
Quality Assurance Project Plan for Baseline Monitoring of WSDOT Highway Runoff

July 2014 Addendum to the March 2014 Revision

Prepared by

Environmental Assessment Program

Washington State Department of Ecology

and

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Stormwater and Watersheds Program

Washington State Department of Transportation



Forward

On March 6, 2014, the Washington State Department of Ecology (Ecology) reissued a National Pollutant Discharge Elimination System (NPDES) and State Waste Discharge Municipal Stormwater General Permit (Ecology, 2014) to the Washington State Department of Transportation (WSDOT), effective April 5, 2014, to April 5, 2019. Under Special Condition S7.B of the reissued 2014 NPDES permit, WSDOT must continue a monitoring program to establish baseline stormwater discharge information from the highway runoff characterization sites described in this Quality Assurance Project Plan (QAPP). In accordance with the new permit, monitoring must continue through September 30, 2014.

Addendum A documents changes that occurred to WSDOT highway runoff monitoring requirements with reissuance of the 2014 NPDES municipal stormwater permit. Addendum B describes a new laboratory contract implemented on June 1, 2014, that replaces previous laboratory services contracts described in this QAPP.

Addendum A

On March 6, 2014, the Washington State Department of Ecology (Ecology) reissued a National Pollutant Discharge Elimination System (NPDES) and State Waste Discharge Municipal Stormwater General Permit (Ecology, 2014) to the Washington State Department of Transportation (WSDOT), effective April 5, 2014, to April 5, 2019. Under Special Condition S7.B of the 2014 permit, WSDOT must continue a monitoring program to establish baseline stormwater discharge information from the highway runoff characterization sites described in this Quality Assurance Project Plan (QAPP). In accordance with the new permit, monitoring must continue through September 30, 2014.

The following identifies and describes the changes that occurred to the highway runoff characterization program under Special Condition S7.B of the reissued 2014 NPDES municipal stormwater permit.

S7.B.1 – This condition requires WSDOT to continue collecting stormwater discharge quality and quantity data from the edge of pavement at its existing highway runoff monitoring sites. The reissued 2014 NPDES municipal stormwater permit establishes an end date for data collection of September 30, 2014.

S7.B.3.a – This condition lists the parameters to be sampled and analyzed as part of the highway runoff characterization program. The reissued permit adds hardness to the list of required water quality parameters.

S7.B.5.a.ii – Under the reissued 2014 NPDES permit, this condition allows WSDOT to collect and report data from up to 20 percent of storm events that were forecast qualifying storms but did not meet the qualifying storm event criteria for rainfall depth. The new permit lowers the rainfall depth criterion from a 0.20-inch to 0.15-inch minimum. This change aligns storm event criteria in the reissued 2014 NPDES permit with requirements in the *Technical Guidance Manual for Evaluating Emerging Stormwater Treatment Technologies: Technology Assessment Protocol – Ecology* (TAPE) (Ecology, 2011).

S7.B.5.b – In addition to the rainfall depth criterion, the reissued 2014 NPDES permit aligns storm event criteria for highway runoff characterization monitoring with the remaining requirements in Ecology's TAPE (Ecology, 2011). This condition details these changes. A qualifying storm event must meet the following conditions:

- i. Rainfall depth: 0.15-inch minimum, no fixed maximum.
- ii. Rainfall duration: Shortest acceptable duration one hour.
- iii. Storm start (antecedent dry period): 6 hours minimum with less than 0.04-inch of rain.
- iv. Storm end (post storm period): 6 hours minimum with less than 0.04-inch of rain.

S7.B.6.a – This condition lists the parameters to be sampled and analyzed from sediment collected at the edge of pavement from each highway monitoring site. The reissued permit adds polychlorinated biphenyls (PCBs) to the list of required parameters.

S7.B.7 – This condition describes reporting requirements for the WSDOT highway runoff monitoring program. The reissued 2014 NPDES permit establishes October 31, 2015, as the due date for the final highway runoff characterization report.

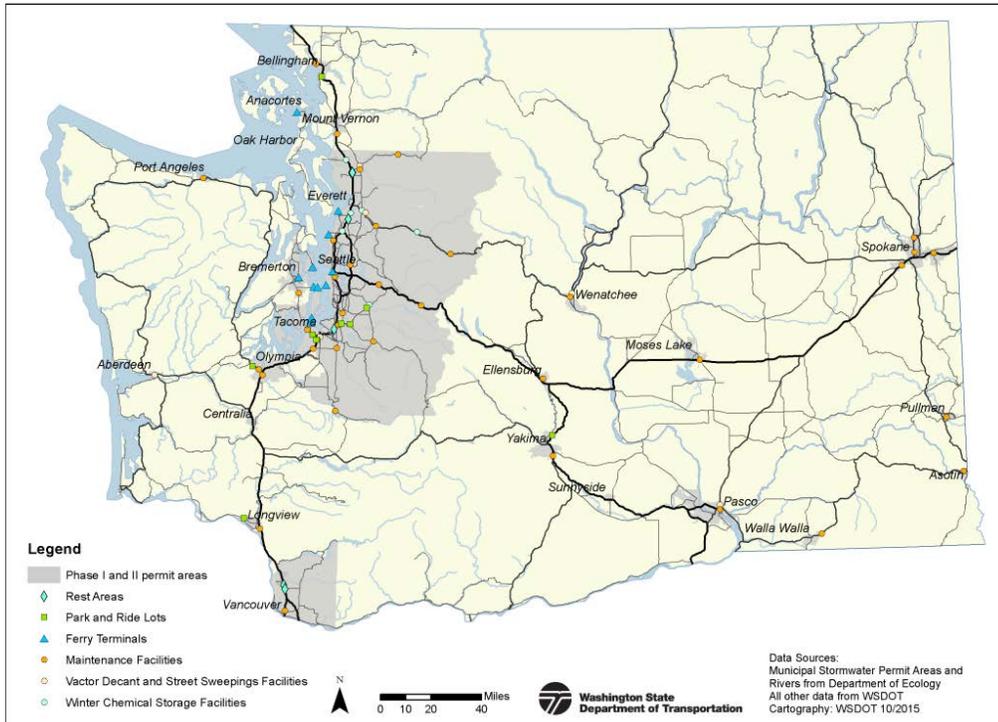


Figure 1 WSDOT NPDES Phase I and Phase II Municipal Stormwater Permit Areas (Updated to reflect 2014 permit coverage area).

Addendum B

On June 1, 2014, the Washington State Department of Transportation (WSDOT) established AmTest, Inc., in Kirkland, Washington as the primary analytical laboratory for the department's stormwater monitoring program. AmTest is an accredited analytical laboratory with the Washington State Department of Ecology (Ecology), and has the ability to achieve acceptable limits of detection for the parameters measured as part of the highway runoff monitoring project.

Not all of the services, methods, and analyses required for the WSDOT highway runoff monitoring program can be performed at the AmTest laboratory in Kirkland. AmTest uses subcontractors to provide a limited number of analytical services. As WSDOT's primary laboratory, AmTest is responsible for managing all subcontracted laboratories to ensure their performance meets all requirements of the highway runoff monitoring program.

The AmTest contract replaces the analytical services agreement with Ecology's Manchester Environmental Laboratory. Establishing AmTest as WSDOT's primary analytical laboratory eliminates the need to communicate with multiple laboratories and streamlines the sample delivery process. Other benefits achieved under this contract include reduced costs for analytical services and availability of AmTest laboratory staff for off hours and weekend sample submittal.

The following *Stormwater Monitoring: Chemical Data Validation Guidance and Criteria, Version 2.0*, updates information in Appendix G of the Quality Assurance Project Plan (QAPP) and presents a complete list of laboratories performing analytical services and their contract required performance criteria, as specified under the June 1, 2014, AmTest contract.

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Washington State Department of Transportation

Stormwater Monitoring: Chemical Data Validation Guidance and Criteria

Version 2.0

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Washington State
Department of Transportation

The Washington State Department of Transportation's (WSDOT's) *Stormwater Monitoring: Chemical Data Validation Guidance and Criteria* is an independent publication and is not affiliated with, nor has it been authorized, sponsored, or otherwise approved by a referenced product's parent company or manufacturer.

Stormwater monitoring work is conducted in response to requirements of WSDOT's NPDES Municipal Stormwater Permit (Ecology, 2014). Instructions presented herein are adapted from published information or were developed by technical experts. Their primary purpose is for internal use by WSDOT's Stormwater Monitoring Group. Described procedures may vary from those used by other WSDOT groups.

WSDOT's stormwater monitoring procedures do not supplant official published definitions or methods.

Distribution of this document does not constitute an endorsement of a particular procedure or method. Any reference to specific equipment, software, manufacturers, or suppliers is for descriptive purposes only and does not constitute an endorsement of a particular product or service by the authors or WSDOT.

Although WSDOT follows these guidelines in most cases, there may be instances in which WSDOT uses an alternative methodology, procedure, or process.

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Acronyms/Abbreviations and Units of Measurement

Acronyms	Abbreviations
%D	percent difference
%D _f	percent drift
%R	percent recovery
%RI	percent relative intensity
%RSD	percent relative standard deviation
%S	percent solids
AES	atomic emission spectrometry
AMU	atomic mass unit
BMP	best management practice
B/N	base and neutral compound
CCAL	continuing calibration
CCB	continuing calibration blanks
CCV	continuing calibration verification
CL	control limit
CLP	contract laboratory program
CRA	reporting limit check sample analysis
CTAS	cobalt thiocyanate activate substance
CWA	Clean Water Act
DFTPP	decafluorotriphenylphosphine
DOC	dissolved organic carbon
Dup	laboratory duplicate
ECD	electron capture detector
Ecology	Washington State Department of Ecology
et al.	and others
FID	flame ionization detector
GC	gas chromatography
GC/MS	gas chromatography/mass spectrometer
HPLC	high performance liquid chromatography
HPLC/MS	high performance liquid chromatography/mass spectrometer
HT	holding time
ICAL	initial calibration
ICB	initial calibration blanks
ICP	inductively coupled plasma
ICP/AES	inductively coupled plasma-atomic emission spectrometry
ICP/MS	inductively coupled plasma-mass spectrometry
ICS	interference check sample
ICSA	interference check sample solution A
ICSAB	interference check sample solution AB
ICV	initial calibration verification
IDL	instrument detection limit
LCL	lower control limit
LCS	laboratory control sample
LCSD	laboratory control sample duplicate
MBAS	methylene blue active substance
MDL	method detection limit
MEL	Washington State Department of Ecology, Manchester Environmental Laboratory
MS	matrix spike

Acronyms	Abbreviations
MSD	matrix spike duplicate
MS4	municipal separate storm sewer system
N/A	not applicable
n/m	narrow mouth
NPDES	National Pollutant Discharge Elimination System
OP	<i>ortho</i> -phosphate
PAHs	polycyclic aromatic hydrocarbons
PS	post-digestion spike
PSD	particle size distribution
QA	quality assurance
QAPP	Quality Assurance Project Plan
QC	quality control
QL	quantitation limit
r	correlation coefficient
r ²	coefficient of determination
RF	response factor
RL	reporting limit
RPD	relative percent difference
RRF	relative response factor
RRT	relative retention time
RSD	relative standard deviation
RT	retention time
RTW	retention time window
SDG	sample delivery group
SIM	selective ion monitoring
SRM	standard reference material
Surr.	surrogate spike compound
TAPE	Guidance for Evaluating Emerging Stormwater Treatment Technologies, Technology Assessment Protocol – Ecology, 2011
TKN	total Kjeldahl nitrogen
TP	total phosphorus
TPH	total petroleum hydrocarbon
TSS	total suspended solids
UCL	upper control limit
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
WAC	Washington Administrative Code
w/m	wide mouth
WSDOT	Washington State Department of Transportation
Units of Measurement	
°C	degrees centigrade
CFU/100mL	colony forming units per 100 milliliters
g	gram, a unit of mass
mg	milligram
mg/Kg	milligrams per kilogram (parts per million)
mg/L	milligrams per liter (parts per million)
mL	milliliters
µg/Kg	micrograms per kilogram (parts per billion)
µg/L	micrograms per liter (parts per billion)
µS/cm	microsiemens per centimeter

WSDOT Stormwater Monitoring: Chemical Data Validation Guidance and Criteria

Introduction

This document contains chemistry data validation protocols and criteria prepared for WSDOT's NPDES Stormwater Monitoring program, as recommended by the USGS report entitled *Scientific Framework for Stormwater Monitoring by the Washington State Department of Transportation* (Sheibley et al., 2009), with supplemental direction provided by (Berwyn, 1999) and (EPA, 2006). The levels of laboratory deliverables—Levels 2a, 2b, 3, and 4—defined herein are based on USEPA *Guidance for Labeling Externally Validated Laboratory Analytical Data for Superfund Use* (EPA, 2009), with supplemental direction provided by (EPA, 2002). This system was selected as the basis for validation because the NPDES program is mandated by the USEPA. WSDOT will combine USEPA levels 3 and 4 into one level referred to as 3+4 and hereto use the reference “WSDOT validation levels” to indicate some deviation from the USEPA levels. USEPA validation levels 2a, 2b, and 3+4 are respectively equivalent to those commonly referred to as Level II, III, and IV by other environmental compliance programs and WSDOT's contract with Cardno TEC.

Validation protocols and criteria presented herein are inclusive of the comprehensive suite of chemistry parameters that have been analyzed for this monitoring program. [Table 1](#) lists current laboratories and contact information of entities performing the referenced analytical work. Analytical methods or techniques irrelevant to the scope of this program (e.g., mercury by cold vapor atomic absorption technique) have been omitted. This document is organized into groups of monitoring parameters based on the types of analytical methodologies as follows:

- Conventional chemistry parameters,
- Metals analysis by ICP and ICP/MS,
- Organic compounds analysis by GC and HPLC, and
- Semi-volatile organic compounds analysis by GC/MS and HPLC/MS methods.

Each group of parameter consists of four tables:

- Validation criteria and respective actions,
- Analysis methods for each of the analytes in the group,
- Sample container, preservation, and holding time requirements, and
- Quality control criteria for the validation.

Table 1 Laboratories Selected for Sample Analyses (Contract Effective May 5th, 2014)

Laboratory Name	Abbreviation	Contact
AmTest, Inc. – Primary Laboratory	AmTest	Project Manager: Aaron Young , Vice President aaron@amtestlab.com Alternate contact: Kathleen Fugiel, President kathyF@amtestlab.com Front Desk: (425) 885-1664
Anatek Labs, Inc. - Subcontractor	Anatek	Kathy Sattler – (509) 838-3999 kathy@anateklabs.com
Analytical Resources, Inc. – Subcontractor	ARI	Mark Harris – (206) 695-6210 markh@arilabs.com
Washington State Department of Transportation – Field Measurements	WSDOT	Fred Bergdolt – (360) 570-6648 bergdof@wsdot.wa.gov

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Validation Guidelines

Table 2a Quality Control Parameters for Various WSDOT Data Validation Levels (Level 2a)

Quality Control Elements	Level 2a			
	Conventional Chemistry Parameters	Metals (ICP/AES & ICP/MS)	Organics (GC & HPLC)	Semi-Volatile Organics (GC/MS & HPLC/MS)
Holding Time and Sample Management	√	√	√	√
Gas Chromatography Coupling with Mass Spectrometry (GC/MS) or High-Performance Liquid Chromatography with Mass Spectrometry (HPLC/MS) Instrument Tuning	N/A	N/A	N/A	
Inductively Coupled Plasma-Mass Spectrometry (ICP/MS) Tuning	N/A		N/A	N/A
Initial Calibration (ICAL)				
Initial Calibration Verification (ICV)				
Continuing Calibration Verification (CCV)				
Initial Calibration Blank and Continuing Calibration Blank (ICB/CCB)			N/A	N/A
Blanks ⁽¹⁾	√	√	√	√
Surrogate Spikes	N/A	N/A	√	√
Multiple Results for One Sample	√	√	√	√
Inductively Coupled Plasma (ICP) Interference Check Sample	N/A		N/A	N/A
Matrix Spike (MS), Matrix Spike Duplicate (MSD), Laboratory Duplicate, or Post-Digestion Spike (PS)	√	√	√	√
Laboratory Control Sample (LCS), Laboratory Control Sample Duplicate (LCSD), and/or Standard Reference Material (SRM)	√	√	√	√
Serial Dilution	N/A		N/A	N/A
Internal Standards	N/A		N/A	
Field Duplicate	√	√	√	√
Reporting Limit Check Sample Analysis (CRA)	N/A		N/A	N/A
Project Reporting Limits (RL)	√	√	√	√
Target Analyte/Compound Identification	N/A	N/A		
Target Analyte/Compound Quantitation				
System Performance				
Overall Data Usability Assessment	√	√	√	√

Table 2a Notes:

N/A – Not applicable

“√” – Indicates the QC parameter is to be reviewed

☐ Indicates the QC parameter is not reviewed in the validation process

Source: USEPA, 2009

[1] Blanks reviewed for Level 2a are limited to method blank and field collected blanks (field blank, trip blank, etc.). Blanks reviewed for Level 2b and Level 3+4 combined are subjected to all blanks, including instrument blanks and initial and continuing calibration blanks.

Table 2b Quality Control Parameters for Various WSDOT Data Validation Levels (Level 2b)

Quality Control Elements	Level 2b			
	Conventional Chemistry Parameters	Metals (ICP/AES & ICP/MS)	Organics (GC & HPLC)	Semi-Volatile Organics (GC/MS & HPLC/MS)
Holding Time and Sample Management	√	√	√	√
Gas Chromatography Coupling with Mass Spectrometry (GC/MS) or High-Performance Liquid Chromatography with Mass Spectrometry (HPLC/MS) Instrument Tuning	N/A	N/A	N/A	√
Inductively Coupled Plasma-Mass Spectrometry (ICP/MS) Tuning	N/A	√	N/A	N/A
Initial Calibration (ICAL)	√	√	√	√
Initial Calibration Verification (ICV)	√	√	N/A	√
Continuing Calibration Verification (CCV)	√	√	√	√
Initial Calibration Blank and Continuing Calibration Blank (ICB/CCB)	√	√	N/A	N/A
Blanks ⁽¹⁾	√	√	√	√
Surrogate Spikes	N/A	N/A	√	√
Multiple Results for One Sample	√	√	√	√
Inductively Coupled Plasma (ICP) Interference Check Sample	N/A	√	N/A	N/A
Matrix Spike (MS), Matrix Spike Duplicate (MSD), Laboratory Duplicate, or Post-Digestion Spike (PS)	√	√	√	√
Laboratory Control Sample (LCS), Laboratory Control Sample Duplicate (LCSD), and/or Standard Reference Material (SRM)	√	√	√	√
Serial Dilution	N/A	√	N/A	N/A
Internal Standards	N/A	√	√	√
Field Duplicate	√	√	√	√
Reporting Limit Check Sample Analysis (CRA)	N/A	√	N/A	N/A
Project Reporting Limits (RL)	√	√	√	√
Target Analyte/Compound Identification	N/A	N/A		
Target Analyte/Compound Quantitation				
System Performance				
Overall Data Usability Assessment	√	√	√	√

Table 2b Notes:

N/A – Not applicable

“√” – Indicates the QC parameter is to be reviewed

☐ Indicates the QC parameter is not reviewed in the validation process

Source: USEPA, 2009

[1] Blanks reviewed for Level 2a are limited to method blank and field collected blanks (field blank, trip blank, etc.). Blanks reviewed for Level 2b and Level 3+4 combined are subjected to all blanks, including instrument blanks and initial and continuing calibration blanks.

Table 2c Quality Control Parameters for Various WSDOT Data Validation Levels (Levels 3+4 Combined)

Quality Control Elements	Levels 3+4 Combined			
	Conventional Chemistry Parameters	Metals (ICP/AES & ICP/MS)	Organics (GC & HPLC)	Semi-volatile Organics (GC/MS & HPLC/MS)
Holding Time and Sample Management	√	√	√	√
Gas Chromatography Coupling with Mass Spectrometry (GC/MS) or High-Performance Liquid Chromatography with Mass Spectrometry (HPLC/MS) Instrument Tuning	N/A	N/A	N/A	√
Inductively Coupled Plasma-Mass Spectrometry (ICP/MS) Tuning	N/A	√	N/A	N/A
Initial Calibration (ICAL)	√	√	√	√
Initial Calibration Verification (ICV)	√	√	N/A	√
Continuing Calibration Verification (CCV)	√	√	√	√
Initial Calibration Blank and Continuing Calibration Blank (ICB/CCB)	N/A	√	N/A	N/A
Blanks ⁽¹⁾	√	√	N/A	N/A
Surrogate Spikes	√	√	√	√
Multiple Results for One Sample	N/A	N/A	√	√
Inductively Coupled Plasma (ICP) Interference Check Sample	√	√	√	√
Matrix Spike (MS), Matrix Spike Duplicate (MSD), Laboratory Duplicate, or Post-Digestion Spike (PS)	N/A	√	N/A	N/A
Laboratory Control Sample (LCS), Laboratory Control Sample Duplicate (LCSD), and/or Standard Reference Material (SRM)	√	√	√	√
Serial Dilution	√	√	√	√
Internal Standards	N/A	√	N/A	N/A
Field Duplicate	N/A	√	√	√
Reporting Limit Check Sample Analysis (CRA)	√	√	√	√
Project Reporting Limits (RL)	√	√	√	√
Target Analyte/Compound Identification	N/A	N/A	√	√
Target Analyte/Compound Quantitation	√	√	√	√
System Performance	√	√	√	√
Overall Data Usability Assessment	√	√	√	√

Table 2c Notes:

N/A – Not applicable

“√” – Indicates the QC parameter is to be reviewed

☐ Indicates the QC parameter is not reviewed in the validation process

Source: USEPA, 2009

[1] Blanks reviewed for Level 2a are limited to method blank and field collected blanks (field blank, trip blank, etc.). Blanks reviewed for Level 2b and Level 3+4 combined are subjected to all blanks, including instrument blanks and initial and continuing calibration blanks.

Table 3 Chemical Data Qualifier Definitions^[1]

Qualifier	Definition
U	The analyte was analyzed for, but was not detected at a level greater than or equal to the level of the reporting limit.
J	The analyte was positively identified and the associated numerical value is approximate; either certain quality control criteria were not met or the concentration of the analyte was below the reporting limit.
NJ	The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical value represents its approximate concentration.
UJ	The analyte was not detected at a level greater than or equal to the reporting limit, and the reported reporting limit may be inaccurate or imprecise.
R	The sample result is unusable because certain quality control criteria were not met.
H	The preparation or analysis was performed past the technical holding time, but data quality may not be significantly affected.
DNR	Do not report this result for the analyte. The result for the analyte was to be reported from an alternative analysis.

Table 3 Notes:

[1] 2008, USEPA. *Contract Laboratory Program National Functional Guidelines for Superfund Organic Methods Raw Data Review*. Publication No. 540-R-08-01. June 2008. <http://www.epa.gov/superfund/programs/clp/guidance.htm>

2010, USEPA. *Contract Laboratory Program National Functional Guidelines for Inorganic Data Review*. Publication No. 540-R-10-011. January 2010. <http://www.epa.gov/superfund/programs/clp/guidance.htm>

Table 4 Chemical Data Qualification Reason Codes

QC Element	Code	Description
Holding Time and Sample Management	PB	Bottle (broken or incorrect)
	PC	Chain of custody issue
	PH	Holding time issue
	PP	Chemical preservation issue
	PT	Temperature preservation issue
	PV	Headspace in volatiles VOA vial
Gas Chromatography Coupling with Mass Spectrometry (GC/MS) or High Performance Liquid Chromatography with Mass Spectrometry (HPLC/MS) Instrument Tuning	IT	Instrument tuning Issue
Inductively Coupled Plasma-Mass Spectrometry (ICP/MS) Tuning		
Initial Calibration (ICAL)	CA	Calibration issues
Initial Calibration Verification (ICV)	ICV	ICV issues
Continuing Calibration Verification (CCV) %D >UCL	CVH	CCV recovery biased high
Continuing Calibration Verification (CCV) %D <LCL	CVL	CCV recovery biased low
Initial Calibration Blank and Continuing Calibration Blank (ICB/CCB)	ICB	Contaminant in ICB/CCB and sample result affected
Blanks	BE	Equipment blank contamination/Trip blank contamination
	BF	Field blank contamination
	BL	Laboratory blank contamination
	BM	Missing blank Information
	BN	Negative laboratory blank contamination
Surrogate Spikes %R >UCL	SSH	Surrogate spike recovery biased high
Surrogate Spike %R <LCL	SSL	Surrogate spike recovery biased low
Multiple Results for One Sample	DNR	Do not report, other result more technically sound (overall assessment)
Inductively Coupled Plasma (ICP) Interference Check Sample	ICS	ICP interference issue
Matrix Spike (MS), Matrix Spike Duplicate (MSD), Laboratory Duplicate, or Post-Digestion Spike (PS)	DL	Laboratory duplicate RPD issue (duplicate, matrix spike duplicate, laboratory control sample duplicate)
	MSH	Matrix spike/matrix spike duplicate recovery biased high
	MSL	Matrix spike/matrix spike duplicate recovery biased low
	PS	Post-digestion spike issue
Laboratory Control Sample (LCS), Laboratory Control Sample Duplicate (LCSD), and/or Standard Reference Material (SRM) %R >UCL	SLH	Laboratory control sample/laboratory control sample duplicate recovery biased high
LCS,LCSD, and/or SRM %R <LCL	SLL	LCS, LCSD, and/or SRM %R biased low
Serial Dilution	SD	Serial dilution issue
Internal Standards recovery >UCL	ISH	Internal standard recovery biased high
Internal Standards recovery <LCL	ISL	Internal standard recovery biased high
Field Duplicate	DF	Field duplicate issue
RL Check Sample Analysis (CRA)	RL	Reporting limit issue
Project Reporting Limits (RL)		
Target Analyte/Compound Identification	TI	Target analyte/compound identification issue
Target Analyte/Compound Quantitation	TQ	Target analyte/compound quantitation issue
	DC	Dual column RPD issue

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QC Element	Code	Description
System Performance	N/A	
Overall Data Usability Assessment	N/A	
Does Not Fit in QC Element Category	MD	Missing deliverables
	MI	Inappropriate analytical method for this parameter
	MQ	No QC results related to this data

A. Conventional Parameters

Table 5 Data Validation Criteria for Conventional Chemistry Parameters

QC Element Subelement	2a	2b	3+4	Acceptance Criteria	Action (use best professional judgment) (-): Nondetected Compounds – (+): Detected Compounds
Holding Times and Sample Management	√	√	√	<ul style="list-style-type: none"> Cooler temperature: ≤6°C Meets preservation and holding time requirements in Table 8 	<ul style="list-style-type: none"> Cooler temperature >6°C: Transit time <24 hours, no action Cooler temperature >6°C: Transit time >24 hours, J(+)/UJ(-) or J(+)/R(-) as justified, based on level of exceedance and type of analyte Preservation requirements not met: J(+)/UJ(-) or J(+)/R(-) as justified, based on type of analyte and required holding time Holding time ≤2x required holding time: J(+)/UJ(-) or J(+)/R(-) as justified, based on type of analyte and severity of holding time exceedance Holding time >2x required holding time: R(+/-) Dissolved organic carbon not filtered or pH in water not analyzed within 15 minutes: H(+/-) pH in water analyzed >24 hours: R(+/-) Dissolved organic carbon filtered >24 hours: R(+/-) Fecal coliform not analyzed within 8 hours but within 24 hours: H(+/-) Fecal coliform analyzed >24 hours: R(+/-)
Initial Calibration (ICAL)		√	√	<p>Where applicable to method:</p> <ul style="list-style-type: none"> At least one blank and five standards to establish ICAL curve Linear regression correlation coefficient (r) >0.995 	<ul style="list-style-type: none"> ICAL not established: R(+/-) ICAL not properly established: Narrate and/or use professional judgment to further qualify data based on the nature of nonconformance, type of analyte, and sample results r <0.995: J(+)/UJ(-)
Initial Calibration Verification (ICV)		√	√	<ul style="list-style-type: none"> Independent source analyzed immediately after calibration. ICV %R = 90-110% For NO₂/NO₃, chloride, sulfate, total phosphorus, <i>ortho</i>-phosphate, and TKN, a low-level standard is analyzed prior to sample analysis Low-level standard %R = 70-130% 	<ul style="list-style-type: none"> ICV %R <90%: J(+)/UJ(-) ICV %R >110%: J(+) Low-level standard %R <70%, sample result >2xRL: No action Low-level standard %R <70%, sample result <2xRL: J(+)/UJ(-) Low-level standard %R >130%, sample result >2xRL: No action Low-level standard %R >130%, sample result <2xRL: J(+)
Continuing Calibration Verification (CCV)		√	√	<p>Where applicable to method:</p> <ul style="list-style-type: none"> Every ten samples, immediately following ICV/ICB and end of analytical sequence CCV %R = 90-110% 	<ul style="list-style-type: none"> CCV not performed properly: Narrate and use professional judgment to evaluate data usability, based on the nature of nonconformance, the type of analyte, and sample results CCV %R <90%: J(+)/UJ(-) CCV %R >110%: J(+)
Initial Calibration Blank and Continuing Calibration Blank (ICB/CCB)		√	√	<p>Where applicable to method:</p> <ul style="list-style-type: none"> After each ICV and CCV every ten samples and end of analytical sequence ICB/CCB concentration absolute value should be <RL 	<ul style="list-style-type: none"> ICB/CCB <RL, sample results ≤RL: U at RL ICB/CCB <RL, sample results >RL: J if sample ≤5x method blank; no action if sample result >5x method blank ICB/CCB ≥RL, sample result ≤RL: U at RL ICB/CCB ≥RL: J if sample result >RL but ≤10x blank; no action if sample result >10x blank ICB/CCB grossly contaminated: R(+/-) Negative ICB/CCB results: J(+)/UJ(-) if sample result < absolute value of 10x ICB/CCB

WSDOT Stormwater Monitoring: Chemical Data Validation Guidance and Criteria

QC Element Subelement	2a	2b	3+4	Acceptance Criteria	Action (use best professional judgment) (-): Nondetected Compounds – (+): Detected Compounds
Blanks – <i>Method Blank</i>	√	√	√	<ul style="list-style-type: none"> One per matrix per batch (not to exceed 20 samples) Less than RL, or all associated sample results >10x the detection in the method blank 	<ul style="list-style-type: none"> Method blank result <RL, sample results ≤RL: U at RL Method blank result <RL, sample results >RL: J if sample ≤5x method blank; no action if sample result >5x method blank Method blank result ≥RL, sample result ≤RL: U at RL Method blank result ≥RL: J if sample result >RL but ≤10x method blank; no action if sample result >10 method blank Method blank grossly contaminated: R(+/-) Negative method blank results: J(+)/UJ(-) if sample result < absolute value of 10x method blank
Blanks – <i>Field Blank</i> <i>Equipment</i> <i>Rinsate Blank</i>	√	√	√	<ul style="list-style-type: none"> Frequency as per QAPP or as needed 	<ul style="list-style-type: none"> Same as method blank
Multiple Results for One Sample	√	√	√	<ul style="list-style-type: none"> Report only one result per analyte 	<ul style="list-style-type: none"> "DNR" results that should not be used to avoid reporting multiple results for one sample
Matrix Spike (MS) or Matrix Spike Duplicate (MSD) – <i>Recovery</i>	√	√	√	<ul style="list-style-type: none"> Refer to Table 7 for specific control criteria No action if sample result > 4x spiking level 	<ul style="list-style-type: none"> Use professional judgment whether all samples in the same batch should be qualified; if lack of accuracy measurement associated with sample analysis, J(+)/UJ(-) all samples in the batch %R <30%: J(+)/R(-) %R ≥ 30% but <LCL: J(+)/UJ(-) %R >UCL: J(+)/no action (-)
MS/MSD, Laboratory Duplicate, or Laboratory Control Sample (LCS)/Laboratory Control Sample Duplicate (LCSD) – <i>RPD</i>	√	√	√	<ul style="list-style-type: none"> Frequency: One MS/MSD, MS/Laboratory Duplicate, or LCS/LCS per matrix per batch RPD <20% for samples >5x RL Difference <RL for samples >RL and <5x RL (may use RPD <35%, Diff <2x RL for solids) 	<ul style="list-style-type: none"> Narrate if frequency not met Use professional judgment whether all samples in the same batch should be qualified If lack of precision measurements associated with sample analysis, J(+)/UJ(-) all samples in the batch RPD or concentration difference outside control criteria: J(+)/UJ(-)
LCS, LCSD, and/or Standard Reference Material (SRM) – <i>Recovery</i>	√	√	√	<ul style="list-style-type: none"> One per matrix per batch Refer to Table 7 for specific control criteria 	<ul style="list-style-type: none"> %R <LCL: J(+)/R(-) all samples in the batch %R > UCL: J(+) all samples in the batch If %R <50%: R(+/-) all samples in the batch If LCS/LCSD RPD >20%: J(+) all samples in the batch
Field Duplicates	√	√	√	<ul style="list-style-type: none"> Solids: RPD <50% or absolute difference <2x RL (for results <5x RL) Aqueous: RPD <35% or absolute difference <1x RL (for results <5x RL) 	<ul style="list-style-type: none"> Criteria not met: J(+)/UJ(-) in both samples
Project Reporting Limits (RL)	√	√	√	<ul style="list-style-type: none"> Reported RL should be ≤RL listed in Table 7, unless justified to raise the RL 	<ul style="list-style-type: none"> Narrate if analyte is not detected and the reported RL exceeded those listed in Table 7 If RL is raised as a result of dilution or matrix effects, evaluate if the dilution or interference is justified; document the finding and resolution in Data Validation Report

WSDOT Stormwater Monitoring: Chemical Data Validation Guidance and Criteria

QC Element Subelement	2a	2b	3+4	Acceptance Criteria	Action (use best professional judgment) (-): Nondetected Compounds – (+): Detected Compounds
Analyte Quantitation			√	<ul style="list-style-type: none"> Perform re-calculation on ICAL, CCV, QC analyses, and sample results to verify that there are no transcription or reduction errors (dilutions, percent solids [%S], sample weights, etc.) on one or more samples 	<ul style="list-style-type: none"> Determine if there is any need to qualify data that are not qualified based on the QC criteria previously discussed Contact the laboratory via WSDOT Project Manager if discrepancies are identified Document findings and resolutions
System Performance			√	<ul style="list-style-type: none"> Examine the raw data for any anomalies (baseline shifts, negative absorbance, omissions, illegibility, etc.) 	<ul style="list-style-type: none"> Determine if there is any need to qualify data that are not qualified based on the QC criteria previously discussed Contact the laboratory via WSDOT Project Manager if discrepancies are identified Document findings and resolutions
Overall Data Usability Assessment – Level 2a	√			<ul style="list-style-type: none"> Check for data points with multiple qualifiers Check for analytes with multiple results 	<ul style="list-style-type: none"> Determine the final data qualifier for a data point in case multiple qualifiers are assigned to the data point Determine the optimal result to be reported for an analyte if multiple results were available for the analyte
Overall Data Usability Assessment – Level 2b		√		<ul style="list-style-type: none"> Check for data points with multiple qualifiers Check for analytes with multiple results Verify that results fall within the calibrated range(s) 	<ul style="list-style-type: none"> Determine the final data qualifier for a data point in case multiple qualifiers are assigned to the data point Determine the optimal result to be reported for an analyte if multiple results were available for the analyte Contact the laboratory via WSDOT Project Manager if discrepancies are identified Document findings and resolutions
Overall Data Usability Assessment – Levels 3+4			√	<ul style="list-style-type: none"> Check for data points with multiple qualifiers Check for analytes with multiple results If reduced volumes were used, verify that appropriate methods and amounts were used in preparing the samples for analysis Verify that results fall within the calibrated range(s) 	<ul style="list-style-type: none"> Determine the final data qualifier for a data point in case multiple qualifiers are assigned to the data point Determine the optimal result to be reported for an analyte if multiple results were available for the analyte Contact the laboratory via WSDOT Project Manager if discrepancies are identified Document findings and resolutions

Table 5 Notes:

Sources: USEPA, 1983; USEPA, 1996; USEPA, 2010; WSDOT(a); WSDOT(b); WSDOT(c); APHA.

Table 6 Laboratories and Methods of Analysis for Conventional Chemistry Parameters

Parameter	Monitoring Type				Methods*	Laboratory (see Table 1)
	NPDES 2014 Hwy. Characterization	NPDES 2016 - 2019 BMP Effectiveness (RA, FT,M)	NPDES 2014 - 2019 BMP Effectiveness (Hwy)	Bioswale Research		
Water Samples						
General Chemistry	Total Chloride	√			USEPA 300.0 Rev. 2.1 (1993) (Ion Chromatography)	AmTest
	Total Sulfate				USEPA 300.0 Rev. 2.1 (1993) (Ion Chromatography)	N/A
	Conductivity ^[1]	√	√	√	Direct Measure	WSDOT
	Alkalinity as CaCO ₃				SM 2320 B-97 (Titration)	N/A
	Particle Size Distribution (PSD) ^[5]		√	√	ASTM D3977-97/TAPE (Laser Diffraction)	ARI
	pH ^{[1][5]}	√	√	√	SM 4500H ⁺ B (Electrometric)	AmTest/ WSDOT
	Temperature ^[1]	√	√	√	Direct measure	WSDOT
	Total Suspended Solids (TSS)	√	√	√	SM 2540D ^[2] (Filtration & Dry Weight)	AmTest
	Dissolved Organic Carbon (DOC)				SM 5310B (High Temp. Combustion)	N/A
Microbial	Fecal Coliform	√			SM 9222D (MF)	AmTest Anatek ^[3]
Surfactants	Methylene Blue Active Substances (MBAS)				SM 5540C (Cationic Transfer/Spectrophotometry)	N/A
	Cobalt Thiocyanate Active Substances (CTAS)				SM 5540D (Cationic and Anionic Transfer/Spectrophotometry)	N/A
Nutrients	Nitrate/Nitrite ^[4]	√	√	√	USEPA 353.2 (Automated Colorimetry)	AmTest
	Ortho-phosphate (OP)	√	√	√	SM 4500-P E (Ascorbic Acid Reduction)	AmTest
	Total Kjeldahl Nitrogen (TKN) ^[4]	√	√	√	USEPA 351.2 (Semi-Automated Colorimetry)	AmTest
	Total Phosphorus (TP)	√	√	√	SM 4500-P E (Ascorbic Acid Reduction)	AmTest
Toxicity	<i>H. azteca</i> 24-hr acute toxicity test ^[1]				ASTM E1192-97 (Acute Toxicity)	N/A
Sediment Samples						
General Chemistry	Particle Size (grain size)	√			ASTM D422 (Sieve/Hydrometer/Hygroscopic Moisture Analyses)	AmTest
	Total Organic Carbon (TOC)	√			USEPA SW-846 9060A (Carbonaceous Analyzer)	AmTest
	Total Solids (%)	√			SM 2540 G (Dry Weight)	AmTest
	Total Volatile Solids (%)				SM 2540 G (Dry Weight)	AmTest

Table 6 Notes:

Parameter information – italicized in grey is not currently applicable to WSDOTs stormwater monitoring activities but may be in the future if future sampling efforts change.

* SM = Standard Methods: <http://www.standardmethods.org/>

USEPA = United States Environmental Protection Agency Method:

http://water.epa.gov/scitech/methods/cwa/methods_index.cfm

ASTM = American Society of Testing and Materials Method: <http://www.astm.org/SITEMAP/index.html>

TAPE = Technology Assessment Protocol – Ecology 2011, *Guidance for Evaluating Emerging Stormwater Treatment Technologies per Washington State Department of Ecology:*

<https://fortress.wa.gov/ecy/publications/summarypages/1110061.html>

MF = Membrane filter

RA = Rest Area

FT = Ferry Terminal

M = Maintenance Facility

[1] Validation criteria for this parameter are not included in this document.

[2] TAPE (Ecology, 2011) requires TSS samples not to exceed 500 microns. A US Standard sieve (#35) or equivalent device may be used for sieving at the lab.

[3] AmTest is the primary laboratory analyzing all samples collected in western WA. Anatek is a subcontracted laboratory analyzing samples collected in the Spokane area.

[4] Optionally collected for research purposes and is not a permit required analyses.

[5] Required for shared Highway and BMP monitoring sites for TAPE (Ecology, 2011) compliance.

Table 7 Method Quality Objectives for Conventional Chemistry Parameters

Parameter	Reporting Limit (RL)	Lab Duplicate (RPD) ^[1]	Matrix Spike (MS)/MS Duplicate (MSD) ^[2] (% Rec)	MS/MSD ^[3] (RPD)	Lab Control Sample (LCS) (% Rec)	
Water Samples^[4]						
General Chemistry	Total Chloride	0.2 mg/L	≤20%	80-120	≤20%	90-110
	<i>Total Sulfate</i>	<i>0.3 mg/L</i>	≤20%	<i>75-125</i>	≤20%	<i>90-110</i>
	Conductivity ^[6]	0.01 μS/cm	N/A	N/A	N/A	N/A
	<i>Alkalinity as CaCO₃</i>	<i>5 mg/L</i>	≤20%	<i>N/A</i>	<i>N/A</i>	<i>80-120</i>
	Particle Size Distribution (PSD)	N/A	≤20%	N/A	N/A	N/A
	pH ^[6]	0.2 units	≤5%	N/A	N/A	N/A
	Temperature ^[6]	0.1°C	N/A	N/A	N/A	N/A
	Total Suspended Solids (TSS)	1.0 mg/L	≤20%	N/A	N/A	81-110
	<i>Dissolved Organic Carbon (DOC)</i>	<i>1.0 mg/L</i>	≤20%	<i>75-125</i>	≤20%	<i>80-120</i>
Microbial	Fecal Coliform	2 min., 2E6 max CFU/100 mL	≤20%	N/A	N/A	N/A
Surfactants	<i>Methylene Blue Active Substances (MBAS)</i>	<i>0.025 mg/L</i>	≤35%	<i>67-133</i>	<i>N/A</i>	<i>80-120</i>
	<i>Cobalt Thiocyanate Active Substances (CTAS)</i>	<i>0.05 mg/L</i>	≤20%	<i>80-120</i>	≤20%	<i>80-120</i>
Nutrients	Nitrate/Nitrite	0.01 mg/L	≤20%	90-110	≤20%	90-110
	<i>Ortho-phosphate (OP)</i>	<i>0.01 mg P/L</i>	≤20%	<i>76-126</i>	≤20%	<i>85-115</i>
	Total Kjeldahl Nitrogen (TKN)	1.0 mg/L	≤20%	69-147	≤20%	80-123
	Total Phosphorus (TP)	0.01 mg P/L	≤20%	88-112	≤20%	90-110
Toxicity	<i>H. azteca 24-hr acute toxicity test^[9]</i>	<i>N/A</i>	<i>N/A</i>	<i>N/A</i>	<i>N/A</i>	<i>N/A</i>
Sediment Samples:^[4]						
General Chemistry	Particle Size (grain size) ^[5]	N/A	≤20% RSD ^[7]	N/A	N/A	N/A
	Total Organic Carbon (TOC)	0.1%	≤20%	70-130	N/A	72-124
	Total Solids (%) ^[5]	N/A	≤20%	N/A	N/A	N/A
	Total Volatile Solids (%)	0.1%	≤20%	N/A	N/A	N/A

Table 7 Notes:

Parameter information – italicized in grey is not currently applicable to WSDOTs stormwater monitoring activities but may be in the future if future sampling efforts change.

CFU = colony forming units

RSD = relative standard deviation

[1] Recommended value. The relative percent difference (RPD) must be ≤ the indicated percentage for results that are >5x reporting limit (RL). Concentration difference values must be ≤2x RL for values that are ≤5x RL.

[2] Recommended value. For inorganics, the *Contract Laboratory Program Functional Guidelines* states the spike recovery limits do not apply when the sample concentration exceeds the spike concentration by a factor of four or more (USEPA, 2010).

- [3] Recommended value. The matrix spike duplicate RPD criteria apply when original and replicate results are $\geq 5x$ RL. Concentration difference of $1x$ RL applies to precision evaluation if either or both original and replicate results are $< 5x$ RL.
- [4] Unless otherwise noted, method quality objectives (matrix spike & LCS values) are based on current performance-based statistics provided by the analytical laboratories. The values are subject to change as the laboratories update their performance control limits as required by the accreditation programs.
- [5] The Measurement Quality Objectives (MQOs) were taken from the Ecology, 2008, Sediment Sampling and Analysis Plan Appendix: www.ecy.wa.gov/pubs/0309043.pdf
- [6] Validation criteria for this parameter are not included in this document. Measurement is taken directly in the field and is not currently lab measured.
- [7] Grain size requires a triplicate analysis; therefore, a relative standard deviation (RSD) is calculated.

Table 8 Quantity, Container, Preservation, and Holding Time Requirements for Conventional Chemistry Parameters

	Parameter	Minimum Quantity Needed for Analysis & QC Samples	Container	Preservative ^{[1][2]}	Holding Time ^[3]
Water Samples					
General Chemistry	Total Chloride ^[5]	Analysis = 10 mL MS & Dup = 10 mL each	250 mL poly bottle if collected alone. 500 mL poly bottle if batched with TSS and pH.	None required.	28 days
	Total Sulfate	Analysis = 100 mL MS & Dup = 100 mL each	500 mL w/m poly bottle	Cool to ≤6°C	28 days
	Conductivity ^[4]	Analysis = 300 mL Dup = 300 mL	500 mL poly, ^[13] glass, or Teflon®	Cool to ≤6°C	Immediately if direct measure; otherwise, 28 days ^[13]
	Alkalinity as CaCO ₃	Analysis = 500 mL (fill bottle full) Dup = 500 mL	500 mL w/m poly bottle	Cool to ≤6°C; fill bottle completely, do not agitate sample ^[13]	14 days
	Particle Size Distribution (PSD)	Analysis = 250 mL Dup = 250 mL	500 mL poly bottle	Cool to ≤6°C	7 days
	pH ^{[5],[6]}	Analysis = 10 mL Dup = 10 mL	250 mL poly bottle if collected alone. 500 mL poly bottle if batched with TSS and total chloride.	None required.	Immediately if direct measure; otherwise, analyze within 15 minutes
	Temperature ^[4]	N/A	N/A	N/A	Immediately if direct measure
	Total Suspended Solids (TSS) ^{[5],[6]}	Analysis = 100 mL Dup = 100 mL	250 mL poly bottle if collected alone. 500 mL poly bottle if batched with pH and total chloride.	Cool to ≤6°C	7 days
	Dissolved Organic Carbon (DOC)	Analysis = 50 mL MS & Dup = 50 mL each	60 mL n/m poly bottle	Filter; ^[9] then add 1:1 HCl to pH<2; cool to ≤6°C	28 days
Microbial	Fecal Coliform	Analysis = 100 mL Dup = 100 mL	250 mL poly autoclaved bottle with preservative ^[8]	Fill EDTA preserved ^[8] bottle to the shoulder; cool to <10°C	6 hours + 2 hours at the lab
Surfactants	Methylene Blue Active Substances (MBAS)	Analysis = 400 mL Dup = 400 mL	1L poly bottle	Cool to ≤6°C	48 hours
	Cobalt Thiocyanate Active Substances (CTAS)	Analysis = 400 mL Dup = 400 mL	1L poly bottle	Cool to ≤6°C	48 hours

Table 8 Quantity, Container, Preservation, and Holding Time Requirements for Conventional Chemistry Parameters

	Parameter	Minimum Quantity Needed for Analysis & QC Samples	Container	Preservative ^{[1][2]}	Holding Time ^[3]
Nutrients	Nitrate/Nitrite ^[7]	Analysis = 10 mL MS & Dup = 10 mL each	250 mL preserved poly bottle if collected alone or batched with TKN and TP.	H ₂ SO ₄ to pH<2; cool to ≤6°C	28 days
	<i>Ortho</i> -phosphate (OP)	Analysis = 25 mL MS & Dup = 25 mL each	250 mL poly bottle	Filter within 15 minutes of collection; ^[9] cool to ≤6°C	48 hours
	Total Kjeldahl Nitrogen (TKN) ^[7]	Analysis = 25 mL MS & Dup = 25 mL each	250 mL preserved poly bottle if collected alone or batched with Nitrate/Nitrite and TP.	H ₂ SO ₄ to pH<2; cool to ≤6°C	28 days
	Total Phosphorus (TP) ^[10]	Analysis = 25 mL MS & Dup = 25 mL each	250 mL preserved poly bottle if collected alone or batched with Nitrate/Nitrite and TKN.	H ₂ SO ₄ to pH<2; cool to ≤6°C	28 days
Toxicity	<i>H. azteca</i> 24-hr acute toxicity test	<i>2 liters total</i>	<i>(4 L) poly cube container</i>	<i>Cool to ≤6°C</i>	<i><36 hours; or <72 hours with approval from Ecology</i>
Sediment Samples					
General Chemistry	Particle Size (grain size)	Analysis = 100 wet g Dup = 100 wet g	1 L glass jar with Teflon® lined lid if batched with all sediment parameters.	Cool to 4°C; Do not freeze ^[11]	6 months ^[11]
	Total Organic Carbon (TOC)	Analysis = 2 wet g MS & Dup = 2 wet g each	1 L glass jar with Teflon® lined lid if batched with all sediment parameters	Cool to 4°C/ May freeze at -18°C at lab ^[11]	14 days; 6 months if frozen ^[11]
	Total Solids (%) ^[12]	Analysis = 10 wet g Dup = 10 wet g	1 L glass jar with Teflon® lined lid if batched with all sediment parameters	Cool to 4°C/ May freeze at -18°C at lab ^[11]	14 days; 6 months if frozen ^[11]
	Total Volatile Solids (%)	Analysis = 20 wet g Dup = 20 wet g	1 L glass jar with Teflon® lined lid if batched with all sediment parameters	Cool to 4°C/ May freeze at -18°C at lab ^[11]	14 days; 6 months if frozen ^[11]

Table 8 Notes:

Parameter information – italicized in grey is not currently applicable to WSDOTs stormwater monitoring activities but may be in the future if sampling efforts change.

Some parameters can be batched in one sample container, e.g., total chloride, pH, and TSS. All sediment parameters can be batched in one sample container.

w/m = wide mouth

n/m = narrow mouth

MS = matrix spike

MSD = matrix spike duplicate

Dup = laboratory duplicate

QC = quality control

poly = polyethylene or high density polyethylene (HDPE). Does not include low density polyethylene (LDPE) per (Table 2, footnote 1 of 40CFR136).

[1] Preservation needs to be done in the field, unless otherwise noted. Ice will be used to cool samples to approximately 6°C.

[2] Preservation per 40 CFR 136, accessed online at and current as of 6/12/2014, unless noted or italicized in grey.

[3] Holding times per 40 CFR 136, accessed online at and current as of 6/12/2014, unless noted or italicized in grey.

[4] Validation criteria for this parameter are not included in this document. Also, measurement is taken directly in the field and is not currently lab measured.

- [5] For highway characterization or shared highway and BMP monitoring sites, a single 500 mL poly bottle is used to collect stormwater for TSS, Chlorides, and pH analyses.
- [6] For BMP effectiveness and Bioswale research monitoring sites, a single 250 mL poly bottle is used to collect stormwater for TSS and pH analyses.
- [7] For BMP effectiveness and Bioswale research monitoring sites, a single 250 mL poly bottle is used to collect stormwater for Nitrate/Nitrite, TKN, and TP analyses.
- [8] Per SM 9222D and 9060A, sample bottles should come sterilized and preserved with EDTA and/or $\text{Na}_2\text{S}_2\text{O}_3$ from the lab prior to collection of samples high in heavy metals (Cu & Zn > 1mg/L) or if an oxidant such as chlorine is suspected to be present. Sample containers from AmTest (used for both E. & W.WA samples) are autoclaved 250 mL w/m HDPE bottles preserved with EDTA.
- [9] 0.45 micron pore size filters.
- [10] For Highway characterization, BMP effectiveness, and Bioswale research monitoring sites a single 250 mL poly bottle is used to collect stormwater for Nitrate/Nitrite, TKN, and TP analyses.
- [11] [Sediment Sampling and Analysis Plan Appendix](#) (Ecology, 2008).
- [12] Permit called for "Total Solids," which is an incorrect term for sediment solids analysis. WSDOT believes the Permit intended to ask for "percent solids" analysis.
- [13] Criteria specified in the 2008 MEL document "Manchester Environmental Laboratory, Lab User's Manual, 9th edition."

B. Metals by ICP/AES and ICP/MS Methods

Table 9 Data Validation Criteria for Metal by ICP/AES and ICP/MS Methods

QC Parameter Subelement	2a	2b	3+4	Acceptance Criteria	Action (use best professional judgment) (-): Nondetected Compounds – (+): Detected Compounds
Holding Times and Sample Management	√	√	√	<ul style="list-style-type: none"> Cooler temperature: ≤6°C Meets preservation and holding time requirements refer to Table 12 	<ul style="list-style-type: none"> Cooler temperature >6°C: Transit time <24 hours, no action Cooler temperature >6°C: Transit time >24 hours, J(+)/UJ(-) if justified Preservation requirements not met: J(+)/UJ(-) Holding time not met: J(+)/UJ(-) if justified Dissolved metals not filtered within 15 minutes but filtered and preserved within 24 hours of collection: H(+/-) Dissolved metals not filtered and preserved within 24 hours: R(+/-)
Inductively Coupled Plasma-Mass Spectrometry (ICP/MS) Tuning		√	√	<ul style="list-style-type: none"> Performed prior to initial calibration Tuning solution should contain proper tuning elements required by the method Scan tuning solution at least five times consecutively, and %RSD <5% Peak widths should be within manufacturer's specification Mass resolution should be <0.1 AMU 	<ul style="list-style-type: none"> Tuning analysis not performed: R(+/-) Tuning analysis not properly performed: Narrate and/or further qualify data Resolution of mass calibration >0.1 AMU: J(+)/UJ(-) %RSD >5%: J(+)/UJ(-)
Initial Calibration (ICAL)		√	√	<ul style="list-style-type: none"> At least one blank and five standards to establish ICAL curve Linear regression correlation coefficient (r) >0.995 y-Axil intercept ≤RL 	<ul style="list-style-type: none"> ICAL not established: R(+/-) ICAL not properly established: Narrate and/or further qualify data r <0.995: J(+)/UJ(-) y-Axil intercept >RL: J(+)/UJ(-)
Initial Calibration Verification (ICV)		√	√	<ul style="list-style-type: none"> Independent source analyzed immediately after calibration ICV %R = 90-110% 	<ul style="list-style-type: none"> %R <75%: J(+)/R(-) %R = 75-89%: J(+)/UJ(-) %R = 111-125%: J(+) %R >125%: R(+)
Continuing Calibration Verification (CCV)		√	√	<ul style="list-style-type: none"> Every ten samples, immediately following ICV/ICB and end of analytical sequence CCV %R = 90-110% 	<ul style="list-style-type: none"> CCV not performed properly: Narrate and/or further qualify data CCV %R <75%: J(+)/R(-) CCV %R = 75-89%: J(+)/UJ(-) CCV %R = 111-125%: J(+) CCV %R >125%: R(+)

Table 9 Data Validation Criteria for Metal by ICP/AES and ICP/MS Methods

QC Parameter Subelement	2a	2b	3+4	Acceptance Criteria	Action (use best professional judgment) (-): Nondetected Compounds – (+): Detected Compounds
Initial Calibration Blank and Continuing Calibration Blank (ICB/CCB)		√	√	Where applicable to method: <ul style="list-style-type: none"> After each ICV and CCV every ten samples and end of analytical sequence ICB/CCB concentration absolute value should be <RL 	<ul style="list-style-type: none"> ICB/CCB <RL, sample results ≤RL: U at RL ICB/CCB <RL, sample results >RL: J if sample ≤5x method blank; no action if sample result >5x method blank ICB/CCB ≥RL, sample result ≤RL: U at RL ICB/CCB ≥RL: J if sample result >RL but ≤10x blank; no action if sample result >10x blank ICB/CCB grossly contaminated: R(+/-) Negative ICB/CCB results: J(+)/UJ(-) if sample result <absolute value of 10x method blank
Blanks – Preparation Method Blank	√	√	√	<ul style="list-style-type: none"> One per matrix per batch (not to exceed 20 samples) Less than RL, or all associated sample results >10x the detection in the method blank 	<ul style="list-style-type: none"> Method blank result <RL, sample results ≤RL: U at RL Method blank result <RL, sample results >RL: J if sample ≤5x method blank; no action if sample result >5x method blank Method blank result ≥RL, sample result ≤RL: U at RL Method blank result ≥RL: J if sample result >RL but ≤10x method blank; no action if sample result >10 method blank Method blank grossly contaminated: R(+/-) Negative method blank results: J(+)/UJ(-) if sample result < absolute value of 10x method blank
Blanks – Field Blank Equipment Rinsate Blank	√	√	√	<ul style="list-style-type: none"> Frequency as per project QAPP or as needed 	<ul style="list-style-type: none"> Same as method blank
Multiple Results for One Sample	√	√	√	<ul style="list-style-type: none"> Report only one result per analyte 	<ul style="list-style-type: none"> "DNR" results that should not be used to avoid reporting multiple results for one sample
Inductively Coupled Plasma (ICP) Interference Check Sample – Interference Check Sample Solution A (ICSA) and Interference Check Sample Solution AB (ICSAB)		√	√	<ul style="list-style-type: none"> Beginning and end of each analytical sequence or every 8 hours ICSAB %R 80%-120% ICSA Absolute value < RL 	<ul style="list-style-type: none"> For samples with Al, Ca, Fe, and Mg >ICSA levels only R(+/-) if %R <50% J(+) if %R > 120% J(+)/UJ(-) if %R= 50% to 79%

Table 9 Data Validation Criteria for Metal by ICP/AES and ICP/MS Methods

QC Parameter Subelement	2a	2b	3+4	Acceptance Criteria	Action (use best professional judgment) (-): Nondetected Compounds – (+): Detected Compounds
Matrix Spike (MS), Matrix Spike Duplicate (MSD), or Post-Digestion Spike (PS) – Recovery	√	√	√	<ul style="list-style-type: none"> If matrix spike performed, post-digestion spike is required Refer to Table 11 for specific control criteria No action if sample result > 4x spiking level If matrix spike %R is outside 75-125%, perform post-digestion spike at 2x the sample concentration 	<ul style="list-style-type: none"> If PS not performed with MS, then narrate Determine if all samples in the same batch should be qualified If lack of accuracy measurement associated with sample analysis, J(+)/UJ(-) all samples in the batch MS %R <30% and PS not performed or PS %R <75%: J(+)/R(-) MS%R <30% and PS %R >75%: J(+)/UJ(-) %R ≥ 30% but <75%: J(+)/UJ(-) %R >125%: J(+)
MS/MSD, Laboratory Duplicate, or Laboratory Control Sample (LCS)/Laboratory Control Sample Duplicate (LCSD) – RPD	√	√	√	<ul style="list-style-type: none"> Frequency: One MS/MSD, MS/Laboratory Duplicate, or LCS/LCS per matrix per batch RPD <20% for samples >5x RL Difference <RL for samples >RL and <5x RL (RPD <35%, Diff <2x RL for solids) 	<ul style="list-style-type: none"> Narrate if frequency not met Use professional judgment whether all samples in the same batch should be qualified If lack of precision measurements associated with sample analysis, J(+)/UJ(-) all samples in the batch RPD or concentration difference outside control criteria: J(+)/UJ(-)
LCS, LCSD, and/or Standard Reference Material (SRM) – Recovery	√	√	√	<ul style="list-style-type: none"> One per matrix per batch Refer to Table 10 for specific control criteria 	<ul style="list-style-type: none"> %R <LCL: J(+)/R(-) %R > UCL: J(+) If %R <50%: R(+/-)
Serial Dilution		√	√	<ul style="list-style-type: none"> Perform a 5x dilution on one sample per matrix per batch %D for the original and diluted analysis should be <10% for original sample concentration >50x MDL (ICP); >100x MDL (ICP/MS) 	<ul style="list-style-type: none"> J(+)/UJ(-) if %D >10% and the analyte concentration is >50x MDL (ICP) or >100x MDL (ICP/MS)
Internal Standards – ICP/MS		√	√	<ul style="list-style-type: none"> Proper number of internal standards - Li (the Li6 isotope); Sc; Y; Rh; Tb; Ho; Lu; or Bi are added to all field and laboratory quality control samples The Percent Relative Intensity (%RI) in the sample shall fall within 60-125% of the response in the calibration blank 	<ul style="list-style-type: none"> Internal standards not added to samples: R(+/-) %RI outside the 60-125% limit: J(+)/UJ(-)

Table 9 Data Validation Criteria for Metal by ICP/AES and ICP/MS Methods

QC Parameter Subelement	2a	2b	3+4	Acceptance Criteria	Action (use best professional judgment) (-): Nondetected Compounds – (+): Detected Compounds
Field Duplicates	√	√	√	<ul style="list-style-type: none"> Solids: RPD <50% or absolute difference <2x RL (for results <5x RL) Aqueous: RPD <35% or absolute difference <1x RL (for results <5x RL) 	<ul style="list-style-type: none"> Criteria not met: J(+)/UJ(-) in both samples
Reporting Limit Check Sample Analysis (CRA)		√	√	<ul style="list-style-type: none"> 2x RL analyzed at beginning of analytical sequence Not required for Al, Ba, Ca, Fe, Mg, Na, K %R = 70%-130% (50%-150% Sb, Pb, Tl) 	<ul style="list-style-type: none"> R(-)/J(+) <2x RL if %R <50% (<30% Sb, Pb, Tl) J(+) <2x RL, UJ(-) if %R 50-69% (30%-49% Sb, Pb, Tl) J(+) <2x RL if %R 130%-180% (150%-200% Sb, Pb, Tl) R(+) <2x RL if %R >180% (200% Sb, Pb, Tl)
Project Reporting Limits (RL)	√	√	√	<ul style="list-style-type: none"> Reported RL should be ≤RL listed in Table 11, unless justified to raise the RL 	<ul style="list-style-type: none"> Narrate if analyte is not detected and the reported RL exceeded those listed in Table 11 If RL is raised as a result of dilution or matrix effects, evaluate if the dilution is justified; document the finding and resolution in Data Validation Report
Target Analyte Quantitation			√	<ul style="list-style-type: none"> If reduced volumes were used, verify that appropriate methods and amounts were used in preparing the samples for analysis Perform recalculation on ICAL, CCV, QC analyses, and sample results to verify that there are no transcription or reduction errors (dilutions, percent solids [%S], sample weights, etc.) on one or more samples 	<ul style="list-style-type: none"> Contact the laboratory via WSDOT Project Manager if discrepancies are identified Document findings and resolutions
System Performance			√	<ul style="list-style-type: none"> Examine the raw data for any anomalies (baseline shifts, negative absorbance, omissions, illegibility, etc.) 	<ul style="list-style-type: none"> Determine if there is any need to qualify data that are not qualified based on the QC criteria previously discussed Contact the laboratory via WSDOT Project Manager if discrepancies are identified Document findings and resolutions
Overall Data Usability Assessment – Level 2a	√			<ul style="list-style-type: none"> Check for data points with multiple qualifiers Check for analytes with multiple results 	<ul style="list-style-type: none"> Determine the final data qualifier for a data point in case multiple qualifiers are assigned to the data point Determine the optimal result to be reported for an analyte if multiple results were available for the analyte

Table 9 Data Validation Criteria for Metal by ICP/AES and ICP/MS Methods

QC Parameter Subelement	2a	2b	3+4	Acceptance Criteria	Action (use best professional judgment) (-): Nondetected Compounds – (+): Detected Compounds
Overall Data Usability Assessment – <i>Level 2b</i>		√		<ul style="list-style-type: none"> • Check for data points with multiple qualifiers • Check for analytes with multiple results • Verify that results fall within the calibrated range(s) 	<ul style="list-style-type: none"> • Determine the final data qualifier for a data point in case multiple qualifiers are assigned to the data point • Determine the optimal result to be reported for an analyte if multiple results were available for the analyte • Contact the laboratory via WSDOT Project Manager if discrepancies are identified • Document findings and resolutions
Overall Data Usability Assessment – <i>Level 3+4</i>			√	<ul style="list-style-type: none"> • Check for data points with multiple qualifiers • Check for analytes with multiple results • Verify that results fall within the calibrated range(s) 	<ul style="list-style-type: none"> • Determine the final data qualifier for a data point in case multiple qualifiers are assigned to the data point • Determine the optimal result to be reported for an analyte if multiple results were available for the analyte • Contact the laboratory via WSDOT Project Manager if discrepancies are identified • Document findings and resolutions

Table 9 Notes:

Sources: USEPA, 1983; USEPA, 1996; USEPA, 2010; WSDOT(a); WSDOT(b); WSDOT(c).

Table 10 Laboratories and Methods of Analysis for Metals

Parameter	Monitoring Type				Methods*	Laboratory (see Table 1)
	NPDES 2014 Hwy. Characterization	NPDES 2017 - 2019 BMP Effectiveness (RA, FT, M)	NPDES 2014 - 2019 BMP Effectiveness (Hwy)	Bioswale Research		
Water Samples						
Metals	Dissolved Cadmium (Cd)	√			USEPA 200.8 (ICP/MS)	AmTest
	Dissolved Copper (Cu)	√	√	√		
	Dissolved Lead (Pb)	√				
	Dissolved Zinc (Zn)	√	√	√		
	<i>Dissolved Calcium (Ca)</i>				USEPA 200.7 Rev. 4.4 (1994) (ICP/AES)	N/A
	<i>Dissolved Magnesium (Mg)</i>					
	<i>Dissolved Sodium (Na)</i>					
	<i>Dissolved Potassium (K)</i>					
	Total Recoverable Cadmium (Cd)	√			USEPA 200.8 (ICP/MS)	AmTest
	Total Recoverable Copper (Cu)	√	√	√		
	Total Recoverable Lead (Pb)	√				
Total Recoverable Zinc (Zn)	√	√	√			
Inorganics	Hardness as CaCO ₃	√	√	√	USEPA 200.7 Rev. 4.4 (1994) (ICP/AES)	AmTest
Sediment Samples						
Metals	Total Recoverable Arsenic (As)	√			USEPA 200.8 (ICP/MS)	AmTest
	Total Recoverable Cadmium (Cd)	√				
	Total Recoverable Copper (Cu)	√				
	Total Recoverable Lead (Pb)	√				
	Total Recoverable Zinc (Zn)	√				
Nutrients	Total Phosphorus (TP)				USEPA 200.7 Rev. 4.4 (1994) (ICP-AES)	AmTest

Table 10 Notes:

Parameter information – italicized in grey is not currently applicable to WSDOTs stormwater monitoring activities but may be in the future if future sampling efforts change.

- * SM = Standard Methods: <http://www.standardmethods.org/>
- USEPA = United States Environmental Protection Agency Method:
http://water.epa.gov/scitech/methods/cwa/methods_index.cfm

RA = Rest Area
 FT = Ferry Terminal
 M = Maintenance Facility

Table 11 Method Quality Objectives for Metals

Parameter	Reporting Limit (RL)	Lab Duplicate ^[1] (RPD)	Matrix Spike (MS)/MS Duplicate (MSD) ^[2] (% Rec)	MS/MSD ^[3] (RPD)	Lab Control Sample (LCS) (% Rec)	
Water Samples^[4]						
Metals	Dissolved Cadmium (Cd)	0.1 µg/L	≤20%	75-125	≤20%	85-115
	Dissolved Copper (Cu)	0.1 µg/L	≤20%	75-125	≤20%	85-115
	Dissolved Lead (Pb)	0.1 µg/L	≤20%	75-125	≤20%	85-115
	Dissolved Zinc (Zn)	5.0 µg/L	≤20%	75-125	≤20%	85-115
	<i>Dissolved Calcium (Ca)</i>	<i>0.025 mg/L</i>	≤20%	<i>75-125</i>	≤20%	<i>85-115</i>
	<i>Dissolved Magnesium (Mg)</i>	<i>0.025 mg/L</i>	≤20%	<i>75-125</i>	≤20%	<i>85-115</i>
	<i>Dissolved Sodium (Na)</i>	<i>0.025 mg/L</i>	≤20%	<i>75-125</i>	≤20%	<i>85-115</i>
	<i>Dissolved Potassium (K)</i>	<i>0.25 mg/L</i>	≤20%	<i>75-125</i>	≤20%	<i>85-115</i>
	Total Recoverable Cadmium (Cd)	0.2 µg/L	≤20%	75-125	≤20%	85-115
	Total Recoverable Copper (Cu)	0.1 µg/L	≤20%	75-125	≤20%	85-115
	Total Recoverable Lead (Pb)	0.1 µg/L	≤20%	75-125	≤20%	85-115
	Total Recoverable Zinc (Zn)	5.0 µg/L	≤20%	75-125	≤20%	85-115
	Inorganics	Hardness as CaCO ₃	1.0 mg/L	≤20%	75-125	≤20%
Sediment Samples^[4]						
Metals	Total Recoverable Arsenic (As)	0.1 mg/Kg dry	≤20%	75-125	≤20%	85-115
	Total Recoverable Cadmium (Cd)	0.1 mg/Kg dry	≤20%	75-125	≤20%	85-115
	Total Recoverable Copper (Cu)	0.1 mg/Kg dry	≤20%	75-125	≤20%	85-115
	Total Recoverable Lead (Pb)	0.1 mg/Kg dry	≤20%	75-125	≤20%	85-115
	Total Recoverable Zinc (Zn)	5.0 mg/Kg dry	≤20%	75-125	≤20%	85-115
Nutrients	Total Phosphorus (TP) ^[5]	0.01 mg/Kg dry	≤20%	N/A	≤20%	63-142

Table 11 Notes:

Parameter information – italicized in grey is not currently applicable to WSDOTs stormwater monitoring activities but may be in the future if future sampling efforts change.

- [1] Recommended value. The relative percent difference (RPD) must be ≤ the indicated percentage for results that are >5x reporting limit (RL). Concentration difference values must be ≤2x RL for values that are ≤5x RL.
- [2] Recommended value. The *Contract Laboratory Program Functional Guidelines* states that the spike recovery limits do not apply when the sample concentration exceeds the spike concentration by a factor of four or more (USEPA, 2010).
- [3] Recommended value. The matrix spike duplicate RPD criteria apply when original and replicate results are ≥5x RL. Concentration difference of 1x RL applies to precision evaluation if either or both original and replicate results are <5x RL.
- [4] Method quality objectives (matrix spike & LCS values) are based on *Contract Laboratory Program Functional Guidelines* for inorganic data review (USEPA, 2010).
- [5] Method quality objectives are based on current performance-based statistics provided by the analytical laboratories. The values are subject to change as the laboratories update their performance control limits as required by the accreditation programs.

Table 12 Quantity, Container, Preservation, and Holding Time Requirements for Metals

Parameter	Minimum Quantity Needed for Analysis & QC Samples	Container	Preservative ^{[1][2]}	Holding Time ^[3]	
Water Samples					
Metals	Dissolved Cd, Cu, Pb, and Zn	Analysis = 50 mL MS & Dup = 50 mL each	250 mL poly bottle acid rinsed if parameters are analyzed together	Filter within 15 minutes of collection ^[4] ; HNO ₃ to pH <2 ^[5]	6 months
	Dissolved Cu and Zn	Analysis = 50 mL MS & Dup = 50 mL each	250 mL poly bottle acid rinsed if parameters are analyzed together	Filter within 15 minutes of collection ^[4] ; HNO ₃ to pH <2 ^[5]	6 months
	<i>Dissolved Ca, Mg, Na, and K</i>	<i>Analysis = 100 mL MS & Dup = 100 mL each</i>	<i>500 mL HDPE bottle with Teflon® lid</i>	<i>Filter within 15 minutes of collection^[4]; HNO₃ to pH <2^[5]</i>	<i>6 months</i>
	Total Recoverable Cd, Cu, Pb, and Zn	Analysis = 50 mL MS & Dup = 50 mL each	250 mL poly bottle acid rinsed if parameters are analyzed together	HNO ₃ to pH <2 ^[5]	6 months
	Total Recoverable Cu and Zn	Analysis = 50 mL MS & Dup = 50 mL each	250 mL poly bottle acid rinsed if parameters are analyzed together	HNO ₃ to pH <2 ^[5]	6 months
Inorganics	Hardness as CaCO ₃	Analysis = 50 mL Dup = 50 mL	250 mL poly bottle acid preserved	HNO ₃ to pH <2	6 months
Sediment Samples					
Metals	Total Recoverable As, Cd, Cu, Pb, Zn	Analysis = 5 wet g MS & Dup = 5 wet g each, if metals parameters are analyzed together.	1 L glass jar with Teflon® lined lid if batched with all sediment parameters.	Cool to 4°C/; May freeze at -18°C at lab ^[6]	6 months; 2 years if frozen ^[6]
Nutrients	Total Phosphorus (TP)	Analysis = 10 wet g MS & Dup = 10 wet g each	1 L glass jar with Teflon® lined lid if batched with all sediment parameters.	Cool to 4°C ^[7]	6 months ^[7]

Table 12 Notes:

Parameter information – italicized in grey is not currently applicable to WSDOTs stormwater monitoring activities but may be in the future if future sampling efforts change.

Some parameters can be batched in one sample container e.g. dissolved metal and total recoverable metal parameters analyzed by the same methods for water. All sediment parameters can be batched in 1 sample container.

w/m = wide mouth

n/m = narrow mouth

MS = matrix spike

MSD = matrix spike duplicate

Dup = laboratory duplicate

QC = quality control

poly = polyethylene or high density polyethylene (HDPE). Does not include low density polyethylene (LDPE) per (Table 2, footnote 1 of 40CFR136).

[1] Preservation needs to be done in the field, unless otherwise noted. Ice will be used to cool samples to approximately 6°C.

- [2] Preservation per 40 CFR 136, accessed online at and current as of 6/12/2014, unless noted or italicized in grey.
- [3] Holding times per 40 CFR 136, accessed online at and current as of 6/12/2014, unless noted or italicized in grey.
- [4] Filtered with a 0.45 µm mesh membrane. May be done at lab if less than 24 hours after sample collection time, results will be J qualified but usable for reporting.
- [5] An aqueous sample may be collected and shipped without acid preservation. However, acid must be added by the lab at least 24 hours before analysis to dissolve any metals that adsorb to the container walls (Table 2, footnote 19 of 40CFR136).
- [6] Sediment Sampling and Analysis Plan Appendix (Ecology, 2008).
- [7] Holding times per USEPA *Contract Laboratory Program, National Functional Guidelines for Inorganic Data Review* (USEPA, 2010).

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C. Organic Parameters by GC and HPLC Methods

Table 13 Data Validation Criteria for Organic Parameters by GC and HPLC Methods

QC Element Subelement	2a	2b	3+4	Acceptance Criteria	Action (use best professional judgment) (-): Nondetected Compounds – (+): Detected compounds
Holding Times and Sample Management	√	√	√	<ul style="list-style-type: none"> Cooler temperature: <6°C Refer to Table 16 for preservation and holding time requirements 	<ul style="list-style-type: none"> Cooler temperature >6°C: Transit time <24 hours, no action Cooler temperature >6°C: Transit time >24 hours, J(+)/UJ(-) or J(+)/R(-) as justified Cooler temperature >15°C for TPH-Gasoline: J(+)/R(-) Preservation requirements not met: J(+)/UJ(-) or J(+)/R(-) as justified, based on type of analyte and required holding time Holding time ≤2x required holding time: J(+)/UJ(-) Holding time >2x required holding time: R(+/-)
Initial Calibration (ICAL)		√	√	<ul style="list-style-type: none"> Established with 5 standards at minimum (6 standards if quadratic fit is used) %RSD<20% for average response factor or average calibration factor Linear regression correlation coefficient (r) >0.995 Coefficient of Determination (r² value) >0.99 for non-linear (quadratic) fit For methods NWTPH-Dx and NWTPH-Gx, %D for each standard should stay within ±15% of the true value 	<ul style="list-style-type: none"> ICAL not established: R(+/-) ICAL not properly established: Narrate and/or further qualify data J(+) if %RSD >20%, r-value <0.99, or r² value <0.99 Use professional judgment if %D outside criteria (±15% of the true value), based on sample results and CCV recovery
Continuing Calibration Verification (CCV)		√	√	<ul style="list-style-type: none"> Percent difference (%D) or percent drift (%D_f) within ±20%, or %R = 80-120% For method NWTPH-Dx, %D and %D_f should be within ±15%, or %R = 85-115% 	<ul style="list-style-type: none"> CCV not performed properly: Narrate and/or use professional judgment to further qualify data J(+) if %D, %D_f, or %R >UCL J(+)/UJ(-) if %D, %D_f, or %R <LCL
Blanks – Method Blank Trip Blank Field Blank Instrument Blank Equipment Rinsate Blank	√	√	√	<ul style="list-style-type: none"> One method blank per matrix per batch (less than 20 samples) Detection <RL 	<ul style="list-style-type: none"> Blank <RL, sample <RL: U at the RL Blank <RL, sample >RL but <5x blank detection: J Blank ≥ RL, sample <RL: U at the RL Blank ≥ RL, sample ≥RL but <blank detection: U Blank ≥ RL, sample ≥RL but <5x blank detection: J Blank ≥ RL, sample ≥5x blank detection: No action

Table 13 Data Validation Criteria for Organic Parameters by GC and HPLC Methods

QC Element Subelement	2a	2b	3+4	Acceptance Criteria	Action (use best professional judgment) (-): Nondetected Compounds – (+): Detected compounds
Surrogate Spikes	√	√	√	<ul style="list-style-type: none"> Added to every field and QC samples Within control limits, refer to Table 15 	<ul style="list-style-type: none"> J(+)/UJ(-) if %R <LCL J(+) if > UCL J(+)/R(-) if any %R <10% No action if 2 or more surrogates are used and only one is <LCL or >UCL No action if %R is outside control limit due to demonstrated matrix effects (e.g., high target and/or non-target chemical levels, acceptable dilution analysis)
Multiple Results for One Sample	√	√	√	<ul style="list-style-type: none"> Report only one result per analyte 	<ul style="list-style-type: none"> "DNR" results that should not be used to avoid reporting multiple results for one sample
Matrix Spike (MS) or Matrix Spike Duplicate (MSD) – Recovery	√	√	√	<ul style="list-style-type: none"> Perform as requested Refer to Table 15 for control limits 	<ul style="list-style-type: none"> Qualify parent sample only unless other QC indicates systematic problems J(+) if both %R >UCL J(+)/UJ(-) if both %R <LCL J(+)/R(-) if both %R <10% No action if only one %R outlier and %R deviation from control limit is <10% No action if parent sample concentration >5x the amount spiked
MS/MSD or Laboratory Duplicate – RPD	√	√	√	<ul style="list-style-type: none"> Perform as requested Refer to Table 15 for control limits 	<ul style="list-style-type: none"> Qualify parent sample only unless other QC indicates systematic problems J(+) if RPD (or absolute concentration difference) >control limit
Laboratory Control Sample, Laboratory Control Sample Duplicate, and/or Standard Reference Material (SRM) – Recovery	√	√	√	<ul style="list-style-type: none"> One set per matrix per batch unless MS/MSD are performed Refer to Table 15 for control limits 	<ul style="list-style-type: none"> Qualify all samples in the batch J(+) if both %R >UCL J(+)/UJ(-) if both %R <LCL J(+)/R(-) if both %R <10% No action if only one %R outlier and %R deviation from control limit is <10%
LCS/LCSD – RPD	√	√	√	<ul style="list-style-type: none"> One set per matrix per batch unless MS/MSD are performed Refer to Table 15 for control limits 	<ul style="list-style-type: none"> Qualify all samples in the batch J(+)/UJ(-) if RPD (or absolute concentration difference) >control limit
Internal Standards (if used)		√	√	<ul style="list-style-type: none"> Internal standard area within 50% to 200% of that for CCV 	<ul style="list-style-type: none"> J(+) if internal standard >100% J(+)/UJ(-) if internal standard <50% J(+)/R(-) if internal standard <25%
Field Duplicates	√	√	√	<p>Solids:</p> <ul style="list-style-type: none"> RPD <50% or absolute difference <2x RL (for results <5x RL) <p>Aqueous:</p> <ul style="list-style-type: none"> RPD <35% or absolute difference <1x RL (for results <5x RL) 	<ul style="list-style-type: none"> If control criteria not met: J(+)/UJ(-)

Table 13 Data Validation Criteria for Organic Parameters by GC and HPLC Methods

QC Element Subelement	2a	2b	3+4	Acceptance Criteria	Action (use best professional judgment) (-): Nondetected Compounds – (+): Detected compounds
Project Reporting Limits (RL)	√	√	√	<ul style="list-style-type: none"> Reported RL should be ≤RL listed in Table 15, unless justified to raise the RL 	<ul style="list-style-type: none"> Narrate if analyte is not detected and the reported RL exceeded those listed in Table 16 If RL is raised as a result of dilution or matrix effects, evaluate if the dilution or interference is justified. Document the finding and resolution in Data Validation Report
Target Compound Identification			√	<ul style="list-style-type: none"> Analyte within RTW on both columns Quantitated using ICAL response calibration factor Higher value from either column reported %D between columns (40%) 	<ul style="list-style-type: none"> J(+) if RPD>40% R(+) if retention time window criterion not met NJ(+) if no confirmation with second column or second analysis (not applicable for NWTPH-Dx and NWTPH-Gx)
Target Compound Quantitation			√	<ul style="list-style-type: none"> Perform re-calculation on ICAL, CCV, QC analyses, and sample results to verify that there are no transcription or reduction errors (dilutions, percent solids [%S]), sample weights, etc.) on one or more samples 	<ul style="list-style-type: none"> Contact the laboratory via WSDOT Project Manager if discrepancies are identified Document findings and resolutions
System Performance			√	<ul style="list-style-type: none"> Examine the raw data for any anomalies (baseline shifts, negative absorbance, omissions, illegibility, etc.) 	<ul style="list-style-type: none"> Determine if there is any need to qualify data that are not qualified based on the QC criteria previously discussed Contact the laboratory via WSDOT Project Manager if discrepancies are identified Document findings and resolutions
Overall Data Usability Assessment – Level 2a	√			<ul style="list-style-type: none"> Check for data points with multiple qualifiers Check for analytes with multiple results 	<ul style="list-style-type: none"> Determine the final data qualifier for a data point in case multiple qualifiers are assigned to the data point Determine the optimal result to be reported for an analyte if multiple results were available for the analyte
Overall Data Usability Assessment – Level 2b		√		<ul style="list-style-type: none"> Check for data points with multiple qualifiers Check for analytes with multiple results Verify that results fall within the calibrated range(s) Verify that the RL is supported with adequate concentration of ICAL standards (RL should be ≥lowest concentration of ICAL standards) 	<ul style="list-style-type: none"> Determine the final data qualifier for a data point in case multiple qualifiers are assigned to the data point Determine the optimal result to be reported for an analyte if multiple results were available for the analyte Contact the laboratory via WSDOT Project Manager if discrepancies are identified Document findings and resolutions

Table 13 Data Validation Criteria for Organic Parameters by GC and HPLC Methods

QC Element Subelement	2a	2b	3+4	Acceptance Criteria	Action (use best professional judgment) (-): Nondetected Compounds – (+): Detected compounds
Overall Data Usability Assessment – Level 3+4			√	<ul style="list-style-type: none"> • Check for data points with multiple qualifiers • Check for analytes with multiple results • Verify all retention times (RTs) are within the determined RT window • If reduced volumes were used, verify that appropriate methods and amounts were used in preparing the samples for analysis • Verify that results fall within the calibrated range(s) • Verify that the RL is supported with adequate concentration of ICAL standards (RL should be ≥lowest concentration of ICAL standards) 	<ul style="list-style-type: none"> • Determine the final data qualifier for a data point in case multiple qualifiers are assigned to the data point • Determine the optimal result to be reported for an analyte if multiple results were available for the analyte • Determine if there is any need to qualify data that are not qualified based on the QC criteria previously discussed • Contact the laboratory via WSDOT Project Manager if discrepancies are identified • Document findings and resolutions

Table 13 Notes:

Sources: USEPA, 1990; USEPA, 1996; USEPA, 2008; WSDOT(a); WSDOT(b); WSDOT(c); Ecology, 1997; APHA.

Table 14 Laboratories and Methods of Analysis for Organic Parameters by GC and HPLC Methods

Parameter	Monitoring Type				Method*	Laboratory (see Table 1)
	NPDES 2014 Hwy. Characterization	NPDES 2017 - 2019 BMP Effectiveness (RA, FT, M)	NPDES 2014 - 2019 BMP Effectiveness (Hwy)	Bioswale Research		
Water Samples						
Organics	Total Petroleum Hydrocarbon - Diesel (NWTPH-Dx)	√	√	√	NWTPH-Dx – Ecology, 1997 Publication No. 97-602 (GC/FID)(GC/MS)(GC/AED)	AmTest
	Total Petroleum Hydrocarbon - Gas (NWTPH-Gx)	√			NWTPH-Gx – Ecology, 1997 Publication No. 97-602 (GC/FID)(GC/PID)(GC/MS)(GC/AED)	AmTest
Herbicides	Glyphosate ^[1] (non-aquatic formula)	√			USEPA 547 (HPLC)	Anatek
	Diuron ^[1]	√			USEPA SW-846 8321 B (HPLC/TS/MS) or (UV Detection)	Anatek
	Dichlobenil, 2,4-D, clopyralid, picloram, triclopyr (ester formula only) ^{[1][2]}	√			USEPA SW-846 8151 A (GC)	AmTest
Sediment Samples						
Organics	TPH-Diesel (NWTPH-Dx)	√			NWTPH-Dx – Ecology, 1997 Publication No. 97-602 (GC/FID)(GC/MS)(GC/AED)	AmTest
	PCB – Aroclors ^[3]	√			USEPA SW-846 8082 A (GC/ECD)	AmTest
Herbicides	Dichlobenil, clopyralid, picloram, triclopyr (ester formula only) ^{[1][2]}	√			USEPA SW-846 8151 A (GC/ECD)	AmTest

Table 14 Notes:

Parameter information – italicized in grey is not currently applicable to WSDOTs stormwater monitoring activities but may be in the future if future sampling efforts change.

* USEPA = United States Environmental Protection Agency Method:

http://water.epa.gov/scitech/methods/cwa/methods_index.cfm

Ecology = Washington State Department of Ecology Method: <http://www.ecy.wa.gov/biblio/97602.html> (Ecology, 1997);

USEPA 1997

RA = Rest Area

FT = Ferry Terminal

M = Maintenance Facility

[1] Required at Highway locations where herbicides listed are applied near the monitoring site vicinity.

[2] WSDOT is required to report only on the ester formula of triclopyr. Triclopyr will be extracted with the other herbicides; however, this method involves hydrolyzing the sample prior to analysis (all forms of triclopyr are transformed into one form). Therefore, more than just the ester formula may be quantified in the result.

[3] Aroclors of interest: Aroclor 1016, Aroclor 1232, Aroclor 1242, Aroclor 1248, Aroclor 1254, Aroclor 1260, Aroclor 1262, and Aroclor 1268.

Table 15 Method Quality Objectives for Organic Parameters by GC and HPLC Methods

Parameter	Reporting Limit (RL)	Lab Duplicate ^[1] (RPD)	Matrix Spike (MS)/MS Duplicate (MSD) (% Rec)	MS/MSD ^[2] (RPD)	Lab Control Sample (LCS) (% Rec)	
Water Samples^[4]						
Organics	Total Petroleum Hydrocarbon (TPH):					
	TPH-Gas (NWTPH-Gx)	0.25 mg/L	≤40%	51-146	≤40%	70-130
	TPH- Diesel (NWTPH-Dx)	0.25 - 0.50 mg/L	≤40%	N/A	≤40%	85-115
	<i>TPH Surrogates:</i>					
	FBP - (for NWTPH-Dx)	N/A	N/A	N/A	N/A	50-150
BFB - (for NWTPH-Gx)	N/A	N/A	N/A	N/A	50-150	
Herbicides	Herbicides:					
	Glyphosate (non-aquatic formula)	25 µg/L ^[3]	≤30%	70-130	≤30%	70-130
	Diuron	0.01 – 1.0 µg/L	≤40%	60-130	≤40%	70-130
	Dichlobenil	0.01 – 1.0 µg/L	≤40%	30-140	≤40%	30-140
	2,4-D	0.01 – 1.0 µg/L	≤40%	30-140	≤40%	30-140
	Clopyralid	0.01 – 1.0 µg/L	≤40%	30-140	≤40%	30-140
	Picloram	0.01 – 1.0 µg/L	≤40%	30-140	≤40%	30-140
	Triclopyr (ester formula only) ^[5]	0.01 – 1.0 µg/L	≤40%	30-140	≤40%	30-140
	<i>Herbicide Surrogate:</i>					
2,4-Dichlorophenyl Acetic Acid	N/A	N/A	N/A	N/A	30-140	
Sediment Samples^[4]						
Organics	Total Petroleum Hydrocarbon (TPH):					
	TPH-Diesel (NWTPH-Dx)	25.0-100.0 mg/Kg dry	N/A	N/A	N/A	85-115
	<i>TPH Diesel Surrogate:</i>					
	FBP	N/A	N/A	N/A	N/A	50-150
	PCB Aroclors:					
	Aroclor 1016	1.25 - 2.5 µg/Kg dry	N/A	30-140	≤50%	70-130
	Aroclor 1232	1.25 - 2.5 µg/Kg dry	N/A	30-140	≤50%	70-130
	Aroclor 1242	1.25 - 2.5 µg/Kg dry	N/A	30-140	≤50%	70-130
	Aroclor 1248	1.25 - 2.5 µg/Kg dry	N/A	30-140	≤50%	70-130
	Aroclor 1254	1.25 - 2.5 µg/Kg dry	N/A	30-140	≤50%	70-130

Parameter	Reporting Limit (RL)	Lab Duplicate (RPD) ^[1]	Matrix Spike (MS)/MS Duplicate (MSD) (% Rec)	MS/MSD ^[2] (RPD)	Lab Control Sample (LCS) (% Rec)	
Organics	Aroclor 1260	1.25 - 2.5 µg/Kg dry	N/A	30-140	≤50%	70-130
	Aroclor 1262	1.25 - 2.5 µg/Kg dry	N/A	30-140	≤50%	70-130
	Aroclor 1268	1.25 - 2.5 µg/Kg dry	N/A	30-140	≤50%	70-130
	<i>PCB Aroclor Surrogates:</i>					
	decachlorobiphenyl (DCBP)	N/A	N/A	N/A	N/A	40-150
	TCMX	N/A	N/A	N/A	N/A	43-135
Herbicides	Herbicides:					
	Dichlobenil	70 µg/Kg dry	N/A	60-140	≤35%	70-130
	Clopyralid	70 µg/Kg dry	N/A	60-140	≤35%	70-130
	Picloram	70 µg/Kg dry	N/A	60-140	≤40%	70-130
	Triclopyr (ester formula only) ^[5]	70 µg/Kg dry	N/A	60-140	≤40%	70-130
	<i>Herbicide Surrogate:</i>					
2,4-Dichlorophenyl Acetic Acid	N/A	N/A	N/A	N/A	35-145	

Table 15 Notes:

Parameter information – italicized in grey is not currently applicable to WSDOTs stormwater monitoring activities but may be in the future if future sampling efforts change.

- [1] Recommended value. The relative percent difference (RPD) must be ≤ the indicated percentage for results that are >5x reporting limit (RL). Concentration difference values must be ≤2x RL for values that are ≤5x RL.
- [2] Recommended value. The matrix spike duplicate RPD criteria apply when original and replicate results are ≥5x RL. Concentration difference of 1x RL applies to precision evaluation if either or both original and replicate results are <5x RL.
- [3] Results for glyphosate analysis between the RL of 25 ug/L and method detection limit (MDL) of 2.5 ug/L will be reported. These results will be qualified as estimates.
- [4] Unless otherwise noted, method quality objectives (matrix spike & LCS values) are based on current performance-based statistics provided by the analytical laboratories. The values are subject to change as the laboratories update their performance control limits as required by the accreditation programs.
- [5] WSDOT is required to report only on the ester formula of triclopyr. Triclopyr will be extracted with the other herbicides; however, this method involves hydrolyzing the sample prior to analysis (all forms of triclopyr are transformed into one form). Therefore, more than just the ester formula may be quantified in the result.

Table 16 Quantity, Container, Preservation, and Holding Time Requirements for Organic Parameters by GC and HPLC Methods

	Parameter	Minimum Quantity Needed for Analysis & QC Samples	Container	Preservative ^{[1][2]}	Holding Time ^[3]
Water Samples					
Organics	Total petroleum hydrocarbon (TPH)-Diesel (NWTPH-Dx)	Analysis = 1 Liter Dup = 1 Liter	1 liter preserved amber n/m glass bottle with Teflon® lined lids	Cool & store at 4°C; holding time to extraction increased if HCl to pH=2 ^[6]	14 days to extraction for preserved water; 7 days to extraction for unpreserved water ^[6]
	TPH-Gas (NWTPH-Gx)	Analysis = 80 mL (fill vials full) Dup = 80 mL	(2) 40 mL preserved clear glass VOA vials with Teflon® coated septum-lined screw tops	Cool & store at 4°C; holding time to extraction increased if HCl to pH=2 ^[6]	14 days to extraction for preserved water; 7 days to extraction for unpreserved water ^[6]
Herbicides	Glyphosate ^[4] (nonaquatic formula)	Analysis = 40 mL MS & MSD = 40 mL each	40 mL preserved ^[5] clear glass VOA vials with Teflon® coated septum-lined screw tops	Cool Na ₂ S ₂ O ₃ preserved ^[5] bottle to ≤6°C; store in dark; Adjust to pH 5-9 or extract within 72 hours of collection	7 days until extraction; 40 days after extraction
	Diuron	Analysis = 1 Liter MS & MSD = 1 Liter each	1 L amber n/m glass bottle with Teflon® lined lids	Cool to ≤6°C; Adjust to pH 5-9 or extract within 72 hours of collection	7 days until extraction; 40 days after extraction
	Dichlobenil, 2,4-D, clopyralid, picloram, triclopyr (ester formula only) ^[4]	Analysis = 1 Liter MS & MSD = 1 Liter each	1 L amber n/m glass bottle with Teflon® lined lids if parameters are analyzed together.	Cool to ≤6°C; Adjust to pH 5-9 or extract within 72 hours of collection	7 days until extraction; 40 days after extraction
Sediment Samples					
Organics	TPH-Diesel (NWTPH-Dx)	Analysis = 30 wet g Dup = 30 wet g	1 L glass jar with Teflon® lined lid if batched with all sediment parameters.	Cool to ≤6°C; May freeze at -18°C at lab ^[6]	14 days until extraction (1 yr if stored frozen at -18°C); 40 days after extraction ^[6]
	PCB – Aroclors	Analysis = 30 wet g Dup = 30 wet g	1 L glass jar with Teflon® lined lid if batched with all sediment parameters.	Cool to 4°C; May freeze at -18°C at lab ^[7]	14 days until extraction (1 yr if stored frozen at -18°C); 40 days after extraction ^[7]
Herbicides	Dichlobenil, clopyralid, picloram, triclopyr (ester formula only) ^[4]	Analysis = 30 wet g Dup = 30 wet g, if herbicide parameters are analyzed together.	1 L glass jar with Teflon® lined lid if batched with all sediment parameters.	Cool to 4°C; May freeze at -18°C at lab ^[7]	14 days until extraction (1 yr if stored frozen at -18°C); 40 days after extraction ^[7]

Table 16 Notes:

Parameter information – italicized in grey is not currently applicable to WSDOTs stormwater monitoring activities but may be in the future if future sampling efforts change.

Some parameters can be batched in one sample container e.g. Dichlobenil, 2,4-D, clopyralid, picloram, and triclopyr (ester formula only) herbicide parameters analyzed by the same method for water. All sediment parameters can be batched in 1 sample container.

w/m = wide mouth

n/m = narrow mouth

MS = matrix spike

MSD = matrix spike duplicate

Dup = laboratory duplicate

QC = quality control

[1] Preservation needs to be done in the field, unless otherwise noted. Ice will be used to cool samples to approximately 6°C.

[2] Preservation per 40 CFR 136, accessed online at and current as of 6/12/2014, unless noted or italicized in grey.

[3] Holding times per 40 CFR 136, accessed online at and current as of 6/12/2014, unless noted or italicized in grey.

[4] Required at Highway characterization locations where herbicides listed are applied near the monitoring site vicinity.

[5] Per USEPA 547, sample should be preserved with Na₂S₂O₃ if an oxidant such as chlorine is suspected to be present. Sample containers from AmTest (used for both E. & W.WA samples) are 40 mL clear glass VOA bottles with preservative already added.

[6] Preservation per Ecology, 1997 Publication No. 97-602 Washington State Department of Ecology Method:

↗ <http://www.ecy.wa.gov/biblio/97602.html>; USEPA, 1997

[7] Sediment Sampling and Analysis Plan Appendix (Ecology, 2008).

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D. Semi-Volatile Organic Compounds by GC/MS and HPLC/MS Methods

Table 17 Data Validation Criteria for Semi-Volatile Organic Compounds by GC/MS and HPLC/MS Methods

QC Element	2a	2b	3+4	Acceptance Criteria	Action (use best professional judgment) (-): Nondetected Compounds – (+): Detected Compounds
Holding Times and Sample Management	√	√	√	<ul style="list-style-type: none"> Cooler temperature: <6°C Refer to Table 20 for preservation and holding time requirements 	<ul style="list-style-type: none"> Cooler temperature >6°C: Transit time <24 hours, no action Cooler temperature >6°C: Transit time >24 hours: J(+)/UJ(-) or J(+)/R(-) as justified, based on type of analyte and holding time Preservation requirements not met: J(+)/UJ(-) or J(+)/R(-) as justified, based on type of analyte and required holding time Holding time ≤2x required holding time: J(+)/UJ(-) Holding time >2x required holding time: R(+/-)
Gas Chromatography Coupling with Mass Spectrometry (GC/MS) or High-Performance Liquid Chromatography with Mass Spectrometry (HPLC/MS) Instrument Tuning		√	√	<ul style="list-style-type: none"> DFTPP for GC/MS Polyethylene glycol or equivalent for HPLC/MS Beginning of each 12-hour period Method or manufacturer acceptance criteria 	<ul style="list-style-type: none"> Tune analysis not performed: R(+/-) all analytes in all samples Tune result did not meet criteria: Use professional judgment
Initial Calibration (ICAL)		√	√	<ul style="list-style-type: none"> Established with 5 standards at minimum %RSD<20% for average response factor (RF) or average calibration factor Correlation coefficient (r value) >0.99 for linear regression Coefficient of determination (r² value) >0.99 for nonlinear (quadratic) fit RF >0.05 A mid-point second source standard (ICV) be analyzed immediately after ICAL; percent difference (%D) should be within ±30% 	<ul style="list-style-type: none"> J(+) if %RSD >20%, r value <0.99, or r² value <0.99 ICV %D <LCL: J(+)/UJ(-) ICV %D >UCL: J(+) Use professional judgment if RF <0.05, based on sample results and CCV recovery; no action if sample detected and CCV acceptable

Table 17 Data Validation Criteria for Semi-Volatile Organic Compounds by GC/MS and HPLC/MS Methods

QC Element	2a	2b	3+4	Acceptance Criteria	Action (use best professional judgment) (-): Nondetected Compounds – (+): Detected Compounds
Initial Calibration Verification (ICV)		√	√	<ul style="list-style-type: none"> ICV performed Percent difference (%D) or percent drift (%D_f) within ±30%, or %R = 70-130% 	<ul style="list-style-type: none"> Narrate if ICV not performed J(+) if %D, %D_f, or %R >UCL J(+)/UJ(-) if %D, %D_f, or %R <LCL Use professional judgment if RF <0.05, based on sample results and CCV recovery: No action if sample detected and CCV acceptable
Continuing Calibration Verification (CCV)		√	√	<ul style="list-style-type: none"> Percent difference (%D) or percent drift (%D_f) within ±20%, or %R = 80-120% RF >0.05 	<ul style="list-style-type: none"> J(+) if %D, %D_f, or %R >UCL J(+)/UJ(-) if %D, %D_f, or %R <LCL Use professional judgment if RF <0.05, based on sample results and CCV recovery: No action if sample detected and CCV acceptable
Blanks – <i>Method Blank</i> <i>Trip Blank</i> <i>Field Blank</i> <i>Instrument Blank</i> <i>Equipment</i> <i>Rinsate Blank</i>	√	√	√	<ul style="list-style-type: none"> One method blank per matrix per batch (less than 20 samples) Detection <RL 	<ul style="list-style-type: none"> Blank <RL, sample <RL: U at the RL Blank <RL, sample >RL but <5x blank detection: J Blank ≥ RL, sample <RL: U at the RL Blank ≥ RL, sample ≥RL but <blank detection: U Blank ≥ RL, sample ≥RL but <5x blank detection: J Blank ≥ RL, sample ≥5x blank detection: No action
Surrogate Spikes	√	√	√	<ul style="list-style-type: none"> Added to every field and QC samples Within control limits refer to Table 19 	<ul style="list-style-type: none"> J(+)/UJ(-) If %R <LCL J(+) If > UCL J(+)/R(-) If any %R <10% No action if 2 or more surrogates are used and only one is <LCL or >UCL No action if %R is outside control limit due to demonstrated matrix effects (e.g., high target and/or non-target chemical levels, acceptable dilution analysis)
Multiple Results for One Sample	√	√	√	<ul style="list-style-type: none"> Report only one result per analyte 	<ul style="list-style-type: none"> "DNR" results that should not be used to avoid reporting multiple results for one sample
Matrix Spike (MS) or Matrix Spike Duplicate (MSD) – <i>Recovery</i>	√	√	√	<ul style="list-style-type: none"> Perform as requested. Refer to Table 19 for control limits 	<ul style="list-style-type: none"> Qualify parent sample only unless other QC indicates systematic problems J(+) if both %R >UCL J(+)/UJ(-) if both %R <LCL J(+)/R(-) if both %R <10% No action if only one %R outlier and %R deviation from control limit is <10% No action if parent sample concentration >5x the amount spiked
MS/MSD or Laboratory Duplicate – <i>RPD</i>	√	√	√	<ul style="list-style-type: none"> Perform as requested. Refer to Table 19 for control limits 	<ul style="list-style-type: none"> Qualify parent sample only unless other QC indicates systematic problems J(+) if RPD (or absolute concentration difference) >control limit

Table 17 Data Validation Criteria for Semi-Volatile Organic Compounds by GC/MS and HPLC/MS Methods

QC Element	2a	2b	3+4	Acceptance Criteria	Action (use best professional judgment) (-): Nondetected Compounds – (+): Detected Compounds
Laboratory Control Sample, Laboratory Control Sample Duplicate, and/or Standard Reference Material (SRM) – Recovery	√	√	√	<ul style="list-style-type: none"> One set per matrix per batch unless MS/MSD are performed Within control limits refer to Table 19 	<ul style="list-style-type: none"> If criteria were not met, qualify all samples in the batch J(+) if both %R >UCL J(+)/UJ(-) if both %R <LCL J(+)/R(-) if both %R <10% No action if only one %R outlier and %R deviation from control limit is <10%
LCS/LCSD – RPD	√	√	√	<ul style="list-style-type: none"> One set per matrix per batch unless MS/MSD are performed Within control limits, refer to Table 19 	<ul style="list-style-type: none"> If criteria were not met, qualify all samples in the batch J(+)/UJ(-) if RPD (or absolute concentration difference) >control limit
Internal Standards		√	√	<ul style="list-style-type: none"> Added to all samples Acceptable range: Internal standard area 50% to 200% of CCAL area RT within 30 seconds of CC RT 	<ul style="list-style-type: none"> J(+) if > 200% J(+)/UJ(-) if <50% J(+)/R(-) if <25% RT>30 seconds, narrate
Field Duplicates	√	√	√	<ul style="list-style-type: none"> Solids: <ul style="list-style-type: none"> RPD <50% or absolute difference <2x RL (for results <5x RL) Aqueous: <ul style="list-style-type: none"> RPD <35% or absolute difference <1x RL (for results <5x RL) 	<ul style="list-style-type: none"> If criteria were not met, J(+)/UJ(-)
Project Reporting Limits (RL)	√	√	√	<ul style="list-style-type: none"> Reported RL should be ≤RL listed in Table 19 unless justified to raise the RL 	<ul style="list-style-type: none"> Narrate if analyte is not detected and the reported RL exceeded those listed in Table 19 If RL is raised as a result of dilution or matrix effects, evaluate if the dilution or interference is justified; document the finding and resolution in Data Validation Report
Target Compound Identification			√	<ul style="list-style-type: none"> Verify all retention times (RTs) are within the determined RT window Examine chromatograms and ion spectra to verify detections of target analytes RRT within 0.06 of standard RRT Ion relative intensity within 30% of standard All ions in standard at >10% intensity must be present in sample 	<ul style="list-style-type: none"> Narrate; further qualify data as needed Contact the laboratory via WSDOT Project Manager if discrepancies are identified Document findings and resolutions

Table 17 Data Validation Criteria for Semi-Volatile Organic Compounds by GC/MS and HPLC/MS Methods

QC Element	2a	2b	3+4	Acceptance Criteria	Action (use best professional judgment) (-): Nondetected Compounds – (+): Detected Compounds
Target Compound Quantitation			√	<ul style="list-style-type: none"> Perform re-calculation on ICAL, CCV, QC analyses, and sample results to verify that there are no transcription or reduction errors (dilutions, percent solids [%S], sample weights, etc.) on one or more samples 	<ul style="list-style-type: none"> Contact the laboratory via WSDOT Project Manager if discrepancies are identified Document findings and resolutions
System Performance			√	<ul style="list-style-type: none"> Examine the raw data for any anomalies (baseline shifts, negative absorbance, omissions, illegibility, etc.) 	<ul style="list-style-type: none"> Determine if there is any need to qualify data that are not qualified based on the QC criteria previously discussed Contact the laboratory via WSDOT Project Manager if discrepancies are identified Document findings and resolutions
Overall Data Usability Assessment – Level 2a	√			<ul style="list-style-type: none"> Check for data points with multiple qualifiers Check for analytes with multiple results 	<ul style="list-style-type: none"> Determine the final data qualifier for a data point in case multiple qualifiers are assigned to the data point Determine the optimal result to be reported for an analyte if multiple results were available for the analyte
Overall Data Usability Assessment – Level 2b		√		<ul style="list-style-type: none"> Check for data points with multiple qualifiers Check for analytes with multiple results Verify that results fall within the calibrated range(s) Verify that the RL is supported with adequate concentration of ICAL standards (RL should be ≥lowest concentration of ICAL standards) 	<ul style="list-style-type: none"> Determine the final data qualifier for a data point in case multiple qualifiers are assigned to the data point Determine the optimal result to be reported for an analyte if multiple results were available for the analyte Contact the laboratory via WSDOT Project Manager if discrepancies are identified Document findings and resolutions
Overall Data Usability Assessment – Level 3+4			√	<ul style="list-style-type: none"> Check for data points with multiple qualifiers Check for analytes with multiple results If reduced volumes were used, verify that appropriate methods and amounts were used in preparing the samples for analysis Verify that results fall within the calibrated range(s) Verify that the RL is supported with adequate concentration of ICAL standards (RL should be ≥lowest concentration of ICAL standards) 	<ul style="list-style-type: none"> Determine the final data qualifier for a data point in case multiple qualifiers are assigned to the data point Determine the optimal result to be reported for an analyte if multiple results were available for the analyte Determine if there is any need to qualify data that are not qualified based on the QC criteria previously discussed Contact the laboratory via WSDOT Project Manager if discrepancies are identified Document findings and resolutions

Table 17 Notes:

Sources: USEPA, 1983; USEPA, 1996; USEPA, 2008; WSDOT(a); WSDOT(b); WSDOT(c).

Table 18 Laboratories and Methods of Analysis for Semi-Volatile Organic Compounds by GC/MS and HPLC/MS

Parameter	Monitoring Type				Methods*	Laboratory (see Table 1)
	NPDES 2014 Hwy. Characterization	NPDES 2017 - 2019 BMP Effectiveness (RA, FT, M)	NPDES 2014 - 2019 BMP Effectiveness (Hwy)	Bioswale Research		
Water Samples						
Semi-Volatile Organics	PAH ^[1] and Phthalate ^[2] compounds	√			USEPA SW-846 Method 8270D (SIM) (GC/MS)	AmTest
	<i>Base/Neutral/Acid extractable semi-volatile compounds (BNAs)-Full List^[5]</i>				<i>USEPA SW-846 Method 8270D (Manchester Modified) (GC/MS)</i>	N/A
	Visible Oil Sheen ^[3]	√	√	√	Observation	WSDOT
Sediment Samples						
Semi-Volatile Organics	PAH ^[1] , Phenolic ^[4] , and Phthalate ^[2] compounds	√			USEPA SW-846 Method 8270D (SIM) (GC/MS)	AmTest

Table 18 Notes:

Parameter information – italicized in grey is not currently applicable to WSDOTs stormwater monitoring activities but may be in the future if sampling efforts change.

* SW: <http://www.epa.gov/osw/hazard/testmethods/sw846/online/index.htm>

EPA: http://water.epa.gov/scitech/methods/cwa/methods_index.cfm

- [1] PAHs of interest: acenaphthene, acenaphthylene, anthracene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[ghi]perylene, benzo[a]pyrene, chrysene, dibenzo[a,h]anthracene, fluoranthene, fluorene, indeno[1,2,3-cd]pyrene, naphthalene, phenanthrene, and pyrene.
- [2] Phthalates of interest: bis(2-Ethylhexyl)phthalate, Butyl benzyl phthalate, Di-n-butyl phthalate, Diethyl phthalate, Dimethyl phthalate, and Di-n-octyl phthalate.
- [3] Validation criteria for this parameter are not included in this document.
- [4] Phenolics, including, at a minimum, but not limited to: Phenol, 2-methylphenol, 4-methylphenol, 2,4-dimethylphenol, pentachlorophenol, benzyl alcohol, and benzoic acid.
- [5] BNAs include: Phenol, Bis(2-Chloroethyl)Ether, 2-Chlorophenol, 1,3-Dichlorobenzene, 1,4-Dichlorobenzene, 1,2-Dichlorobenzene, Benzyl Alcohol, 2-Methylphenol, Bis(2-chloro-1-methylethyl) ether, N-Nitrosodi-n-propylamine, 4-Methylphenol, Hexachloroethane, Nitrobenzene, Isophorone, 2-Nitrophenol, 2,4-Dimethylphenol, Bis(2-Chloroethoxy)Methane, Benzoic Acid, 2,4-Dichlorophenol, 1,2,4-Trichlorobenzene, Naphthalene, 4-Chloroaniline, Hexachlorobutadiene, 4-Chloro-3-Methylphenol, 2-Methylnaphthalene, 1-Methylnaphthalene, Hexachlorocyclopentadiene, 2,4,6-Trichlorophenol, 2,4,5-Trichlorophenol, 2-Chloronaphthalene, 2-Nitroaniline, Dimethyl phthalate, 2,6-Dinitrotoluene, Acenaphthylene, 3-Nitroaniline, Acenaphthene, 2,4-Dinitrophenol, 4-Nitrophenol, Dibenzofuran, 2,4-Dinitrotoluene, Diethyl phthalate, Fluorene, 4-Chlorophenyl-Phenylether, 4-Nitroaniline, 4,6-Dinitro-2-Methylphenol, N-Nitrosodiphenylamine, 1,2-Diphenylhydrazine, Triethyl citrate, 4-Bromophenyl phenyl ether, Hexachlorobenzene, Tris(2-chloroethyl) phosphate(TCEP), Pentachlorophenol, Phenanthrene, Anthracene, Caffeine, 4-nonylphenol, Carbazole, Di-N-Butylphthalate, Triclosan, Fluoranthene, Pyrene, Bisphenol A, Retene, Butyl benzyl phthalate, Benz[a]anthracene, 3,3'-Dichlorobenzidine, Chrysene, Bis(2-Ethylhexyl) Phthalate, Di-N-Octyl Phthalate, Benzo(b)fluoranthene,

Benzo(k)fluoranthene, Benzo(a)pyrene, 3B-Coprostanol, Cholesterol, Indeno(1,2,3-cd)pyrene, Dibenzo(a,h)anthracene, Benzo(ghi)perylene.

Table 19 Method Quality Objectives for Semi-Volatile Organic Compounds by GC/MS and HPLC/MS Methods

Parameter	Reporting Limit	Lab Duplicate ^[1] (RPD)	MS/MSD (% Rec)	MS/MSD ^[3] (RPD)	LCS/Surrogate Spike ^[2] (% Rec)
Water Samples^[5]					
Direct Observation:					
Visible Oil Sheen ^[4]	Yes/No	N/A	N/A	N/A	N/A
PAH Compounds:					
Acenaphthene	0.1 µg/L	≤40%	25-150	≤40%	70-130
Acenaphthylene	0.1 µg/L	≤40%	20-112	≤40%	70-130
Anthracene	0.1 µg/L	≤40%	20-155	≤40%	70-130
Benzo[a]anthracene	0.1 µg/L	≤40%	28-140	≤40%	70-130
Benzo[b]fluoranthene	0.1 µg/L	≤40%	20-160	≤40%	70-130
Benzo[k]fluoranthene	0.1 µg/L	≤40%	21-157	≤40%	70-130
Benzo[ghi]perylene	0.1 µg/L	≤40%	21-175	≤40%	70-130
Benzo[a]pyrene	0.1 µg/L	≤40%	35-140	≤40%	70-130
Chrysene	0.1 µg/L	≤40%	20-130	≤40%	70-130
Dibenzo[a,h]anthracene	0.1 µg/L	≤40%	20-170	≤40%	70-130
Fluoranthene	0.1 µg/L	≤40%	20-147	≤40%	70-130
Fluorene	0.1 µg/L	≤40%	24-131	≤40%	70-130
Indeno[1,2,3-cd]pyrene	0.1 µg/L	≤40%	31-163	≤40%	70-130
Naphthalene	0.1 µg/L	≤40%	26-134	≤40%	70-130
Phenanthrene	0.1 µg/L	≤40%	46-125	≤40%	70-130
Pyrene	0.1 µg/L	≤40%	21-174	≤40%	70-130
PAH Surrogates:					
D ₅ -Nitrobenzene	N/A	N/A	N/A	N/A	22-114
2-Fluorobiphenyl	N/A	N/A	N/A	N/A	17-113
D ₁₄ -Terphenyl	N/A	N/A	N/A	N/A	30-142
Phthalates:					
Bis(2-Ethylhexyl)phthalate	1.0 µg/L	≤40%	37-165	≤40%	70-130
Butyl benzyl phthalate	1.0 µg/L	≤40%	40-140	≤40%	70-130
Di-n-butyl phthalate	1.0 µg/L	≤40%	33-164	≤40%	70-130
Diethyl phthalate	1.0 µg/L	≤40%	32-136	≤40%	70-130
Dimethyl phthalate	1.0 µg/L	≤40%	18-133	≤40%	70-130
Di-n-octyl phthalate	1.0 µg/L	≤40%	24-136	≤40%	70-130
Phthalate Surrogates:					
D ₅ -Nitrobenzene	N/A	N/A	N/A	N/A	22-114
2-Fluorobiphenyl	N/A	N/A	N/A	N/A	17-113
D ₁₄ -Terphenyl	N/A	N/A	N/A	N/A	30-142
Base/Neutral/Acid Extractable Semi-Volatile Compounds (BNAs)-Full List:					
<i>Phenol</i>	0.33 µg/L ^[6]	≤40%	30-100 ^[7]	≤40%	41-100 ^[7]
<i>Bis(2-Chloroethyl)Ether</i>	0.17 µg/L ^[6]	≤40%	65-110	≤40%	65-110
<i>2-Chlorophenol</i>	0.33 µg/L ^[6]	≤40%	46-104	≤40%	66-109
<i>1,3-Dichlorobenzene</i>	0.08 µg/L ^[6]	≤40%	30-100 ^[7]	≤40%	30-100 ^[7]
<i>1,4-Dichlorobenzene</i>	0.08 µg/L ^[6]	≤40%	30-100 ^[7]	≤40%	30-100 ^[7]
<i>1,2-Dichlorobenzene</i>	0.08 µg/L ^[6]	≤40%	30-100 ^[7]	≤40%	30-100 ^[7]

Table 19 Method Quality Objectives for Semi-Volatile Organic Compounds by GC/MS and HPLC/MS Methods

	Parameter	Reporting Limit	Lab Duplicate ^[1] (RPD)	MS/MSD (% Rec)	MS/MSD ^[3] (RPD)	LCS/Surrogate Spike ^[2] (% Rec)
	Benzyl Alcohol	0.83 µg/L ^[6]	≤40%	30-100 ^[7]	≤40%	30-100 ^[7]
	2-Methylphenol	0.83 µg/L ^[6]	≤40%	30-100 ^[7]	≤40%	55-117
Semi-Volatile Organics	bis(2-chloro-1-methylethyl) ether	0.08 µg/L ^[6]	≤40%	63-105	≤40%	63-105
	N-Nitrosodi-n-propylamine	0.08 µg/L ^[6]	≤40%	46-124	≤40%	60-128
	4-Methylphenol	0.83 µg/L ^[6]	≤40%	30-100 ^[7]	≤40%	43-127
	Hexachloroethane	0.08 µg/L ^[6]	≤40%	30-100 ^[7]	≤40%	30-79 ^[7]
	Nitrobenzene	0.08 µg/L ^[6]	≤40%	48-113	≤40%	67-108
	Isophorone	0.17 µg/L ^[6]	≤40%	46-100 ^[7]	≤40%	50-103
	2-Nitrophenol	0.17 µg/L ^[6]	≤40%	51-115	≤40%	64-115
	2,4-Dimethylphenol	0.83 µg/L ^[6]	≤40%	58-122	≤40%	59-127
	Bis(2-Chloroethoxy)Methane	0.08 µg/L ^[6]	≤40%	46-124	≤40%	65-116
	Benzoic Acid	1.67 µg/L ^[6]	≤40%	30-100 ^[7]	≤40%	30-100 ^[7]
	2,4-Dichlorophenol	0.83 µg/L ^[6]	≤40%	49-125	≤40%	66-115
	1,2,4-Trichlorobenzene	0.08 µg/L ^[6]	≤40%	30-100 ^[7]	≤40%	30-100 ^[7]
	Naphthalene	0.08 µg/L ^[6]	≤40%	34-114	≤40%	34-114
	4-Chloroaniline	3.33 µg/L ^[6]	≤40%	30-150 ^[7]	≤40%	30-150 ^[7]
	Hexachlorobutadiene	0.08 µg/L ^[6]	≤40%	30-100 ^[7]	≤40%	30-100 ^[7]
	4-Chloro-3-Methylphenol	0.83 µg/L ^[6]	≤40%	50-133	≤40%	60-129
	2-Methylnaphthalene	0.08 µg/L ^[6]	≤40%	30-112 ^[7]	≤40%	30-112 ^[7]
	1-Methylnaphthalene	0.08 µg/L ^[6]	≤40%	33-110	≤40%	33-110
	Hexachlorocyclopentadiene	0.33 µg/L ^[6]	≤40%	30-100 ^[7]	≤40%	30-100 ^[7]
	2,4,6-Trichlorophenol	0.33 µg/L ^[6]	≤40%	66-118	≤40%	51-141
	2,4,5-Trichlorophenol	0.33 µg/L ^[6]	≤40%	56-130	≤40%	46-141
	2-Chloronaphthalene	0.17 µg/L ^[6]	≤40%	30-127 ^[7]	≤40%	30-127 ^[7]
	2-Nitroaniline	1.67 µg/L ^[6]	≤40%	30-145 ^[7]	≤40%	64-136
	Dimethyl phthalate	0.17 µg/L ^[6]	≤40%	73-126	≤40%	74-122
	2,6-Dinitrotoluene	0.33 µg/L ^[6]	≤40%	71-130	≤40%	65-131
	Acenaphthylene	0.08 µg/L ^[6]	≤40%	46-118	≤40%	46-118
	3-Nitroaniline	0.33 µg/L ^[6]	≤40%	30-123 ^[7]	≤40%	30-150 ^[7]
	Acenaphthene	0.08 µg/L ^[6]	≤40%	30-150 ^[7]	≤40%	30-150 ^[7]
	2,4-Dinitrophenol	0.83 µg/L ^[6]	≤40%	71-139	≤40%	42-135
	4-Nitrophenol	0.83 µg/L ^[6]	≤40%	30-100 ^[7]	≤40%	30-134 ^[7]
Dibenzofuran	0.17 µg/L ^[6]	≤40%	47-126	≤40%	47-126	
2,4-Dinitrotoluene	0.33 µg/L ^[6]	≤40%	71-118	≤40%	64-136	
Diethyl phthalate	0.17 µg/L ^[6]	≤40%	79-117	≤40%	77-123	
Fluorene	0.08 µg/L ^[6]	≤40%	50-134	≤40%	50-134	
4-Chlorophenyl-Phenylether	0.08 µg/L ^[6]	≤40%	58-110	≤40%	47-113	

Table 19 Method Quality Objectives for Semi-Volatile Organic Compounds by GC/MS and HPLC/MS Methods

	Parameter	Reporting Limit	Lab Duplicate ^[1] (RPD)	MS/MSD (% Rec)	MS/MSD ^[3] (RPD)	LCS/Surrogate Spike ^[2] (% Rec)	
	4-Nitroaniline	0.33 µg/L ^[6]	≤40%	30-150 ^[7]	≤40%	30-150 ^[7]	
	4,6-Dinitro-2-Methylphenol	1.67 µg/L ^[6]	≤40%	80-128	≤40%	67-133	
	N-Nitrosodiphenylamine	0.17 µg/L ^[6]	≤40%	30-150 ^[7]	≤40%	30-150 ^[7]	
	1,2-Diphenylhydrazine	0.08 µg/L ^[6]	≤40%	50-150	≤40%	50-150	
	Triethyl citrate	0.33 µg/L ^[6]	≤40%	35-143	≤40%	30-123 ^[7]	
	4-Bromophenyl phenyl ether	0.17 µg/L ^[6]	≤40%	61-136	≤40%	47-113	
	Hexachlorobenzene	0.08 µg/L ^[6]	≤40%	52-129	≤40%	53-114	
	Tris(2-chloroethyl) phosphate (TCEP)	0.08 µg/L ^[6]	≤40%	50-150	≤40%	50-150	
	Pentachlorophenol	0.08 µg/L ^[6]	≤40%	52-140	≤40%	64-140	
	Phenanthrene	0.17 µg/L ^[6]	≤40%	63-126	≤40%	63-126	
Semi-Volatile Organics	Anthracene	0.17 µg/L ^[6]	≤40%	66-121	≤40%	66-121	
	Caffeine	0.17 µg/L ^[6]	≤40%	30-100 ^[7]	≤40%	62-114	
	4-nonylphenol	0.33 µg/L ^[6]	≤40%	30-150 ^[7]	≤40%	77-150 ^[7]	
	Carbazole	0.17 µg/L ^[6]	≤40%	59-139	≤40%	59-139	
	Di-N-Butylphthalate	0.08 µg/L ^[6]	≤40%	73-148	≤40%	70-150 ^[7]	
	Triclosan	0.08 µg/L ^[6]	≤40%	43-150 ^[7]	≤40%	54-126	
	Fluoranthene	0.17 µg/L ^[6]	≤40%	72-124	≤40%	72-124	
	Pyrene	0.17 µg/L ^[6]	≤40%	64-140	≤40%	64-140	
	Bisphenol A	0.33 µg/L ^[6]	≤40%	30-150 ^[7]	≤40%	30-150 ^[7]	
	Retene	0.17 µg/L ^[6]	≤40%	73-136	≤40%	75-135	
	Butyl benzyl phthalate	0.33 µg/L ^[6]	≤40%	80-150	≤40%	30-150 ^[7]	
	Benzo[a]anthracene	0.17 µg/L ^[6]	≤40%	84-130	≤40%	84-130	
	3,3'-Dichlorobenzidine	0.17 µg/L ^[6]	≤40%	30-150 ^[7]	≤40%	30-150 ^[7]	
	Chrysene	0.17 µg/L ^[6]	≤40%	82-128	≤40%	82-128	
	bis(2-Ethylhexyl) Phthalate	0.17 µg/L ^[6]	≤40%	61-131	≤40%	80-128	
	Di-N-Octyl Phthalate	0.83 µg/L ^[6]	≤40%	61-148	≤40%	75-135	
	Benzo(b)fluoranthene	0.08 µg/L ^[6]	≤40%	71-140	≤40%	71-140	
	Benzo(k)fluoranthene	0.08 µg/L ^[6]	≤40%	73-141	≤40%	73-141	
	Benzo(a)pyrene	0.08 µg/L ^[6]	≤40%	70-145	≤40%	70-145	
	3B-Coprostanol	1.67 µg/L ^[6]	≤40%	30-150 ^[7]	≤40%	30-150 ^[7]	
	Cholesterol	1.67 µg/L ^[6]	≤40%	30-150 ^[7]	≤40%	30-140 ^[7]	
	Indeno(1,2,3-cd)pyrene	0.08 µg/L ^[6]	≤40%	61-139	≤40%	61-139	
	Dibenzo(a,h)anthracene	0.08 µg/L ^[6]	≤40%	65-130	≤40%	65-130	
	Benzo(ghi)perylene	0.17 µg/L ^[6]	≤40%	61-141	≤40%	61-141	
	Base/Neutral/Acid Extractable Semi-Volatile Compounds (BNAs)-Surrogates:						
		2-Fluorophenol	N/A	N/A	N/A	N/A	30-150 ^[7]
		Phenol-D ₅	N/A	N/A	N/A	N/A	30-150 ^[7]
	2-Chlorophenol-D ₄	N/A	N/A	N/A	N/A	44-112	

Table 19 Method Quality Objectives for Semi-Volatile Organic Compounds by GC/MS and HPLC/MS Methods

Parameter	Reporting Limit	Lab Duplicate ^[1] (RPD)	MS/MSD (% Rec)	MS/MSD ^[3] (RPD)	LCS/Surrogate Spike ^[2] (% Rec)
<i>Bis(2-Chloroethyl)Ether-D₈</i>	N/A	N/A	N/A	N/A	50-150
<i>1,2-Dichlorobenzene-D₄</i>	N/A	N/A	N/A	N/A	30-150 ^[7]
<i>4-Methylphenol-D₈</i>	N/A	N/A	N/A	N/A	50-150
<i>Nitrobenzene-D₅</i>	N/A	N/A	N/A	N/A	50-118
<i>2-Nitrophenol-D₄</i>	N/A	N/A	N/A	N/A	30-120 ^[7]
<i>2,4-Dichlorophenol-D₃</i>	N/A	N/A	N/A	N/A	50-150
<i>4-Chloroaniline-D₄</i>	N/A	N/A	N/A	N/A	30-120 ^[7]
<i>2-Fluorobiphenyl</i>	N/A	N/A	N/A	N/A	30-116 ^[7]
<i>Dimethylphthalate-D₆</i>	N/A	N/A	N/A	N/A	50-150
<i>Acenaphthylene-D₈</i>	N/A	N/A	N/A	N/A	50-150
<i>4-Nitrophenol-D₄</i>	N/A	N/A	N/A	N/A	30-120 ^[7]
<i>Fluorene-D₁₀</i>	N/A	N/A	N/A	N/A	50-150
<i>4,6-Dinitro-2-methylphenol-D₂</i>	N/A	N/A	N/A	N/A	50-150
<i>Anthracene-D₁₀</i>	N/A	N/A	N/A	N/A	50-150
<i>Pyrene-D₁₀</i>	N/A	N/A	N/A	N/A	57-134
<i>Terphenyl-D₁₄</i>	N/A	N/A	N/A	N/A	42-145
<i>Benzo(a)pyrene-D₁₂</i>	N/A	N/A	N/A	N/A	50-150
Sediment Samples^[5]					
PAH Compounds:					
Acenaphthene	70 µg/Kg dry	N/A	47-145	40%	70-130
Acenaphthylene	70 µg/Kg dry	N/A	33-145	40%	70-130
Anthracene	70 µg/Kg dry	N/A	27-133	40%	70-130
Benzo[a]anthracene	70 µg/Kg dry	N/A	33-143	40%	70-130
Benzo[a]pyrene	70 µg/Kg dry	N/A	17-163	40%	70-130
Benzo[b]fluoranthene	70 µg/Kg dry	N/A	24-159	40%	70-130
Benzo[ghi]perylene	70 µg/Kg dry	N/A	0-219	40%	70-130
Benzo[k]fluoranthene	70 µg/Kg dry	N/A	11-162	40%	70-130
Chrysene	70 µg/Kg dry	N/A	17-168	40%	70-130
Dibenzo[a,h]anthracene	70 µg/Kg dry	N/A	0-227	40%	70-130
Fluoranthene	70 µg/Kg dry	N/A	26-137	40%	70-130
Fluorene	70 µg/Kg dry	N/A	59-121	40%	70-130
Indeno[1,2,3-cd]pyrene	70 µg/Kg dry	N/A	0-171	40%	70-130
Naphthalene	70 µg/Kg dry	N/A	21-133	40%	70-130
Phenanthrene	70 µg/Kg dry	N/A	54-135	40%	70-130
Pyrene	70 µg/Kg dry	N/A	52-115	40%	70-130
PAH Surrogates:					
Terphenyl-D ₁₄	N/A	N/A	N/A	N/A	18-157
2-Fluorobiphenyl	N/A	N/A	N/A	N/A	27-134
Nitrobenzene-D ₅	N/A	N/A	N/A	N/A	25-128
Phenols:					
Phenol	70 µg/Kg dry	N/A	30-140	40%	70-130
Benzyl alcohol	70 µg/Kg dry	N/A	30-140	40%	70-130

Table 19 Method Quality Objectives for Semi-Volatile Organic Compounds by GC/MS and HPLC/MS Methods

Parameter	Reporting Limit	Lab Duplicate ^[1] (RPD)	MS/MSD (% Rec)	MS/MSD ^[3] (RPD)	LCS/Surrogate Spike ^[2] (% Rec)
2-methylphenol	70 µg/Kg dry	N/A	30-140	40%	70-130
4-methylphenol	70 µg/Kg dry	N/A	30-140	40%	70-130
2,4-dimethylphenol	70 µg/Kg dry	N/A	30-140	40%	70-130
pentachlorophenol	70 µg/Kg dry	N/A	30-140	40%	70-130
Benzoic acid	70 µg/Kg dry	N/A	30-140	40%	70-130
Phenol Surrogates:					
D ₅ -Nitrobenzene	N/A	N/A	N/A	N/A	25-128
2-Fluorobiphenyl	N/A	N/A	N/A	N/A	27-134
D ₁₄ -Terphenyl	N/A	N/A	N/A	N/A	18-157
Phthalates:					
<i>bis</i> (2-Ethylhexyl)phthalate	70 µg/Kg dry	N/A	8-158	40%	70-130
Butyl benzyl phthalate	70 µg/Kg dry	N/A	0-152	40%	70-130
Di-n-butyl phthalate	70 µg/Kg dry	N/A	1-118	40%	70-130
Diethyl phthalate	70 µg/Kg dry	N/A	0-114	40%	70-130
Dimethyl phthalate	70 µg/Kg dry	N/A	0-112	40%	70-130
Di-n-octyl phthalate	70 µg/Kg dry	N/A	4-155	40%	70-130
Phthalate Surrogates:					
D ₅ -Nitrobenzene	N/A	N/A	N/A	N/A	25-128
2-Fluorobiphenyl	N/A	N/A	N/A	N/A	27-134
D ₁₄ -Terphenyl	N/A	N/A	N/A	N/A	18-157

Table 19 Notes:

Parameter information – italicized in grey is not currently applicable to WSDOTs stormwater monitoring activities but may be in the future if future sampling efforts change.

- [1] Recommended value. The relative percent difference (RPD) must be ≤ the indicated percentage for values that are >5x reporting limit (RL). Concentration difference value must be 2x RL for values that are ≤5x RL.
- [2] For PAHs, phthalates, and BNAs, both deuterated and non-deuterated monitoring compounds are the surrogate standards.
- [3] Recommended value. The matrix spike duplicate RPD criteria apply when original and replicate results are ≥5x reporting limit. Concentration difference of 1xRL applies to precision evaluation if either or both original and replicate results are <5x reporting limit.
- [4] Validation criteria for this parameter are not included in this document.
- [5] Unless otherwise noted, method quality objectives (matrix spike & LCS values) are based on current performance-based statistics provided by the analytical laboratories. The values are subject to change as the laboratories update their performance control limits as required by the accreditation programs.
- [6] The RL used is based on laboratory recommendations on achievable RLs.
- [7] The control limit has been adjusted to cope with project-specific accuracy control goals and is based on a recommendation of industry standard. A minimum lower control limit (LCL) of 30%, a minimum upper control limit (UCL) of 100% and a maximum UCL of 150% has been set forth as project accuracy control goals. The control limits have been adjusted accordingly as denoted.

Table 20 Quantity, Container, Preservation, and Holding Time Requirements for Semi-Volatile Organic Compounds by GC/MS and HPLC/MS Methods

Parameter	Minimum Quantity Needed for Analysis & QC Samples	Container	Preservative ^{[1][2]}	Holding Time ^[3]	
Water Samples					
Semi-Volatile Organics	PAH compounds ^[5]	Analysis = 1 Liter MS & MSD = 1 Liter each	1 Liter amber n/m glass bottle with Teflon® lid if analyzed alone or combined with Phthalates.	Store in dark; cool to ≤6°C; lab preserve with Na ₂ S ₂ O ₃ and adjust pH to 6-9 ^[4]	7 days until extraction; 40 days after extraction
	Phthalates ^[6]	Analysis = 1 Liter MS & MSD = 1 Liter each	1 Liter amber n/m glass bottle with Teflon® lid if analyzed alone or combined with PAHs.	Store in dark; cool to ≤6°C	7 days until extraction; 40 days after extraction
	<i>Base/Neutral/Acid extractable semi-volatile compounds (BNAs)^[8]</i>	<i>Analysis = 1 Liter MS & MSD = 1 Liter each</i>	<i>1 liter amber glass bottle with Teflon® lined lids</i>	<i>Store in dark; cool to ≤6°C</i>	<i>7 days until extraction, 40 days after extraction</i>
	Visible Oil Sheen ^[9]	N/A	N/A	N/A	N/A
Sediment Samples					
Semi-Volatile Organics	PAH ^[5]	Analysis = 30 wet g Dup = 30 wet g, if analyzed alone or combined with Phthalates and Phenolics.	1 L glass jar with Teflon® lined lid if batched with all sediment parameters.	Cool to ≤6°C; standard: may freeze at -18°C at lab ^[10]	14 days until extraction (1 yr if stored frozen at -18°C); 40 days after extraction ^[10]
	Phthalates ^[6]	Analysis = 30 wet g Dup = 30 wet g, if analyzed alone or combined with PAH and Phenolics.	1 L glass jar with Teflon® lined lid if batched with all sediment parameters.	Cool to ≤6°C; standard: may freeze at -18°C at lab ^[10]	14 days until extraction (1 yr if stored frozen at -18°C); 40 days after extraction ^[10]
	Phenolics ^[7]	Analysis = 30 wet g Dup = 30 wet g, if analyzed alone or combined with PAH and Phenolics.	1 L glass jar with Teflon® lined lid if batched with all sediment parameters.	Cool to ≤6°C; standard: may freeze at -18°C at lab ^[10]	14 days until extraction (1 yr if stored frozen at -18°C); 40 days after extraction ^[10]

Table 20 Notes:

Parameter information – italicized in grey is not currently applicable to WSDOTs stormwater monitoring activities but may be in the future if future sampling efforts change.

Some parameters can be batched in one sample container e.g. PAH and phthalate parameters analyzed by the same method for water. All sediment parameters can be batched in 1 sample container.

w/m = wide mouth

n/m = narrow mouth

MS = matrix spike

MSD = matrix spike duplicate

Dup = laboratory duplicate

[1] Preservation needs to be done in the field, unless otherwise noted. Ice will be used to cool samples to approximately 6°C.

- [2] Preservation per 40 CFR 136, accessed online at and current as of 6/12/2014, unless noted or italicized in grey.
- [3] Holding times per 40 CFR 136, accessed online at and current as of 6/12/2014, unless noted or italicized in grey.
- [4] Per USEPA 8270D, sample should be preserved with $\text{Na}_2\text{S}_2\text{O}_3$ if an oxidant such as chlorine is suspected to be present. The lab will add $\text{Na}_2\text{S}_2\text{O}_3$ and adjust pH to 6-9 upon sample receipt.
- [5] PAHs of interest: acenaphthene, acenaphthylene, anthracene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[ghi]perylene, benzo[a]pyrene, chrysene, dibenzo[a,h]anthracene, fluoranthene, fluorene, indeno[1,2,3-cd]pyrene, naphthalene, phenanthrene, and pyrene.
- [6] Phthalates of interest: bis(2-Ethylhexyl)phthalate, Butyl benzyl phthalate, Di-n-butyl phthalate, Diethyl phthalate, Dimethyl phthalate, and Di-n-octyl phthalate.
- [7] Phenolics: Phenol, 2-Methylphenol, 4-Methylphenol, 2,4-Dimethylphenol, pentachlorophenol, benzyl alcohol, and benzoic acid.
- [8] BNAs include: Phenol, Bis(2-Chloroethyl)Ether, 2-Chlorophenol, 1,3-Dichlorobenzene, 1,4-Dichlorobenzene, 1,2-Dichlorobenzene, Benzyl Alcohol, 2-Methylphenol, Bis(2-chloro-1-methylethyl) ether, N-Nitrosodi-n-propylamine, 4-Methylphenol, Hexachloroethane, Nitrobenzene, Isophorone, 2-Nitrophenol, 2,4-Dimethylphenol, Bis(2-Chloroethoxy)Methane, Benzoic Acid, 2,4-Dichlorophenol, 1,2,4-Trichlorobenzene, Naphthalene, 4-Chloroaniline, Hexachlorobutadiene, 4-Chloro-3-Methylphenol, 2-Methylnaphthalene, 1-Methylnaphthalene, Hexachlorocyclopentadiene, 2,4,6-Trichlorophenol, 2,4,5-Trichlorophenol, 2-Chloronaphthalene, 2-Nitroaniline, Dimethyl phthalate, 2,6-Dinitrotoluene, Acenaphthylene, 3-Nitroaniline, Acenaphthene, 2,4-Dinitrophenol, 4-Nitrophenol, Dibenzofuran, 2,4-Dinitrotoluene, Diethyl phthalate, Fluorene, 4-Chlorophenyl-Phenylether, 4-Nitroaniline, 4,6-Dinitro-2-Methylphenol, N-Nitrosodiphenylamine, 1,2-Diphenylhydrazine, Triethyl citrate, 4-Bromophenyl phenyl ether, Hexachlorobenzene, Tris(2-chloroethyl) phosphate(TCEP), Pentachlorophenol, Phenanthrene, Anthracene, Caffeine, 4-nonylphenol, Carbazole, Di-N-Butylphthalate, Triclosan, Fluoranthene, Pyrene, Bisphenol A, Retene, Butyl benzyl phthalate, Benz[a]anthracene,3,3'-Dichlorobenzidine, Chrysene, Bis(2-Ethylhexyl) Phthalate, Di-N-Octyl Phthalate, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(a)pyrene, 3B-Coprostanol, Cholesterol, Indeno(1,2,3-cd)pyrene, Dibenzo(a,h)anthracene, Benzo(ghi)perylene.
- [9] Validation criteria for this parameter are not included in this document.
- [10] Sediment Sampling and Analysis Plan Appendix (Ecology, 2008b).

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