



**Addendum 3 to
Quality Assurance Monitoring Plan**

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



April 2016

Publication No. 16-03-101

Publication Information

Addendum

This addendum is on the Department of Ecology's website at <https://fortress.wa.gov/ecy/publications/SummaryPages/1603101.html>

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

Cover photo of Hood Canal by Laura Hermanson.

Data for this project will be available on Ecology's Environmental Information Management (EIM) website at www.ecy.wa.gov/eim/index.htm. Search Study ID MarineWater.

Activity Tracker code

Ecology's Activity Tracker code for this addendum is 01-800.

Original Publication

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

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Addendum 3 to Quality Assurance Monitoring Plan

Long-Term Marine Waters Monitoring, Water Column Program

April 2016

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Carol Smith, Client, representing EAP Management Team

Date: April 2016

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Signatures are not available on the Internet version.
EAP: Environmental Assessment Program

3.0 Background

This document describes the 2016 sampling effort for Ecology’s Long-Term Marine Flights Monitoring Program. It is an addendum to *Quality Assurance Monitoring Plan: Long-Term Marine Waters Monitoring, Water Column Program* (Bos, 2015). In 2016, 37 core stations, and 1 rotational station, and 2 sediment team core stations will be sampled. Additional sampling will be added for fecal coliform bacteria, enterococci bacteria, total organic carbon (TOC), total nitrogen (TN), particulate organic carbon (POC), particulate organic nitrogen (PN), and testing a new instrument, the Submersible Ultraviolet Nitrate Analyzer (SUNA). This Quality Assurance Monitoring Plan (QAMP) addendum specifies which stations and parameters will be sampled in 2016 and also describes the addition of TOC, TN, POC, and PN sampling collection at a subset of stations.

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 describes the roles and responsibilities of people involved with the Marine Waters Monitoring Program. All are employees of the Washington State Department of Ecology.

Table 1. Organization of project staff and responsibilities.

Staff	Title	Responsibilities
<p>Julia Bos Marine Monitoring Unit Western Operations Section Ecology - EAP Phone: (360) 407-6674</p>	<p>Monitoring Coordinator, Data Management, Data Analyst, Publications Author</p>	<p>Writes the QAPP. Oversees 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.</p>
<p>Christopher Krembs Marine Monitoring Unit Western Operations Section Ecology - EAP Phone: (360) 407-6675</p>	<p>Senior Oceanographer, Lead Presentations & Publications Author</p>	<p>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.</p>
<p>Skip Albertson Marine Monitoring Unit Western Operations Section Ecology - EAP Phone: (360) 407-6675</p>	<p>Physical Oceanographer, Data Analyst, Modeler, Publications Author</p>	<p>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.</p>
<p>Mya Keyzers Marine Monitoring Unit Western Operations Section Ecology - EAP Phone: (360) 407-6395</p>	<p>Author & Marine Flight Lead Technician</p>	<p>Conducts field sampling, laboratory analysis and instrument maintenance. Records & manages field information. Conducts QA review, analyzes, and interprets data. Writes reports and data summaries.</p>
<p>Laura Hermanson Marine Monitoring Unit Western Operations Section Ecology - EAP Phone: (360) 407-0273</p>	<p>Marine Flight Technician</p>	<p>Conducts field sampling, laboratory analysis and instrument maintenance. Records & manages field information. Conducts QA review, analyzes, and interprets data. Writes reports and data summaries.</p>
<p>Carol Maloy Marine Monitoring Unit Western Operations Section Ecology - EAP Phone: (360) 407-6742</p>	<p>Unit Supervisor</p>	<p>Provides internal review of the QAPP, approves the budget, and approves the final QAPP.</p>
<p>Dale Norton Western Operations Section Ecology - EAP Phone: (360) 407-6596</p>	<p>Section Manager</p>	<p>Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.</p>
<p>William R. Kammin Ecology - EAP Phone: (360) 407-6964</p>	<p>Ecology Quality Assurance Officer</p>	<p>Reviews the draft QAPP and approves the final QAPP.</p>

5.4 Project schedule

Table 2. Proposed schedule for completing the field, and laboratory work, data processing, review, OC, 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	Laura Hermanson
Internal (Ecology) laboratory analyses completed	1 month post-collection (chlorophyll a samples)	Laura Hermanson
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	Laura Hermanson
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, Laura Hermanson
Internal laboratory data	1 month post-analyses	Laura Hermanson
External laboratory data	Quarterly, one quarter post-collection	Mya Keyzers
Environmental Information System (EIM) database		
EIM data loaded	Same month as collection	Julia Bos
EIM QA	4 months after sampling year complete	Julia Bos
EIM complete	4 months after sampling year complete	Julia Bos
Monthly reports		
Monthly condition summary generated	1 month post-collection	Julia Bos
Monthly summary posted to web	1 month post-collection	Christopher Krembs
Annual Assessment - data products & written summary		
Draft assessments & products due	3 months after sampling year complete	Christopher Krembs, Julia Bos, Skip Albertson, Mya Keyzers, Laura Hermanson
Final reviews & QAQC summarized	4 months after sampling year complete	Christopher Krembs, Julia Bos
Final summary due on web	4 months after sampling year complete	Christopher Krembs
Final data posted and performance measures reported		
Final data & analytical plots due on web	4 months after sampling year complete	Christopher Krembs, Skip Albertson
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

5.6 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. Projected budget for 2016 Marine Flight operations.

UW Marine Chemistry Lab Analyses¹			
Type	Cost/unit	Qty.	Cost
Seawater Nutrient Analysis ²	16.75	1320	\$ 22,110.00
Salinity Analysis	19.25	156	\$ 3,003.00
Dissolved Oxygen reagents	585.00	2	\$ 1,170.00
Subtotal			\$ 26,283.00
Manchester (MEL) Lab Analyses			
Particulate organic carbon & nitrogen ²	42.50	528	\$ 22,440.00
Particulate filters	0.90	528	\$ 475.20
Total Nitrogen ²	40.00	528	\$ 21,120.00
Total Organic Carbon ²	30.00	528	\$ 15,840.00
Subtotal			\$ 59,875.20
Sensor Cost			
Company			Cost
Seabird Inc.			\$ 4,000.00
WET Labs Inc.			\$ 3,000.00
Biospherical Instruments Inc.			\$ 200.00
Subtotal			\$ 7,200.00
Transportation Cost			
Company			Cost
Kenmore Air Seaplanes ³			\$ 114,000.00
Port of Olympia			\$ 600.00
Subtotal			\$ 114,600.00
Shannon Point Marine Science Center			
Research Vessel ⁴	\$110.00	88	\$ 9,680.00
Lab fee	\$200.00	12	\$ 2,400.00
Subtotal			\$ 12,080.00
Total			\$ 220,038.20

¹Costs include 15.6% overhead

² Includes lab check standards and blanks sent with every batch.

³State Contract No. 04413

⁴ Inter-agency Agreement No. C1400008

6.1 Measurement Quality Objectives

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 the Ecology's Manchester Environmental Laboratory (MEL). Any labs conducting analyses for the marine waters monitoring program are accredited through Ecology's Laboratory Accreditation Program.

All work is expected to meet the 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%	1 mg/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
*Alkalinity	10%	5%	1µM/kg
*Dissolved Inorganic Carbon	10%	5%	1µM/kg
Dissolved Oxygen	5%	5%	0.05 mg/L
Marine Nitrate	10%	5%	0.15 µM
Marine Nitrite	10%	5%	0.01 µM
Marine Ammonium	10%	5%	0.05 µM
Marine Orthophosphate	10%	5%	0.02 µM
Marine Silicate	10%	5%	0.21 µM
Chlorophyll a	10%	N/A	0.02 µg/L
Salinity	5%	5%	0.002 PSU

*Not currently collected

7.1.2.2 Sampling schedule

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 1 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 6 regional surveys a month as opposed to 5, 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.

For 2015, the stations WPA001 and GYS004 were changed from core to rotational, as these stations are in rivers and exhibit freshwater rather than marine characteristics. These 2 stations will not be sampled in 2016. This results in a total of 37 core, 1 rotational station, and 2 sediment team core stations. This year the regions will be grouped as:

- Strait of Juan de Fuca (Straits)
- Coastal Bays (Marine Flight (MF1))
- San Juans/North Sound/Whidbey Basin (MF2)
- Admiralty Inlet/Central Sound (MF3)
- South Sound (MF4)
- Hood Canal (MF5)

See Table 5 and Figures 1-7.

Stations are sampled at intervals no less than 3 weeks apart to ensure reasonable adherence to a monthly sampling scheme.

Table 5. 2016 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	Depth (m)	Record	Record Length (yrs)	Justification
Marine Flight 1: Coast	GYS008	Mid-S. Channel	46 56.2388	123 54.7934	Western Olympic	6	1974 - 76, 1983 - present	35	represents mid Grays Harbor, south
	GYS016	Damon Point	46 57.2053	124 05.5770	Western Olympic	11	1982 - 1987, 1991 - present	29	represents outer Grays Harbor, north
	WPA004	Toke Point	46 41.9800	123 58.1240	Lower Columbia	14	1973-1975, 1977-present	41	represents north Willapa Bay
	WPA113	Bay Center	46 38.6400	123 59.5800	Lower Columbia	11	1997-2000, 2006-present	12	represents mouth of (NW) Willapa Bay
	WPA006	Nahcotta Channel	46 32.7226	123 58.8097	Lower Columbia	21	1991-present	24	represents central Willapa Bay
	WPA007	Long Island, S. Jenson Pt.	46 27.1893	124 00.5672	Lower Columbia	14	1991-2008, 2013-present	19	represents SW Willapa Bay
	WPA008	Naselle River mouth	46 27.7890	123 56.4760	Lower Columbia	14	1996-2008, 2013-present	14	represents SE Willapa Bay, off Naselle R.
	WPA003	Willapa River, John. Slough	46 42.2392	123 50.2431	Lower Columbia	10	1973-present	42	represents north Willapa Bay, off Willapa R.
Marine Flight 2: North	PTH005	Port Townsend	48 04.9889	122 45.8767	Eastern Olympic	26	1977-1978, 1991-2002, 2005-present	24	represents waters off city of Port Townsend
	RSR837	Rosario Strait	48 36.9896	122 45.7775	Nooksack/San Juan	56	2009-present	6	represents waters in Rosario Strait
	GRG002	Strait of Georgia	48 48.4896	122 57.2446	Nooksack/San Juan	190	1988-present	27	represents Strait of Georgia end member
	BLL009	Bellingham Bay	48 41.1564	122 35.9771	Nooksack/San Juan	16	1977-present	38	represents waters off city of Bellingham
	BLL040	Bellingham Bay	48 41.0382	122 32.2920	Nooksack/San Juan	26	NA	26	represents waters of Bellingham
	SKG003	Skagit Bay	48 17.7893	122 29.3763	Island/Snohomish	24	1990-1991, 1994-1998, 2007-present	15	represents Whidbey Basin
	SAR003	Saratoga Passage	48 06.4557	122 29.4925	Island/Snohomish	149	1977-present	38	represents Whidbey Basin
	PSS019	Possession Sound	48 00.6556	122 18.0750	Island/Snohomish	101	1980-present	35	represents waters off city of Everett
PSS008	Possession Sound	47 58.5400	122 13.2000	Island/Snohomish	37	1994, 1995, 1997, 1998	22	represents waters off city of Everett	
Marine Flight 3: Central	ADM001	Admiralty Inlet	48 01.7888	122 37.0760	Kitsap & Cedar/Green	148	1975-1987, 1992-present	35	represents waters within Admiralty Inlet
	ADM003	S. of Admiralty Inlet	47 52.7390	122 28.9917	Kitsap & Cedar/Green	210	1988-1991, 1996-present	21	represents waters S. of Admiralty sills
	PSB003	Puget Snd. Main Basin	47 39.5891	122 26.5745	Kitsap & Cedar/Green	40-50	1976-present	39	represents Puget Sound Main Basin
	ELB015	Elliott Bay	47 35.7892	122 22.1743	Cedar/Green	82	1991-present	24	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	23	represents S. Puget Sound main axis
	CMB003	Commencement Bay	47 17.4226	122 27.0074	South Puget Sound	150	1976-present	39	represents waters off city of Tacoma
Marine Flight 4: South	BUD005	Budd Inlet	47 05.5224	122 55.0918	Eastern Olympic	15	1973-present	42	represents waters off city of Olympia
	DNA001	Dana Passage	47 09.6890	122 52.3083	Eastern Olympic	40	1984-85, 1989-present	28	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	21	represents S. Puget Sound near Nisqually
	GOR001	Gordon Point	47 10.9891	122 38.0743	E. Oly & Kitsap & SPS	160-170	1996-present	18	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-pre	31	represents waters within Carr Inlet
	CSE001	Case Inlet	47 15.8724	122 50.6583	Eastern Olympic	55	1978-1993, 95-96, 1998-99, 2009-presen	26	represents waters within Case Inlet
	SIN001	Sinclair Inlet	47 32.9557	122 38.6083	Kitsap	16	1973-1987, 1991-present	38	represents waters off city of Bremerton
	OAK004	Oakland Bay	47 12.8056	123 04.6590	Eastern Olympic	15	1974-75, 1977-present	40	represents waters off city of Shelton
Marine Flight 5: Hood Canal	HCB007	Hood Canal, Lynch Cv.	47 23.8889	122 55.7755	Kitsap & E. Olympic	21	1990-1996, 1998-2007, 2011-present	21	very low DO, assess duration & coverage
	HCB004	Hood Canal, Sisters Pt.	47 21.3723	123 01.4924	Kitsap & E. Olympic	55	1975-1987, 1990-present	38	represents southern Hood Canal
	HCB003	Hood Canal, Eldon	47 32.2722	123 00.5760	Kitsap & E. Olympic	144	1976-92, 1994-96, 1998-2007, 2010-pre	34	very low DO, assess duration & coverage
	HCB010	Hood Canal, S of Bangor	47 40.2000	122 49.2000	Kitsap & E. Olympic	100	2005-present	10	represents northern Hood Canal
	HCB013	Hood Canal	47 50.2548	122 37.7370	N of Hood Canal Bridge	20	NA	0	represents entrance of Hood Canal
Straits	SJF000	Strait of Juan de Fuca	48 25.0000	123 01.5000	S. of San Juan Island	180	2000 - present	15	represents northern Strait of Juan de Fuca
	SJF001	Strait of Juan de Fuca	48 20.0000	123 01.5000	SE of Hein Bank	160	2000 - present	15	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	15	represents southern Strait of Juan de Fuca
	ADM002	N. of Admiralty Inlet	48 11.2391	122 50.5770	Island & E. Olympic	82	1980-present	34	represents waters entering Admiralty Inlet



Figure 1. All 2016 Ecology long-term marine water column monitoring station locations. The 20 particulate pilot project stations are highlighted with a white star.

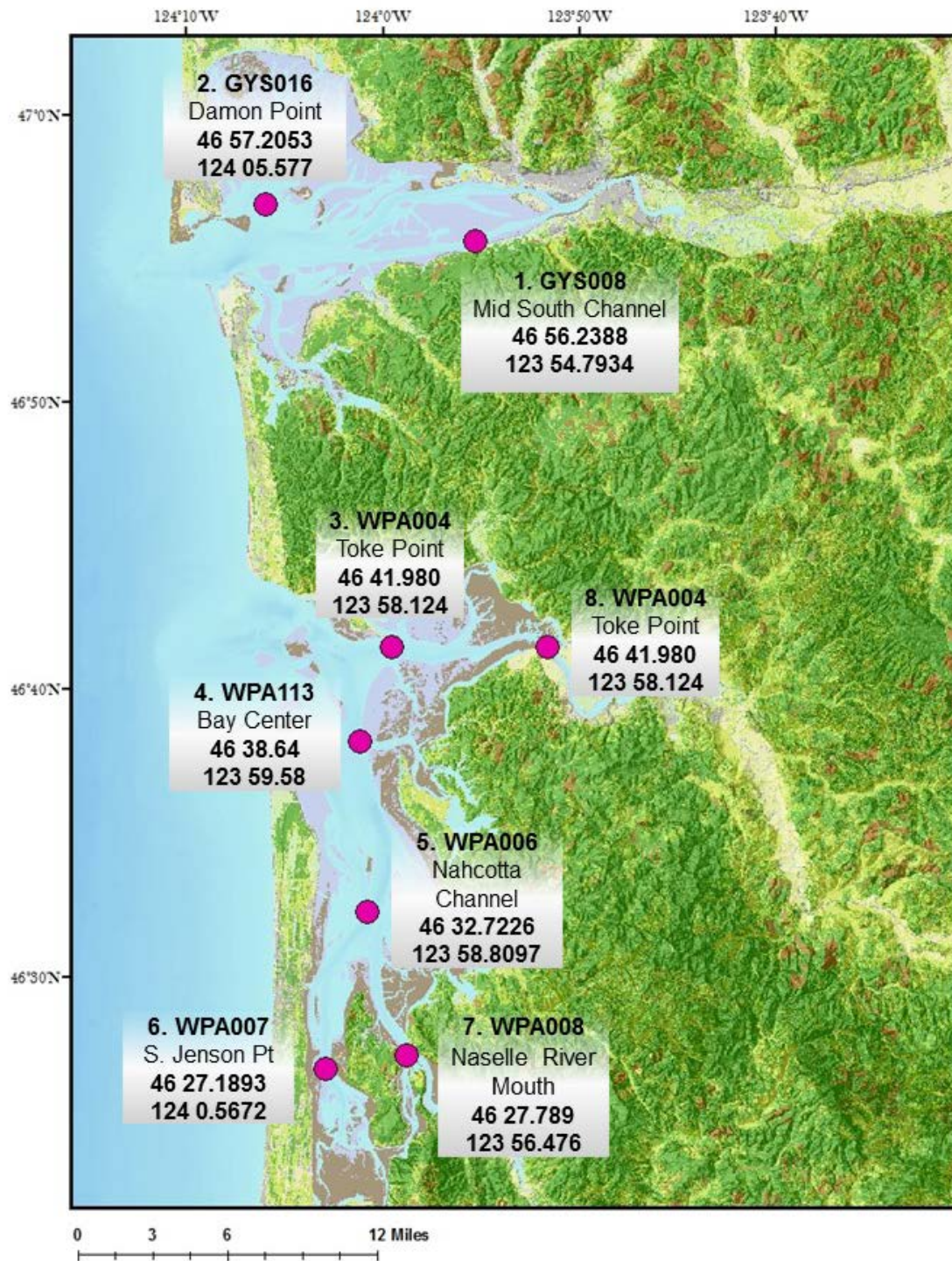


Figure 2. 2016 Marine Flight 1 (MF1) Coast sampling stations.

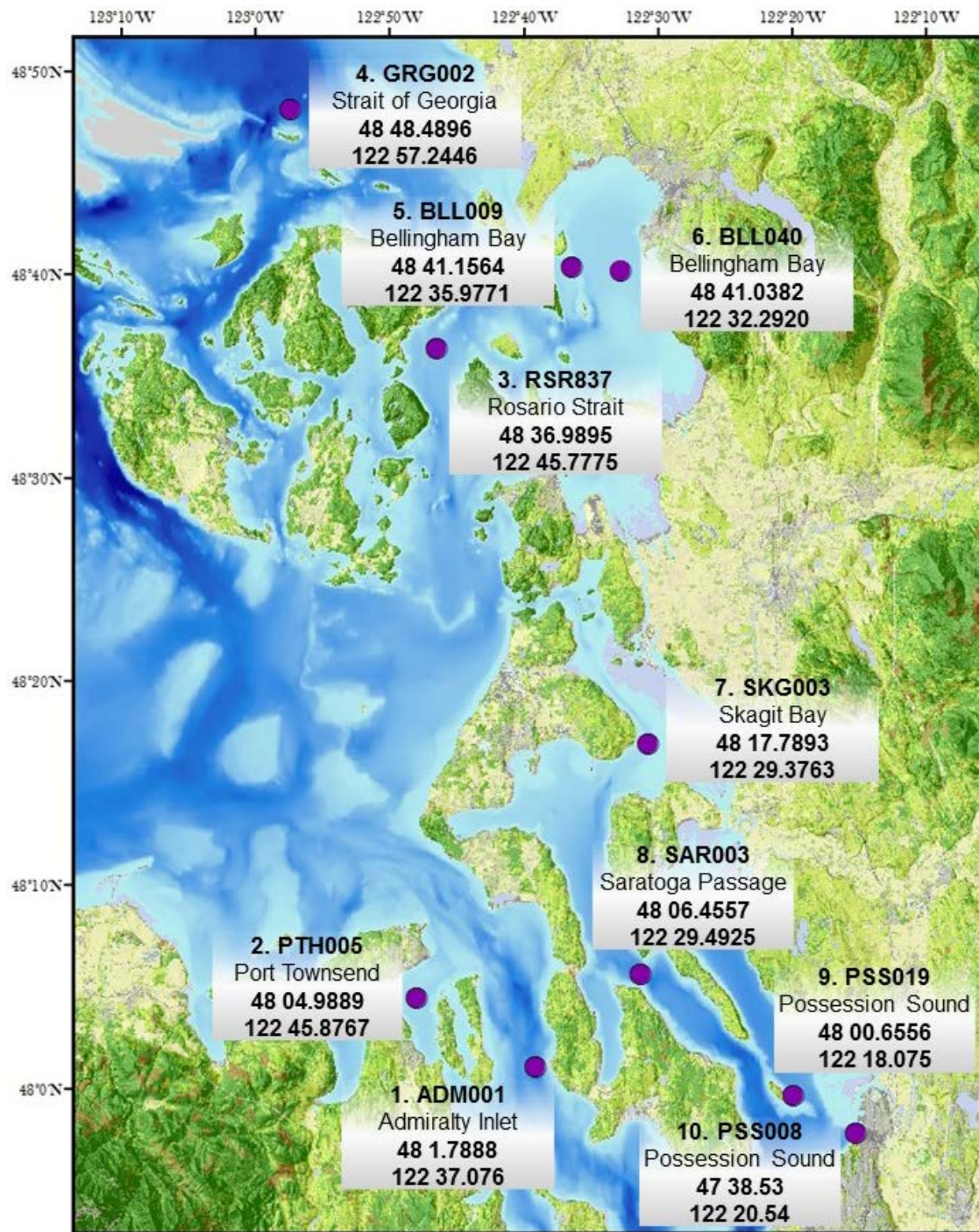


Figure 3. 2016 Marine Flight 2 (MF2) North Sound sampling stations.

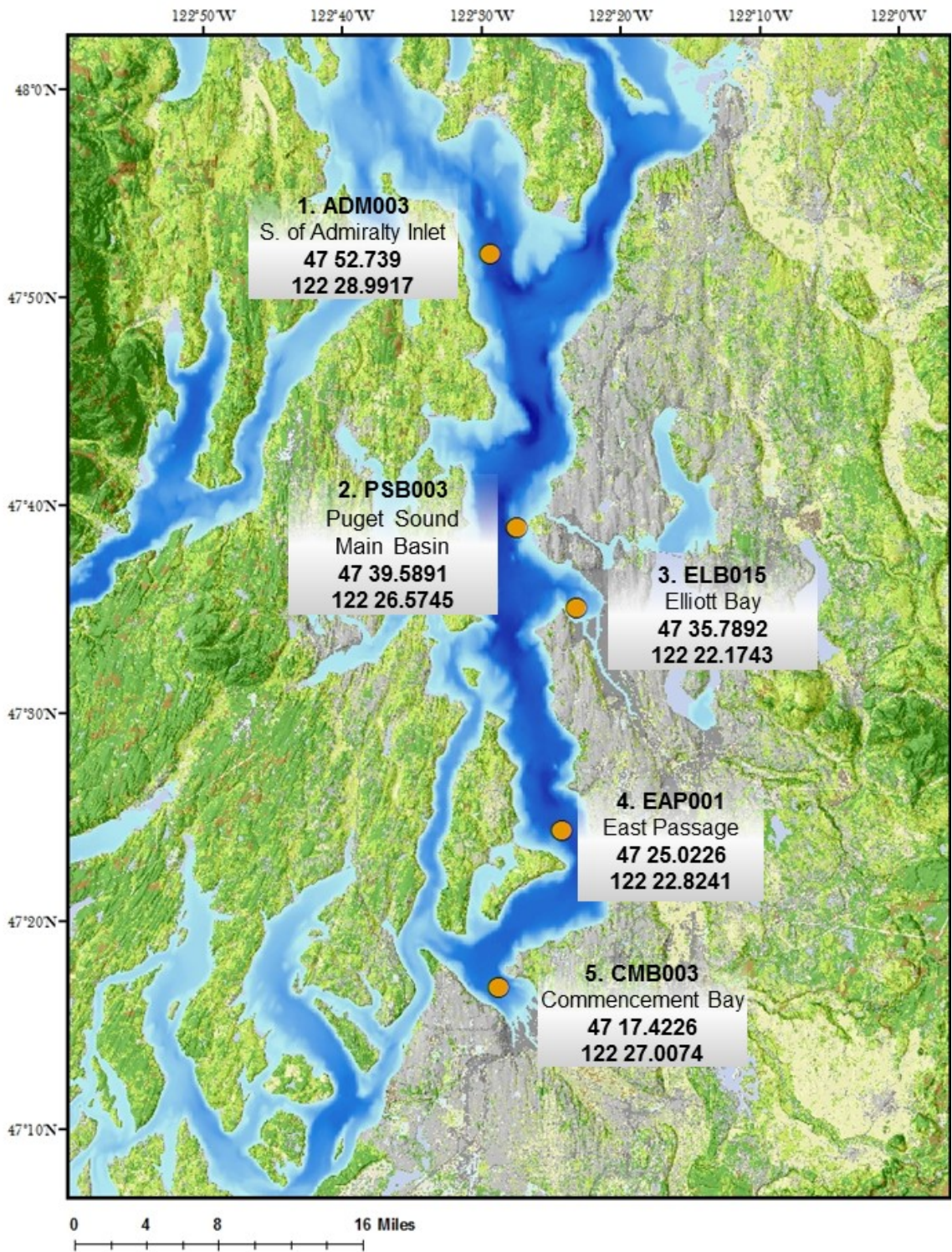


Figure 4. 2016 Marine Flight 3 (MF3) Central Sound sampling stations.

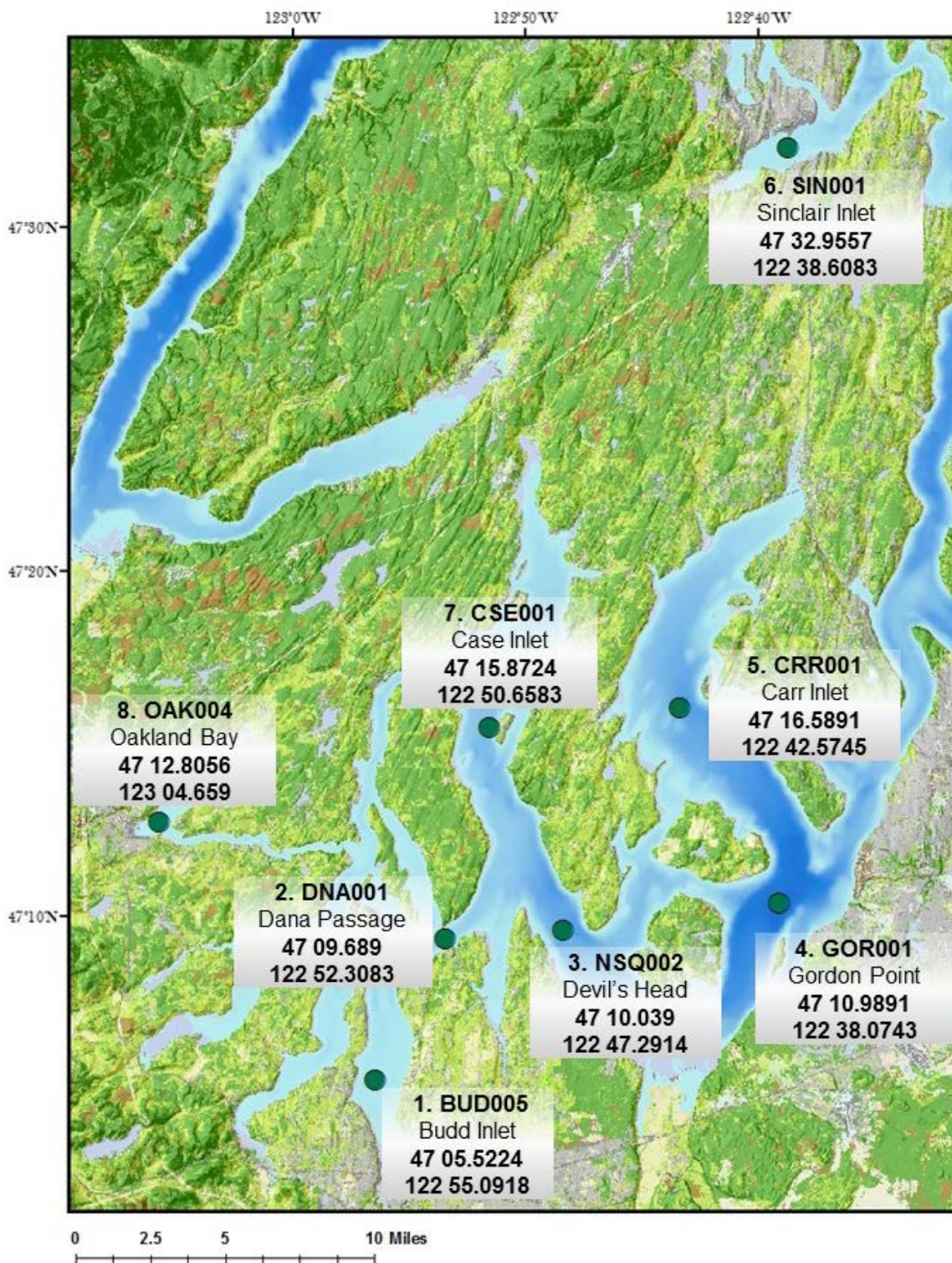


Figure 5. 2016 Marine Flight 4 (MF4) South Sound sampling stations.

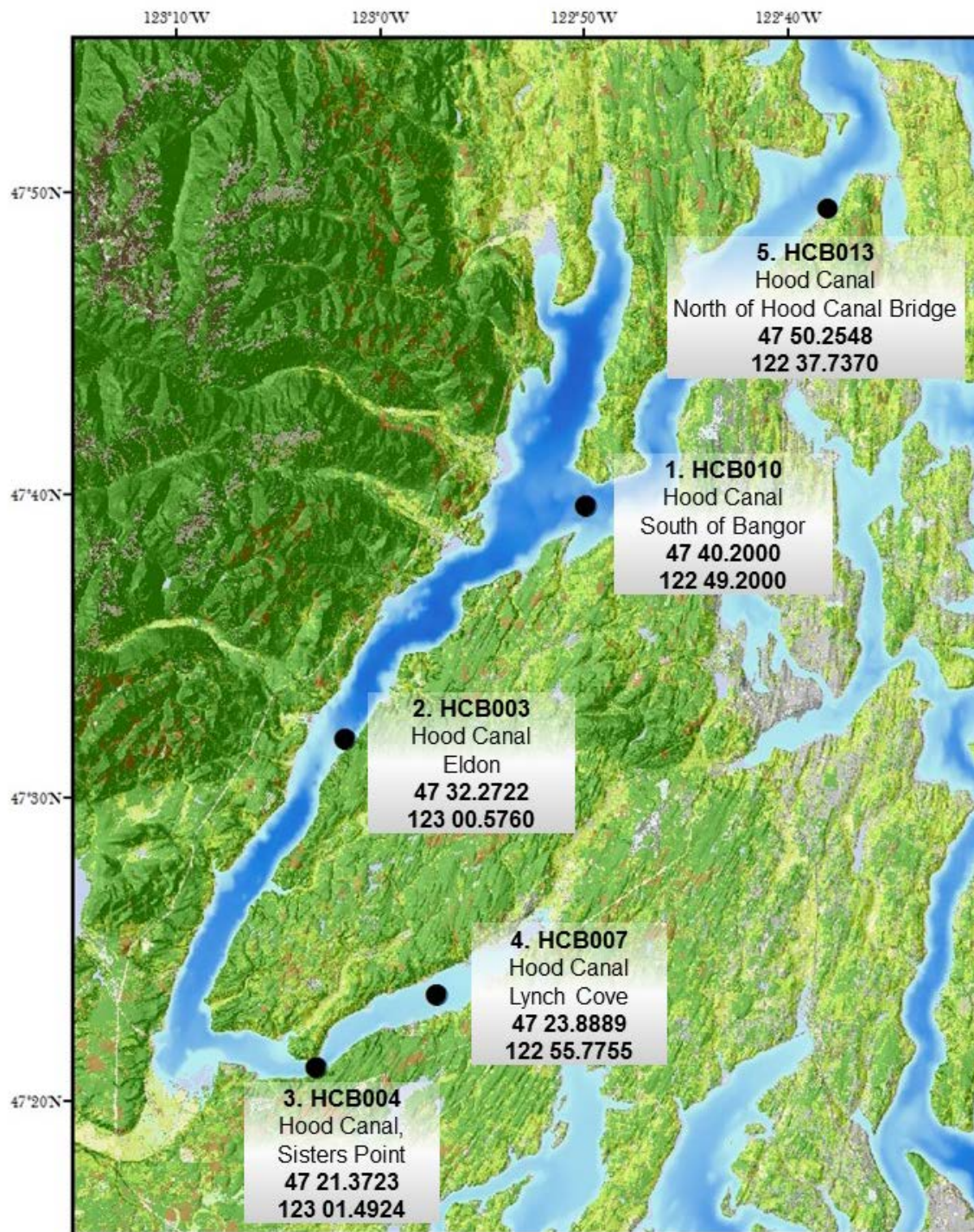


Figure 6. Marine Flight (MF5) Hood Canal sampling stations.

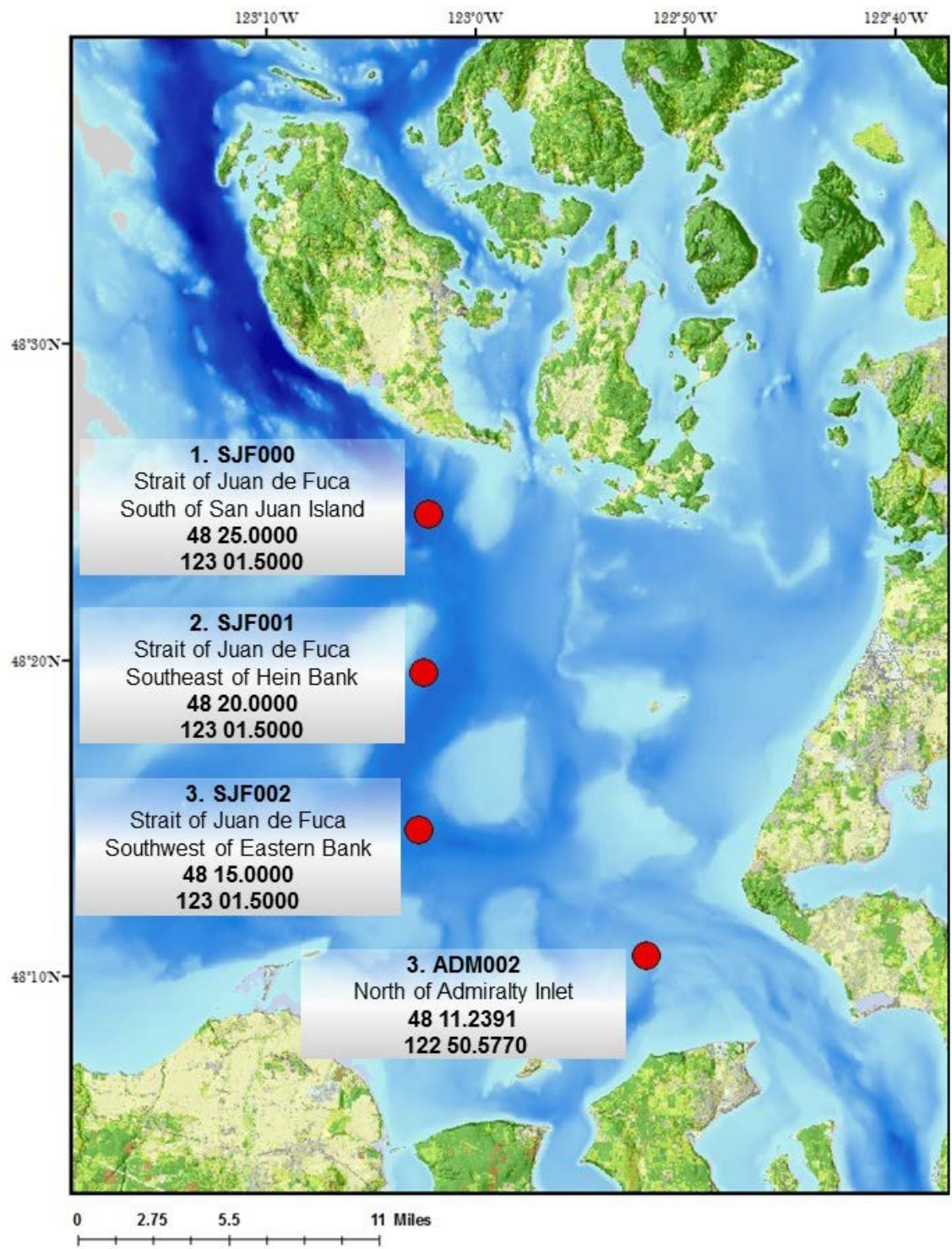


Figure 7. 2016 Strait JEMS sampling stations.

Table 6. Projected water sample collection plan for 2016 listing depths (in meters) for each sample type collected at each station.

Station	Nutrients	Chlorophyll	POC & PN	TOC	TN	Dissolved Oxygen	Salinity	Enterococci Bacteria	Fecal Coliform Bacteria	Approximate Water Depth (m)
Marine Flight 1										
GYS008	0	0						0.0	0.0	6
GYS016	0, 10	0, 10				near bottom (NB)		0.0	0.0	11
WPA004	0, 10, 10, 10	0, 10, 10, 10					10			14
WPA113	0, 10	0, 10				NB				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 Samples:										
8	17	17				3	2	4	4	
Marine Flight 2										
ADM001	0, 10, 30	0, 10, 30				NB				148
PTH005	0, 10, 10, 10	0, 10, 10, 10								26
RSR837	0, 10, 30	0, 10, 30				NB				56
GRG002	0, 10, 30	0, 10, 30					30			190
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
PSS008	0, 10, 30, NB	0, 10, 30	10, NB	10, NB	10, NB					37
PSS019	0, 10, 30	0, 10, 30				NB				101
Total Samples:										
10	33	28	11	11	11	3	2			
Marine Flight 3										
ADM003	0, 10, 30, NB	0, 10, 30	10, NB	10, NB	10, NB	30				210
PSB003	0, 10, 30, NB	0, 10, 30	10, NB	10, NB	10, NB					40-50
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 Samples:										
5	22	17	11	11	11	3	2			
Marine Flight 4										
BUD005	0, 0, 0, 10, NB	0, 10, 10, 10	10, NB	10, NB	10, NB		10			15
DNA001	0, 10, 30, NB	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
SIN001	0, 10, NB	0, 10	10, NB	10, NB	10, NB					16
CSE001	0, 10, 30, NB	0, 10, 30	10, NB	10, NB	10, NB	30				55
OAK004	0, 10	0, 10								15
Total Samples:										
8	30	23	13	13	13	5	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
HCB013	0, 10, NB		10, NB	10, NB	10, NB					20
Total Samples:										
5	20	15	9	9	9	2	2			
Straits										
SIF000	0, 30, 80, 140	0, 30, 80, 140				0, 30, 80, 140				161
SIF001	0, 30, 80, 140	0, 0, 0, 30, 80, 140				0, 30, 80, 140				144
SIF002	0, 30, 80, 140, 140	0, 30, 80, 140				0, 30, 80, 140, 140	0, 140			142
ADM002	0, 10, 30, 80	0, 10, 30, 80				80	80			82
Total Samples:										
4	18	18				15	3			
Annual Total:										
Station	Nutrients	Chlorophyll	POC & PN	TOC	TN	Dissolved Oxygen	Salinity	Enterococci Bacteria	Fecal Coliform Bacteria	
40	140	118	44	44	44	31	13	4	4	

7.3.1 Changes to the Sampling Process Design

Enterococci and Fecal Coliform Bacteria

The Marine Flight Program is conducting additional sampling at two stations in Grays Harbor for enterococci and fecal coliform bacteria. Ecology's Southwest Region Water Quality and Industrial Sections are currently assessing the impact of the industrial discharge from Cosmo Specialty Fiber's (CSF) facility on the receiving water body, Grays Harbor. This sampling effort will cover 12 months, beginning in August of 2015 and ending in August of 2016. For more information see *2015 Addendum 2 to Quality Assurance Monitoring Plan: Long-Term Marine Waters Monitoring, Water Column Program* (Keyzers and Bos, 2015).

Particulate Organic Material Carbon and particulate Nitrogen

Analyses of Ecology's long-term marine monitoring data indicate increases of dissolved nitrate and phosphate and a change in the balance of macro-nutrients and silicate. These changes affect growth conditions of phytoplankton at the base of the food web. The observed changes in nutrients could either be the result of decreased uptake by phytoplankton, increased nitrogen and phosphate loading, or a combination of the two. 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 better, Ecology will begin a particulate pilot project as a collaboration between Marine Waters water column group and sediment group. Starting in April 2016 through June 2017 in addition to the routine sampling the marine group will collect total organic carbon (TOC), total nitrogen (TN), particulate organic carbon (POC), and particulate organic 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.

The goal of this collaboration is to address the following:

- Determine how organic particle export to deep water and the benthos is changing.
- Quantify pools of unaccounted nutrients in the form of organic material (OM) in relation to inorganic nutrient trends.
- Utilize organic material (OM) cycling to explain patterns in water and sediment quality.
- Quantify and determine the loss of OM and how these change or vary over time.
- Determine if pools of OM have changed qualitatively and quantitatively from various sources (rivers to sediment).
- Establish important pathways of pollution and toxic transport in context of changing human and climate pressures.

Table 7. Projected water sample collection plan for 2016-17 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	
PSS008	Possession Sound - Port Gardner Bay Pier 3	47.98148	-122.22347	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			
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	

Station Id	Station location	Latitude	Longitude	Station type	MW particulates	Sediment chemistry	Benthos	TOC and Grain Size Only
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			

Excessive nitrogen loading is a key cause for accelerating primary production and eutrophication (Pearl, 2009). Nitrogen loading occurs in the form of both dissolved and particulate nitrogen. Long-term increases of dissolved nutrients in Puget Sound emphasize the need to quantify pools of nutrients present in all forms, including the particulate phase (Krembs, 2013). To date, Ecology has only routinely collected nutrients in the dissolved phase. Dissolved nutrients quickly transform into organic biomass and are removed from the dissolved phase, hence escaping detection. Estimating nutrients in the form of organic nitrogen and phosphate is therefore important to assess overall nutrient trends in Puget Sound.

In addition to sampling TOC, TN, PN, and POC, we will be able to calculate dissolved organic material (DOC). TOC is the fundamental unit of energy in food web and biogeochemical studies (Azam and Smith, 1991). TOC is made of a dissolved DOC and particulate POC fraction with very different attributes in the environment. While bulk DOC concentrations tend to support moderate bacterial activity and are neutrally buoyant, POC are hotspots of microbial activity which sink quickly through the water column. POC therefore constitutes a vector of energy and material transport to greater depth (Smith et al., 1992). First we plan to augment our sampling with POC measurements to provide key information that can help link observed changes in the food web at the surface with oxygen demand and observed benthic changes at greater depth (Turley and Mackie, 1994). Evolving water quality, toxic fate and transport, and food web models will benefit from this information and help address unaccounted detrital pools being introduced to Puget Sound from land.

Presently, POC in Puget Sound is sometimes estimated from in situ chlorophyll *a* (chl *a*) concentrations, using an assumed ratio of carbon to chl *a*. This approach makes assumptions of predictable relationship between chl *a* and POC based on published data. However, this does not account for a large pool of non-photosynthetic organic carbon (e.g., organic detrital material introduced by rivers and decaying macroalgae). The detrital pool of POC, while not associated with living phytoplankton, is largely unknown in Puget Sound. Yet at times it figures significantly in the overall respiration and uptake of oxygen in Puget Sound. Puget Sound changes in response to human and climatic pressures, and we observe species shifts occurring on a large scale (e.g., *Noctiluca*) with very different organic carbon attributes. Estimating POC from chl *a* alone, therefore, results in inaccuracies because of the uncertainty of assumed ratios of

nutrients to chl *a*. Therefore, measuring PN in addition to dissolved macro-nutrients resolves this critical gap for understanding nutrient cycling in Puget Sound.

In addition, the relationship between chl *a*, POC, and ideally TOC need to be seasonally and geographically refined (Westberry et al., 2010). Ongoing monitoring data of POC and chl *a* pigment concentration of phytoplankton will support chl *a* as proxy for phytoplankton biomass in the future. Continuous POC sampling in conjunction with PN will provide valuable data for water quality models that incorporate land-based organic material loadings to Puget Sound, closing an important data gap (Ahmed, 2014).

The key goals of this sampling are to:

- Quantify pools of nutrients (nitrogen) in the particle phase to understand overall nitrogen trends in Puget Sound.
- Calibrate organic carbon estimates for chl *a* as proxy and provide site and seasonal specific estimates (baseline and trends) on organic material in the upper mixed layer.
- Develop a tool to explore unaccounted organic nitrogen and carbon sources to Puget Sound that might affect dissolved oxygen consumption and respiration at depth.

Satlantic SUNA V2 nitrate sensor

To quantify nitrogen in Puget Sound, Ecology will collect continuous vertical nitrate measurements as part of the routine monitoring. Starting in 2016 we plan to test a Satlantic Submersible Ultraviolet Nitrate Analyzer (SUNA) V2 (or equivalent) to our SBE25*plus* CTD instrument package. 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 and extend measurements to full depth.
- 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.
- Extend nitrate information from 0, 10, and 30 meter point samples to full water column depth resolution.

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 100 μ L super-saturated HgCl ₂ . 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.	Up to 100 days once filtered and stored at -20C
Chlorophyll <i>a</i>	UNESCO, 1994 (JGOFS Protocols)	125 mL clean brown polyethylene bottles	Store on ice - filter immediately upon arrival at lab. Filter stored frozen in 90% acetone.	1 month
Dissolved Nutrients	UNESCO, 1994 (JGOFS Protocols)	125 ml clear acid-washed plastic bottles	Store on ice- filter immediately upon collection – filtrate frozen.	3 months
Dissolved Oxygen	UNESCO, 1994 (JGOFS Protocols) *1st sample collected	130 mL clean, dry borosilicate glass stoppered volumetric flasks	Fix with MnCl ₂ & 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
Secchi Disk Depth	Lower in water until disk disappears, then bring up until it reappears-record reading	NA	NA	NA

*Not currently collected

8.1.1 CTD Data Collection

Beginning in 2015 the CTD instrument package was upgraded from a Seabird Electronics SBE25 to a SBE25*plus*. The SBE25*plus* has an internal pressure sensor and a faster sampling rate, providing more measurements per second, thus improving data quality and vertical resolution for several parameters. This upgrade does not change field operations or methods. Principles of CTD and sensor operations are described in manufacturer operating manuals. Instructions for optimum CTD data collection are outlined in these manuals.

9.0 Measurement Methods

9.2 Lab procedures table

Nutrient and salinity samples are analyzed at University of Washington's Marine Chemistry Laboratory in Seattle, Washington using various analytical methods described in Table 10. Dissolved oxygen and chlorophyll *a* samples are analyzed at Ecology's Marine Laboratory using analytical methods described in Table 10. POC, PN, TOC, TN are analyzed at Ecology's Manchester Environmental Laboratory (MEL) in Port Orchard, Washington using various analytical methods described in Table 9.

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	1 ug/L
Total Nitrogen (TN)	MEL	SM 4500-N B	15-50 µM	0.01 µM
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
*Alkalinity				
*Dissolved Inorganic Carbon				
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 µM	0.15 µM
Marine Nitrite	MCL	Armstrong et al., 1967	0.00 - 2.00 µM	0.01 µM
Marine Ammonium	MCL	Slawyk & MacIsaac, 1972	0.00 - 10.00 µM	0.05 µM
Marine Orthophosphate	MCL	Bernhardt & Wilhelms,	0.00 - 4.00 µM	0.02 µM
Marine Silicate	MCL	Armstrong et al., 1967	0.00 - 200.00 µM	0.21 µM
Chlorophyll <i>a</i>	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

*Not currently collected

ML - Ecology's Marine Laboratory

MCL - UW's Marine Chemistry Laboratory

MEL - Ecology's Manchester 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 (QC) Procedures

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 2016 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 Appendix F 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)
- “Blind” SRMs submitted to the laboratory

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)	$\leq 20\%$	5%	✓	✓	✓	✓	✓	✓	✓	✓
Total Nitrogen (TN)	$\leq 20\%$	5%	✓	✓	✓	✓	✓	✓	✓	✓
Particulate Organic Carbon and particulate nitrogen (POC & PN)	$\leq 20\%$	5%	✓	✓	✓	✓	✓	✓	✓	✓
Chlorophyll a	10%	NA	✓	✓		✓	✓	✓	✓	✓
Dissolved Oxygen	5%	NA	✓	✓		✓	✓	✓	✓	✓
Nitrate	10%	5%	✓	✓	✓	✓	✓	✓	✓	✓
Nitrite	10%	5%	✓	✓	✓	✓	✓	✓	✓	✓
Ammonium	10%	5%	✓	✓	✓	✓	✓	✓	✓	✓
Orthophosphate	10%	5%	✓	✓	✓	✓	✓	✓	✓	✓
Silicate	5%	5%	✓	✓	✓	✓	✓	✓	✓	✓
Salinity	10%	5%	✓	✓		✓	✓	✓		✓

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, data associated with the batch is flagged by the reviewer. 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

Starting in 2016 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 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)	Replicates (30 or less samples)	Blanks per Batch
Laboratory Samples				
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 ₄)	5 point standardization	2 - 3	2	2
Nitrate (NO ₃)	5 point standardization	2 - 3	2	2
Nitrite (NO ₂)	5 point standardization	2 - 3	2	2
Orthophosphate (PO ₄)	5 point standardization	2 - 3	2	2
Silicate (SiO ₄)	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
<i>~ Nutrients, dissolved oxygen and chlorophyll a are replicated in the field.</i>				
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

*Calibration standards ran every 10 samples.

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18.0 Appendix A. Glossary, Acronyms, and Abbreviations

Particulate Nitrogen (PN). Particulate matter is defined as suspended particles in seawater having a size greater than 0.45 μM . 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 μM . The particulate organic carbon fraction of total organic carbon is defined as organic matter that is larger than 0.45 μM . 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.