STANDARD OPERATING PROCEDURE (SOP)

"Water Quality Sample Processing"

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Reviewed by:

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PROCEDURAL SECTION

1.0 SCOPE AND APPLICATION

1.1 This SOP covers the initial processing and preservation of water quality samples collected for analysis of pH, alkalinity, turbidity, apparent color, specific conductivity, total and volatile suspended solids, soluble reactive phosphorus, dissolved and total P, ammonia$_{tot}$, nitrate + nitrite, dissolved and total N, dissolved and total organic carbon, major cations (Ca, Mg, Na, K), metals (e.g. Fe, Mn), and major anions (SO4, Cl, F).

1.2 It assumes that one 1-liter sample has been collected for measurement of turbidity, apparent color, and suspended solids, 1-2 syringes have been collected for analysis of pH and alkalinity, and one 1-liter sample has been collected for the analysis of the remaining water quality parameters.

2.0 SUMMARY OF METHOD

A. Definitions - N/A

B. Health and Safety Warnings - Lab coats, gloves, and safety glasses should be worn when working with acids. Addition of strong acids to samples for preservation should be done under a hood.

C. Interferences - Samples can be contaminated through hand contact (e.g. Na, Cl, PO_4), through contact with unclean surfaces, through aerial deposition (dust), or through dissolution of acid aerosols released from strong acids. Disposable gloves should be worn when processing samples to avoid hand contact. Samples and filters should not be touch directly; filters may be handled with forceps. Samples should not be left standing uncovered. Samples should be processed in the order described below to avoid cross-contamination from acids used in preservation. Ideally, acidification of samples with HNO_3 or H_3PO_4 should take place in a room other than that used for processing of nutrient or anion samples. Samples should be divided and filtered within 24 hours of collection. Samples must be shaken well before splitting; otherwise sample characteristics will be biased and subsequent analyses invalid. Nutrient and organic carbon samples may deteriorate (mineralize) if left at room temperature for too long; these should be kept at 4°C until processing, and then analyzed or frozen or preserved with acid until analysis.

3.0 PERSONNEL QUALIFICATIONS -

3.1 Personnel should be familiar with general lab safety practices and steps necessary

to avoid contaminating samples. Personnel preparing samples for the first time should be supervised by a staff member familiar with these procedures, and blanks samples be prepared and processed to ensure good techniques have been followed.

4.0 MATERIALS AND PROCEDURES

4.1 Materials

4.1.1 Nalgene-type filtration units (250 mL capacity), Vacuum pump, or hand pump, or lab vacuum (least desirable), Vacuum tubing or thick-walled Tygon tubing

4.1.2 Ultrex HNO_3 (or equivalent)

4.1.3 Phosphoric acid (H_3PO_4) 50%

4.1.4 Calibrated Eppendorf (or equivalent) pipettes (Repeating Eppendorf or 10-100 µL pipette)

4.1.5 Deionized water in wash bottle

4.1.6 10% HCl in wash bottle

4.1.7 10% HNO_3 in wash bottle

4.1.8 Membrane filters (Millipore) ($\leq$ 0.45 µ pore diameter; 47 mm diameter) and forceps

4.1.9 Glass fiber filters as prefilters for turbid samples (47 mm diameter, e.g. GF A/E)

4.1.10 Pre-cleaned sample bottles (see pages 10-11 for volumes needed)

4.1.11 Pre-printed sample labels (corresponding to numbers on field-collected samples)

4.1.11.1 Sample numbers on the 1-L composite samples (C-nnnn) should match those on the subsamples poured off and/or filtered from the main sample

4.1.12 Sample tracking sheet

4.2 Sample filtering (for filtered sample processing)

4.2.1 Clean and soak filtration apparatus for at least one hour in deionized (DIW) water or 10% HCl or 10% HNO_3 prior to filtering samples.

4.2.2 Rinse each filtration apparatus at least 3x with DI water prior to filtering samples.

4.2.2.1 Use forceps when handling o-rings to avoid contamination.

4.2.2.2 When putting filtration apparatus back together, check to make sure that all o-rings are in place and in good condition to prevent leakage.

4.2.2.3 Using clean forceps, place filter(s) on the base of the filtration apparatus.

4.2.2.3.1 Do not touch filter or inside of filtration unit with your hands; disposable gloves should be worn.

4.2.2.3.2 Make sure filter is centered and does not overlap around edges of unit.

4.2.2.4 Replace top of filtering apparatus on bottom and tighten using the white ring around bottom of top unit, while holding down top of unit.

4.2.2.5 Wiggle the top of the unit to make sure it is screwed down snugly; if it is not, it will leak around the edges.

4.2.3 Filter **cation, anion, dissolved nutrient, and dissolved organic carbon** subsamples from 1-L composite sample (C-nnnn) bottle as follows:

4.2.3.1 **Anion** and samples will be filtered with the DI-water washed filtration apparatus.

4.2.3.2 **Nutrient** samples will be filtered with the HCl-washed filtration apparatus.

4.2.3.3 **Cation and organic carbon** samples will be filtered with the HNO_3 -washed filtration apparatus.

4.2.4 The composite sample (C-nnnn) should be shaken thoroughly before dividing into samples as to eliminate analysis bias.

4.2.5 Put approximately 20 mL of sample from composite (C-nnnn) bottle into the top of the unit, swirl, and apply suction to the filter.

4.2.5.1 The filtering apparatus is attached to the vacuum tubing and uses the vacuum pump to suction.

4.2.5.2 Release vacuum from base of unit by releasing cap on side port of filtration unit.

4.2.6 Swirl the water around the bottom of the apparatus and discard, or use to rinse out subsample bottles if only a small amount of parent sample is available.

4.2.6.1 Rinse pre-cleaned cation (M), anion (AN), nutrient (FN), or organic carbon (FC) bottle with **a little** filtered sample and discard before filling bottle completely

4.2.7 Fill FN bottle to just below neck to allow for sample expansion during freezing. Place FN bottle in freezer, AN bottle in refrigerator, and FC and M bottles in hood for acid additions.

4.2.8 Rinse filtering apparatus with appropriate 10% acid solution and 3X DIW between samples.

4.2.8.1 If an organic matter film builds up on the HCl-apparatus, it may need to be wiped out or scrubbed and re-soaked before additional use.

4.2.9 If sample is very turbid, a pre-filter may be needed on top of the membrane filter.

4.3 <u>Sample splitting (for unfiltered sample processing)</u>

4.3.1 The composite sample (C-nnnn) should be shaken thoroughly before dividing into samples as to eliminate analysis bias.

4.3.2 The composite sample © for unfiltered samples will be poured into 2 sample bottles: 1) **unfiltered nutrients** (labeled UN-nnnn) and 2) **total**

organic carbon (labeled UC-nnnn).

4.3.3 Fill UN bottle to **just below neck** to allow for sample expansion during freezing. Place UN bottle in freezer, and UC bottle in hood for acid additions.

4.3.4 See Figure 1 below for summary of sample splitting and preservation steps.

4.4 Sample preservation

4.4.1 Freeze nutrient samples (FN, UN).

4.4.2 Refrigerate anion samples (AN).

4.4.3 Acidify cation (M) samples to pH 1-2 with Ultrex HNO3 and refrigerate. (Start with 100 uL, check pH , add in 50 uL increments until desired pH).

4.4.3.1 Check pH on a subset of samples by pouring a small amount of sample into a beaker and testing with pH paper.

4.4.4 Acidify organic carbon samples (FC, UC) to pH 1-2 with 50% phosphoric acid (use 4 drops ~50uL then check pH) and refrigerate.

4.4.4.1 Check pH on a subset of samples by pouring a small amount of sample into a beaker and testing with pH paper.

4.5 Sample storage and tracking

4.5.1 Samples will be stored in CT rooms (refrigerated samples: UC, FC, AN, M) or in the core freezer (FN, UN) in labeled boxes by sample type.

4.5.2 Check the labels on the shelves for the proper location of different sample types for the WSDT project.

4.5.2.1 The box should be labeled with the date, batch number (corresponds to date of collection, e.g. 6/10/97 = batch 610), team, project, sample type, and holding time. Use preprinted labels provided for this purpose.

4.5.3 Fill out sample tracking sheet with each sample set processed.

5.0 DATA ACQUISITION, CALCULATIONS, AND DATA REDUCTION

A. Computer Hardware and Software - Sample tracking sheets are generated in Paradox after sample numbers are entered from water quality sample field sheets into the R:\WATERSHD\WQ97\SAMPLES.DB file and WQTRACK.SAS is run.

B. Data Management and Records Management - See Water Quality Information Management Plan for details. Samples are tracked by a unique sample code and batch number (corresponding to collection date).

6.0 QUALITY CONTROL AND QUALITY ASSURANCE SECTION

6.1 Field sample blanks, field bottle blanks, and field duplicate samples are all processed the same as blind samples at this point. Laboratory filter blanks are done with every filtering event. These blanks are used in analyses for background determinations.

6.2 QA sample types are recorded on field sheet sample forms and tracked through the information management system.

7.0 REFERENCES

7.1 APHA. 1992. Standard methods for the examination of water and wastewater, 18th edition. American Public Health Association, Washington, D.C.

7.2 U.S. EPA. 1983. Methods for chemical analysis of water and wastes. U.S. Environmental Protection Agency, Cincinnati, Ohio. EPA_600/4-79-020.

7.3 U.S. EPA. 1988. Chemical characteristics of streams in the Mid-Atlantic and Southeastern United States (National Stream Survey - Phase I): Volume I: Population descriptions and physico-chemical relationships. Office of Acid Deposition, Environmental Monitoring and Quality Assurance, Washington, D.C. EPA/600/3-88/021a.

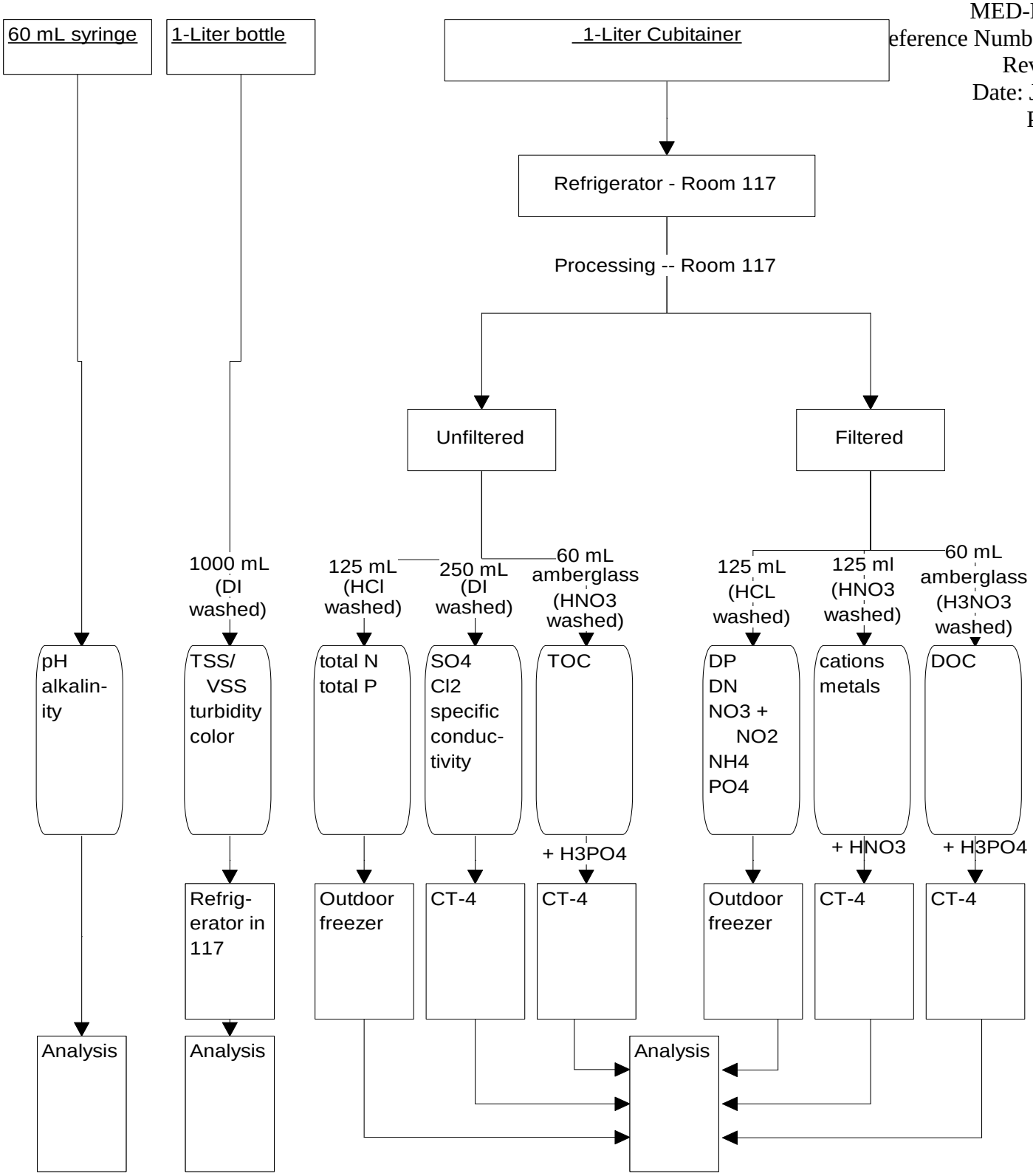
60 mL syringe
1-Liter bottle
1-Liter Cubitainer
Refrigerator - Room 117
Processing -- Room 117
Unfiltered
Filtered
1000 mL (DI washed)
125 mL (HCl washed)
250 mL (DI washed)
60 mL amberglass (HNO3 washed)
125 mL (HCL washed)
125 ml (HNO3 washed)
60 mL amberglass (H3NO3 washed)
pH alkalin-ity
TSS/ VSS turbidity color
total N total P
SO4 Cl2 specific conduc-tivity
TOC
DP DN NO3 + NO2 NH4 PO4
cations metals
DOC
+ H3PO4
+ HNO3
+ H3PO4
Refrig-erator in 117
Outdoor freezer
CT-4
CT-4
Outdoor freezer
CT-4
CT-4
Analysis
Analysis
Analysis

Table 1. Water quality sample collection and preservation procedures.

Parameter	Container	Sample volume	Bottle preparation	Sample preservation	Sample holding times
Bulk sample composite	Polyethylene	1000 mL	Deionized water wash	Storage at 4°C	24 hours
Bulk sample: total suspended solids volatile suspended solids turbidity color	Polyethylene	1000 mL	Deionized water wash	Storage at 4°C	 7 days 7 days 24 hr 48 hr
Unfiltered nutrients: total phosphorus total nitrogen	Polyethylene	125 mL	10% HCl wash	Storage at 0°C	6 months
Filtered nutrients: dissolved phosphorus dissolved nitrogen orthophosphate ammonium nitrate + nitrite	Polyethylene	125 mL	10% HCl wash	Filtration (0.45µ), storage at 0°C	6 months 6 months 6 months 6 months 28 days 6 months
Cations: Ca, Mg, Na, K	Polyethylene	125 mL	10% HNO_3 wash	Filtration, Acidification with Ultrex HNO_3, storage at 4°C	6 months
Organic carbon: dissolved total	Glass amber bottles w teflon lined cap	60 mL	10% HNO_3 wash	Acidification with H_3PO_4, storage at 4°C	 6 months 6 months
Anions: SO_4, Cl specific conductivity	Polyethylene	125 mL	Deionized water wash	Store at 4°C	 28 days 28 days
Alkalinity, pH	Polyethylene syringe	60 mL	Deionized water wash	Store at 4°C	24 hrs

Field sheet for collection of water quality samples

Date(mm/dd/yy)_____ Time (0000-2400)_____
Sampler initials_____/_____

Site code_____ Sample collected on WQ transect? 1 Yes 2 No

If no, what direction from WQ transect? 1 Upstream 2 Downstream
If no, what distance (meters) from WQ transect? _____

weather 1 sun 2 partly cloudy
3 overcast
4 rain 5 sleet
6 snow

wind 1 calm 2 breeze 3 windy

Sample Code _____ Samples collected: 1 L C(omp) ___ 1 L S(S)___ 60 mL syringes____

Sample type 1 event/snowmelt 2 baseline 3 Field sample blank
4 Field bottle blank

Field duplicate 1 Yes 2 No

Collection method 1 Masterflex pump 2 Integrated grab sample

Water surface width across stream at sampling point (cm): _____

Water depth at 10-15 evenly spaced points across stream at sampling point (cm):

____ ____ _____ _____ ____ ____ _____ _____ ____ ____ _____ _____ ____ ____ _____

Water velocity at 10-15 evenly spaced points across channel (m/s, in same order as above):

____ ____ _____ _____ ____ ____ _____ _____ ____ ____ _____ _____ ____ ____ _____

Additional notes: