DEPARTMENT OF ECOLOGY
State of Washington

Addendum 1 to Quality Assurance Monitoring Plan

Long-Term Marine Waters Monitoring Water Column Program

February 2022

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Addendum 1 to
Quality Assurance Monitoring Plan

Long-Term Marine Waters Monitoring, Water Column Program

by Marine Monitoring Unit (MMU) staff listed below

February 2022

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EAP: Environmental Assessment Program
MMU: Marine Monitoring Unit

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The numbered headings in this document correspond to the headings used in the original QAMP. Only relevant sections are included; therefore, some numbered headings are missing.

3.0 Background

This document describes changes planned for 2022 to the sampling effort by the Department of 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* (Keyzers, Bos, and Albertson, 2020). This Quality Assurance Monitoring Plan (QAMP) addendum specifies which stations and parameters will be sampled during 2022.

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 standard operating procedures (SOPs).

4.0 Project Description

4.4 Tasks required

4.4.1 Data collection

On a year-round, monthly basis, we collect vertical water column profile data for salinity, temperature, dissolved oxygen, turbidity, water clarity, in situ fluorescence, chlorophyll *a*, and dissolved inorganic nutrient species (nitrate, nitrite, ammonium, orthophosphate, silicate), total nitrogen, total organic carbon, particulate organic carbon, particulate nitrogen, dissolved inorganic carbon, and total alkalinity. These are collected at 39 marine water sampling stations, based on directives from the original Puget Sound monitoring plan for the water column.

Sampling is conducted monthly to maintain a long-term record of water column conditions. Year-round sampling is necessary because many parameters, such as chlorophyll, nutrients, salinity and dissolved oxygen, change seasonally. Sampling is conducted during all 12 months to capture hydrographic trends and to provide a complete data set for analysis of temporal trends (MMC, 1988).

Changes for 2022 sampling tasks

As of July 1, 2021, we discontinued the collection of pH data via SeaBird SBE 18 pH sensors due to data quality issues associated with the operation of glass electrodes in waters with salinity gradients. Going forward, pH data will be calculated using dissolved inorganic carbon and total alkalinity data following established methods. See Appendix A: *Memo on changes to methods for the assessment of marine pH* and the referenced article, *Ocean Acidification Monitoring at Ecology's Greater Puget Sound Stations* (Gonski et al., 2019).

5.0 Organization and Schedule

5.1 Key individuals and their responsibilities

Table 1. Roles and responsibilities of staff involved with the Marine Waters Monitoring (MWM) program

All staff work for the Department of Ecology's Environmental Assessment Program (EAP).

Staff Name	Title	Responsibilities
Christopher Krembs MMU, WOS Phone: (360) 407-6675	Senior Oceanographer	Determines monitoring and data assessment strategy. Generates indicators of water quality conditions. Leads data review, analysis, interpretation, and reporting. Develops information products. Writes publications and presentations delivered to the agency and public. Performs and publishes EOPS aerial surveys.
Micah Horwith MMU, WOS Phone: (360) 485-5473	Ocean Acidification Senior Scientist	Coordinates ocean acidification science within Ecology. Provides recommendations to management to address ocean acidification. Oversees data compilation and analysis and reports findings.
Skip Albertson MMU, WOS Phone: (360) 407-6676	Physical Oceanographer	Analyzes and reports on 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.
Julia Bos MMU, WOS Phone: (360) 280-8369	Oceanographer	Manages data workflow, processing, and QA review. Analyzes, and interprets data, and manages data in both the EAPMW and EIM database systems. Generates analytical and QC products and develops tools. Writes reports and data summaries.
Natural Resource Scientist 2 (NRS2) MMU, WOS	Marine Waters Field Lead	Coordinates and conducts field sampling, laboratory analysis, instrument calibrations and instrument maintenance. Records and manages field information. Conducts QA review; analyzes and interprets data. Writes reports and data summaries.
Elisa Rauschl MMU, WOS Phone: (360) 407-6687	Marine Waters Field Scientist	Conducts field sampling, laboratory analysis, instrument calibrations, and instrument maintenance. Records & manages field information. Conducts QA review, analyzes, audits, and interprets data.
Natalie Coleman MMU, WOS Phone: (360) 790-5152	Ocean Acidification Scientist	Provides expertise to OA parameters. Leads/assists with field sampling. Conducts QA review, analyzes, audits, and interprets ocean acidification data. Assists with sensor assessment and annual calibrations. Writes reports and data summaries.
Julianne Ruffner MMU, WOS Phone: (360) 407-6742	Unit Supervisor	Provides internal review of the QAMP and addenda, manages the budget, and approves the final QAMP and QAMP addenda.
Stacy Polkowske WOS Phone: (360) 464-0674	Section Manager	Reviews and approves the final QAMP addendum.
Alan Rue Phone: (360) 871-8801	MEL Director	Reviews and approves the final QAMP addendum.
Arati Kaza Phone: (360) 407-6964	Ecology QA Officer	Reviews the draft QAMP and approves the final QAMP addendum.

EIM: Environmental Information Management database
MEL: Manchester Environmental Laboratory
MMU: Marine Monitoring Unit
QA: Quality Assurance;
QAMP: Quality Assurance Monitoring Plan
WOS: Western Operations Section

5.4 Proposed project schedule

Table 2 provides a summary of the routine activities conducted during a routine sampling year under the monitoring plan.

Table 2. Proposed schedule for completing field and laboratory work, data entry into EIM, and reports.

Field and laboratory work (sample collection & analyses, instrument deployment, and data retrieval)	Due date	Lead staff
Field work (sample and data collection) completed	Monthly	NRS2, N. Coleman, E. Rauschl
Internal laboratory (MML, MEL) analyses completed	1 month post collection (chlorophyll *a* samples, salinity, bath winklers, total organic carbon, total nitrogen, particulate carbon and nitrogen.)	NRS2, N. Coleman, E. Rauschl
External laboratory (UW, PMEL) analyses completed	3 months post collection (nutrients, TA/DIC samples)	NRS2, N. Coleman
Aerial observation photos for Eyes Over Puget Sound (EOPS) survey completed	Once a month or as needed	C. Krembs
Data receipt, processing and upload to EAPMW database		
Instrument and sensor data	Same month as collection	J. Bos, NRS2
Internal laboratory data (MML, MEL)	1 month post analyses	E. Rauschl, NRS2
External laboratory data (UW, PMEL)	3 months post analyses	NRS2, N. Coleman
Data Review and QA/QC (including sensor performance)		
Instrument and sensor data, data adjustments	1 month post collection	J. Bos, S. Albertson, NRS2, C. Krembs, E. Rauschl
Sensor assessment bath and performance tests	1 month pre collection	NRS2, N. Coleman, E. Rauschl
Factory & in-house calibrations	Annually pre collection	J. Bos, N. Coleman, E. Rauschl, NRS2
Internal laboratory data (MML, MEL)	2 months post analyses	E. Rauschl, J. Bos, NRS2, N. Coleman, C. Krembs,
External laboratory data (UW, PMEL)	4 months post analyses	S. Albertson, J. Bos, N. Coleman, M. Horwith, NRS2, C. Krembs, E. Rauschl
Environmental Information System (EIM) database		
EIM Study ID	MarineWater	
EIM data loaded	6 months after sampling year completed	J. Bos, N. Coleman, M. Horwith
EIM data entry review	6 months after sampling year completed	J. Bos, N. Coleman, M. Horwith
EIM complete	6 months after sampling year completed	J. Bos, N. Coleman, M. Horwith
Annual reporting & Performance Measures		
Eyes Over Puget Sound (EOPS) Publication	Monthly or as needed	C. Krembs
PSEMP Puget Sound Marine Waters Report	Annually in April	S. Albertson, J. Bos, C. Krembs
Final data products & QA/QC summarized	Annually in May	C. Krembs, S. Albertson, J. Bos
Final Performance data quality objectives calculated and submitted to Office of Financial Management	Annually in July	J. Bos

MML = Marine Monitoring Laboratory; MEL = Manchester Environmental Laboratory
UW = University of Washington; PMEL = Pacific Marine Environmental Laboratory
TA/DIC = total alkalinity / dissolved inorganic carbon

5.5 Budget and funding

Estimated budgets for 2022 are in Tables 3–5 below. These tables do not include ocean acidification samples (TA/DIC) to PMEL as they are supported by a different funding source. This is not the entire cost of the program as it excludes some items such as staffing, some internal laboratory samples and supplies, and some field equipment costs (e.g., repairs, administrative costs.

Table 3. 2022 budget (estimate) for contract costs of the long-term marine water column monitoring data collection.

Vendor	Cost
SeaBird Scientific Equipment	$20,500
Kenmore Air Harbor Inc.	$25,020
Ecology's R/V Skookum	$28,500
Shannon Point Marine Science Center	$40,440
Total	$114,460

Table 4. 2022 budget (estimate) for internal laboratory (MEL) cost only.

Parameter	Number of Samples	Number of QA Samples	Total Number of Samples	Cost Per Sample	Lab Subtotals
Particulate Organic Carbon and Nitrogen	480	48	528	$46.00	$24,288.00
Total Organic Carbon	480	48	528	$35.00	$18,480.00
Total Nitrogen	480	48	528	$20.00	$10,560.00
				Lab Grand Total:	$53,328.00

Table 5. 2022 budget (estimate) for external laboratory cost only.

Parameter	Number of Samples	Number of QA Samples	Total Number of Samples	Cost Per Sample	Lab Subtotals
Nutrients	1464	144	1620	$16.80	$27,216.00
Salinity	24	0	24	$19.80	$475.20
				Lab Grand Total:	$27,691.20

6.0 Quality Objectives

6.1 Data quality objectives

The main data quality objectives (DQOs) for this project are to (1) collect monthly vertical sensor profile measurements for the entire marine water column, (2) collect water samples from multiple depths at 39 core stations, and (3) analyze all water samples using internal and external laboratory facilities. These objectives will be met by following a detailed sample collection plan (see Section 7.2) which is specific for each station. These are ideal objectives which might change and need to be adjusted for various sampling constraints (e.g., weather, instrument or vessel failures, and programming errors).

The number of results will also vary depending on water depth and tide levels. These results should be representative of the southern Salish Sea and Coastal Bays. The sensor measurements and water sample analysis will use standard methods to obtain results that meet measurement quality objectives (MQOs) that are described below. The results will be used to describe long-term patterns, including status and trends for more comprehensive marine water quality assessments in context of climate, hydrology, and ocean boundary conditions for this region.

6.2 Measurement quality objectives

Tables 6 and 7 show the MQOs for the methods used for sensor measurements and water sample analysis.

6.2.1 Targets for precision, bias, and sensitivity

Table 6. Measurement quality objectives (MQOs) for laboratory analyses of water samples.

Laboratory	Parameter	Relative Percent Difference (RPD) or Relative Standard Deviation (RSD)	Recovery Limits (%)	Reporting Limit[1]	Method Detection Limit (MDL) or Lowest Concentration of Interest
PMEL	Total Alkalinity	<0.5%	<0.25%	NA	±0.1% µmol kg^{-1}
PMEL	Dissolved Inorganic Carbon	<0.5%	<0.25%	NA	±0.1% µmol kg^{-1}
MEL	Particulate Organic Carbon	≤ 20%	±10%	NA	16.5 µg/L
MEL	Particulate Nitrogen	≤ 20%	±10%	NA	0.78 µg/L
MEL	Total Organic Carbon	≤ 20%	±10%	NA	0.12 mg/L
MEL	Total Nitrogen	≤ 20%	±20%	NA	0.014 mg/L
UW MCL	Dissolved Inorganic Nitrate	10%	5%	NA	0.15 µM
UW MCL	Dissolved Inorganic Nitrite	10%	5%	NA	0.01 µM
UW MCL	Dissolved Inorganic Ammonia	10%	5%	NA	0.05 µM
UW MCL	Dissolved Inorganic Orthophosphate	10%	5%	NA	0.02 µM
UW MCL	Dissolved Inorganic Silica	10%	5%	NA	0.21 µM
UW MCL	Salinity	5%	5%	NA	0.002 PSU
MML)	Salinity	5%	NA	NA	0.05 PSU
MML	Chlorophyll *a*	10%	NA	NA	0.02 µg/L

[1] See Table 10

PMEL = Pacific Marine Environmental Laboratory
MEL = Manchester Environmental Laboratory
UW MCL = University of Washington Marine Chemistry Laboratory
MML = Marine Waters Laboratory

Table 7. Measurement quality objectives (MQOs) for field instrument measurement methods.

Measurement - Field	Precision (relative standard deviation, RSD)	Bias (% deviation from true value)	Manufacturer (Model Number)	Mfg reported range	Mfg reported accuracy	Lowest Value
Conductivity	10%	5%	Sea-Bird Electronics (SBE4)	0.0 to 7.0 Siemens/meter (S/m)	0.0003 S/m	1 µS/cm
Density	10%	5%	Sea-Bird Electronics	dependent on T,C	dependent on T,C	0.1 $\square_t$
Dissolved Oxygen	NA	0.45 mg/L at 7.62 mg/L	Precision Sensing (PreSens) Fibox4 + Optode Dipping Probe (PSt3)	0 to 45 mg/L	±0.4% O_2 at 20.9% O_2	.015 mg/L
Dissolved Oxygen	5%	5%	Sea-Bird Electronics (SBE43)	0 to 120% of saturation	2% of saturation	0.05 mg/L
Fluorescence	10%	5%	WET Labs, Inc. (ECOFLNTU)	0 to 50 µg Chl/L	0.025 µg Chl /L	0.1 µg Chl /L
Light Transmission	10%	5%	WET Labs, Inc. (C-Star)	0 to 100%	99% R^2	0.01%
Nitrate	10%	15%	Satlantic SUNA; SUNAV2	0.5 to 2000 µM	±2µM or ±10% of reading, whichever is greater under lab conditions	2.4 µM
Pressure	5%	1%	Sea-Bird Electronics (SBE29 or SBE25plus integrated)	0 to 500m	0.1% of full scale range	0.1 decibars
Temperature	0.025 °C	0.05 °C	Sea-Bird Electronics (SBE3)	-5.0 to +35 °C	0.001 °C	0.01 °C
Turbidity	10%	5%	WET Labs, Inc. (ECOFLNTU)	0 to 25 NTU	0.01 NTU	0.1 NTU

7.0 Study Design

7.2 Field data collection

7.2.1 Sampling locations and frequency

The annual 2022 station routes, map, and sampling plans are listed below in Figure 1 and Table 8.

Regions covered are:

- Coastal Bays
- South Sound
- Hood Canal
- Central Sound
- Admiralty/Whidbey
- San Juan Islands
- Strait of Juan de Fuca

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

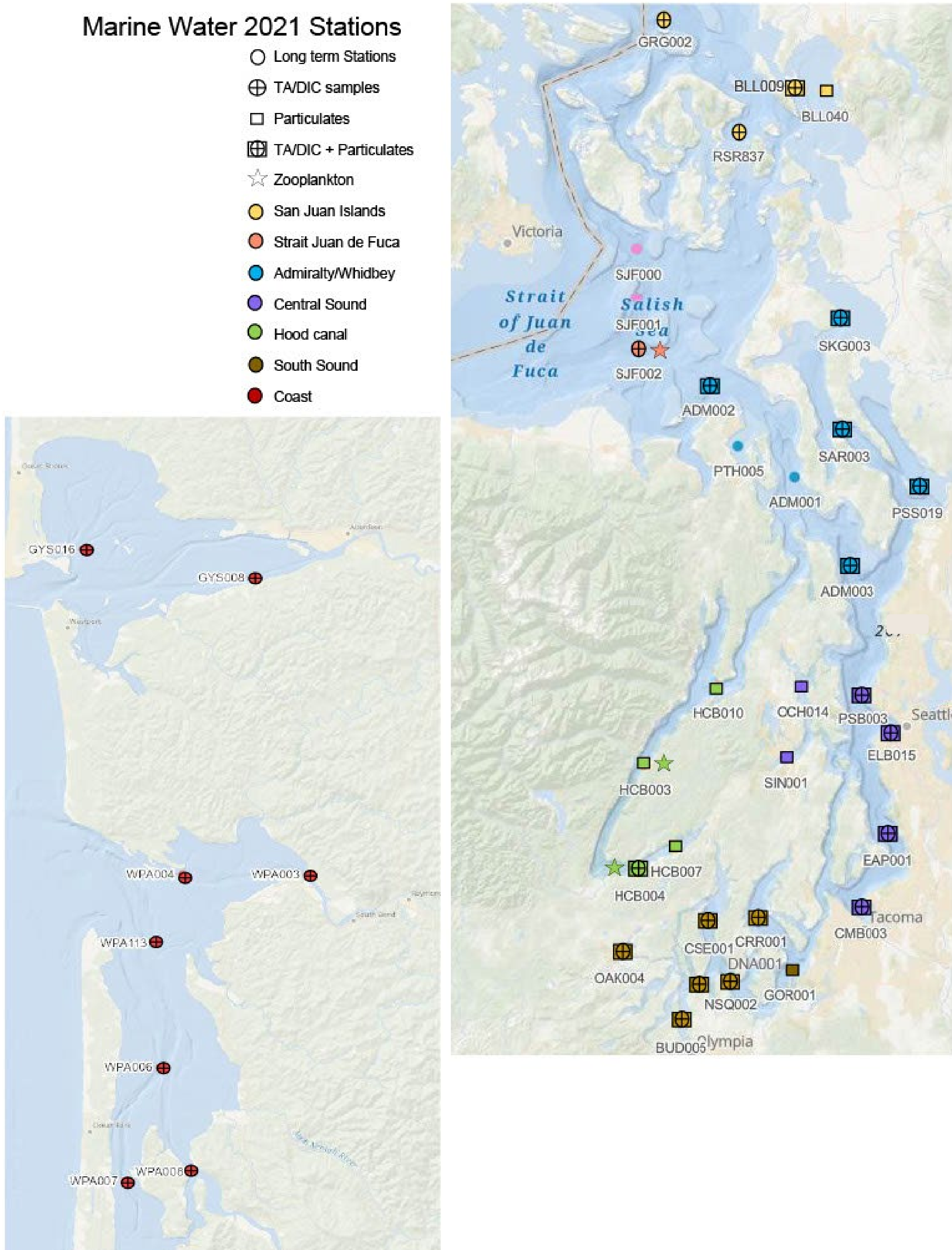

Figure 1. Map of 2022 stations and routes

Table 8. Regional Station Locations

Regional Survey	Station ID	Location	Latitude (N NAD83 (deg.dec min)	Longitude (W NAD83 deg.dec min)	WQMA[a]	Depth (m)	Record	Record Length (yrs)	Justification
Coast	GYS008	Mid-S. Channel	46 56.2388	123 54.793	Western Olympic	6	1974 - 76, 1983 - present	41	represents mid Grays Harbor, south
	GYS016	Damon Point	46 57.2053	124 5.577	Western Olympic	11	1982 - 1987,1991 - present	35	represents outer Grays Harbor, north
	WPA004	Toke Point	46 41.98	123 58.124	Lower Columbia	14	1973-1975, 1977-present	47	represents north Willapa Bay
	WPA113	Bay Center	46 38.64	123 59.580	Lower Columbia	11	2006-present	18	represents mouth of (NW) Willapa Bay
	WPA006	Nahcotta Channel	46 32.7226	123 58.809	Lower Columbia	21	1991-present	29	represents central Willapa Bay
	WPA007	Long Island, S. Jenson Poin	46 27.1893	124 0.567	Lower Columbia	14	1991-2008, 2013-present	25	represents SW Willapa Bay
	WPA008	Naselle River mouth	46 27.789	123 56.476	Lower Columbia	14	1996-2008, 2013-present	20	represents SE Willapa Bay, off Naselle R.
	WPA003	Willapa River, John. Slough	46 42.2392	123 50.243	Lower Columbia	10	1973-present	48	represents north Willapa Bay, off Willapa R.
San Juan Islands	GRG002	Strait of Georgia	48 48.4896	122 57.245	Nooksack/San Juan	190	1988-present	33	represents Strait of Georgia end member
	BLL009	Bellingham Bay	48 41.1564	122 35.977	Nooksack/San Juan	16	1977-present	44	represents waters off city of Bellingham
	BLL040	Bellingham Bay	48 41.0382	122 32.292	Nooksack/San Juan	26	2016-present	5	represents waters off city of Bellingham Bay
	RSR837	Rosario Strait	48 36.9896	122 45.778	Nooksack/San Juan	56	2009-present	12	represents waters in Rosario Strait
Strait of Juan de Fuca	SJF000	Strait of Juan de Fuca	48 25	123 1.500	S. of San Juan Island	180	2000 - present	21	represents northern Strait of Juan de Fuca
	SJF001	Strait of Juan de Fuca	48 20	123 1.500	SE of Hein Bank	160	2000 - present	21	represents central Strait of Juan de Fuca
	SJF002	Strait of Juan de Fuca	48 15	123 1.500	SW of Eastern Bank	145	2000 - present	21	represents southern Strait of Juan de Fuca
Admiralty Inlet - Whidbey Basin	PTH005	Port Townsend	48 4.9889	122 45.877	Eastern Olympic	26	1977-1978, 1991-2002, 2005-presen	30	represents waters off city of Port Townsend
	ADM001	Admiralty Inlet	48 1.7888	122 37.076	Kitsap & Cedar/Green	148	1975-1987, 1992-present	41	represents waters within Admiralty Inlet
	ADM002	N. of Admiralty Inlet	48 11.2391	122 50.577	Island & E. Olympic	82	1980-present	40	represents waters entering Admiralty Inlet
	ADM003	S. of Admiralty Inlet	47 52.739	122 28.992	Kitsap & Cedar/Green	210	1988-1991, 1996-present	27	represents waters S. of Admiralty sills
	SKG003	Skagit Bay	48 17.7893	122 29.376	Island/Snohomish	24	1990-1991, 1994-1998, 2007-presen	21	represents Whidbey Basin
	SAR003	Saratoga Passage	48 6.4557	122 29.493	Island/Snohomish	149	1977-present	44	represents Whidbey Basin
	PSS019	Possession Sound	48 0.6556	122 18.075	Island/Snohomish	101	1980-present	41	represents waters off city of Everett
Hood Canal	HCB007	Hood Canal, Lynch Cove	47 23.8889	122 55.775	Kitsap & E. Olympic	21	1990-1996, 1998-2007, 2010-presen	27	very low DO, assess duration & coverage
	HCB004	Hood Canal, Sisters Point	47 21.3723	123 1.492	Kitsap & E. Olympic	55	1975-1987, 1990-present	44	represents southern Hood Canal
	HCB003	Hood Canal, Eldon	47 32.2722	123 0.576	Kitsap & E. Olympic	144	1976-92, 1994-96, 1998-2007, 2010-	40	very low DO, assess duration & coverage
	HCB010	Hood Canal, S of Bangor	47 40.2	122 49.200	Kitsap & E. Olympic	100	2005-present	16	represents northern Hood Canal
Central	OCH014	Port Orchard Channel	47 40.2924	122 35.971	Bainbridge Basin	20	2019-present	3	represents outer Dyes Inlet
	PSB003	Puget Sound Main Basin	47 39.5891	122 26.575	Kitsap & Cedar/Green	40	1976-present	45	represents Puget Sound Main Basin
	SIN001	Sinclair Inlet	47 32.9557	122 38.608	Kitsap	16	1973-1987, 1991-present	42	represents waters off city of Bremerton
	ELB015	Elliott Bay	47 35.7892	122 22.174	Cedar/Green	82	1991-present	30	represents waters off city of Seattle
	EAP001	East Passage	47 25.0226	122 22.824	Kitsap & Cedar/Green	200	1988-1991, 94-95, 1997-present	29	represents S. Central Puget Sound main axis
	CMB003	Commencement Bay	47 17.4226	122 27.007	outh Central Puget Sou	150	1976-present	45	represents waters off city of Tacoma
South	BUD005	Budd Inlet	47 5.5224	122 55.092	Eastern Olympic	15	1973-present	46	represents waters off city of Olympia
	DNA001	Dana Passage	47 9.689	122 52.308	Eastern Olympic	40	1984-85, 1989-present	34	represents southernmost reach of Puget Sound
	NSQ002	Devil's Head	47 10.039	122 47.291	E. Oly & Kitsap & SPS	100	1984-85, 1996-present	27	represents Puget Sound near Nisqually
	GOR001	Gordon Point	47 10.9891	122 38.074	E. Oly & Kitsap & SPS	160-170	1996-present	24	represents Puget Sound south of Narrows
	CRR001	Carr Inlet	47 16.5891	122 42.575	Eastern Olympic	95	1977-93, 95-96, 1998-2003, 2006,20	36	represents waters within Carr Inlet
	CSE001	Case Inlet	47 15.8724	122 50.658	Eastern Olympic	55	1978-1993, 1995-96,1998-99, 2009-|	32	represents waters within Case Inlet

7.2.2 Field parameters and laboratory analytes to be measured

For the 2022 monitoring year, we plan to use one CTD package to measure hydrographic conditions at each station. The package includes sensors that will measure conductivity (salinity), temperature, depth (pressure), dissolved oxygen, nitrate, in vivo chlorophyll fluorescence, turbidity, and light transmission. Using one CTD package means we (1) will always have a set of replicate sensors in storage, and (2) are able to swap or replace sensors that exhibit issues or damage with a newly calibrated, operational replacement sensor.

Table 9 lists the sensor measurements and lab samples that we will collect in 2022. One change we are making is to analyze the bottle salinity samples in house using a benchtop salinity probe via methods in Coleman, 2021 (in publication, SOP EAP053). Also see Appendix B: *Memo on proposed methods for pilot project of in-house salinity sensor testing*. We will continue to send two salinity bottle samples that we collect from the monthly sensor assessment bath to University of Washington Marine Lab per month for independent verification of sensor operations. The 48 bottles of salinities collected concurrently with TA/DIC samples will be analyzed monthly by the Marine Waters team.

Table 9. Sample types and depths (in meters) for Marine Waters Monitoring (MWM) parameters.

Parameters	Depth (meters)	Parameter Type
Weather & Conditions	NA	Observation
Temperature	0 to Near-bottom	Sensor
Conductivity (salinity)	0 to Near-bottom	Sensor
Dissolved Oxygen	0 to Near-bottom	Sensor
Nitrate	0 to Near-bottom	Sensor
Light Transmission	0 to Near-bottom	Sensor
Turbidity	0 to Near-bottom	Sensor
Fluorescence	0 to Near-bottom	Sensor
Pressure	0 to Near-bottom	Sensor
Chlorophyll *a* and Pheopigments	0, 10, 30, [1]80	Water sample
Dissolved Inorganic Nitrate	0, 10, 30, [1]80, [1]140, Near-bottom	Water sample
Dissolved Inorganic Nitrite	0, 10, 30, [1]80, [1]140, Near-bottom	Water sample
Dissolved Inorganic Ammonium	0, 10, 30, [1]80, [1]140, Near-bottom	Water sample
Dissolved Inorganic Orthophosphate	0, 10, 30, [1]80, [1]140, Near-bottom	Water sample
Dissolved Inorganic Silicate	0, 10, 30, [1]80, [1]140, Near-bottom	Water sample
Total Alkalinity	0, 30	Water sample
Dissolved Inorganic Carbon	0, 30	Water sample
Particulate Organic Carbon	10, Near-bottom	Water sample
Particulate Nitrogen	10, Near-bottom	Water sample
Total Organic Carbon	10, Near-bottom	Water sample
Total Nitrogen	10, Near-bottom	Water sample
Salinity	0, 30	Water sample

[1]80 and 140m samples collected at Strait of Juan de Fuca sites (SJF00#) sites only.

8.0 Field Procedures

8.2 Measurement and sampling procedures

For 2022 marine water column monitoring, the instrument package used will be the SBE25plus "boat package", serial number 1146. This package will be configured to transition between "real-time" user-controlled niskin bottle closure and "pre-programmed" niskin bottle closure controlled by an automatic firing module (AFM). The SBE25plus sampling rate is 16 Hz. To optimize the sample resolution for each 0.5m depth bin, we will lower the CTD at a rate no faster than 0.5 m/sec to meet these sampling objectives:

- The sensors have time to respond to changes in the water column accurately.
- The resulting water column hydrographic structure will have higher resolution, especially in the upper layers where steep gradients may exist.
- Measurement errors due to rapid sampling and steep parameter gradients such as rapid changes in temperature are reduced.

Figure 2. Instrument package (CTD)

Another change for 2022 monitoring is that station sampling will no longer be conducted by floatplane. Monthly site visits will be accomplished using two research vessels: Ecology's boat (R/V Skookum) and Shannon Point Marine Science Center's boats (R/V Magister).

Sampling from a vessel makes it possible to collect more water samples and support collaborations, yet the flexibility to collect rotational stations is more limited. Because vessels can handle more inclement weather such as fog and bigger waves, a vessel provides more opportunities to sample. Samples are collected using a winch attached to the vessel to lower and retrieve instruments and water sampling equipment.

At all core stations, complete CTD profiles of the entire water column are collected. Water sample type collection varies from station to station. Which waters samples are collected at a particular station depends on several factors such as depth, collaborations, budget, and historical precedent and strategic importance.

Table 10 shows the sampling plan for each of the 39 stations, showing which parameters are collected by depth. Samples are collected from 0, 10, 30, 80, 140 meters depth and near-bottom (NB), depending on parameter and location. Replicate samples are also listed for each survey, by depth and location.

Table 10. Individual Sampling Plans for the 39 Stations Sampled Monthly

Route	Parameters								
Station	**Nutrients**	**Chlorophyll**	**POC & PN**	**TOC**	**TN**	**TA/DIC**	**Salinity**	**DO**	**Zooplankton**
Coast	**Depths collected**								
GYS008	0	0				0	0		
GYS016	0,10	0,10				0	0	10	
WPA004	0,10,10,10	0,10,10,10				0	0		
WPA113	0,10	0,10				0	0		
WPA006	0,10	0,10				0	0	10	
WPA007	0,10	0,10				0	0		
WPA008	0,10	0,10				0	0		
WPA003	0,10	0,10				0	0		
Totals:	**17**	**17**	**0**	**0**	**0**	**8**	**8**	**2**	**0**
Hood Canal									
HCB007	0,10,NB	0,10	10,10,NB	10,10,NB	10,10,NB			NB	
HCB004	0,10,10,10,30	0,10,10,10,30				0,30,30	0,30,30	NB	Complete profile vertical tow
HCB003	0,10,30,NB	0,10,30	10,NB	10,NB	10,NB			NB	Complete profile vertical tow
HCB010	0,10,30,NB	0,10,30	10,NB	10,NB	10,NB			NB	
Totals:	**16**	**13**	**7**	**7**	**7**	**3**	**3**	**4**	**2**
South Sound									
BUD005	0,10,NB	0,10	10,NB	10,NB	10,NB	0	0		
DNA001	0,10,30	0,10,30				0,30	0,30		
NSQ002	0,10,30,NB	0,10,30	10,NB	10,NB	10,NB	0,30	0,30		
GOR001	0,10,30,NB	0,10,30	10,NB	10,NB	10,NB			NB	
CRR001	0,10,30,NB	0,10,30	10,10,NB	10,10,NB	10,10,NB	0,30	0,30	NB	
CSE001	0,10,30,NB	0,10,30	10,NB	10,NB	10,NB	0,30	0,30	NB	
OAK004	0,10,10,10	0,10,10,10				0,0	0,0		
Totals:	**26**	**21**	**11**	**11**	**11**	**11**	**11**	**3**	**0**
Central									
OCH014	0,10,NB		10,NB	10,NB	10,NB				
PSB003	0,10,30,NB	0,10,30	10,NB	10,NB	10,NB	0,30	0,30	NB	
SIN001	0,10,NB	0,10	10,NB	10,NB	10,NB				
ELB015	0,10,30,NB	0,10,30	10,10,NB	10,10,NB	10,10,NB	0,30	0,30		
EAP001	0,10,30,NB	0,10,30	10,NB	10,NB	10,NB	0,30	0,30	NB	
CMB003	0,0,0,10,30,NB	0,0,0,0,30	10,NB	10,NB	10,NB	0,30	0,30	NB	
Totals:	**24**	**16**	**13**	**13**	**13**	**8**	**8**	**3**	0
San Juans									
BLL009	0,10,NB	0,10	10,NB	10,NB	10,NB	0	0		
BLL040	0,10,NB		10,NB	10,NB	10,NB			NB	
RSR837	0,10,30	0,10,30				0,30	0,30		
GRG002	0,10,30	0,10,30				0,30,30	0,30,30	NB	
Totals:	**12**	**8**	**4**	**4**	**4**	**6**	**6**	**2**	**0**

Route	Parameters								
Station	**Nutrients**	**Chlorophyll**	**POC & PN**	**TOC**	**TN**	**TA/DIC**	**Salinity**	**DO**	**Zooplankton**
Strait of Juan de Fuca									
SJF000	0,30,80,140	0,30,80						140	
SJF001	0,30,80,140	0,0,0,30,80						140	
SJF002	0,30,80,140,140,140	0,30,80				0,30,30	0,30,30		40-0 & 120-80
Totals:	**14**	**11**	0	0	0	**3**	**3**	**2**	**2**
Admiralty/ Whidbey									
PTH005	0,10, ,30	0,10,10,10,30							
ADM001	0,10,30	0,10,30							
ADM002	0,10,30	0,10,30				0,30	0,30	NB	
ADM003	0,10,30,NB	0,10,30	10,NB	10,NB	10,NB	0,30	0,30		
SKG003	0,10,NB	0,10	10,10,NB	10,10,NB	10,10,NB	0	0		
SAR003	0,10,30,NB	0,10,30	10,NB	10,NB	10,NB	0,30	0,30	NB	
PSS019	0,10,30, NB	0,10,30	10,NB	10,NB	10,NB	0,30	0,30	NB	
Totals:	**26**	**21**	**9**	**9**	**9**	**9**	**9**	**3**	**0**
Monthly Totals:									
Station Count	**Nutrients**	**Chlorophyll**	**POC & PN**	**TOC**	**TN**	**TA/DIC**	**Salinity**	**DO**	**Zooplankton**
39	**135**	**107**	**44**	**44**	**44**	**48**	**48**	**19**	**4**

8.8 Other activities

We will continue to collect zooplankton samples for the Salish Sea Marine Survival Project (SSMSP) at the Strait of Juan de Fuca station, SJF002, along with two vertical net tows for zooplankton at Hood Canal stations HCB003 and HCB004. For more information on SSMSP see *Pacific Salmon Foundation. Salish Sea Marine Survival Project –2017-2018 Research Plan* (Riddell, 2016).

9.0 Laboratory Procedures

9.1 Lab procedures table

Table 11 lists the laboratory methods we will use to analyze water samples during 2022.

Table 11. Laboratory Measurement Methods

Measurement Lab Analyte	Matrix	Expected Range	Reporting Limit	Analytical Methods
Total Alkalinity	Seawater	500-2180 (μmol kg^{-1})	±0.1% μmol kg^{-1}	Dickson et al. (2003); Dickson et al. (2007) (SOP 3b)
Dissolved Inorganic Carbon	Seawater	550-2160 (μmol kg^{-1})	±0.1% μmol kg^{-1}	Dickson et al. (2007) (SOP 2); Johnson et al. (1985, 1987, 1993)
Particulate Organic Carbon	Seawater	40-15000 μg/L	40 μg/L	EAP 440.0
Particulate Nitrogen	Seawater	1-1600 μg/L	5 μg/L	EPA 440.0
Total Organic Carbon	Seawater	1-8 mg/L	0.5 mg/L	SM 5310B
Total Nitrogen	Seawater	0.025-1.00 mg/L	0.025 mg/L	SM 4500NB
Dissolved Inorganic Nitrate	Seawater	0.00 - 40.00 μM	0.15 μM	EPA 353.4; Armstrong, 1967
Dissolved Inorganic Nitrite	Seawater	0.00 - 2.00 μM	0.01 μM	EPA 353.4; Armstrong, 1967
Dissolved Inorganic Ammonium	Seawater	0.00 - 10.00 μM	0.05 μM	EPA 349; Slawyk & MacIsaac, 1972
Dissolved Inorganic Orthophosphate	Seawater	0.00 - 4.00 μM	0.02 μM	EPA 365.5; Bernhardt & Wilhelms, 1967
Dissolved Inorganic Silicate	Seawater	0.00 - 200.00 μM	0.21 μM	EPA 366; Armstrong, 1967
Chlorophyll *a*	Seawater	0.00 - 200.00 μg/L	0.01 mg/L	EPA 445.0
Salinity	Seawater	0.00 - 36.00 PSU	0.002 PSU	UNESCO, 1994
Salinity	Seawater	0.05 – 39.00 PSU	0.05 PSU	Ecology SOP EAP053; Coleman, 2021

12.0 Audits and Reports

12.1 Field, laboratory, and other audits

Every month we conduct data audits on sensor and laboratory data after the data have been processed and uploaded to the EAPMW database. We conduct annual audits for every sampling year after data have been finalized. These audits occur four to six months after the sampling year is completed.

To audit laboratory data, we track, reconcile, and monitor the status of samples delivered to all labs for analyses, and we track any problems that arise. After the sampling year is completed, we conduct several audits to assess overall attainment, identify missing or erroneous results, and summarize overall completeness.

We audit sensor data results from initial collection through data processing and review to finalization. We monitor counts by month and station, auditing at multiple points in the workflow, looking for missing, duplicate, or irregular data results. In the final step, we audit our EAPMW database and, after loading, the agency EIM database. This tracking to determine "conservation of data points" ensures that all data have been flagged appropriately and that no data are overlooked, duplicated, or lost.

12.2 Responsible personnel

Table 12. Staff responsible for data quality assurance and audits

Marine Monitoring Staff	Title	Responsibilities
Christopher Krembs	Senior Oceanographer	Audits of historical sensor and laboratory data sets. Monthly participation in CTD data reviews. Monthly data statistical analysis of bath sensor assessment. Leads routine data finalization work and special data QC & management projects.
Micah Horwith	Ocean Acidification Senior Scientist	Leads data statistical analysis, QA/QC and audits of the TA/DIC and salinity data. Monthly review of the TA/DIC field and laboratory data. Leads routine O.A. data finalization work.
Skip Albertson	Physical Oceanographer	Monthly review of the CTD temperature, salinity, and density data. Rotating data duties to run monthly audits at all stages of QC. Does variety of audits on an as-needed basis. Leads routine data finalization work and special data QC & management projects.
Julia Bos	Oceanographer	Business lead for marine waters data management with EAP Information Technology group; monthly review of CTD dissolved oxygen, and nitrate data. Rotating data duties to run monthly audits at all stages of QC. Conducts routine, historical, and current data audits; leads routine data finalization work and special data QC & management projects.
NRS2	Marine Waters Field Lead	Monthly review of the CTD fluorescence data. Leads the monthly tracking, reconciliation, QA/QC and audits of field and laboratory data. Supports variety of audits on an as-needed bases.
Elisa Rauschl	Marine Waters Field Scientist	Monthly review of the CTD transmissometer and turbidity data. Monthly tracking, reconciliation, QA/QC and audits of field and laboratory data. Supports variety of audits on an as-needed bases.
Natalie Coleman	Ocean Acidification Scientist	Leads the tracking, reconciliation, QA/QC and audits of the TA/DIC and salinity data and other field and lab data. Monthly review of the TA/DIC field and laboratory data. Supports variety of audits on an as-needed basis.

15.0 References

Coleman, Natalie. 2021. Standard Operating Procedure EAP053, Version 1.0: Marine Water Salinity Sample Analysis. (In Publication.) Washington State Department of Ecology, Olympia.

Gonski, S., C. Krembs, and G. Pelletier. 2019. Quality Assurance Project Plan; Ocean Acidification Monitoring at Ecology's Greater Puget Sound Stations. Washington State Department of Ecology, Olympia. Publication 19-03-102. https://apps.ecology.wa.gov/publications/SummaryPages/1903102.html

Riddell, B. 2016. Pacific Salmon Foundation. Salish Sea Marine Survival Project –2017-2018 Research Plan. PSF, 300-1682 West 7th Ave., Vancouver BC Canada V6J 4S6. https://marinesurvivalproject.com/wp-content/uploads/Strait-of-Georgia-Marine-Survival-Research-Plan-2017-2018.pdf

Appendices

Appendix A. Memo on changes to methods for the assessment of marine pH

06/14/2021
prepared by Micah Horwith, Ocean Acidification Senior Scientist

Summary
In 2018 EAP adopted state-of-the-art practices to monitor ocean acidification (OA). The Marine Waters Group (MWG) now collects OA bottle samples to measure dissolved inorganic carbon (DIC) and total alkalinity (TA) through a partnership with the National Oceanic and Atmospheric Administration (NOAA). The exacting accuracy and precision of these data are necessary to detect the gradual effects of anthropogenic CO_2 on marine chemistry amidst natural variation.

Since 1989 the MWG has used glass electrode sensors to monitor marine pH. Best practices in OA science now recommend against the use of glass electrode sensors in marine waters, especially when pH measurements are taken consecutively at stations with different salinities.

DIC and TA data can be used to calculate pH with a high degree of certainty. Comparisons between pH calculated from DIC and TA in bottle samples and coincident pH values from the glass electrode sensor indicate poor sensor performance. To ensure defensible data, the MWG will discontinue the use of glass electrode sensors for pH on 07/01/2021 and thereafter calculate and report pH based on DIC and TA values in OA bottle samples.

Assessing the problem
OA threatens marine ecosystems and human livelihoods, and Ecology is the first state agency in the country to conduct OA monitoring to assess and respond to this threat. Since October 2018, the MWG has collected OA bottle samples at 20 stations across greater Puget Sound each month. EAP contracts with NOAA to analyze DIC and TA in each sample and aims to achieve 'climate-quality' objectives of $\pm 2 \mu mol*kg^{-1}$ for both parameters. In a recent publication, we report that our program is achieving this goal. Our OA data can therefore support decision making on important topics, including the efficacy of CO_2 regulations and nutrient reduction efforts.

The MWG has measured pH using glass electrode sensors on its conductivity-temperature-depth (CTD) package since 1989. To evaluate these data, we compared coincident CTD glass electrode pH to pH calculated from DIC and TA in OA bottle samples from October 2018 to October 2020. We found that CTD glass electrode pH data are unreliable (Fig. A-1):

- CTD glass electrode pH is only weakly correlated with OA bottle pH
- CTD glass electrode pH is off by 0.175 units on average
- Only 48% of CTD glass electrode pH values achieve the manufacturer's stated accuracy

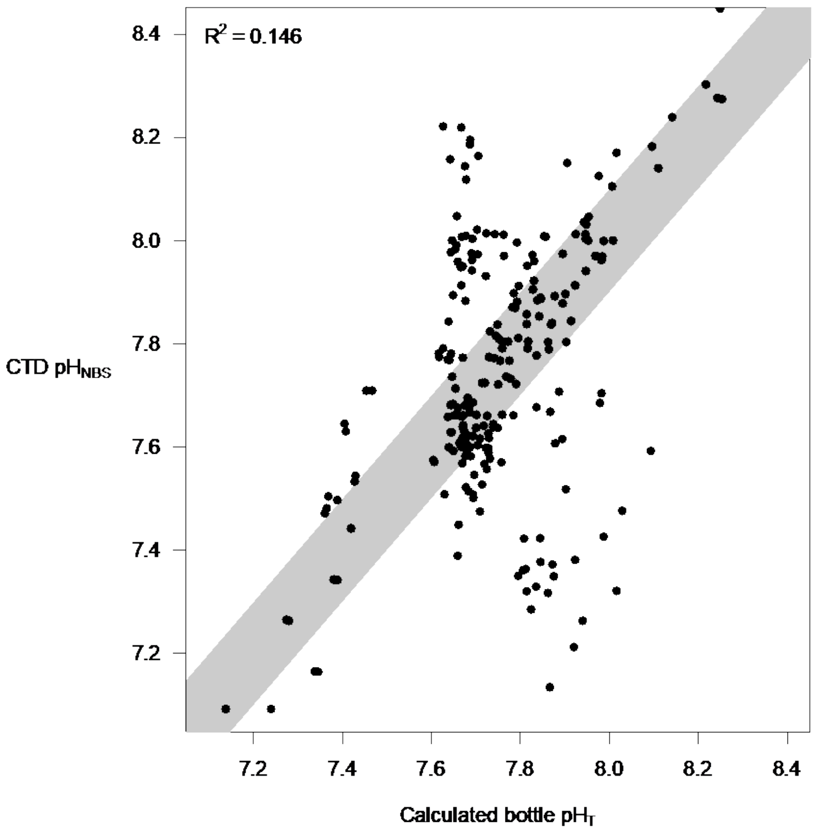

Figure A-1.: pH calculated from OA bottle samples vs. coincident pH from CTD glass electrode sensor. *Shaded area represents manufacturer's stated accuracy of ±0.1 pH units.*

Anthropogenic CO_2 has caused pH in the global oceans to decline by ~0.1 units, and so sensor uncertainty of ±0.175 units is inadequate to assess OA. In comparison, calculated pH from OA bottle samples achieves uncertainty of ±0.003 units.

Best practices for OA science have matured over the past decade, and glass electrodes are no longer recommended for the measurement of marine pH. This is due largely to the effects of shifting ionic strength as glass electrodes move between calibration standards and marine water, or between marine waters with different salinities. For MWG monitoring, this manifests as short-term drift which we can see within a given field day. Station sample order is one of the best predictors of CTD pH (Fig. A-2):

- the CTD glass electrode sensor overestimates pH early in the day
- the CTD glass electrode sensor underestimates pH later in the day

It is difficult to correct for this short-term drift, because it depends on the exact differences in salinity between stations, on calibration practices and media, and on electrode age and material composition. Unfortunately, the historic dataset of glass electrode pH data back to 1989 is likely unsuitable for the analysis of OA conditions. Fortunately, EAP is now collecting and calculating OA data – including pH – that meet the highest standards for data quality.

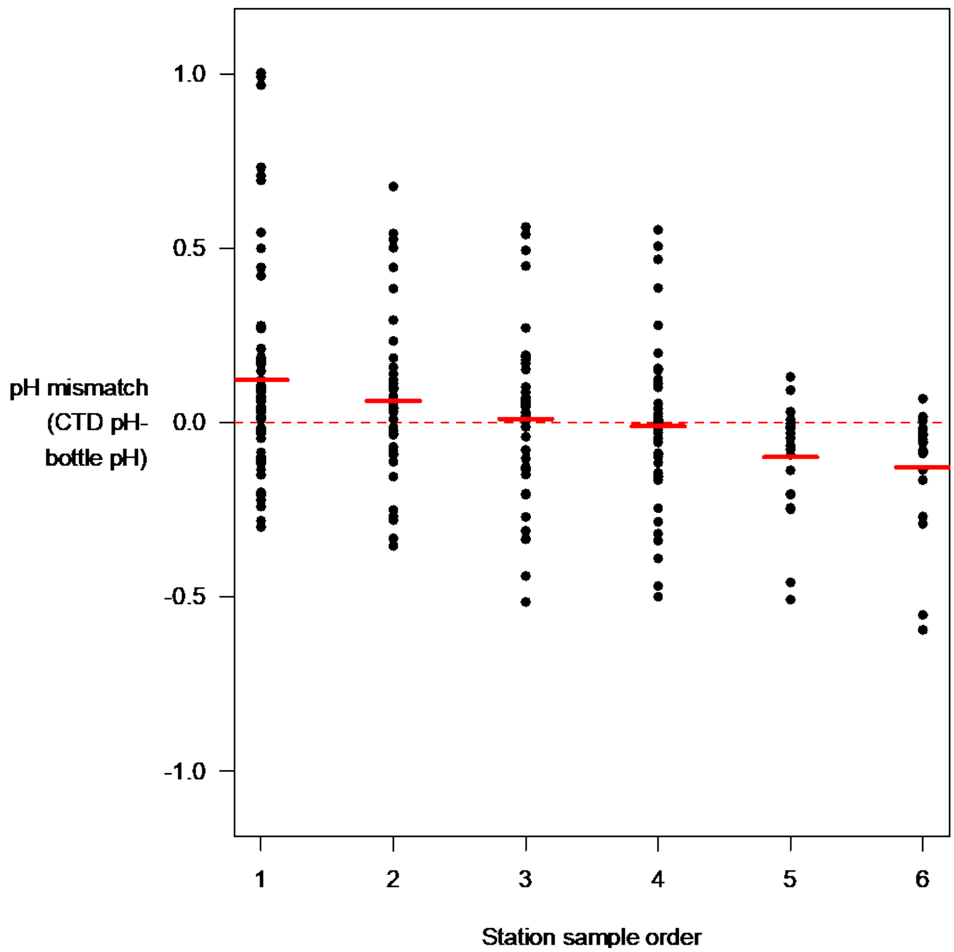

Figure A-2. Station sample order (1 is the first station of the day, and 6 the last) vs. mismatch between CTD glass electrode pH and pH calculated from coincident OA bottle samples.

Solution

We will end the use of glass electrode sensors for pH measurement in marine waters on 07/01/2021. The MWG will continue to calculate and report highly accurate and defensible marine pH data through our OA bottle samples. In the future we may wish to expand the collection of OA bottle samples to better capture regional variation in OA conditions.

In addition to improving the quality of EAP data on marine pH, ending the use of glass electrode sensors will have other benefits. In-house calibration and maintenance of the sensor currently consumes roughly 22 hours per month of staff time, which will be redirected to analysis and reporting of OA data. Manufacturer calibrations and electrode replacements cost thousands of dollars annually, which will be redirected towards other OA science priorities.

As EAP data on marine pH are incorporated into future water quality assessments, we aim to provide the highest quality measurements of regional OA conditions. Washington State and the Department of Ecology have already made substantial investments to monitor OA conditions by following state-of-the-art practices. We have enough evidence to confidently rely on pH data from these new methods, and to discontinue the use of a sensor based on technology that is unreliable in marine waters.

Appendix B. Memo on proposed methods for pilot project of in-house salinity sensor testing

To: Annette Hoffmann, Environmental Assessment Program Manager, and PMT
From: Julianne Ruffner, Marine Monitoring Unit Supervisor
Through: Stacy Polkowske, Western Operations Section Manager
Re: Testing of new salinity sensor
Date: November 23, 2020

<u>Proposed methods for pilot project of in-house salinity sensor testing</u>

Motivation

Salinity is an important variable needed for high precision TA/DIC analysis. We propose to perform an in-house salinity measurements for the support of OA samples in order to significantly reduce the costs and efforts associated with external analysis of salinity samples and sample tracking. Additional benefits include an expedited data turnaround and data quality control to remain in step with other water quality variables from the Marine Monitoring Group.

Proposed steps to ensure highest data quality of salinity measurements supporting OA work

*The following are proposed methods to pilot test an in-house salinity sensor that could eventually replace the external UW lab salinity analysis for the concurrent TA/DIC samples. The verification of present CTD salinity sensors requiring a higher precision for salinity analysis are not part of this proposal. Pending feedback from the group, these measurements would be in addition to the normal UW CTD salinity measurements and would start in December 2020 allowing for a side by side testing of internal and external salinity measurements. If comparisons between UW salinity and this sensor salinity are <0.5% relative percent difference over a period of 3 months we propose to pursue a full change away from UW measured salinity to support OA work while leaving CTD calibrations salinity samples in place.

Ensuring high data by using accepted salinity standards

To preserve the integrity and cost of standards, all 40 salinity samples from 1 month of sampling will be tested using the following methods in one batch before being sent off to UW for concurrent analysis. I've spoken with Aaron Morello at UW and he mentioned many good points about precision and standards that are factored into the following methods. He also offered to sell us the exact standards UW uses every month when we do a delivery, as UW gets a bulk discount.

Cost considerations

*Current salinity analysis from UW costs $880/month and as the first step in the analysis process for Total Alkalinity by NOAA-PMEL, can add additional days to weeks and deliveries to our monthly workflow. Since Covid-19, PMEL no longer will accept and "hold" any samples for TA analysis that don't already have salinity data. This is a change from pre-Covid when they would sometimes store samples for us until we updated them with the salinity information from UW.

Cost and efforts saved

*With this proposed method, the new monthly cost of salinity analysis would be $144/month and would reduce at least one trip to Seattle every month, cutting our wait time for salinity data from days/weeks to the 1.5 hours every month it would take to complete this analysis in house. After the <u>initial cost of $432 and 20 hours of work over 3 months</u>, the monthly savings would be $736 and at least one personnel delivery trip to Seattle using a motor pool vehicle. In addition, in-house analysis may reduce mistakes that can happen in delivery/transfer and handling by multiple people. With the current Covid-19 environment in-house analysis would also reduce exposure of employees, motor pool organization, and delivery scheduling conflicts.

<u>Test of new salinity sensor</u>

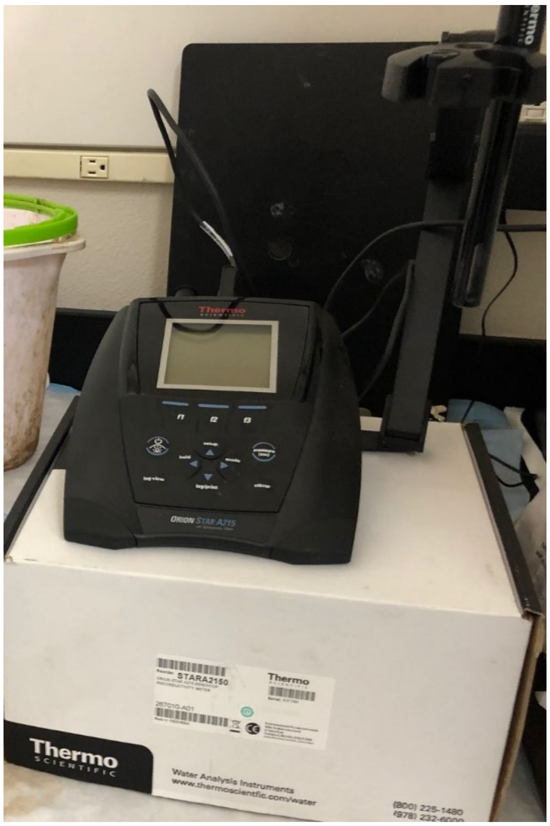

Figure B-1. ThermoFisher Scientific 4-electrode conductivity cell.

These instructions apply to a ThermoFisher Scientific-4 electrode conductivity cell. (Figure B-1)

In between sampling days, leave probe soaking in beaker of 0.692 ppt standard (also the conditioning solution). For longer periods of no use, store probe dry after rinsing with DI water.

After pressing “on” button display should read “sal 0.000 ppt”. If it doesn’t, use “mode” button to change between *cond* and *sal.*

1. The probe should be calibrated before every use using two standards-Low (0.69 ppt, also conditioning solution) and High (35.00 ppt). Standards should be replaced every month.
2. At the beginning of calibration, hit the F1 button under the screen to the left and lower the dry probe into the Low standard so that the entire gap at the bottom of the probe is submerged and hit “next”. The screen should show P1-692 ppm/1413 µS/cm at the top with a large display blinking “ready” until the reading is shown. If the reading matches the known concentration exactly, hit “accept” and then “next” and repeat process with High standard. If

reading does no match, hit "edit" and manually enter the known concentration before moving on to High standard. After High standard step is complete hit "cal done", rinse probe with DI water and dry with KimWipe.

3. Lower probe into beaker of DI water and hit "measure". Wait until ppt reading stabilizes (the blinking light above the numeric display will go from "stabilizing" to "ready"). Reading for DI water must not exceed 0.05 ppt. Dry probe with Kimwipe and move on to sample bottles.
4. Repeat step 3 for measurement of 10.00 ppt standard
5. Decant 40mL of salinity sample from brown field bottle into 40mL glass vial using pipette, then immediately reseal sample bottle. Lower the probe into the vial and hit the "measure" button and wait until ppt reading stabilizes (the blinking light above the numeric display will go from "stabilizing" to "ready"). Record reading, date, and sample number in tracking sheet. Remove probe, rinse with DI water, dry with KimWipe and repeat process with remaining sample vials.

   **Take special care to use separate pipette tips to decant from sample bottle into vial to avoid contamination.*
6. At the end of measuring samples, use "measure" button on the Low and High standards and record values in the tracking sheet with date to see if there is drift over the sampling period.

   **Results from the tracking sheet will be compared to values received from UW to determine if this sensor performs with enough accuracy to make changes to the current QAMP.*

cc: Arati Kaza, Environmental Assessment Program Quality Assurance Officer