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Addendum 6 to Quality Assurance Monitoring Plan

Long-Term Marine Waters Monitoring, Water Column Program

July 2019
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Cover photo: Four pictures of the Ecology boat, R/V Skookum, tied up at the Westport Marina. Top left: length of the boat. Top right: rear view of the back deck. Bottom right: picture of the bow. Bottom left: the CTD package on the rear deck of the boat. All photos by Mya Keyzers using a Go Pro Hero 5.

Addendum 6 to Quality Assurance Monitoring Plan

Long-Term Marine Waters Monitoring, Water Column Program

July 2019

Approved by:

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

3.0 Background

This document describes changes to the sampling effort for Ecology's Long-Term Marine Waters Monitoring Program planned for 2019. The purpose of the program is to examine and report marine water quality on a regular, long-term basis. Its objectives are to understand existing conditions in the context of environmental factors, identify spatial and temporal trends, and provide high-quality information from sensor and lab sample collection.

This is an addendum to the *Quality Assurance Monitoring Plan: Long-Term Marine Waters Monitoring, Water Column Program* (Bos, 2015). This Quality Assurance Monitoring Plan (QAMP) addendum specifies changes to the original QAMP and past addendums. These changes include which stations and parameters will be sampled in 2019. 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 20 stations for ocean acidification (OA)-relevant parameters of total alkalinity (TA) and dissolved inorganic carbon (DIC) (Gonski, 2019). Ecology received a National Estuary Program grant that will fund a two-year ocean acidification study. This study will begin in late 2018, and it will closely follow the methods of the 2014–2015 QAPP, *Puget Sound total alkalinity and dissolved inorganic carbon pilot project plan* (Keyzers, 2014). The focus of this new 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. See the QAPP, *Ocean Acidification Monitoring at Ecology's Greater Puget Sound Stations* (Gonski, 2019), for more detailed information.

We have offered boat time to our colleagues at Padilla Bay National Estuarine Research Reserve (NERR) to support the Salish Sea bottom water microbial respiration project funded through September 2019. Their staff will ride along on the North, Admiralty Inlet, and South Sound routes to collect respiration samples from near bottom water. The NERR staff will bring all the supplies and conduct the sampling and analysis at the 15 stations. Marine Waters simply provides the sampling platform; all detailed information about the respiration project can be found in the QAPP, *Spatial and seasonal variability in Salish Sea bottom water microbial respiration*, currently in draft format (Apple, 2019).

All required sections not mentioned in this addendum are discussed in the original QAMP, Addendums 1–5, 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
Skip Albertson Marine Monitoring Unit Western Operations Section Phone: 360-407-6676	Physical Oceanographer	Analysis and reporting of climate, weather, and ocean indicators. Generates data and QC products and analytical tools. Conducts QA review of data, analyzes, audits, and interprets data. Writes reports and data summaries.
Allison Brownlee Marine Monitoring Unit Western Operations Section Phone: 360-407-6687	Marine Field Scientist	Conducts field sampling, laboratory analysis, instrument calibrations, and instrument maintenance Records and manages field information. Conducts QA review, analyzes, audits, and interprets data.
Julia Bos Marine Monitoring Unit Western Operations Section Phone: 360-407-6674	Oceanographer	Writes the QAMP. Manages data workflow, processing, and QA review. Analyzes, and interprets data, and manages data in EIM data management system. Generates data and QC products and analytical tools. Writes reports and data summaries.
Stephen Gonski Marine Monitoring Unit Western Operations Section Phone: 360-407-6517	Marine Field Scientist	Provides expertise to QA parameters. Assists with field sampling. Conducts QA review, analyzes, audits, and interprets the TA and DIC data.
Mya Keyzers Marine Monitoring Unit Western Operations Section Phone: 360-407-6395	Marine Waters Field Lead	Coordinates all parties for the field and laboratory work. Conducts field sampling, laboratory analysis, and instrument maintenance. Oversees monitoring program field and laboratory activities. Conducts QA review. Writes reports and data summaries.
Christopher Krembs Marine Monitoring Unit Western Operations Section Phone: 360-407-6675	Senior Oceanographer	Determines monitoring strategy and advises agency on water quality. Generates index/indicators of water quality conditions. Generates data products for agency and interagency communication. Lead author of publications and presentations.
Carol Maloy Marine Monitoring Unit Western Operations Section Phone: 360-407-6730	Unit Supervisor	Provides internal review of the QAMP and QAMP Addendums. Approves the budget and approves the final QAMP and QAMP Addendums.
Dale Norton Western Operations Section Phone: 360-407-6596	Section Manager	Reviews the project scope and budget, trans progress, reviews the draft QAMP and QAMP Addendums, and approves the final QAMP and QAMP Addendums.
Arati Kaza Quality Assurance Officer Phone: 360 407-6964	Ecology Quality Assurance Officer	Reviews the draft QAMP, QAMP Addendums, and approves the final QAMP and QAMP Addendums.

5.2 Special Training and Certification

Any special training needed for the TA/DIC sampling is covered in the QAPP *Ocean Acidification Monitoring at Ecology's Greater Puget Sound Stations* (Gonski, 2019).

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.

Field and laboratory work	Due date	Lead staff
Field work (sample collection)	Monthly	Mya Keyzers
Internal (Ecology) laboratory analyses	3 days (DO samples, TOC, TN, POC/PN) post collection	Allison Brownlee
Internal (Ecology/MEL) laboratory analyses	1 month post collection (chlorophyll *a* samples)	Allison Brownlee
External UW and PMEL laboratory analyses completed	3 months post collection (nutrient, TA/DIC samples)	Mya Keyzers, Stephen Gonski

*PMEL = Pacific Marine Environmental Lab

Data receipt or processing and upload to EAPMW (Marine Waters)	Due date	Lead staff
Instrument and sensor data	Same month as collection	Julia Bos
Internal laboratory data	1 month post analysis	Mya Keyzers, Allison Brownlee, Sandy Weakland
External laboratory data	3 month post analysis	Mya Keyzers, Stephen Gonski

Data review and QA/QC	Due date	Lead staff
Instrument and senor data	1 month post collection	Julia Bos, Christopher Krembs, Skip Albertson, Mya Keyzers, Allison Brownlee, Stephen Gonski
Internal laboratory data	1 month post analysis	Allison Brownlee, Mya Keyzers, Sandy Weakland, Valerie Partridge
External laboratory data	Quarterly, one quarter post collection	Julia Bos, Stephen Gonski

Environmental Information System (EIM) database	Due date	Lead staff
EIM data loaded	4 months after sampling year completed	Julia Bos
EIM QA	4 months after sampling year completed	Julia Bos
EIM complete	4 months after sampling year completed	Julia Bos
Annual assessment – data products and written summary	**Due date**	**Lead staff**
Draft assessments and products due	3 months after sampling year complete	Christopher Krembs, Julia Bos, Skip Albertson, Mya Keyzers, Allison Brownlee
Final reviews	4 months after sampling year complete	Christopher Krembs, Julia Bos
Final data posted and performance measures reported	**Due date**	**Lead staff**
Final performance calculated and submitted to OFM	Annually in July	Julia Bos

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 award from the EAP Near Term Action National Estuary Program grant.

Type	Cost	Comments
Near Term Action National Estuary Program grant (EPA)	$370,785	Funding for two years. Addresses ocean acidification. Add measurements of total alkalinity (TA) and dissolved inorganic carbon (DIC).

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

Most labs conducting analyses for the marine waters monitoring program are accredited through Ecology's Laboratory Accreditation Program if a lab does not have an accreditation a waiver form must be approved prior to sampling. Seawater nutrient and salinity sample analyses are conducted by the accredited University of Washington Marine Chemistry Laboratory (UW-MCL). Dissolved oxygen (Winkler) and chlorophyll *a* samples are analyzed by the accredited Marine Lab (ML) of Ecology's Marine Monitoring Unit. POC, PN, TOC, and TN analyses are conducted by Ecology's accredited Manchester Environmental Laboratory (MEL). Total Alkalinity (TA) and Dissolved Inorganic Carbon (DIC) samples are analyzed by the NOAA Pacific Marine Environmental Lab (PMEL) under a waiver of accreditation (Gonski, 2019).

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 TA/DIC laboratory samples (Gonski, 2019).

MQO →	Precision		Bias			Sensitivity
Parameter	**Field Duplicate Samples**	**Matrix Spike-Duplicates**	**Verification Standards (CRM)**	**Matrix Spikes**	**Surrogate Standards**	**Resolution within expected range**
	Relative Percent Difference (%RPD)		Recovery Limits (%)			Concentration (µmol kg^{-1})
DIC	<0.5%	N/A	<0.25%	N/A	N/A	±0.1%
TA	<0.5%	N/A	<0.25%	N/A	N/A	±0.1%

7.0 Study Design

7.1 Study boundaries

7.1.2 Sampling location and frequency

7.1.2.1 Core Station Monitoring & Locations

Thirty-nine long-term monitoring stations are sampled 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 seven regional surveys a month as opposed to six, 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.

There are 39 total stations for 2019: 37 core waters stations and 2 sediment team core stations. This year the regions will be grouped as:

- San Juan Islands (Shannon Point Marine Science Center).
- Admiralty Inlet (Shannon Point Marine Science Center).
- Coastal Bays (Ecology).
- North Sound (Shannon Point Marine Science Center).
- Central Sound (Ecology).
- South Sound (Ecology).
- Hood Canal (Ecology).

Ecology will sample four of the regions, while Shannon Point Marine Center (SPMC) will sample the San Juan Islands, Admiralty Inlet, and North Sound stations through our interagency agreement with Western Washington University.

See Figures 1 and 2 as well as Table 5 for a list of the long-term monitoring stations and some of their characteristics. Table 5 has the complete monthly water sample collection plan for 2019 including routes, stations, parameters, depths, and counts.

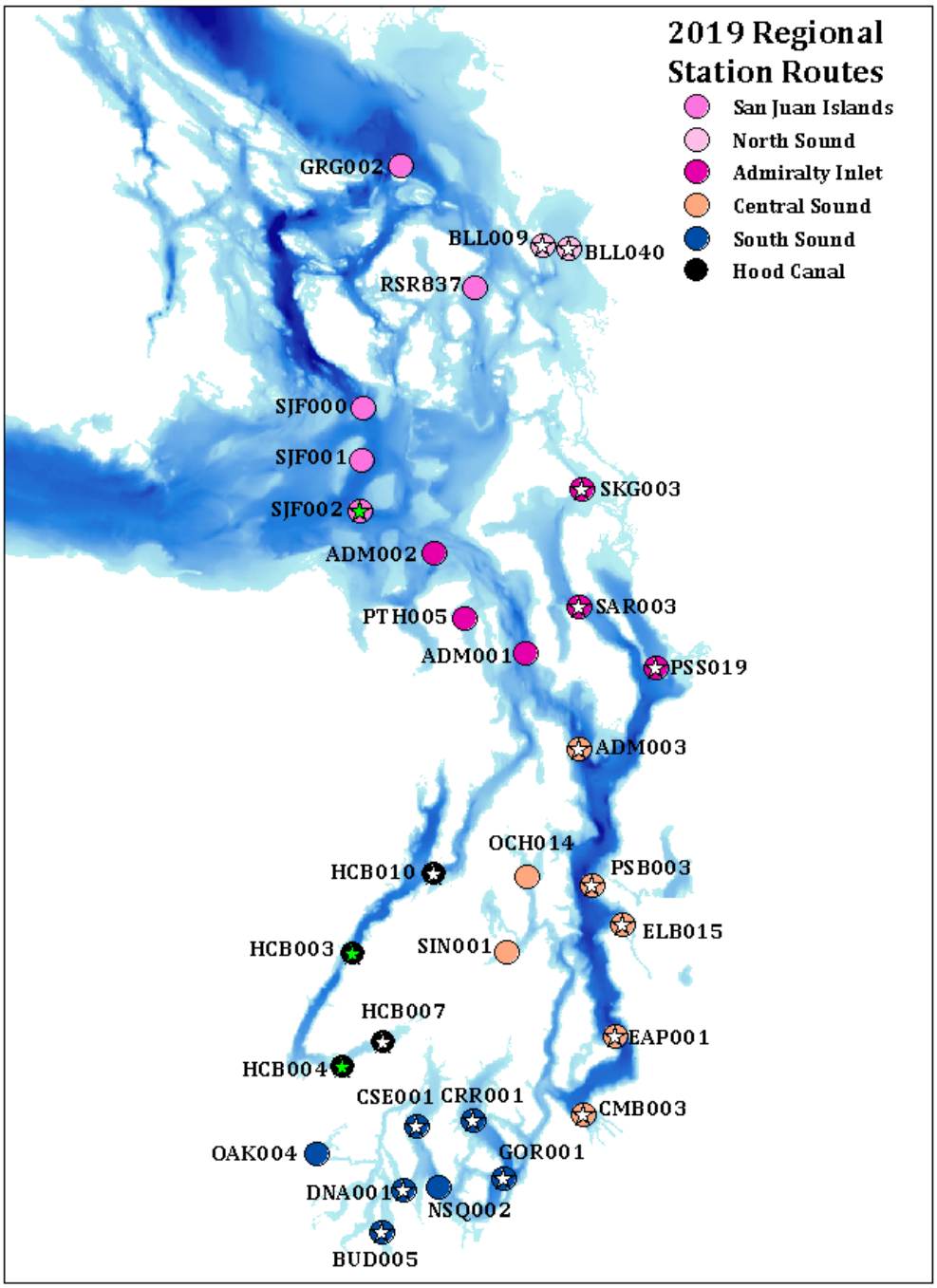

Figure 1. 2019 Ecology long-term marine water column monitoring station locations. The 20 particulate pilot project stations are highlighted with a white star; the three zooplankton stations are highlighted with a green star.

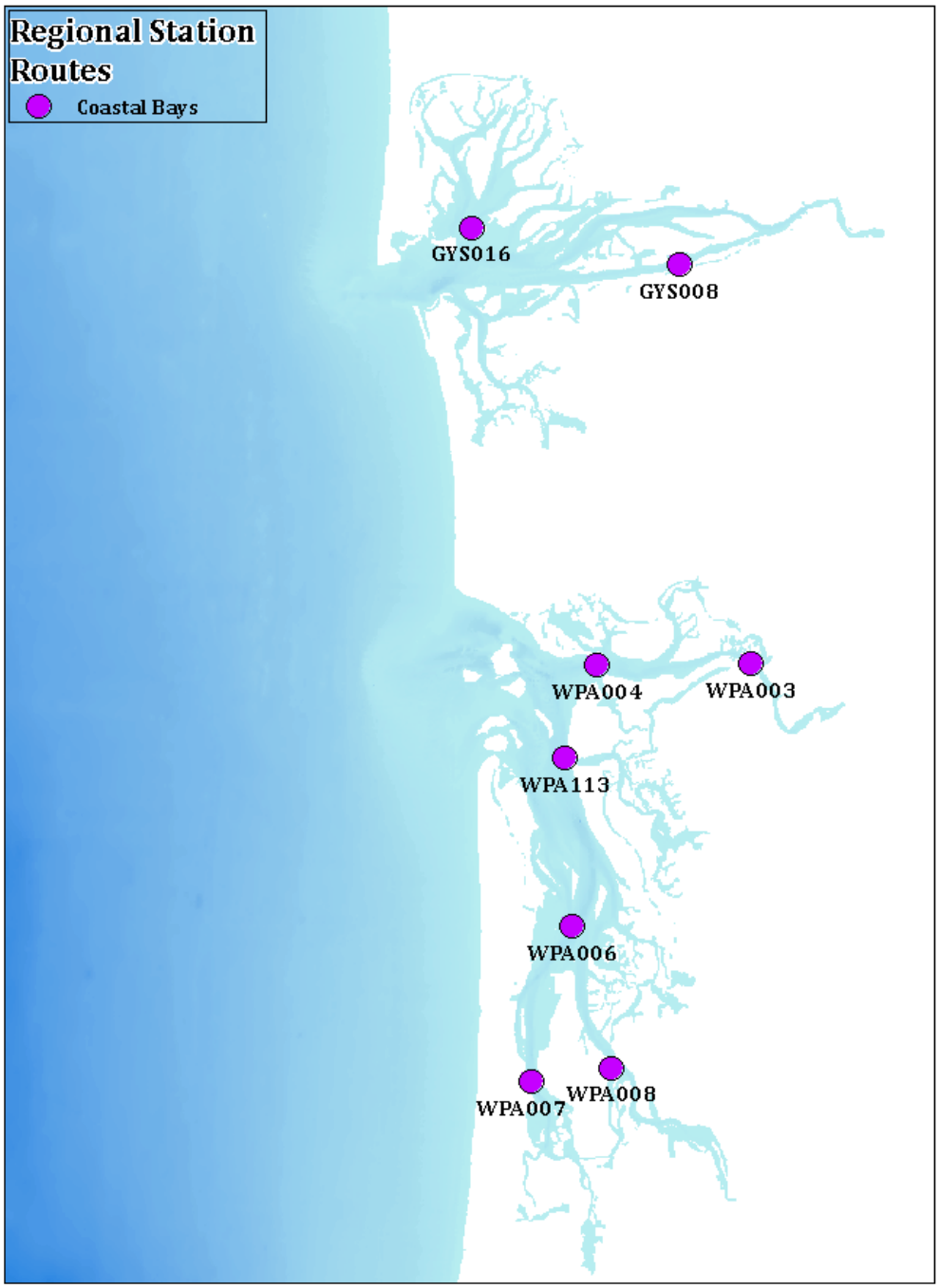

Figure 2. 2019 Locations of Ecology long-term marine water column monitoring stations in Willapa Bay and Grays Harbor.

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

Table 5. 2019 list of stations for Ecology long-term marine water column monitoring.

Regional Survey	Station ID	Location	Lat. N NAD83 (deg/dec_min)		Long. W (NAD83) (deg/dec_min)		WQMA[a]	Depth (m)[b]	Record	Record Length (yrs)	Justification
Coast	**GYS008**	Mid-S. Channel	46	56.2388	123	54.7934	Western Olympic	6	1974 - 76, 1983 - present	38	represents mid Grays Harbor, south
	GYS016	Damon Point	46	57.2053	124	05.5770	Western Olympic	11	1982 - 1987,1991 - present	32	represents outer Grays Harbor, north
	WPA004	Toke Point	46	41.9800	123	58.1240	Lower Columbia	14	1973-1975, 1977-present	44	represents north Willapa Bay
	WPA113	Bay Center	46	38.6400	123	59.5800	Lower Columbia	11	1997-2000, 2006-present	15	represents mouth of (NW) Willapa Bay
	WPA006	Nahcotta Channel	46	32.7226	123	58.8097	Lower Columbia	21	1991-present	27	represents central Willapa Bay
	WPA007	Long Island, S. Jenson Pt.	46	27.1893	124	00.5672	Lower Columbia	14	1991-2008, 2013-present	22	represents SW Willapa Bay
	WPA008	Naselle River mouth	46	27.7890	123	56.4760	Lower Columbia	14	1996-2008, 2013-present	17	represents SE Willapa Bay, off Naselle R.
	WPA003	Willapa River, John. Slough	46	42.2392	123	50.2431	Lower Columbia	10	1973-present	45	represents north Willapa Bay, off Willapa R.
North	**BLL009**	Bellingham Bay	48	41.1564	122	35.9771	Nooksack/San Juan	16	1977-present	41	represents waters off city of Bellingham
	BLL040	Bellingham Bay	48	41.0382	122	32.2920	Nooksack/San Juan	26	2016-present	29	represents waters of Bellingham
Central	**OCH014**	Brownsville	47	40.2924	122	35.9712	Banbridge Basin	20	2019-present	0	represents outer Dyes Inlet
	ADM003	S. of Admiralty Inlet	47	52.7390	122	28.9917	Kitsap & Cedar/Green	210	1988-1991, 1996-present	24	represents waters S. of Admiralty sills
	PSB003	Puget Snd. Main Basin	47	39.5891	122	26.5745	Kitsap & Cedar/Green	40-50	1976-present	42	represents Puget Sound Main Basin
	SIN001	Sinclair Inlet	47	32.9557	122	38.6083	Kitsap	16	1973-1987, 1991-present	41	represents waters off city of Bremerton
	ELB015	Elliott Bay	47	35.7892	122	22.1743	Cedar/Green	82	1991-present	27	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	26	represents S. Puget Sound main axis
	CMB003	Commencement Bay	47	17.4226	122	27.0074	South Puget Sound	150	1976-present	42	represents waters off city of Tacoma
South	**BUD005**	Budd Inlet	47	05.5224	122	55.0918	Eastern Olympic	15	1973-present	43	represents waters off city of Olympia
	DNA001	Dana Passage	47	09.6890	122	52.3083	Eastern Olympic	40	1984-85, 1989-present	31	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	24	represents S. Puget Sound near Nisqually
	GOR001	Gordon Point	47	10.9891	122	38.0743	E. Oly & Kitsap & SPS	160-170	1996-present	21	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	34	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	29	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
Hood Canal	**HCB007**	Hood Canal, Lynch Cv.	47	23.8889	122	55.7755	Kitsap & E. Olympic	21	1990-1996, 1998-2007, 2011-present	24	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	41	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-present	37	very low DO, assess duration & coverage
	HCB010	Hood Canal, S of Bangor	47	40.2000	122	49.2000	Kitsap & E. Olympic	100	2005-present	13	represents northern Hood Canal
San Juan Islands	**SJF000**	Strait of Juan de Fuca	48	25.0000	123	01.5000	S. of San Juan Island	180	2000 - present	18	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	18	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	18	represents southern Strait of Juan de Fuca
	RSR837	Rosario Strait	48	36.9896	122	45.7775	Nooksack/San Juan	56	2009-present	9	represents waters in Rosario Strait
	GRG002	Strait of Georgia	48	48.4896	122	57.2446	Nooksack/San Juan	190	1988-present	30	represents Strait of Georgia end member
Admiralty Inlet	**PTH005**	Port Townsend	48	04.9889	122	45.8767	Eastern Olympic	26	1977-1978, 1991-2002, 2005-present	27	represents waters off city of Port Townsend
	ADM001	Admiralty Inlet	48	01.7888	122	37.0760	Kitsap & Cedar/Green	148	1975-1987, 1992-present	38	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
	SKG003	Skagit Bay	48	17.7893	122	29.3763	Island/Snohomish	24	1990-1991, 1994-1998, 2007-present	18	represents Whidbey Basin
	SAR003	Saratoga Passage	48	06.4557	122	29.4925	Island/Snohomish	149	1977-present	41	represents Whidbey Basin
	PSS019	Possession Sound	48	00.6556	122	18.0750	Island/Snohomish	101	1980-present	38	represents waters off city of Everett

[a]Water Quality Management Area
[b]Depth averaged from the maximum depth we have sampled to over the stations data recorded.

Table 6. Projected monthly water sample collection plan for 2019 listing depths (in meters) for each sample type collected at each station.

Station	Nutrients	Chlorophyll	POC & PN	TOC	TN	TA/DIC	Respiration	Dissolved Oxygen	Zooplankton	Salinity	Approximate Station Depth (m)
Coast											
GYS008	0	0									6
GYS016	0, 10	0, 10						10			11
WPA004	0, 10, 10, 10	0, 10, 10, 10									14
WPA113	0, 10	0, 10									11
WPA006	0, 10	0, 10						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**	0	0	0	0	0	**2**	**0**	**0**	
North											
BLL009	0, 10, NB	0, 10	10, NB	10, NB	10, NB	0	NB				16
BLL040	0, 10, NB		10, NB	10, NB	10, NB		NB, NB	10			26
Total Samples:											
2	**6**	**2**	**4**	**4**	**4**	**1**	**3**	1	0	0	
Central											
OCH014	0, 10, NB		10, NB	10, NB	10, NB						20
ADM003	0, 10, 30, NB	0, 10, 30	10, NB	10, NB	10, NB	0, 30				-	210
PSB003	0, 10, 30, NB	0, 10, 30	10, NB	10, NB	10, NB	0, 30					40-50
SIN001	0, 10, NB	0, 10	10, NB	10, NB	10, NB						16
ELB015	0, 10, 30, NB	0, 10, 30	10, 10, NB	10, 10, NB	10, 10, NB	0, 30					82
EAP001	0, 10, 30, NB	0, 10, 30	10, NB	10, NB	10, NB	0, 30		10			200
CMB003	0, 0, 0, 10, 30, NB	0, 0, 0, 0, 30	10, NB	10, NB	10, NB	0, 30		10			150
Total Samples:											
7	**28**	**19**	**15**	**15**	**15**	**10**	0	**2**	0	**0**	
South Sound											
BUD005	0, 10, NB	0, 10, NB	10, NB	10, NB	10, NB	0	NB				15
DNA001	0, 10, 30	0, 10, 30				0, 30	NB	10, 10, 10			40
NSQ002	0, 10, 30, NB	0, 10, 30	10, NB	10, NB	10, NB	0, 30	NB				100
GOR001	0, 10, 30, NB	0, 10, 30	10, NB	10, NB	10, NB		NB	10			160-170
CRR001	0, 10, 30, NB	0, 10, 30	10,10, NB	10,10, NB	10,10, NB	0, 30	NB				95
CSE001	0, 10, 30, NB	0, 10, 30	10, NB	10, NB	10, NB	0, 30	NB	10			55
OAK004	0, 10, 10, 10	0, 10, 10, 10				0, 0	NB			0, 0	15
Total Samples:											

Station	Nutrients	Chlorophyll	POC & PN	TOC	TN	TA/DIC	Respiration	Dissolved Oxygen	Zooplankton	Salinity	Approximate Station Depth (m)
7	**26**	**21**	**11**	**11**	**11**	**11**	**7**	**5**	0	**2**	
Hood Canal											
HCB007	0, 10, NB	0, 10	10,10, NB	10,10, NB	10,10, NB						21
HCB004	0, 10, 10, 10 30	0, 10, 10, 10 30				0, 30, 30		10	ü	30, 30	55
HCB003	0, 10, 30, NB	0, 10, 10, 10	10, NB	10, NB	10, NB				ü		144
HCB010	0, 10, 30, NB	0, 10, 30	10, NB	10, NB	10, NB			30			100
Total Samples:											
4	**16**	**12**	**7**	**7**	**7**	**2**	0	**2**	**2**	**2**	
San Juan Islands											
SJF000	0, 30, 80, 140	0, 30, 80, 140						140			161
SJF001	0, 30, 80, 140	0, 0, 0, 30, 80, 140						80			144
SJF002	0, 30, 80, 140, 140, 140	0, 30, 80, 140				0, 30		80	ü		142
RSR837	0, 10, 30	0, 10, 30				0, 30		10			56
GRG002	0, 10, 30	0, 10, 30				0, 0, 30		10		0, 0, 30	190
Total Samples:											
5	**20**	**20**	0	0	0	**7**	0	**5**	**1**	**3**	
Admiralty Inlet											
PTH005	0, 10, 10, 10	0, 10, 10, 10					NB				26
ADM001	0, 10, 30	0, 10, 30					NB				148
ADM002	0, 10, 30, 80	0, 30, 80				0, 30	NB	30			82
SKG003	0, 10, NB	0, 10	10, 10, NB	10, 10, NB	10, 10, NB	0, 0	NB			0, 0, 30	24
SAR003	0, 10, 30, NB	0, 10, 30	10, NB	10, NB	10, NB	0, 30	NB	10			149
PSS019	0, 10, 30	0, 10, 30	10, NB	10, NB	10, NB	0, 30	NB	10			101
Total Samples:											
6	**21**	**18**	**7**	**7**	**7**	**9**	**6**	**3**	0	**3**	
Monthly Total:											
Station Count	**Nutrients**	**Chlorophyll**	**POC & PN**	**TOC**	**TN**	**TA/DIC**	**Respiration**	**Dissolved Oxygen**	**Zooplankton**	**Salinity**	**Approximate Station Depth (m)**
39	**134**	**109**	**44**	**44**	**44**	**40**	**16**	**20**	**3**	**10**	**NA**

Notes for Table 6
NB: Water collected from near bottom water column depth.
Depth averaged from the maximum depth we have sampled to over the stations data recorded.

8.0 Field Procedures

Field procedures for the TA/DIC sampling are covered in the QAPP *Ocean Acidification Monitoring at Ecology's Greater Puget Sound Stations* (Gonski, 2019)**.**

9.0 Laboratory Procedures

9.1 Lab procedures table

All laboratory analytical methods for OA parameters are described in Table 7. Total alkalinity and dissolved inorganic carbon will be analyzed at the Pacific Marine Environmental Laboratory (PMEL) in Seattle, Washington.

Table 7. Lab measurement methods, expected range of results and reporting limits for TA/DIC data.

Analyte	Sample Matrix	Samples (Number/ Arrival Date)	Expected Range of Results	Resolution within expected range	Sample Prep Method	Analytical (Instrumental) Method
DIC	Seawater	40 samples/month	1050-2300 µmol kg^{-1}	±0.1%	n/a	Dickson *et al*. (2007) (SOP 2); Johnson *et al.* (1985, 1987, 1993)
TA	Seawater	40 samples/month	1100-2300 µmol kg^{-1}	±0.1%	n/a	Dickson *et al.* (2003); Dickson *et al.* (2007) (SOP 3b)

9.2.1 Analyte

Analytes are listed in Table 7.

9.2.4 Expected range of results

Expected ranges for analytical results are listed in Table 7.

9.2.5 Analytical method

Analytical methods are listed in Table 7.

9.2.6 Sensitivity/Method Detection Limit (MDL)

Sensitivity is reported as “Resolution within expected range” in Table 7.

10.0 Quality Control Procedures

10.1.1 Tables of field and lab quality control required

Table 8 includes summary of laboratory quality control steps for the TA/DIC samples. The Ecology QA Glossary included in the Appendix contains definitions of the various types of QC samples, including:

- Standard Reference Materials (SRM)
- Certified Reference Materials (CRM)
- Lab Control Samples (LCS)

Table 8. A summary of laboratory quality control steps for TA and DIC samples.

Lab Measurement	Precision-Relative Percent Difference (RPD)	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 Alkalinity	±0.1%	N/A		✓	✓	✓		✓	✓	✓
Total Dissolved Inorganic Carbon	±0.1%	N/A		✓	✓	✓		✓	✓	✓

10.5.2 Water Sample QA/QC Procedures

10.5.2.1 Replicate Sample Collection

Field replicates for TA/DIC are collected from different niskin bottles from the same depth. DIC is sensitive to headspace equilibration, so you cannot use the same niskin to collect multiple samples. Of the 40 monthly samples, 10% will serve as the field replicates for the current work. The relative percent difference (%RPD) for field replicate samples should not exceed the MQO of 0.5% shown in Table 3. If the results fall outside of established limits, data associated with the batch are flagged by the reviewer. Any measurement problem that cannot be resolved for a specific sample is given a data quality flag.

Starting in 2019, we will be using a PreSens dissolved oxygen (DO) optode sensor during the field surveys as a performance check of the SBE 43 oxygen sensor. The process will be gradually refined as we get to know the instrument, eventually replacing sensor performance checks now performed by Winkler samples. We plan to use the PreSens sensor for sensor verification at increased frequency at the sample frequency/interval currently used by Winkler samples.

10.5.2.2 Analytical Replicates

Laboratory replicates (replicate analyses of a single sample from the same bottle) may be run for TA only. If laboratory replicates for TA are performed, any such analyses are subject to the same MQO as the field replicates. It is not part of the plan to have any laboratory splits performed for either DIC or TA.

10.5.2.3 Certified Reference Materials

CRMs are included with every sample batch. Specific to DIC and TA measurements, certified reference materials (CRMs; Dickson *et al.*, 2003) provided by A.G. Dickson of Scripps Institution of Oceanography (SIO) are used to calibrate analyzers at PMEL. The DIC, TA, and salinity values of the CRMs (found at: https://www.nodc.noaa.gov/ocads/oceans/Dickson_CRM/batches.html) are measured and certified during preparation at SIO prior to distribution and use (Dickson *et al.*, 2007). 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.

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Appendix A. 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 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.

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_2), carbonic acid (H_2CO_3), bicarbonate anion (HCO_3^-), and carbonate (CO_3^{2-}).

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_2) 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 under-saturated 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.

90th percentile: An estimated portion of a sample population based on a statistical determination of distribution characteristics. The 90th 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.

Nutrient species include: Nitrite, nitrate, o-phosphate, silicate, and ammonium.

Acronyms and Abbreviations

DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
EAPMW	Environmental Assessment Program Marine Waters
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
et al.	And others
MEL	Manchester Environmental Laboratory
MQO	Measurement quality objective
OFM	Office of Financial Management
QA	Quality assurance
PMEL	Pacific Marine Environmental Laboratory
PN	Particulate Nitrogen
POC	Particulate Organic Carbon
PON	Particulate Organic Nitrogen
QAMP	Quality Assurance Monitoring Plan
QAQC	Quality Assurance Quality Control
RSD	Relative standard deviation
SOP	Standard operating procedures
TA/DIC	Total Alkalinity/Dissolved Inorganic Carbon
TN	Total Nitrogen
TOC	Total Organic Carbon
UW	University of Washington
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
µg/g	micrograms per gram (parts per million)
µg/L	micrograms per liter (parts per billion)
µM	micromolar (a chemistry unit)
µS/cm	microsiemens per centimeter, a unit of conductivity
µmol kg^{-1}	micromoles per kilogram

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)

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)

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)

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)

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)

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)

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

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