Addendum to

Quality Assurance Monitoring Plan: Stream Ambient Water Quality Monitoring: Correction of Responsibilities and Addition of Analytes

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SUBJECT:	**ADDENDUM TO QUALITY ASSURANCE MONITORING PLAN: STREAM AMBIENT WATER QUALITY MONITORING: CORRECTION OF RESPONSIBILITIES AND ADDITION OF ANALYTES** **PUBLICATION NUMBER: 03-03-200ADD#1** **PROJECT CODE: AT-07-545-2 & 08-047**

Background

The River and Stream Monitoring Program has been collecting water quality data in more or less the same way since 1988. The most recent Quality Assurance Monitoring Plan (QAMP) was completed in 2003 (Hallock and Ehinger) and our basic objectives, study design, and quality control procedures remain the same. However, since 2003 there have been a few changes:

- Some of the personnel have changed, as has the organization.
- We have added more *runs* because of requests (and funding) for additional stations.
- At some stations, we are measuring additional water quality constituents because of requests from clients.

This addendum is intended to document these changes. The original QAMP (Hallock and Ehinger, 2003) applies except as modified in this addendum.

Organization

Shifting personnel may not always be updated in a new addendum to the QAMP. However, the Environmental Assessment (EA) Program has recently reorganized in a manner that bears directly on quality control procedures. Specifically, the EA Program has regionalized and designated Technical Coordination Teams (TCT) to facilitate cross-region communications and maintain data collection and processing consistency. The Freshwater (FW) TCT will, among other things, regularly review written procedures, periodically observe samplers, and develop training schedules.

Personnel involved in stream monitoring and their duties are listed in Table 1.

Table 1. Ambient monitoring personnel and areas of responsibility (replaces Hallock and Ehinger 2003, Table 1).

Personnel	Region	Phone	Primary Duties
Brad Hopkins	Statewide	360.407.6686	Unit lead for statewide issues
Martha Maggi	Western WA	360.407.6453	Unit lead for Western Washington issues
Gary Arnold	Eastern WA	509.454.4244	Section lead for Eastern Washington issues
George Onwumere	Western WA	360.407.6730	FWTCT management sponsor
Dave Hallock	Statewide	360.407.6681	Data management; miscellaneous data analyses and reports; substitute sampler; FWTCT lead
Chris Coffin	Central	509.454.4257	Central Region ambient monitoring; TMDL effectiveness monitoring
Jim Ross	Eastern	509.329.3425	Eastern Region ambient monitoring; TMDL effectiveness monitoring; metals monitoring quality control assessment
Bill Ward	Southwestern	360.407.6621	Southwestern Region ambient monitoring; continuous temperature monitoring; equipment procurement; SOP maintenance
Craig Homan	Northwestern	425.649.7008	Northwestern Region ambient monitoring and TMDL projects
Casey Clishe	Western	360.407.6691	Olympic Peninsula ambient monitoring; surface water hydrology

The four sampling *runs* referred to in Hallock and Ehinger (2003) may at times be increased depending on personnel available, logistics, the number of stations, and funding. The number of runs may affect who does the sampling and the sampling schedule but all procedures are identical for all runs. These additional runs also share the same requirements for collecting quality control samples as specified in the QAMP for the four basic runs. At present there are two additional runs, besides the usual four: one covers the Olympic Peninsula and the other several Snake River tributaries.

Measurement Quality Objectives

Clients occasionally request and fund the collection of additional water quality constituents at some or all stations beyond those routine analytes we sample. The objectives for requesting particular analytes vary. TMDL modelers, for example, may need total organic carbon; permit writers need alkalinity and hardness (which we plan to collect at all stations in water year (WY) 2008).

Measurement quality objectives (MQOs) for various analytes are specified in Table 2; we expect the client requesting the analyte to ensure that these MQOs are appropriate for the intended use. Accuracy MQOs are to be applied to individual results obtained from field constituents during calibration checks, i.e., the measurement should not exceed the known or replicate value by more than the amount shown. Precision MQOs are to be compared against the average relative standard deviation of at least 10 field split pairs collected during a water year (Mathieu, 2006). Bias MQOs are based on individual laboratory control sample spike recoveries and applied by Manchester Environmental Laboratory (MEL) in accordance with their quality control procedures.

Table 2. Measurement Quality Objectives (replaces Hallock and Ehinger 2003, Table 3).

Analyte	Accuracy (deviation or % deviation from true or replicate value)	Precision (% relative standard deviation)	Bias (% Recovery)
Field Constituents (Routine)			
Conductivity	± 5 µs/cm at 100 µs/cm	10%	NA
Oxygen	± 0.2 mg/L	10%	NA
pH	± 0.10 std. units	10%	NA
Temperature	± 0.2 ºC	10%	NA
Turbidity	± 10%	15%	NA
Lab Constituents (Routine)			
Ammonia-N	NA	10 %	80-120
Fecal coliform (>20 cfu/100mL)	NA	50% of pairs <20%; 90% of pairs <50%	NA
Nitrate+Nitrite-N	NA	10 %	80-120
Nitrogen, total	NA	10 %	80-120
Phosphorus, soluble reactive	NA	10 %	80-120
Phosphorus, total	NA	10 %	80-120
Solids, total suspended	NA	15 %	80-120
Turbidity	NA	15%	95-105
Lab Constituents (Sampled by Special Request)			
Alkalinity	NA	10 %	80-120
Biochemical oxygen demand	NA	25%	85-115
Biochemical oxygen demand, ultimate	NA	25%	80-120
Chloride	NA	5 %	90-110
Hardness	NA	10 %	80-120
Nitrogen, total dissolved	NA	10 %	80-120
Organic carbon, dissolved	NA	10 %	80-120
Organic carbon, total	NA	10 %	80-120
Phosphorus, total dissolved	NA	10 %	80-120
Sediment, suspended concentration (SSC)	NA	15 %	80-120

Field Procedures

We have slightly modified the field procedures discussed in the 2003 QAMP. All samples (except oxygen and bacteria) are now collected in passengers attached to the stainless oxygen sampling bucket (the redesigned sampler is described in Hallock, 2006). Previously, we collected only nutrients and suspended sediment in passengers. Samples for specially requested analytes are generally obtainable as aliquots from these same passengers, usually from the acid-washed nutrient bottle. We will collect samples for biochemical oxygen demand (BOD) and ultimate BOD in a glass jug or other large container and fill the sample container with a funnel.

We are currently re-writing our detailed protocols (Ward et al., 2001) as standard operating procedures. When complete, these will be posted on the EA Program's intranet pages (http://aww.ecology/programs/eap/index.html). In many cases, they will also be published on the EA Program's Quality Assurance internet site (http://www.ecy.wa.gov/programs/eap/quality.html).

Shipment of samples, preservatives, and sample holding times conform to requirements in MEL's User's Manual (Ecology, 2005) (Table 10), and are shown in Table 3.

Table 3. Container type, required water volume, method of preservation, and maximum permissible holding times for lab-analyzed samples are listed below (replaces Hallock and Ehinger 2003, Table 10).

Analyte	Container Type	Sample Volume (mL)	Preservation	Holding Time
Routine Constituents				
Ammonia-N	poly	125	adjust to pH<2 w/ $H_2SO_4$and cool to 4°C	28 days
Fecal coliform	Autoclaved glass or poly	250 or 500	cool < 4°C	24 hrs
Nitrate+Nitrite-N	poly	125	adjust to pH <2 w/ H_2SO_4 and cool to <4°C	28 days
Nitrogen, total	poly	125	adjust to pH<2 w/ $H_2SO_4$and cool to <4°C	28 days
Phosphorus, soluble reactive	brown poly	125	filter in field and cool to <4°C	48 hrs
Phosphorus, total (EPA200.8)	poly	60	adjust to pH<2 w/ HCl and cool to <4°C	28 days
Phosphorus, total (SM4500PI)	poly	60	adjust to pH<2 w/ H_2SO_4 and cool to <4°C	28 days
Solids, suspended	poly	1000	cool to <4°C	7 days
Turbidity	poly	500	cool to <4°C	48 hrs
Constituents Sampled by Special Request				
Alkalinity	poly (can be combined with chloride)	500	cool < 4°C; fill bottle completely	14 days
Biochemical oxygen demand	cubitainer	1 gal	cool < 4°C; keep dark	48 hrs
Biochemical oxygen demand, ultimate	cubitainer	1 gal	cool < 4°C; keep dark	48 hrs
Chloride	poly (can be combined with alkalinity)	500 ml	cool < 4°C	28 days
Hardness	poly	125	adjust to pH<2 w/ $H_2SO_4$and cool to <4°C	6 months
Nitrogen, total dissolved	poly	125	adjust to pH<2 w/ $H_2SO_4$and cool to <4°C	28 days
Organic carbon, dissolved	poly	60	adjust to pH<2 w/ HCl and cool to <4°C	28 days
Organic carbon, total	poly	60	adjust to pH<2 w/ HCl and cool to <4°C	28 days
Phosphorus, total dissolved	poly	60	adjust to pH<2 w/ HCl and cool to <4°C	28 days
Sediment, suspended (SSC)	poly	1000	cool to <4°C	7 days

Laboratory Procedures

Most analytical methods are the same as those specified in Hallock and Ehinger (2003). The only significant change is the addition of another analytical method for the analysis of total phosphorus. Table 4 lists current analytical methods and lower reporting limits for both routinely sampled constituents and additional analytes that may be requested.

Table 4. Laboratory analytical methods and reporting limits (replaces Hallock and Ehinger 2003, Table 11).

Analyte	Sample Matrix	Number of Samples[a]	Method	Reference[b]	Lower Reporting Limit
Routine Constituents					
Ammonia-N	Total	984	Automated phenate	SM4500NH3H	0.01 mg/L
Fecal coliform	NA	984	Membrane filter	SM9222D	1 colony per 100 mg/L
Nitrate+Nitrite-N	Total	984	Automated cadmium reduction	SM4500NO3I	0.01 mg/L
Phosphorus, soluble reactive	Dissolved	984	Automated ascorbic acid	SM4500PG	0.003 mg/L
Solids, suspended	Total	984	Gravimetric	SM2540D	1 mg/L
Nitrogen, total	Total	984	Persulfate digestion, cadmium reduction	SM4500NB	0.025 mg/L
Phosphorus, total	Total	984	Ascorbic acid with manual digestion	SM4500PI	0.01 mg/L
Phosphorus, total	Total		ICP-MS	EPA200.8	0.001 mg/L
Turbidity	Total	984	Nephelometric	SM2130	0.5 NTU
Constituents Sampled by Special Request					
Alkalinity	Total	Various	Titration to pH end point	SM2320B	5 mg/L
Biochemical oxygen demand	Total	Various	Change in dissolved oxygen after incubation	SM5210B	>=2 mg/L
Biochemical oxygen demand, ultimate	Total	Various	Change in dissolved oxygen after incubation; ammonia, NO_2, NO_3	SM5210C	>=2 mg/L
Chloride	Total	Various	Ion Chromatography	SM4110C	0.1 mg/L
Hardness	Total	Various	Ca and Mg by, ICP	SM 2340B	~0.3 mg/L
Nitrogen, total dissolved	Dissolved	Various	Persulfate digestion, cadmium reduction	SM4500NB	0.025 mg/L
Organic carbon, dissolved	Dissolved	Various	CO_2 conversion, NDIR detection	EPA415.1	1 mg/L
Organic carbon, total	Total	Various	CO_2 conversion, NDIR detection	EPA415.1	1 mg/L
Phosphorus, total dissolved	Dissolved	Various	ICP-MS	EPA200.8	0.001 mg/L
Sediment, suspended (SSC)	Total	Various	Gravimetric	ASTMD3977B	1 mg/L

[a] Approximate annual total based on 12 samples per station, 82 stations per year. Does not include quality control samples or additional stations.
[b] SM=Standard Methods (APHA 1998); EPA=Environmental Protection Agency (EPA, 1983).

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