DEPARTMENT OF ECOLOGY
State of Washington

Addendum to Quality Assurance Monitoring Plan

Stream Ambient Water Quality Monitoring: Correction of Objectives, Responsibilities, and Addition of Analytes

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Addendum

This addendum is an addition to an original Quality Assurance Monitoring Plan. The addendum is not a correction (errata) to the original plan.

This addendum is available on the Department of Ecology's website at www.ecy.wa.gov/biblio/0303200Addendum2.html.

Original Publication

Quality Assurance Monitoring Plan: Stream Ambient Water Quality Monitoring

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DEPARTMENT OF ECOLOGY
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THROUGH: Brad Hopkins, Unit Supervisor, Freshwater Monitoring Unit, Western Operations Section

FROM: Dave Hallock, Freshwater Monitoring Unit, Western Operations Section

SUBJECT: **Addendum to Quality Assurance Monitoring Plan: Stream Ambient Water Quality Monitoring: Correction of Objectives, Responsibilities, and Addition of Analytes**

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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 an addendum produced in 2007 (Hallock, 2007). Our basic study design and quality control procedures remain the same. However, since 2007 there have been a few changes. This addendum documents these changes and supersedes the previous addendum (Hallock, 2007). The original QAMP (Hallock and Ehinger, 2003) applies except as modified in this addendum.

Organization

Since the original QAMP was written, the Environmental Assessment (EA) Program has 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, among other duties, regularly reviews written procedures, periodically observes samplers, and develops training schedules.

In 2012, the FWTCT required that samplers be trained by a single designated trainer (to maintain consistency). In addition, to be eligible to conduct ambient monitoring, samplers must have participated in monitoring within the previous 9 months. If eligibility has lapsed, the designated trainer must re-qualify the sampler.

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 and FWTCT management sponsor
Bob Cusimano	Western WA	360.407.6596	Section lead for Western Washington issues
Gary Arnold	Eastern WA	509.454.4244	Section lead for Eastern Washington issues
Dave Hallock	Statewide	360.407.6681	Data management; data analyses and reports; ambient monitoring; FWTCT lead
Jim Ross	Eastern WA	509.329.3425	Technical lead for Eastern Region ambient monitoring
Bill Ward	Southwestern WA	360.407.6621	Ambient monitoring; continuous temperature monitoring; equipment procurement; SOP maintenance; designated trainer
Various field staff	Statewide	N/A	Ambient monitoring. The designated trainer maintains a list of qualified ambient samplers.

The four sampling *runs* referred to in Hallock and Ehinger (2003) may at times be increased or modified 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. All runs share the same requirements for collecting quality control samples as specified in the QAMP for the four basic runs.

Project Description: Objectives

Beginning with water year (WY) 2011 (October 2010-September 2011), we added a new station type (sentinel) and revised the objectives for basin stations. These changes were made after considerable discussion and with the consensus of the FWTCT. The process was documented in an unpublished "White Paper" (Hallock, 2010). Station types and objectives are listed below:

- **Long-term stations** (same as before): Monitored every year to track water quality changes over time (trends), assess inter-annual variability, and collect current water quality information. These stations are generally located near the mouths of major rivers, below major population centers, where major streams enter the state, or upstream from most human-caused sources of water quality problems.

- **Basin stations** (new objectives): Selected to support the "Water Quality Assessment" process and Clean Water Act (303(d)) listings (http://ecy.wa.gov/programs/wq/303d/index.html). Specific objectives are to:

- Confirm current category 5 ("Polluted waters") listings: Some listings are based on old or suspect data; we hope recent data of known quality will help to remove from the category 5 list those waterbodies that currently support standards.
- Determine a category for currently unlisted waterbodies.
- Better define current category 5 listings.
- Resolve category 2 listings ("Waters of concern")
- Identify "high quality" Tier III waters.

- **Special project stations** (same as before): Sampled to address a particular question, and usually supported by funding external to the ambient monitoring program. We may not sample these stations for the entire usual suite of sampled parameters or we may sample extra parameters.

- **Sentinel sites** (new station type): These are effectively "long-term" stations but with different objectives:
  - Support Ecology's probabilistic "watershed health" monitoring program.
  - Characterize reference conditions.
  - Provide trend data for reference conditions.
  - Monitor climate change.

Measurement Quality Objectives

Measurement quality objectives (MQOs) for various analytes are specified in Table 2. For analytes sampled by request, 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.

The pH accuracy MQO is being increased to 0.2 standard units because we have changed our procedures for conducting calibration checks. We now conduct calibration checks with buffers from a different manufacturer than those that used to calibrate the meter. This procedure will help us recognize bad buffers but it also introduces error due to imprecision in the pH of the buffers.

We also routinely monitor total and dissolved metals at several stations every other month. Metals procedures and quality control requirements are discussed in Hopkins (1996).

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 data; permit writers need alkalinity and hardness data, which we collected at all stations in WY 2008.

Most recently, we are planning to collect total recoverable phosphorus (TRP) at Spokane River stations. Advanced wastewater treatment methods are being employed in the Spokane basin in an effort to meet the requirements of the Lake Spokane dissolved oxygen TMDL. Dischargers believe the characteristics of the effluent have changed enough to question some basic assumptions used in modeling, especially regarding the bioavailability of phosphorus. These TRP data may be used in determining whether TRP or total phosphorus should be used for modeling and permitting.

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 have re-written our detailed protocols (Ward et al., 2001) as standard operating procedures (Ward, 2007).

Shipment of samples, preservatives, and sample holding times conform to requirements in MEL's *Lab Users Manual* (Ecology, 2008) (Table 10), and are shown in Table 3.

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 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	± 0.2 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/100 mL)	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
Chlorophyll	NA	25 %	NA
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
Phosphorus, total reactive	NA	10 %	80-120
Sediment, suspended concentration (SSC)	NA	15 %	80-120

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
Chlorophyll	Poly, brown	1 L	cool < 4°C	24 hrs to filtration; 28 days after filtration
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
Phosphorus total reactive	brown poly	125	cool to <4°C	48 hrs
Sediment, suspended (SSC)	poly	1000	cool to <4°C	14 days

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	0.005 mg/L
Phosphorus, total	Total	984	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
Chlorophyll	Total	Various	Fluorometric	SM10200H3	0.05 ug/L
Hardness	Total	Various	Ca and Mg by, ICP	SM2340B	~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
Phosphorus, total reactive	Total	Various	Automated ascorbic acid	SM4500PG	0.003 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).

Table 5. Proposed schedule for completing field and laboratory work, data entry into EIM, and reports.

Field and laboratory work	Due date	Lead staff
Field work completed	Ongoing	Various
Laboratory analyses completed	Ongoing	
Environmental Information System (EIM) database		
EIM user study ID	AMS001, AMS001A-E, AMS001-2	
Product	Due date	Lead staff
EIM data loaded	Quarterly	Dave Hallock
EIM QA	There is no manual EIM data entry	
EIM complete	EIM is compared to primary database annually.	Dave Hallock
Final report		
Author lead / support staff	Dave Hallock/Bill Ward/Jenny Hall/Maggie Bell-McKinnon	
Schedule		
Draft due to supervisor	Ongoing-April	
Draft due to client/peer reviewer	Ongoing-May	
Draft due to external reviewer(s)	No external client	
Final (all reviews done) due to publications coordinator	July	
Final report due on web	September	

References

APHA (American Public Health Association), 2005. Standard Methods for the Examination of Water and Wastewater. 21st Edition. Washington, D.C.

Ecology, 2008. Manchester Environmental Laboratory, Lab Users Manual, 9th Edition, Washington State Department of Ecology, Manchester, WA.

Hallock, D., 2006. River and Stream Water Quality Monitoring Report for Water Year 2005. Washington State Department of Ecology, Olympia, WA. 18 pages + appendices. Publication No. 06-03-032. www.ecy.wa.gov/biblio/0603032.html

Hallock, D. and W. Ehinger, 2003. Quality Assurance Monitoring Plan: Stream Ambient Water Quality Monitoring. Washington State Department of Ecology, Olympia, WA. 27 pages. Publication No. 03-03-200. www.ecy.wa.gov/biblio/0303200.html

Hallock, D., 2007. Addendum to Quality Assurance Monitoring Plan: Stream Ambient Water Quality Monitoring: Correction of Responsibilities and Addition of Analytes. Washington State Department of Ecology, Olympia, WA. 11 pages. Publication No. 03-03-200ADD#1. www.ecy.wa.gov/biblio/0303200add1.html

Hallock, D., 2010. White Paper: Sampling Design for Ambient Basin Stations. June 4, 2010. Washington State Department of Ecology, Olympia, WA. 13 pages. Unpublished Report.

Hopkins, B., 1996. Ambient Metals Project Proposal - Final Quality Assurance Project Plan. Washington State Department of Ecology, Environmental Investigations and Laboratory Services Program, Olympia, WA. 19 pp. + appendices. March 1996.

Mathieu, N., 2006. Replicate Precision for 12 TMDL Studies and Recommendations for Precision Measurement Quality Objectives for Water Quality Parameters. Washington State Department of Ecology, Olympia, WA. 15 pages. Publication No. 06-03-044. www.ecy.wa.gov/biblio/0603044.html

Ward, W., B. Hopkins, D. Hallock, C. Wiseman, R. Plotnikoff, and W. Ehinger, 2001. Stream Sampling Protocols for the Environmental Monitoring and Trends Section. Washington State Department of Ecology, Olympia, WA. 31 pages + appendices. Publication No. 01-03-036. www.ecy.wa.gov/biblio/0103036.html

Ward, W. 2007. Standard Operating Procedures for the Collection, Processing, and Analysis of Stream Samples, Version 1.0. Washington State Department of Ecology, Olympia, WA. SOP Number EAP034. www.ecy.wa.gov/programs/eap/quality.html

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