Master Protocol

Yukon River Synoptics

Lab Operations (processing)

Homogenize jerican sample and transfer to clean Teflon Churn

Churn Sampling:

(see Lab flow chart for samples taken from churn)

Prior to collecting sample, rinse churn with copious amounts of DI water
Rinse churn with ~500 ml sample water. When using the paddle to mix the Churn sample, **be sure not to scrap the sides of the Churn with the paddle** (this may scratch the Teflon coating). Person filling the bottles from the Churn wears Poly gloves at all times.

Aiken: DOC Characterization

DOC samples: Collected straight from Teflon churn using the Geopump and filtered through in-line capsule filter into 40 ml brown glass vial. Label with site name, date, time. Keep chilled.

Fractionation samples: Collected straight from Teflon churn using the Geopump and filtered through in-line capsule filter into three 1-L brown glass bottles. Label with site name, date, time. Keep chilled

Michel: Tritium

Tritium: Whole water sample from the Churn collected into a 500 ml Poly bottle. Fill to the top (no rinsing). Cap, label with site name, date, and time. Store at room temp.

Barber: POP's

Whole water from selected sites (see flow chart).
Be sure no detergents or plastics other than silicon are in contact with any of the sampling equipment.

Coplen: D/^{18}O, Nitrate Isotopes

1. Fill 60 ml clear glass vial (poly seal cap) to overflowing with water taken from churn.
2. Cap the vial, making sure there are no air bubbles in the vial.
3. Label vial with site, date, time.
4. Store at room temp.

Kendall: Nitrate Isotopes

From the in-line filter capsule (from churn), fill 2 60ml HDPE bottle per site. Label the bottles with site name, date and time. Bottles are frozen.

Brabets: Sediment fractions samples

Fill a 1-L Poly bottle with whole water from the Churn. Label with site name, date and time. Store at room temp.

Reddy: major anions

From the in-line filter capsule (from churn), collect two 125 ml Poly bottles.
Label bottles with site name, date and time. Store chilled.

Taylor: Major cautions, trace metals, nutrients, Hg

Bottle type	Analyte	Filtration	Processing
Clear plastic, 125-mL bottle	Metals	Gelman	Filter (preserve with 2 ml of nitric acid)
Blue capped clear glass, 125-mL bottle	Hg	Nuclepore	Filter (preserve with 4 ml of nitric acid)
Green capped clear glass, 60-ml bottle	Hg filter	Nuclepore	Preserve with 2 ml of nitric acid
Amber plastic, 30-mL bottle	Nutrients	Gelman	Filter and chill

One time Hg Holding Bottle Calibration:

Upon arrival in the field, the 500 ml Teflon holding bottle for Hg will need to be calibrated. Calibration can be accomplished either by taring the bottle with an appropriate balance and weighing each sample to be filtered (be sure balance can handle the weight of the bottle plus the sample) or by adding a known amount of water with a graduated cylinder and marking the level at 5 or 10 ml intervals throughout the range expected for the sample (ie. 150 to 200 ml).

Cleaning of the churn and Teflon holding bottles prior to sampling and in between sampling

DI rinse the Teflon holding bottles.
DI rinse the churns followed by a rinse with the river water, prior to sample collection.

Splitting of the sample

After the sample is composited in the Teflon-coated 20 L churn, carefully insert the paddle. Churn the composite with a consistent continuous motion for one minute without breaking the surface, prior to splitting the samples. When ready to split the sample, rinse the Hg holding bottle with the sample (use gloves to keep from touching any sample collected). Collect the samples in their respective bottles by opening the spigot and allowing a continuous flow as the sample is dispensed from the churn. Fill the Hg holding bottle with the sample to a volume of between 150 and 200 ml of sample, (use gloves to keep from touching any sample collected), tightly cap, keep cool as possible until processing (ie. keep out of direct sunlight), and record the total volume.

Hg Filtration

With gloved hands open the filter apparatus and rinse the filter support, place a filter (shiny side up) on the filter support and assemble the filter apparatus. Rinse the filtration funnel and filter by passing the rinsing solutions through the filter using dilute nitric followed by a quick DI rinse and discard the rinse solutions (use approx. 15-20 ml for rinses). Finally with sample bottle (120 ml clear glass) in place pour the entire sample into the filter funnel and filter approximately 15-20 ml to rinse the bottle. Discard the rinse solution, replace the sample bottle and filter until the sample bottle is nearly full (leave room for the preservative). Remove the sample bottle when nearly full and add 4 ml of distilled HNO_3, cap tightly. Continue filtering until all the sample has been passed through the filter, if necessary, rinse any sediment in the filter funnel through the filter with DI water.

When all of the sample sediment has been collected on the filter and no more liquid is observed dripping from the filter apparatus, release the pressure and disassemble the apparatus. Remove the filter and place in a 60 ml clear glass bottle, add 2 ml of distilled HNO_3 and cap tightly.

Gelman cartridge filtration from the churn

After collecting the splits of the sample, remove the paddle (preferably store it in the other churn if it is not in use, otherwise, lay the paddle on a clean Kimwipe). Insert the DI-rinsed Teflon tube into the churn with gloved hands. Use the lid to hold the tube in place. Do not allow the tube to extend to the very bottom of the churn. Begin pumping the sample. Rinse filter with a minimum of 1 filter-capsule volume of water prior to beginning collection of filtrate (this rinse may be used for other purposes). Rinse the Taylor sample bottles with a small volume of filtered sample and discard before collection (~5 ml). Sample bottles should be filled in the following order: 1) nutrients; 2) metals. Preserve the filtered samples as indicated above.

Labeling bottles

Please include the following on the label:

- Site
- Yukon Project
- Howard Taylor
- Sample Type
- Date
- Time
- Total volume filtered (**for Hg only; estimate to the nearest 1 ml**)

Blank requests

DI water blank

Collect a sample of the deionized water in the field and submit in individual sample bottles for metals, Hg and nutrients, preserved as described in the table.

Process blank

Process a portion of the deionized water through the various processing steps, including the churn and Gelman filtration. Preserve as indicated above in table.

Kraemer: U Isotopes

Fill 2 1-L Poly bottles with capsule filtered Churn water. Label with site name, date and time. Store at room temp.

Raymond: 14C Sampling

Put QFF filter inline before the capsule filter.

14C-POC and 14C-DOC.

The goal here is to collect POC on the filter (at least 150 ug of material), obtaining enough organic carbon for a C14-POC sample while capturing some of the filtered water in the clear polycarbonate bottles for C14-DOC. These samples can come from the churn and basically involve a simple filtration. Connect the filter holder to the peristaltic pump tubing (I have supplied a few lengths of tubing just in case your tubing doesn't fit the filter holders). Remove the white nubbin and start the pump at a slow pump. Allow the filter holder to fill completely with water, dispelling any air. Place the white nubbin back on. KEEP TRACK OF THE TOTAL FILTER VOLUME. Begin filtering at a moderately slow pump speed.

For Yukon mainstem samples:

Let the first 100 ml pass through the filter (filter rinse). Use a graduated cylinder to track the volume. After 100ml has been filtered, put 100ml of filtered water in one of the labeled 125ml clear polycarbonate bottles. After this continue to filter into the graduated cylinder, filling to 200 ml (total filter volume will be 300 ml). Label bottle "Raymond-14DOC", site name, date, time, Site ID #. Keep chilled in dark.

For glacial melt tribs (no sed):

Same as mainstem sample EXCEPT a total of 2 L will be filtered.

For tribs between the two above:

Observe filter to determine if there is >150 ug material. Sample volumes will likely range from 300 ml to 2 L.

When finished filtering, pass a few liters of air through the filter using the peristaltic pump to dry the filter. The filter gets placed in one of the small labeled vials. The vial is placed on ice and frozen at the first opportunity. The water collected for DOC in the 125ml polycarb bottle gets acidified with 1ml of the phosphoric acid and placed on ice and frozen at the first opportunity.

Group: GFF Filters

1. From Hold Bottles (See flow chart)
2. Use manifold filtering system (4 filter towers). Clean with DI after each use.
3. Follow flow chart for filter-type collection, number and storage.
4. Using SS forceps, place GFFs on filtration rigs with grain running left to right
5. With the exception of the POC/PN and SED/OM filters (Reddy), the more material, the better. The Reddy filters need only have color. Do not "cake " material on these filters. **NOTE**: the SED/OM filter comes from the pre-weighed filters stored in the petri dishes.
6. Mix well the Hold bottle sample and pour into a graduated cylinder, record the volume and pour into the filter funnel making sure all the material is transferred to the funnel. A DI squirt bottle can be used to rinse remaining material from the cylinder but DO NOT record the DI rinse volume.
7. Turn on the vacuum pump and filter the sample. If enough material is on the filter, pump for an additional 30 seconds to tightly pull the material to the filter. If there is not enough material, repeat #7.
    a. Krabbenhoft; For one of the CNS filters: After filtering adequate sample volume; turn the stopcock to the closed position and add approx. 15mL of 10% HCl to filter tower with the filter in place. Allow to stand for 15-20 minutes or until effervescences ceases.
8. While the pump is still running, remove the filter funnel and inspect the part 20 minutes or until any visible effervescence stops of the rim in contact with the GFF. If there is material caked to the rim, squirt it off and on to the GFF surface while the vacuum is still on, then turn off the pump.
9. Break the vacuum. Using SS forceps and touching only the outside of the filters, fold each filter in half with the grain and material on inside of the fold. Place filters next to each other in the Al foil pouch. **Exception:** The SED/OM filters go back into their petri dishes (not folded, facing up)
10. Fold the Al pouch over the filters sealing them (do not tape shut). Label all foil packets with site name, date and time and **TOTAL VOLUME FILTERED**.
11. Rinse filtration rigs with DI-water for next sampling.

Krabbenhoft: Mercury Grabs

Mercury-sample processing

Filtration—practical considerations:

Filters used for filtered-water samples will be analyzed for particulate total mercury (PTHg) and particulate methylmercury (PMHg). If the particle concentration is very low, filter an entire liter for PTHg, and an entire liter for PMHg. At modest particle concentrations, evidenced by slowing filtration rates, ~500 mL is sufficient for each filter.

High particle-concentration waters may require several filter changes to filter sufficient volumes for water samples—in such cases, retain only one filter for PTHg, and one filter for PMHg, noting the volume (mass) of water filtered through each filter. You need not calculate sample volumes that pass through subsequent filters, after the PTHg and PMHg samples have been collected.

Filtration method:

a) Weigh a filled 1-L Teflon sample bottle. Record mass, in grams (if weight exceeds the balance limit, you need to weigh the empty 500 mL collection bottle).

b) <u>500 mL FTHg sample and PTHg sample</u>:
   1. Prepare vacuum filtration chamber. Install a combusted 47 mm diameter quartz fiber filter (QFF) in the filtration support. {Photo}
   2. Discard the 1% HCl from a 500 mL FTHg bottle.
   3. Place open bottle inside vacuum desicator, positioned directly beneath the teflon tube.
   4. Close filtration chamber. Attach vacuum pump line.
   5. Agitate raw-water 1-L sample bottle to keep well mixed (do this frequently during the filtration process), and begin pouring small volumes of raw water into top of filter chamber.
   6. Filter into the 500 mL FTHg bottle, triple rinsing the bottle with small amounts (~10-20 mL) of filtered sample before filling the bottle to the shoulder. Leave >20 mL of headspace for addition of preservative and lab reagents.
   7. Re-cap the FTHg bottle; re-bag; and label outer bag with all sample information.
   8. If the filter has collected a noticeable particle load—evidenced by slowing filtration rates—remove the PTHg filter and place in Teflon petri dish. At low particle loads, filter the remaining water in the first 1-L sample bottle.

c) Repeat step b for FMHg and PMHg using 250 mL FMHg bottle.

d) When filtration is complete, weigh bottle; calculate and record the mass of water (in grams) that passed through the filter. Place filter in its Teflon petri dish; cover with stackable petri dish. Record all necessary sample identification and volume information.

e) <u>Particulate Hg samples</u>: When filtration is complete, and the QFF filters are stacked in their petri dishes, tape the petri dishes together to prevent separation during sample storage and shipping. Place petri dishes in zip-seal bag. Ensure that all sample information is recorded on the bags. Place bagged filters in a cooler stocked with dry ice or frozen, bagged blue ice packs. Keep particulate Hg samples frozen or chilled in field. Upon return to office, store in freezer until all mercury sampling is complete.

f) When filtration is complete, empty any water that has spilled in filtration chamber; re-bag chamber in a clean plastic bag for use at the next site. Place used Teflon filtration parts into a bag to be returned to the WDMRL for cleaning and reuse.

Preservation:

Preserve filtered-water samples with low-mercury 6 *N* HCl preservative as soon after collection as practical. This is the most susceptible step in the process, in terms of contaminating the sample and the HCl preservative. This step may be delayed for a few hours after sampling if it can be done in a more controlled environment. If multiple sites per day are to be sampled, then all samples should be preserved in one sitting at the end of the day, thereby minimizing the number of times the HCl preservative is opened. The WDMRL provides the HCl and measurement vial.

a) At a clean workspace (see above processing notes), using CH / DH procedures, prepare a sample-processing chamber with a new plastic bag.
b) Rinse the measurement vial three times with small volumes of 6 *N* HCl preservative. Collect waste HCl in a waste vessel.
c) Fill the vial to the 10 mL mark and pour into the 500 mL THg bottle. Repeat for all THg to be preserved.
d) Fill measurement vial to the 5 mL mark, and pour into the 250 mL MHg bottle. Repeat for all MHg samples to be preserved.
e) Reseal all bottles. Sample bottles and HCl preservative should be sealed as tightly as possible by hand. **Do not** wrench tighten (recommended in some publications) because it damages threads in the bottle caps. Re-bag bottles in their zip-seal bags.
f) Do not use all of the HCl because the laboratory must analyze the remaining solution. Save at least 30 mL. Return HCl and vial with samples. Write the preservative HCl bottle id in the space to the right of the total mercury bar codes. Use care when handling HCl preservative.
g) Transport and store preserved water samples in a cool, dark environment. When sampling for your study unit is complete (or if a break of more than 1 week occurs in your sampling schedule), express-ship samples to the WDML. **Do not** store or ship preserved water samples on ice—ice meltwater invariably invades the sealed bags, potentially compromising the sample bottles' clean environment. **Do not** expose samples to light or heat.

In addition to these grab samples from each cross section, a 1-L sample will be collected from the Teflon churn at 5 selected sites for method and equipment comparison (grab vs. EDI). Blank collection from the churn will also be required; one before the first use of a churn and one after a field cleaning or two.