10.0 mL
- *Plastic Pipette Tip Covers (n = 30)
- Plastic Pipette Tip Cover *labeled* "NaOH"
- Graduated Cylinder with top, 100 mL
- 40x50mm Funnels (n = 5), labeled:
 - NitraVer[®] X
 - PhosVer® 3
 - Nitrogen Persulfate
 - TN Reagent A
 - TN Reagent B
 - Potassium Persulfate



- Test'N'Tube Cooling Racks (60 16mm (¾") wells)
- *Test Tube Kimwipes®
- *Clipboard: Data Sheets, Pens, Sharpie
- * Masking tape
- *Garbage Disposal (n = 4), labeled for:
 - Hazard
 - Single Use Trash
 - Single Use Recycle
 - Reusable
- Material Safety Data Sheets, First Aid
- pH adjusting equipment, including:
 - New Sample Jars (n = 30)
 - _D pH Meter
 - *pH Calibration Fluids (250mL jars, standards, DI water)
 - *Phenol Red
 - _D Dropper
 - Graduated Cylinder with top, 100 mL
 - Green Dial Pipette
 - Glass Pipette Tip, 0.1-1.0 mL
 - *Hydrochloric Acid
 - *DI Water
 - PPE (heavy jacket, heavy gloves, goggles, face mask, sink, fresh air)
- *Orthophosphate Reagents:
 - PhosVer® 3 Reagent Pillow Packs
 - Hach DR900 Sample Vials (reusable)
- *Nitrate Reagent Sets (#53):
 - n = 50 TestNTube Vials
 - $n = 50 \text{ NitraVer}^{\mathbb{R}} \text{ Reagent Pillow Packs}$
- *Nitrite Reagent Sets (#83):
 - n = 50 TestNTube Vials
 - n = 6 Empty vials with caps for blanks
 - DI Water, 100mL
- *Total Nitrogen Reagent Sets (#17 AND #21):
 - $_{0}$ n = 50 TestNTube Vials #1 (MSDS M01349) [#17]
 - n = 50 Nitrogen Persulfate Pillow Packs [#17]
 - $_{\Box}$ n = 50 TestNTube Vials #2 (SDS M00933) [#21]
 - n = 50 Reagent A Pillow Packs [#21]
 - n = 50 Reagent B Pillow Packs [#21]
 - DI Water, 100mL [#21]
- *Total Phosphorus Reagent Sets (#26):



- $_{\Box}$ n = 50 TestNTube Vials
- n = 50 Potassium Persulfate Pillow Packs
- $_{\Box}$ $n = 50 \text{ PhosVer}^{\textcircled{R}}$ 3 Reagent Pillow Packs
- Sodium Hydroxide Solution, 100mL
- DI Water, 100 mL

D. Cleaning

- A clean, clear workspace with sink and fresh air
- Dish bins (n = 3), labeled for:
 - HCl Acid
 - Luminox
 - Waste Disposal/Dilution
- Drying racks
- Bottle brush
- _ Tongs
- *DI water. jug
- *DI water, squeeze bottle
- *Liquinox®
- *Hydrochloric Acid (1:1 solution)
- Hydrochloric Acid disposal bucket
- Baking Soda
- Uinegar
- Graduated Cylinder
- _D pH Meter
- *Garbage Disposal (n = 4), labeled for:
 - Hazard
 - Single Use Trash (*emptied and relined since analysis*)
 - Single Use Recycle (with used Test N' Tube vials)
 - Reusable (with used Hach sample cells and other used equipment)
- Plastic bin/buckets to collect cleaned, used Test N' Tubes to recycle
- The Hach Safety Datasheets binder
- Personal Protective Equipment, including:
 - Elbow-length rubber gloves
 - Goggles
 - Heavy canvas jacket
 - Full length pants and closed toe shoes

II. SITE SELECTION

A. Watershed Scale

- River (main stem) sites should be chosen for:
 - Consistent spatial distribution relative to other sites on the river



- Locations above and below major tributaries to quantify effects
- Tributary sites should be chosen for:
 - Prioritization, specifically:
 - A...a. <u>1st Priority Tributaries</u>: chosen for consistent spatial distribution as well as for having one or more important factors (high volume, trout spawning habitat/thermal refugia, major irrigation source, land use conflicts, etc.), sampled at the mouth
 - A...b. <u>2nd Priority Tributaries:</u> chosen for consistent spatial distribution but lacking any of the factors described for 1st priority tributaries, sampled at the mouth
 - A...c. <u>3rd Priority Sites/Tributaries:</u> which are (a) additional sites on a 1st or 2nd priority tributary to monitor confounding factors (i.e., upstream of an irrigation diversion, point source, or tributary mouth), or (b) additional tributaries that are severely modified by land use (mining, irrigation).
 - Accessible locations near the *mouth* of the tributary at least 10m upstream from the main stem (1st, 2nd, and 3rd Priority Tributaries), or *upstream* above and/or below major inputs, diversions, etc. (3rd Priority Sites)
 - Avoiding bridges, culverts, pipes, and other instream structures that could contaminate samples

B. Local Scale

- All water sampling sites (river and tributary) should be:
 - Safely and legally accessible
 - Fully within the body of water listed in the site description
 - Not influenced by nearby bodies of water (i.e., > 10m above the stream's mouth, and away from water entering the stream from a tributary
 - In flowing current (not an eddy or backwater) as close as possible to the thalweg
 - As close as possible to additional site description information provided (e.g., photos, maps, narrative descriptions)

C. Site Establishment

- A.1. Enter metadata into the RiverNET Site Location Database:
 - A.1.A. **Site ID**: Alphanumeric identifier with (a) first 3 letters of site name, and (b) unique number (e.g., "Yel1")
 - A.1.B. **Site Name**: Full name. Make sure that descriptive adjectives such as "upper" and "lower" follow the full name and are separated by columns (e.g., "Mill Creek, upper"), unless they are part of the proper name (e.g., "Upper Deer Creek"). All main stem sites should include the name of the



river and a specific location separated by a hyphen (e.g., "Yellowstone River - Gardiner Airport")

- A.1.C. Latitude: Decimal Degrees
- A.1.D. **Longitude**: Decimal Degrees
- A.1.E. Watershed: Descriptive name of the watershed
- A.1.F. **Tributary?**: Binary (1 = yes, 0 = no) indicating whether river (main stem) or tributary site
- A.1.G. Water Quality?: Binary indicating whether water quality samples are collected
- A.1.H. **Water Quantity?**: Binary indicating whether water quantity data are collected
- A.1.I. **Observation Types**: Used for categorizing datastreams
- A.1.J. Group: Descriptive name of sites sharing locational attributes
- A.1.K. **Order**: Arrangement of sites within a group
- A.1.L. Rating Curve; Min Stage; Max Stage: If applicable, the current rating curve formula calculated for each site and the range of stages for which it is applicable (stage where rating curve produces a discharge of 0 for the minimum, and highest stage recorded in rating table for the maximum)
- A.1.M. **Stage:Depth Correction**: Distance, in feet, between 0-level on staff gauge and the stream bed
- A.1.N. **Max Channel Width (m)**: Distance, in meters, between the high water marks (monumented with rebar stakes) on either side of the staff gauge in water *quantity* monitoring sites
- A.1.O. **Device Serial #s**: Manufacturer serial numbers from any instream monitoring devices
- A.1.P. **Device YERC ID #s**: In-house ID numbers from any instream monitoring devices
- A.1.Q. **Device Maintenance Logs**: Maintenance logs from any instream monitoring devices
- A.1.R. **Notes**: Any important notes pertaining to the site
- A.2. Include additional information to help locate the site such as:
 - ➤ Narrative descriptions of the site as well as parking and access info
 - > Photos of the site from multiple angles
 - > Clear, hand-drawn map of the site that includes:
 - Parking spot and approach route
 - Important landmarks
 - Exact sample collection site
 - Compass rose
 - Anything else that would help future crews locate the site



III. Sample Collection

A. Sampling & Analysis Frequency

| Season | Dates | Routine Sampling/ In-House Analysis | Duplicate Sampling/ External Analysis |
|---------------------|------------------|--|--|
| Pre-Growing Season | April-June | Once | Once |
| Growing Season | July-September | Bi-Weekly | Once |
| Post-Growing Season | October-December | Once | Once |

B. Preparation

- A.1. Gather equipment:
 - Sample Coolers:
 - Coolers (2 blue YERC cooler for routine samples, 3 red Energy Labs coolers for duplicate samples)
 - Gallon Ziploc® freezer bags (with the traditional double seal, NOT the sliding zipper locks)
 - Cube ice (~20 lbs/cooler)
 - Routine Samples (all sampling events):
 - Carrying Tote
 - 750 mL HDPE jars + lids (n = 30), labeled with a unique ID number
 - Latex Gloves
 - Watch
 - Fully Charged Smartphone (i.e., GPS, camera)
 - _a Thermometer
 - _D pH Meter
 - Extra Batteries
 - Protocols
 - Clipboard: Data Sheets, Pens, Maps
 - Waders, Wading Boots, Wading Belt
 - Personal clothing (+ extra dry layers) and equipment
 - First Aid Kit, Emergency Vehicle Tools, etc.
 - Ice-filled blue YERC coolers (n = 2)
 - Duplicate Samples (seasonal sampling events):
 - Energy Labs Sample Collection Kits (n = 18)



- 1 extra Ziploc® bag for garbage
- Paper Towels (for drying sample jars)
- $_{\circ}$ 60 mL syringes (n = 15)
- 25 mm diam/45 um pore size Syringe Filters (n = 30)
- DI Water
- Protocols
- Energy Labs Chain of Custody Form
- Energy Labs Custody Seals
- Energy Labs Shipping Labels
- YERC Review for Completeness Form
- Packing Tape (n = 2 full rolls)
- Ice-filled red Energy Labs coolers (n = 3)

* IMPORTANT NOTE ABOUT ENERGY LABS MATERIALS: to obtain these materials, a <u>Bottle Order</u> must be submitted to Energy Labs at least **2 weeks** before the sampling event, which includes:

- a. The previous fill bottle order number (if available)
- b. The quote number provided by DEQ/Energy Labs on approval of the Volunteer Monitoring application
- c. The parameters being tested
- d. Contact information
- e. And be sure to check "Ship to my address" before submitting
- Other (see also **I. EQUIPMENT**):
 - Waders, wading boots, wading belt
 - Appropriate clothing (rain gear, extra dry layers, etc.)
 - First Aid/Safety Equipment
- A.2. Prepare sample coolers:
 - 2A.1.a. Fill gallon Ziploc® bags about 75% full of cubed ice, and tightly seal
 - 2A.1.b. Put about 20 lbs worth of ice packs into each cooler
 - 2A.1.c. Periodically check ice packs, replacing those that are melted
 - 2A.1.d. As samples are collected, arrange them and the ice packs so that they are well surrounded by ice
 - > DO NOT put loose ice in the cooler
 - > DO NOT use reusable blue ice packs
 - > DO NOT use low-quality freezer bags or those with the slidy zippers

C. Routine Sampling (for in-house analysis):

- **A.1.** Collect one unfiltered grab sample at each sample site:
 - 1A..a. Select a location that represents the body of water being sampled



- and isn't influenced by nearby water bodies, wade out into the current as close to the thalweg as is safely possible, and face upstream
- 1A..b. Avoid stirring up sediment with your footing
- 1A..c. Fill the sample jar by reaching upstream
- 1A..d. Triple rinse the sample jar and lid with natural water from the sample site, dispensing it downstream
- 1A..e. After triple rinsing the jar and lid, collect the sample, close the lid tightly, record the jar number on the datasheet, and store the sample in the ice pack-filled blue cooler
- **A.2.** Collect pH and water temperature (*required*), and other environmental parameters like visual algae coverage assessments (*optional*), and record on the Water Quality Field Datasheet
- **A.3.** Record additional observations about:
 - Unique circumstances that might affect that sample
 - Natural observations of hydrologic/riparian ecology phenomena such as evidence of beaver, aquatic insect, and/or fish activity
 - Anything else that seems interesting, in the "Notes" section of the datasheet

D. <u>Duplicate Sampling (for external analysis)*</u>

- A.1. Collect three unfiltered and one filtered grab samples (see table below) at the 15 top priority sites (all Yellowstone River main stem and 1st Priority Tributary sites)
 - 1A..a. Use same location where routine sample was collected, and approach collection site the same way (avoid stirring up sediment, face upstream, etc.)
 - 1A..b. Triple rinse all sample jars and lids as with routine samples, *using* filtered water instead of natural water for the orthophosphate sample jar
 - 1A..c. Fill each sample jar about 80% of the way, leaving some headspace
 - 1A..d. Individual parameters have their own sample jars, some of which require further processing (preservatives, filtration, etc.):

| Sample Jar | Parameter | Preservative | Filter? |
|----------------|-----------------|--------------|---------|
| White-Capped | Total Nitrogen | No | No |
| Square 250 mL | | | |
| White-Capped 1 | Total Suspended | No | No |
| L | Solids | | |



| Yellow-Capped Square 500 mL | Total Phosphorus, Nitrate+Nitrite | YES - Add one yellow- capped H ₂ SO ₄ vial to collected sample and invert 3 times to mix, wearing gloves and handling/ disposing of the vial with care | No |
|--------------------------------|---|--|--|
| White-Capped Round 120 mL | Orthophosphate | No | YES - Triple rinse and collect sample using 60 CC syringe + 45 um filter, handling the filter with care when filling syringe/rinsing sample jar and avoiding touching it with your hands or any other object |

- 1A..e. Dry the sample jars with paper towels, and clearly label with site name, date, *TIME WHEN 1st ARRIVED AT SITE*, and mark filtered/unfiltered.
- 1A..f. Arrange them in their Ziploc® bag so that they will remain upright with the labels facing out
- 1A..g. Store in an ice pack-filled red cooler
- A.2. Collect *field duplicates* at two randomly selected sites per sampling event
 - 2A.2.a. Follow all duplicate sample collection protocols (III-D) above
 - 2A.2.b. Label the bottles/chain of custody form with "SITE ID *FD*"
- A.3. Collect one *field blank* at one randomly selected site per sampling event
 - 3A.3.a. Fill all sample jars with DI water transported to the site
 - 3A.3.b. Label the bottles/chain of custody form with "SITE ID *FB*"
 - 3A.3.c. Handle the completed field blank with the regular samples
- A.4. Complete the Energy Labs Chain of Custody form, including:
 - A.3.A. **Account Information** with:
 - *DEQ* contact information
 - Quote # assigned by Energy Labs/DEQ
 - Fill bottle order # from Energy Labs
 - A.4.B. **Report Information** with:
 - *your* contact information
 - A.4.C. **Page Numbers** (in upper right corner)
 - A.4.D. **Project Information** with:
 - Project Name supplied by DEQ
 - lead tech's name under Sampler Name
 - "No" checked for EPA/State Compliance
 - A.4.E. **Sample Identification** (rows) with:
 - Site IDs as written on the Sampling & Analysis Plan and on the



- sample jar labels
- Date and Time of collection (important that the time be consistent between the Chain of Custody form, all the sample jar labels for a given site, and the datasheet: we suggest recording the time when first arrived at the site)
- Number of containers (i.e., 4)
- Matrix (i.e., **W**)

A.4.F. **Analysis Requested** (columns) with:

- Parameters being tested
- Xs in the cells of rows for each sample to be tested for that parameter
- A.4.G. Signature of the lead tech on the 1st Relinquished By line, with
 - Printed name
 - Date and Time when samples are complete and about to be shipped
 - Signature
- A.5. Detach the original (white) copy of the Chain of Custody form (keep the yellow carbon copy for own records), seal it inside the Ziploc® bag it came in, and enclose it in one of the red Energy Labs coolers along with the samples
- * VOLUNTEER MONITORING APPLICATION: to obtain external lab support from Montana DEQ's Volunteer Monitoring (VM) Program, one must first:
- 1. Contact the DEQ water quality bureau (i.e., Katie Makarowski, <u>kmakarowski@mt.gov</u>, November 2019) and ask to be added to the Volunteer Monitoring Program contact list
- 2. Keep an eye out for the Call For Applications, which usually comes out in early spring
- 3. Prepare a Sampling & Analysis Plan (see **Appendix A** for an example). This will take some time, so best to get it started before the Call For Applications goes out.
- 4. Prepare a Volunteer Monitoring application (attached to the Call For Applications), and submit it, plus the Sampling & Analysis Plan, and other required material by the deadline listed on the Call For Applications.
- 5. The application will then be reviewed, after which it will be (a) rejected, (b) accepted, or (c) provisionally accepted with revisions.
- 6. All VM data must also be entered into MT-eWQX at the end of the season.

IV. TRANSPORTING & STORING SAMPLES

A. <u>Transporting</u>

- A.1. Upon collection, transfer samples to ice pack-filled coolers (see **III.B.2**)
 - Ensure lids are screwed on tightly and samples are upright
- A.2. Monitor the temperature inside the coolers and maintain *BETWEEN*



32°F AND 42°F, adding fresh ice packs if necessary

A.3. Deliver the samples (routine samples to the home office/lab for in-house analysis, or duplicate samples to the UPS store for external analysis) as soon as possible, ideally the same day as collected

B. Shipping (duplicate samples for Energy Labs)

- A.1. Obtain the original datasheet, Energy Labs Chain of Custody form, and YERC Review For Completeness form
- A.2. Remove samples from the coolers, and check that the information on each sample jar label matches the information on the Chain of Custody form
- A.3. Return samples to the coolers, ensuring they are upright and well packed in ice packs (adding fresh ice packs if necessary)
- A.4. Ensure that a temperature blank bottle is present inside each cooler, and that the completed Chain of Custody form is resealed in a Ziploc® bag and returned to one of the coolers
- A.5. Sign and date one Energy Labs Custody Seal for each cooler, and attach to span the gap between the cooler body and lid
- A.6. Attach an Energy Labs Shipping Label to each cooler
- A.7. Remove previous shipping labels
- A.8. Wrap the cooler/lid at least four times with clear packing tape, covering the Custody Seal and Shipping Label as well
- A.9. Complete the YERC Review For Completeness form
- A.10. Drop off prepared coolers at the nearest UPS Store, and get a receipt
- A.11. Attach the (a) original datasheet, (b) completed Review For Completeness form, (c) carbon copy of the completed Chain of Custody form, and (d) UPS receipt together, and file them at the office

C. Storing (routine samples for in-house analysis)

All samples should be analyzed as soon as possible: routine samples analyzed in house with Hach DR900 colorimeters should be analyzed the same day they are collected. If samples must be stored overnight:

- A.1. Obtain equipment:
 - 2 new, clean, labeled sample jar/sample
 - Masking tape (for jar labels)
 - 1 60cc syringe/sample
 - 1 45um filter/sample
 - _D pH meter
 - 0.1-1.0 pipette with glass tip
 - 0.1 Mol Hydrochloric Acid (HCl) solution (see below)
 - 5N Sodium Hydroxide solution
 - Refrigerator or cooler with renewed ice packs
 - PPE (gloves, goggles, long sleeves
 - A clean and clear workspace with a sink and fresh air
- A.2. Filter 25mL of each sample into one of the clean sample jars for the



- Orthophosphate test, labeled with the original jar number and "Filtered for PO4"
- A.3. Add 10mL of each sample to the other clean sample jar for the Total Phosphorus, Total Nitrogen, and Nitrate tests, check the current pH, adjust it to pH 2 by adding ~0.34mL of 0.1 Mol HCl solution/pH unit/10mL sample (about 2.25-2.5mL of 0.1 Mol HCl solution for a sample with pH 9; NOTE: Hach methods call for *sulfuric* acid addition), and label the jar with the original jar jumber and "pH adjusted"
 - To make a 0.1 Mol HCl solution:
 - A.3..1. Obtain equipment and supplies:
 - 10 mL graduated cylinder with top
 - 0.1-1.0 mL pipette
 - _n HCl
 - DI water
 - HDPE jar with lid
 - PPE (mask, heavy gloves, goggles, heavy jacket)
 - clean clear work environment (sink, fresh air)
 - A.3..2. Add 0.1 mL HCl to 25 mL DI water in the graduated cylinder, cover with top, swirl to mix
 - A.3..3. Store in HDPE bottle labeled "0.1 Mol HCl solution", use pipette to measure/add to samples
- A.4. Store these treated samples with the original sample jars (which will be used for the Nitrite tests) in a refrigerator or cooler maintained between 32-42 F with fresh ice packs for up to 48 hours
- A.5. Before analyzing the samples:
 - Allow all sample jars (original and treated) to heat up to room temperature
 - Readjust the pH-adjusted samples to pH 7 by adding 5N Sodium Hydroxide solution, checking the pH with a pH meter as you go

V. <u>IN-HOUSE SAMPLE ANALYSIS (WITH HACH DR900)</u>

A. Hach Method Details

| Parameter | Method | Measurement Range | Resolution | Accuracy |
|---------------------|---------------------------------------|----------------------|------------|-------------------------|
| Nitrate (HR)* | Chromotropic acid (Hach 10020) | 0.2 to 30 mg/L | 0.2 mg/L | \pm 0.5 mg/L |
| Nitrite | Diazotization (Hach 10019) | 0.003 to 0.500 mg/L | 0.003 mg/L | \pm 0.006 mg/L |
| Orthophosphate | Ascorbic acid (Hach 8048) | 0.02 to 2.50 mg/L | 0.02 mg/L | $\pm 0.02 \text{ mg/L}$ |
| Total Nitrogen | Persulfate digestion (Hach 10071) | 0.5 to 25.0 mg/L | 0.4 mg/L | ± 0.5 mg/L |
| Total Phosphorus | Acid persulfate digestion (Hach 8190) | 0.06 to 3.50 mg/L | 0.06 mg/L | ± 0.07 mg/L |



* The Hach Nitrate (LR) method uses a cadmium reduction method that we determined to be too hazardous (cadmium exposure) for RiverNET applications

B. Analysis Setup

- 1. Prepare a clean, clear workspace
- 2. Remove all samples from cooler/refrigerator, and allow to warm up to room temperature

| | temper | ature |
|----|--------|--|
| 3. | Obtain | equipment and supplies: |
| | | Computer with access to database (optional) |
| | | *Latex Gloves |
| | | PPE (Goggles, Face Masks, Long Sleeve/Full Toe) |
| | | Hach DR900 Colorimeters ($n = 2$) |
| | | 16mm Well Adaptor for DR900 ($n = 2$) |
| | | Hach DRB200 Reactor (double block) |
| | | Black Pipette TenSette |
| | | Glass Pipette Tip, 1.0-10.0 mL |
| | | *Plastic Pipette Tip Covers ($n = 30$) |
| | | Plastic Pipette Tip Cover labeled "NaOH" |
| | | Graduated Cylinder with top, 100 mL |
| | | 40x50mm Funnels ($n = 5$), labeled: |
| | | NitraVer® X |
| | | PhosVer® 3 |
| | | Nitrogen Persulfate |
| | | TN Reagent A |
| | | TN Reagent B |
| | | Potassium Persulfate |
| | | Test'N'Tube Cooling Racks (60 16mm (¾") wells) |
| | | *Test Tube Kimwipes® |
| | | *Clipboard: Data Sheets, Pens, Sharpie |
| | | Must include complete field data sheet with locations, jar numbers |
| | | collection times and dates, and pH and temperature observations |
| | | * Masking tape |
| | | *Garbage Disposal (hazard, single use-trash, single use-recycle, reusable) |
| | | Material Safety Data Sheets, 1st Aid |
| | | *Orthophosphate Reagents: |
| | | PhosVer® 3 Reagent Pillow Packs |
| | | Hach DR900 Sample Vials (reusable) |
| | | *Nitrate Reagent Sets (#53): |
| | | n = 50 TestNTube Vials |

 $n = 50 \text{ NitraVer}^{\mathbb{R}} \text{ Reagent Pillow Packs}$



- □ *Nitrite Reagent Sets (#83):
 - $_{\Box}$ n = 50 TestNTube Vials
 - n = 6 Empty vials with caps for blanks
 - DI Water, 100mL
- □ *Total Nitrogen Reagent Sets (#17 AND #21):
 - n = 50 TestNTube Vials #1 (MSDS M01349) [#17]
 - n = 50 Nitrogen Persulfate Pillow Packs [#17]
 - $_{\Box}$ n = 50 TestNTube Vials #2 (SDS M00933) [#21]
 - n = 50 Reagent A Pillow Packs [#21]
 - n = 50 Reagent B Pillow Packs [#21]
 - DI Water, 100mL [#21]
- □ *Total Phosphorus Reagent Sets (#26):
 - n = 50 TestNTube Vials
 - $_{\Box}$ n = 50 Potassium Persulfate Pillow Packs
 - $n = 50 \text{ PhosVer}^{\mathbb{R}}$ 3 Reagent Pillow Packs
 - Sodium Hydroxide Solution, 100mL
 - DI Water, 100 mL
- 4. Adjust pH of treated samples back to pH 7 (if necessary; see Section IV.C.5)
- 5. Using the Sharpie permanent marker, label one plastic pipette tip cover for each sample jar (these will be used to draw water from the sample jars for each test without cross-contaminating the samples), and one with "B" for DI water blanks
- 6. Create a new sheet on the Water Quality Analysis Database (see Section VII.A.1)
- 7. **IDENTIFY SAMPLES SELECTED FOR DUPLICATE ANALYSES**. In order to validate the precision of our in-house results, **TWO** samples must be **randomly selected** from **each sampling event**, and **ALL** parameters must be tested a total of **THREE** times for each of these samples

C. Methods, By Parameter*

- * Click on parameter titles to link to original Hach protocols
 - **■** General instructions for all tests:
 - Wear latex gloves, goggles, and long sleeves throughout testing
 - To add water (samples or blanks) to test vials, use the TenSette pipette, glass pipette tip, and *appropriately labeled* plastic pipette tip covers (disposable), being careful not to mix tip covers and contaminate samples
 - To add Powder Pillow reagents to test vials, use *appropriately labeled* funnels (reusable)
 - For tests that use Test N' Tube vials, first insert the plastic 16mm adapter into the DR900s test well. Remove the 16mm adapter for test that use reusable sample vials (i.e., Orthophosphate)
 - Note the different DRB200 Reactor temperature settings for the Total



Nitrogen and Total Phosphorus tests

- At the end of each test:
 - Discard used Test N' Tube vials into the garbage receptacle labeled for single-use recycle
 - Discard used Powder Pillow packaging into garbage receptacle labeled for single-use trash
 - Carefully place used reusable sample vials into receptacle labeled for reusable items
 - > Set aside labeled plastic pipette tips to be used in subsequent tests until all testing is complete, then discard them into the garbage receptacle labeled for **single-use trash**
- Before starting any analyses, review all hazards and first aid procedures described in Sections VI.C, X.B, and X.C, and in the Hach Material and Safety Data Sheets (see Section XI). Always wear your Personal Protective Equipment. Be very careful whenever handling, storing, or working with any of these chemicals. And most importantly, if you feel unsure, unprepared, or unsafe in any way:

DO NOT PROCEED

AND IMMEDIATELY NOTIFY YOUR SUPERVISOR!

You have both the **RIGHT** and **RESPONSIBILITY** to stop and/or refuse to participate in any operation that you feel is not safe!

A.i. Nitrate, HR (Hach Method 10020, Reagent Set # 53)

- A.i.1. Power on DR900 and start program 344 N, Nitrate HR, TNT
- A.i.2. Label one **NitraVer**® **X Reagent A** Test N' Tube vial for each sample jar
- A.i.3. Prepare and run the **blank**:
 - 3A.i.3.a. Add 1 mL of sample to the Test N' Tube vial
 - 3A.i.3.b. Cap vial and invert 10 times to mix
 - 3A.i.3.c. Clean vial with Kimwipes®
 - 3A.i.3.d. Insert vial into DR900
 - 3A.i.3.e. Press **ZERO** on DR900, and wait until it reads 0.00 mg/L NO₃-N
 - 3A.i.3.f. Remove vial from DR900



- A..4. Prepare and run the **sample**:
 - 4A..4.a. Add one **NitraVer**® **X Reagent B** Powder Pillow to the same vial
 - 4A..4.b. Cap vial and invert 10 times to mix
 - 4A..4.c. Clean vial with Kimwipes®
 - 4A..4.d. Insert vial into DR900
 - 4A..4.e. Start **5 minute timer** on DR900 and wait for reaction to occur
 - 4A..4.f. After timer has elapsed, press **READ** to obtain result
 - 4A..4.g. Record result
- A..5. Repeat steps 3-4 for remaining samples
- A.ii. Nitrite (Hach Method 10019, Reagent Set #83)
 - A..1. Power on DR 900 and start program 345 N, Nitrite LR TNT
 - A..2. Label one **NitriVer**® **3 Nitrite** Test N' Tube vial for each sample jar
 - A..3. Prepare a **sample**:
 - 3A..1.a. Add 5 mL of sample to the Test N' Tube vial
 - 3A..1.b. Cap vial and shake to mix (the sample may turn pink if nitrite is present)
 - 3A..1.c. Set aside, and start 20 minute timer on DR900
 - 3A..1.d. As the reaction occurs, move to Step 4
 - A..4. Prepare and run the **blank**:
 - 4A..1.a. Add **5 mL of sample** to one of the *empty* Test N' Tube vials included in the Reagent Set (#83) for the sample blanks (NOT one of the NitriVer® 3 Nitrite Test N' Tube vials)*
 - 4A..1.b. Clean blank test vial with Kimwipes®
 - 4A..1.c. Insert blank test vial into DR900
 - 4A..1.d. Press **ZERO** on DR900, and wait until it reads 0.00 mg/L NO₂-N
 - NOTE: This step in the original Hach instructions (step #5) says to "fill and empty Test 'N Tube vial with 5mL sample" -- we presume this is an error and that it should read "fill an empty..."
 - A..5. After timer has elapsed, run the **sample**:
 - 5A..5.a. Clean sample test vial with Kimwipes®
 - 5A..5.b. Insert sample test vial into DR900
 - 5A..5.c. Press **READ** on DR900
 - 5A..5.d. Record result
 - A...6. Rinse the **blank** test vial **3 times** with **DI water** so it can be reused*
 - > NOTE: Although DI water is included in the Reagent Set (#83),



and only 6 empty blank Test N' Tube vials are included in a single Reagent Set for testing 50 samples, the original Hach instructions do not include any information about rinsing and reusing the empty blank vials.

A..7. Repeat steps 3-6 for remaining samples

A.iii. Orthophosphate (AKA Phosphorus, Reactive (Orthophosphate); Hach Method 8048)

- A..1. Label the **sample** and **blank** test vials:
 - 1A..1.a. Place a piece of masking tape on each of **2** reusable Hach sample vials
 - 1A..1.b. Write the sample jar number on the masking tape on one of the vials, and the sample jar number plus "B" on the masking tape on the other vial
- A..2. Power on DR 900 and start program **490 P, React. PP**
- A..3. Prepare **sample** test vial:
 - 3A..1.a. Add **10 mL of sample** to the reusable test vial labeled with *just* the sample jar number
 - 3A..1.b. Add one **PhosVer**® **3 Phosphate Reagent** Powder Pillow to sample test vial
 - 3A..1.c. Cap vial and shake vigorously for **30 seconds**
 - 3A..1.d. Set aside, and start the **2 minute timer** on the DR900
- A..4. Prepare blank test vial:
 - 4A..1.a. Add **10 mL of sample** to the reusable test vial labeled with the sample jar number plus "B"
- A..5. After the timer elapses, run the **blank**:
 - 5A..1.a. Clean blank test vial with Kimwipes®
 - 5A..1.b. Insert blank test vial into DR900
 - 5A..1.c. Press **ZERO** on DR900, and wait until it reads 0.00 mg/L PO_4^{3-}
- A..6. Run the **sample:**
 - 6A..6.a. Clean sample test vial with Kimwipes®
 - 6A..6.b. Insert sample test vial into DR900
 - 6A..6.c. Press **READ** on DR900
 - 6A..6.d. Record result

A..7. Repeat steps 1-6 for remaining samples

A.iv. Total Nitrogen (Hach Method 10071, Reagent Sets #17 and #21)

- A..1. Power on **DRB200 reactor** and preheat both blocks to $105\,\mathrm{C}$
- A..2. Label the Test N' Tube vials:



- 2A..1.a. Label one Test N' Tube vial from **EACH** of the Reagent Sets (#17 and #21) for **each** of the sample jars (then return those from Reagent Set #21 to their packaging for now)
- 2A..1.b. Label **one** Test N' Tube vial from Reagent Set #17 **ONLY** with a "B" for the blank (which can be reused for all tests conducted on the same day)
- A..3. Prepare the **samples** and the **blank** Test N' Tube vials from *Reagent Set #17*:
 - 3A..1.a. Add the contents of one **Nitrogen Persulfate** Powder Pillow to **each** of the labeled Test N' Tube vials from Reagent Set #17 (those with the sample jar numbers and the one labeled "B")
 - 3A..1.b. Add **2mL of sample** to its labeled Test N' Tube vial from Reagent Set #17
 - 3A..1.c. Cap vial and shake vigorously for **30 seconds** (make sure the cap is tight)
 - 3A..1.d. Repeat Steps 3a-3c for remaining samples
 - 3A..1.e. Add **2mL of DI water** to the Test N' Tube vial from Reagent Set #17 labeled "B"
 - 3A..1.f. Cap vial and shake vigorously for **30 seconds** (make sure the cap is tight)
- A..4. Digest samples and blank:
 - 4A..1.a. Insert prepared sample test vials and the prepared blank test vial into the DRB200 reactor, and close the lid
 - 4A..1.b. Start **30 minute timer** on the DRB200
 - 4A..1.c. When the timer elapses, **immediately** remove all the vials and place them in the cooling rack (CAUTION: the vials will be hot)
 - 4A..1.d. Allow vials to cool to room temperature before proceeding
- A..5. Power on DR900 and start program **350 N, Total LR TNT**
- A..6. Add remaining Pillow Pack reagents to vials:
 - 6A..1.a. Add one **Total Nitrogen (TN) Reagent** *A* Pillow Pack to each of the vials
 - 6A..1.b. Cap vials and shake vigorously for 15 seconds
 - 6A..1.c. Set aside and start 3 minute timer on the DR900
 - 6A..1.d. When the timer elapses, add one **Total Nitrogen (TN) Reagent** *B* Pillow Pack to each of the vials
 - 6A..1.e. Cap vials and shake vigorously for 15 seconds
 - 6A..1.f. Set aside and start 2 minute timer on the DR900
 - 6A..1.g. When the timer elapses, proceed to next step
- A..7. Prepare the **samples** and the **blank** Test N' Tube vials from *Reagent Set #21*:
 - 7A..1.a. Add **2mL** of *digested* samples and blank to their respective labeled Test N' Tube vials from Reagent Set #21
 - 7A..1.b. Cap vials and *slowly* invert 10 times (vials will become warm)



- 7A..1.c. Set aside and start 5 minute timer on the DR900
- 7A..1.d. When the timer elapses, proceed to next step
- A..8. Run blank
 - 8A..1.a. Clean blank test vial with Kimwipes®
 - 8A..1.b. Insert blank test vial into DR900
 - 8A..1.c. Press **ZERO** on DR900 and wait until it reads 0.00 mg/L N
 - 8A..1.d. Set blank test vial aside to use on other tests
- A..9. Run sample
 - 9A..9.a. Clean sample test vial with Kimwipes®
 - 9A..9.b. Insert sample test vial into DR900
 - 9A..9.c. Press **READ** on DR900
 - 9A..9.d. Record result
- A..10. Repeat Steps 8-9 for remaining samples
- A.v. Total Phosphorus (Hach Method 8190, Kit # 26)
 - A..1. Power on **DRB200 reactor** and preheat both blocks to $150\,\mathrm{C}$
 - A..2. Label one **Total Phosphorus** Test N' Tube vial for each sample jar
 - A..3. Prepare samples:
 - A..3.a. Add 5mL of each sample to its labeled test vial
 - A..3.b. Add one **Potassium Persulfate** Powder Pillow to each test vial
 - A..3.c. Cap and shake test vials to dissolve powder
 - A..4. Digest samples:
 - A..4.a. Insert prepared test vials into DRB200 Reactor, and close the lid
 - A..4.b. Start **30 minute timer** on DRB200
 - A..4.c. When the timer elapses, remove vials and place them in the cooling rack (CAUTION: the vials will be hot)
 - A..4.d. Allow vials to cool to room temperature before proceeding A..5. When the vials have cooled to room temperature:
 - A..5.a. Add **2mL of 1.54N Sodium Hydroxide** Standard Solution (included in Kit #26) into each vial using the pipette, glass pipette tip, **and the plastic tip cover labeled "NaOH"**
 - A..5.b. Cap vial and invert to mix
 - A..6. Zero DR900 for one sample:
 - A..6.a. Clean sample test vial with Kimwipes®
 - A..6.b. Insert into DR900
 - A..6.c. Press **ZERO** on DR900, and wait until it reads 0.00 mg/L PO_4^{3-}
 - A..7. Add reagent to sample:



- A..7.a. Add one **PhosVer**[®] **3** Powder Pillow to vial
- A..7.b. Cap vial and shake for **30 seconds**
- A..7.c. Set aside and start **2 minute timer** on DR900 (finish running sample within 8 minutes of timer elapsing)
- A..8. Run sample:
 - A..8.a. Clean sample test vial with Kimwipes®
 - A..8.b. Insert vial into DR900
 - A..8.c. Press **READ** on DR900
 - A..8.d. Record result
- A..9. Repeat Steps 6-8 for remaining samples
- D. **Methods**, all parameters [total elapsed time at start of step : time required for step]
 - * Time estimates recorded in hours, assuming 30 tests/parameter using double block DRB200 reactor and two DR900 colorimeters, ~12-12.5 hours total
 - * For individual steps, refer to **Section V.C:** "Methods, by parameter"
 - A.1. Setup [0.0 : 0.75]
 - 1A..a. Prepare clean, clear workspace
 - 1A..b. Turn on DRB200 Reactor, and preheat both blocks to $150 \, \text{C} \sim 30$ minutes to preheat
 - 1A..c. Remove samples to warm to room temperature
 - 1A..d. Adjust pH of samples stored overnight (add 30 minutes to time estimate)
 - 1A..e. Layout all remaining equipment and supplies
 - 1A..f. Label plastic pipette tip covers with sample jar ID numbers
 - A.2. Start Total Phosphorus *digestion* [0.75 : 0.75]:
 - 2A..a. Prep samples (Steps v.2-v.3); ~15 minutes
 - 2A..b. Digest samples for 30 minutes (Step v.4)
 - A.3. Start Nitrate tests [1.0 : 1.5]:
 - 3A..a. Steps i.1-i.5; ~6 minutes/test
 - A.4. Finish Total Phosphorus digestion [1.5 : NA]
 - 4A..a. Move TP vials to cooling rack
 - A.5. Start Total Nitrogen *digestion* [1.5 : 0.75]
 - 5A..a. Reset temperature setting on both blocks of DRB200 to $105\,\mathrm{C}$
 - 5A..b. Prep samples (Steps iv.2-iv.3); ~15 minutes
 - 5A..c. Digest samples for 30 minutes (Step V.C.iv.3)
 - A.6. Continue Nitrate tests [1.75 : NA]
 - A.7. Finish Total Nitrogen digestion [2.25 : NA]
 - 7A..a. Move TN vials to cooling rack



- A.8. Finish Nitrate tests [2.75 : NA]
- A.9. Start Nitrite tests [2.75 : 5.25]
 - 9A..a. Steps **ii.1-ii.7**; ~21 minutes/test
- A.10. Clean reusable Hach DR900 Sample Tubes (n = 30) from previous testing between Nitrite tests; see **VI.B.x**
- A.11. Finish Nitrite tests [8.0 : NA]
- A.12. Start/Finish Orthophosphate tests [8.0 : 0.75]
 - 12A..a. Steps iii.1-iii.7; ~3 minutes/test
- A.13. Start/Finish Total Phosphorus *tests* [8.75 : 0.75]
 - 13A..a. Steps v.5-v.9; ~ 3 minutes/test
- A.14. Start/Finish Total Nitrogen *tests* [11.5 : 2.75]
 - 14A..a. Steps **iv.4-iv.10**; ~11 minutes/test
- A.15. Cleanup [11.5 : 0.5]
 - 15A..a. Inventory consumables
 - 15A..b. Empty all trash
 - 15A..c. Secure reusable supplies to be cleaned later
 - 15A..d. Return equipment to shelves

VI. <u>CLEANING</u>

A. Setup

- A.1. Clear a desk and floor space large enough to comfortably move about
- A.2. Clear an area for placement of the Hydrochloric Acid disposal bucket
- A.3. Alert all office/laboratory personnel of the presence of the Hydrochloric Acid disposal bucket (including any who come in while you are cleaning)
- A.4. Lay out all of the necessary cleaning supplies in your cleared area to include:
 - Dish bins (n = 3), labeled for:
 - HCl Acid
 - Luminox
 - Waste Disposal/Dilution
 - Drying racks
 - Bottle brush
 - Tongs
 - DI water (jug; check for sufficient amount)
 - DI water squeeze bottle
 - Liquinox® solution (jug; check for sufficient amount)
 - Hydrochloric Acid ACS grade (jug; check for sufficient amount)
 - Hydrochloric Acid disposal bucket
 - Baking Soda
 - Vinegar
 - Graduated Cylinder



- _D pH Meter
- *Garbage Disposal (n = 4), labeled for:
 - Hazard
 - Single Use Trash (emptied and relined since analysis)
 - Single Use Recycle (with used Test N' Tube vials)
 - Reusable (with used Hach sample cells and other used equipment)
- Plastic bin/buckets to collect cleaned, used Test N' Tubes to recycle
- The Hach Safety Datasheets binder
- Personal Protective Equipment, including:
 - Latex gloves
 - Elbow-length rubber gloves
 - Goggles
 - Heavy canvas jacket
 - Be wearing full length pants and closed toe shoes
- A.5. Don all Personal Protective Equipment, and keep it on for all steps involving reagent disposal or Hydrochloric Acid washes.
- A.6. Remember: Hydrochloric acid and the chemicals used in the reagents are extremely dangerous! Review all hazards and first aid procedures described in Sections VI.C, X.B, and X.C, and in the Hach Material and Safety Data Sheets (see Section XI). Always wear your Personal Protective Equipment. Be very careful whenever handling, storing, or working with any of these chemicals. And most importantly, if you feel unsure, unprepared, or unsafe in any way:

DO NOT PROCEED

AND IMMEDIATELY NOTIFY YOUR SUPERVISOR!

You have both the **RIGHT** and **RESPONSIBILITY** to stop and/or refuse to participate in any operation that you feel is not safe!

B. Sample Collection (Field) Equipment

- Sample Jars
 - A..1. Submerge in Liquinox® bath, scrub inside and out with the bottle brush, and rinse **three** times in *Liquinox® solution*
 - A..2. Rinse **five** times in *cold tap water*
 - A..3. Rinse **three** times in *DI water* from squeeze bottle
 - A..4. Set on the *inside* of the drying racks
 - A..5. Pour Liquinox[®] solution down the drain, and rinse out the bin
 - A...6. Pour extra DI water from the squeeze bottle back into the DI water bucket/jug, and place squeeze bottle and cap on the drying rack
 - A..7. Allow equipment to dry for at least 12 hours, and put it all away as

soon as it is dry

Coolers

- A..1. After sample analysis, clean out any debris from coolers with running water and soap as necessary
- A..2. Leave cooler lids open and/or turn coolers upside down to allow for drying
- A..3. **DO NOT close cooler lid and store until inside of coolers is 100% dry!** If you do, and they get moldy, you have to clean them out!

Other field equipment

- A..1. Remove all dirt debris from equipment
- A..2. Dispose of all waste materials in appropriate trash bin
- A..3. Make sure all equipment is dry before storing

C. Sample Analysis (Lab) Equipment

Reusable Hach Sample Cells

- A..1. Prepare Liquinox® bath in dish bin marked "Liquinox" and Hydrochloric Acid bath (1:1 HCl:DI Water solution) in dish bin marked "HCl Acid", placing them on the counter in a way that **THEY WON'T GET BUMPED OR SPILLED**, with the HCl Acid bath closest to the sink
- A..2. Clean each sample cell one at a time by:
 - 2A...a. Submerging the sample cell in the Liquinox® bath, scrubbing it inside and out with the bottle brush, and rinsing it at least **three** times in the Liquinox® solution
 - 2A...b. Using the tongs, submerge the sample cell in the Hydrochloric Acid bath, lightly swirl it around, and remove it using the tongs, holding it low over the sink (so that it doesn't fall far and break in case you drop it from the tongs). BE EXTREMELY CAREFUL USING HYDROCHLORIC ACID (HCl)! AND BE MINDFUL OF WHERE YOU SET DOWN THE TONGS IN BETWEEN SAMPLE CELLS (try to place them upright against the side of the HCl Acid bin so that the handles are above the acid bath, so long as you don't bump them into the bath.) IF HCl GETS ON THE SKIN, IMMEDIATELY RINSE AREA IN COLD WATER, WASH WITH SOAP AND WATER, AND NOTIFY YOUR SUPERVISOR
 - 2A...c. Rinse the sample cell inside and out **five** times using cold tap water (you can now handle it without the tongs)
 - 2A...d. Rinse the sample cell inside and out **three** times with DI water from the squeeze bottle
 - 2A...e. Set it on one of the **exterior pegs** on the drying racks so that the cell hangs upside down



- A...3. Pour the HCl bath into the Hydrochloric Acid disposal bucket, thoroughly rinse out the bin and the tongs with cold tap water with the tap running for five minutes [CITATION?], and return the Hydrochloric Acid disposal bucket to its lower shelf in the gear room. Notify your supervisor when the bucket is half full. AND BE CAREFUL!
- A..4. Allow the sample cells and HCl equipment (HCl Acid bin, tongs) to dry for at least 12 hours, and put it all away as soon as it is dry
- Other laboratory equipment (funnels, pipette, pipette tips, graduated cylinders, etc.)
 - Follow the same steps as you would for the **Sample Jars** in **Section VI.B**

D. Chemical Disposal (by parameter)*†

- * Click on chemical/reagent titles to link to original Hach Material Safety Data Sheets available on various online sources: <u>click here</u> to request latest versions from Hach † Dispose of all chemicals, reagents and used test vials in accordance with <u>local</u> regulations and environmental legislation
 - A..i. Nitrate, HR (Hach Method 10020, Kit # 53
 - NitraVer® X Test 'N Tube Reagent (Hach MSDS M00933)
 - NitraVer® X Nitrate Reagent B (Hach MSDS M00411)
 - D....1. Pour contents of used Test 'N Tubes into Waste Disposal/Dilution bin
 - D....2. Slowly add **5 times** that volume of cold water (~150mL for 30 samples)
 - D....3. Add baking soda to adjust pH between 6 and 9
 - D....4. Open cold water tap, and slowly pour contents of bin down the drain
 - D....5. Leave cold water running to flush system for 5 minutes
 - D....6. Rinse empty Test N' Tube vials in cold water as it is flushing the system
 - D....7. Discard plastic cap in **Single Use-Trash** disposal
 - D....8. Discard glass Test N' Tube in **bin/buckets** for recycling

A..ii. Nitrite (Hach Method 10019, Kit # 83)

- NitriVer® 3 Test 'N Tube Reagent (Hach MSDS M00055)
 - D....9. Pour contents of used Test 'N Tubes into **Waste Disposal/Dilution** bin
 - D....10. Slowly add enough cold water to make a <5% solution (~6L for 30 samples)
 - D....11. Add baking soda to adjust pH between 6 and 9.



- D....12. Open cold water tap, and slowly pour the reacted material to the drain
- D....13. Leave cold water running to flush system for 5 minutes
- D....14. Rinse empty Test N' Tube vials in cold water as it is flushing the system
- D....15. Discard plastic cap in **Single Use-Trash** disposal
- D....16. Discard glass Test N' Tube in **bin/buckets** for recycling

A..iii. Phosphorus, Reactive (Orthophosphate) (Hach Method 8048)

- PhosVer® 3 Reagent (Hach MSDS M00035)
 - D....17. Pour contents of used sample cells into **Waste Disposal/Dilution** bin
 - D....18. Slowly add enough cold water until the bin is **80% full**
 - D....19. Open cold water tap, and slowly pour contents of bin down the drain
 - D....20. Leave cold water running to flush system for 5 minutes
 - D....21. Rinse empty reusable sample cells in cold water as it is flushing the system
 - D....22. Carefully place sample cells into the EMPTY bin labeled for "HCl Acid" (there SHOULD NOT be any acid solution in this bin at this time)

A..iv. Total Nitrogen (Hach Method 10071, Kits #17 and #21)

- TN Digestion Test N' Tube [1st] (Hach MSDS M01349)
- Nitrogen Persulfate (Hach MSDS M00039)
- TN Reagent A (Hach MSDS M00247) *2nd MSDS in linked pdf
- TN Reagent B (Hach MSDS M01059)*3rd MSDS in linked pdf
- TN Test N' Tube Reagent [2nd] (Hach MSDS M00933)
 - * 4th MSDS in linked pdf
 - A..iv..1. Pour contents of used sample cells into **Waste Disposal/Dilution** bin
 - A..iv..2. Slowly add enough cold water to make a <5% solution (~1.2L for 30 samples)
 - A..iv..3. Open cold water tap, and slowly pour contents of bin down the drain
 - A..iv..4. Leave cold water running to flush system for 5 minutes



- A..iv..5. Rinse empty Test N' Tube vials in cold water as it is flushing the system
- A..iv..6. Discard plastic cap in **Single Use-Trash** disposal
- A..iv..7. Discard glass Test N' Tubes in **bin/buckets** for recycling

A..v. Total Phosphorus (Hach Method 8190, Kit # 26)

- TP Test N' Tube Reagent (Hach MSDS M01616)
- Potassium Persulfate (Hach MSDS M00039)
- PhosVer® 3 Reagent (Hach MSDS M00035)
- Sodium Hydroxide Solution 1.54N (Hach MSDS M01622)
 - A..v..1. Pour contents of used Test 'N Tubes into **Waste Disposal/Dilution** bin
 - A..v..2. Slowly add **5 times** that volume of cold water (~*1L for 30 samples*)
 - A..v..3. Check pH with pH meter, and adjust pH between 6 and 9 by adding baking soda (if pH>9) or vinegar (if pH<6)
 - A..v..4. Open cold water tap, and slowly pour contents of bin down the drain
 - A..v..5. Leave cold water running to flush system for 5 minutes
 - A..v..6. Rinse empty Test N' Tube vials in cold water as it is flushing the system
 - A..v..7. Discard plastic cap in **Single Use-Trash** disposal
 - A..v..8. Discard glass Test N' Tube in **bin/buckets** for recycling

A..vi. Other Chemicals

- Hydrochloric Acid [used in cleaning] (Hach MSDS M00218)
 - D....23. Pour used solution into HCl Acid bin
 - D....24. **SLOWLY** add enough cold water to make a <5% solution (~5L for 250mL of 1:1 HCl:DI Water cleaning solution)
 - D....25. Add baking soda to adjust pH between 6 and 9
 - D....26. Open cold water tap, and slowly pour contents of bin down the drain
 - D....27. Leave cold water running to flush system for 5 minutes
- Phenol Red [used in adjusting pH] (Hach MSDS M00349)
 - D....28. Pour used solution into **Waste Disposal/Dilution** bin



- D....29. Slowly add 5 times that volume of cold water
- D....30. Open cold water tap, and slowly pour contents of bin down the drain
- D....31. Leave cold water running to flush system for 5 minutes
- Phosphate Standard Solution 1.0mg/L (Hach MSDS M00224)
- Sodium Hydroxide 5.0N Solution (Hach MSDS M00438)
- <u>Nitrate Nitrogen Standard Solution (Hach MSDS M00757)</u>
- All other chemicals or solutions like expired reagents or unknown chemicals
 - D....32. **DO NOT** release into environment
 - D....33. Collect material in HDPE bucket, and dispose at a hazardous waste collection site (contact local waste disposal administration for locations/times)

E. Storage

- Make sure all used equipment (sample collection equipment, analysis equipment, cleaning equipment) is clean, dry, and in good operating order before putting it away -- notify your supervisor immediately if anything is damaged and needs to be repaired or replaced
- For long-term storage (>1 month) of electronic equipment, remove disposable batteries, bunch the batteries together with a rubber band or tape, and store them together with the equipment
- As soon as you are done using equipment and it is ready to be put away, put it
 away on the labeled shelves or bins in a clean, dry, secure location outside of
 direct sunlight
- DO NOT store any analysis equipment or reagents on open shelves or other locations exposed to dust, humidity, etc., as environmental exposure can contaminate the equipment and/or affect the reagents. Store them in clean, dry enclosed containers
- For all consumables (reagents, single-use supplies, etc.), update the inventory at the end of the day
- For hazardous materials (e.g., cleaning solutions, used chemicals being stored for hazardous waste disposal), store them in **clearly labeled** containers made of an **appropriate material** for the material being stored (e.g., HDPE for hydrochloric acid), with a **securely attached lid**, and on a **bottom shelf** where they will not fall if dropped or tipped over. Where ever such materials are stored, **restrict access** to children, pets, and other unauthorized personnel. For all potentially hazardous materials, **review product label** for other storage instructions



VII. <u>DATA MANAGEMENT</u>

A. Data Entry

- A.1. Before beginning analysis, open the <u>Water Quality Analysis Database</u> and create a new sheet (tab):
 - 1A.1.a. Click the + sign on the lower left corner (in Google Sheets)
 - 1A.1.b. Rename the new sheet with the date (MMDDYYYY) that the samples were **collected**
 - 1A.1.c. Click and drag the new sheet to the end of the list of tabs (so it is arranged in chronological order
 - 1A.1.d. Open the 1st sheet named "TEMPLATE"*
 - ➤ The current template is defined for the 2019 Upper Yellowstone RiverNET -- adjust as necessary for programs with different/additional sites or parameters
 - 1A.1.e. Click the cell in the upper left corner (above the numbered column of rows and to the left of the lettered row of columns in Google Sheets) to select all, and COPY
 - 1A.1.f. Open your new sheet, click the A1 cell, and PASTE
- A.2. During analysis, enter data as it becomes available into the new sheet, which has **one row per parameter for each sample** (columns listed here in *italics* are fixed on the template or produce results from a built-in formula, and **do not require data entry**; other specific instructions are [*italicized in brackets*] in column descriptions here):
 - A.2.A. *Site ID*: alphanumeric identifier from <u>RiverNET Site Location</u>
 <u>Database</u>
 - A.2.B. *Site Name*: listing order, hyphen, full site name
 - A.2.C. **Jar** #: ID number on sample jar used in that event (will vary for each event as sampling jars are cleaned and reused)
 - A.2.D. **Volunteer**: binary, 1 = volunteer collected sample, 0 = staff collected sample [preset to 0 on template: adjust as needed]
 - A.2.E. **Collection Time**: hh:mm in 24-hour format
 - A.2.F. Collection Date: mm/dd/yyyy
 - A.2.G. *Parameter*: one full parameter name per row*
 - ➤ The "Nitrate+Nitrite" row has formulas that automatically sum the individual Nitrate and Nitrite rows -- no data entry required for Column **H** ("Value 1")
 - > Data entered for the "pH" and "Temperature"
 - A.2.H. **Value 1**: the result from one test
 - A.2.I. Value 2: the result from a replicate test of the same sample [if



- applicable, otherwise enter "NA"]
- A.2.J. **Value 3**: the result from a replicate test of the same sample [*if applicable, otherwise enter* "NA"]
- A.2.K. Average Value: automatically calculates average of columns g-i
- A.2.L. **Standard Deviation**: automatically calculates standard deviation of Columns **G-I** [*if columns* **H-I** *are* "NA", *manually change this cell to* "NA"]
- A.2.M. **Energy Labs Value**: result from external duplicate analysis [*if applicable, otherwise enter* "NA"]
- A.2.N. **Confidence Interval**: automatically calculates confidence interval based on a Normal distribution [*if columns* **H-I** *are* "NA", *manually change this cell to* "NA"]
- A.2.O. *CI Population*: number of samples used in confidence interval calculation
- A.2.P. **CI Plus**: upper limit of confidence interval around average value [if columns **H-I** are "NA", manually change this cell to "NA"]
- A.2.Q. **CI Minus**: lower limit of confidence interval around average value [*if columns* **H-I** *are* "NA", *manually change this cell to* "NA"]
- A.2.R. Collector Initials: fml (first, middle, last name) of tech who collected sample
- A.2.S. Analyst Initials: fml of tech who analyzed sample
- A.2.T. Enterer Initials: fml of tech who entered data
- A.2.U. **QA/QC Initials**: fml of tech who checked entered data for quality control
- A.2.V. **Notes:** any observations, questions, concerns, etc. from any of the technicians (collector, analyst, enterer, QA/QC), including their initials
- A.3. Save the spreadsheet
- A.4. Click the cell in the upper left corner (above the numbered column of rows and to the left of the lettered row of columns in Google Sheets) of the completed sheet you just entered data into to select all, and COPY
- A.5. Open the sheet/tab named "2019_ALL"*, scroll down to the first clear row below all previously entered data (or the first row if this was the first data collection event for the season), click on the first cell in the upper left corner, and PASTE
 - ➤ Select appropriate sheet/tab with name corresponding to the year of sampling, or create a new one if needed
- A.6. Save the spreadsheet
- General data entry considerations:
 - **DO NOT** leave any cells blank: all cells must have a value, so enter "NA"



- (all caps, without the quotation marks) for any cell with no other information to enter
- If an error is found: in Column **O** ("Notes") enter (a) the original erroneous value, (b) an explanation of the problem, how you detected it, and how you resolved it, and (c) your initials, THEN replace it with the correct value
- Ensure consistency in all names and naming conventions, date/time formats, decimal formats, etc. throughout database
- Ensure accuracy of all values being entered. Mistakes are easy to make with lots of tedious data entry, and can cause problems in subsequent analyses that may be difficult to identify. So take your time, double check your work against the original data (i.e., field datasheet, Hach colorimeter screen), and take a break if you start feeling bored/tired/distracted.

ACCURATE DATA ENTRY IS CRITICAL FOR THIS AND ALL OTHER PROJECTS!

B. Quality Assurance/Quality Control

- ➤ **Before** data analysis procedures take place, it is the **project manager**'s responsibility to ensure that all technicians:
 - Are adequately trained
 - Have all necessary equipment in proper functioning condition
 - Are fully prepared to safely and effectively complete the tasks at hand
- ➤ *After* data analysis procedures take place, it is the **project manager**'s responsibility to ensure:
 - All data entry procedures have been followed, including double checking that data on Water Quality Field Data Sheets matches data entered into the Water Quality Analysis Database
 - That the new data is complete, consistent, and properly labeled
 - That any questions, comments, or issues addressed in the Notes sections of both the Water Quality Field Data Sheets and the Water Quality Analysis Database have been resolved
 - That the entered data appears to be within the range of expected values
 - ➤ Any suspected outliers must be examined and validated before proceeding
- > At the end of every season it is the project manager's responsibility to:
 - Test all Hach DR900 Colorimeters for every parameter monitored using Hach standard solutions, recording results in a **calibration log** that includes (a) device ID numbers (i.e., S/N), (b) date of test, (c) parameter tested, (d) standard solution reported value, (e) actual measured value, (f) manufacturer reported accuracy range for method, (g) whether the actual



measured value fell within the method's accuracy range around the standard solution reported value (yes or no), and (h) notes

- ➤ Any "nos" in **column g** above must be reported to Hach customer service and resolved before the next sampling event
- > The calibration log must be digitized and backed up with project data and documentation, and available for inspection as needed
- Ensure that all equipment is clean and in working order, prepared for storage (i.e., batteries removed), and stored in the proper location

C. Data Storage and Processing

- 1. All data must be **backed up** in multiple, separate, secure locations. The Google Sheet database is stored on the Cloud, providing one secure location. Other locations may include:
 - A computer hard drive (easy access, moderate durability, moderate protection)
 - An external hard drive stored in a fire file (difficult access, low durability, high protection)
 - A separate Cloud-based server (moderate access, high durability, high protection)
- 2. Backup the database as soon as data entry is complete for one event
- 3. After backing up the data:
 - 3a. Open the "2019_ALL" sheet/tab (or whichever year-appropriate sheet/tab you pasted new data into in **Step VII.A.5** above
 - 3b. Click "Download" under the File menu [Google Sheets, otherwise "Save As" in Excel], and select "Comma-separated values (.csv)"
 - 3c. Name the new .csv with the date (mmddyyyy) of the most recent sample collection date and the prefix "WQ_" (i.e, "WQ_09162019.csv" for data with a most recent sample collection date of September 16, 2019)
 - 3d. Save the new .csv in the "2-Analysis" folder in the RiverNET shared folder

VIII. DATA ANALYSIS

A. Graphical Analysis (2019 VERSION - SUBJECT TO REVISION)

- A.1. On a personal computer, download:
 - A.1.a. Both the "WaterQuality_R" R file and the .csv you created in **Step VII.B.3** from the <u>RiverNET/2-Analysis folder</u>
 - A.1.b. Up to date versions of <u>RStudio</u> and <u>R</u> from the Internet (unless you already have them installed)



- A.2. Create a new folder named "RiverNET_WaterQuality", save the downloaded R file in this folder, save the RStudio and R program files into a new subfolder here named "R" (if needed), and create another subfolder named "Plots" (NOTE: this step is for initial setup, and does not need to be repeated in subsequent analyses using the same computer)
- A.3. Save the downloaded .csv file in the new RiverNET WaterQuality folder
- A.4. Install RStudio and R (if needed), and open the WaterQuality_R R file
- A.5. Check **Line 11** (setwd...), and update the path to where you stored the new RiverNET WaterQuality folder
- A.6. Edit **Line 12** (WQa<-read.csv...) so that the name of the .csv enclosed in quotation marks matches that of the .csv you downloaded and saved in the RiverNET_WaterQuality folder (including the quotation marks and the ".csv" suffix)
- A.7. Select the entire body of code (by either quadruple clicking one of the lines, or by clicking the front of the first line and dragging your cursor through the last line while holding Shift)
- A.8. Run the code (by either pressing Ctrl+Enter on a PC, or by clicking the Run button with the green arrow icon above and center-right of the RStudio code dialogue window (upper left quadrant)
- A.9. When the code has completed running, plots will appear in the RStudio plot window (lower right quadrant): click on the backward facing arrow in the upper right corner of the plot window until it turns gray and you have reached the first plot (labeled "Nitrate+Nitrite Yellowstone River")
- A.10. Drag the edges of the RStudio plot window to expand it to fill your whole screen, then export the plot by:
 - A.10.a. Clicking "Export" on top of the plot window, and selecting "Save as image..."
 - A.10.b. Clicking the "Directory" button in the resulting popup box, and browsing to/selecting the RiverNET_Water/Plots folder you created in **Step 2**, then clicking "Open"
 - A.10.c. Changing the file name to correspond with the plot title
 - A.10.d. Clicking "Save"
- A.11. Click on the forward facing arrow in the upper right corner of the RStudio plot window, and repeat **Step 10** for the remaining plots

B. Interpreting Results

Interpret the plots as follows:

■ Results are shown through colored bar charts. Read these using the scale on the left side of the plot (Y-axis) as you would an old fashioned mercury thermometer: as the value increases, so does the height of the bar. The plots are further arranged so that the data can be visually assessed and



- compared in a meaningful and relevant way.
- Each parameter is plotted individually (named in the plot title), each bar represents a single sample site (described in the plot legend), and each group of bars represents a single sampling event (labeled by date on the plot's bottom (X) axis). The scales on the Y-axis are fixed for each parameter based on the range of values observed across the entire dataset: that way, data from different sample sites/sampling events can be visually compared.
- Sample sites are further grouped and arranged by geography:
 - Yellowstone River *main stem* sites are grouped together, are ordered from upstream to downstream, and share a *continuous blue color spectrum* because these sites and their order are related being on the same body of water
 - *Tributary* sites are grouped based on similar geography, ordered from upstream to downstream relative to the Yellowstone River, but DO NOT share a continuous color spectrum because each tributary is independent of the others
- In addition to the colored bar charts, control/quality assurance assessments are also displayed:
 - **gray lines** on *each* colored bar show the analysis equipment manufacturer's reported **accuracy range** the reported value shown by the colored bar could've actually fallen anywhere within the gray lines
 - black lines shown on *some* colored bars show the confidence interval we calculated for those results after randomly selecting two samples per sampling event, splitting the samples, repeating the analyses three times for each, and calculating the resulting averages and standard deviations if we were to repeat the analysis a fourth time, we would be 95% confident that the result would fall within these black lines, based on the variance within the previous analyses
 - clear bars with black outlines overlaying *some* of the colored bars show independent lab results from an EPA-certified lab (Energy Labs in Helena) that we use to validate and calibrate data from our less sensitive in-house analysis equipment these values should match up with our values, and if they don't, then further review is needed
- To interpret these QA/QC assessments:
 - HIGH QUALITY: samples for which the top of the colored bar, the black lines (if available), and the top of the clear bar (if available) all fall within the gray lines are **accurate** *and* **precise**
 - MODERATE QUALITY: samples for which the top of the colored bar and the top of the clear bar, but *not* the black lines, are within the gray lines are accurate *but not* precise
 - LOW QUALITY (1): samples for which the top of the colored bar and the black lines, but *not* the top of the clear bar, are within the



- gray lines are precise but not accurate
- LOW QUALITY (2): samples for which neither the black lines nor the clear bar are within the gray lines can be considered *neither* accurate *nor* precise
- UNKNOWN QUALITY (1): samples with no confidence interval, but that do have a clear bar within the gray lines, are accurate with *unknown* precision
- UNKNOWN QUALITY (2): samples with no independent lab results, but that do have a black lines within the gray lines, are **precise with** *unknown* **accuracy**
- UNKNOWN QUALITY (3): samples with neither confidence intervals nor independent lab results have *unknown* accuracy and precision
- Not all of samples have a confidence interval: we randomly select ~10% of the sample sites on a given sampling event to conduct these analyses, as conducting them for every sample would be cost and time prohibitive. Nor, for the same reason, do we have independent lab results for every sample: we collect duplicate samples for all of our Yellowstone River main stem sites and all of our top priority tributary sites during three seasonally significant sampling events (pre-growing season; growing season; post-growing season
- Nor is there necessarily a sample for every sample site, every sampling event: although rare, some sites might not have been sampled because of access, weather, timing, or other issues, and later in the season, some tributary sites go dry. In other cases, the sample might have been collected, but a problem during analysis resulted in no available (NA) data.
 - These NAs should not be confused with zeros: a site with no colored bar and *without* grey lines indicates that no data is available (NA) for whatever reason, whereas a site with no colored bar but *with* grey accuracy lines indicates that the sample was collected, the analysis was completed, and the result was zero.
- In addition to data, the Total Nitrogen and Total Phosphorus plots for tributaries of the Upper Yellowstone also show horizontal lines indicating the Montana Department of Environmental Quality's "Base Numeric Nutrient Standard" a water quality threshold indicating the recommended maximum value for the growing season (July 1 September 30). This threshold only applies to tributaries, and only during the growing season.

C. Posting Results Online

After the plots have been visually inspected and their quality assured:

- 1. Log on to SquareSpace, open the YERC website for editing, and navigate to the "RiverNET Water QUALITY Monitoring" page
- 2. Click "EDIT" in the gray dialogue box that appears when you hover over the top



- of that page (white space, NOT the gray banner at the very top)
- 3. Scroll down to the plots, hover over the first one until a gray "GALLERY" dialogue box appears, and click "EDIT"
- 4. Remove the existing images, and replace them by uploading the new plots you just created for that parameter, ordering them (1) Yellowstone River, (2) Yankee Jim Tributaries, (3) West Bank Tributaries, (4) East Bank Tributaries, and click "SAVE"
- 5. Repeat **Steps 3-4** for remaining parameters
- 6. When finished, click "SAVE" in the upper left corner
 - ➤ It is also recommended that you periodically create blog posts on the website's **Field Notes** section interpreting results, interesting findings, potential sources of confusion, and other material, in an easy-reading, jargon-free article aimed at engaging and informing a popular audience -- see YERC Website Maintenance Instructions for step-by-step instructions

IX. SAFETY

A. Field Safety

- General Safety Considerations:
 - ➤ As with all YERC projects, human safety is Priority #1, minimizing resource impact is #2, and accomplishing project objectives is #3, in that order. If you can not do the job safely or without severely harming the study subject or its surroundings, DON'T DO IT!
 - ➤ Always carry a first aid kit. Field techs and volunteers should also maintain up-to-date CPR and First Aid certifications
 - ➤ Be mindful of the **weather**, and don't be on the water if **thunderstorms** are approaching: if you hear thunder or see lightning, it is already too late
 - > Dress appropriately and bring extra dry layers
 - ➤ Be careful **driving** to/from collection sites, parking, and getting out of the car/crossing the road in traffic
 - ➤ Be careful working on **slippery river rocks** ("they are a lot harder than you are" -- Clarence Rostad)
 - ➤ Avoid excessive **sun exposure**, which could result in severe sunburns, heat exhaustion, or heat stroke
 - > Be **courteous and respectful** of other river users, interacting with them and answering questions as best you can
 - > You have both the right and the responsibility to shut down any operation that you feel is unsafe or that you are otherwise uncomfortable with



■ Swift Water Safety

- Adequate safety precautions should be taken prior to entering the field as fast-moving water, unstable banks, and adverse weather conditions present a hazard that could result in serious injury or death
- > Personal floatation devices must be worn whenever boats or other watercraft are used, or when wading in over knee deep water
- ➤ Wading belts must be worn whenever waders are used

■ Wildlife Safety

- ➤ Dangerous wildlife including bears, mountain lions, bison, elk, moose, rattlesnakes, bees, and others **WILL** be encountered in the field: take appropriate precautions
- ➤ Always be **aware of your surroundings**, and never enter an area where visibility is restricted without having **multiple escape routes**
- **Be bear aware at all times**, which includes:
 - Always carry bear spray (in an accessible location like on a hip belt or external pack strap, NOT inside a backpack) and know how to use it
 - Travel in **groups** (at least 2 people, ideally 3 or more)
 - Make lots of **noise** especially when entering areas that are already noisy or where visibility is restricted (running water, wind in trees, thick vegetation, blind corners, etc.)
- Always check the **expiration date** on your bear spray canister, and only carry unexpired bear spray. Expired canistered may be used for training (just make sure you spray them **downwind** while practicing!) Inert bear spray canisters for training may also be purchased.
- ➤ DO NOT leave bear spray canisters inside a closed vehicle, as they can overheat in the sun and explode. Leave them outside, or enclose them inside a sealed PVC case
- > If you encounter a bear:
 - DO NOT make eye contact
 - slowly back away (DO NOT RUN!) while talking softly to the bear
 - ready your bear spray
 - leave the area
- ➤ If the bear charges or follows you, spray a sweeping 2 second burst of bear spray LOW and between the bear and you to make a floating wall of bear spray. If it continues past that, spray directly in the bears face, remembering to spray LOW as it approaches so you don't shoot over the



top of it. **If it charges and hits you**, curl in a ball so as to protect your face, chest, and stomach; cover the back of your neck with your hands OR continue to spray your bear spray if possible; and stay still and calm so that the bear feels that the threat (i.e., you) is neutralized. **If the bear seems predatory** (i.e., it is trying to eat you, not just defend itself) fight back.

- For elk and bison, use **extra caution** around cows during **calving season** (early May-late June) and bulls during the **rut** (mid July-mid October)
- At all times of the year, keep an eye on elk and bison herds, watch where they are moving, and consider not entering an area if it appears as though a herd is moving that way
- Animals acting wary, snorting and stomping, and/or raising their tails may be displaying signs of aggression and should be given plenty of space.
 BUT DO NOT ASSUME THEY WILL ALWAYS DISPLAY SIGNS OF AGGRESSION: ALL ANIMALS MAY ACT SUDDENLY AND UNPREDICTABLY!
- ➤ If you get charged by an elk or bison, RUN! (unlike with bears or other predators)
- Yellowstone National Park regulations mandate that visitors stay at least 100 yards from bears and wolves, and 25 yards from bison, elk, moose, and other large mammals. Those distances are WAY TOO CLOSE: YERC field techs and volunteers must maintain at least double those distances!
- ➤ If someone is bitten by a **snake**: **REMOVE** the victim and rescuers from the area where the snake was, **REMOVE** any jewelry that will cause restrictions with swelling, **RAISE** the bit body part above heart level, **RELAX** the victim to further reduce heart rate, and **RELAY** the victim to professional medical help. **DO NOT** apply ice to the bite or attempt to cut and suck out venom like in old Western movies
- ➤ Before entering the field with any new partners, be aware if anyone has a bee allergy or any other allergies that could be triggered in the field. If anyone does have an allergy, make sure they carry proper medication (e.g., Epipens) and avoid allergens or areas where allergens may be encountered. Consider carrying an antihistamine such as Benadryl in your first aid kit

B. Laboratory Safety

- **Before** starting any procedure, make sure you:
 - Have read and fully understand all safety procedures and chemical information,



- Have all proper equipment in full working order including Personal Protective Equipment, and
- Are confident that you have been fully trained and are fully prepared to handle the task at hand

If any one of these conditions is not met **DO NOT PROCEED** and notify your supervisor **IMMEDIATELY!**

- ➤ Use **Personal Protective Equipment** at all times, including:
 - Latex gloves
 - Elbow-length rubber gloves
 - Goggles
 - Face mask
 - Full sleeve shirt and pants, and closed toe shoes
 - For cleaning procedures using hydrochloric acid, wear a heavy canvas jacket in addition to the above PPE required for all procedures
- Prepare a clean and cleared workspace to complete laboratory procedures, including the pathway between the workspace and storage area
- ➤ Workspace MUST include instant access to a **sink** with cold running water and adequate **ventilation** (e.g., local exhaust, fume hood, respirator)
- Alert all personnel in the vicinity when handling dangerous chemicals and provide Personal Protective Equipment for others who will be assisting or handling chemicals and reagents.
- ➤ Hold chemicals away from face when mixing them or adding them to vials
- > **DO NOT** breath dust/fumes/gas/mist/vapors/spray from chemicals
 - If you do, seek fresh air IMMEDIATELY
- ➤ **DO NOT** get any chemicals on your eyes/skin/clothing
 - If you do, remove the affected clothing and rinse the affected body parts in cold water IMMEDIATELY

> If anyone

- Appears unwell at any time,
- Displays any symptoms such as rash, burning sensation, itching, trouble breathing, or any other allergy or asthma-like symptoms, or
- There is any question about potential exposure:

Immediately remove all personnel, close and contain the workspace, and seek medical help

- > Do not drink, eat, smoke in area where toxic chemicals are used
- ➤ Be aware of the specific procedures for chemicals you will be handling by reviewing their Material Safety Data Sheets (see **Section X**: References)
 - YERC considers **ALL** chemicals used in these procedures to be **hazardous** to human and animal health and to the environment, and they must be stored, handled, and disposed of appropriately
- > Only use reagents, equipment, etc. as directed in manufacturer instructions and project protocols
- > Only use equipment that is in proper working order. DO NOT use damaged or modified equipment
- > Never pipette by mouth. Always use mechanical pipette



- Clean up spills promptly according to published procedures for the specific chemical
- > Empty all disposal containers in the dumpster or other designated disposal areas as soon as procedures are complete
- Remember: Review all hazards and first aid procedures described in the safety data sheets. Always wear your Personal Protective Equipment. Be very careful whenever handling, storing, or working with any of these chemicals. And most importantly, if you feel unsure, unprepared, or unsafe in any way, **DO NOT PROCEED AND IMMEDIATELY CONTACT YOUR SUPERVISOR!** You have both the **RIGHT** and **RESPONSIBILITY** to stop and/or refuse to participate in any operation that you feel is not safe.

C. Laboratory First Aid

- > All labs must have:
 - First Aid Kit
 - Fire Extinguisher(s) suitable for electric and chemical fires
 - Sink, shower, and/or eye rinse station with cold running water
 - Soap
 - Access to fresh air
 - Binder with Material Safety Data Sheets for ALL chemicals being used
 - Immediate communication access to medical help (i.e., fully charged phone)
 - Clearly posted phone numbers to access medical help:
 - > LOCAL EMERGENCY RESPONSE: 911
 - > POISON CONTROL HOTLINE: 1-800-222-1222

If any one of these items is not available or inadequate **DO NOT PROCEED** and notify your supervisor **IMMEDIATELY!**

- First Aid Measures by Nature of Injury for NON-HAZARDOUS chemicals
 - Inhalation
 - Remove to fresh air
 - > Seek medical help if symptoms persist
 - Eye Contact



- ➤ Rinse thoroughly with plenty of water for at least 15 minutes, lifting and lowering eyelids
- > Seek medical help if symptoms persist
- Skin Contact
 - ➤ Wash skin with soap and water
 - > Seek medical help if symptoms persist
- Ingestion
 - > Clean mouth with water and drink plenty of water afterwards
 - > Seek medical help if symptoms persist
- First Aid Measures by Nature of Injury for **HAZARDOUS** chemicals
 - Inhalation
 - Remove to fresh air and keep at rest in comfortable position for breathing
 - > Seek medical help if symptoms persist
 - Eye Contact
 - ➤ Rinse immediately with plenty of water lifting and lowering eyelids
 - Remove contact lenses if present and easy to do under the circumstances
 - > Contact 911/Poison Control immediately: immediate medical help is required
 - Skin Contact
 - > Remove contaminated clothing immediately
 - > Rinse skin with water for at least 15 minutes
 - > Contact 911/Poison Control immediately: immediate medical help is required
 - Ingestion
 - > Rinse mouth. **DO NOT** induce vomiting.
 - > Contact 911/Poison Control immediately: immediate medical help is required

X. REFERENCES

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XI. <u>GLOSSARY</u>

Blank: a blank solution is a solution that contains deionized water or little to no analyte of interest and is used to calibrate laboratory instruments (i.e. Hach DR 900)

Chain of Custody: (CoC), in legal contexts, is the chronological documentation or paper trail that records the sequence of custody, control, transfer, analysis, and disposition of physical or electronic evidence

Colorimeter: the device that measures the <u>absorbance</u> of particular <u>wavelengths</u> of <u>light</u> by a specific <u>solution</u>. This device is commonly used to determine the <u>concentration</u> of a known <u>solute</u> in a given solution by the application of the <u>Beer–Lambert law</u>, which states that the concentration of a solute is proportional to the absorbance



Data Quality Control (QC): refers to comparing hard copy datasheets and notes to the electronic database and correcting and data entry mistakes using the hard copy data sheets as the reference

Data Quality Assurance (QA): refers to the set of processesses used to assure the quality of the data result by using external validation methods, duplicate samples, and blanks

DI Water: Deionized water (DI water, DIW or de-ionized water), often synonymous with demineralized water/DM water, is water that has had almost all of its mineral ions removed, such as cations like sodium, calcium, iron, and copper, and anions such as chloride and sulfate

Dropper: is a device used to transfer small quantities of liquids

Google Drive: a cloud storage service from Google that lets users store and synchronize digital content across computers, laptops and mobile devices, including Android-powered tablet and smartphone devices

Grab Sample: refers to a small representative subset of a larger quantity of water (or other media) collected at one location and at one point in time

Graduated Cylinder: a cylinder used to measure the volume of a liquid. It has a narrow cylindrical shape. Each marked line on the graduated cylinder represents the amount of liquid that has been measured

Hach DR 900: A multi-parameter handheld water testing reactor with over 90 colorimetric parameters for use in the most demanding field environments

Hach DRB 200: A reactor for digestions of metals, nutrients, or biological culture samples. The DRB 200 is pre-programmed with Hach digestion procedures with dual heating blocks

HDPE Jar: (high density polyethylene) plastic jars offer a mildly stiff impact resistant jar with a great moisture barrier

Kimwipe[®]: General purpose wipes used to remove link and electrostatic discharge from glass laboratory instruments

Liquinox[®]: a critical cleaning liquid detergent used to clean laboratory instruments without leaving any interfering residues. It is extremely mild and completely soluble in hard and soft water

Montana DEQ: The Montana Department of Environmental Quality is charged with protecting a clean and healthy environment as guaranteed to our citizens by our State Constitution

Parameter: Chemical characteristics of water of interest to be analyzed. (i.e. pH, total nitrogen etc.)

Parametric Analysis: the study of the influence of different parameters on the solution of the problem

pH Meter: A pH meter is a scientific instrument that measures the hydrogen-ion activity in water-based



solutions, indicating its acidity or alkalinity expressed as pH

Pipette: a laboratory tool commonly used in chemistry, biology and medicine to transport a measured volume of liquid, often as a media dispenser

Pipette Tip: Pipette tips are used with pipettes and pipettors to speed processing and reduce cross-contamination

PPE: Personal protective equipment (PPE) is protective clothing, helmets, goggles, or other garments or equipment designed to protect the wearer's body from injury or infection. The hazards addressed by protective equipment include physical, electrical, heat, chemicals, biohazards, and airborne particulate matter

Powder Pillow: small packets of reagents provided by Hach with associated Test N' Tubes for each digestion procedure

Sample Cell: small glass bottle with a stopper used to measure a sample with a small volume

Standard Solution: a solution containing a precisely known concentration of an element or a substance

Test N' Tube: test tubes provided with appropriate reagent for designated Hach method

Zeroing Out: To reset some device that counts or measures something back to zero. (i.e. Hach DR 900)

XII. APPENDIX

A. <u>RiverNET Upper Yellowstone River Sampling & Analysis Plan</u> (example image-click for link; also available online at <u>www.yellowstoneresearch.org/rivernet</u>)





Yellowstone Ecological Research Center RiverNET Community Water Monitoring Program Upper Yellowstone River Watershed Sampling and Analysis Plan

Prepared for the Montana Department of Environmental Quality April2019

Prepared by:

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Patrick Cross Ecologist/Lab Manager, Yellowstone Ecological Research Center 2048 Analysis Dr. Ste. B | Bozeman, MT 59718

Approvals:

Katie Makarowski (Montana DEQ VM Lab Analysis Program Manager

Michelle Hauer (Montana DEQ QA Officer)

Date

5/29/19

Date

B. <u>RiverNET Site Location Database</u> (example image-click for link)



| Notes | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | 47 |
|--|--------------------------------|--------------------------------------|--------------------------------|---|--------------------------------|---------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------------|--------------------------------|--------------------------------|--------------------------------|----------------------------------|--------------------------------|--------------------------------|---|--------------------------------|--------------------------------|--------------------------------|--------------------------------|---|--|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|---|---|-------------------|
| e Maintenance | NA | NA | NA | NA | https://docs.goog | × | NA | NA | https://docs.goog | NA | Miles (does goog | mps: (docs poor | NA | NA | NA | NA | NA | NA | Mips: (Mors goog | NA | Mips: (docs poor | NA | NA | NA | NA | Miles. (Bocs goog | https://docs.goog | NA | https://docs.goog | NA | NA | NA | |
| Device YERC ID #: | NA | NA | NA | NA | 9-100EQN | NA | NA | NA | MDC2001-10 | NA | NDC2001-1 | MD22001-2 | NA | NA | NA | NA | NA | NA | MX2001-6 | NA | MD22001-3 | NA | NA | NA | NA | NDC2001-5 | 7-100CXV | NA | NDC2001-4 | NA | NA | NA | 7.7 |
| e Devices Serial #s I | NA | NA | NA | NA | 20665424 | NA | NA | NA | 20665460 | NA | 20449344 | 20449345 | NA | NA | NA | NA | NA | NA | 20593597 | NA | 20393593 | NA | NA | NA | NA | 20593595 | 30593596 | NA | 20593594 | NA | NA | NA | 19000008066 |
| Depth Correction (f | NA | NA | NA | NA | 0 | 0 | NA | NA | 0.25 | NA | 1.208 | 2.042 | NA | NA | NA | NA | NA | NA | 177.0 | NA | -0.18 | NA | NA | NA | NA | 0.625 | 0.854 | NA | 0.542 | NA | NA | NA | ; |
| Stage, Max Stage age: Depth Correction (fe Devices Serial 43 | NA | NA | NA | NA | -141.78+171.32s, 0.83; 1.3 | -13.34+79.45x; 0.17; 0.7 | NA | NA | 28.16+134.05x, -0.21; 0.5 | NA | 41.8+209.81x, -0.19, 0.81 | 36.19+159.25x, -0.22; 0.44 | NA | NA | NA | -12.77+93.76x, NA; NA | NA | 83.95+148.34x, NA; N. | 37.02+92.49x, -0.4; 0.42 | 33.48+140.41x, NA, NA | 19.33+224.63x; 0.14; 1.4 | NA | NA | -8.15+186.19x, NA; NA | 61.65+51.58x, NA; NA | 32.37+127.3x; 0.26; 1.0 | 19.28+111.32x; 0.45; 1.9 | 103.52+33.6x, NA, NA | 49.43.45.25.4x, 0.16; 0.9 | 5.59+128.03x, NA, NA | NA | NA | ij |
| Order | 1 | 1 | 67 | 64 | m | , | * | w | 1 | | 4 | m | *1 | + | 61 | 40 | *1 | 1 | - | 4 | + | ţ- | 60 | vo | 64 | 64 | - | 17 | m | * | g, | 10 | 1 |
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| Observation Types | WeterQuality | WaterQuality | | WaterQuality | WaterQuality:Water Quantity | WaterQuality:Water Quantity | WaterQuality | | WaterQuality:Water Quantity | WeterQuality | | WaterQuality:Water Quantity | WaterQuality | WeterQuality | | WaterQuality | WeterQuality | WaterQuantity | WaterQuality:Water Quantity | WaterQuantity | WaterQuality:Water Quantity | WaterQuality | WaterQuality | WaterQuality | WaterQuantity | WaterQuantity | WeterQuantity | 100 | WaterQuality:Water Quantity | WaterQuality | WaterQuality | WeterQuality | |
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| Quality? | | | | | | | | | | | | | | | | | | 0 | | 0 | | | | | 0 | 0 | 0 | 0 | | | | | |
| Tributary? | - | 0 | - | 0 | , | - | - | - | , | 0 | - | 1 | 1 | 0 | - | 1 | 0 | | | 1 | - | 0 | 0 | 1 | , | - | 1 | 1 | 1 | 1 | 0 | 0 | |
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| Long | -110.70039 | -110.73794 | -110.74589 | -110.79016 | -110.80634 | -110.81286 | -110.83945 | -110.87528 | -110.9086 | -110.902 | -110.8315 | -110.86668 | -110.82704 | -110.77301 | -110.70985 | -110.75401 | -110.704 | -109.93336 | -110.69962 | -109.79162 | -110.649 | -110.637 | -110.62 | -110.56789 | -109.90333 | -110.9039 | -110.77164 | -109.83289 | -110.55551 | -110.5217 | -110.583 | -110.566 | |
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| Site Name | Gardiner Niver | Vellouvione River - Gardiner Airport | Landslide Oreak | Yellowstone River - Corwin Springs Fishing Access | Mulberia Creek | Cedar Creek | Joe Brown Creek | Sphinn Creak | Tom Miner Creek | Yellowstone River - Tom Miner Bridge | Lower Big Creek | Upper Big Creak | Dry Creek Pre-Diversion | Vellowstone Kiver - Reedfly Farm | Emigrant Gulch | Fridley Creek, South Fork | Yellowstone River - Gray Ond Fishing Access | Big Timber Creak | Eight Mile Creek | Lower Deer Creek | Mill Creek, lower | Yellowstone River - Das Beiley Fishing Access | Vellowstone River - Mallards Rest Fishing Access | Pins Creek, Joner | Otter Creek | Rock Creak | Six Mile Creek | Upper Dear Creak | Mill Creak, upper | Pins Creak, upper | Yellowstone River - Pine Creek Fishing Access | Yellowstone Kiver - Carters Bridge Fishing Access | |
| | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |

C. <u>RiverNET Water Quality Field Datasheet</u> (example image-click for link)



| Date (mm/dd/yyyy): | AAAA/pp/ | 1 | | | | | | |
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| Yel7 | | | | | | | | |
| Pin1 | | | | | 41 | | | |
| Pin2 | | | | | 10 | | | |
| Yel8 | | | | | | | | |
| Yel9 | | | | | - 10 | | | |
| Additional Mason | Maker | | | | | | | |
| Hadrona | Notes | | | | | | | |
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D. RiverNET Water Quality Analysis Database (example image-click for link)



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