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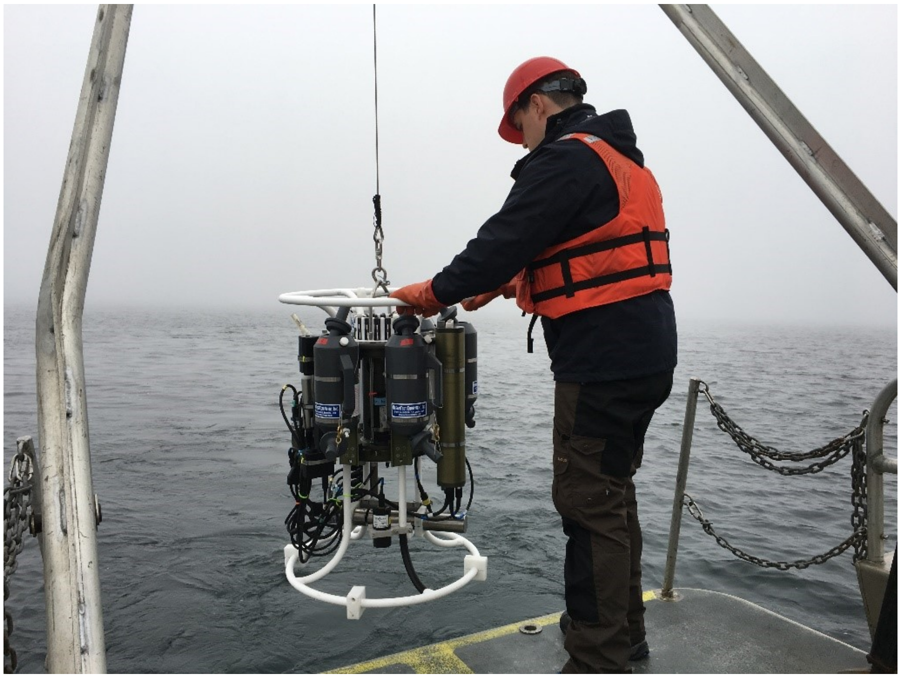

Quality Assurance Project Plan

Ocean Acidification Monitoring at Ecology's Greater Puget Sound Stations

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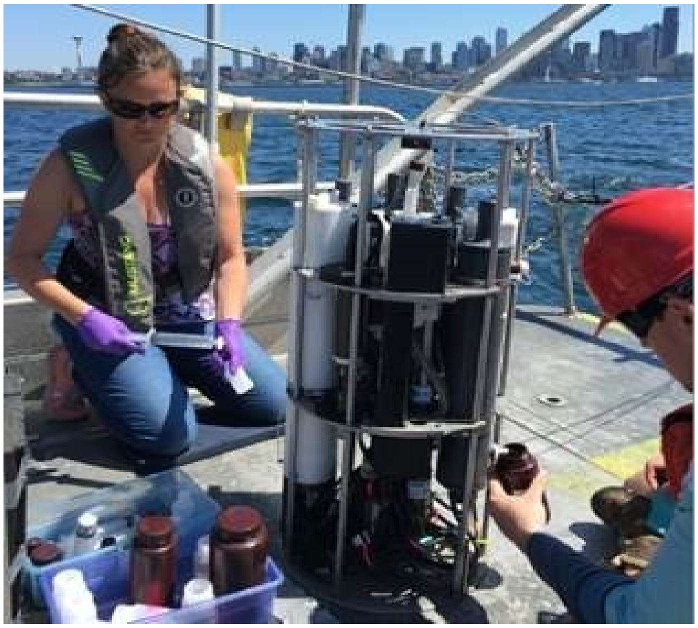

Ecology staff collecting water samples in Elliott Bay by Seattle. Photo taken by Carol Maloy.

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Cover photo: Ecology staff performing marine monitoring work in Elliott Bay by Seattle. Photo taken by Carol Maloy.

Quality Assurance Project Plan

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January 2019

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EAP: Environmental Assessment Program

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2.0 Abstract

The Washington State Department of Ecology (Ecology) is conducting a large-scale study to characterize the spatiotemporal variability of total dissolved inorganic carbon (DIC) and total alkalinity (TA) in Puget Sound as well as the greater Salish Sea. This work will enhance the frequency and coverage of existing monitoring, and provide an avenue for continued monitoring of these ocean acidification (OA) relevant parameters in Puget Sound and the Salish Sea. This will expand marine CO_2 chemistry and OA data records across the diverse spectrum of seascapes spanning from freshwater- to marine-dominated systems within Puget Sound and the Salish Sea.

Ecology will accomplish this with the following steps:

- Quantify ocean acidification (OA) relevant parameters (DIC and TA) in Puget Sound and the Salish Sea over space, time, and depth.
- Integrate marine, estuarine, and river alkalinity measurements to ensure consistency of analysis and reporting so that the land-ocean influences of climate change may be characterized.
- Conduct comparative exploratory analysis of the Salish Sea Model (SSM) output and observations to uncover notable features or relationships to investigate further. (For background on the Salish Sea model, see section 3.1.)

The focus of this study will be to:

- Determine the range of DIC and TA at 20 of the 39 stations in Ecology's long-term marine monitoring network.
- Assess the regional and seasonal marine CO_2 chemistry and OA dynamics in the upper water column of estuarine and marine systems across the Salish Sea.

3.0 Background

3.1 Introduction and problem statement

When carbon dioxide (CO_2) is absorbed by seawater, it forms carbonic acid ($\mathrm{H_2CO_3}$), a weak acid which releases hydrogen ions ($\mathrm{H^+}$) and reduces the pH of seawater upon dissociation into bicarbonate ($\mathrm{HCO_3^-}$) and carbonate ($\mathrm{CO_3^{2-}}$) ions. This collection of chemical transformations is often referred to as ocean acidification (OA). In turn, OA drives changes in the marine CO_2 system by (1) increasing total dissolved inorganic carbon (DIC) and partial pressure of CO_2 ($p\mathrm{CO_2}$) and (2) reducing the $\mathrm{CO_3^{2-}}$ ion concentration and saturation states of biologically important calcium carbonate ($\mathrm{CaCO_3}$) minerals such as aragonite (Ω_{Arag}) and calcite (Ω_{Calc}).

Alkalinity plays an important part in how well seawater can buffer subsequent acidification mediated by the absorption of CO_2. 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, seawater is supersaturated with respect to $\mathrm{CaCO_3}$ minerals ($\Omega > 1$) providing favorable conditions for calcifying organisms to build their skeletons and shells. However, continued ocean acidification or a reduced capacity of the water to buffer the absorption of CO_2 and transformation into $\mathrm{H_2CO_3}$ over time is causing marine waters to become more corrosive and undersaturated with respect to $\mathrm{CaCO_3}$ minerals ($\Omega < 1$), specifically aragonite. Such conditions favor mineral dissolution and negatively affect the ability of calcifying organisms to produce and maintain their skeletons and shells (Millero, 2013; Zeebe and Wolf-Gladrow, 2001).

The traditional definition of OA (described above) is largely restricted to the open ocean. The open ocean's relative isolation from population centers and terrestrial inputs insulate it from the range of processes that modulate and contribute to more pronounced changes in the marine CO_2 system of estuarine and coastal ocean environments (Duarte *et al.*, 2013). Estuaries and the coastal ocean are part of the "coastal zone" and are among the most biogeochemically active environments on the planet (Borges *et al.*, 2005). In the coastal zone, acidification is driven by a complex interplay of biological, chemical, and physical processes that vary in scale among different geographical regions (Duarte *et al.*, 2013). One physical process that can affect acidification within the coastal zone is upwelling along the continental shelf, which brings deep water with high inorganic nutrients, low oxygen, and low pH landward (Feely *et al.*, 2008). Also, river discharge often transports freshwaters depleted in alkalinity, calcium ($\mathrm{Ca^{2+}}$), and $\mathrm{CO_3^{2-}}$ ions relative to marine waters (Harris *et al.*, 2013; Moore-Maley *et al.*, 2016), reducing seaward buffering capacities and $\mathrm{CaCO_3}$ mineral saturation states (Moore-Maley *et al.*, 2016; Vargas *et al.*, 2016).

Net community production, or the balance between photosynthesis and respiration, modulate acidification in the coastal zone as these biological processes act as CO_2-consuming and CO_2-producing processes, respectively. (Aufdenkampe *et al.*, 2011; Duarte *et al.*, 2013). Additionally, changes in river DIC and/or TA over time alter DIC and alkalinity export and buffer capacity and acidification in the coastal zone (Cai *et al.*, 2008; Ingrosso *et al.*, 2016; Raymond and Cole, 2003; Raymond *et al.*, 2008). This happens through a combination of changes in chemical and/or physical weathering within watersheds, land use practices, and freshwater delivery. Because of the numerous processes influencing marine CO_2 chemistry and acidification in the coastal zone, acidification rates in this environment are often an order of magnitude greater than those observed in the open ocean (Duarte *et al.*, 2013; Provoost *et al.*, 2010; Wootton and Pfister, 2012). Accordingly, focused and intensive studies of the magnitude and drivers of acidification in estuaries and the coastal ocean are warranted (Kapsenberg *et al.*, 2017).

The marine CO_2 system is comprised of four measurable parameters: TA, DIC, pCO_2, and pH. Using any two measured parameters, the remainder of the marine CO_2 system can be constrained and the remaining marine CO_2 system parameters can be calculated including Ω_{Arag}, Ω_{Calc}, and $\mathrm{HCO_3^-}$ and $\mathrm{CO_3^{2-}}$ ion concentrations (Dickson *et al.*, 2007). Marine CO_2 system calculations can be performed in programs such as CO2SYS (Pierrot *et al.*, 2006) or Seacarb (Gattuso *et al.*, 2016). This requires using two measured marine CO_2 system parameters together with *in situ* temperature, salinity, nutrients (specifically phosphate $(\mathrm{PO_4^{3-}})$ and silicate $(\mathrm{SiOH_4})$), and the required sets of dissociation constants (Dickson *et al.*, (2007). For further discussion of these calculations, please see Section 14.3.

In recent years, the Washington State Department of Ecology (Ecology) performed a pilot study to test the feasibility of adding sampling for DIC and TA from a floatplane to the ongoing Marine Flight Program (Keyzers, 2014, 2016). While collecting samples for DIC and TA from a floatplane was not deemed feasible (Keyzers, 2016), the marine CO_2 system data generated from the first phase of this project provided valuable insights into the seasonal variability of Ω_{Arag} in the surface waters of Puget Sound (Pelletier *et al.*, 2018).

The work conducted for this QAPP will serve as Phase II of that work. Phase II will expand and refine Ecology's OA monitoring efforts in Puget Sound and the Salish Sea, and will hereafter be referred to as the **O**cean Acidification **M**onitoring at **E**cology's **G**reater Puget Sound St**A**tions (OMEGA) Project. Sampling will be performed by boat, enabling water collection from Niskin bottles that are integrated with conductivity-temperature-depth (CTD) sensor packages thereby replacing water sample collection using a peristaltic pump on a floatplane. Niskins will allow collection of defined water samples from multiple depths in the water column, thereby expanding the previously restricted and poorly defined sampling of water near the surface (Keyzers, 2016). An additional benefit of sampling by boat is the elimination of the spatiotemporal mismatches between DIC and TA samples and CTD measurements caused by floatplane drift. This should improve agreement between pH calculated from DIC and TA and CTD pH measurements collected using a SeaBird SBE 18 pH sensor. It also has the potential to facilitate a retrospective investigation of Ecology's large historical pH dataset (Keyzers, 2014, 2016).

OMEGA will be carried out in cooperation with the Salish Sea Modeling Team within the Environmental Assessment Program (EAP) at Ecology. The Salish Sea Model (SSM) was developed by Pacific Northwest National Laboratory in collaboration with Ecology and the U.S. Environmental Protection Agency (EPA). The SSM is a three-dimensional circulation and water quality model that simulates the processes affecting dissolved oxygen (DO) and water quality throughout the Salish Sea, which includes Puget Sound (McCarthy *et al.*, 2018). In recent years, the SSM was expanded to incorporate marine CO_2 system and ocean acidification modeling capabilities by adding DIC and TA as state variables and accounting for a range of *in situ* biogeochemical processes that produce and consume DIC and TA (Pelletier *et al.*, 2017). When the model was calibrated to 2008 conditions, SSM simulations identified a number of areas of concern for present and future acidification that included portions of South Sound, Port Susan, Skagit Bay, Whidbey Basin, and central Puget Sound (Bianucci *et al.*, 2018; Pelletier *et al.*, 2017).

Our ability to use the SSM as a tool to evaluate human impacts on water quality conditions in the Salish Sea hinges on the availability of representative environmental data (McCarthy *et al.*, 2018). Recent, comprehensive, and spatially representative datasets of Salish Sea and Puget Sound DIC and TA as model inputs and validations are needed. These will improve the model's ability to characterize current OA dynamics and model utility when evaluating sensitivity of OA dynamics in response to current and future spatial and temporal changes in DIC and TA (Bianucci *et al.*, 2018; McCarthy *et al.*, 2018; Pelletier *et al.*, 2017). To close the data gaps, sampling for DIC and TA will be expanded from 6 to 20 of the 39 stations in Ecology's long-term marine monitoring network across the Salish Sea. The station locations include many of the areas of concern for previously identified acidification. For information regarding the specific locations to be sampled, please see Section 7.2.1.

3.2 Study area and surroundings

U.S. waters of the Salish Sea

The Salish Sea extends from the north end of the Strait of Georgia and Desolation Sound to the south end of the Puget Sound and west to the mouth of the Strait of Juan de Fuca including the inland marine waters of Washington (USA) and southern British Columbia (Canada). These separately named bodies of water form a single estuarine ecosystem, the Salish Sea (Figure 1).

The Puget Sound study area is part of the larger Salish Sea ecosystem, and regional and local Puget Sound processes are influenced and regulated by large-scale ocean and climate drivers. Other influences include the hydrodynamic connection and exchange between basins of the Salish Sea as well as seaward-flowing freshwater inputs entering the Salish Sea.

The Salish Sea is connected to the Pacific Ocean primarily via the Strait of Juan de Fuca (with relatively slight tidal influence from the north around Vancouver Island and through Johnstone Strait). The Strait of Juan de Fuca is bounded by Vancouver Island and the Olympic Peninsula. In addition to the Gulf Islands and the San Juan Islands, the watershed contains the lower Fraser River Delta and the Puget Lowlands as well as Hood Canal, Tacoma Narrows, and Deception Pass (Freelan, 2009).

The geomorphology of the area includes a variety of landforms with interconnected shallow estuaries and bays, deep glacially scoured basins and fjords, and broad channels and river mouths. It is bounded by three major mountain ranges: the Olympics to the west, the mountains of Vancouver Island to the north, and the Cascade Range to the east. A regional depression extends from British Columbia to Oregon and includes the Puget lowlands between the Olympic and Cascade Mountains. The Puget Sound region of the Salish Sea is the flooded area of these lowlands (Burns, 1985).

The Puget Sound study area defined by the Marine Waters Monitoring Program encompasses marine basins, channels, and embayments in northwest Washington from the U.S./Canada border to the southern-most inlets near Olympia and Shelton; this includes Puget Sound proper, Whidbey Basin, Hood Canal, and portions of Admiralty Inlet, the San Juan Islands, and the eastern portion of the Strait of Juan de Fuca **(**Figure 2). The study area extends for about 200 km and ranges in width from 10 to 40 km (Kennish, 1998).

Figure 1. Map of U.S. and Canadian waters of the Salish Sea, courtesy of Stephen Freelan, Western Washington University, 2009.

Puget Sound basins

The Strait of Juan de Fuca connects to the Strait of Georgia via Haro Strait on the west side of San Juan Islands and via Rosario Strait to the east of this island group. Boundary Bay, Bellingham Bay and Padilla Bay all border the Straits to the east. South of this junction, Puget Sound is connected to the Strait of Juan de Fuca primarily via Admiralty Inlet. This region is referred to as the San Juan/North Sound region by the MWM program. Puget Sound is also connected less significantly to the eastern straits via Deception Pass at the north end of Whidbey Island and through Swinomish Slough which connects Skagit and Padilla Bays. The Puget Sound study area is further subdivided bathymetrically into four basins, where each basin is a depression and is separated from the others by a barrier (sill) or a shoaling of the seafloor.

The entrance to the Main Basin of Puget Sound is constricted by a sill at Admiralty Inlet, and includes both Admiralty Inlet and the Central Basin. Whidbey Basin connects to the Main Basin to the east, and as there is no true sill defining this basin, it is considered an appendage to the Main Basin. Both Whidbey and Central Basins are defined by deep passages, river deltas, mudflats, tidelands, and island shorelines. South Puget Sound is separated from the Central Basin by a sill and a constricted passage called Tacoma Narrows. This basin consists of deep passages, many islands, and multiple finger inlets; it has the most shoreline of any of the basins. Hood Canal is the smallest of the Puget Sound basins, and connects to the west side of the Main Basin at Admiralty Inlet. It has limited tidelands, bays, coves and mudflats in contrast to the other basins. South of the entrance to Hood Canal lies a shallow sill, constricting exchange between Hood Canal and the Main Basin (Burns, 1985).

Puget Sound has depths up to 300 m; its depth over the sills that constrict water exchange ranges from 44 m at the Narrows to 60 m at Admiralty Inlet. Puget Sound has an area of 2632 km^2, a volume of 168 km^3, 2141 km of shoreline and 303 km^2 of tideland (Burns, 1985).

Circulation in Puget Sound is driven by a complex mix of freshwater inputs, tides, and winds. Puget Sound has been characterized as a two-layered estuarine system with marine waters entering at the sill in Admiralty Inlet from the Strait of Juan de Fuca at depths of 100 to 200 m and freshwater entering from a number of large streams and rivers. The Fraser River in British Columbia is the largest freshwater source in the Salish Sea region and directly influences the San Juan Islands and eastern Straits area. Major rivers entering Puget Sound include the Skagit, Stillaguamish, Snohomish, Cedar, Duwamish, Puyallup, and Nisqually (Figure 2). The Skagit, Stillaguamish, and Snohomish rivers account for more than 75% of the freshwater input into the Sound.

Up to two-thirds of the freshwater outflow in Puget Sound is downwelled upon reaching Admiralty Inlet, mixed with deep ocean water and recirculated in the Sound (Ebbesmeyer *et al.*, 1984). This causes residence time for water in the Central basin to range from 160 to 290 days in isolated inlets and restricted deep basins in Hood Canal and southern Puget Sound (Khangaonkar *et al.*, 2012).

Both relatively undeveloped rural areas and highly developed urban and industrial areas border the Puget Sound. Approximately 17% of the watershed tributary to U.S. waters of the Salish Sea is developed land that represents a combination of residential, commercial/urban, and agricultural lands or alpine areas (Herrera, 2011). Major urban centers include the cities of Bellingham, Everett, Seattle, Bremerton, Tacoma, and Olympia, all of which are located at the mouths of large river systems that feed into Puget Sound's largest estuarine embayments. Approximately 7 million people live within the drainage basin of the Salish Sea (sometimes referred to as the Puget Sound – Georgia Basin watershed); this population includes the cities of Vancouver, Victoria, Nanaimo, Port Angeles, and Port Townsend, in addition to the Puget Sound cities mentioned above (Freelan, 2009).

Figure 2. Ecology Marine Waters Monitoring study sites in Puget Sound and Coastal Bay study areas.

3.2.1 History of study area

The earliest routine observations of water properties in Puget Sound date back to June, 1932, when the Department of Oceanography at the University of Washington (UW) conducted longitudinal surveys of Puget Sound basins aboard the R/V Brown Bear. Surveys continued throughout the 1950s, 60s, and 70s. Measurements were taken routinely for salinity, temperature, and dissolved oxygen. Silicate, nitrate, nitrite, alkalinity, orthophosphate, and other parameters were measured at select stations (Collias *et al.*, 1970). Since this trailblazing work was undertaken, Marine Ambient Monitoring in Puget Sound and the greater Salish Sea has continued in various forms up to the present day. For a more thorough discussion of the history of Marine Ambient Monitoring in Puget Sound and the Salish Sea, please see Bos *et al.* (2015).

3.2.2 Summary of previous studies and existing data

Fassbender *et al.* (2018) performed a systematic data compilation of marine CO_2 system data spanning the entire U.S. Pacific Northwest including data for Puget Sound and U.S. Territorial Waters of the Salish Sea. This paper provides maps and tables summarizing the geographical locations, observation periods, measured parameters, numbers of measurements, and data storage locations for existing marine CO_2 chemistry datasets collected during hydrographic cruises. Also summarized in this paper are data gathered through monitoring buoys, moorings, and other monitoring activities by the following groups:

- Washington State Department of Ecology.
- National Oceanic and Atmospheric Administration (NOAA).
- University of Washington (UW).
- Washington Ocean Acidification Center (WOAC).
- Other agencies and programs within the study area.

Fassbender *et al.* (2018) also established average monthly DIC and TA seasonal cycles for several major regions of the Salish Sea over the observation period of the aggregated dataset (1970 – 2015). However, the problem with adhering to reported average ranges is that these data ranges tend to be biased toward the portion of the range with the most measurements and may not reflect the full DIC and TA ranges in the Salish Sea (Feely *et al.*, 2010; Pelletier *et al.*, 2018).

Marine CO_2 system data from Canadian Territorial Waters of the Salish Sea (mainly Strait of Georgia, the Fraser River Delta, Haro Strait, and the northern Strait of Juan de Fuca) are summarized in Ianson *et al.* (2016), Moore-Maley *et al.* (2016), and Moore-Maley *et al.* (2018). The Department of Fisheries and Oceans (DFO), Environment and Climate Change Canada, and University of British Columbia collected these data between 2001 and 2016. The same active dataset is used across all three publications.

These studies (and numerous others not explicitly discussed) have resolved the seasonality and temporal variability of the marine CO_2 system in different regions of the Salish Sea and established expected DIC and TA ranges representative of Puget Sound and the Salish Sea. For further context, DIC and TA ranges published from previous marine CO_2 chemistry studies in the Salish Sea are presented in Table 1.

Table 1. Measured DIC and TA ranges from previous studies in our study area.

Study	**Region of Salish Sea**	**TA (µmol kg^{-1})**		**DIC (µmol kg^{-1})**	
		Min	**Max**	**Min**	**Max**
Fassbender *et al.*, 2018	U.S.	1795	2140	1628	2075
Feely *et al.*, 2010	U.S.	2018	2129	1881	2053
Pelletier *et al.*, 2018	U.S.	1510	2021	1431	2038
Ianson *et al.*, 2016; Moore-Maley *et al.*, 2016; Moore-Maley *et al.*, 2018	Canadian	1100	2300	1050	2300

3.2.3 Parameters of interest and potential sources

Primary parameters of interest for the present study include ocean acidification relevant parameters of total dissolved inorganic carbon (DIC) and total alkalinity (TA). Secondary parameters of interest include pH, temperature, salinity, and nutrients already collected as a part of Ecology's Long-Term Marine Waters Monitoring, Water Column Program (Bos *et al.*, 2015). For further discussion of the Quality Objectives, Methods, Quality Control Procedures, and Data Verification protocol for secondary parameters of interest, please see Bos *et al.* (2015) and Brownlee (2018).

Dissolved inorganic carbon exists as four species in aquatic systems: aqueous carbon dioxide $\left(\mathrm{CO_2(aq)}\right)$, carbonic acid $(\mathrm{H_2CO_3})$, bicarbonate $(\mathrm{HCO_3^-})$, and carbonate $(\mathrm{CO_3^{2-}})$. In solution, the first two species are relatively difficult to distinguish from one another and are often together referred to as $\mathrm{CO_2^*}$. The equilibrium speciation of dissolved inorganic carbon in aquatic systems is governed by pH and temperature, meaning changes in either parameter changes the relative proportions of each species. For example, at pH 4.3, pH 8.3, and pH 12.6, the dominant inorganic carbon species are $\mathrm{CO_2^*}$, $\mathrm{HCO_3^-}$, and $\mathrm{CO_3^{2-}}$, respectively (Zeebe & Wolf-Gladrow, 2001).

DIC is supplied to aquatic systems within the coastal zone through:

- CO_2 from the atmosphere from the burning of fossil fuels.
- Delivery of DIC from rivers and other point (e.g., wastewater treatment plants) and non-point (terrestrial runoff) sources.
- Mixing with groundwater.
- Landward transport of upwelled waters from the continental shelf.
- Direct addition from precipitation.
- Exchange with benthic sediments.
- Biogeochemical processes that produce CO_2 like heterotrophic respiration (Cai *et al.*, 2003; Millero, 2013).

Dissolved organic carbon (DOC) or dissolved organic matter (DOM) supplied to aquatic systems by a number of the aforementioned pathways can also be respired and oxidized into DIC. *In situ* biogeochemical transformation of DOC and DOM into DIC will also contribute to DIC inventories (Millero, 2013).

Total alkalinity in aquatic systems is mainly comprised of bicarbonate, carbonate, borate, and silicate alkalinity with smaller contributions from nitrogen, phosphorous, and sulfur species (Dickson *et al.*, 2007). Alkalinity in aquatic systems is primarily derived from the chemical and/or physical weathering of the carbonate, silicate, and other minerals on land and within watersheds; it is then delivered to the aquatic system by rivers, groundwater, and other point and non-point sources (Cai *et al.*, 2003; Millero, 2013). A small fraction of alkalinity can also be derived from organic compounds of various types (Cai *et al.*, 1998; Hammer *et al.*, 2017). Within aquatic systems, alkalinity can be also produced (added) and consumed (removed) through a host of biogeochemical processes (Millero, 2013) as well as added to or sequestered from aquatic systems through exchange with benthic sediments (Lukawska-Matuszewska *et al.*, 2018; Millero, 2013).

3.2.4 Regulatory criteria or standards

Marine pH calculated from DIC and TA data generated by this study will be used for evaluation of compliance with the Washington State water quality standards for marine pH (better known as the Aquatic Life pH Criteria in Marine Water) established under Washington Administrative Code (WAC) 173-201A-210. Current compliance targets for this parameter are summarized below in Table 2.

Table 2. Washington State Aquatic Life pH Criteria in Marine Water.

Use Category	**pH Units**
Extraordinary quality	pH must be within the range of 7.0 and 8.5 with a human-caused variation within the above range of less than 0.2 units
Excellent quality	pH must be within the range of 7.0 and 8.5 with a human-caused variation within the above range of less than 0.5 units
Good quality	Same as Excellent quality
Fair quality	pH must be within the range of 6.5 and 9.0 with a human-caused variation within the above range of less than 0.5 units

The data will also be integrated into marine CO_2 chemistry datasets utilized as part of the broader regional OA community work to distinguish between natural variability and regional and global anthropogenic variations in the marine CO_2 system of the Salish Sea. In addition, the data will likely be used in the future if there are evaluations for potential new water quality standards for OA variables (e.g., Ω_{Arag} and/or thresholds for adverse effects on pelagic and benthic calcifiers).

3.3 Water quality impairment studies

This section is not applicable to the current work.

3.4 Effectiveness monitoring studies

This section is not applicable to the current work.

4.0 Project Description

4.1 Project goals

- Quantify parameters relevant to ocean acidification (OA) such as total dissolved inorganic carbon (DIC) and total alkalinity (TA), in Puget Sound and the Salish Sea over space, time, and depth.
- Integrate marine, estuarine, and river alkalinity measurements to ensure consistency of analysis and reporting so that the land-ocean influences of climate change may be characterized.
- Conduct comparative exploratory analysis of the Salish Sea Model (SSM) output and observations to uncover notable features or relationships to be further investigated.

4.2 Project objectives

1. Collect 960 water samples for analysis of DIC and TA from 20 stations at two depths (0 and 30 m). Samples will be collected by boat over a 24-month observation period across Puget Sound and the larger Salish Sea.
2. Collect simultaneous nutrient and salinity samples alongside DIC and TA samples already integrated into Ecology's Long-Term Marine Waters Monitoring, Water Column Program.
3. Perform hydrocasts of conductivity-temperature-depth (CTD) sensors to collect accompanying oceanographic (temperature and salinity) data to be used with DIC and TA samples.
4. Explore historical TA datasets from the Salish Sea and ensure collected TA data adheres to appropriate analysis and reporting practices across the entire salinity (S) gradient from freshwater (S=0, rivers) to seawater (S=35, open ocean).
5. Provide DIC and TA data of acceptable quality to serve as model inputs in separate work to recalibrate the Salish Sea Model (SSM) to more recent datasets (relative to past work using a DIC and TA dataset from 2008 detailed in Pelletier *et al.* (2017)).
6. Provide DIC and TA data of acceptable quality that will be used in separate work to validate SSM simulations.
    - Assess model skill in recreating marine CO_2 chemistry and OA dynamics embodied in the collected data.
    - Identify anomalies between model output and measured data to be targeted for further investigation.

4.3 Information needed and sources

The types of data of to be collected for OMEGA are equivalent to the data collected during Phase I (Keyzers, 2014, 2016). Briefly, samples for DIC, TA, and nutrients will be collected at selected monitoring stations. Temperature and salinity data taken from CTD output will also be used in concert with those samples; however, salinity samples will be collected more frequently for this project than they currently are under Ecology's Long-Term Marine Waters Monitoring, Water Column Program. For more information, please see Sections 7.2.2 and 10.1.

Existing historical marine CO_2 chemistry datasets that will be used to provide context for the present work are discussed in Section 3.2.2. The collected DIC and TA data only comprise a very small part of the data required for the SSM. The data needs of the SSM are addressed in detail in Roberts *et al.* (2015) and McCarthy *et al.* (2018).

4.4 Tasks required

As sampling for DIC and TA will be integrated into the existing Ecology Long-Term Marine Waters Monitoring, Water Column Program, please see Bos *et al.* (2015) for a discussion of the general tasks for that work (Project Objectives #1, #2, and #3). For a discussion of the tasks needed to run and validate the SSM (Project Objectives #5 and #6), please refer to Roberts *et al.* (2015) and McCarthy *et al.* (2018).

To address Project Objective #4, research on the techniques and assumptions of the different analytical methods associated with total alkalinity analyses for salinities ranging from freshwater (S=0) and seawater (S=35) will be performed.

4.5 Systematic planning process used

This QAPP describing OMEGA represents the systematic planning process for this project.

5.0 Organization and Schedule

5.1 Key individuals and their responsibilities

Table 3. Organization of project staff and responsibilities.

Staff	Title	Responsibilities
Stephen Gonski Marine Monitoring Unit Western Operations Section Phone: 360-407-6517	Project Manager	Writes the QAPP. Oversees field sampling and transportation of samples to the laboratory. Conducts QA review of data and analyzes and interprets data. Writes the draft report and final report.
Christopher Krembs Marine Monitoring Unit Western Operations Section Phone: 360-407-6675	Senior Oceanographer	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. Reviews QAPP.
Greg Pelletier Modeling & TMDL Unit Western Operations Section Phone: 360-407-6485	Modeling Lead	Determines modeling strategy. Determines appropriate analysis, review, and interpretative methods for data reduction and reporting. Generates modeling products. Reviews QAPP.
Mya Keyzers Marine Monitoring Unit Western Operations Section Phone: 360-407-6395	Marine Monitoring Lead Technician	Conducts field sampling, laboratory analysis, and instrument maintenance. Records and manages field information. Conducts QA review and analyzes and interprets data. Reviews QAPP.
Allison Brownlee Marine Monitoring Unit Western Operations Section Phone: 360-407-6687	Marine Monitoring Technician	Conducts field sampling, laboratory analysis, and instrument maintenance. Records and manages field information. Conducts QA review and analyzes and interprets data. Reviews QAPP.
Julia Bos Marine Monitoring Unit Western Operations Section Phone: 360-407-6674	Data Management Lead	Conducts QA review and analyzes and interprets data. Enters data into EAPMW and EIM data management systems. Support data analysis, coding, and reporting. Reviews QAPP.
Carol Falkenhayn Maloy Marine Monitoring Unit Western Operations Section Phone: 360-407-6742	Unit Supervisor for the Project Manager	Creates the project scope and budget, and tracks progress. Provides internal review of the QAPP, approves the budget, and approves the final QAPP.
Cristiana Figueroa-Kaminsky Modeling & TMDL Unit Western Operations Section Phone: 360-407-7392	Unit Supervisor for the Modeling Lead	Approves modeling strategy. Oversees modeling products.
Dale Norton Western Operations Section Phone: 360-407-6596	Section Manager for the Project Manager	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Arati Kaza Statewide Coordination Section Phone: 360-407-6964	Quality Assurance Officer	Reviews the draft QAPP and approves the final QAPP. May comment on draft project report.

EIM: Environmental Information Management database
QAPP: Quality Assurance Project Plan

5.2 Special training and certifications

Sampling for total dissolved inorganic carbon (DIC) and total alkalinity (TA) will be incorporated into Ecology's Long-Term Marine Waters Monitoring, Water Column Program. For a list of the special trainings and certifications completed by marine monitoring staff involved in this work, please refer to Bos *et al.* (2015).

Trainings for all field staff on sample collection, preservation, and storage methods specific to DIC and TA (discussed in Section 8.2) will be provided prior to the start of sample collection. Trainings will also be conducted as new field staff join the sampling team over the 24-month period of work.

5.3 Organization chart

See Table 3 (above) for the list of key individuals, their project positions, and their responsibilities for this project.

5.4 Proposed project schedule

Table 4. Proposed schedule for completing field and laboratory work, data entry into EIM, and reports.

Field and laboratory work	**Due date**	**Lead staff**
Fieldwork completed	September 2020	Stephen Gonski
Laboratory analyses completed	December 2020	
Environmental Information System (EIM) database		
EIM Study ID	MarineWater	
Product	**Due date**	**Lead staff**
EIM data loaded	Quarterly starting January 2019	Julia Bos
EIM data entry review	Quarterly starting January 2019	Allison Brownlee
EIM complete	April 2021	Julia Bos
Final report		
Author lead / Support staff	Stephen Gonski / Christopher Krembs, Greg Pelletier	
Schedule		
Draft due to supervisor	March 2020	
Draft due to client/peer reviewer	March 2020	
Draft due to external reviewer(s)	April 2020	
Final (all reviews done) due to publications coordinator (Jill)	May 2020	
Final report due on web	June 2020	

5.5 Budget and funding

This budget does not include the full cost of OMEGA. It is limited to direct expenses for the specific elements listed in Table 5 below.

Table 5. Tentative project budget and funding.

Funding Category					Available Funds
Laboratory Analysis (PMEL and UW Marine Chemistry Lab)					$126,000
Miscellaneous Laboratory Goods and Services					$8,016
Miscellaneous Equipment Costs					$2,082
Parameter	**Number of Samples**	**Number of QA Samples**	**Total Number of Samples**	**Cost Per Sample**	**Lab Subtotal**
DIC-TA (PMEL)	864	96	960	$125.00	$120,000
Salinity (UW Marine Chemistry Lab)	–	–	288	$19.30	$5558

In addition to sending water samples to NOAA's Pacific Marine Environmental Laboratory (PMEL) for DIC and TA analysis, some water samples will likely be sent to the College of Earth, Ocean, and Atmospheric Sciences (CEOAS) at Oregon State University (OSU) for analysis of DIC and partial pressure of carbon dioxide ($p\mathrm{CO}_2$) by Burke-o-Lator (B-o-L). The cost of DIC and $p\mathrm{CO}_2$ analysis at OSU will be $25 per sample.

For clarification regarding the number of salinity samples to be collected and analyzed, please see Section 10.1.

6.0 Quality Objectives

6.1 Data quality objectives

The main data quality objective (DQO) for this project is to collect and analyze a minimum of 960 water samples representative of different parts of the Salish Sea. The analysis will use standard methods to obtain total dissolved inorganic carbon (DIC) and total alkalinity (TA) that meet the measurement quality objectives (MQOs) described below. The analysis will also be compared to results of previous marine CO_2 chemistry and ocean acidification (OA) studies conducted in the Salish Sea summarized in Section 3.2.2.

6.2 Measurement quality objectives

6.2.1 Targets for precision, bias, and sensitivity

Water samples collected in the field and analyzed in the laboratory have an inherent amount of error. Concerns about precision and consistency in sample collection will be minimized by following the appropriate Standard Operating Procedures (SOPs). Further, the MQOs for the project results, expressed in terms of acceptable precision, bias, and sensitivity, are described in this section and summarized in Table 6 below.

Table 6. Measurement quality objectives.

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**			**Percent of 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%

6.2.1.1 Precision

Precision is a measure of variability between results of replicate measurements that is due to random error, and is usually assessed by using replicate field measurements or laboratory analyses. Duplicate samples for DIC and TA will be collected in the field at the surface (0 m) at three monitoring stations (GRG002, OAK004, and SKG003) and 30 m depth at one monitoring station (HCB004) every month over the 24-month observation period to assess precision. For more information on the stations selected for DIC and TA sampling, please see Table 7. When duplicate samples are collected, two Niskin bottles will be fired at the same depth, and one sample for DIC and TA will be collected from each Niskin bottle. Duplicate samples comprise 4 of the 40 monthly DIC and TA samples collected. Duplicate samples will primarily serve as field replicates and comprise 10% of the total monthly DIC and TA samples collected. Secondarily, these duplicate samples will serve as a check of station representativeness.

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. Laboratory splits will not be performed for neither DIC nor TA. Please refer to Section 10.1 for more information.

6.2.1.2 Bias

Bias is defined as the difference between the population mean and the true value of the parameter being measured (Lombard and Kirchmer, 2004). Specific to DIC and TA measurements, analyzers for these parameters are calibrated against certified reference materials (CRMs) (Dickson *et al.*, 2003) provided by A.G. Dickson of Scripps Institution of Oceanography. The DIC, TA, and salinity values of the CRMs[1] are measured and certified during preparation at Scripps Institution of Oceanography prior to distribution and use (Dickson *et al.*, 2007). CRMs are also routinely employed as method checks to quantify and correct for any analyzer drift occurring during analysis (Wang *et al.*, 2017) which would yield unrepresentative DIC and TA values of the measured samples and impart increased bias to those measurements. Standard analytical methods for DIC and TA routinely achieve $\leq$0.1% accuracy with respect to CRMs, and samples measured using analyzers calibrated with CRMs are assumed to possess the same accuracy.

6.2.1.3 Sensitivity

Sensitivity is a measure of the capability of a method to detect a substance. Sensitivity of standard analytical methods for DIC and TA are inherently difficult to assess and state outright since different measurement methods optimized for certain concentration ranges and mediums (e.g., freshwater, seawater, sea ice melt, or sediment porewater) exist. Concentration ranges of standard analytical methods vary. NOAA's Pacific Marine Environmental Laboratory (PMEL) accurately and precisely measures DIC and TA in the ranges between 1500 and 2500 µmol kg^{-1} and 1500 and 2400 µmol kg^{-1}, respectively (Alin, 2018; Ostendorf, 2018). However, it is important to note that simple modifications to standard analytical methods may be employed based on the anticipated DIC, TA, and salinity ranges of the water samples to be measured. Such modifications would be employed based on the ranges of the expected results for the current study (DIC: 1050 – 2300 µmol kg^{-1}; TA: 1100 – 2300 µmol kg^{-1}). For more information on method modifications, please see Section 9.3.

6.2.2 Targets for comparability, representativeness, and completeness

6.2.2.1 Comparability

It is important that data collected and analyzed for long-term monitoring by different technicians or monitoring groups are comparable. In order to ensure comparable data collection techniques, we use the same methods and procedures whenever possible for collecting and analyzing DIC and TA data throughout the program.

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[1] https://www.nodc.noaa.gov/ocads/oceans/Dickson_CRM/batches.html

The following SOPs and accompanying procedures will be used:

- DIC and TA sampling and storage – SOP 1 of Dickson *et al.* (2007)
- DIC Analysis – SOP 2 of Dickson *et al.* (2007) based on Johnson *et al.* (1985, 1987)
- TA Analysis – SOP 3b of Dickson *et al.* (2007) based on Dickson *et al.* (2003)
- DIC & $p\mathrm{CO_2}$ Analysis by Burke-o-Lator (B-o-L) – (Bandstra *et al.,* 2006; Hales *et al.*, 2004).
- Modified procedures for analyzing discrete water samples using B-o-L – (Bandstra *et al.,* 2006; Barton *et al.*, 2012; Hales *et al*, 2005).

6.2.2.2 Representativeness

The long-term marine waters monitoring program is designed to collect data that represents the study area across seasonal cycles including spatial and temporal variations. By collecting data monthly, wide varieties of seasonal conditions are represented. Regional sampling surveys are conducted over five different days a month, with no set date or condition imposed for any survey. Surveys are conducted monthly with at least three weeks between consecutive visits to the same region.

By sampling 20 select marine sites at 0 m and 30 m, the data will represent the surface waters and upper water column of regions of the Salish Sea in which the stations are located, including spatial variation. As this work will focus on the river-dominated shelf regions of the Salish Sea, the majority of the selected stations are located near the discharge points of many major rivers flowing into the U.S. Territorial Waters of the Salish Sea.

Sampling variability between technicians will be controlled by strictly following standard operating procedures and collecting quality control samples, but natural spatial and temporal variability may contribute greatly to overall variability in the parameter value.

6.2.2.3 Completeness

EPA has defined completeness as a measure of the amount of valid data needed to be obtained from a measurement system to meet study objectives. The completeness objective for this study is that 95% of all data collected meet measurement quality objectives. There is no attainment objective established given the safety considerations specific to marine water sampling. We make all efforts to complete all sampling every month to avoid gaps in the data record.

Reasons why sampling may be cancelled:

1. Severe weather that prevents vessels from sailing. To mitigate this, Ecology schedules multiple backup dates.
2. Malfunctioning equipment. To minimize this risk, we maintain interchangeable sets of auxiliary equipment, ensure equipment is well maintained, and check functionality prior to starting fieldwork.
3. Measurement/data quality objectives are not met. To minimize this occurrence, we conduct regular pre- and post-sampling assessments of all procedures and equipment to ensure all are operating correctly.

6.3 Acceptance criteria for quality of existing data

Results from this study will be compared to existing DIC and TA data for Puget Sound and the Salish Sea; comparisons will be limited to those that were collected under an approved QAPP or that have undergone a full data quality verification process.

6.4 Model quality objectives

This section is not applicable to the present work.

7.0 Study Design

7.1 Study boundaries

The Washington State Department of Ecology (Ecology) currently carries out long-term ambient monitoring at 39 core marine stations across U.S. Territorial Waters of the Salish Sea and Washington State Coastal Bays. Salish Sea stations are divided among five regions – San Juan Islands and Admiraly Inlet, North Puget Sound, Central Puget Sound, South Puget Sound, and Hood Canal. For a more thorough discussion of the 2018 core station locations and monitoring program carried out by Ecology, please see Brownlee (2018).

Samples for total dissolved inorganic carbon (DIC) and total alkalinity (TA) are to be collected at 20 of the 39 core marine monitoring stations within Ecology's Long-Term Marine Waters Monitoring network. The majority of the stations are generally located in the more dynamic river-dominated and freshwater-forced shelf regions of the Salish Sea.

Please refer to the map of the study area with the selected stations for DIC and TA included in Figure 3 below. Sole DIC and TA sampling stations are designated by a red dot. A few sampling stations selected for DIC and TA monitoring are co-located with regional OA monitoring buoys. University of Washington (UW) and their educational and tribal partners (e.g., Se'lhaem Buoy in Bellingham Bay operated in partnership with the Lummi Nation and Northwest Indian College) operate these buoys with funds provided by the Northwest Association of Networked Ocean Observing Systems (NANOOS) (hereafter referred to as UW-NANOOS buoys). Finally, other sampling stations are co-located Washington Ocean Acidification Center (WOAC) plankton tow sites.

As shown in Figure 3:

- Stations co-located with UW-NANOOS buoys are designated by a yellow dot.
- Stations co-located with WOAC plankton tow sites are designated by a purple dot.
- Stations co-located with both UW-NANOOS buoys and WOAC plankton tow sites are designated by an orange dot.

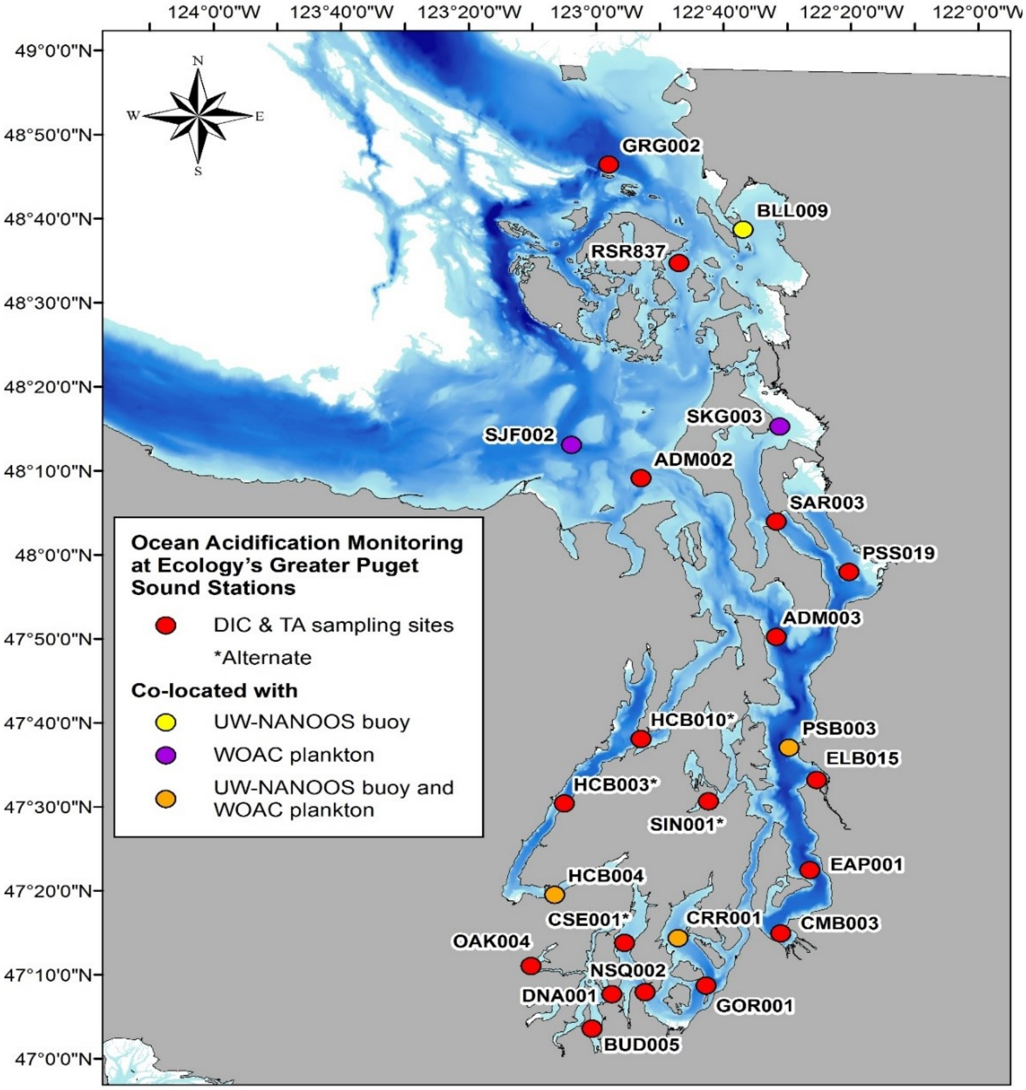

Figure 3. Map showing boundaries of study area.

7.2 Field data collection

Samples for DIC and TA will be collected once a month from 20 marine stations within Ecology's Long-Term Marine Monitoring Network across the Salish Sea during Ecology's regularly scheduled ambient monitoring fieldwork activities. Water samples for DIC and TA will always be collected by boat from 4-L Niskin bottles attached to a Rosette-Niskin package equipped with a conductivity-temperature-depth (CTD) sensor package at depths of 0 m or 0 m and 30 m depending on approximate bottom depths of the selected stations. Sample collection for DIC and TA will continue for 24 months or until available funding is exhausted. Table 7 summarizes the marine monitoring stations selected for DIC and TA sampling.

Table 7. List of Ecology stations selected for DIC and TA sampling.

Station	Location	Basin	Sampling Region	Latitude NAD83 (deg/dec min)	Longitute NAD83 (deg/dec min)	County	WRIA	Max depth	Sample Depths
ADM002	Admiralty Inlet (north) – Quimper Pn.	Admiralty Inlet	North/Central Sound	48 11.239	122 50.577	Jefferson	17	82	0, 30
ADM003	Admiralty Inlet (south)	Admiralty Inlet	North/Central Sound	47 52.739	122 28.992	Kitsap	15	210	0, 30
BLL009	Bellingham Bay – Pt. Frances	San Juan Island/Georgia St.	North Sound	48 41.156	122 35.977	Whatcom	01	20	0
BUD005	Budd Inlet – Olympia Shoal	South Basin	South Sound	47 5.522	122 55.092	Thurston	13	15	0
CMB003	Commencement Bay – Browns Point	Puget Sound Main Basin	Central Sound	47 17.423	122 27.007	Pierce	10	150	0, 30
CRR001	Carr Inlet – Off Green Point	South Basin	South Sound	47 16.589	122 42.575	Pierce	15	95	0, 30
DNA001	Dana Passage – S. of Brisco Point	South Basin	South Sound	47 9.689	122 52.308	Thurston	13	40	0, 30
EAP001	East Passage – SW of Three Tree Point	Puget Sound Main Basin	Central Sound	47 25.023	122 22.824	King	09	213	0, 30
ELB015	Elliott Bay – E. of Duwamish Head	Puget Sound Main Basin	South Sound	47 35.789	122 22.174	King	09	82	0, 30
GOR001	Gordon Point	South Basin	South Sound	47 10.989	122 38.074	Pierce	15	168	0, 30
GRG002†	Georgia Strait – N. of Patos Island	San Juan Island/Georgia St.	North Sound/San Juans	48 48.490	122 57.245	San Juan	02	190	0, 0, 30
HCB004†	Hood Canal – Gt. Bend, Sisters Point	Hood Canal Basin	Hood Canal	47 21.372	123 1.492	Mason	14	55	0, 30, 30
NSQ002	Nisqually Reach – Devils Head	South Basin	South Sound	47 10.039	122 47.291	Pierce	13	101	0, 30
OAK004†	Oakland Bay – Near Eagle Point	South Basin	South Sound	47 12.806	123 4.659	Mason	14	19	0, 0
PSB003	Puget Sound Main Basin – West Point	Puget Sound Main Basin	Central Sound	47 39.589	122 26.575	King	08	67	0, 30
PSS019	Possession Sound – Gedney Island	Whidbey Basin	Whidbey Basin	48 0.656	122 18.075	Snohomish	07	101	0, 30
RSR837	Rosario Straight	San Juan Island/Georgia St.	North Sound/San Juans	48 36.990	122 45.778	San Juan	2	56	0, 30
SAR003	Saratoga Passage – East Point	Whidbey Basin	Whidbey Basin	48 6.456	122 29.493	Island	06	149	0, 30
SJF002	Strait of Juan de Fuca – SW of Eastern Bank	Strait of Juan de Fuca	North Sound/San Juans	48 15.0	123 01.5	San Juan	2	145	0, 30
SKG003†	Skagit Bay – Str. Point (Red Buoy)	Whidbey Basin	Whidbey Basin	48 17.789	122 29.376	Island	06	24	0, 0
CSE001‡	Case Inlet – S. Heron Island	South Basin	South Sound	47 15.872	122 50.658	Pierce	15	58	TBD
HCB003‡	Hood Canal, Eldon	Hood Canal Basin	Hood Canal	47 32.2722	123 0.576	Mason	14	144	TBD
HCB010‡	Hood Canal – Send Creek, Bangor	Hood Canal Basin	Hood Canal	47 40.2	122 49.2	Kitsap	15	100	TBD
SIN001‡	Sinclair Inlet – Naval Shipyards	Main Basin	Central Sound	47 32.956	122 38.608	Kitsap	15	16	TBD

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† Denotes QA stations where field replicates will be collected at specified depths
‡ Denotes alternate stations

7.2.1 Sampling locations and frequency

For a map of the stations selected for DIC and TA sampling, please refer to Figure 3 (above).

Many studies that previously characterized the marine CO_2 system of the Salish Sea have been regionally biased as they have largely focused on investigating marine CO_2 chemistry dynamics in its seaward reaches where high salinity waters subjected to relatively greater oceanic forcing are found (Fassbender *et al.*, 2017). As a result, there is a notable lack of marine CO_2 chemistry measurements in river-influenced Salish Sea waters (Fassbender *et al.*, 2017), which are generally accepted to be waters of $S<20$ (Moore-Maley *et al.*, 2018). With these considerations, OMEGA will focus on the measurement of DIC and TA as well as the characterization of OA dynamics in the shallow, river-dominated shelf regions of the Salish Sea subject to seasonally variable freshwater forcing.

The majority of fisheries and shellfish and bivalve aquaculture confined to these nearshore regions (Washington State Blue Ribbon Panel on Ocean Acidification, 2012) contribute an estimated $150,000,000 to Washington State's economy. This further justifies shifting Ecology's OA focus to the landward reaches of the Salish Sea. Finally, improved spatial coverage of DIC and TA data around major rivers flowing into the Salish Sea is critically needed to improve the Salish Sea Model (SSM) (Bianucci *et al.*, 2018).

Based on SSM runs, Pelletier *et al.* (2017) identified several regions of concern for OA within Puget Sound proper including the South Sound, Whidbey Basin, and waters around major urban centers concentrated in central Puget Sound. Coincidentally, many of these regions are also located near the outflow points of major rivers, which include the Skagit, Stillaguamish, Snohomish, Duwamish/Green, Puyallup, Nisqually, and Deschutes Rivers. All of these rivers impart prominent local control over and drive salinity decreases in their surrounding nearshore waters during their peak flow periods. Furthermore, the first three rivers discharging into Whidbey Basin are responsible for more than two-thirds of the gauged river input within Puget Sound proper (Banas *et al.*, 2015). Notwithstanding, the differences in the OA dynamics in the surrounding waters of these rivers may help characterize relative contributions of rain-fed and snowmelt-/glacial-fed river systems to OA in Puget Sound. Accordingly, stations in those regions of Puget Sound (Whidbey Basin, central Puget Sound, and South Sound) around those major rivers were selected for DIC and TA sampling.

Station HCB004 was selected for its proximity to the discharge point of the Skokomish River, which represents the largest source of freshwater to Hood Canal (Banas *et al.*, 2015). An additional consideration when selecting stations for DIC and TA sampling was the co-location of sampling stations with regional OA monitoring buoys within the Salish Sea (UW-NANOOS buoys – yellow stations in Figure 3) and WOAC plankton tow sites (purple stations in Figure 3). This was considered for station HCB004 and the UW-NANOOS profiling buoy at Twanoh in southern Hood Canal. At such stations, marine CO_2 system data captured in water samples and measured by co-located *in situ* biogeochemical sensors in the same location at the same time can be compared and used to check the accuracy of either type of measurement. Water samples collected next to monitoring buoys can also help assess the degree to which the water sample data and sensor measurements match and can be used to further identify biofouling effects and/or sensor failure (Bresnahan *et al.*, 2014). Conversely, when water samples are collected further away from these buoys in the same water body, water sample data and associated sensor data can help elucidate and track the influence of freshwater and/or marine water intrusions as they propagate through a specific body of water (e.g., Bellingham Bay).

Admiralty Inlet represents the main conduit of exchange between the Strait of Juan de Fuca and Puget Sound proper, so stations located within Admiralty Reach (ADM002 and ADM003) were selected to monitor the waters entering northern Puget Sound from the deep waters of the Pacific Ocean. Station SJF002 was selected for similar reasons, but as it remains outside of Admiralty Reach, it will be free of biogeochemical modifications of incoming waters to Puget Sound mediated by estuarine return flow mixing from surface to depth at Admiralty Inlet. SJF002 is also co-located with a Washington Ocean Acidification Center (WOAC) zooplankton tow site.

Moving south from the Strait of Georgia, station GRG002 was selected because of its proximity to the mouth of Fraser River and its seasonal inclusion in the Fraser River plume. The Fraser River discharges into the Strait of Georgia along the southwestern coast of British Columbia just upstream of the Haro Strait (Ianson *et al.*, 2016). It represents the largest single source of freshwater to the Salish Sea, accounting for more than 50% of the freshwater contained within Puget Sound during late summer/early fall low-flow periods for Puget Sound rivers between late August and early October. In Bellingham Bay, station BLL009 was selected because it is adjacent to the mouth of the Nooksack River, which seasonally predominates Bellingham Bay year-round (Banas *et al.*, 2015). In Rosario Strait, station RSR837 was selected because it occupies a zone of intense mixing where waters converge from the following sources:

- The Fraser River plume moving south from the Strait of Georgia.
- Bellingham Bay adjacent to the Nooksack River moving west.
- The Strait of Juan de Fuca moving north.

As logistics permit, stations BLL009, PSS019, SAR003, and SKG003 may be dropped in favor of alternative sampling stations in Hood Canal (HCB003 and HCB010) and terminal inlets of South Sound (Case Inlet – CSE001) and central Puget Sound (Sinclair Inlet – SIN001) (see Section 7.5.1 for more information). Stations HCB003 and HCB010 in Hood Canal are located near the discharge points of the Hamma Hamma River and Dosewallips/Duckabush Rivers, respectively. Stations CSE001 and SIN001, located in terminal inlets, were selected based on the need to improve SSM resolution in these shallow, niche environments that experience substantial biogeochemical variability (Pelletier *et al.*, 2017). If available funding and ship time permits, additional stations may be added, and sampling may be undertaken more frequently than once a month.

7.2.2 Field parameters and laboratory analytes to be measured

The collection and analysis of water samples for DIC and TA will be integrated with the suite of biogeochemical parameters already included in the Long-Term Marine Waters Monitoring, Water Column Program. For a list of the parameters, please Bos *et al.* (2015).

NOAA’s Pacific Marine Environmental Laboratory (PMEL) will carry out principal analysis of water samples for DIC and TA. Over the course of the project, some water samples will likely be sent to the College of Earth, Ocean, and Atmospheric Sciences (CEOAS) at Oregon State University (OSU) to be analyzed for DIC and partial pressure of carbon dioxide (pCO_2). These latter analyses will serve as a check of the DIC measured by PMEL.

CTD salinities during the early phase of this project will be confirmed by laboratory analyses of salinity samples simultaneously collected alongside water samples for DIC and TA. Laboratory analyses of salinity samples will be carried out by University of Washington's Marine Chemistry Laboratory as per Bos *et al.* (2015). Collection of salinity samples will be curtailed once sufficient agreement between laboratory-measured and CTD-measured salinities has been verified. For more information, please see Section 10.1.

7.3 Modeling and analysis design

DIC and TA data will be collected to support future modeling activities. However, the current work will not entail modeling, so this section is not applicable.

7.3.1 Analytical framework

This section is not applicable to the current work.

7.3.2 Model setup and data needs

This section is not applicable to the current work.

7.4 Assumptions in relation to objectives and study area

A common misconception about monthly ambient sampling is that it captures the full range of environmental variability inherent to one of Ecology's marine monitoring stations. Instead, monthly samples and measurements only provide representative snapshots of environmental conditions and cannot resolve short-term event-scale variability at a given location.

Although we take steps to ensure representativeness, data users must be careful not to overstate these measurements. DIC and TA measurements collected once a month cannot ascertain cross-channel, surface, or temporal variability on their own. This is the case for measurements taken when values change rapidly with the tide, on the diurnal period, or during storms, weather events, or high river flows. We use the existing ocean acidification (OA) monitoring activities carried out by agencies and universities in the USA and Canada to supplement our data.

Therefore, it is assumed that this work will be carried out over a temporal and spatial scale to capture the seasonal variability of DIC and TA across the entire study area. It is also assumed that this work will provide long-term context for the paucity of spatiotemporal coverage of DIC and TA measurements throughout the Salish Sea embodied in existing datasets. This will be achieved by providing 24 months of DIC and TA data across the Salish Sea to supplement existing OA monitoring work currently underway in the region.

7.5 Possible challenges and contingencies

7.5.1 Logistical problems

Sampling via boat may be conducted in more challenging conditions such as stronger winds or higher waves; however, no boat-based sampling is conducted after dark, or during stormy conditions necessitating small craft advisories from the National Weather Service. The consequence of this problem is more gaps in sampling events during wintertime (more storm events).

The proposed marine monitoring stations located in Bellingham Bay near the discharge point of the Nooksack River (BLL009) and Whidbey Basin (PSS019, SAR003, and SKG003) are currently sampled by floatplane on the North Sound Flight (MF2) (Brownlee, 2018). As sampling for DIC and TA by floatplane was deemed not to be feasible (Keyzers, 2016), these stations will be added to the list of stations sampled as part of the Joint Effort to Monitor the Strait (JEMS) Program carried out by staff of the Shannon Point Marine Center (Bos *et al.*, 2015) as logistics permit. The details regarding the addition of these stations to the JEMS Program will be determined at a later date.

7.5.2 Practical constraints

Data collection is not conducted under adverse or unsafe conditions. In addition, data collection may be suspended when access is denied or operations prohibited by federal agencies such as the U.S. Coast Guard or an arm of the military such as the U.S. Navy. Data collection may be cancelled or curtailed when budget constraints result in staff reductions or limited availability of resources such as equipment, supplies, laboratory analyses, or calibration and maintenance services.

Data assessment may be limited or not performed when data collection is suspended, equipment fails to generate data that meet quality standards or when budget constraints result in staff reductions or limitations to resources such as equipment and supplies, analytical laboratory or information management services.

Any circumstance that interferes with data collection and quality will be noted and discussed in reports and data summaries.

7.5.3 Schedule limitations

Sampling via boat may be conducted in more challenging conditions such as stronger winds or higher waves; however, sampling is not conducted after dark, nor in stormy conditions resulting in small craft advisories. The result is that there are more gaps in sampling events during wintertime (more stormy periods) and data could be biased.

8.0 Field Procedures

8.1 Invasive species evaluation

Use of a dedicated boat kept at a saltwater marina with little opportunity for contact with invasive species means that there is low risk for transporting invasive species from one water body to another. Marine waters monitoring staff minimize the spread of aquatic organisms by following protocols set in Standard Operating Procedures to Minimize the Spread of Invasive Species, Ecology's SOP EAP070 (Parsons, 2012). This document is on the Ecology QA Website.

8.2 Measurement and sampling procedures

Ecology field methods for collecting samples for total dissolved inorganic carbon (DIC) and total alkalinity (TA) have been informed by SOP 1 of Dickson *et al.* (2007). To collect one 500-mL DIC and TA sample, a total volume of 2.5 L of water is needed. Samples will be collected from Niskin bottles using Tygon tubing following filtration through Whatman 0.45 µm Polyethersulfone (PES) filters by bottom-filling and overflowing into triple-rinsed 500-mL borosilicate glass bottles. Filtration is performed to remove particulate matter from the sample. Samples will be overflowed at least two times the sample volume to minimize the effects of CO_2 invasion into the water sample while sampling. Samples will then be fixed with 200 µL of saturated mercuric chloride ($HgCl_2$) aboard ship or after returning to the lab depending on logistics and safety. Sample bottles will then be sealed (to ensure they remain gas-tight) and inverted several times to disperse the $HgCl_2$ throughout the entirety of the sample. DIC and TA samples will be stored in cool (~4°C), dark conditions until analysis.

DIC and TA will be analyzed at NOAA's Pacific Marine Environmental Laboratory (PMEL) in Seattle. For more information, please see Section 9.1.

8.3 Containers, preservation methods, and holding times

Table 8. Sample containers, preservation, and holding times.

Parameter	Matrix	Minimum Quantity Required	Container	Preservative	Holding Time
DIC/TA	Seawater	500 mL	500-mL borosilicate glass bottles	200 µL of saturated mercuric chloride ($HgCl_2$). Apply Apiezon® L grease to stopper, insert, and twist to remove all air. Store in cool (~4°C), dark conditions.	6 months

8.4 Equipment decontamination

By nature of ambient monitoring, Marine Waters Monitoring (MWM) staff avoid sampling in waters that contain high levels of contaminants, such as oil spills or toxic substances. If contact is suspected, staff follow all recommended protocols from instrument manufacturers for cleaning and re-calibrating sensors. If non-sensor sampling equipment is contaminated, staff follow Ecology's SOP EAP090, *Decontamination of Sampling Equipment for Use in Collecting Toxic Chemical Samples,* when cleaning equipment.

8.5 Sample ID

All water samples collected are labeled with station, depth, and sample identification numbers based on bottle numbers, and these are recorded in the field log. Each sample is automatically given a unique identification number once loaded to the database, which is then transferred to analyses logs (for internal lab samples) or chain of custody forms sent to external labs. All sample bottles are reconciled against forms to verify completeness as samples move through the analytical process.

8.6 Chain-of-custody

Field measurements are collected in a field notebook and will be entered into Microsoft Excel® spreadsheets after returning from the field. Chain of custody forms are filled out by hand after returning from the field using the appropriate observational and measured data. An example of the Chain of Custody form can be found in Appendix A. If DIC and TA sample information can be integrated into electronic flight logs, chain of custody forms for DIC and TA samples may be generated electronically.

When samples are ready for external laboratory analysis, laboratories are contacted to schedule delivery. Advanced notice is given so that transfer is successful and samples are kept in optimal storage conditions at all times during transport and transfer.

Chain of custody logs are delivered to the lab with the corresponding samples in order to manage sample counts, scheduling, and tracking analysis. Once the samples are delivered, lab personnel log in each sample and assign a unique lab number, using sample label numbers and dates. Each unique laboratory sample number must correspond to a particular date, station, and depth.

When data results are received from labs, chain of custody forms are reconciled with data to ensure complete delivery and correct invoicing for all results. If a discrepancy exists, research and investigation of the discrepancy are conducted in coordination with the lab(s) until the problem is resolved.

8.7 Field log requirements

Sampling for DIC and TA will be integrated into Ecology's current Long-Term Marine Waters Monitoring Program. With the exception of data specific to the collection of the DIC and TA samples, supporting physical, chemical, and bio-optical data synoptically collected and recorded will be pulled from Long-Term Marine Waters Monitoring Program desktop flight forms. For the collection of the DIC and TA samples, the following information will be recorded while in the field:

1. Date and Time.
2. Full name of person who took the sample.
3. Location of Project (Marine Flight number and name).
4. Location: Station, Latitude, Longitude, Depth, and Niskin Bottle Number.
5. Sample ID.
6. Comments (e.g., conditions when sampling, problems with sample collection, or unusual circumstances that might affect results).

All information will be recorded in waterproof notebooks using permanent waterproof ink. All corrections will be made with single line strikethroughs accompanied by initials and dates. If the above information can be integrated into existing electronic desktop flight forms, data for DIC and TA samples will be collected electronically in lieu of collection by paper-and-ink methods as previously described.

8.8 Other activities

Sampling for DIC and TA will be integrated into Ecology's current Long-Term Marine Waters Monitoring Program data quality control and plotting routines, data handling, and data storage procedures. For a discussion of these activities, please see Bos *et al.* (2015).

Specific to the collection of DIC and TA samples, trainings for all field staff on sample collection, preservation, and storage methods discussed in Section 8.2 will be provided prior to the start of sample collection. Trainings will also be conducted as new field staff join the sampling team over the 24-month period of work.

9.0 Laboratory Procedures

9.1 Lab procedures table

For each analysis performed, Table 9 lists information specific to the laboratory procedures used to analyze water samples. Dissolved inorganic carbon (DIC) and total alkalinity (TA) will be analyzed at NOAA's Pacific Marine Environmental Laboratory (PMEL) and DIC and partial pressure of CO_2 (pCO_2) will be analyzed at Oregon State University (OSU).

Table 9. Measurement methods (laboratory).

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)
DIC	Seawater	TBD	1050 – 2300 µmol kg^{-1}	±0.2%	n/a	Bandstra *et al.* (2006); Barton *et al.* (2012); Hales *et al.* (2004, 2005)
pCO_2	Seawater	TBD	90 – 1450 µatm[§]	±2%	n/a	Bandstra *et al.* (2006); Barton *et al.* (2012); Hales *et al.* (2004, 2005)

At PMEL, DIC is analyzed coulometrically following methods summarized in SOP 2 of Dickson *et al.* (2007) with minor modifications to accommodate newer, state-of-the-art equipment. PMEL analyzers consist of a coulometer coupled with a Dissolved Inorganic Carbon Extractor (DICE). The DICE system is a modernized version of the Single Operator Multi-parameter Metabolic Analyzer (SOMMA) carbon extractor developed and refined by Johnson *et al.* (1985, 1987,

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[§] Range of pCO_2 calculated from DIC and TA of surface water samples as described in Pelletier *et al.* (2018)

1993). Specific information regarding minor modification to this SOP employed at PMEL is described below:

1. Section 4 states SOMMA systems are used to analyze DIC. The SOMMA is no longer used and has been replaced with the DICE.
2. Section 4.3 states a model 5011 or 5012 coulometer (UIC Inc., Joliet, IL, USA) is used. Instead, a 5015O coulometer (UIC Inc, Joliet, IL, USA) is used. The 5015O coulometer is a newer improved model of the 5011 coulometer.
3. Section 5.1 states nitrogen gas (> 99.995% pure) is used as the CO_2-free carrier gas. In addition to nitrogen gas, a CO_2 Free Air Generator (Domnick Hunter, Model CO2RP015) is also used to remove CO_2 from compressed air and generate a CO_2-free carrier gas.
4. Section 5.2 states the carrier gas is run through soda Ascarite II. Instead, the carrier gas (nitrogen gas or CO_2-free air) is run through soda lime (Greeley, 2018).

At PMEL, TA is measured using the two-stage, open-cell, potentiometric titration method discussed in Dickson *et al.* (2003) and summarized in SOP 3b of Dickson *et al.* (2007). In their specific application, PMEL employs three minor modifications to this SOP described below:

1. Section 4.1 states that a 125 cm^3 plastic screw-cap bottle is used. This type of bottle is not used. Instead, a 125 mL beaker is used to weigh out ~130g of sample.
2. Section 4.4 states Metrohm Dosimat anti-diffusion tip is used. The anti-diffusion is no longer used.
3. Section 4.6.1 is not applicable to Ecology's DIC and TA samples. A sample transfer device is used when at sea, and a balance is not an appropriate way to measure out the sample. When running samples in the lab, they will be weighed out gravimetrically (Ostendorf, 2018).

PMEL uses Certified Reference Materials (CRMs) to check precision and accuracy of all DIC and TA analyses (Greeley, 2018; Ostendorf, 2018).

Some water samples will likely be sent to OSU for simultaneous analysis of DIC and pCO_2 using a Burke-o-Lator (B-o-L). The B-o-L was first designed to simultaneously measure DIC and pCO_2 while a source of seawater was pumped and flowed continuously through the instrument (Bandstra *et al.*, 2006; Hales *et al.*, 2004). B-o-L analytical procedures were later modified to allow discrete water samples to be analyzed for DIC and pCO_2 (Bandstra *et al.*, 2006; Barton *et al.*, 2012; Hales *et al.*, 2005). First, DIC is analyzed by withdrawing a constant flow of sample from the sample bottle, which is then acidified to convert all sample DIC to aqueous carbon dioxide (CO_2). The evolved CO_2 is then stripped from solution and passed through a membrane contactor unit. Second, pCO_2 is analyzed by recirculating headspace gas in a closed loop through the remaining sample liquid and gas detector. For both parameters, gas-phase CO_2 is measured by non-dispersive infrared absorption (Hales *et al.*, 2017).

9.2 Sample preparation method(s)

Besides filtering during sample collection as discussed in Section 8.2, no sample preparation methods are required for the current work.

9.3 Special method requirements

At PMEL, SOPs 2 and 3b (2007) describe measurement of DIC between the range of 1500 and 2500 µmol kg^{-1} and TA between the range 1500 and 2400 µmol kg^{-1}. Low salinity (e.g., $S<10$) measured in the field by CTD sensor packages may indicate DIC and TA less than 1500 µmol kg^{-1} or outside of the ranges of DIC and TA routinely measured by PMEL. If this is observed, the SOPs will need to be altered at least to include sets of lower concentration standards for DIC and TA made using sodium bicarbonate ($NaHCO_3$) or sodium carbonate (Na_2CO_3), which will then be used to calibrate DIC and TA analyzers.

In this event, PMEL will provide Ecology's Project Manager with details of any proposed SOP changes. Ecology will approve the revised procedures in advance of sample analysis or re-analysis. Detailed information pertaining to the accommodation and implementation of PMEL method modifications for DIC and TA less than 1500 µmol kg^{-1} as well as their results will be documented in the final report for this project described in greater detail in Section 12.3.

9.4 Laboratories accredited for methods

The analytical techniques employed at PMEL for analysis of DIC and TA in seawater and the future applications of any modified analytical techniques for DIC and TA less than 1500 µmol kg^{-1} in estuarine waters of the Salish Sea are relatively novel. For these and other reasons, Ecology has an existing Laboratory Accreditation Waiver on file for DIC and TA analyses. Please see Appendix B for a copy of this waiver.

In the future, before water samples collected over the 24-month observation period are sent to OSU for DIC and pCO_2 analysis, a Laboratory Accreditation Waiver will be acquired prior to this stage of the work.

10.0 Quality Control Procedures

10.1 Table of field and laboratory quality control

Ecology will collect 40 samples per month for total dissolved inorganic carbon (DIC) and total alkalinity (TA) over 24 months at marine monitoring stations across the Salish Sea. Of these 40 monthly samples, 10% will serve as the field replicates for this work. The relative percent difference (RPD) for field replicate samples should not exceed the MQO of 0.5% discussed in Section 6.2.1. 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. More details on field and laboratory quality control methods can be found in Table 10 below.

Table 10. Quality control samples, types, and frequency.

Parameter	Field		Laboratory			
	Blanks	Replicates	Check Standards	Method Blanks	Analytical Duplicates	Matrix Spikes
DIC	n/a	4/month	See Below	n/a	See Below	n/a
TA	n/a	4/month	See Below	n/a	See Below	n/a

Outside of existing Ecology quality control procedures, NOAA's Pacific Marine Environmental Laboratory (PMEL) also uses Certified Reference Materials (CRMs) provided by A. G. Dickson of Scripps Institution of Oceanography to routinely check the accuracy and precision of their DIC and TA analyses. For DIC analysis at PMEL, CRMs are run at the beginning of the day and may be run additionally during a given day's analyses at the discretion of the laboratory analyst. For TA analysis at PMEL, CRMs are run at the beginning and end of a given day's analyses and after each 10 – 15 samples depending on the total number of samples analyzed on a given day. At PMEL, replicate analyses for TA of the same sample from the same bottle may be run and are done at the discretion of the laboratory analyst. Any such laboratory replicates for TA are subject to the same MQOs for field replicates discussed in Section 6.2.1. At PMEL, no analogous analyses for DIC are performed. Laboratory splits of DIC and TA samples are also not performed at PMEL (Alin, 2018).

All CRM analyses should not exceed the MQO of 0.25% discussed in Section 6.2.1. 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 is given a non-passing data quality flag.

External to the quality control procedures for DIC and TA analyses discussed above, an independent verification of CTD salinity against laboratory-measured salinities will be conducted. A full set of salinity samples (40 samples) will be simultaneous collected alongside DIC and TA samples each month for the first three months (120 total samples). This is done to verify the accuracy of CTD salinity values and assess the CTD's utility in using these salinities to directly constrain the marine CO_2 system over the course of this work. Salinity is measured using established benchtop methods and will be compared against redundant CTD salinities to assess the accuracy of the CTD-measured values. After the first three months, salinity samples will be collected alongside all DIC and TA samples at QA stations (GRG002, HCB004, OAK004, and SKG003) at the depths where field replicates are collected as discussed in Sections 6.2.1.1. This will be done for the remaining 21 months (168 additional samples) to ensure CTD salinity accuracy is maintained. This yields 288 total salinity samples as described in Table 5 in Section 5.5.

Deviations from the plan outlined above will be discussed and executed as necessary as the project progresses. A full summary of the CTD salinity verification approach and accompanying sampling regiment along with its final cost and results will be included in the final report for this project (described in Section 12.3).

10.2 Corrective action processes

QC results may indicate problems with data during the course of the project. Staff and external lab analysts will follow prescribed procedures to quickly resolve problems. Options for corrective action may include:

- Retrieving missing information.
- Re-analyzing samples (if sufficient volume remains and maximum holding time is not exceeded).
- Collecting additional samples (as logistics and available funding permits).
- Increasing the number of field replicates collected over the course of the 24-month observational period.
- Increasing the number of salinity samples simultaneously collected alongside DIC and TA samples previously specified in Section 10.1.
- Qualifying results using QC codes.

11.0 Data Management Procedures

Data and information management are critical to maintaining an efficient, organized, long-term monitoring system capable of generating high quality, up-to-date, and informative products for managers and scientists. Data used for analysis and reporting that is distributed to the public must pass all QA/QC tests. The Marine Waters Monitoring (MWM) group has invested considerable resources in maintaining and updating data processing and storage structures to facilitate rapid distribution of high-quality monitoring data and products. There are several levels of information management required in this system:

- Field, lab, and CTD data management (database of final data results that pass QA/QC).
- Document management (e.g., lists, SOPs, procedures, logs, and forms).
- Original data file management (raw sensor and lab results).
- Analytical and QA/QC information management (e.g., summary statistics, calibration information, equations, and other analysis information).
- Reports, observations, and other products (e.g., analytical results, graphs, photos, and video).

Figure 4 shows the overall organization of the data workflow and products generated by the Marine Waters group. It is essential for information and products to be thoughtfully organized for efficient and reliable output. The MWM group uses well-managed information and file systems to make this possible.

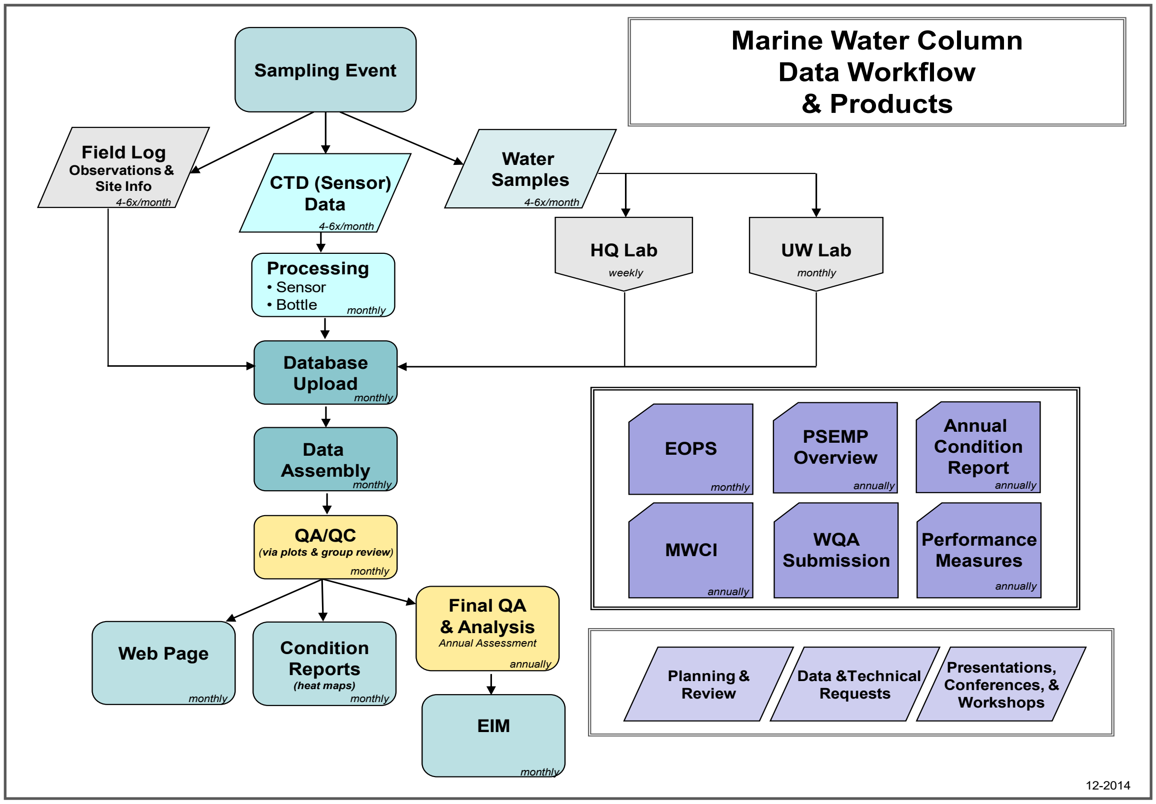

Figure 4. Marine Waters data workflow and data products.

11.1 Data recording and reporting requirements

All field and laboratory data will be transferred to Ecology's (Environmental Information Management (EIM) database. Procedures for recording laboratory results and transferring them to EIM[**] . During this work, 100% of the dataset will be reviewed for data entry errors. Errors will be recorded, discussed among the project team, and consensus corrections will be made.

11.2 Laboratory data package requirements

Laboratory reports and results for marine water sample analysis performed by external labs are typically sent as files attached to an email. These are reconciled and reviewed for completeness and correctness then loaded into the Marine Waters Monitoring data management system (EAPMW). Laboratory results generated by the internal Marine Lab are entered into digital forms and stored on a secure network server. All digital files are stored as unprocessed data, here referred to as "raw" data, in folders organized by monitoring year. All laboratory results are reviewed, loaded to the EAPMW database, and further assessed using QA/QC procedures. All data are given QC codes when finalized.

All data from labs include:

- Raw data results for all parameters measured at each station in electronic format.
- QA sample results.
- A narrative or report with methods used, any problems with the analyses, corrective actions taken, changes to the referenced method, and an explanation of data qualifiers.
- All associated QC results; this includes results for all required field and analytical (laboratory) control replicates, laboratory control (check) samples, reference materials or standards, and method blanks.
- Any qualification of the results.

NOAA's Pacific Marine Environmental Laboratory (PMEL) provides verified data packages for all data analyzed. Laboratories and contractors submit interim data packages including information for data verification to the monitoring coordinator.

All data received from external providers are verified and reviewed by MWM staff against the MQOs listed in Section 6 and the verification process described in Section 13. Any discrepancies are discussed with the laboratories or contractors for amendment. Once data have been reviewed and verified, MWM staff enter final QC information into the EAPMW database and finalize the data.

11.3 Electronic transfer requirements

Data that is generated electronically is then transferred in the form of various files such as spreadsheets, database forms, and recorded instrument files converted to simple text formats. All

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[**] https://ecology.wa.gov/Research-Data/Data-resources/Environmental-Information-Management-database

data are transferred to a secure, shared network server within 24 hours of receipt or generation. Field measurements and notes pertinent to DIC and TA samples will be collected in a field notebook and entered into Microsoft Excel® spreadsheets or transcribed over to Microsoft Word® as soon as possible after returning from the field. This will join all electronic files and data on the same secure, shared network server. Long-term marine monitoring information is organized in annual folders with subfolders organized by topic or data parameter type. Higher-level folders are used to organize other digital files by type, including project data and information, multi-program documents such as inventories, forms and lists, procedures, manuals, software programs, equipment information, manuals, and other related information.

11.4 EIM/STORET data upload procedures

The Marine Waters Monitoring database (EAPMW) is an SQL server database connected to Ecology's EIM data system. Data generated by this program are stored on EAPMW then transferred to EIM. The data is considered provisional until all QA/QC activities have been completed successfully. All data that passes QA/QC are finalized and stored in EIM for subsequent transfer to STORET.

11.5 Model information management

DIC and TA data will be collected to support future modeling activities. This project will not entail modeling, so this section is not applicable to the current work.

12.0 Audits and Reports

12.1 Field, laboratory, and other audits

For collection of samples for total dissolved inorganic carbon (DIC) and total alkalinity (TA), there are no specific audits of field sampling planned. All Ecology field staff, however, will receive training on sample collection, preservation, and storage methods (discussed in Section 8.2) before sample collection begins. Any field staff joining this work after the initial training will receive necessary training when they first start.

Once sampling for DIC and TA begins, the data will be incorporated into the existing monthly data audits for Ecology's Long-Term Marine Waters Monitoring, Water Column Program. For more information regarding these monthly data audits, please refer to Bos *et al.* (2015).

12.2 Responsible personnel

Any data audits involving the DIC and TA data from this project will performed by:

- The Project Manager.
- Project staff within Ecology's Marine Monitoring and Modeling and TMDL Units.
- Scientists of NOAA's Pacific Marine Environmental Laboratory (PMEL).

Other auditing participants will be incorporated when possible. Potential participants include representatives of regional ocean acidification (OA) research partners:

- University of Washington.
- Northwest Association of Networked Ocean Observing Systems.
- Pacific Northwest National Laboratory.
- Washington Ocean Acidification Research Center.
- Western Washington University.
- Shannon Point Marine Center.
- Padilla Bay National Estuarine Research Reserve.

12.3 Frequency and distribution of reports

Monthly and quarterly progress reports will be written. They will include details on the work performed and progress made toward project goals for the reporting period.

A final report will be prepared that describes detailed methods, data quality assessment outcomes, results, lessons learned from the project, and recommendations for future work. Analogous information specific to modifications of PMEL analytical techniques for DIC and TA less than 1500 μmol kg^{-1} as well as the CTD salinity verification scheme will be included in the final report. The final report will also include analyses of the data collected and comparisons of the data collected with existing marine CO_2 chemistry datasets. The Project Manager's position is currently scheduled to end on June 30, 2020. Therefore, the final report will not cover the full

24 months of data. A cut-off date to determine the amount of data to be incorporated into the final report will be decided at a later date by the Project Manager and other project staff. If additional funding is secured to extend the Project Manager's position, the final report will provisionally include the full 24 months of data. In addition, the final report will evaluate the success of achieving the objectives and performance measures identified in the project plan. The final report will be submitted by June 30, 2020.

12.4 Responsibility for reports

The final report will be prepared, written, revised, and submitted by the Project Manager.

13.0 Data Verification

Data verification and review is conducted by the MWM group by examining all field and laboratory-generated data to ensure:

1. Specified methods and protocols were followed.
2. Data are consistent, correct, and complete, with no errors or omissions.
3. Data specified in the Study Design section (Section 7.0) were obtained.
4. Results for QC samples as specified in the Measurement Quality Objectives (Section 6.0) and Quality Control (Section 10.0) sections accompany the sample results.
5. Established criteria for QC results were met.
6. Data qualifiers (QC codes) are properly assigned.

13.1 Field data verification, requirements, and responsibilities

Throughout field sampling, the lead technician and all crew members are responsible for carrying out station-positioning, sample-collection, and sensor-deployment procedures as specified. Technicians will systematically review all field documents (e.g., field logs, chain-of-custody sheets, and sample labels) to ensure data entries are consistent, correct, and complete, with no errors or omissions. A second staff person will be required to check the work of the staff person who primarily collected or generated data results. This will be done while fieldwork is underway and when all staff have returned from the field.

13.2 Laboratory data verification

Lab technicians verify sample and data disposition by conducting continual tracking and reconciliation procedures. A second staff person always checks the work of the staff person who primarily collected or generated data results.

13.3 Validation requirements, if necessary

Once sampling is complete, all data are finalized and all QA/QC is completed. The data will then be made available for review by the Puget Sound Ecosystem Monitoring Program Marine Waters work group. This group includes scientists with specialized knowledge of marine CO_2 chemistry and ocean acidification.

13.4 Model quality assessment

This section is not applicable to the current work.

13.4.1 Calibration and validation

This section is not applicable to the current work.

13.4.2 Analysis of sensitivity and uncertainty

This section is not applicable to the current work.

14.0 Data Quality and Usability Assessment

14.1 Process for determining project objectives were met

Data from laboratory QC procedures as well as results from field replicates provide information to determine if MQOs have been met. All sample results and all analyses from the laboratory and the sensor deployments are examined for completeness. Processing logs and laboratory reports are scrutinized for adherence to specified methods and QA/QC requirements.

If MQOs are met, the quality of the data is considered usable for meeting project objectives. If MQOs have not been met, the data will undergo examination to determine whether they are still usable and whether the quantity is sufficient to meet project objectives.

14.2 Treatment of non-detects

Non-detects for analytes of total dissolved inorganic carbon (DIC) and total alkalinity (TA) are not expected for Salish Sea samples and do not require a separate data treatment in the context of the present work.

14.3 Data analysis and presentation methods

DIC and TA data received from NOAA's Pacific Marine Environmental Laboratory (PMEL) will be used to constrain the marine CO_2 system using programs like CO2SYS (Pierrot *et al.*, 2006) or Seacarb (Gattuso *et al.*, 2016) together with *in situ* temperature, salinity, and nutrients (specifically phosphate $(\mathrm{PO_4^{3-}})$ and silicate $(\mathrm{SiOH_4})$). In these calculations, we will use the inorganic carbon dissociation constants from Lueker *et al.* (2000) for all data with salinity (S) >16 and the inorganic carbon dissociation constants from Millero *et al.* (2006) for all data with S<16. The borate-to-salinity ratio from Uppstrom (1974) will be used in these calculations. The dissociation constant for bisulfate $(\mathrm{K_s})$ from Dickson (1990) will be used in these calculations as well. Inputs for the above parameters to be used to constrain the marine CO_2 system match those used in analogous calculations performed during model runs of the Salish Sea Model (SSM) (Pelletier *et al.*, 2017).

For all DIC and TA data, once the marine CO_2 system is constrained, data will be tabulated and compared with existing historical marine CO_2 chemistry datasets for the Salish Sea. This will help us assess whether the data generated falls within known data ranges for DIC, TA, partial pressure of CO_2 $(p\mathrm{CO_2})$, pH, and saturation states of aragonite (Ω_{Arag}) and calcite (Ω_{Calc}) in the Salish Sea. Graphical visualizations of all data will also be created using programs such as MATLAB and Ocean Data View. Additional parameters may undergo equivalent analyses as needs arise in the future.

While this work does not entail modeling, DIC and TA data compiled and tabulated will be used to corroborate the predictions of the Salish Sea Model (SSM). These data will also be used to run future sensitivity experiments to help improve the forecasting of future ocean acidification (OA) scenarios in the Salish Sea via the SSM. Model predictions will be compared with observations to determine model skill metrics (e.g., to estimate model bias and root-mean-square error).

14.4 Sampling design evaluation

In order to characterize the spatial and depth variability of DIC and TA in the river-dominated and freshwater-forced shelf regions of the Salish Sea, these parameters are sampled at 20 stations at 0 m (more dynamically-forced) and 30 m (more statically forced) depths. Marine monitoring stations located near the discharge points of many major rivers are integrated into this study design and further justify this assertion. River endmembers include the Nooksack, Skagit, Stillaguamish, Snohomish, Dumawish/Green, Puyallup, Deschutes, and Skokomish Rivers along with contingency plans for additional stations near the mouths of the Dosewallips, Duckabush, and Hamma Hamma Rivers in Hood Canal.

Temporal context for existing marine CO_2 chemistry datasets of shorter temporal resolutions in the Salish Sea are provided by monthly sampling for 24 months. This will help fill temporal gaps and capture the regional seasonality of DIC, TA, and OA in Puget Sound and the Salish Sea. Thus, this study will support our regional OA research partners and allow them to enhance their understanding of the temporal variability of OA across the Salish Sea. The degree of variability in DIC and TA characterized by this work will also be used to assess and inform if increased sampling frequencies are needed to characterize regional OA dynamics in the Salish Sea.

The present sampling design was informed by marine CO_2 chemistry and OA data gaps (both directly- and indirectly-stated by relevant peer-reviewed scientific literature) identified for Puget Sound and the greater Salish Sea. The OA component of Ecology's ongoing monitoring program is determined by resource availability including budget and staff, and program capabilities and capacity. Moving forward, the data generated from this project will help provide context for and inform the design of future marine CO_2 chemistry and OA studies undertaken in the Salish Sea in conjunction with the following parties:

- Pacific Coast Shellfish Growers Association.
- Pacific Shellfish Institute.
- Pacific Northwest Tribes.
- Washington Ocean Acidification Center.
- University of Washington.
- Western Washington University.
- National Oceanic and Atmospheric Administration.
- Northwest Association of Networked Ocean Observing Systems.
- Pacific Northwest National Laboratory.
- Padilla Bay National Estuarine Research Reserve.
- King County.
- Other regional OA research partners.

14.5 Documentation of assessment

A discussion of topics relevant to the data quality assessment will be included in the final report for this project, which is discussed in detail in Section 12.3.

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16.0 Appendices

Appendix A. PMEL DIC-TA Sample Chain of Custody Form

Date Sent	Project	FO#	Sample #s	# Samples	Date Analyzed	Data File Name	Month Invoiced	Date Data Rec'd
	SPSMEM	PF321302						

Date	Station	Latitude	Longitude	Temp (ºC)	Salinity	Depth	Sample ID	Volume (mL)

Appendix B. PMEL Laboratory Accreditation Waiver

Department f Ecology

Request to Waive Required Use of Accredited Lab

Use form ECY 070-152a for a waiver for Microbial Source Tracking (MST)

Reference: Executive Policy 22-02

Date:	9/11/2018	**Program:**	EAP
Name of Requester:	Stephen Gonski	**Work Phone:**	360-407-6517

Project Name: Ocean Acidification Monitoring at Ecology's Greater Puget SoundStations (continuation of 2014 Pilot)

Test(s) for which a waiver is requested:

Total dissolved inorganic carbon (DIC) and total alkalinity (TA) will be measured in marine and estuarine waters by NOAA's Pacific Marine Environmental Laboratory (PMEL) following SOPs described in Dickson *et al.* (2007) (Guide to Best Practices for Ocean CO_2 Measurements. PICES Special Publication 3, IOCCP Report No. 8. October 2007).

Justification for Request:

- ☐ Data quality goal does not warrant accreditation [1]
- ☒ There is no lab accredited to do the test(s) [2]
- ☐ EAP Lab Accreditation Section cannot accredit for test(s) [3]
- ☐ There is no accredited lab in a reasonable distance [4]
- ☒ No lab can be accredited in time to meet the need [4]
- ☒ Other (explain in narrative)

Narrative (Explain the above checked boxes):

This is a continuation of a pilot project, begun in 2014, that has used the same contract lab to analyze the same parameters using the same methods. The original **Request to Waive Required Use of Accredited Lab** neither identified the laboratory that would perform the analyses nor did it identify DIC as one of the parameters to be analyzed. Finally, Ecology does not yet accredit laboratories for the methods described in Dickson *et al.* (2007).

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[1] Screening data, for example may not necessitate use of an accredited lab.

[2] Check the Lab Accreditation website or Contact the EAP Lab Accreditation Unit, or both.

[3] Contact the EAP Lab Accreditation Unit

[4] Check the Lab Accreditation website or Contact the EAP Lab Accreditation Unit, or both.

Request for Waiver to Required Use of Accredited Lab, continued

Associated Quality Control Tests

Exemption from the requirement to use an accredited lab does not relieve the data user from the requirement to assure lab data meets quality objectives. Reviewing quality control (QC) test results, routinely performed as part of the lab accreditation process, becomes an especially important issue for the user of data coming from a non-accredited lab. Mark below the QC tests the lab will be required to report along with the environmental data. Refer to this description of QC tests, if needed, to determine the significance of each test.

☐ Check standards
☐ Method Blanks
☐ Matrix Spikes
☐ Matrix Spike Duplicates
☒ Duplicates (field and laboratory)
☐ Surrogates
☐ Laboratory Splits
☒ Standard/Certified Reference Materials

When completed, save the request and submit it to the Agency's QA Officer by e-mail.

Approval Signatures:

Thomas H Gries 9-10-18
Ecology Quality Assurance Officer / Date
(ACTING)

9-17-18
Environmental Assessment Program Manager or Ecology Deputy Director / Date

Appendix C. Glossaries, Acronyms, and Abbreviations

Glossary of General Terms

Total Alkalinity (TA): 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.

Ambient: Background or away from point sources of contamination.

Anthropogenic: Human-caused.

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.

CTD: A set of sensors (conductivity-temperature-depth) combined into an instrument package used for collecting continuous water column profile data. The CTD is equipped with sensors to measure additional variables and a pump to draw water through the sensors. Profiles at each station are collected from the sea surface (top bin = 0.5 m) to the sea bottom. The CTD and sensors are operated and maintained according to manufacturer's recommended protocols, with factory calibration occurring annually.

Dissolved Inorganic Carbon (DIC): The sum of inorganic carbon species in a solution. The inorganic carbon species include aqueous carbon dioxide ($\mathrm{CO_2(aq)}$), carbonic acid (H_2CO_3), bicarbonate ($\mathrm{HCO_3^-}$), and carbonate ($\mathrm{CO_3^{2-}}$). CO_2(aq) and H_2CO_3 are often together referred to as $\mathrm{CO_2^*}$.

Non-point source: Chemical compounds and species that enter any waters of the state from any dispersed land-based or water-based activities, including but not limited to atmospheric deposition, surface-water runoff from agricultural lands, urban areas, or forest lands, subsurface or underground sources, or discharges from boats or marine vessels not otherwise regulated under the NPDES program. Generally, any unconfined and diffuse source of a chemical compound or species. Legally, any source of a chemical compound or species that does not meet the legal definition of "point source" in section 502(14) of the Clean Water Act.

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.

Ocean Acidification (OA): When carbon dioxide (CO_2) is absorbed by seawater, it forms carbonic acid ($\mathrm{H_2CO_3}$), a weak acid which releases hydrogen ions ($\mathrm{H^+}$) and reduces the pH of seawater upon dissociation into bicarbonate ($\mathrm{HCO_3^-}$) and carbonate ($\mathrm{CO_3^{2-}}$) ions. This collection of chemical transformations is often referred to as ocean acidification (OA). In turn, OA drives changes in the marine CO_2 system by increasing total dissolved inorganic carbon (DIC) and partial pressure of CO_2 ($p\mathrm{CO_2}$) and reducing the $\mathrm{CO_3^{2-}}$ ion concentration and saturation states of biologically important calcium carbonate ($\mathrm{CaCO_3}$) minerals such as aragonite (Ω_{Arag}) and calcite (Ω_{Calc}). In areas where most life now congregates in the ocean, seawater is supersaturated with respect to $CaCO_3$ minerals ($\Omega > 1$) providing favorable conditions for calcifying organisms to build their skeletons and shells. However, continued ocean acidification or a reduced capacity of the water to buffer the absorption of CO_2 and transformation into H_2CO_3 over time is causing marine waters to become more corrosive and undersaturated with respect to $CaCO_3$ minerals ($\Omega < 1$), specifically aragonite. Such conditions favor mineral dissolution and negatively affects the ability of calcifying organisms to produce and maintain their skeletons and shells.

Parameter: A physical chemical or biological property whose values determine environmental characteristics or behavior.

pH: pH is the negative logarithm of the activity of the (solvated) hydronium ion, more often expressed as the measure of the hydronium ion concentration. pH is a measure of the acidity and basicity 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 has ten times less hydronium ion activity than one with a pH of 7.

Point source: Source that discharges at a specific location from pipes, outfalls, and conveyance channels to a surface water. Examples of point source discharges include municipal wastewater treatment plants, municipal stormwater systems, industrial waste treatment facilities, and construction sites where more than 5 acres of land have been cleared.

Watershed: A drainage area or basin in which all land and water areas drain or flow toward a central collector such as a stream, river, or lake at a lower elevation.

Acronyms and Abbreviations

B-o-L	Burke-o-Lator
CEOAS	College of Earth, Ocean, and Atmospheric Sciences at Oregon State University
CRM	Certified Reference Material
CTD	Conductivity-temperature-depth (see Glossary above)
DFO	Department of Fisheries & Oceans (Canada)
DIC	Dissolved inorganic carbon (see Glossary above)
DICE	Dissolved Inorganic Carbon Extractor
DO	Dissolved oxygen (see Glossary above)
DOC	Dissolved organic carbon
DOM	Dissolved organic material
DQO	Data quality objective
EAP	Environmental Assessment Program
EAPMW	Marine Waters Monitoring database
Ecology	Washington State Department of Ecology
e.g.	For example
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
et al.	And others
JEMS	Joint Effort to Monitor the Strait
LAU	Laboratory Accreditation Unit
MQO	Measurement quality objective
MWM	Marine Waters Monitoring
NANOOS	Northwest Association of Networked Ocean Observing Systems
NOAA	National Oceanic & Atmospheric Administration
OSU	Oregon State University
$p\mathrm{CO}_2$	Partial pressure of carbon dioxide (CO_2)
PMEL	Pacific Marine Environmental Laboratory
OA	Ocean acidification (see Glossary above)
OMEGA	**O**cean Acidification **M**onitoring at **E**cology's **G**reater Puget Sound St**A**tions
QA	Quality assurance
QAPP	Quality Assurance Project Plan

QC	Quality control
RPD	Relative percent difference
RSD	Relative standard deviation
S	Salinity
SOMMA	Single Operator Multi-parameter Metabolic Analyzer
SOP	Standard operating procedures
SSM	Salish Sea Model
TA	Total alkalinity (see Glossary above)
TBD	To be determined
USA	United States of America
USGS	United States Geological Survey
UW	University of Washington
WA	Washington State
WAC	Washington Administrative Code
WOAC	Washington Ocean Acidification Center

Units of Measurement

°C	degrees centigrade
kg	kilogram, a unit of mass equal to 1,000 grams
m	meter
L	liter
mL	milliliter
mole	an International System of Units (IS) unit of matter
µatm	microatmospheres
µL	microliter
µm	micrometer
µmol	micromole or one-millionth of a mole
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 sample mean and the true value. Bias usually describes a systematic difference reproducible over time and is characteristic of both the measurement system and the analyte(s) being measured. Bias is a commonly used data quality indicator (DQI). (Kammin, 2010; Ecology, 2004)

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

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

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

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

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

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

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

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

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

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

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

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

Data validation: An analyte-specific and sample-specific process that extends the evaluation of data beyond data verification to determine the usability of a specific data set. It involves a detailed examination of the data package, using both professional judgment and objective criteria, to determine whether the MQOs for precision, bias, and sensitivity have been met. It may also include an assessment of completeness, representativeness, comparability, and integrity, as these criteria relate to the usability of the data set. Ecology considers four key criteria to determine if data validation has actually occurred. These are:

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

Examples of data types commonly validated would be:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Split sample: A discrete sample subdivided into portions, usually duplicates (Kammin, 2010)

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

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

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

References for QA Glossary

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