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State of Washington

Quality Assurance Project Plan

Salish Sea Acidification Model Development

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Quality Assurance Project Plan

Salish Sea Acidification Model Development

May 2015

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EAP: Environmental Assessment Program

SCS: Statewide Coordination Section

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2.0 Abstract

Several monitoring programs indicate low and declining pH and related parameters in the marine waters of the Pacific Northwest (Feely et al., 2012; Wootton and Pfister, 2012; Murray et al., 2015). Global atmospheric carbon dioxide levels have been identified as the dominant contributor (Washington Ocean Acidification Blue Ribbon Panel, 2012). Regional human contributions may exacerbate low levels of pH or aragonite saturation state in the Salish Sea. Aragonite is the form of calcium carbonate used in many shell-building organisms. If aragonite saturation is low or undersaturated, organisms may not be able to build shells, which could result in a cascade of impacts to the food web. Regional human contributions are those sources that originate from within the Puget Sound and Salish Sea watershed, including point sources. Pacific Ocean conditions include the influence of global atmospheric carbon dioxide and ocean conditions.

The present project will examine how various regional sources impact acidification in the Salish Sea, including Puget Sound. Recently models have quantified the relative impacts of regional human nutrient sources on dissolved oxygen in the Salish Sea (Roberts et al., 2014).

The purpose of this Quality Assurance Project Plan (QAPP) is to describe details of a plan to (1) expand the existing Salish Sea Model to evaluate pH and aragonite saturation state and (2) quantify the influences of regional and global carbon and nutrient sources. This QAPP is based on the previously published acidification model approach document (Long et al., 2014) that identifies the technical approach for simulating the carbon cycle. It proposes adding total dissolved inorganic carbon and alkalinity as state variables, including source and sink terms related to air-sea exchange, respiration, photosynthesis, nutrient gains and losses, sediment fluxes, and boundary conditions. Boundary conditions would account for both Pacific Ocean upwelled water and regional human nutrient contributions and air emissions around the Salish Sea.

This effort will assess the relative contribution of regional sources and will identify what regions or seasons are more influenced by regional sources within Salish Sea waters. This project does not include new sampling prior to model development. Therefore, an important component will be an assessment of the uncertainty in the predictions that are based on the best available information. This will guide how the information could be used by Salish Sea managers.

Acknowledgements

This project is funded wholly or in part by the United States Environmental Protection Agency (EPA) under assistance agreement PC-00J20101 -4 to the Washington State Department of Ecology. The contents of this document do not necessarily reflect the views and policies of EPA, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

3.0 Background

The Washington State Ocean Acidification Blue Ribbon Panel report (2012) and Scientific Summary (Feely et al., 2012) provide important context. Long et al. (2014) Section 1.0 describes the historical and scientific background regarding acidification. We summarize key topics, but refer to previously published documents for details.

This modeling effort was identified as a Key Early Action of the Washington State Blue Ribbon Panel on Ocean Acidification (Washington State Blue Ribbon Panel on Ocean Acidification, 2012). The panel was appointed by Governor Christine Gregoire to identify the causes and consequences of ocean acidification. A fundamental question is how much of the low pH is caused by nutrients reaching the Salish Sea from point source discharges, increased river nitrogen and carbon, and atmospheric emissions of nitrogen and carbon. Managers must understand the relative contributions of these regional human sources compared with the influences of global atmospheric carbon dioxide increases that have decreased the pH of the Pacific Ocean.

3.1 Study area and surroundings

Long et al. (2014) Section 1.0 describes the study area, climate, Pacific Ocean influences, and regional watershed influences. Figure 1 presents the land areas discharging to the Salish Sea that are part of this project.

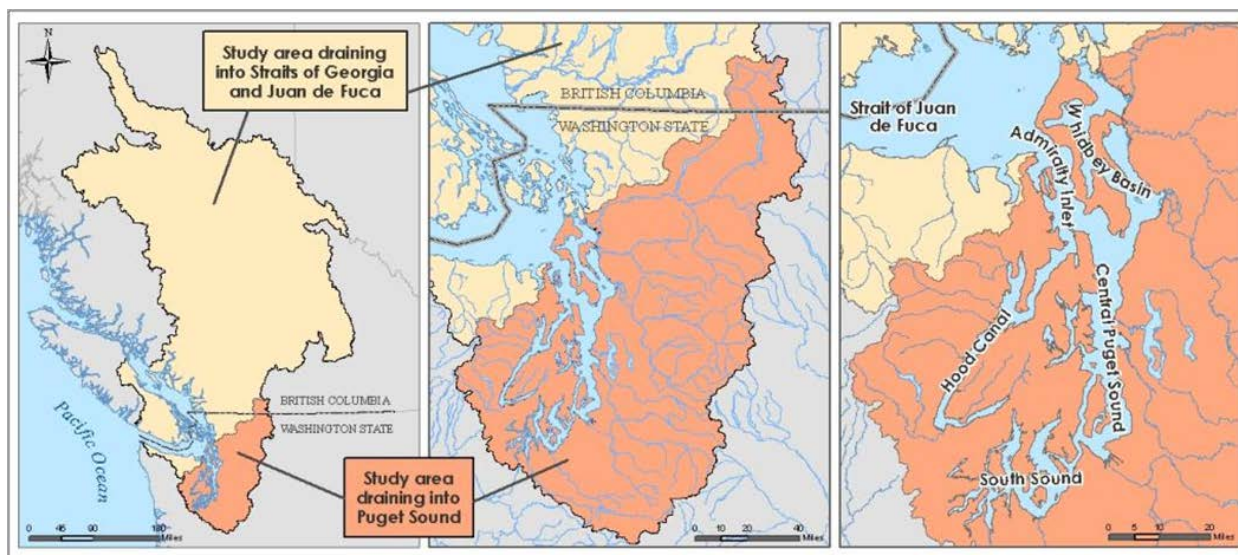


Figure 1. Salish Sea (Puget Sound, Strait of Georgia, Strait of Juan de Fuca) with land areas discharging to marine waters within the model domain. (Source: Long et al., 2014)

3.1.1 Logistical problems

This project does not include any field work, so there are no logistical problems. Primary information gaps are described in Long et al. (2014) Section 4.7.

3.1.2 History of study area

The study area and human uses are briefly described in Sackmann (2009). The Washington State Blue Ribbon Panel on Ocean Acidification (2012) describes when and how ocean acidification concerns were first identified as well as what was known as of that publication date. Washington Sea Grant (2014) and its partners updated key scientific findings since 2012.

3.1.3 Parameters of interest

Long et al. (2014) Section 1.0 describes the parameters of interest in acidification modeling. Washington State has established water quality criteria for pH, which can affect marine life. In addition, aragonite saturation state can interfere with the metabolic processes of shell-building organisms (Washington State Blue Ribbon Panel on Ocean Acidification, 2012). While Washington does not have water quality criteria for aragonite saturation state, the parameter has received strong interest as it is likely to affect shell-building organisms (summarized in Waldbusser et al., 2014).

3.1.4 Results of previous studies

Previous investigations are summarized in Washington State Blue Ribbon Panel on Ocean Acidification (2012), Long et al. (2014), and Washington Sea Grant (2014). Several studies add to the understanding of the region. Murray et al. (2015) reported pH, alkalinity, and total dissolved inorganic carbon (DIC) from the San Juan Islands. They attribute 22% of the carbon to increases in global atmospheric carbon dioxide (CO₂) since preindustrial conditions. Wootton and Pfister (2012) identified a declining trend near Tatoosh Island, in the Strait of Juan de Fuca greater than the trend in Hawaii (Doney et al., 2009). No previous effort has evaluated the impacts of regional human contributions relative to impacts from the Pacific Ocean and global atmospheric carbon dioxide. A separate modeling effort will focus on short-term forecasts of acidic conditions (MacCready et al., 2013).

3.1.5 Regulatory criteria or standards

Washington State has established water quality criteria for marine pH under Washington Administrative Code (WAC) 173-201A-210. Table 1 and Figure 2 summarize the aquatic life pH criteria for marine water and the use designations by location in the Salish Sea.

Table 1. Washington State aquatic life pH criteria for marine water.

Use Category	pH Units
Extraordinary quality	pH must be within the range of 7.0 to 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 to 8.5 with a human-caused variation within the above range of less than 0.5 units.
Good quality	pH must be within the range of 7.0 to 8.5 with a human-caused variation within the above range of less than 0.5 units.
Fair quality	pH must be within the range of 6.5 to 9.0 with a human-caused variation within the above range of less than 0.5 units.

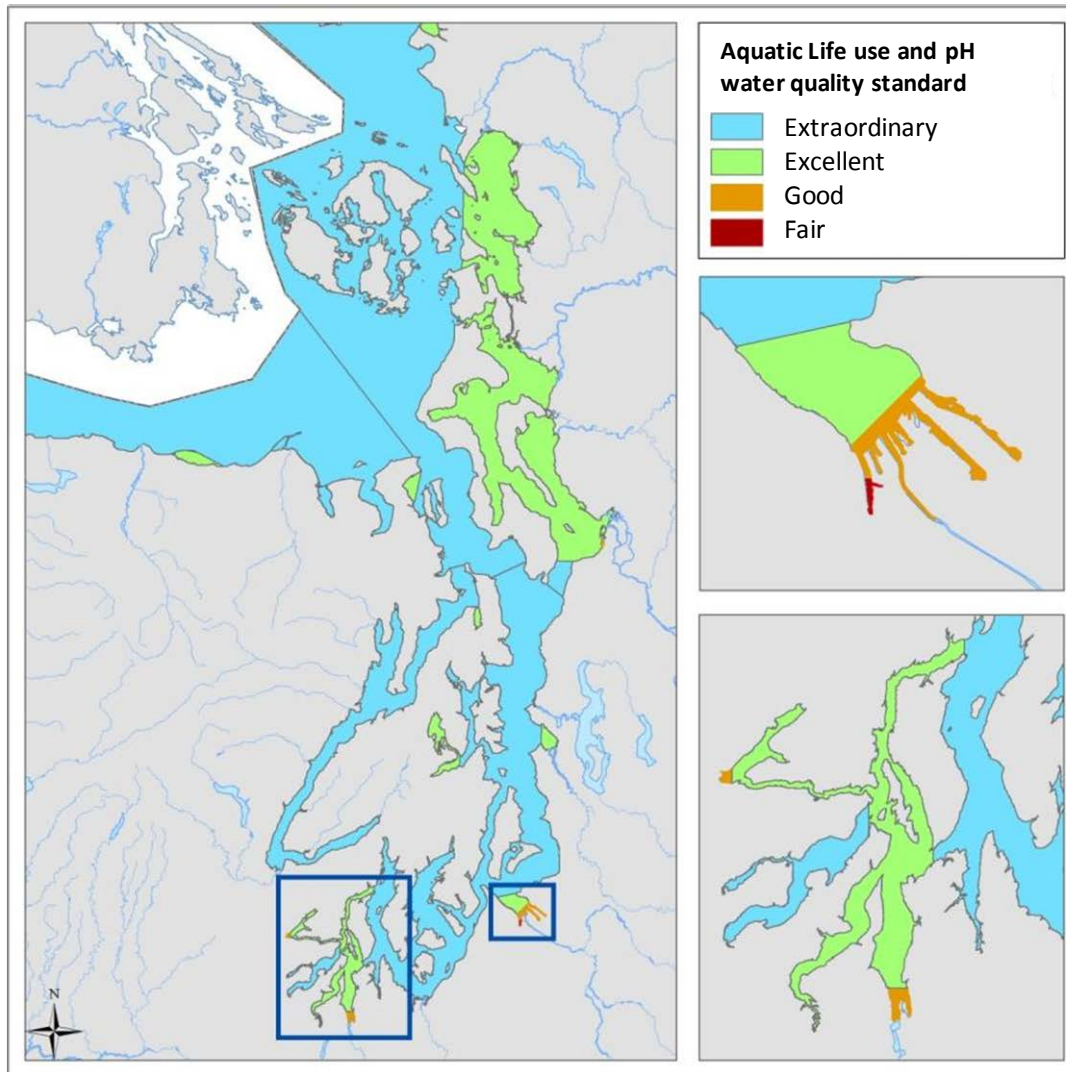


Figure 2. Washington State aquatic life use designations for the Salish Sea.

Washington State has not established water quality criteria for aragonite saturation. In 2012, the Washington State Department of Ecology (Ecology) requested that EPA lead the development of any change in water quality criteria related to acidification. Several individual research efforts are evaluating impacts on different biota at different aragonite saturation states; however, no consensus exists regarding what level of saturation state might protect biota.

We will compare model-predicted aragonite saturation state with values of 1.0 and 2.0. Saturation states below 1.0 favor dissolution or non-formation of aragonite-based shells, but other biotic impacts have been documented at higher saturation states. For example, Waldbusser et al. (2014) summarizes impacts to native *Olympia* oysters at a saturation state of 1.4 (Hettinger et al., 2012) and commercial non-native species at 1.5 to 2.0 (Barton et al., 2012). Therefore, model results will be compared against both values until either scientific consensus or regulatory action identifies alternative values for aragonite saturation state.

4.0 Project Description

4.1 Project goal

The project goal is to evaluate the relative impacts of regional human contributions to Pacific Ocean influences on acidification in the Salish Sea based on best available information. The final report will recommend appropriate next steps based on the level of certainty in the results.

4.2 Project objectives

The project objectives include the following:

- Expand the existing Salish Sea circulation and biogeochemical model (Khangaonkar et al. (2012 a, b) to include acidification parameters. Specifically, we will add state variables for total dissolved inorganic carbon (DIC) and total alkalinity to the Salish Sea model. The original model development described in Sackmann (2009) is currently being updated to include the sediment diagenesis capabilities described in Roberts et al. (2015).
- Calibrate the model to the best available information on pH and related parameters in the Salish Sea. The effort will focus on the calibration time period of 2006 and 2007 described in Khangaonkar et al. (2012 a, b). We will also consult data available from other time periods with more abundant acidification-related data to supplement data from 2006 and 2007. The calibration will include evaluating the model sensitivity.
- Evaluate the likely relative impacts of the Pacific Ocean and regional human contributions on acidification, which may vary by time of year, by basin, or vertically within the water column. This will include uncertainty in the predictions.
- Recommend next steps and identify potential management actions consistent with the level of certainty of the predictions.

4.3 Information needed and sources

Long et al. (2014) Section 4.0 details information needs for boundary conditions and model comparison data as well as the availability of that information. These include:

- Water column monitoring data from Ecology's marine ambient monitoring program.
- Supplemental data from the National Oceanic and Atmospheric Administration (NOAA), Research Vessel (R/V) Bold, and the University of Washington (UW).
- River and wastewater treatment plant inputs.
- Atmospheric partial pressure of carbon dioxide ($p\text{CO}_2$) from the Space Needle and over Washington coastal waters.
- Rate parameters.

Section 4.7 of Long et al. (2014) identifies primary information gaps that include:

- Vertical mixing
- Sediment fluxes
- Biological processes
- Marine water alkalinity, pCO₂, or total DIC
- Process studies for rate parameters

These data could improve the model calibration if improved information becomes available.

Long et al. (2014) Section 3.0 and Khangaonkar et al. (2012 a, b) describe the FVCOM-ICM model of the Salish Sea. Appendix A of Long et al. (2014) describes the model theory that will be implemented to expand the capabilities of the Salish Sea model.

4.4 Target population

The target conditions (population) in terms of constituents are pH and aragonite saturation state in the water column and changes from natural conditions due to influences from the Pacific Ocean and regional human sources of nitrogen and carbon to water and air.

4.5 Study boundaries

Figure 3 presents the model domain and grid of the Salish Sea. See Section 3.1, Long et al. (2014), and Sackmann (2009) for a description of the study area. Figure 1 presents the watershed boundary.

Water Resource Inventory Area (WRIA) and 8-digit Hydrologic Unit Code (HUC) numbers for the study area

The study area includes Water Resource Inventory Areas (WRIAs) 1 through 19 and eight-digit Hydrologic Unit Code (HUC) numbers 171100001 through 17110021.

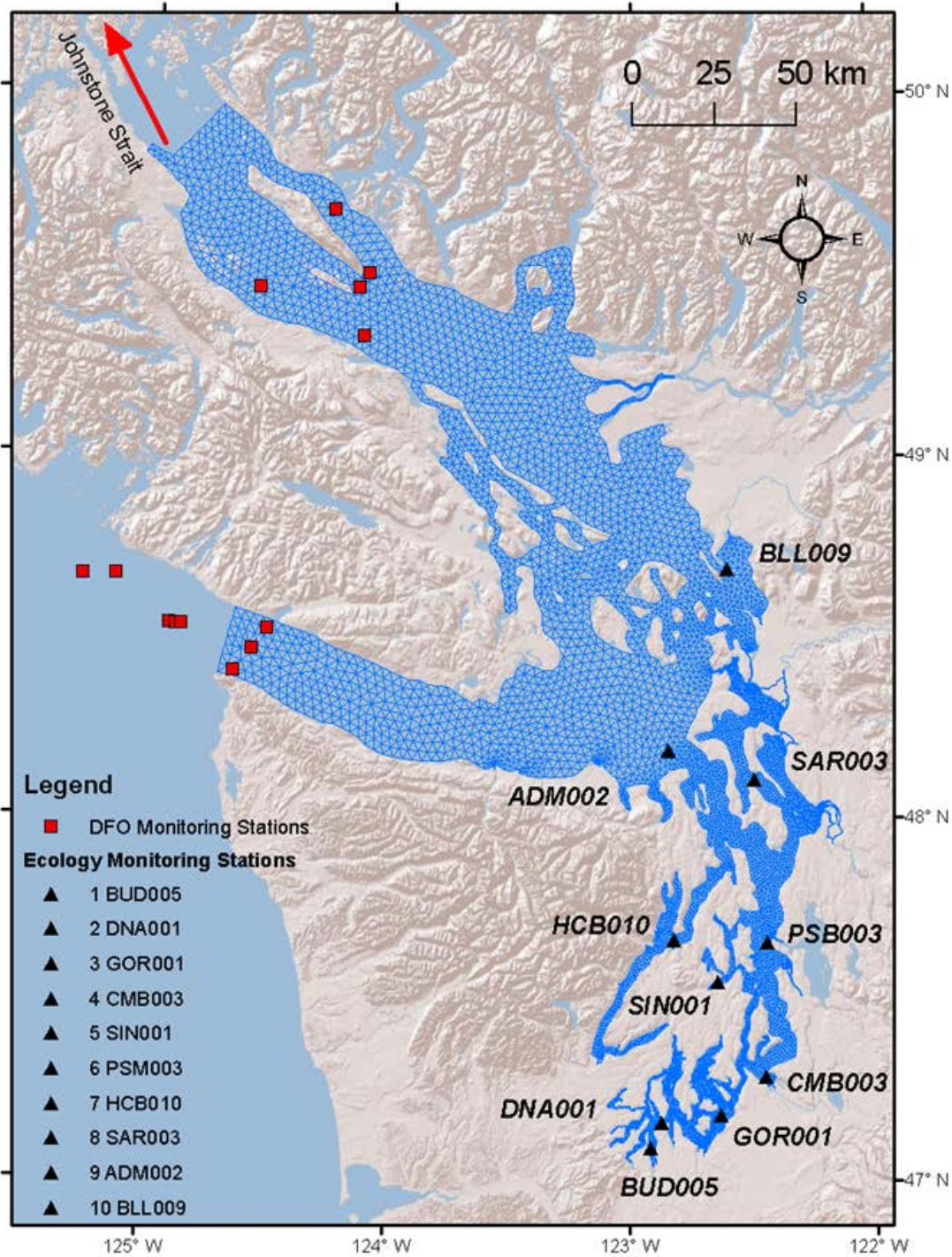


Figure 3. Circulation and water quality model grid with marine ambient monitoring stations. (Source: Khangaonkar et al., 2012b.)

4.6 Tasks required

The project will include several tasks:

- Implement software changes to add total DIC and total alkalinity to the Salish Sea biogeochemical model.
- Test software changes on idealized systems with analytical solutions.
- Apply updated code to the Salish Sea and calibrate the model to best available data for carbon cycle parameters. This model has been calibrated previously to nutrient, oxygen, and algae processes (Khangaonkar et al., 2012 a, b). Assess the sensitivity of acidification-related parameters such as pH and aragonite saturation to input data and rate parameters.
- Evaluate the relative impacts of the Pacific Ocean and regional human contributions on pH and aragonite saturation, which likely vary by time of year, by basin, and vertically within the water column. Assess uncertainty.
- Present regular progress to Ecology programs and stakeholders at key project steps.
- Document findings in the draft and final project reports.

4.7 Practical constraints

There are no or minimal logistical (e.g., field or lab) constraints for this project. Computational requirements and constraints, such as unmet data needs or unknown data quality, are described in Long et al. (2014) Section 4.7. One data set that will be considered for calibration is Ecology's marine ambient pH data. These data are currently undergoing re-evaluation first by Ecology (Krembs, 2015) and second by the Washington Ocean Acidification Center by Fassbender (2014). We will use the product of the Washington Ocean Acidification Center analysis if available during calibration. In lieu of that product, we will consider the product of Ecology's re-evaluation.

4.8 Systematic planning process

This QAPP, the QAPPs approved for related work on dissolved oxygen (Sackmann, 2009; Roberts et al., 2015), and the model approach document (Long et al., 2014) reflect a systematic planning process.

5.0 Organization and Schedule

5.1 Key individuals and their responsibilities

Table 2 lists the individuals involved in this project. All are employees of Ecology unless otherwise noted.

Table 2. Organization of project staff and responsibilities.

Staff (all are EAP except PNNL)	Title	Responsibilities
Will Kendra SCS Phone: 360-407-6698	Client	Clarifies scope of the project. Provides internal review of the QAPP and approves the final QAPP.
Mindy Roberts MIS, SCS Phone: 360-407-6804	Project Manager	Directs project. Writes the QAPP. Oversees project activities. Writes the draft report and final report.
Greg Pelletier MIS, SCS Phone: 360-407-6485	Principal Investigator	Assists in writing model theory portions of the QAPP. Participates in model evaluation. Develops software tests and evaluates results.
Teizeen Mohamedali MIS, SCS Phone: 360-715-5209	Modeling Assistant	Develops boundary conditions, applies the model, and post-processes the results. Participates in model evaluation. Assists in drafting the report.
Tarang Khangaonkar PNNL Phone: 206-528-3053	PNNL Project Manager	Oversees software development and testing. Guides the application to Salish Sea and participates in model performance evaluation. Assists in review of results and provides overall PNNL project management.
Wen Long PNNL Phone: 206-528-3056	PNNL Model Developer	Assists in development and incorporation of pH kinetics into FVCOM-ICM framework. Assists in applying the model, post-processing the results and model documentation.
Laura Bianucci PNNL Phone: 206-528-3414	PNNL Model Developer	Leads the development of a carbonate chemistry module into FVCOM-ICM and its application into the Salish Sea model. Assists in post-processing and documentation of model application and tests.
Karol Erickson MIS, SCS Phone: 360-407-6694	Unit Supervisor for the Project Manager	Provides internal review of the QAPP, approves the budget, and approves the final QAPP.
Will Kendra SCS Phone: 360-407-6698	Section Manager for the Project Manager	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Jessica Archer WOS Phone: 360-407-6596	Section Manager for the Study Area	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Tom Gries Phone: 360-407-6327	NEP Quality Assurance Officer	Reviews the draft QAPP and recommends its approval.
William R. Kammin Phone: 360-407-6964	Ecology Quality Assurance Officer	Reviews and approves the draft QAPP and the final QAPP.

Notes for Table 2:

EAP: Environmental Assessment Program

EIM: Environmental Information Management database

MIS: Modeling and Information Support Unit

NEP: National Estuary Program

PNNL: Pacific Northwest National Laboratory

QAPP: Quality Assurance Project Plan

SCS: Statewide Coordination Section

WOS: Western Operations Section

5.2 Special training and certifications

Key project personnel have previous experience developing and applying biogeochemical models in the Salish Sea environment.

5.3 Organization chart

Table 2 lists the key individuals, their current positions, and their responsibilities for this project.

5.4 Project schedule

Table 3 presents the proposed schedule for this project.

Table 3. Proposed schedule for completing field and laboratory work, data entry into EIM, and reports.

Field and laboratory work	Due date	Lead staff
Field work completed	Not applicable	Not applicable
Laboratory analyses completed	Not applicable	
Environmental Information System (EIM) database		
EIM Study ID	Not applicable	
Product	Due date	Lead staff
EIM data loaded	Not applicable	Not applicable
EIM data entry review	Not applicable	Not applicable
EIM complete	Not applicable	Not applicable
Model development	Due date	Lead staff
Setup and testing	June 2015	PNNL
Calibration to Salish Sea conditions	December 2015	PNNL and Ecology
Establishing modeling capability at Ecology	June 2016	PNNL
Application to Salish Sea conditions	June 2016	Ecology and PNNL
Final report		
Author lead / Support staff	Roberts / Pelletier / Mohamedali / Khangaonkar / Long / Bianucci	
Schedule		
Draft due to supervisor	May 2016	
Draft due to client/peer reviewer	May 2016	
Draft due to external reviewer(s)	June 2016	
Final (all reviews done) due to publications coordinator	August 2016	
Final report due on web	September 2016	

PNNL: Pacific Northwest National Laboratory

5.5 Limitations on schedule

The two tasks producing the largest uncertainty in the project schedule are (1) model setup and testing and (2) calibration. These will be managed through frequent communication and coordination within the modeling team.

5.6 Budget and funding

Table 4 presents the project budget funded by the National Estuary Program (NEP) grants. The totals do not include costs for some Ecology staff time funded through other state or federal sources.

Table 4. Project budget and funding.

Parameter	PNNL budget – Amendment 8 (DSM25)	PNNL budget – Amendment 10 (in progress)	Ecology budget*	Project team total
Quality Assurance Project Plan	\$12,120			\$12,120
Model setup and testing	\$96,960			\$96,960
Model calibration	\$96,960			\$96,960
Model application	\$32,320	\$32,320	\$37,500	\$102,140
Project report		\$24,240	\$5,000	\$29,240
Project management		\$12,120		\$12,120
Total	\$238,360	\$68,680	\$42,500	\$349,540

* Does not include in-kind contributions for Ecology staff funded through other state and federal sources.

6.0 Quality Objectives

6.1 Decision Quality Objectives (DQOs)

The overall project goal is to assess the relative impacts of (1) Pacific Ocean and (2) regional human sources on acidification in the Salish Sea. As described in Long et al. (2014), this work has not been attempted to date, and information gaps exist. We cannot establish decision quality objectives for model acceptance a priori. The final report will summarize model performance, will describe how model skill affects the interpretation and uncertainty of the results, and will recommend next steps that could include management actions or further projects.

6.2 Measurement Quality Objectives

Not applicable; no field measurements are included. Section 7.5 describes an ongoing evaluation of the quality of a key acidification-related data set. The final report will summarize the data used in the model calibration and evaluation.

6.2.1 Targets for Precision, Bias, and Sensitivity

6.2.1.1 Precision

Not applicable; no field measurements are included.

6.2.1.2 Bias

Not applicable; no field measurements are included.

6.2.1.3 Sensitivity

Not applicable; no field measurements are included. See Section 7.1.2 for model sensitivity and uncertainty.

6.2.2 Targets for Comparability, Representativeness, and Completeness

6.2.2.1 Comparability

No field measurements are included. No previous modeling project has evaluated the relative influences of the Pacific Ocean and regional human sources on acidification in the Salish Sea.

6.2.2.2 Representativeness

No field measurements are included. We will document the representativeness of the data described in Long et al. (2014) Section 4.0, Section 7.5 below, and currently being compiled by the Washington Ocean Acidification Center (Fassbender, 2014) in the final report.

6.2.2.3 Completeness

Not applicable; no field measurements are included.

6.2.3 Targets and Goals for Modeling

We will assess model performance using both root-mean-squared-error (RMSE) and bias for salinity, temperature, nitrate plus nitrite, pH, total DIC, total alkalinity, and chlorophyll a (algae) for all stations with sufficient data. At a minimum, we will evaluate the error of pH predictions compared with Ecology's re-analysis of the historical database (Krembs, 2015) in the event that the Washington OA Center analysis is delayed or not completed. We will also consider other sources of pH data, as described in Long et al. (2014).

These measures of model accuracy will be evaluated as time series in the surface and bottom layers. In addition, we will check the vertical profiles for characteristic shapes identified in the ambient monitoring program and other information sources with acceptable data from Long et al. (2014).

Calibration will focus on representing seasonal pH concentrations throughout the model domain. The overall process will be to describe the bulk of the data, and short-term effects of ephemeral events or those affecting limited areas may not be represented.

Because of the uncertain state-of-the-art in model performance criteria, the inherent error in input and observed data, and the approximate nature of model formulations, absolute criteria for model acceptance or rejection are not appropriate for this effort. We cannot establish acceptance criteria a priori, nor is there a body of literature with which to compare or support criteria for performance of estuarine acidification models. The final report will summarize model results and performance and will compile results from relevant existing studies and any new studies published in the interim.

7.0 Sampling Process Design (Experimental Design)

7.1 Study Design and Model Selection

Sackmann (2009) describes the initial Salish Sea circulation and biogeochemical model development. Khangaonkar et al. (2012 a, b) and Roberts et al. (2014) summarize the model setup and calibration results and application to current and future scenarios that isolate the influences of Pacific Ocean and regional human sources on dissolved oxygen in the Salish Sea.

Long et al. (2014) Section 3.0 describes the modeling framework for adding acidification parameters to the Salish Sea model. The model application will use the best available information described in Long et al. (2014) Section 4.0 with supplemental information in Section 7.5 below.

We will develop and apply the model in three phases:

1. Model setup and testing
2. Calibration to existing information
3. Application to scenarios

7.1.1 Model setup and testing

Long et al. (2014) Appendix A presents the model equations, and Long et al. (2014) Section 5.1 describes FVCOM-ICM model performance tests. Subroutines in acidification simulation will be set up and tested against idealized conditions where analytical solutions are available. As described in Long et al. (2014), these include:

- Exact solution with a batch reactor
- One-dimensional, steady-state channel case
- One-dimensional, dynamic channel case

Once the tests are complete for idealized conditions, the subroutines will be coupled with the FVCOM-ICM code and the implementation tested for errors before beginning calibration. The Excel formulation of CO2SYS (Pelletier et al., 2015), after the work of Lewis and Wallace (1998), will be used in model setup and testing. Orr et al. (2015) recently published a comparison among carbonate chemistry calculation packages and found that Pelletier et al. (2015) was consistent with the Matlab version of CO2SYS (Lewis and Wallace, 1998).

7.1.2 Calibration approach

Sackmann (2009) describes the general approach to calibrating the biogeochemical model of the Salish Sea, focusing on dissolved oxygen. We will follow the same protocols for acidification parameters, further described in Long et al. (2014) Section 5.2 for Salish Sea acidification conditions. We will continue with the baseline year of 2006; however, we will also evaluate alternative baseline years if they facilitate model calibration.

Rate constants are described in Appendix A of Long et al. (2014) based on best available information.

The model calibration effort will consist of running the model and comparing the results to observed data for total DIC, total alkalinity, and pH. Few continuous data records are available for pH or related variables, or cover limited locations. Most data are profiles such as those collected monthly by Ecology across multiple stations, UW or NOAA seasonal cruises, or a single station sampled once in a day, week, or month. Therefore, the data may not characterize the full diel cycle that could influence pH and related parameters in the euphotic zone. Data will be mapped to the corresponding model computational element and layer for comparison with model output.

Performance criteria are based on both quantitative and qualitative measures. Quantitative measures will rely on root-mean-squared error (RMSE) and bias assessed throughout the model domain and throughout the period of simulation. Because of the uncertainty and lack of available literature on model performance criteria, the inherent error in input and observed data, and the approximate nature of model formulations, absolute criteria for model acceptance or rejection are not appropriate for this effort. We will focus on the model's ability to represent overall pH throughout the study area and seasonal patterns in acidification parameters such as aragonite saturation state calculated from other carbon cycle parameters.

Because acidification has not been evaluated before in the Salish Sea, and very few estuarine ocean acidification modeling studies have been published including measures of model skill (Fennel et al., 2008; Artioli et al., 2012; Artioli et al. 2013; Hauri et al., 2013), we have insufficient a priori information on critical conditions. One of the objectives is to identify what times of year, basins or bays, or critical locations in the water column are most critical for pH or aragonite saturation.

Several sensitivity tests will be performed during calibration. The purpose is to identify which boundary conditions or rate parameters are most influential. These may include Pacific Ocean boundary conditions, surface winds, ammonia preference in nutrient uptake, precipitation, remineralization of particulate organic carbon and dissolved organic carbon under different oxygen regimes, denitrification, as well as sediment fluxes of total DIC. The results of perturbing the various boundary conditions and rate constants will be summarized in a semi-quantitative assessment of uncertainty.

7.1.3 Application to scenarios

Following calibration, the model will simulate several sets of scenarios, including:

- Current Pacific Ocean conditions with natural regional contributions (no human nitrogen or carbon air emissions or water discharges). This is the baseline condition against which other scenarios will be compared.
- Current Pacific Ocean conditions with current water emissions (natural and human) but no air emissions. By comparing the results of this scenario against the baseline condition, regional human water-based impacts will be identified.

- Current Pacific Ocean conditions with current air emissions but only natural water inputs (no human nitrogen or carbon). By comparing the results of this scenario against the baseline condition, regional human air-based impacts will be identified.

The regional water inputs for both wastewater treatment plants and rivers are summarized in Mohamedali et al. (2011).

We will also evaluate a limited number of alternative Pacific Ocean conditions for the modeling that will be developed in collaboration with external advisors. These could include historical conditions at a particular time and/or potential future conditions, based on varying Pacific Ocean carbon parameters, oxygen, or nitrogen. These scenarios would identify impacts from various Pacific Ocean conditions.

7.1.4 Computational requirements

Long et al. (2014) Section 7.4 describes the computational requirements of the Salish Sea model. The model updates for acidification will not change the overall computational requirements.

7.2 Maps or diagram

Figure 1 presents the boundaries of the study area, and Figure 3 shows the model domain and computational grid. Long et al. (2014) provides links to monitoring stations with available data collected by Ecology. The approach document also referenced monitoring conducted by the UW, NOAA, Canada's Department of Fisheries and Oceans, and others. Some data are available from www.nanoos.org.

Figure 4 identifies Ecology's core monitoring stations in the Salish Sea. Section 7.5 describes ongoing data quality evaluations and presents maps of data collection locations.

7.3 Assumptions underlying design

The model framework and assumptions underlying the study design are described in Long et al. (2014) Section 3.0 and Appendix A. No new environmental data will be developed.

From that document, major assumptions include the following:

- Estimating alkalinity from salinity is a reasonable proxy since very few data are available (Section 3.4 of Long et al., 2014)
- Chlorophyll is a reasonable proxy to describe spatial and temporal patterns in phytoplankton abundance (Section 4.7 of Long et al., 2014)
- Calcium availability does not limit aragonite saturation state (Section 4.7 of Long et al., 2014)
- Dissociation constants, especially under low salinity, are reasonably described by available literature (Section 4.7 of Long et al., 2014).

7.4 Relation to objectives and site characteristics

The study design supports the objectives of the project. Because limited information exists and the approach has not been attempted previously in the Salish Sea or elsewhere, we will report model errors, will describe how those errors affect interpretation, and will recommend how the results could be used to inform management questions.

7.5 Characteristics of existing data

Available data and primary information gaps are described in Section 4.0 of Long et al. (2014). An ongoing collaboration among Ecology, UW, and NOAA will compile and evaluate ambient monitoring data collected by Ecology and others for pH and related parameters to establish a representative baseline for pH both geographically and seasonally. This effort is led by the Washington Ocean Acidification Center at the UW. Ecology's historical pH data are currently being re-evaluated (Krembs, 2015) and delivered to the Washington Ocean Acidification Center, where a project is funded to evaluate data quality and analyze the collective data sets of UW, NOAA, and Ecology (Fassbender, 2014). One of the products is an evaluation of the quality of these data both in terms of sensor performances and environmental context; no quality evaluation is currently available. This has been identified as an important information gap not just for this project but for overall regional knowledge of ocean acidification (Washington State Blue Ribbon Panel on Ocean Acidification, 2012).

Figure 5 shows the locations of current and historical buoys deployed through the UW and others, while Figure 6 identifies pH data from fixed locations. Figure 7 summarizes the stations surveyed during PRISM cruises; however, pH and related variables were only monitored in the February 2008 cruise. Values are not available for other cruises. Figure 8 identifies stations monitored by Canada's Department of Fisheries and Oceans as part of the Line P program (DFO, 2015).



Figure 4. Ecology's Marine ambient monitoring program core stations. (Source: Bos et al., 2015.)

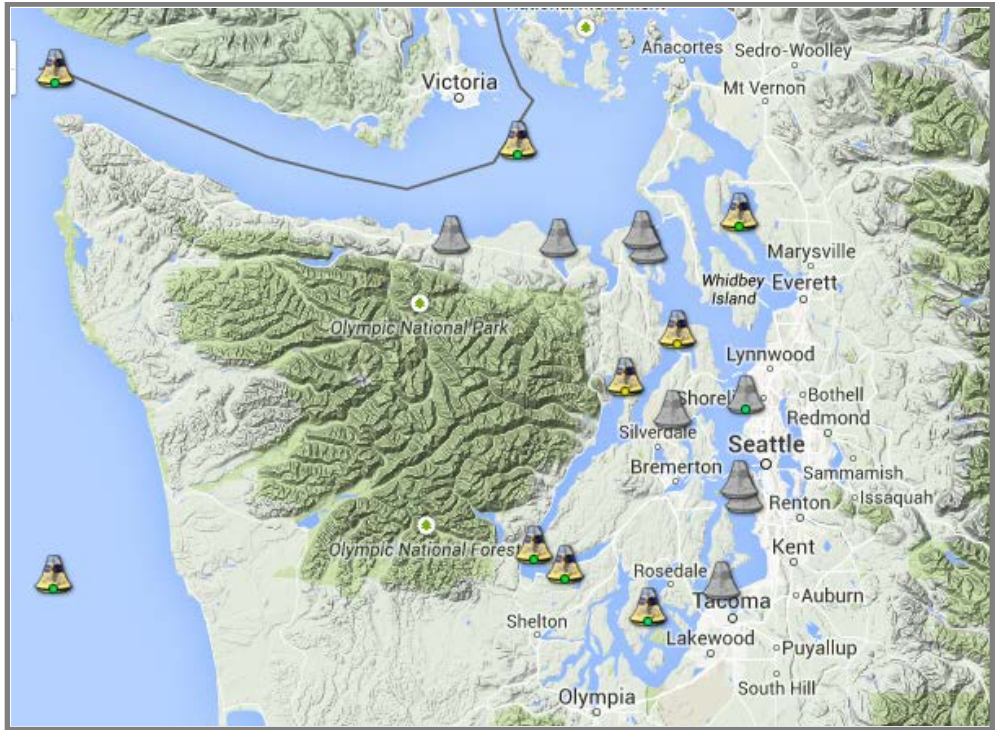


Figure 5. ORCA buoys currently in operation (yellow) and previous deployments (gray). (Source: www.nanoos.org.)

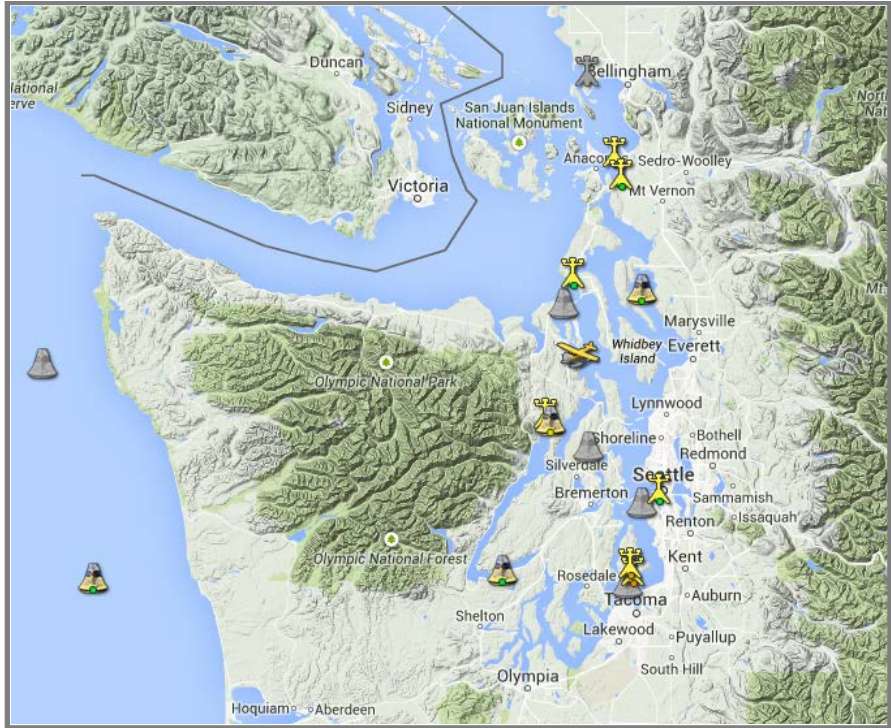


Figure 6. Sites with pH data, including ORCA buoys and land-based stations. (Source: www.nanoos.org.)

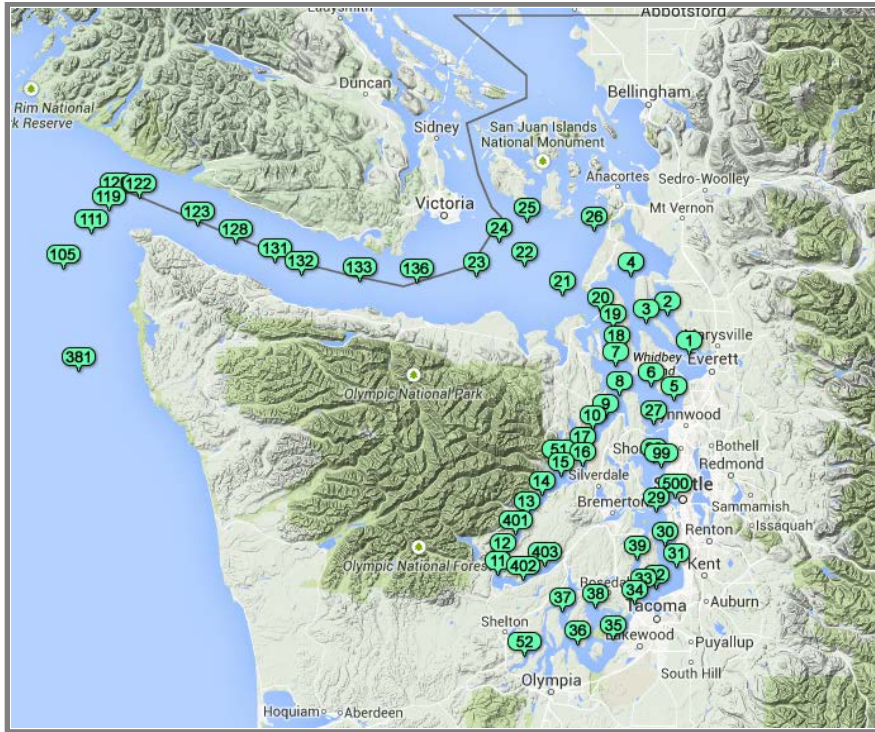


Figure 7. Stations visited during the University of Washington's PRISM cruises. (Source: nvs.nanoos.org/CruisePrism.)

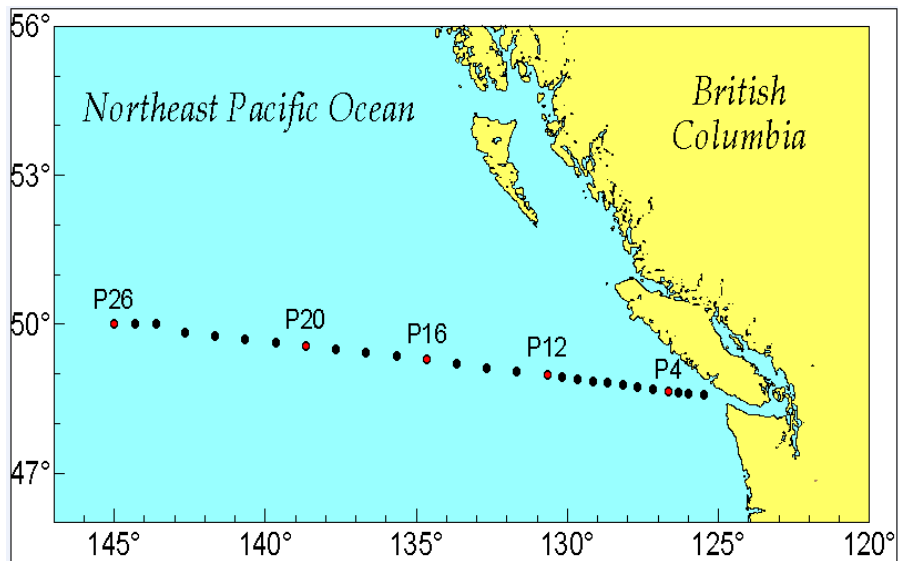


Figure 8. Stations monitored during Station P cruises by Canada's Department of Fisheries and Oceans. (Source: Miller et al., 2010).

Figure 9 presents preliminary pH data from Ecology’s ambient monitoring program from 1992 to 2013. These include monthly grab samples at 26 stations in Puget Sound or the Straits. The figure compiles data throughout the water column using electrode-based marine pH sensors that are widely used for water quality monitoring programs in the US. Within the technical limitations of the sensor, Ecology’s pH data represent both good data and best estimates available. Following a recent in-depth reanalysis and re-calculation of pH data based on raw voltage sensor outputs, a detailed quality control (QC) process was performed, and a significant improvement of the existing data set was achieved (Krembs, 2015). The strength of the data set is its spatial and temporal scale and the statistical power of the large data set.

While the accuracy of the absolute magnitudes of the pH values is part of the Washington Ocean Acidification Center evaluation (Fassbender, 2014), the relative patterns likely represent the range of variability over time and by location. The goal of the modeling effort is to capture the spatial variability in measured pH, using the model. For example, we will check the relative magnitudes and range of variability from the model against these data by station as part of an initial calibration step. We will document these and other data consulted in the model calibration and application in the final report.

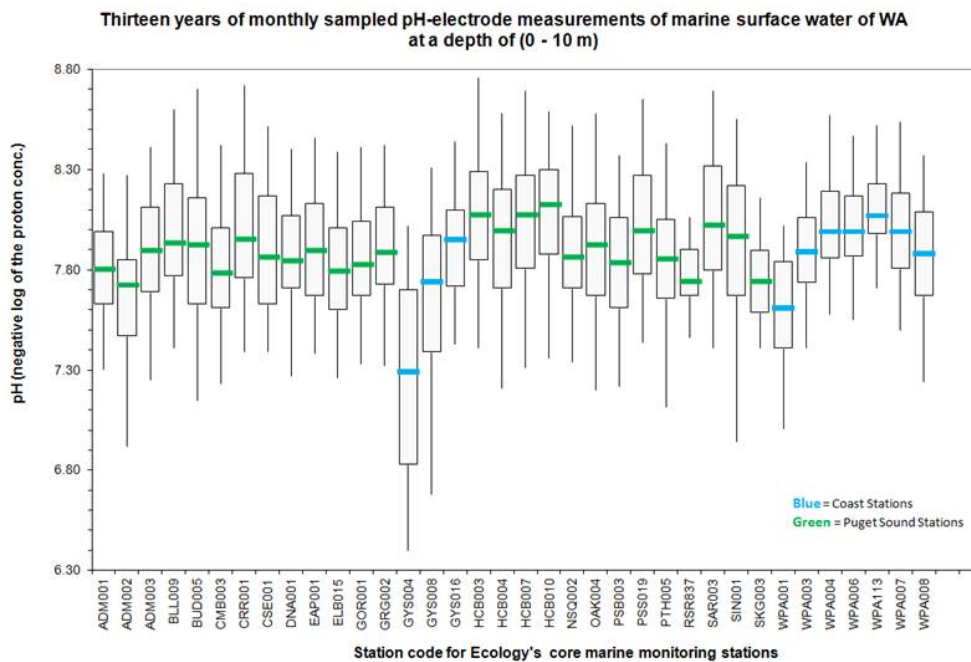


Figure 9. Preliminary pH data from Ecology's ambient monitoring program for 1992-2013. (Source: Krembs, 2015.)

Data are undergoing a quality assurance (QA) evaluation by the Washington OA Center and will be updated as better information becomes available.

8.0 Sampling Procedures

8.1 Field measurement and field sampling SOPs

Not applicable; no sampling or laboratory analysis is planned.

8.2 Containers, preservation methods, holding times

Not applicable; no sampling or laboratory analysis is planned.

8.3 Invasive species evaluation

Not applicable; no sampling or laboratory analysis is planned.

8.4 Equipment decontamination

Not applicable; no sampling or laboratory analysis is planned.

8.5 Sample ID

Not applicable; no sampling or laboratory analysis is planned.

8.6 Chain-of-custody, if required

Not applicable; no sampling or laboratory analysis is planned.

8.7 Field log requirements

Not applicable; no sampling or laboratory analysis is planned.

9.0 Measurement Methods

9.1 Field procedures table/field analysis table

Not applicable; no sampling or laboratory analysis is planned.

9.2 Lab procedures table

Not applicable; no sampling or laboratory analysis is planned.

9.3 Sample preparation method(s)

Not applicable; no sampling or laboratory analysis is planned.

9.4 Special method requirements

Not applicable; no sampling or laboratory analysis is planned.

9.5 Lab(s) accredited for method(s)

Not applicable; no sampling or laboratory analysis is planned.

10.0 Quality Control (QC) Procedures

10.1 Table of field and lab QC required

Not applicable; no sampling or laboratory analysis is planned.

10.2 Corrective action processes

No sampling or laboratory analysis is planned. See Section 7.1.1 for model setup and testing, and Section 7.1.2 for model calibration and sensitivity testing. Calibration is, by nature, an iterative process that converges on minimizing model skill to a level consistent with understanding of underlying processes and data gaps. We will evaluate model skill and interpret model output considering uncertainty.

11.0 Data Management Procedures

11.1 Data recording/reporting requirements

Not applicable; no sampling or laboratory analysis is planned.

11.2 Laboratory data package requirements

Not applicable; no sampling or laboratory analysis is planned.

11.3 Electronic transfer requirements

Not applicable; no sampling or laboratory analysis is planned.

11.4 Acceptance criteria for existing data

Sackmann (2009 and 2011) and Roberts et al. (2014 and 2015) summarize information needed for early iterations of FVCOM-ICM. Long et al. (2014) summarizes additional information needed to parameterize and calibrate the acidification model.

An important consideration is that Ecology's water column data are currently undergoing extensive evaluation first by Ecology and then by the Washington Ocean Acidification Center, as described in Section 7.5 above. We will substitute vetted data sets as they are available and will appropriately describe uncertainty and limitations of the modeling that result from data uncertainty in the final report. The final report will also cite and summarize the retrospective QC screening procedures by Ecology and the Washington Ocean Acidification Center that produces the data set used in this project.

We will use the best available information from reputable sources such as Ecology, NOAA, and UW. Data used for calibration will be acceptable if they are obtained from reputable sources such as scientific publications, government documents, and other reports that represent systematic planning processes, documented quality assurance reviews, and peer review. We will evaluate the quality of all data used to compare with model-predicted ocean acidification and will describe the information sources and uses in the final report.

11.5 EIM/STORET data upload procedures

Not applicable; no sampling or laboratory analysis is planned.

11.6 Model information management procedures

Roberts et al. (2015) describes model information management procedures for the Salish Sea model. We will follow the same procedures for expanding the capabilities to simulate acidification parameters.

12.0 Audits and Reports

12.1 Number, frequency, type, and schedule of audits

No field or laboratory data are planned, so audits do not apply. For modeling efforts, interim results are evaluated internally within the project team to determine progress toward calibration. Interim results are also shared externally with stakeholders as presentations. The final project report will be consistent with Ecology's peer review and publications guidelines.

12.2 Responsible personnel

Table 2 lists staff responsibilities. The project team collaborates on interim results review.

12.3 Frequency and distribution of report

One project report is planned; however, interim results are shared with external stakeholders.

12.4 Responsibility for reports

Table 3 lists the personnel responsibilities for the final report.

13.0 Data Verification

13.1 Field data verification, requirements, and responsibilities

Not applicable; no sampling or laboratory analysis is planned.

13.2 Lab data verification

Not applicable; no sampling or laboratory analysis is planned.

13.3 Validation requirements, if necessary

Not applicable; no sampling or laboratory analysis is planned.

13.3 Model calibration and evaluation

13.3.1 Methods Overview

Calibration refers to the process of adjusting model parameters within physically defensible ranges until the resulting predictions give the best possible match with observed data. Model evaluation is the process used to determine whether a model and its analytical results are of sufficient quality to serve as the basis for a decision and whether the model is capable of approximating the real system of interest (EPA, 2009). Some efforts refer to this as validation, confirmation, or verification.

Model calibration is an iterative procedure that combines quantitative comparison with measured data and qualitative assessments regarding the underlying processes. We will use both goodness of fit statistics and visual comparison of predicted and observed time series and depth profiles for pH, and related parameters (Krause et al., 2005). The goal is to maximize model skill consistent with our understanding of the underlying processes.

Figure 10 summarizes the model setup, testing, and calibration process for the acidification model. Once the acidification code development and testing are complete, we will run the model for the baseline 2006 conditions, using the previous dynamic boundary conditions described in Roberts et al. (2014) and Mohamedali et al. (2011). We will compare predicted results for water column parameters with best available data until the project team has optimized model skill while considering the inherent limitations of the available data. If 2006 data are not sufficient to calibrate the model, we will consult data for other years and will consider updating the baseline year for calibration. The calibration will be presented to external stakeholders before proceeding with scenario evaluation.



Figure 10. Process for acidification model development, calibration, and application.

Long et al. (2014) Appendix A presents the model summary and rate parameters.

13.3.2 Targets and Goals

See Section 6.2.3.

13.3.3 Sensitivity and Uncertainty Analyses

Model sensitivity analyses are described in Section 7.1.2.

Due to the limited data currently available for acidification parameters in the Salish Sea, we will quantify uncertainty of the predictions. This will distinguish, where possible, between uncertainty related to the underlying data and uncertainty in our fundamental understanding and representation of the processes. See Section 14.1 for related information.

14.0 Data Quality (Usability) Assessment

14.1 Process for determining whether project objectives have been met

The project goal is to evaluate the relative influences of the Pacific Ocean and regional human sources of nitrogen and carbon on acidification in the Salish Sea. This will use the best available information, yet recognizes the limitations of that data. Long et al. (2014) Section 4.0 identifies available data as well as significant information gaps, which have been recognized regionally (Washington State Blue Ribbon Panel on Ocean Acidification, 2012). Rather than target a specific model quality objective, we will evaluate the quality of the source information, the understanding of fundamental processes affecting acidification, and the certainty of the initial assessment of relative impacts in the final report.

The focus is on relative impacts rather than on the absolute magnitudes of pH or aragonite saturation. We will compare model output with measured pH where available during calibration. Scenarios will be evaluated as changes from natural conditions or other baselines for both pH and aragonite saturation state. We will compare model output with pH criteria and two aragonite saturation state levels described in Section 3.1.5, describing how uncertainty affects the findings.

The outcome will be an initial assessment of the relative source contributions as well as the likely relative influences of different processes. We will provide a semi-quantitative assessment of the uncertainty of the findings similar to that used for the relative influences of different Pacific Ocean and human sources on dissolved oxygen in the Salish Sea (see Roberts et al., 2014, Figure 49).

The final report will include interpretation and next steps. If the results are not certain enough to support specific management actions, we will recommend activities that would decrease uncertainty in the most influential parameters. We will also identify what geographic areas or seasons of the year are most influenced by the Pacific Ocean or regional human sources of nitrogen or carbon.

14.2 Data analysis and presentation methods

Not applicable; no sampling or laboratory analyses are planned.

14.3 Treatment of non-detects

Not applicable; no sampling or laboratory analysis is planned.

14.4 Sampling design evaluation

Not applicable; no sampling or laboratory analysis is planned.

14.5 Documentation of assessment

The final project report will document the results of this project. In addition, we will present interim findings at key project steps to stakeholders.

15.0 References

- Artioli, Y., J.C. Blackford, M. Butenschön, J.T. Holt, S.L. Wakelin, H. Thomas, A. Boges. J.I. Acllen. 2012. The carbonate system in the North Sea: Sensitivity and model validation. *Journal of Marine Systems* 102-104: 1-13. http://www.co2.ulg.ac.be/pub/artioli_et_al_2012.pdf.
- Artioli, Y., J.C. Blackford, G. Nondal, R.G.J. Bellerby, S.L. Wakelin, J.T. Holt, M. Butenschön, J.I. Allen. 2013. Heterogeneity of impacts of high CO₂ on the North Western European Shelf. *Biogeosciences* 11:601-612. Doi: 10.5194/bg-11-601-2014. https://www.researchgate.net/publication/258758267_Heterogeneity_of_impacts_of_high_CO2_on_the_North_Western_European_Shelf.
- Barton, A., B. Hales, G.G. Waldbusser, C. Langdon, and R.A. Feely. 2012. The Pacific oyster, *Crassostrea gigas*, shows negative correlation to naturally elevated carbon dioxide levels: Implications for near-term ocean acidification effects. *Limnology and Oceanography* 57: 698-710. doi: 10.4319/lo.2012.57.3.0698.
- Bos, J., M. Keyzers, L. Hermanson, C. Krembs, and S. Albertson. 2015. Quality Assurance Monitoring Plan: Long-Term Marine Waters Monitoring, Water Column Program. Washington State Department of Ecology Publication No. 15-03-101. <https://fortress.wa.gov/ecy/publications/SummaryPages/1503101.html>
- Department of Fisheries and Oceans. 2015. Line P Program, URL: <http://www.pac.dfo-mpo.gc.ca/science/oceans/data-donnees/line-p/index-eng.html>.
- Doney, S.C., V.J. Fabry, R.A. Feely, and J.A. Kleypas. 2009. Ocean acidification: The other CO₂ problem. *Annual Review of Marine Science* 1:169-192. DOI: 10.1146/annurev.marine.010908.163834.
- EPA. 2009. Guidance on the Development, Evaluation, and Application of Environmental Models. Office of the Science Advisor, Council for Regulatory Environmental Modeling. EPA/100/K-09/003.
- Fassbender, A.J. 2014. Collaborating to build strategic scientific infrastructure for long-term ocean acidification monitoring and prediction in Washington State. Proposal to Postdocs Applying Climate Expertise (PACE) Partners (NOAA Pacific Marine Environmental Laboratory, University of Washington Joint Institute for the Study of Ocean Atmosphere, Washington State Department of Ecology).
- Feely, R.A., T. Klinger, J.A. Newton, and M. Chadsey. 2012. Scientific Summary of Ocean Acidification in Washington State Marine Waters. NOAA OAR Special Report.
- Fennel, K., J. Wilkin, M. Previdid, and R. Najjar. 2008. Denitrification effects on air-sea CO₂ flux in the coastal ocean: Simulations for the northwest North Atlantic. *Geophysical Research Letters* L24608, doi:10.1029/2008GL036147.

https://www.researchgate.net/publication/228697840_Denitrification_effects_on_air-sea_CO2_flux_in_the_coastal_ocean_Simulations_for_the_northwest_North_Atlantic

Hauri, C., N. Gruber, M. Vogt, S.C. Doney, R.A. Feely, Z. Lachkar, A. Leinweber, A.M.P. McDonnell, M. Munnich, and G.-K. Plattner. 2013. Spatiotemporal variability and long-term trends of ocean acidification in the California Current System. *Biogeosciences* 10:193-216 doi: 10.5194/BG-10-193-2013. <http://www.biogeosciences.net/10/193/2013/bg-10-193-2013.pdf>

Hettinger, A., E. Sanford, T.M. Hill, A.D. Russell, K.N.S. Sato, J. Hoey, M. Forsch, H.N. Page, and B. Gaylord. 2012. Persistent carry-over effects of planktonic exposure to ocean acidification in the Olympia oyster. *Ecology* 93:2758-2768.

Khangaonkar, T., B. Sackmann, W. Long, T. Mohamedali, and M. Roberts. 2012 a. Simulation of annual biogeochemical cycles of nutrient balance, phytoplankton bloom(s), and DO in Puget Sound using an unstructured grid model. *Ocean Dynamics*. (2012) 62:1353–1379. DOI 10.1007/s10236-012-0562-4.

Khangaonkar T, W Long, B Sackmann, T Mohamedali, and M Roberts. 2012 b. Puget Sound Dissolved Oxygen Modeling Study: Development of an Intermediate Scale Water Quality Model. PNNL-20384 Rev 1, prepared for the Washington State Department of Ecology (Publication No. 12-03-049), by Pacific Northwest National Laboratory, Richland, Washington.

Krause, D., D.P. Boyle, and F. Base. 2005. Comparison of different deficiency criteria for hydrological model assessment. *Advances in Geoscience* 5:89-97.

Krembs, Christopher. 2015. Personal communication with Mindy Roberts by email January 27, 2015.

Lewis, E. and D.W.R. Wallace. 1998. Program Developed for CO₂ System Calculations, ORNL/CDIAC-105, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory.

Lombard, S. and C. Kirchmer. 2004. Guidelines for Preparing Quality Assurance Project Plans for Environmental Studies. Washington State Department of Ecology, Olympia, WA. Publication No. 04-03-030.

<https://fortress.wa.gov/ecy/publications/SummaryPages/0403030.html>

Long, W., T. Khangaonkar, M. Roberts, and G. Pelletier. 2014. Approach for Simulating Acidification and the Carbon Cycle in the Salish Sea to Distinguish Regional Source Impacts. Washington State Department of Ecology Publication No. 14-03-002.

<https://fortress.wa.gov/ecy/publications/SummaryPages/1403002.html>.

MacCready, P., N. Banas, and S. Siedlecki. 2013. Proposal for the Development of an Ocean Acidification Forecast Model. Submitted to the Washington Ocean Acidification Center.

Miller, L.A., Christian, M. Davelaar, W.K. Johnson, and J. Linguanti. 2010. Carbon Dioxide,

Hydrographic and Chemical Data Obtained During the Time Series Line P Cruises in the North-East Pacific Ocean from 1985-2010. http://cdiac.ornl.gov/ftp/oceans/CLIVAR/Line_P.data/. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, US Department of Energy, Oak Ridge, Tennessee. doi: 10.3334/CDIAC/otg.CLIVAR_Line_P_2009.

Mohamedali, T., M. Roberts, B. Sackmann, and A. Kolosseus. 2011. Puget Sound Dissolved Oxygen Model Nutrient Load Summary for 1999-2008. Washington State Department of Ecology Publication No. 11-03-057.

<https://fortress.wa.gov/ecy/publications/SummaryPages/1103057.html>

Murray, J.W., E. Roberts, E. Howard, M. O'Donnell, C. Bantam, E. Carrington, M. Foy, B. Paul, and A. Fay. 2015. An inland sea high nitrate-low chlorophyll (HNLC) region with naturally high pCO₂. *Limnology and Oceanography*. doi: 10.1002/lno.10062.

Orr, J.C., J.-M. Epitalon, and J.-P. Gattuso. 2015. Comparison of ten packages that compute ocean carbonate chemistry. *Biogeosciences* 12:1483-1510. doi: 10.5194/bg-12-1483-2015.

Pelletier, G., E. Lewis, and D. Wallace. 2015. CO2SYS.XLS: A calculator for the CO₂ system in seawater for Microsoft Excel/VBA. Washington State Department of Ecology, Olympia, WA and Brookhaven National Laboratories, Upton, NY. www.ecy.wa.gov/programs/eap/models.html.

Roberts, M., G. Pelletier, T. Khangaonkar, and W. Long. 2015. Quality Assurance Project Plan: Salish Sea Dissolved Oxygen Modeling Approach: Sediment-Water Interactions. Washington State Department of Ecology Publication No. 15-03-103.

<https://fortress.wa.gov/ecy/publications/SummaryPages/1503103.html>.

Roberts, M., T. Mohamedali, B. Sackmann, T. Khangaonkar, and W. Long. 2014. Dissolved Oxygen Assessment for Puget Sound and the Straits: Impacts of Current and Future Human Nitrogen Sources and Climate Change through 2070. Washington State Department of Ecology Publication No. 14-03-007.

Sackmann, B. 2009. Quality Assurance Project Plan: Puget Sound Dissolved Oxygen Modeling Study: Intermediate-scale Model Development. Washington State Department of Ecology Publication No. 09-03-110.

<https://fortress.wa.gov/ecy/publications/summarypages/0903110.html>.

Sackmann, B. 2011. Addendum to Quality Assurance Project Plan: Puget Sound Dissolved Oxygen Modeling Study Intermediate-scale Model Development. Washington State Department of Ecology Publication No. 09-03-110Addendum1.

<https://fortress.wa.gov/ecy/publications/SummaryPages/0903110Addendum1.html>.

WAC 173-201A. Water Quality Standards for Surface Waters in the State of Washington Washington State Department of Ecology, Olympia, WA.

www.ecy.wa.gov/laws-rules/ecywac.html

Waldbusser, G., B. Hales, C.J. Langdon, B.A. Haley, P. Schrader, E.L. Brunner, M.W. Gray, C.A. Miller, and I. Gimenez. 2014. Saturation-state sensitivity of marine bivalve larvae to ocean acidification. *Nature Climate Change* 15 December 2014, doi: 10.1038/NCLIMATE2479.

Washington State Blue Ribbon Panel on Ocean Acidification. 2012. Ocean Acidification: From Knowledge to Action. Adelsman, H., L. Whitely Binder, M. Chadsey (editors). Washington State Department of Ecology Publication No. 12-01-015.

Washington Sea Grant. 2014. Ocean Acidification in the Pacific Northwest. May 2014 fact sheet. <http://wsg.washington.edu/our-northwest/ocean-acidification/>

Washington State Blue Ribbon Panel on Ocean Acidification. 2012. Ocean Acidification: From Knowledge to Action, Washington State's Strategic Response. H. Adelsman and L. Whitely Binder (eds). Washington Department of Ecology, Olympia, Washington. Publication no. 12-01-015. <https://fortress.wa.gov/ecy/publications/publications/1201015.pdf>.

Wootton, J.T. and C.A. Pfister. 2012. Carbon system measurements and potential climatic drivers at a site of rapidly declining ocean pH. PLOS One 7(12): e53396. doi:10.1371/journal.pone.0053396.

16.0 Figures

The figures in this QAPP are inserted after the first mention in the text.

17.0 Tables

The tables in this QAPP are inserted after the first mention in the text.

18.0 Appendix. Glossaries, Acronyms, and Abbreviations

Glossary of General Terms

Acidification: Reduction in the pH of the ocean over an extended period of time, caused primarily by the update of carbon dioxide from the atmosphere.

Ambient: Background or away from point sources of contamination. Surrounding environmental condition.

Critical condition: When the physical, chemical, and biological characteristics of the receiving water environment interact with the effluent to produce the greatest potential adverse impact on aquatic biota and existing or designated water uses. For steady-state discharges to riverine systems, the critical condition may be assumed to be equal to the 7Q10 flow event unless determined otherwise by the department.

Dissolved oxygen: A measure of the amount of oxygen dissolved in water.

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

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

Point source: Source of pollution 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.

Pollution: Contamination or other alteration of the physical, chemical, or biological properties of any waters of the state. This includes change in temperature, taste, color, turbidity, or odor of the waters. It also includes discharge of any liquid, gaseous, solid, radioactive, or other substance into any waters of the state. This definition assumes that these changes will, or are likely to, create a nuisance or render such waters harmful, detrimental, or injurious to (1) public health, safety, or welfare, or (2) domestic, commercial, industrial, agricultural, recreational, or other legitimate beneficial uses, or (3) livestock, wild animals, birds, fish, or other aquatic life.

Salish Sea: Formal name recognized by the U.S. and Canada to describe the estuarine waters that include the Strait of Juan de Fuca, Strait of Georgia, Puget Sound and all adjoining waters.

Sediment: Soil and organic matter that is covered with water (for example, river or lake bottom).

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

DIC	Dissolved inorganic carbon
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
et al.	And others
NOAA	National Oceanic and Atmospheric Administration
QAPP	Quality Assurance Project Plan
PNNL	Pacific Northwest National Laboratory
UW	University of Washington
WAC	Washington Administrative Code

Units of Measurement

ft	feet
g	gram, a unit of mass
kg	kilograms, a unit of mass equal to 1,000 grams
kg/d	kilograms per day
km	kilometer, a unit of length equal to 1,000 meters
m	meter
mg	milligram
psu	practical salinity units
s.u.	standard units

Quality Assurance Glossary

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Examples of data types commonly validated would be:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Method Detection Limit (MDL): This definition for detection was first formally advanced in 40CFR 136, October 26, 1984 edition. MDL is defined there as the minimum concentration of

an analyte that, in a given matrix and with a specific method, has a 99% probability of being identified, and reported to be greater than zero. (Federal Register, October 26, 1984)

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

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

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

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

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

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

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

Quality Assurance 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:

$$[\text{Abs}(a-b)/((a + b)/2)] * 100$$

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: The term split sample denotes when a discrete sample is further subdivided into portions, usually duplicates. (Kammin, 2010)

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

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

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

References for QA Glossary

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

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

USEPA, 1997. Glossary of Quality Assurance Terms and Related Acronyms. U.S. Environmental Protection Agency. <http://www.ecy.wa.gov/programs/eap/quality.html>

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

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