



# Addendum 5 to Quality Assurance Monitoring Plan

# **Long-Term Marine Waters Monitoring, Water Column Program**

February 2018 Publication No. 18-03-105

#### **Publication Information**

Each study conducted by the Washington State Department of Ecology (Ecology) must have an approved Quality Assurance Project Plan. The plan describes the objectives of the study and the procedures to be followed to achieve those objectives. After completing the study, Ecology will post the final report of the study to the Internet.

This Quality Assurance Monitoring Plan is available on Ecology's website at <a href="https://fortress.wa.gov/ecy/publications/SummaryPages/1803105.html">https://fortress.wa.gov/ecy/publications/SummaryPages/1803105.html</a>

Data for this project will be available on Ecology's Environmental Information Management (EIM) website at EIM Database. Search Study ID MarineWater.

Ecology's Activity Tracker Code for this study is 01-800.

#### **Original Publication**

Quality Assurance Project Plan: Long-Term Marine Waters Monitoring, Water Column Program. Publication No. 15-03-101. https://fortress.wa.gov/ecy/publications/SummaryPages/1503101.html

#### **Author and Contact Information**

Allison Brownlee P.O. Box 47600 Environmental Assessment Program Washington State Department of Ecology Olympia, WA 98504-7600

Communications Consultant: phone 360-407-6834.

Washington State Department of Ecology – <a href="https://ecology.wa.gov">https://ecology.wa.gov</a>

Location of Ecology Office	Phone
Headquarters, Lacey	360-407-6000
Northwest Regional Office, Bellevue	425-649-7000
Southwest Regional Office, Lacey	360-407-6300
Central Regional Office, Union Gap	509-575-2490
Eastern Regional Office, Spokane	509-329-3400

**Cover photo:** Float plane departing Swantown Marina in Olympia (by Allison Brownlee)

Any use of product or firm names in this publication is for descriptive purposes only and does not imply endorsement by the author or the Department of Ecology.

Accommodation Requests: To request ADA accommodation including materials in a format for the visually impaired, call Ecology at 360-407-6834. People with impaired hearing may call Washington Relay Service at 711. People with speech disability may call TTY at 877-833-6341.

# Addendum 5 to **Quality Assurance Monitoring Plan**

# Long-Term Marine Waters Monitoring, Water Column Program

February 2018

### Approved by:

Signature:	Date:
Allison Brownlee, Author / Field Scientist, EAP	
Signature:	Date:
Mya Keyzers, Co-author / Project Manager, EAP	
Signature:	Date:
Christopher Krembs, Author / Principal Investigator, EAP	
Signature:	Date:
Carol Falkenhayn Maloy, Author's Unit Supervisor, EAP	
Signature:	Date:
Dale Norton, Author's Section Manager, EAP	
Signature:	Date:
Alan Rue, Acting Director, Manchester Environmental Laboratory	
-	
Signature:	Date:

Bill Kammin, Ecology Quality Assurance Officer

Signatures are not available on the Internet version.

EAP: Environmental Assessment Program

# **Table of Contents**

		Page
3.0	Background	6
5.0	Organization and Schedule	7 8
6.0	Quality Objectives	9
7.0	Study Design	11 11
8.0	Field Procedures	29
9.0	Laboratory Procedures  9.1 Lab procedures table  9.2.1 Analyte  9.2.4 Expected range of results  9.2.5 Analytical method  9.2.6 Sensitivity/Method Detection Limit (MDL)	30 31 31
10.0	Quality Control Procedures	32 32
15.0	References	37
Appe	endix. Glossaries, Acronyms, and Abbreviations	38

# **List of Figures**

	Page
Figure 1.	All 2018 Ecology long-term marine water column monitoring station locations. The 20 particulate pilot project stations are highlighted with a white star, the 2 zooplankton & particulate stations are highlighted with a green star, and the 2 stations that are sampled on different routes depending on time of year are split color
Figure 2.	2018 Marine Flight 1 (MF1) Coast sampling stations
Figure 3.	2018 Marine Flight 2 (MF2) North Sound sampling stations. The particulate pilot project stations are highlighted with a white star. Stations HCB013 and SIN001 (purple/orange symbol) are sampled on MF2 by plane October-March, and on MF3 by boat April-September
Figure 4.	2018 Marine Flight 3 (MF3) Central Sound sampling stations. The particulate pilot project stations are highlighted with a white star. Stations HCB013 and SIN001 (purple/orange symbol) are sampled on MF2 by plane October-March, and on MF3 by boat April-September
Figure 5.	2018 Marine Flight 4 (MF4) South Sound sampling stations. The particulate pilot project stations are highlighted with a white star19
Figure 6.	2018 Marine Flight 5 (MF5) Hood Canal sampling stations. The particulate pilot project stations are highlighted with a white star. The green stars represent stations that are sampled for both particulates and zooplankton20
Figure 7.	2018 San Juans and Admiralty Inlet stations sampled by the Shannon Point Marine Center (SPMC)

# **List of Tables**

Page	3
Table 1. Organization of project staff and responsibilities.	7
Table 2. Proposed schedule for completing the field and laboratory work, data processing, review, QAQC, storage in a database, and reports	8
Table 3. Budget presented to the Program Management Team for the 2017-2019 biennium Marine Flight operations.	9
Table 4. Measurement quality objectives for marine water column laboratory samples1	0
Table 5. 2018 station list for Ecology long-term marine water column monitoring1	2
Table 6. Projected monthly water sample collection plan for 2018 listing depths (in meters) for each sample type collected at each station	2
Table 7. Projected water sample collection plan for 2018 listing each sample type collected at each station by the waters or sediment group	6
Table 8. Field sample collection methods for ambient water column monitoring2	9
Table 9. Lab measurement methods, expected range of results and reporting limits for marine data	1
Table 10. A summary of quality control steps for field measurements3	3
Table 11. Quality assurance/quality control procedures for water column parameter analysis in the laboratory	6

# 3.0 Background

This document describes changes planned for 2018 to the sampling effort for Ecology's Long-Term Marine Waters Monitoring Program. It is an addendum to *Quality Assurance Monitoring Plan: Long-Term Marine Waters Monitoring, Water Column Program* (Bos, 2015). This Quality Assurance Monitoring Plan (QAMP) addendum specifies which stations and parameters will be sampled in 2018. Thirty seven core stations and two sediment team core stations will be sampled for standard water column parameters. Additional sampling will be included at a subset of stations for total organic carbon (TOC), total nitrogen (TN), particulate organic carbon (POC), and particulate nitrogen (PN).

A new instrument called a Submersible Ultraviolet Nitrate Analyzer (SUNA) was tested in 2017 at the stations sampled by Shannon Point Marine Center. Starting in January, a new suite of sensors will be compiled for use while sampling Ecology stations by boat. This larger boat package will include a SUNA sensor and will be used at all stations sampled by boat. A collaboration with the Salish Sea Marine Survival Project will take place monthly at two stations in Hood Canal. Staff from the Hood Canal Salmon Enhancement Group will collect one vertical plankton net tow at each of these two stations to quantify zooplankton.

The purpose of the program is to examine and report marine water quality on a regular, long-term basis. Its objectives are to understand current existing conditions in the context of environmental factors, identify spatial and temporal trends, and provide high-quality information from sensor and lab sample collection.

All required sections not mentioned in this addendum are discussed in the original QAMP and referenced SOPs.

# 5.0 Organization and Schedule

# 5.1 Key individuals and their responsibilities

Table 1. Organization of project staff and responsibilities.

Staff	Title	Responsibilities
Julia Bos Marine Monitoring Unit Western Operations Section EAP Phone: (360) 407-6674	Monitoring Coordinator, Data Management, Data Analyst, Publications Author	Writes the QAMP. Oversees JEMS monitoring program - field and laboratory activities. Conducts QA review, analyzes and interprets data, and enters data into EIM/data management system. Writes reports and data summaries.
Christopher Krembs Marine Monitoring Unit Western Operations Section EAP Phone: (360) 407-6675	Senior Oceanographer, Lead Presentations & Publications Author	Determines monitoring strategy. Generates index/indicators of water quality conditions. Determines appropriate analysis, review and interpretative methods for data reduction and reporting. Generates data products. Lead author of publications and presentations.
Skip Albertson Marine Monitoring Unit Western Operations Section EAP Phone: (360) 407-6675	Physical Oceanographer, Data Analyst, Modeler, Publications Author	Analysis & reporting of climate, weather and ocean indicators. Generates data products and analytical tools. Conducts QA review of data, analyzes and interprets data. Writes reports and data summaries.
Mya Keyzers Marine Monitoring Unit Western Operations Section EAP Phone: (360) 407-6395	Marine Flight Lead Scientist	Conducts field sampling, laboratory analysis, and instrument maintenance. Records & manages field information. Conducts QA review, analyzes and interprets data. Writes reports and data summaries.
Allison Brownlee Marine Monitoring Unit Western Operations Section EAP Phone: (360) 407-0273	Marine Flight Scientist	Conducts field sampling, laboratory analysis and instrument maintenance. Records & manages field information. Conducts QA review, analyzes and interprets data. Writes reports and data summaries.
Carol Falkenhayn Maloy Marine Monitoring Unit Western Operations Section EAP Phone: (360) 407-6742	Unit Supervisor	Provides internal review of the QAMP, approves the budget, and approves the final QAMP.
Dale Norton Western Operations Section EAP Phone: (360) 407-6596	Section Manager	Reviews the project scope and budget, tracks progress, reviews the draft QAMP, and approves the final QAMP.
William R. Kammin Phone: (360) 407-6964	Ecology Quality Assurance Officer	Reviews the draft QAMP and approves the final QAMP.

EAP: Environmental Assessment Program, Department of Ecology

EIM: Environmental Information Management database

QAMP: Quality Assurance Project Plan

# 5.4 Proposed project schedule

Table 2. Proposed schedule for completing the field and laboratory work, data processing, review, QAQC, storage in a database, and reports.

Activity	Due date	Lead staff	
Field and laboratory work			
Field work (sample collection) completed	Monthly	Mya Keyzers	
Internal (Ecology) laboratory analyses completed	3 days (DO samples) post-collection	Allison Brownlee	
Internal (Ecology) laboratory analyses completed	1 month post-collection (chlorophyll <i>a</i> samples)	Allison Brownlee	
External UW and MEL laboratory analyses completed	3 months post-collection (nutrient, TOC, and POC/PN samples)	Mya Keyzers	
Data receipt or processing and	upload to EAPMW (Marine Waters)		
Instrument & sensor data	Same month as collection	Julia Bos	
Internal laboratory data	1 month post-analyses	Allison Brownlee	
External laboratory data	1 month post-analyses	Mya Keyzers	
Data review and QAQC			
Instrument & sensor data	1 month post-collection	Julia Bos, Christopher Krembs, Skip Albertson, Mya Keyzers, Allison Brownlee	
Internal laboratory data	1 month post-analyses	Allison Brownlee	
External laboratory data	Quarterly, one quarter post-collection	Mya Keyzers	
Annual Assessment - data prod	ucts & written summary		
Draft assessments & products due	3 months after sampling year complete	Christopher Krembs, Julia Bos, Skip Albertson, Mya Keyzers, Allison Brownlee	
Final reviews & QAQC 4 months after sampling year com		Christopher Krembs, Julia Bos	
Final data posted and performa	nce measures reported		
Final performance calculated & submitted to OFM	Annually in July	Julia Bos	

EAP: Environmental Assessment Program

EIM: Environmental Information Management database

QAMP: Quality Assurance Monitoring Plan

UW: University of Washington

## 5.5 Budget and funding

This budget does not include the full cost of the monitoring program. It is limited to direct expenses for the specific elements below.

Table 3. Budget presented to the Program Management Team for the 2017-2019 biennium Marine Flight operations.

Туре	Cost	Comments
MEL Lab (Particulates)	\$119,750	Particulates study, 24 months of sampling at 20 stations.
Vessel (Skookum)	\$25,500	
Nutrient Analyses (UW)	\$67,937	UW Marine Chem Lab: inorganic nutrients and salinity.
Marine Flights (Kenmore Air) <sup>2</sup>	\$158,389	
Shannon Point Contract	\$83,740	
NEW Near Term Action National Estuary Program grant (EPA)	[\$370,785]	Funding for two years (2018-2020). Addresses ocean acidification: Adds total alkalinity (TA) and dissolved inorganic carbon (DIC) measurements.
2017-2019 Biennium Total	\$455,316	Excludes NTA grant

MEL: Manchester Environmental Laboratory

UW: University of Washington

UWW: University of Western Washington <sup>1</sup>Inter-agency Agreement No. C1400008

# 6.0 Quality Objectives

## 6.1 Measurement quality objectives (MQOs)

## 6.1.1 Targets for precision, bias, and sensitivity

#### **6.1.1.5** Laboratory MQOs

Seawater nutrient and salinity sample analyses are conducted by the University of Washington Marine Chemistry Laboratory (UW-MCL). Dissolved oxygen (Winkler) and chlorophyll *a* samples are analyzed by the Marine Lab (ML) of the Marine Waters Monitoring Group. POC, PN, TOC, and TN analyses are conducted by Ecology's Manchester Environmental Laboratory (MEL). Any labs conducting analyses for the marine waters monitoring program are accredited through Ecology's Laboratory Accreditation Program. Sampling for total alkalinity (TA) and dissolved inorganic carbon (DIC) will not begin until an appropriate staff member is appointed.

<sup>&</sup>lt;sup>2</sup>State Contract No. 04413

Once collected, those samples will be processed by the Pacific Marine Environmental Laboratory (PMEL) and a waiver of accreditation will be obtained.

All work is expected to meet the quality control (QC) requirements of the analytical methods used for this project. These requirements are summarized in the Measurement Procedures and Quality Control Procedures sections of this document and in the standard operating procedures (SOPs) used for each analysis. Many of these procedures can also be found in detail in the Puget Sound Estuary Program (PSEP) Protocols (1997).

Table 4. Measurement quality objectives for marine water column laboratory samples.

This table summarizes measurement quality objectives for "analytical laboratory" values for marine data. Ecology is responsible for verifying all MQOs are met.

Measurement - Laboratory	Precision (relative standard deviation, RSD)	Accuracy (Bias) (% deviation from true value)	Lowest Value (reporting limit)
Total Organic Carbon (TOC)	≤ 20%	5%	500 ug/L
Total Nitrogen (TN)	≤ 20%	5%	25 ug/L
Particulate Nitrogen (PN)	≤ 20%	5%	62.3ug/L
Particulate Organic Carbon (POC)	≤ 20%	5%	10.5 ug/L
Total Alkalinity*	±0.1%	N/A	N/A
Dissolved Inorganic Carbon*	±0.1%	N/A	N/A
Dissolved Oxygen	5%	5%	0.05 mg/L
Marine Nitrate	10%	5%	0.15 μΜ
Marine Nitrite	10%	5%	0.01 μΜ
Marine Ammonium	10%	5%	0.05 μΜ
Marine Orthophosphate	10%	5%	0.02 μΜ
Marine Silicate	10%	5%	0.21 μΜ
Chlorophyll a	10%	N/A	0.02 μg/L
Salinity	5%	5%	0.002 PSU

<sup>\*</sup>Not currently collected

# 7.0 Study Design

## 7.1 Study boundaries

### 7.1.2 Sampling location and frequency

#### 7.1.2.1 Core Station Monitoring & Locations

Core long-term monitoring stations are visited once a month, year-round, to ensure that all major seasonal hydrographic conditions are observed. Since not all stations can be visited in one day, stations are aligned by region and separated into regional surveys conducted every month for the most efficient operations. This year the stations are divided into six regional surveys a month as opposed to five, as previously done. Fewer stations per survey allow for more flexibility to adapt to weather delays, seasonally limited daylight hours, and weather-dependent activities such as the *Eyes Over Puget Sound* (EOPS) aerial surveys.

In 2015, stations WPA001 and GYS004 were changed from core to rotational, as these stations are in rivers and exhibit freshwater rather than marine characteristics. These two stations will not be sampled in 2018. This results in a total of 39 stations: 37 core waters stations and 2 sediment team core stations. This year the regions will be grouped as:

- San Juans and Admiralty Inlet (Shannon Point Marine Science Center)
- Coastal Bays (Marine Flight 1)
- North Sound (Marine Flight 2)
- Central Sound (Marine Flight 3)
- South Sound (Marine Flight 4)
- Hood Canal (Marine Flight 5)

Ecology will sample all Marine Flight (MF) stations, while the San Juans and Admiralty Inlet stations will be contracted to the Shannon Point Marine Center (SPMC).

See Table 5 and Figures 1-7.

Stations are sampled at intervals no less than three weeks apart to ensure reasonable adherence to a monthly sampling scheme. Due to lower station attainment by plane during the winter months, MF3 will be sampled by boat between October and March. Two stations (HCB013 and SIN001) are hard to reach by boat and will be added to the MF2 route by plane during those months.

Table 5. 2018 station list for Ecology long-term marine water column monitoring.

Flight	Station ID	Location	Lat. N NAD83 (deg/dec_min)	Long. W (NAD83) (deg/dec_min)	WQMA <sup>a</sup>	Depth (m)	Record	Record Length (yrs)	Justification
Marine	GYS008	Mid-S. Channel	46 56.2388	123 54.7934	Western Olympic	6	1974 - 76, 1983 - present	37	represents mid Grays Harbor, south
Flight 1	GYS016	Damon Point	46 57.2053	124 05.5770	Western Olympic	11	1982 - 1987,1991 - present	31	represents outer Grays Harbor, north
	WPA004	Toke Point	46 41.9800	123 58.1240	Lower Columbia	14	1973-1975, 1977-present	43	represents north Willapa Bay
	WPA113	Bay Center	46 38.6400	123 59.5800	Lower Columbia	11	1997-2000, 2006-present	14	represents mouth of (NW) Willapa Bay
	WPA006	Nahcotta Channel	46 32.7226	123 58.8097	Lower Columbia	21	1991-present	26	represents central Willapa Bay
	WPA007	Long Island, S. Jenson Pt.	46 27.1893	124 00.5672	Lower Columbia	14	1991-2008, 2013-present	21	represents SW Willapa Bay
	WPA008	Naselle River mouth	46 27.7890	123 56.4760	Lower Columbia	14	1996-2008, 2013-present	16	represents SE Willapa Bay, off Naselle R.
	WPA003	Willapa River, John. Slough	46 42.2392	123 50.2431	Lower Columbia	10	1973-present	44	represents north Willapa Bay, off Willapa R.
Marine	BLL009	Bellingham Bay	48 41.1564	122 35.9771	Nooksack/Sa n Juan	16	1977-present	40	represents waters off city of Bellingham
Flight 2	BLL040	Bellingham Bay	48 41.0382	122 32.2920	Nooksack/Sa n Juan	26	NA	28	represents waters of Bellingham
	SKG003	Skagit Bay	48 17.7893	122 29.3763	Island/Snoho mish	24	1990-1991, 1994-1998, 2007-present	17	represents Whidbey Basin
	SAR003	Saratoga Passage	48 06.4557	122 29.4925	Island/Snoho mish	149	1977-present	40	represents Whidbey Basin
	PSS019	Possession Sound	48 00.6556	122 18.0750	Island/Snoho mish	101	1980-present	37	represents waters off city of Everett
Marine	SIN001	Sinclair Inlet	47 32.9557	122 38.6083	Kitsap	16	1973-1987, 1991-present	40	represents waters off city of Bremerton
Flight 2/3 <sup>b</sup>	HCB013	Hood Canal	47 50.2548	122 37.7370	N of Hood Canal Bridge	20	NA	2	represents entrance of Hood Canal
Marine	ADM003	S. of Admiralty Inlet	47 52.7390	122 28.9917	Kitsap & Cedar/Green	210	1988-1991, 1996-present	23	represents waters S. of Admiralty sills
Flight 3	PSB003	Puget Snd. Main Basin	47 39.5891	122 26.5745	Kitsap & Cedar/Green	40-50	1976-present	41	represents Puget Sound Main Basin

Flight	Station ID	Location	Lat. N NAD83 (deg/dec_min)	Long. W (NAD83) (deg/dec_min)	WQMA <sup>a</sup>	Depth (m)	Record	Record Length (yrs)	Justification
Marine Flight 3(cont.)	ELB015	Elliott Bay	47 35.7892	122 22.1743	Cedar/Green	82	1991-present	26	represents waters off city of Seattle
	EAP001	East Passage	47 25.0226	122 22.8241	Kitsap & Cedar/Green	200	1988-1991, 94-95, 1997- present	25	represents S. Puget Sound main axis
	CMB003	Commenceme nt Bay	47 17.4226	122 27.0074	South Puget Sound	150	1976-present	41	represents waters off city of Tacoma
Marine	BUD005	Budd Inlet	47 05.5224	122 55.0918	Eastern Olympic	15	1973-present	44	represents waters off city of Olympia
Flight 4	DNA001	Dana Passage	47 09.6890	122 52.3083	Eastern Olympic	40	1984-85, 1989-present	30	represents south reach of Southern Puget Sound
	NSQ002	Devil's Head	47 10.0390	122 47.2914	E. Oly & Kitsap & SPS	100	1984-85, 1996-present	23	represents S. Puget Sound near Nisqually
	GOR001	Gordon Point	47 10.9891	122 38.0743	E. Oly & Kitsap & SPS	160-170	1996-present	20	represents S. Puget Sound south of Narrows
	CRR001	Carr Inlet	47 16.5891	122 42.5745	Eastern Olympic	95	1977-93, 95-96, 1998-2003, 2006,09-present	33	represents waters within Carr Inlet
	CSE001	Case Inlet	47 15.8724	122 50.6583	Eastern Olympic	55	1978-1993, 95-96,1998-99, 2009-present	28	represents waters within Case Inlet
	OAK004	Oakland Bay	47 12.8056	123 04.6590	Eastern Olympic	15	1974-75, 1977-present	43	represents waters off city of Shelton
Marine	HCB007	Hood Canal, Lynch Cv.	47 23.8889	122 55.7755	Kitsap & E. Olympic	21	1990-1996, 1998-2007, 2011-present	23	very low DO, assess duration & coverage
Flight 5	HCB004	Hood Canal, Sisters Pt.	47 21.3723	123 01.4924	Kitsap & E. Olympic	55	1975-1987, 1990-present	40	represents southern Hood Canal
	НСВ003	Hood Canal, Eldon	47 32.2722	123 00.5760	Kitsap & E. Olympic	144	1976-92, 1994-96, 1998- 2007, 2010-present	36	very low DO, assess duration & coverage
	НСВ010	Hood Canal, S of Bangor	47 40.2000	122 49.2000	Kitsap & E. Olympic	100	2005-present	12	represents northern Hood Canal
SPMC <sup>c</sup>	SJF000	Strait of Juan de Fuca	48 25.0000	123 01.5000	S. of San Juan Island	180	2000 - present	17	represents northern Strait of Juan de Fuca
SI MC	SJF001	Strait of Juan de Fuca	48 20.0000	123 01.5000	SE of Hein Bank	160	2000 - present	17	represents central Strait of Juan de Fuca
	SJF002	Strait of Juan de Fuca	48 15.0000	123 01.5000	SW of Eastern Bank	145	2000 - present	17	represents southern Strait of Juan de Fuca
	RSR837	Rosario Strait	48 36.9896	122 45.7775	Nooksack/Sa n Juan	56	2009-present	8	represents waters in Rosario Strait

Flight	Station ID	Location	Lat. N NAD83 (deg/dec_min)	Long. W (NAD83) (deg/dec_min)	WQMA <sup>a</sup>	Depth (m)	Record	Record Length (yrs)	Justification
SPMC <sup>c</sup> (cont.)	GRG002	Strait of Georgia	48 48.4896	122 57.2446	Nooksack/Sa n Juan	190	1988-present	29	represents Strait of Georgia end member
	PTH005	Port Townsend	48 04.9889	122 45.8767	Eastern Olympic	26	1977-1978, 1991-2002, 2005-present	26	represents waters off city of Port Townsend
	ADM001	Admiralty Inlet	48 01.7888	122 37.0760	Kitsap & Cedar/Green	148	1975-1987, 1992-present	37	represents waters within Admiralty Inlet
	ADM002	N. of Admiralty Inlet	48 11.2391	122 50.5770	Island & E. Olympic	82	1980-present	37	represents waters entering Admiralty Inlet

 <sup>&</sup>lt;sup>a</sup> Water Quality Management Area
 <sup>b</sup> Stations are sampled October-March on MF2 by plane, and April-September on MF3 by boat.
 <sup>c</sup> Shannon Point Marine Center

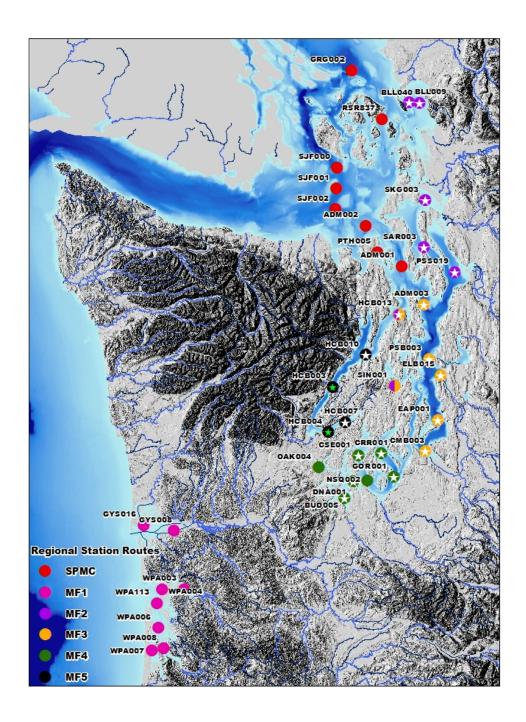


Figure 1. All 2018 Ecology long-term marine water column monitoring station locations. The 20 particulate pilot project stations are highlighted with a white star, the 2 zooplankton & particulate stations are highlighted with a green star, and the 2 stations that are sampled on different routes depending on time of year are split color.

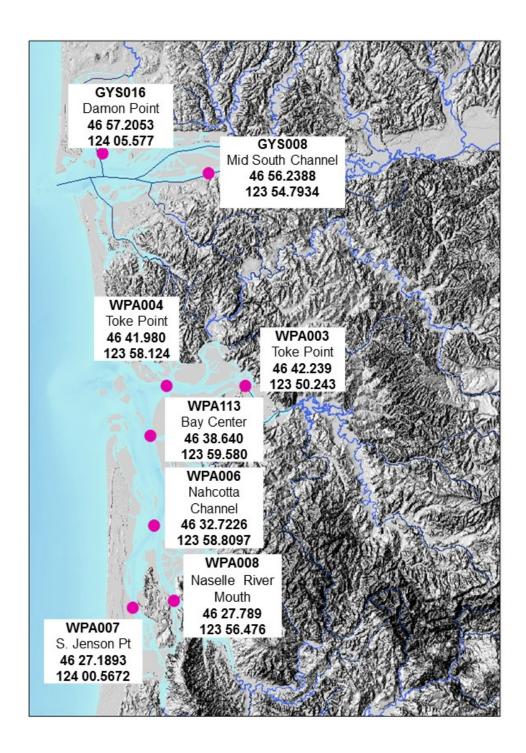


Figure 2. 2018 Marine Flight 1 (MF1) Coast sampling stations.

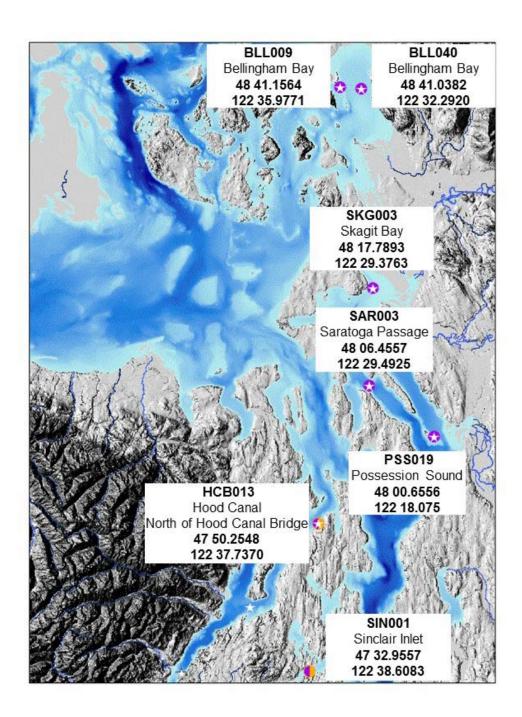


Figure 3. 2018 Marine Flight 2 (MF2) North Sound sampling stations. The particulate pilot project stations are highlighted with a white star. Stations HCB013 and SIN001 (purple/orange symbol) are sampled on MF2 by plane October-March, and on MF3 by boat April-September.

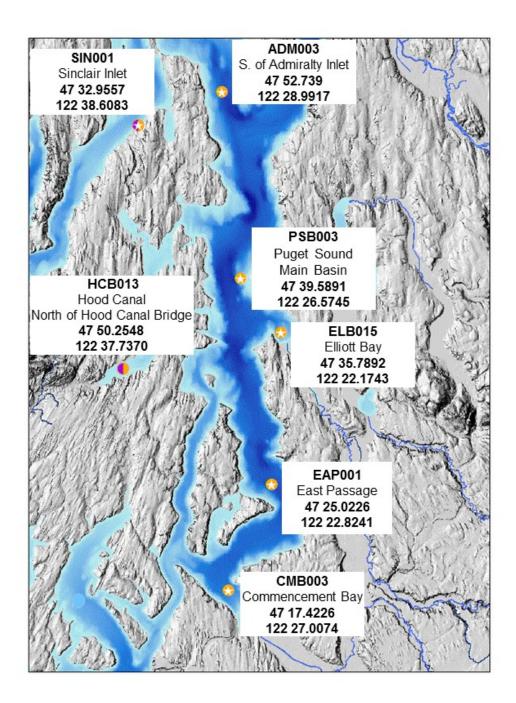


Figure 4. 2018 Marine Flight 3 (MF3) Central Sound sampling stations. The particulate pilot project stations are highlighted with a white star. Stations HCB013 and SIN001 (purple/orange symbol) are sampled on MF2 by plane October-March, and on MF3 by boat April-September.

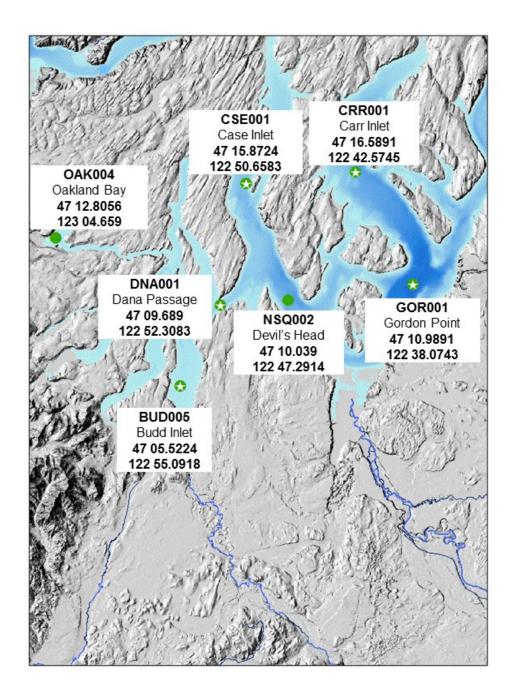


Figure 5. 2018 Marine Flight 4 (MF4) South Sound sampling stations. The particulate pilot project stations are highlighted with a white star.

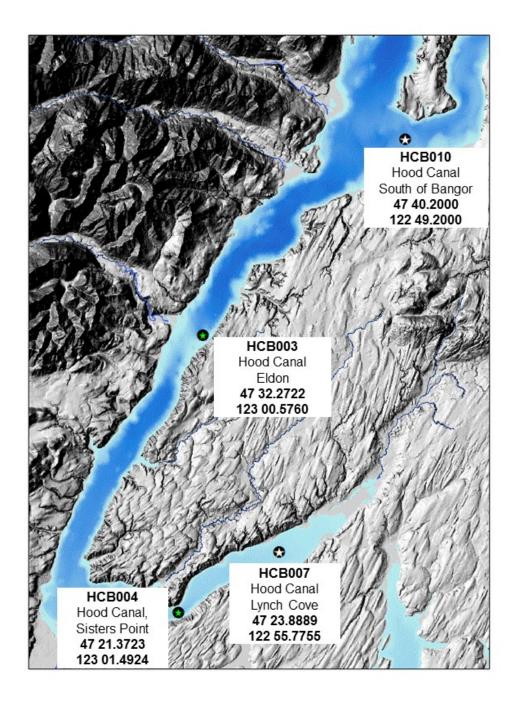


Figure 6. 2018 Marine Flight 5 (MF5) Hood Canal sampling stations. The particulate pilot project stations are highlighted with a white star. The green stars represent stations that are sampled for both particulates and zooplankton.

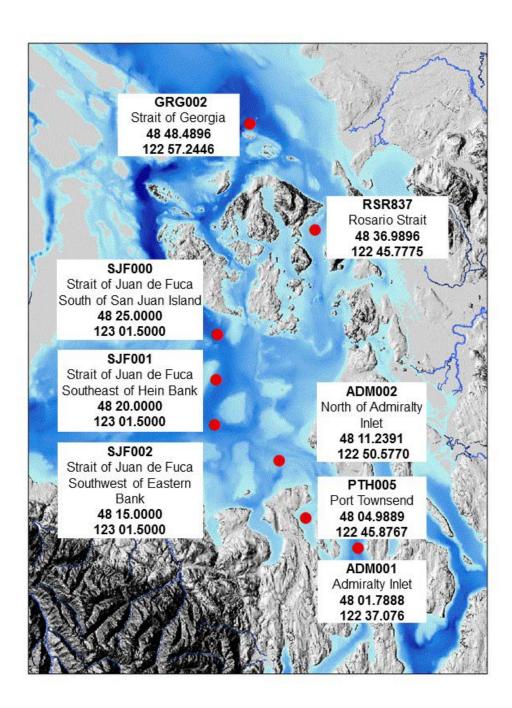


Figure 7. 2018 San Juans and Admiralty Inlet stations sampled by the Shannon Point Marine Center (SPMC).

Table 6. Projected monthly water sample collection plan for 2018 listing depths (in meters) for each sample type collected at each station.

Station	Nutrients*	Chlorophyll	POC & PN	тос	TN	Dissolved Oxygen	Zooplankton	Salinity	Approximate Station Depth (m)
Marine Flight 1									
GYS008	0	0							6
GYS016	0, 10	0, 10				near bottom (NB)			11
WPA004	0, 10, 10, 10	0, 10, 10, 10						10	14
WPA113	0, 10	0, 10							11
WPA006	0, 10	0, 10				NB		10	21
WPA007	0, 10	0, 10							14
WPA008	0, 10	0, 10							14
WPA003	0, 10	0, 10							10
Total MF1 Samples:	17	17	0	0	0	2	0	2	
Marine Flight 2	Sampled on MF2 h	y plane Oct-Mar ar	nd by boat Ap	r- Sep					
BLL009	0, 10, NB	0, 10	10,NB	10,NB	10,NB				16
BLL040	0, 10, NB		10,NB	10,NB	10,NB				26
SKG003	0, 10, NB	0, 10	10, 10, NB	10, 10, NB	10, 10, NB			10	24
SAR003	0, 10, 30, NB	0, 10, 30	10,NB	10,NB	10,NB				149
PSS019	0, 10, 30	0, 10, 30	10,NB	10,NB	10,NB	NB			101
Total MF2 Samples:	16	10	11	11	11	1	0	1	
Marine Flight 2/3									
HCB013	0, 10, NB		10,NB	10,NB	10,NB				20
SIN001	0, 10, NB	0, 10	10,NB	10,NB	10,NB				16
Total MF2/3 Samples:	6	2	4	4	4	0	0	0	
Marine Flight 3									
ADM003	0, 10, 30, NB	0, 10, 30	10,NB	10,NB	10,NB			=	210
PSB003	0, 10, 30, NB	0, 10, 30	10,NB	10,NB	10,NB				40-50

Station	Nutrients*	Chlorophyll	POC & PN	тос	TN	Dissolved Oxygen	Zooplankton	Salinity	Approximate Station Depth (m)
ELB015	0, 10, 30, NB	0, 10, 30	10, 10, NB	10, 10, NB	10, 10, NB			10	82
EAP001	0, 10, 30, NB	0, 10, 30	10,NB	10,NB	10,NB	30			200
CMB003	0, 0, 0, 10, 30, NB	0, 10, 10, 10, 30	10,NB	10,NB	10,NB	30		30	150
Total MF3 Samples:	22	17	11	11	11	2	0	2	
Marine Flight 4									
BUD005	0, 0, 0, 10, NB	0, 10, 10, 10	10,NB	10,NB	10,NB		T	10	15
DNA001	0, 10, 30	0, 10, 30				30, 30, 30			40
NSQ002	0, 10, 30, NB	0, 10, 30	10,NB	10,NB	10,NB				100
GOR001	0, 10, 30, NB	0, 10, 30	10,NB	10,NB	10,NB	30		30	160-170
CRR001	0, 10, 30, NB	0, 10, 30	10,10, NB	10,10, NB	10,10, NB				95
CSE001	0, 10, 30, NB	0, 10, 30	10,NB	10,NB	10,NB	30			55
OAK004	0, 10	0, 10							15
Total MF 4 Samples:	26	21	11	11	11	5	0	2	
Marine Flight 5									
HCB007	0, 0, 0, 10, NB	0, 10	10,10, NB	10,10, NB	10,10, NB			10	21
HCB004	0, 10, 30	0, 10, 30				30	✓		55
HCB003	0, 10, 30, NB	0, 10, 10, 10	10,NB	10,NB	10,NB		✓		144
HCB010	0, 10, 30, NB	0, 10, 30	10,NB	10,NB	10,NB	30		30	100
Total MF5 Samples:	16	12	7	7	7	2	2	2	
<b>Shannon Point Marine</b>	Center								
SJF000	0, 30, 80, 140	0, 30, 80, 140				0, 30, 80, 140			161
SJF001	0, 30, 80, 140	0, 0, 0, 30, 80, 140				0, 30, 80, 140			144
SJF002	0, 30, 80, 140, 140, 140	0, 30, 80, 140				0, 30, 80, 140, 140, 140		0, 140	142
ADM002	0, 10, 30, 80	0, 30, 80				80		80	82

Station	Nutrients*	Chlorophyll	POC & PN	тос	TN	Dissolved Oxygen	Zooplankton	Salinity	Approximate Station Depth (m)
RSR837	0, 10, 30	0, 10, 30				NB			56
GRG002	0, 10, 30	0, 10, 30						30	190
ADM001	0, 10, 30	0, 10, 30				NB			148
Total SPMC Samples:	31	30	0	0	0	17	0	4	

Monthly Total:										
Station	Nutrients	Chlorophyll	POC & PN	тос	TN	Dissolved Oxygen	Zooplankton	Salinity		
39	134	109	44	44	44	29	2	13		

<sup>\*</sup>Nutrient species included: Nitrite, nitrate, phosphate, silicate, and ammonium.

#### 7.1.3 Parameters to be determined

#### Particulate Organic Material Carbon and Particulate Nitrogen

Analyses of Ecology's long-term marine monitoring data indicate increases of dissolved inorganic nitrate and phosphate relative to ocean source water and a change in the balance of macro-nutrients and silicate (Krembs, 2012, Moore et al., 2016). These changes affect growth conditions of phytoplankton at the base of the food web. The observed changes in inorganic nutrients could either be the result of decreased uptake by phytoplankton, increased nitrogen and phosphate loading, changes in estuarine circulation patterns in respond to climate impacts, or a combination of the three. The long-term change has potential implications for marine food web structure, energy transfer, particle export, and higher trophic levels such as fish.

To understand these processes and to include the organic pools or nutrients, Ecology will continue a particulate pilot project as a collaboration between Marine Waters water column group and sediment group which started in April 2016 and will continue through 2019. In addition to the routine sampling, the marine group will collect total organic carbon (TOC), total nitrogen (TN), particulate organic carbon (POC), and particulate nitrogen (PN) from 2 depths; 10m and near bottom (NB) from 20 stations that overlap core sediment and core waters stations. Samples will be kept at 4°C and delivered to the Manchester Lab the day after collection where the samples will be handled according to standard methods explained in Table 9. An additional goal of this collaboration is to refine temporal and spatial relationships between chlorophyll *a* and estimates of POC to support modeling efforts.

Table 7. Projected water sample collection plan for 2018 listing each sample type collected at each station by the waters or sediment group.

Station Id	Station location	Latitude	Longitude	Station type	MW particulates	Sediment chemistry	Benthos	TOC and Grain Size Only
3	Strait of Georgia	48.87025	-122.97842	Sediment		X	X	
GRG002	Georgia Strait - N of Patos Island	48.80817	-122.95408	Water				
4	Bellingham Bay	48.68397	-122.53820	Sediment	X	X	X	
BLL009	Bellingham Bay - Pt. Frances	48.68593	-122.59962	Water	X		X	X
209R	Skagit Bay	48.29533	-122.48850	Sediment		X	X	
SKG003	Skagit Bay - Str. Point (Red Buoy)	48.29648	-122.48960	Water	X			
19	Saratoga Passage	48.09792	-122.47134	Sediment		X	X	
SAR003	Saratoga Passage - East Point	48.10760	-122.49155	Water	X			
21	Port Gardner/ Everett Harbor	47.98547	-122.24283	Sediment		X	X	
PSS019	Possession Sound	48.01092	-122.30125	Water	X			
119	Admiralty Inlet	47.87615	-122.48217	Sediment		X	X	
ADM003	Admiralty Inlet (south)	47.87898	-122.48320	Water	X			
29	Shilshole	47.70075	-122.45403	Sediment		X	X	
PSB003	Puget Sound Main Basin - West Point	47.65982	-122.44292	Water	X			
191	Central	47.59842	-122.37581	Sediment			X	X
ELB015	Elliott Bay-East of Duwamish Head	47.59648	-122.36957	Water	X			
34	Sinclair Inlet	47.54708	-122.66208	Sediment		X	X	
SIN001	Sinclair Inlet - Naval Shipyards	47.54927	-122.64347	Water	X			
38	Point Pully (3 Tree Point)	47.42833	-122.39363	Sediment		X	X	
EAP001	East Passage - SW of Three Tree Point	47.41705	-122.38040	Water	X			
281	Commencement Bay	47.29229	-122.44193	Sediment			X	X
CMB003	Commencement Bay- Browns Point	47.29038	-122.45012	Water	X			
40	Thea Foss Waterway	47.26130	-122.43730	Sediment			X	X
CMB006	Commencement Bay - Mouth of City WW	47.26149	-122.43735	Water				
44	East Anderson Island	47.16133	-122.67358	Sediment		X	X	
GOR001	Gordon Point	47.18315	-122.63457	Water	X			
265	Carr Inlet	47.25240	-122.66572	Sediment		X	X	
CRR001	Carr Inlet-Off Green Point	47.27648	-122.70958	Water	X			
252	Case Inlet	47.26957	-122.85101	Sediment		X	X	
CSE001	Case Inlet-S. Heron Island	47.26453	-122.84430	Water	X			

Station Id	Station location	Latitude	Longitude	Station type	MW particulates	Sediment chemistry	Benthos	TOC and Grain Size Only
52	W. of Devils Head, Case Inlet (Nisqually Reach)	47.17060	-122.78051	Sediment		X	X	
NSQ002	W. of Devils Head, Case Inlet (Nisqually Reach)	47.16732	-122.78819	Water	X			
49	Budd Inlet	47.07997	-122.91347	Sediment		X	X	
BUD005	Budd Inlet - Olympia Shoal	47.09203	-122.91820	Water	X			
13R	Hood Canal (north of bridge)	47.83758	-122.62895	Sediment	X	X	X	
222	Hood Canal	47.67821	-122.81466	Sediment		X	X	
HCB010	Hood Canal - Send Creek, Bangor	47.67000	-122.82000	Water	X			
HCB003	Hood Canal - Central	47.53787	-123.00960	Water	X		X	X
305R	Lynch Cove	47.39717	-122.93124	Sediment		X	X	
HCB007	Hood Canal - Lynch Cove	47.39815	-122.92959	Water	X			

#### Satlantic SUNA V2 nitrate sensor

To begin quantifying nitrogen in Puget Sound, the Shannon Point Marine Center collected continuous vertical nitrate measurements as part of Ecology's routine monitoring at the San Juans/Admiralty Inlet stations throughout 2017. In early 2018 we plan to build a larger CTD package specifically for Ecology boat sampling which can hold additional sensors including a Satlantic Submersible Ultraviolet Nitrate Analyzer (SUNA) V2. Principles of operation for this sensor are described in manufacturer manuals. Instructions for optimum data collection are outlined in these manuals.

The goals of continuous vertical nitrate measurements are to:

- Improve representativeness of dissolved inorganic nitrate measurements in surface water.
- Extend nitrate information from 0, 10, and 30 meter point samples to full water column depth resolution.
- Provide nitrate data for monthly condition updates in relationship with other vertical profiles. Currently, lab sample results are received much later.
- Provide information for nitrate maxima, minima, and nitrogen load in association with identifiable water masses to support information on nitrate transport in Puget Sound.

#### **Total Alkalinity and Dissolved Inorganic Carbon**

The Washington State Department of Ecology (Ecology) conducted a pilot study from 2014-2015 (Keyzers, 2014) to characterize the carbonate system in Puget Sound by sampling total alkalinity (TA) and dissolved inorganic carbon (DIC) from select stations and to test the practicality of adding such sampling to routing monitoring. Results from the pilot study found seasonal variation in aragonite saturation in relation to pH, chlorophyll *a*, and pCO2 (Keyzers, 2016). The pilot study demonstrated a feasibility of sampling from the boat, but proved difficult by plane. Ecology has received a National Estuary Program grant which will fund a two year ocean acidification study which will begin in late 2018 and closely follow the methods of the pilot study. The focus of this study will determine the range of TA, DIC, and pH within Puget Sound, and further assess the seasonal variability in relation to other variables collected through our routine monitoring program. A separate QAMP will be prepared prior to the start of this study.

# 8.0 Field Procedures

# 8.1 Field measurement and field sampling SOPs

Table 8. Field sample collection methods for ambient water column monitoring.

Sample Parameter	Collection Method or Sensor	Sample Container	Preservation Method	Holding Time
Alkalinity & Dissolved Inorganic Carbon (DIC)	UNESCO, 1994 (JGOFS Protocols)	500 mL pre- combusted, acid- washed, borosilicate glass, stoppered volumetric flasks	Preserve sample with 0.2 mL super-saturated HgCl <sub>2</sub> . Apply Apiezon® L grease to stopper, insert & twist to remove all air. Store in cool, dark conditions.	3 months
Total Organic Carbon (TOC)	SM5310B	125mL quality certified HDPE poly bottle	1:1 HCL, ice upon collection	28 days store at 0°C - 6°C.
Total Nitrogen (TN)	SM 4500-N B	125mL 1:1 quality certified HDPE poly bottle	1:1 H2SO4, ice upon collection	28 days store at 0°C - 6°C.
Particulate Organic Carbon and Particulate Nitrogen (POC & PN)	EPA 440.0	1 L poly amber quality certified bottle	Store on ice. Filter ASAP upon arrival at the laboratory. Store at -20C.	Up to 100 days once filtered and stored at -20C
Chlorophyll a	UNESCO, 1994 (JGOFS Protocols)	125 mL clean brown polyethylene bottles	Store on ice. Filter immediately upon arrival at lab and place filter in 90% acetone.  Store frozen.	1 month
<sup>a</sup> Dissolved Nutrients	UNESCO, 1994 (JGOFS Protocols)	125 mL clear acid- washed plastic bottles	Filter immediately upon collection and place on ice. Store frozen.	3 months when stored frozen.
Dissolved Oxygen	UNESCO, 1994 (JGOFS Protocols) *1st sample collected	130 mL clean, dry borosilicate glass stoppered volumetric flasks	Fix with MnCl <sub>2</sub> & NaOH-NaI azide reagents. Stopper & shake. Store in cold, dark conditions. Upon arrival at lab, shake again and apply DI cap.	5 days
Salinity	UNESCO, 1994 (JGOFS Protocols)	250 mL brown equilibrated polyethylene bottles	Keep in a well-sealed container.	6 months

<sup>&</sup>lt;sup>a</sup> Nutrient species included: Nitrite, nitrate, phosphate, silicate, and ammonium.

#### 8.1.1 CTD Data Collection

Beginning in 2018, a new CTD instrument package will be built for sampling by boat. Due to the small nature of the plane, a smaller unit must be used which minimizes the amount of sensors it can accommodate. In order to add new sensors such as the SUNA V2, a larger frame is required. This new boat package will be built using existing sensors with the addition of the boat only sensors such as the SUNA.

# 9.0 Laboratory Procedures

# 9.1 Lab procedures table

All laboratory analytical methods are described in Table 9. Nutrient and salinity samples are analyzed at University of Washington's Marine Chemistry Laboratory (MCL) in Seattle, Washington. Dissolved oxygen and chlorophyll *a* samples are analyzed at Ecology's Marine Laboratory (ML). Samples of POC, PN, TOC, TN are analyzed at Ecology's Manchester Environmental Laboratory (MEL) in Port Orchard, Washington. Total alkalinity and dissolved inorganic carbon will be analyzed at the Pacific Marine Environmental Laboratory (PMEL) in Seattle, Washington.

Table 9. Lab measurement methods, expected range of results and reporting limits for marine data.

Measurement – Lab Analyte	Lab	Analytical Method	Expected Range of Results	Reporting Limit
Total Organic Carbon (TOC)	MEL	SM5310B	0 - 3000 ug/L	500 ug/L
Total Nitrogen (TN)	MEL	SM 4500-N B 15-50 μM		0.01 μΜ
Particulate Nitrogen (PN)	MEL	EPA 440.0	140-380 ug/L	1 ug
Particulate Organic Carbon (POC)	MEL	EPA 440.0	0 - 3000 ug/L	1 ug
*Total Alkalinity	PMEL	Dickson et al. 2003, 2007 (SOP3b)	1400-2200 μmol/kg	N/A
*Dissolved Inorganic Carbon	PMEL	Johnson et al. (1985, 1987, 1993, 1999), Johnson (1992), Dickson et al. 2007 (SOP2)	1300-2200 μmol/kg	N/A
Dissolved oxygen	ML	Carpenter, 1966	0.00 - 15.00 mg/L	0.01 mg/L
Marine Nitrate	MCL	Armstrong et al., 1967	0.00 - 40.00 μΜ	0.15 μΜ
Marine Nitrite	MCL	Armstrong et al., 1967	0.00 - 2.00 μΜ	0.01 μΜ
Marine Ammonium	MCL	Slawyk & MacIsaac, 1972	0.00 - 10.00 μΜ	0.05 μΜ
Marine Orthophosphate	MCL	Bernhardt & Wilhelms, 1967	0.00 - 4.00 μΜ	0.02 μΜ
Marine Silicate	MCL	Armstrong et al., 1967	0.00 - 200.00 μΜ	0.21 μΜ
Chlorophyll a	ML	EPA, 1997	0.00 - 60.00 μg/L	0.01 mg/L
Salinity	MCL	Grasshoff et al., 1999	0.00 - 36.00 PSU	0.01 PSU

<sup>\*</sup>Not currently collected

ML - Ecology's Marine Laboratory

MCL - UW's Marine Chemistry Laboratory

MEL - Ecology's Manchester Environmental Laboratory

PMEL - Pacific Marine Environmental Laboratory

## 9.2.1 Analyte

Analytes are listed in Table 9.

## 9.2.4 Expected range of results

Expected ranges for analytical results are listed in Table 9.

## 9.2.5 Analytical method

Analytical methods are listed in Table 9.

# 9.2.6 Sensitivity/Method Detection Limit (MDL)

Sensitivity is reported as "Reporting Limit" in Table 9.

# 10.0 Quality Control Procedures

# 10.1 Table of field and lab quality control (QC) required

Ecology will adhere to all quality control procedures outlined in the original QAMP (Bos, 2015). Likewise, Ecology will use the measurement quality objectives defined in the original QAMP to assess quality/usability of the collected data. The sections below discuss specific modifications to our quality assessment and quality control procedures for the 2018 sampling year.

## 10.1.1 Tables of field and lab QC required

Table 10 identifies our quality objectives for marine waters data and steps that we follow toward meeting these objectives. Table 11 includes types and numbers of QC samples collected for each sampling survey. The Ecology QA Glossary included in the Appendix contains definitions of the various types of QC samples, including:

- Blanks, both lab and field
- Duplicates, both lab and field
- "Standards" or Standard Reference Materials (SRM)
- Lab Control Samples (LCS)

Table 10. A summary of quality control steps for field measurements.

Lab Measurement	Precision (relative standard deviation, %RSD)	Accuracy (% from true value)	Instrument Control Check Using Blanks	Laboratory Standards Check	Laboratory Control Samples	Replicate Analysis	Method Detection Limits Check	Preliminary Review and Flagging of Raw Data	Graphical & Statistical Data Review and Flagging	Annual Review Assessments
Total Organic Carbon (TOC)	≤20%	5%	<b>√</b>	<b>✓</b>	<b>√</b>	<b>√</b>	<b>√</b>	<b>√</b>	<b>✓</b>	$\checkmark$
Total Nitrogen (TN)	≤20%	5%	<b>√</b>	<b>✓</b>	<b>√</b>	<b>√</b>	<b>√</b>	<b>√</b>	<b>✓</b>	<b>✓</b>
Particulate Organic Carbon and Particulate Nitrogen (POC & PN)	≤20%	5%	<b>✓</b>	<b>✓</b>	<b>✓</b>	<b>✓</b>	<b>✓</b>	<b>✓</b>	<b>✓</b>	<b>✓</b>
Total Alkalinity	±0.1%	N/A	<b>√</b>		<b>√</b>	✓		<b>√</b>	<b>√</b>	<b>✓</b>
Dissolved Inorganic Carbon	±0.1%	N/A	<b>√</b>		<b>√</b>	✓		<b>√</b>	<b>√</b>	<b>✓</b>
Chlorophyll a	10%	N/A	$\checkmark$	$\checkmark$		✓	<b>√</b>	$\checkmark$	$\checkmark$	$\checkmark$
Dissolved Oxygen	5%	N/A	<b>√</b>	<b>√</b>		✓	<b>√</b>	<b>√</b>	<b>√</b>	<b>✓</b>
Nitrate	10%	5%	<b>√</b>	<b>√</b>	✓	✓	✓	<b>√</b>	<b>√</b>	<b>√</b>
Nitrite	10%	5%	<b>√</b>	<b>✓</b>	<b>√</b>	<b>√</b>	<b>√</b>	<b>√</b>	<b>✓</b>	<b>✓</b>
Ammonium	10%	5%	<b>√</b>	<b>√</b>	<b>√</b>	✓	✓	<b>√</b>	<b>√</b>	<b>√</b>
Orthophosphate	10%	5%	<b>√</b>	<b>√</b>	<b>✓</b>	<b>✓</b>	<b>✓</b>	<b>√</b>	<b>√</b>	<b>√</b>
Silicate	5%	5%	<b>√</b>	<b>√</b>	<b>√</b>	<b>√</b>	<b>√</b>	<b>√</b>	<b>√</b>	<b>√</b>
Salinity	10%	5%	<b>√</b>	<b>✓</b>	<b>√</b>	<b>✓</b>	<b>✓</b>	<b>√</b>	<b>✓</b>	<b>√</b>

## 10.5.2 Water sample QA/QC procedures

#### 10.5.2.1 Replicate Sample Collection

Triplicate samples will be collected during every field event to help determine field and sampling variability. At one station, three samples taken in succession from the same Niskin sampling bottle will be collected in order to conduct a quantitative determination of homogeneity of conditions, along with precision of sampling methods. Parameters to be replicated include dissolved oxygen (monthly), nutrients (every survey), and chlorophyll *a* (every survey). Due to water volume constraints, one field split, not triplicate, samples will be collected for each TOC, TN, and POC, PN on every survey.

#### 10.5.2.2 Analytical Replicates

Total variation in lab samples are assessed by collecting replicate samples from the same Niskin sampling bottle for all parameters at 5% or more of sites. These replicates are used to assess whether the data quality objectives for precision were met. If the objectives were not met, the data are qualified. In addition, Ecology's Manchester Environmental Laboratory, UW's Marine Chemistry Laboratory, and Ecology's Marine Laboratory all routinely perform replicate sample analyses using sample splits within laboratory batches for quality control purposes. The difference between field and laboratory variability is a measure of the sample field variability.

#### 10.5.2.3 Laboratory control samples

For testing laboratory performance and analyst proficiency, check standards or laboratory control samples of known concentrations are included with every sample batch. Recovery percentage is calculated from these results and therefore, can be used as a measure of analytical accuracy and bias. If the results fall outside of established limits, the reviewer flags data associated with the batch. Any measurement problem that cannot be resolved is given a data quality flag.

To assess the quality of our nutrient data, we conduct laboratory performance and analyst proficiency tests of the analytical lab, using low nutrient seawater laboratory control samples of known concentrations from Ocean Scientific International Ltd. (GPO). They are included with every sample batch. Recovery percentage is calculated from these results and therefore can be used as a measure of analytical accuracy and bias. If the results fall outside of established limits, data associated with the batch are flagged by the reviewer as estimates. Any measurement problem that cannot be resolved is given a data quality flag.

#### 10.5.2.3 Certified Reference Materials

A standard reference material sample from the Ocean Scientific International Ltd will be sent to the laboratory to assess analytical lab performance, along with field split sample collection, and laboratory control samples.

#### 10.5.2.4 Laboratory Blanks

#### Blanks

Blanks of low nutrient seawater will be used to test the nutrient field and analytical laboratory conditions for each survey. These blanks will be handled like field samples to determine if contamination occurs during any stage of the sampling or analytical laboratory processes. To test the POC/PN field and analytical laboratory conditions, blanks of deionized water will be collected at the beginning and end of each filtration.

An additional two unfiltered blanks of low nutrient seawater (LNSW) will be included with each sample batch submitted to the lab for analysis. These blanks serve to determine if samples could be contaminated during processing and analysis and also if they can be used to determine low level bias.

Table 11. Quality assurance/quality control procedures for water column parameter analysis in the laboratory.

Analytical Parameters	Calibration and Standardization	Lab control (check) samples - or- standards (30 or less samples)	Replicate s (30 or less samples)	Blanks per Batch
	Laboratory Sampl	les		
Total Organic Carbon (TOC)	5 point standardization	5*	1 per 20 or less	1 per 20 or less
Total Nitrogen (TN)	5 point standardization	5*	1 per 20 or less	1 per 20 or less
Particulate Organic Carbon and Particulate Nitrogen (POC & PN)	Single point or multi-point dependent upon the expected range of sample results	5*	1 per 20 or less	1 per 20 or less
Ammonia (NH <sub>4</sub> )	5 point standardization	2 - 3	2	2
Nitrate (NO <sub>3</sub> )	5 point standardization	2 - 3	2	2
Nitrite (NO <sub>2</sub> )	5 point standardization	2 - 3	2	2
Orthophosphate (PO <sub>4</sub> )	5 point standardization	2 - 3	2	2
Silicate (SiO <sub>4</sub> )	5 point standardization	2 - 3	2	2
Chlorophyll & phaeopigments	Calibration - 2x/year	4 total - 2 high, 2 low	3	2 - method 2 - reagent
Dissolved Oxygen	3 point standardization	3	3	2
Salinity	1 (batch)	1	1	2
~ Nutrients, dissolved oxygen and chlorophyll a are replicated in the field.				
	CTD Sensors			
pH (electrode sensor)	5 point calibration	NA	NA	NA
Light Transmission	2 point calibration (high & low)	NA	NA	NA
Dissolved oxygen (Clark cell - membrane)	Standardization - full saturation	NA	NA	NA

<sup>\*</sup> Calibration standards ran every 10 samples.

## 15.0 References

Bos, J., 2015. Quality Assurance Monitoring Plan: Long-Term Marine Waters Monitoring, Water Column Program. Washington State Department of Ecology, Olympia, WA. Publication No. 15-03-101. <a href="https://fortress.wa.gov/ecy/publications/SummaryPages/1503101.html">https://fortress.wa.gov/ecy/publications/SummaryPages/1503101.html</a>

EPA, 1997. Method 440.0 rev. 1.4. Determination of Carbon and Nitrogen in Sediments and Particulates of Estuarine/Coastal Waters Using Elemental Analysis. U.S. Environmental Protection Agency.

GPO (The U.S. Government Publishing Office). 40 CFR Appendix B to Part 136 - Definition and Procedure for the Determination of the Method Detection Limit-Revision 1.11. <a href="http://www.gpo.gov/fdsys/granule/CFR-2011-title40-vol23/CFR-2011-title40-vol23-part136-appB/content-detail.html">http://www.gpo.gov/fdsys/granule/CFR-2011-title40-vol23/CFR-2011-title40-vol23-part136-appB/content-detail.html</a>

Grasshoff, K., M. Ehrhardt, K. Kremling. 1999. Methods of seawater analysis. 3rd. ref. ed. Verlag Chemie GmbH, Weinheim. 600 pp.

Keyzers, M. 2014. Quality Assurance Project Plan: Puget Sound total alkalinity and dissolved inorganic carbon pilot project. Washington Department of Ecology, Olympia, Washington. Publication no. 14-03-116.

https://fortress.wa.gov/ecy/publications/SummaryPages/1403116.html

Keyzers, M. 2016. Puget Sound Total Alkalinity and Dissolved Inorganic Carbon Pilot Project. Washington Department of Ecology, Olympia Washington. Publication no. 16-03-032. <a href="https://fortress.wa.gov/ecy/publications/SummaryPages/1603032.html">https://fortress.wa.gov/ecy/publications/SummaryPages/1603032.html</a>

Krembs C. 2012. Marine Water Condition Index: Washington State Department of Ecology, Olympia, Washington. https://fortress.wa.gov/ecy/publications/SummaryPages/1203013.html

Moore S. K., R. Wold, K. Stark, J. Bos, P. Williams, K. Dzinbal, C. Krembs and J. Newton (Eds). PSEMP Marine Waters Workgroup. 2016. Puget Sound marine waters: 2015 overview. www.psp.wa.gov/PSEMP/PSmarinewatersoverview.php

Manchester Environmental Laboratory SOP 710080, Total Organic Carbon and Dissolved Organic Carbon in Water by Standard Method 5310B (Combustion and NDIR Detection). Washington State Department of Ecology, Manchester, Washington.

# Appendix. Glossaries, Acronyms, and Abbreviations

### **Glossary of General Terms**

**Conductivity:** A measure of water's ability to conduct an electrical current. Conductivity is related to the concentration and charge of dissolved ions in water.

**Dissolved oxygen (DO):** A measure of the amount of oxygen dissolved in water.

**Nutrient:** Substance such as carbon, nitrogen, and phosphorus used by organisms to live and grow. Too many nutrients in the water can promote algal blooms and rob the water of oxygen vital to aquatic organisms.

**Particulate Nitrogen (PN):** Particulate matter is defined as suspended particles in seawater having a size greater than 0.45 uM. The particulate nitrogen fraction of total nitrogen can be determined by separating dissolved from particulate fractions by filtration.

**Particulate Organic Carbon (POC):** Particulate matter is defined as suspended particles in seawater having a size greater than 0.45 uM. The particulate organic carbon fraction of total organic carbon is defined as organic matter that is larger than 0.45 uM. POC inputs to the sea are divided into two categories: allochthonous inputs from land and atmosphere and autochthonous (internal) inputs from biogenic material formed from *in situ* photosynthesis or decomposition of organic matter or organisms.

**Particulate Organic Nitrogen (PON):** The fraction of particulate nitrogen that is from biogenic material, such as material formed from *in situ* photosynthesis or decomposition of organic matter or organisms

**Total Nitrogen (TN):** Total nitrogen is the amount of nitrogen found in water and consists of dissolved nitrogen (DN) and particulate nitrogen (PN) of either organic or inorganic sources.

**Total Organic Carbon (TOC):** Total organic carbon is the amount of carbon found in an organic compound and is often used as a non-specific indicator of water quality. Total organic carbon consists of dissolved (DOC) and particulate organic carbon (POC) and is therefore affected by pronounced fluctuations in suspended solids in riverine systems. Sources of organic carbon in fresh and marine waters include living material and waste materials and effluents. Organic matter from living material may arise directly from plant photosynthesis or indirectly from terrestrial organic matter.

**pH:** A measure of the acidity or alkalinity of water. A low pH value (0 to 7) indicates that an acidic condition is present, while a high pH (7 to 14) indicates a basic or alkaline condition. A pH of 7 is considered to be neutral. Since the pH scale is logarithmic, a water sample with a pH of 8 is ten times more basic than one with a pH of 7.

**Dissolved Inorganic Carbon (DIC):** The sum of inorganic carbon species in a solution. The inorganic carbon species include carbon dioxide (CO<sub>2</sub>), carbonic acid (H<sub>2</sub>CO<sub>3</sub>), bicarbonate anion (HCO<sub>3</sub><sup>-</sup>), and carbonate (CO<sub>3</sub><sup>2-</sup>).

**Alkalinity:** measures the ability of a solution to neutralize acids to the equivalence point of carbonate or bicarbonate. The alkalinity is equal to the stoichiometric sum of the bases in solution.

Ocean Acidification (OA): When carbon dioxide (CO<sub>2</sub>) is absorbed by seawater, chemical reactions occur that reduce seawater pH, carbonate ion concentration, and saturation states of biologically important calcium carbonate minerals. These chemical reactions are termed "ocean acidification" or "OA" for short. Calcium carbonate minerals are the building blocks for the skeletons and shells of many marine organisms. In areas where most life now congregates in the ocean, the seawater is supersaturated with respect to calcium carbonate minerals. This means there are abundant building blocks for calcifying organisms to build their skeletons and shells. However, continued ocean acidification is causing many parts of the ocean to become undersaturated with these minerals, which is likely to affect the ability of some organisms to produce and maintain their shells.

**Turbidity:** A measure of water clarity. High levels of turbidity can have a negative impact on aquatic life.

**90<sup>th</sup> percentile:** An estimated portion of a sample population based on a statistical determination of distribution characteristics. The 90<sup>th</sup> percentile value is a statistically derived estimate of the division between 90% of samples, which should be less than the value, and 10% of samples, which are expected to exceed the value.

## **Acronyms and Abbreviations**

DO Dissolved oxygen

DOC Dissolved organic carbon

Ecology Washington State Department of Ecology

EIM Environmental Information Management database

et al. And others

GIS Geographic Information System software

GPS Global Positioning System

MEL Manchester Environmental Laboratory

MQO Measurement quality objective

QA Quality assurance PN Particulate Nitrogen

POC Particulate Organic Carbon
PON Particulate Organic Nitrogen
RSD Relative standard deviation
SOP Standard operating procedures

TN Total Nitrogen
TOC Total organic carbon
WQA Water Quality Assessment

#### WRIA Water Resource Inventory Area

#### Units of Measurement

°C degrees centigrade

m meter

mg/L milligrams per liter (parts per million)

mg/L/hr milligrams per liter per hour

mL milliliter

mmol millimole or one-thousandth of a mole ng/g nanograms per gram (parts per billion) ng/L nanograms per liter (parts per trillion)

NTU nephelometric turbidity units

psu practical salinity units

ug/g micrograms per gram (parts per million)
ug/L micrograms per liter (parts per billion)

uM micromolar (a chemistry unit)

uS/cm microsiemens per centimeter, a unit of conductivity

### **Quality Assurance Glossary**

**Accreditation:** A certification process for laboratories, designed to evaluate and document a lab's ability to perform analytical methods and produce acceptable data. For Ecology, it is "Formal recognition by (Ecology)...that an environmental laboratory is capable of producing accurate analytical data." [WAC 173-50-040] (Kammin, 2010)

**Accuracy:** The degree to which a measured value agrees with the true value of the measured property. USEPA recommends that this term not be used, and that the terms precision and bias be used to convey the information associated with the term accuracy. (USGS, 1998)

**Analyte:** An element, ion, compound, or chemical moiety (pH, alkalinity) which is to be determined. The definition can be expanded to include organisms, e.g., fecal coliform, Klebsiella. (Kammin, 2010)

**Bias:** The difference between the population mean and the true value. Bias usually describes a systematic difference reproducible over time, and is characteristic of both the measurement system, and the analyte(s) being measured. Bias is a commonly used data quality indicator (DQI). (Kammin, 2010; Ecology, 2004)

**Blank:** A synthetic sample, free of the analyte(s) of interest. For example, in water analysis, pure water is used for the blank. In chemical analysis, a blank is used to estimate the analytical response to all factors other than the analyte in the sample. In general, blanks are used to assess possible contamination or inadvertent introduction of analyte during various stages of the sampling and analytical process. (USGS, 1998)

**Calibration:** The process of establishing the relationship between the response of a measurement system and the concentration of the parameter being measured. (Ecology, 2004)

**Check standard:** A substance or reference material obtained from a source independent from the source of the calibration standard; used to assess bias for an analytical method. This is an obsolete term, and its use is highly discouraged. See Calibration Verification Standards, Lab Control Samples (LCS), Certified Reference Materials (CRM), and/or spiked blanks. These are all check standards, but should be referred to by their actual designator, e.g., CRM, LCS. (Kammin, 2010; Ecology, 2004)

**Comparability:** The degree to which different methods, data sets and/or decisions agree or can be represented as similar; a data quality indicator. (USEPA, 1997)

**Completeness:** The amount of valid data obtained from a project compared to the planned amount. Usually expressed as a percentage. A data quality indicator. (USEPA, 1997)

Continuing Calibration Verification Standard (CCV): A QC sample analyzed with samples to check for acceptable bias in the measurement system. The CCV is usually a midpoint calibration standard that is re-run at an established frequency during the course of an analytical run. (Kammin, 2010)

**Control chart:** A graphical representation of quality control results demonstrating the performance of an aspect of a measurement system. (Kammin, 2010; Ecology 2004)

**Control limits:** Statistical warning and action limits calculated based on control charts. Warning limits are generally set at +/- 2 standard deviations from the mean, action limits at +/- 3 standard deviations from the mean. (Kammin, 2010)

**Data Integrity:** A qualitative DQI that evaluates the extent to which a data set contains data that is misrepresented, falsified, or deliberately misleading. (Kammin, 2010)

**Data Quality Indicators (DQI):** Commonly used measures of acceptability for environmental data. The principal DQIs are precision, bias, representativeness, comparability, completeness, sensitivity, and integrity. (USEPA, 2006)

**Data Quality Objectives (DQO):** Qualitative and quantitative statements derived from systematic planning processes that clarify study objectives, define the appropriate type of data, and specify tolerable levels of potential decision errors that will be used as the basis for establishing the quality and quantity of data needed to support decisions. (USEPA, 2006)

**Data set:** A grouping of samples organized by date, time, analyte, etc. (Kammin, 2010)

**Data validation:** An analyte-specific and sample-specific process that extends the evaluation of data beyond data verification to determine the usability of a specific data set. It involves a detailed examination of the data package, using both professional judgment, and objective criteria, to determine whether the MQOs for precision, bias, and sensitivity have been met. It

may also include an assessment of completeness, representativeness, comparability and integrity, as these criteria relate to the usability of the data set. Ecology considers four key criteria to determine if data validation has actually occurred. These are:

- Use of raw or instrument data for evaluation.
- Use of third-party assessors.
- Data set is complex.
- Use of EPA Functional Guidelines or equivalent for review.

Examples of data types commonly validated would be:

- Gas Chromatography (GC).
- Gas Chromatography-Mass Spectrometry (GC-MS).
- Inductively Coupled Plasma (ICP).

The end result of a formal validation process is a determination of usability that assigns qualifiers to indicate usability status for every measurement result. These qualifiers include:

- No qualifier, data is usable for intended purposes.
- J (or a J variant), data is estimated, may be usable, may be biased high or low.
- REJ, data is rejected, cannot be used for intended purposes (Kammin, 2010; Ecology, 2004).

**Data verification:** Examination of a data set for errors or omissions, and assessment of the Data Quality Indicators related to that data set for compliance with acceptance criteria (MQOs). Verification is a detailed quality review of a data set. (Ecology, 2004)

**Detection limit** (limit of detection): The concentration or amount of an analyte which can be determined to a specified level of certainty to be greater than zero. (Ecology, 2004)

**Duplicate samples:** Two samples taken from and representative of the same population, and carried through and steps of the sampling and analytical procedures in an identical manner. Duplicate samples are used to assess variability of all method activities including sampling and analysis. (USEPA, 1997)

**Field blank:** A blank used to obtain information on contamination introduced during sample collection, storage, and transport. (Ecology, 2004)

**Initial Calibration Verification Standard (ICV):** A QC sample prepared independently of calibration standards and analyzed along with the samples to check for acceptable bias in the measurement system. The ICV is analyzed prior to the analysis of any samples. (Kammin, 2010)

**Laboratory Control Sample (LCS):** A sample of known composition prepared using contaminant-free water or an inert solid that is spiked with analytes of interest at the midpoint of the calibration curve or at the level of concern. It is prepared and analyzed in the same batch of regular samples using the same sample preparation method, reagents, and analytical methods employed for regular samples. (USEPA, 1997)

**Matrix spike:** A QC sample prepared by adding a known amount of the target analyte(s) to an aliquot of a sample to check for bias due to interference or matrix effects. (Ecology, 2004)

**Measurement Quality Objectives** (MQOs): Performance or acceptance criteria for individual data quality indicators, usually including precision, bias, sensitivity, completeness, comparability, and representativeness. (USEPA, 2006)

**Measurement result:** A value obtained by performing the procedure described in a method. (Ecology, 2004)

**Method:** A formalized group of procedures and techniques for performing an activity (e.g., sampling, chemical analysis, data analysis), systematically presented in the order in which they are to be executed. (EPA, 1997)

**Method blank:** A blank prepared to represent the sample matrix, prepared and analyzed with a batch of samples. A method blank will contain all reagents used in the preparation of a sample, and the same preparation process is used for the method blank and samples. (Ecology, 2004; Kammin, 2010)

**Method Detection Limit (MDL):** This definition for detection was first formally advanced in 40CFR 136, October 26, 1984 edition. MDL is defined there as the minimum concentration of an analyte that, in a given matrix and with a specific method, has a 99% probability of being identified, and reported to be greater than zero. (Federal Register, October 26, 1984)

**Percent Relative Standard Deviation (%RSD):** A statistic used to evaluate precision in environmental analysis. It is determined in the following manner:

$$%RSD = (100 * s)/x$$

where s is the sample standard deviation and x is the mean of results from more than two replicate samples (Kammin, 2010)

**Parameter:** A specified characteristic of a population or sample. Also, an analyte or grouping of analytes. Benzene and nitrate + nitrite are all "parameters." (Kammin, 2010; Ecology, 2004)

**Population:** The hypothetical set of all possible observations of the type being investigated. (Ecology, 2004)

**Precision:** The extent of random variability among replicate measurements of the same property; a data quality indicator. (USGS, 1998)

**Quality Assurance (QA):** A set of activities designed to establish and document the reliability and usability of measurement data. (Kammin, 2010)

**Quality Assurance Monitoring Plan (QAMP):** A document that describes the objectives of a project, and the processes and activities necessary to develop data that will support those objectives. (Kammin, 2010; Ecology, 2004)

**Quality Control (QC):** The routine application of measurement and statistical procedures to assess the accuracy of measurement data. (Ecology, 2004)

**Relative Percent Difference (RPD):** RPD is commonly used to evaluate precision. The following formula is used:

$$[Abs(a-b)/((a+b)/2)] * 100$$

where "Abs()" is absolute value and a and b are results for the two replicate samples. RPD can be used only with 2 values. Percent Relative Standard Deviation is (%RSD) is used if there are results for more than 2 replicate samples (Ecology, 2004).

**Replicate samples:** Two or more samples taken from the environment at the same time and place, using the same protocols. Replicates are used to estimate the random variability of the material sampled. (USGS, 1998)

**Representativeness:** The degree to which a sample reflects the population from which it is taken; a data quality indicator. (USGS, 1998)

**Sample (field):** A portion of a population (environmental entity) that is measured and assumed to represent the entire population. (USGS, 1998)

**Sample (statistical):** A finite part or subset of a statistical population. (USEPA, 1997)

**Sensitivity:** In general, denotes the rate at which the analytical response (e.g., absorbance, volume, meter reading) varies with the concentration of the parameter being determined. In a specialized sense, it has the same meaning as the detection limit. (Ecology, 2004)

**Spiked blank:** A specified amount of reagent blank fortified with a known mass of the target analyte(s); usually used to assess the recovery efficiency of the method. (USEPA, 1997)

**Spiked sample:** A sample prepared by adding a known mass of target analyte(s) to a specified amount of matrix sample for which an independent estimate of target analyte(s) concentration is available. Spiked samples can be used to determine the effect of the matrix on a method's recovery efficiency. (USEPA, 1997)

**Split sample:** A discrete sample that is further subdivided into portions, usually duplicates. (Kammin, 2010)

**Standard Operating Procedure (SOP):** A document which describes in detail a reproducible and repeatable organized activity. (Kammin, 2010)

**Surrogate:** For environmental chemistry, a surrogate is a substance with properties similar to those of the target analyte(s). Surrogates are unlikely to be native to environmental samples. They are added to environmental samples for quality control purposes, to track extraction efficiency and/or measure analyte recovery. Deuterated organic compounds are examples of surrogates commonly used in organic compound analysis. (Kammin, 2010)

**Systematic planning:** A step-wise process which develops a clear description of the goals and objectives of a project, and produces decisions on the type, quantity, and quality of data that will be needed to meet those goals and objectives. The DQO process is a specialized type of systematic planning. (USEPA, 2006)

#### **References for QA Glossary**

Ecology, 2004. Guidance for the Preparation of Quality Assurance Project Plans for Environmental Studies. <a href="https://fortress.wa.gov/ecy/publications/SummaryPages/0403030.html">https://fortress.wa.gov/ecy/publications/SummaryPages/0403030.html</a>

Kammin, B., 2010. Definition developed or extensively edited by William Kammin, 2010. Washington State Department of Ecology, Olympia, WA.

USEPA, 1997. Glossary of Quality Assurance Terms and Related Acronyms. U.S. Environmental Protection Agency.

USEPA, 2006. Guidance on Systematic Planning Using the Data Quality Objectives Process EPA QA/G-4. U.S. Environmental Protection Agency. <a href="http://www.epa.gov/quality/qs-docs/g4-final.pdf">http://www.epa.gov/quality/qs-docs/g4-final.pdf</a>

USGS, 1998. Principles and Practices for Quality Assurance and Quality Control. Open-File Report 98-636. U.S. Geological Survey. http://ma.water.usgs.gov/fhwa/products/ofr98-636.pdf