Washington State Department of Ecology

Environmental Assessment Program

Standard Operating Procedures for Marine Waters Data Quality Assurance and Quality Control

Version 1.0

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SIGNATURES ON FILE

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Although Ecology follows the SOP in most instances, there may be instances in which the Ecology uses an alternative methodology, procedure, or process.

SOP Revision History

Revision Date	Rev number	Summary of changes	Sections	Reviser(s)
4/13/2016	1.0	Initial publication		Kammin

Environmental Assessment Program

Standard Operating Procedure for Marine Waters Data Quality Assurance and Quality Control

1.0 Purpose and Scope

1.1 This document is the Environmental Assessment Program (EAP) Standard Operating Procedure (SOP) for a system of quality assessment (QA) and quality control (QC) procedures conducted for marine water quality data collected under the long-term Marine Waters Monitoring Program.

1.2 Marine waters monitoring is driven by key questions about the long-term conditions of Washington's marine waters. Part of answering these questions is determining the data to collect and setting quality objectives to ensure the data can fulfill the needs. Good QA procedures are used to determine if data collected meets the quality objectives. High data quality is mandatory for Ecology's Long-Term Monitoring Program and ensure that trends accurately reflect true environmental change. We have implemented an overall data quality assessment (QA) system which includes routine data quality control (QC) procedures during all phases of the data life cycle including internal peer group reviews to ensure that our data meet highest quality standards. Data quality codes are applied to datasets allowing users to decide the appropriate level of quality for their analyses.

1.3 This document describes test procedures for QC of measurements and analyses performed on marine waters data that are part of the overall QA system. Observations covered by these procedures are collected as a measure of water quality in Washington state marine water bodies, some in real-time or near-real-time settings. Many of these procedures were established in 1991 for the Puget Sound Water Quality Authority, after the Marine Waters Monitoring program was formalized and mandated by the state legislature (PSEP, 1991, 1997). Many of these procedures have been updated and improved over the years, as methods and technology has evolved.

1.4 Post-processing and post-deployment data treatment and adjustment issues are not part of the scope of this document and are described in a separate procedure, Standard Operating Procedure for Marine Waters Data Processing. Bos, J. and S. Albertson, SOP No. EAP089.

2.0 Applicability

2.1 This SOP represents a set of tests and procedures for a variety of data types. The goal is to improve QA/QC through documented, reproducible standard processes. Although certain tests are recommended, thresholds for tests may vary among and within the marine waters monitoring programs and projects, depending upon technology, location seasonality and type of deployment and sampling. For example, the upper limit for DO observations for an instrument moored in deeper coastal waters might not be suitable for use in a shallow nutrient-rich bay.

3.0 Definitions

3.1 The following list of definitions includes terms relevant to the marine waters monitoring program. There may be undefined terms used in this document and it is assumed the user can infer the meaning of these terms. An extensive list of definitions specific to QA and QC can be found on Ecology's Quality Assurance website.

3.2 **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)

3.3 **Calibration:** A procedure for comparing the signal from an instrument with known or standard materials for e.g. turbidity, temperature, pressure, salinity, and other parameters. The process of establishing the relationship between the response of a measurement system and the concentration of the parameter being measured. (Ecology, 2004)

3.4 **Check standard:** A substance or reference material obtained from a source independent from the calibration standard source; 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. (i.e. CRM, LCS, etc.) (Kammin, 2010; Ecology, 2004)

3.5 **Chlorophyll *a*:** Pigment that allows plants, including algae, to convert sunlight into organic compounds in the process of photosynthesis. Chlorophyll *a* is the predominant type found in algae and phytoplankton, and its abundance is a good indicator of the amount of algae present.

3.6 **Clarity:** A qualitative measurement of the ability of water to transmit light. Clarity can be assessed using transmissometer and turbidity sensors (see 3.41).

3.7 **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.

3.8 **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)

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

3.10 **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)

3.11 **CTD (Conductivity-Temperature-Depth):** A set of sensors that is combined into a submersible instrument package used for collecting continuous data of conductivity, temperature, and depth in the water. The CTD can be equipped with auxiliary sensors to measure additional variables and a pump to draw water through or pass by the sensors. The CTD and auxiliary sensors are operated and maintained according to manufacturer's recommended protocols, with factory calibration occurring annually. It is commonly used in both marine and freshwater applications.

3.12 **Derived Data:** Derived data are defined or calculated using other data, called base or primary (raw) data. An example of a derived data variable is the density of seawater, calculated using salinity, temperature, and pressure, based on the equation of state for seawater.

3.13 **Dissolved Oxygen (DO):** The amount of gaseous oxygen (O_2) dissolved in water. Oxygen gets into water by diffusion from the surrounding air, by aeration (rapid movement), and as a product of photosynthesis. It is consumed by respiration and decay processes, as well as in some chemical reactions. Dissolved oxygen levels are used as an indicator of water quality.

3.14 **Fluorometer:** An instrument that provides an indication of the concentration of a given material by measuring the amount of fluorescence attributed to the material. For example, a fluorometer provides an excitation beam at a wavelength that is known to cause fluorescent emission from chlorophyll and measures light at a wavelength that matches the chlorophyll emission. As a result, the amount of chlorophyll-containing algal biomass can be estimated through in situ fluorescence.

3.15 **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)

3.16 **Instrument Detection Limit (IDL):** The minimum quantity of analyte or the concentration equivalent which gives an analyte signal equal to three times the standard deviation of the background signal at the selected wavelength, mass, retention time, absorbance line, etc.

3.17 **Interquartile Range:** In descriptive statistics, the interquartile range (IQR) is a measure of variability. Quartiles divide a rank-ordered data set into four equal parts. The IQR is equal to the difference between the upper and lower quartiles, such that 25% of the results are above and below those values, respectively. $IQR = Q3 - Q1$. It is the most significant basic robust measure of scale.

3.18 **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)

3.19 **Material Safety Data Sheet (MSDS):** MSDSs provide both field staff and emergency personnel with proper procedures for handling or working with a particular substance. MSDSs include information such as physical data (e.g., melting point, boiling point, flash point, etc.), toxicity, health effects, first aid, reactivity, storage, disposal, protective equipment, and spill/leak clean up procedures.

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

3.21 **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)

3.22 **Method Detection Limit (MDL) -** This definition for detection was first formally advanced in Federal Register, 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)

3.23 **Niskin Bottle:** Water sampling bottle used to collect sub-surface water for subsequent measurements. Niskin bottles are plastic tubes (PVC) with spring-loaded end caps, an air-vent valve at one end and a dispensing stopcock at the other.

3.24 **Nutrient:** A substance such as nitrate, nitrite, silicate, ammonium and phosphate. These compounds are used by organisms to live and grow. Nutrient measurements are used as an indicator of water quality.

3.25 **Parameter:** A distinguishing physical, chemical or biological property whose values determine environmental characteristics or behavior.

3.26 **Percentile:** An estimated portion of a sample population based on a statistical determination of distribution characteristics. For example, the 90th percentile value is a statistically derived estimate of the division between 90% of samples, which should be less than the value, and 10% of samples, which are expected to exceed the value.

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

Percent relative standard deviation, %RSD = 100 * (s/x) where s = sample standard deviation, and x = sample mean (Kammin, 2010)

3.28 **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.

3.29 **Photosynthetically Active Radiation (PAR):** Wavelengths - roughly 400 - 700 nanometers—of incoming sunlight that can be absorbed by plants for photosynthesis.

3.30 **Phytoplankton:** Free-floating aquatic flora that convert inorganic compounds into complex organic compounds using light. This process of primary productivity supports the pelagic food-chain. Phytoplankton vary in size from less than 1 to several hundred µm.

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

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

Abs|a-b|/((a+b)/2) * 100

Where a and b are 2 sample results, and abs() indicates absolute value

RPD can be used only with 2 values. If there are more than two values, use %RSD.

(Ecology, 2004)

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

3.34 **Salinity:** Salinity is the total amount of dissolved material in grams in one kilogram of sea water.

3.35 **Secchi Disk:** Measures transparency of the water using an 8-inch diameter white disk attached to a rope. The rope is marked at 0.5 meter intervals for easy determination of depth. This also specifies the depth resolution of the measurement.

3.36 **Secchi Depth:** Depth in the water at which a deployed secchi disk is no longer visible. It is usually the average between the depth at which the disk is no longer visible when it is lowered into the water and the depth at which it is again visible as the disk is raised. The secchi depth can be used to estimate the amount of colored substances (i.e., phytoplankton, algae, and detritus) in the water. Changes can be caused by sediment runoff from land or increased phytoplankton populations. Changes in secchi depth over time are used as an indicator of water quality.

3.37 **Secondary Data**: Data from sources other than the Marine Waters Monitoring Program, used for advanced analyses or contextual interpretation of monitoring data. An example of a secondary data source is stream flow data from the USGS.

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

3.39 **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)

3.40 **Transmissivity (light transmission):** A measure of light scattering and absorption through a defined distance of the water, reported as a percent or ratio of light received relative to light that was originally transmitted. Light transmission is used as an indicator of water quality, providing information about water clarity, light absorption and light scattering (beam attenuation)

3.41 **Turbidity:** A measure of water clarity at a specified wavelength of light. High levels of turbidity can have a negative impact on aquatic life.

3.42 **303(d) list:** Section 303(d) of the federal Clean Water Act, requiring Washington State to periodically prepare a list of all surface waters in the state for which beneficial uses of the water – such as for drinking, recreation, aquatic habitat, and industrial use – are impaired by pollutants. These are water quality-limited estuaries, lakes, and streams that fall short of state surface water quality standards and are not expected to improve within the next two years.

4.0 Personnel Qualifications/Responsibilities

4.1 Experience with oceanographic or marine waters data collection, analysis and interpretation.

4.2 Training and experience working with basic statistical and graphical analysis.

4.3 Training and experience with software programs e.g., Excel, Powerpoint and if possible, some MATLAB or statistical software and tool development skills.

4.4 Typical Job Class performing SOP: Natural Resource Scientist 1/2/3/4, Environmental Engineer 1/2/3/4/5, Environmental Specialist 1/2/3/4/5.

5.0 Equipment, Reagents, and Supplies

Equipment consists of computer hardware and appropriate software with connection to data files and databases stored on shared Ecology network servers.

6.0 Summary of Procedure

6.1 QA system description.

6.1.1 The ongoing effort to provide high quality data occurs in many steps before, during and after data collection. Figure 1 provides a high-level summary of our QA system and QC steps.

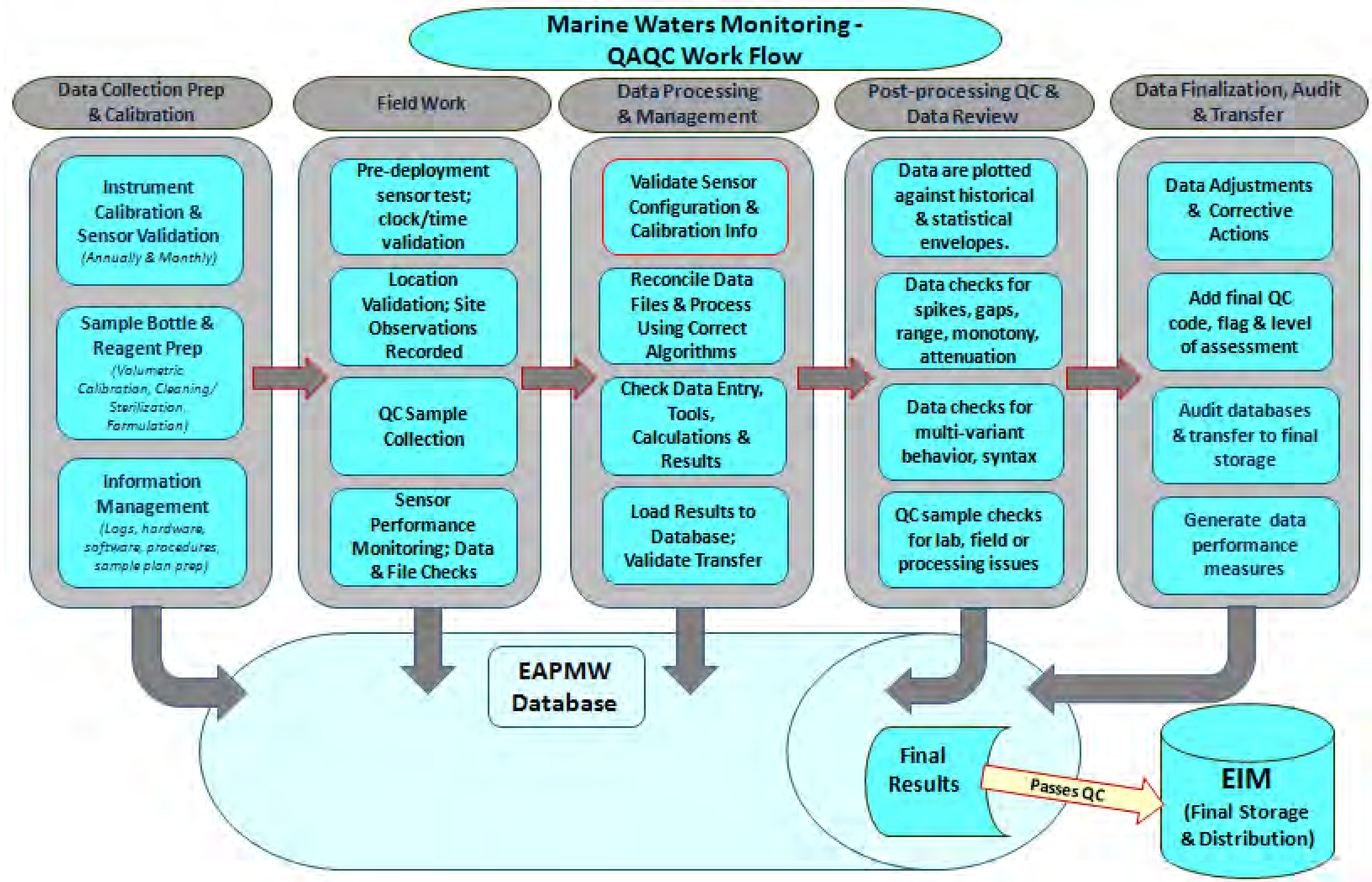


Figure 1. Marine Waters Monitoring data QA system with QC steps.

6.1.2 Essentially, all QA and QC activities for the Marine Waters Monitoring Program can be segmented into specific categories that occur at key intervals in the data life cycle:

- I. Preliminary QC - activities prior to data collection
- II. Data Collection QC – activities during field sampling
- III. Post-Data Collection & Analysis QC – activities during lab sample analysis & sensor checks
- IV. Data Preparation & Processing QC – activities during data entry, calculations, processing and management
- V. Post-Processing or Analytical Data QC – activities such as statistical analyses, sensor signal checks, and contextual checks
- VI. Final QA – activities such as database, web and product audits, to determine if data quality objectives have been met

6.1.3 Our QA system includes multiple actions to ensure all data collection, reporting and analyses are of high quality and appropriate for assessing marine water quality. We emphasize using standard, validated and scientifically recommended procedures which are thoroughly documented and independently reviewed for appropriate and correct application. Our QA system includes the following key elements incorporated into the data life cycle.

1. Meeting QA/QC objectives.
2. Training and performance checks of personnel.
3. Calibrating/validating equipment & proper maintenance.
4. Performing proper sample custody.
5. Performing proper data and information management.
6. Conducting repetitive sensor performance assessment or verification.
7. Field measurement and analytical laboratory QC procedures.
8. Data verification and validation through routine data review.
9. Periodic data usability (method) assessment.
10. Conducting audits.
11. Performance measure evaluation.

6.1.4 The first five activities are discussed at length in Quality Assurance Monitoring Plans (QAMPs) with specific application to the different Marine Waters Monitoring programs. Sensor performance assessment procedures to validate sensors are described in QAMPs, and relevant SOPs while treatment of the assessment results are discussed briefly in this SOP. The last five elements on the list - analytical lab and field QC procedures, data verification and validation through data review and data usability assessments are described in this SOP. Conducting audits and performance measure evaluation are described in program QAMPs and briefly in this document.

6.1.5 These procedures are conducted using any current and available oceanographic data QAQC standards. Yet, current practices and technologies for oceanographic sampling and marine monitoring continue to evolve. Different types of data (sensor, discrete laboratory sample analyses, field observations) require unique data QC techniques. As technology evolves, steps in the QC process change also. Therefore, the current routines used for QAQC activities for data review and assessment are published and updated every 3 years in this SOP.

6.2 Field measurement (CTD or Sensor) QC procedures – before and during data collection.

6.2.1 A major prerequisite for establishing QC standards for field sensor data collection is a strong QA program. A national consensus amongst a broad group of oceanographers and marine scientists is that good QC requires good QA, and good QA requires dedicated, good scientists, engineers, and technicians. An effective QA effort continuously strives to ensure that end data products are of high value and to prove they are free of error. (US IOOS, 2012)

6.2.2 For this reason, the Marine Waters Monitoring program has implemented multiple levels of QA to test performance and operation of sensors before, during and after deployment and engage in routine, frequent assessment to determine if measurement procedures are functioning as expected and generating high quality data. Technicians routinely collect a variety of quality control samples and conduct evaluations to test whether quality objectives are being met, in the field and in the lab. After data collection and processing, data is subjected to several QC tests, including coordinated statistical and graphical review by multiple staff members. Each datum is given an overall “pass” or “fail” QC code, any qualifying QC flags and a code for level of assessment. Tables of current QC codes can be found on the Marine Waters Monitoring website.

6.2.3 Table 1 lists criteria for quality objectives specified for marine water column variables, including precision, accuracy, measurement ranges and reporting limits. Table 2 lists basic analytical procedures used to test that these objectives are met. Since the tests performed for these assessments may change with advancing technology in sensor or laboratory methods, this SOP will be updated every 3 years. The overall QA/QC objectives may change depending on the monitoring plan, study design or with advancing technology in sensor or laboratory methods. Any changes are noted in annual updates to be published as an addendum to the monitoring QAMPs.

Measurement - **Field**	Precision (as % relative standard deviation, RSD)	Accuracy (% difference from true value)	Mfg (Model Number)	Mfg reported range	Mfg reported accuracy	Lowest Value
Chlorophyll Fluorescence	10%	5%	WET Labs, Inc. (ECO-FLNTU)	0–50 µg/l Chl	[1]0.025 µg/l Chl	0.1 µg/l Chl
Conductivity (C)	10%	5%	Sea-Bird Electronics (SBE4)	0.0 - 7.0 Siemens/meter (S/m)	0.0003 S/m	1 uS/cm
Density	10%	5%	Sea-Bird Electronics	dependant on T,C	dependant on T,C	0.1 s_t
Dissolved Oxygen	5%	5%	Sea-Bird Electronics (SBE43)	0 - 120% of saturation	2% of saturation	0.05 mg/L
Light Transmission	10%	5%	WET Labs, Inc. (C-Star)	0-100%	[2]99% R^2	0.01%
PAR (Photosynthetically Active Radiation)	5%	5%	Biospherical Instruments, Inc. (QSP-2200)	1.4x10-5 µE/(cm2·sec) to 0.5 µE/(cm2·sec)	± 5%	0.01%
pH	10%	N/A	Sea-Bird Electronics (SBE18)	0 - 14 pH	0.1 pH	0.1 pH
Pressure	5%	1%	Sea-Bird Electronics (SBE29)	0-500m	0.1% of full scale range	0.1 db
Temperature (T)	5%	1%	Sea-Bird Electronics (SBE3)	-5.0 to +35 °C	0.001 °C	0.01 °C
Turbidity	10%	5%	WET Labs, Inc. (ECO-FLNTU)	0-25 NTU	0.01 NTU	0.1 NTU

Table 1. A summary of quality control objectives, measurement ranges and reporting limits for field sensor measurements.

Field Measurement	**Precision** (relative standard deviation), %RSD	**Accuracy or Bias** (% from true value)	Annual manufacturer calibration & report review	Pre-deployment validation via lab seawater bath or other standard	In field sensor checks & assessment	Preliminary data processing and flags applied	Graphical & statistical data review & QC codes applied	Comparison to QC samples or standards: adjustments & corrections applied	Annual review& final data assessment
Conductivity	10%	5%	✓	✓	✓	✓	✓		✓
Density	10%	5%	✓	✓	✓	✓	✓		✓
Dissolved Oxygen	5%	5%	✓	✓	✓	✓	✓	✓	✓
Fluorescence	10%	5%	✓	✓	✓	✓	✓	✓	✓
Light Transmission	10%	5%	✓	✓	✓	✓	✓		✓
PAR	5%	5%	✓	✓	✓	✓	✓		✓
pH	10%	10%	✓	✓	✓	✓	✓	✓	✓
Pressure	5%	1%	✓	✓	✓	✓	✓		✓
Salinity	10%	5%	✓	✓	✓	✓	✓	✓	✓
Temperature	1%	1%	✓	✓	✓	✓	✓		✓
Turbidity	10%	5%	✓	✓	✓	✓	✓		✓

Table 2. A summary of quality control objectives and QC procedures for field sensor measurements.

6.2.4 QC procedures start prior to sensor deployment with industry-standard, well-controlled sensor calibration by a manufacturer at the factory. The primary instrument used for Marine Waters Monitoring is a Sea-Bird Electronics, Inc. (SBE) CTD package. The CTD is a system composed of multiple specialized sensors that will give accurate and precise results when properly calibrated and maintained. High quality, controlled manufacturer calibrations help assure that quality objectives can be met. Maintenance and calibration procedures are fully described in various operating manuals and application notes for the specific sensors used. A full list of sensor models is included in Table 1. References for specific manuals and application notes for each sensor can be found at various manufacturer websites, including SBE, WET Labs, Satlantic and Biospherical Instruments, Inc. Calibrations are performed at the factory for all sensors on an annual basis, with servicing and repairs occurring as needed. With each calibration, the manufacturer generates a new set of calibration coefficients. In addition to providing a new set of calibration coefficients, the manufacturer also reports on drift and loss of sensitivity relative to the previous calibration. The most recent calibration coefficients are applied to the data during processing prior to storage in the database.

6.2.5 A schedule listing the frequency of factory calibrations is listed in Table 3. The calibration and maintenance schedule tracks age and behavior of sensors over each instrument's operational lifetime. Sensors returning from annual calibration are tested prior to deployment, using a seawater bath as well as standards and other reasonable tests to determine proper and correct operation. If performance checks and data review indicate that instrument performance may be compromised from original factory state, the problem is investigated and resolved, and instruments are returned to the manufacturer for diagnostics and repair, as needed. Sensor calibration histories are preserved to track sensor behavior and characterize reasonable operation and correct measurement by each sensor. Two other SOPS, EAP086 and EAP087 provide information on sensor assessment via controlled seawater baths.

Sensor	Monthly In-House Performance Assessment	Annual Factory Calibrations
Conductivity[2,3]	X	X
Temperature		X
Pressure		X
Dissolved Oxygen[2,3]	X	X
pH[1,4]	X	X
Transmissometer[1]	X	X
Fluorescence[3]	X	X
Turbidity		X
Photosynthetically Active Radiation (PAR)		X

[1] Bi-monthly calibration
[2] Monthly performance check via lab bath
[3] Performance check using in-situ samples
[4] During factory calibrations, pH sensor is checked for internal electrolyte and electrical connections. Probe to be replaced annually.

Table 3. CTD calibration and maintenance schedule.

All calibration/validation data are recorded in appropriate separate sensor forms and archived in the data management file system. Calibration and sensor performance verification results are maintained in the database. Sensor behavior and aging are tracked via control charts or other appropriate analytical tools.

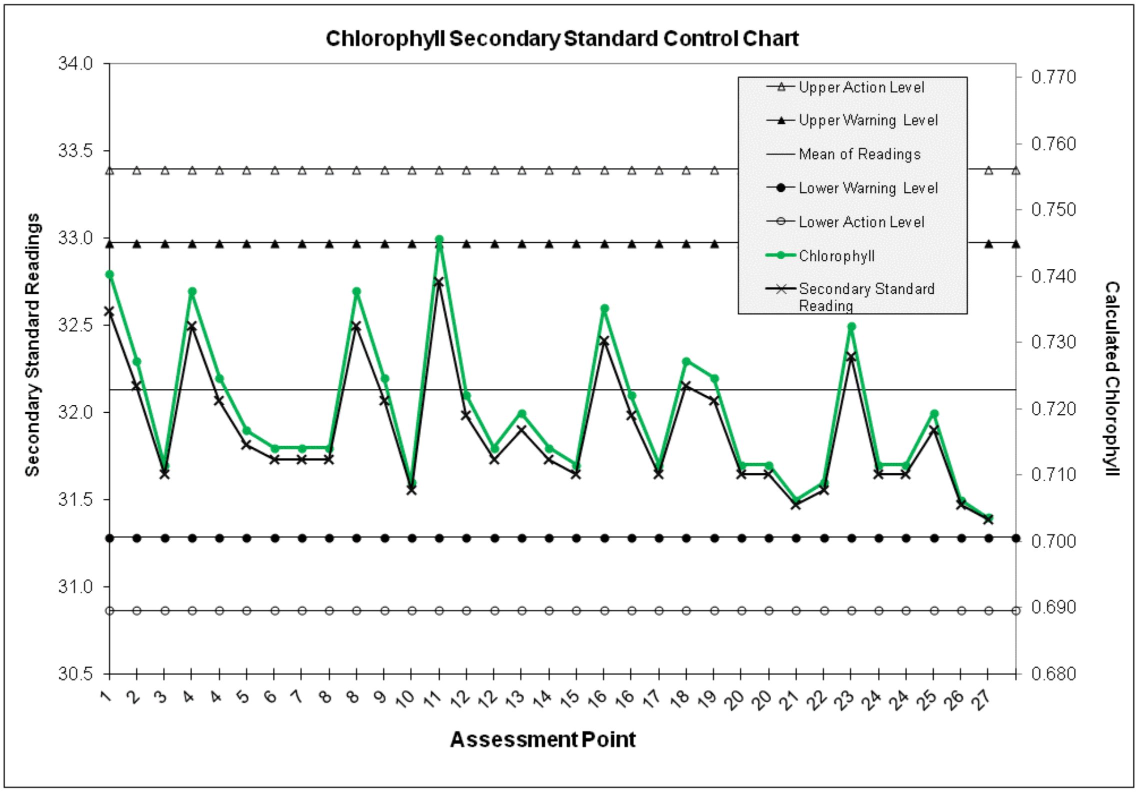


Figure 2. Example of an instrument control chart used to assess and track performance of a Turner Designs fluorometer.

6.2.6 Pre-survey performance tests of instruments are conducted and compared to expected value ranges determined by sensor-specific performance testing and to specifications determined during factory calibration. Technicians test instrument packages under controlled conditions to ensure proper operations prior to any field survey. Table 6 lists MQOs for CTD sensor performance testing in the lab.

6.2.7 During sensor deployments, several test readings are taken, using standards or other available tests to ensure proper configuration and operation. Technicians take voltage and frequency readings during flights, mooring servicing and boat surveys, before and after every sensor deployment to ensure reasonable operation of all sensors. These tests are immediately evaluated to identify any sensor issues or failures during sampling. Examples of typical readings from vertical profiles are shown in Table 4. These measurements are reviewed and compared to the range (minimum and maximum) of all good test results for each respective sensor using plotting tools. If a sensor malfunctions, the problem is immediately recognized through these sensor performance readings. If a problem is detected and confirmed in the field using plotting tools, then data collection is suspended. Once the problem is resolved and the sensor repaired or replaced, data collection can resume.

Voltage Channel	1	2	3	4	5	6	7	8	9	10
Voltage Description	CTD Alkaline Batteries/5.0161	CTD Lithium Battery/3.873	Pressure	Pressure Temperature	Dissolved Oxygen	pH	Transmission	Fluorescence	Turbidity	Photosynthetically Active Radiation
Sensor SN	2538854-0381	2538854-0381	290559	290559	430049	180530	CST-850PR	FLNTURT-299	FLNTURT-299	20351
Month	March-2013	March-2013	March-2013	March-2013	March-2013	March-2013	March-2013	March-2013	March-2013	March-2013
Count	*772*	*772*	*772*	*772*	*772*	*772*	*772*	*772*	*722*	*722*
Average	2.406	1.317	4.408	1.452	2.981	2.909	2.948	0.091	0.375	2.789
Min	2.166	1.278	4.399	1.269	2.267	2.128	0.337	0.055	0.243	1.645
Max	2.649	1.364	4.422	1.567	3.295	2.987	4.598	0.18	0.603	3.423

Table 4. Example of raw CTD voltage readings from one month used for pre-survey validation and as a coarse QA range test in the field prior to CTD casts. The pH sensor is soaked in pH 8 buffer for reading. No other sensors are controlled using standard reference materials for this test.

6.3 CTD QC Sample Collection.

6.3.1 During field deployments, independent QC samples are collected to validate measurements for salinity, dissolved oxygen (DO) chlorophyll *a* fluorescence and nitrate. Independent QC verification samples provide information about sensor behavior during field deployments between scheduled lab or field bath assessments. These QC samples also provide a way to determine if sensors have drifted, are damaged, or have failed during deployment. Verification samples for salinity measurements, and reference samples for dissolved oxygen, chlorophyll *a* fluorescence and nitrate are collected during each daily survey to compare with sensor values and verify CTD sensor performance. These reference samples are used to adjust data as appropriate, according to methods documented in Ecology SOP No. 088.

6.3.2 Water samples, including dissolved oxygen (DO) are collected at stations with little to no vessel drift to minimize effects of rapidly changing horizontal water masses. DO samples are not collected from areas with rapidly changing vertical oxygen gradients due to stratification, upwelling, tide or meteorological fronts. DO samples are collected from near bottom depths at more stable sites, and from a variety of sites with a range of oxygen conditions to capture the natural range of oxygen levels. Chlorophyll a and nitrate samples are collected from 0, 10 and 30 meters to capture a variety of levels observed in the upper water column. Salinity samples are collected at a few various locations throughout the day to cover a range of expected salinities.

6.3.3 Should the CTD values differ substantially from the analyzed water samples, CTD data are "flagged" until differences are resolved. At the end of a sampling year, as part of data finalization, independent verification sample results are analyzed and used to determine if there were any substantial anomalies in quantitative sensor measurements. If anomalies are found, lab and sensor data are checked for any QC flags such as outlier, gap, or contextual issues which may explain the difference. If the lab sample is good, depending on the severity of the difference (e.g. <0.1 PSU), a “pass” QC flag is applied to the sensor data if no issues are found. Figure 3 shows a typical result for analyses of independent (salinity) lab samples against sensor data, confirming validity of the sensor data.

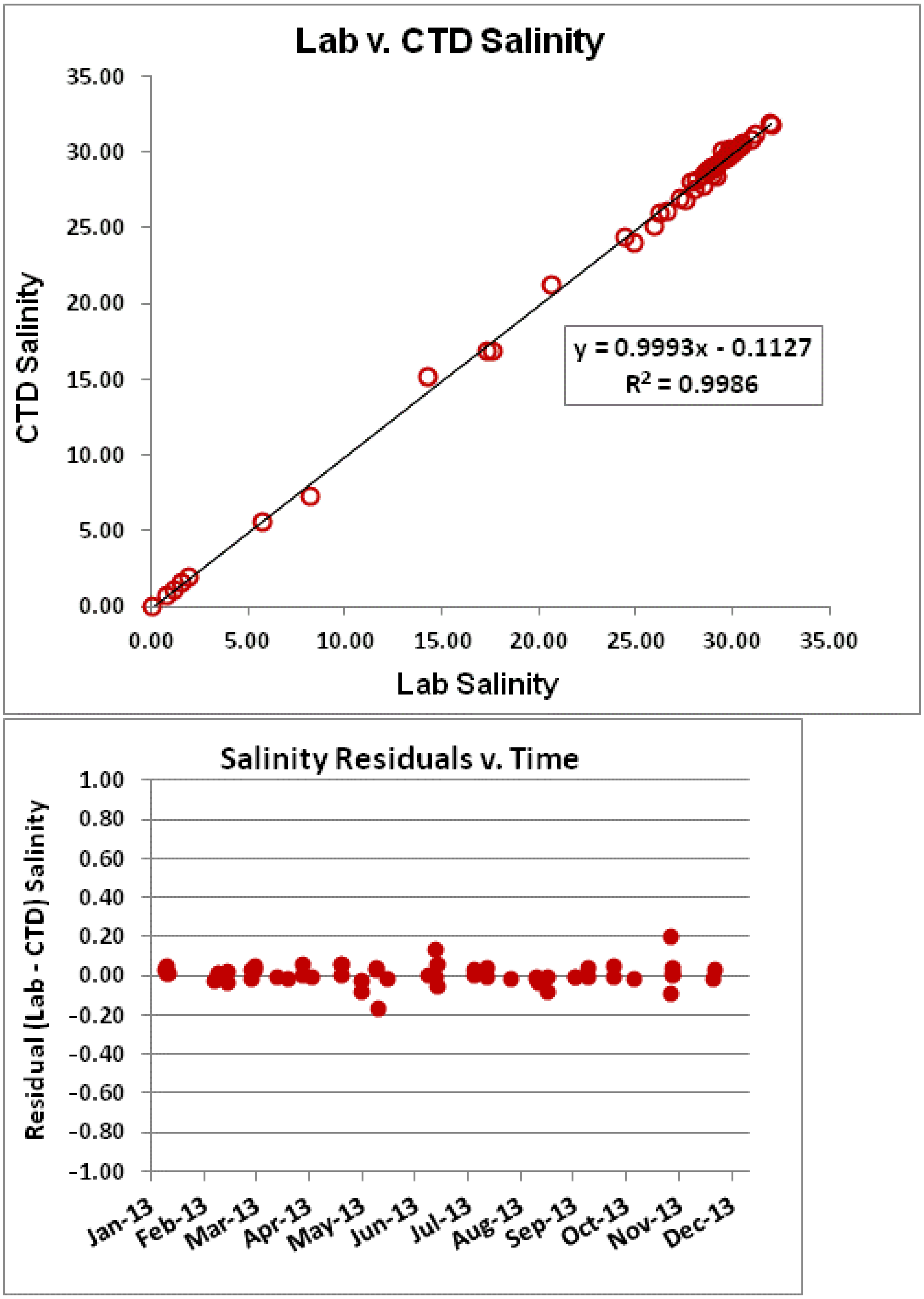


Figure 3. Example plots of sensor validation using independent lab samples.

6.4 CTD Field Replicates.

6.4.1 Due to the nature of marine water column sampling via a Lagrangian approach, that is drifting with a water parcel and currents rather than holding one static position, replicate CTD casts in the field do not provide a good test of precision. At some sites, currents and winds cause the vessel to drift a significant amount, and along with rapidly changing water conditions, replicate casts collected one after another provide a measure of field variability in space and time rather than a test of CTD precision and accuracy. For this reason, the MWM group uses independent, *in situ* QC sample collection and lab testing under controlled conditions (e.g. such as a bath) to perform QA of CTD performance.

6.5 Laboratory-based CTD QC procedures via seawater bath assessment of CTDs

6.5.1 A seawater bath is set up and maintained at Ecology's Marine lab. This bath is used to assess clean, recently factory-calibrated sensors prior to deployment, and monthly to track sensor performance during the course of a sampling year. More information on this procedure can be found in the document Marine Waters Oxygen and Supporting Sensor Performance Assessment - Lab Procedures, (Friedenberg et al., 2014).

6.5.2 For the laboratory bath procedure, a reference CTD-DO (SBE 37-SMP-IDO) is used to evaluate the performance of field instruments before and after deployments. The lab reference and field sensors are run side-by-side in a semi-controlled seawater bath where environmental effects from currents, advection and weather are minimized. A side-by-side (paired sample) approach generates a data volume adequate for a statistically robust comparison. For dissolved oxygen this type of sampling is referred to as "reference sampling" (Sea-Bird Electronics Application Note 64-2, 2012).

6.5.3 Every 3 months, the calibration of the reference instrument is checked against laboratory methods to ensure highest data quality. To minimize air exposure and dissolved oxygen bias in Winkler samples, the lab bath is maintained near 100% dissolved oxygen saturation. Both a CTD with a field SBE 43 dissolved oxygen sensor to be deployed and a reference CTD (SBE 37-SMP-IDO) are placed in the laboratory bath and programmed to take samples concurrently. Dissolved oxygen measurements between the field CTD and the reference instrument are quantitatively compared to assess field sensor performance (stability, slope and offset) and whether measurement quality objectives for accuracy and precision are met.

6.5.4 For dissolved oxygen, a sensor passes the instrument-based performance check if values fall within 2% of the reference instrument measurements (i.e. the paired bath measurement values are within 98-102% of each other). Any instrument that does not pass performance checks is not deployed and is removed from the instrument pool for additional diagnostics. The instrument-to-instrument comparison ratio is confirmed quarterly by laboratory analysis (Winkler DO replicates). The instrument should fall within 5% of the established Winkler to DO sensor ratio, based on ongoing sensor control methods. The Carpenter method for DO titrations is used to determine the dissolved oxygen concentration in collected reference samples (Bos, J., 2012). Verification DO samples are analyzed by staff in the Ecology's Marine Laboratory.

6.5.5 For pressure, performance is verified in the bath by confirming whether values are near expected pressure values, given the depth of the bath water, and whether there are continuous, stable measurements and general agreement with the reference instrument held at the same depth within the bath.

6.5.6 For salinity, which is derived from the CTD's conductivity measurements, performance is verified based on agreement (difference <0.2 PSU) between the reference CTD and the assessed CTD. In general, sensors are expected to hold their calibration well within measured quality objectives (McPhaden et al., 1990). Verification salinity samples are sent to the UW's Marine Chemistry Laboratory for analysis.

6.5.7 For temperature, sensor performance is based on agreement (difference <0.2 °C) between the reference CTD and the assessed CTD.

6.6 Analytical Laboratory (Discrete Water) Sample QC Procedures – pre- and during sample collection.

6.6.1 QC procedures for discrete water samples results via laboratory analyses start prior to sample collection and analyses with several pre-collection activities. These include:

- Verification that lab instrument calibrations are current and instrument meets control criteria based on standards analysis.
- Verification that all methods and standards are up-to-date.
- Verification that chemicals and reagents are current (not expired).
- verification that all equipment and sample bottles are properly cleaned and prepped, certified or calibrated as required by methods used.

In addition to QC activities that occur before and during sample collection, analytical laboratories perform additional QC procedures throughout sample analyses and result calculations. These procedures are not covered in this SOP and are reported in method procedures or reports generated by each lab.

6.6.2 Prior to sample collection, all information necessary for sample management and analysis is defined and appropriately documented. During collection, information is recorded and verified by a second staff member for correctness and completeness.

6.6.3 Along with regular environmental samples, QC samples are collected or generated at the lab to accompany each batch of samples. These include:

- Blanks, both lab and field
- Replicate samples
- "Standards" or Standard Reference Materials (SRM)
- Lab Control Samples (LCS)
- "Blind" SRMs submitted to the laboratory

The Ecology QA Glossary contains definitions of the various types of QC samples. The QC samples have MQOs (evaluation criteria) associated with them and are described in Tables 5 and 6. Specified criteria must be met to obtain fully usable data.

6.6.4 **Replicate Sample Collection.** Replicate samples for dissolved oxygen, nutrients, and chlorophyll *a* are collected during every long-term monitoring survey to determine field and sample variability. Ten percent of sites are sampled to conduct a quantitative determination of homogeneity of conditions, along with precision and bias of sampling methods. When servicing moorings, replicate samples are taken for dissolved oxygen from a sensor performance bath test and chlorophyll *a* concentrations from seawater collected with a Niskin sampler.

6.6.5 **Analytical Replicates.** Total variation in lab samples is assessed by collecting replicates from the same Niskin sampling bottle for all parameters at 5% -10% of sites. These replicates are used to assess whether the data quality objectives for precision were met. If the objectives are not met, the data are qualified. In addition, Ecology's Manchester Environmental Laboratory, UW's Marine Chemistry Laboratory, and Ecology's Marine Laboratory all routinely perform replicate sample analyses using sample splits within laboratory batches for quality control purposes. The difference between analytical field replicates and laboratory replicate results is a measure of the field sample variability.

6.6.6 **Laboratory Performance Samples.** For testing laboratory performance and analyst proficiency, check standards or laboratory control samples of known concentrations are included with every sample batch. Recovery percentage is calculated from these results and therefore, can be used as a measure of analytical accuracy and bias. If the results fall outside of established limits, data associated with the batch is flagged by the reviewer. Any measurement problem that cannot be resolved is given a data quality flag.

6.6.7 **Blanks.** Blanks are prepared and analyzed in each laboratory to determine if samples were contaminated during processing and analysis. Blanks are run before and after each batch of samples and compared to established acceptance limits. Blank results are reported by each lab and are included with each dataset. Blank results are evaluated by the MWM group and receive final approval from the monitoring coordinator or senior oceanographer.

6.6.7.1 A positive blank can indicate laboratory contamination. Blanks are important to measure to determine the accuracy of low level samples near the detection limits. Blank responses are used to determine method detection limits (MDLs) and in some cases, to apply data quality flags to sample batches. Table 6 lists the QAQC samples used to perform quality assessment of laboratory procedures and data results.

Lab Measurement	Precision (relative standard deviation, %RSD)	Accuracy (% from true value)	Instrument Control Check Using Blanks	Laboratory Standards Check	Laboratory Control Samples	Replicate Analysis	Method Detection Limits Check	Preliminary Review and Flagging of Raw Data	Graphical & Statistical Data Review and Flagging	Annual Review Assessments
Chlorophyll a	10%	NA	✓	✓		✓	✓	✓	✓	✓
Dissolved Oxygen	5%	NA	✓	✓		✓	✓	✓	✓	✓
Nitrate	10%	5%	✓	✓	✓	✓	✓	✓	✓	✓
Nitrite	10%	5%	✓	✓	✓	✓	✓	✓	✓	✓
Ammonium	10%	5%	✓	✓	✓	✓	✓	✓	✓	✓
Orthophosphate	10%	5%	✓	✓	✓	✓	✓	✓	✓	✓
Silicate	5%	5%	✓	✓	✓	✓	✓	✓	✓	✓
Salinity	10%	5%	✓	✓		✓	✓	✓		✓

Table 5. A summary of quality control steps for analytical lab samples.

Analytical Parameters	Calibration or Standard Curve Response Verification	LCS or CVS (per sample batch)	Replicates (per sample batch)	Blanks (per sample batch)
Laboratory Samples				
Ammonia (NH_4)	5 point standardization	2 - 3	2	2
Nitrate (NO_3)	5 point standardization	2 - 3	2	2
Nitrite (NO_2)	5 point standardization	2 - 3	2	2
Orthophosphate (PO_4)	5 point standardization	2 - 3	2	2
Silicate (SiO_4)	5 point standardization	2 - 3	2	2
Chlorophyll & phaeopigments	Instrument calibration - 2x/year	4 total - 2 high, 2 low	3	2 - method 2 - reagent
Dissolved Oxygen	3 point standardization	3	3	2
Salinity	1 per batch	1	1	2
~ Nutrients, dissolved oxygen and chlorophyll a are replicated in the field.				
CTD Sensors				
pH (electrode sensor)	5 point calibration	NA	NA	NA
Light Transmission	2 point calibration (high & low)	NA	NA	NA
Dissolved oxygen (Clark cell - membrane)	Standardization - full saturation	NA	NA	NA

Table 6. Quality assurance/quality control procedures for water sample analysis and sensor performance testing in the laboratory.

6.7 Data Processing QC Procedures

6.7.1 Quality control for data processing consists of a few basic activities, best performed prior to processing to reduce the need for more extensive work later such as tracking down errors and redoing work, and to avoid propagating errors.

Processing and data adjustment activities often are not given adequate attention. This is unfortunate because errors can still occur after data have been collected. Just as field, instrument or technician performance could introduce measurement error, data processing staff may potentially introduce processing error, sometimes systematically. Often a few errors are responsible for the majority of QC issues. To reduce effort, and possibly minimize error, checks are performed throughout the field collection period and data processing rather than waiting until the end of data collection. The burden of QC programming and checking should not be underestimated.

The QC activities during processing are:

- Verifying all source information and files.
- Checking source data and data files for correctness.

- Checking source data and files for completeness (e.g. if 20 samples were collected, there should be 20 sample results).
- Checking data processing tools and software for correct operation, formatting, calculation, and references.
- Documenting any necessary data processing results or confirmations, especially any issues or exceptions that occur during processing and would be informative for further data analyses and finalization.

These activities apply to all types of data collected for processing – sensor measurements, analytical lab samples and field observations and to any secondary data used for more advanced analyses or contextual assessment.

6.8 Data verification and validation through routine data review. (Post Data Processing QC)

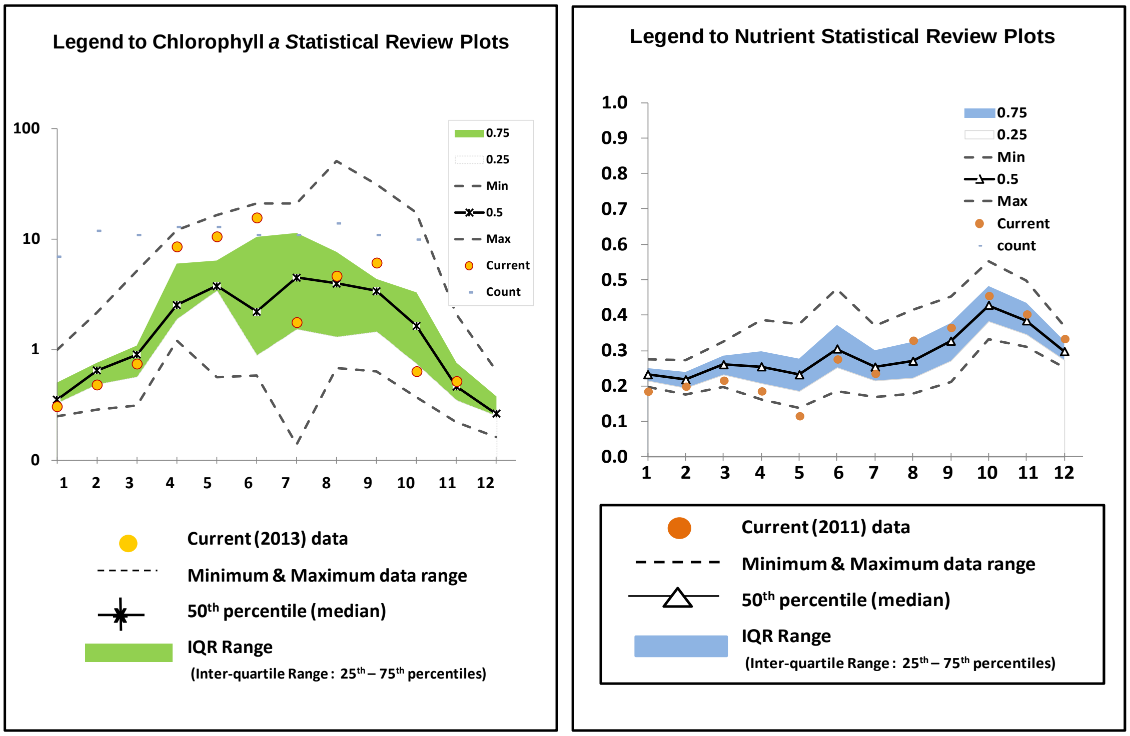
6.8.1 One of the most critical phases of quality control occurs during post-processing of all data, prior to comprehensive data analysis. At this step, multiple types of tests and analyses are performed, included statistical and graphical exploration of lab and sensor data.

6.8.2 Post Processing QC for laboratory data

6.8.2.1 **QC Tests.** All lab data results are subjected to the following tests:

- **Range check.** Do data fall within the expected ranges?
- **Gap or missing value check.** Are any expected results missing?
- **Spurious results check.** Are any values negative or of an unreasonable magnitude?
- **Outlier check.** Do any results fall outside the expected data pattern, either being too high or too low?
- **Climatology check.** Do results seem reasonable compared to historical results – range and pattern?
- **Neighbor check.** Do results seem reasonable compared to results from the same site, same day or similar depths?
- **Seasonality check.** Do results reflect seasonal processes or effects or are they extraordinarily different?

These tests use statistical and graphical analyses, and a suite of numerical and auditing/reconciliation procedures. Figures 5a and 5b show examples of graphs used to determine spurious results, outliers, climatology, seasonality, and neighbor checks.



Figures 5a and 5b. Examples of statistical graphs used to apply QC tests to lab sample results.

6.8.2.2 **Analysis of Replicates.** All replicate samples are treated as follows:

Step 1. Replicate lab samples are paired with the nearest 0.5m sampling depth recorded by the AFM (Automatic Firing Module) during vertical profiles or by collection times recorded on field or sensor bath test logs during moored instrument operations. When servicing a mooring, one or two sets of replicates may be collected: 1) water samples are paired with collection times of a moored instrument before and after deployment; 2) water samples are drawn from a field bath during a sensor performance test and paired with CTD sampling times.

Step 2. Depths or times between field replicates are compared (e.g., samples collected out of different Niskin bottles at identical depth or differing times). At a vertical difference > 0.25m depth, or a significant time difference (>5 min.) for mooring deployments or baths, samples are "disqualified" as replicates and treated as unique samples.

Step 3. If field replicates meet sampling depth or time criteria, an average, standard deviation and coefficient of variance (relative standard deviation) are calculated. The same metrics are also calculated for lab replicates. This requires that at least 3 replicates be collected for every event.

Note: Variance results outside of MQOs are evaluated to determine if field or lab procedures have created a systematic bias in the results and if samples need to be rejected. Typically, higher variance is associated with samples of very low concentrations. In these cases, small relative differences are checked against proportion of concentration and if the concentration is very low, high variance may be considered acceptable.

6.8.2.3 **Analyses of blanks.** For Marine Waters Monitoring lab sample collection, the type of blank used depends on the parameter, and thus the type of analysis for blank results varies by parameter. For each parameter listed in Table 7 below, the type of blank is denoted, along with the test procedure and criteria for passing or failing the test.

Lab Blanks QC Summary				
Dissolved Oxygen (mg L^{-1})	**Type**	**Analysis Test Method**	**Method Criteria**	**Comment**
Blanks	Spiked Blank	Recovery Efficiency	2 blanks run & must be within $\pm$.001 uL of each other	DI water spiked with surrogate analyte - KIO_3 - equivalent to .001 normality
Chlorophyll *a* (µg L^{-1})	**Type**	**Analysis Test Method**	**Method Criteria**	**Comment**
Laboratory Reagent Blanks (LRB)	DI Water	Threshold Exceedance	$\leq$ 3x MDL (based on acetone blanks)	A 2° test determines if blank exceeds 3% of lowest sample concentration.
Filtration Reagent Blanks (FRB)	Method Blank	Threshold Exceedance	$\leq$ 3x LRB	A 2° test determines if blank exceeds 5% of lowest sample concentration.
Nutrients (µM)	**Type**	**Analysis Test Method**	**Method Criteria**	**Comment**
Ortho-Phosphate - PO_4 Silicic Acid (aka Silicate) - SiO_4 Nitrate - NO_3 Nitrite - NO_2 Ammonium - NH_4	*Method Blank	Threshold Exceedance	$\leq$ 3x Reported Blank Concentration	*Blank based on seawater matrix with known low level concentrations of analyte. Blank to test reagent contamination.
Salinity (PSU)	**Type**	**Analysis Test Method**	**Method Criteria**	**Comment**
Blanks	DI Water	Threshold Exceedance	$\leq$ 3x MDL	

Table 7. Lab blanks included in Marine Waters QC analytical procedures.

6.8.2.4 **Analyses of Standards.** As for laboratory blanks, standards are analyzed with every batch of lab samples. Depending on the parameter and the type of analyses different types of standards are used. Standards can consist of certified reference materials (CRMs), laboratory control standards (LCSs) and calibration verification standards (CVSs). These standards are used to test for bias in a measurement system. For each parameter listed in Table 8 below, the type of standard is denoted, along with the test procedure and criteria for passing or failing the test.

Lab Standards QC Summary				
Dissolved Oxygen (mg L^{-1})	**Type**	**Analysis Test Method**	**Method Criteria**	**Comment**
Standards	ICV	Recovery Efficiency	3 standards run. Must be within ±.001 uL (titrant dispensed) of each other	DI water spiked with surrogate analyte - KIO_3 - equivalent to .01 normality
Chlorophyll *a* (µg L^{-1})	**Type**	**Analysis Test Method**	**Method Criteria**	**Comment**
Standards	CRMs - 1° stds.	Calibration	Establish measurement relationship.	Calibration performed annually.
Standards	CRMs - 2° stds.	Control Limits	Results within ± 2 std deviations of the mean, consistently.	Results within ± 3 std deviations of the mean, otherwise corrective action needed.
Nutrients (µM)	**Type**	**Analysis Test Method**	**Method Criteria**	**Comment**
Ortho-Phosphate - PO_4	ICV	Calibration Verification	Establish measurement relationship.	Calibration performed before and after every sample run.
Silicic Acid (aka Silicate) - SiO_4				
Nitrate - NO_3				
Nitrite - NO_2				
Ammonium - NH_4				
Ortho-Phosphate - PO_4	LCS	Recovery Efficiency	± 5% of known concentration	"Blind" control samples created with CRMs.
Silicic Acid (aka Silicate) - SiO_4				
Nitrate - NO_3				
Nitrite - NO_2				
Ammonium - NH_4				
Ortho-Phosphate - PO_4	CCV	Recovery Efficiency	± 5% of known concentration	2° test to monitor system bias during analytical runs.
Silicic Acid (aka Silicate) - SiO_4				
Nitrate - NO_3				
Nitrite - NO_2				
Ammonium - NH_4				
Salinity (PSU)	**Type**	**Analysis Test Method**	**Method Criteria**	**Comment**
Standards	CRM	Calibration	Establish measurement relationship.	Calibration performed before and after every sample run.

Table 8. Lab standards included in Marine Waters QC analytical procedures.

6.8.2.5 **Detection Limits.** For each type of analyses, various detection limits are established as a measurement quality objective. For analyses at Ecology's Marine Lab (ML), we establish an Instrument Detection Limit (IDL) based on the analyses of method blanks. For EPA method 445.0 the background is a solution of 90% acetone. For dissolved oxygen analyses, the determination of instrument detection limit is by replication of spiked or fortified blanks within a recovery efficiency range equivalent to $\pm$.001 µL sodium thiosulphate. Any sample batches with blanks that exceed expected IDLs are flagged as an "estimate" due to potential contamination revealed by analyses of blanks.

Method detection limits are established for each analytical lab parameter by analyses of multiple (at least 7) replicates of seawater containing the analyte at 5 times the concentration of the estimated detection limit. Table 9 includes the MDLs for all analytical lab parameters. If any reported sample results fall below the MDL, that sample result is flagged as an "estimate."

Measurement - Lab Analyte	Lab	Analytical Method	Expected Range of Results	Method Detection Limit
Dissolved oxygen	ML	Carpenter, 1966	0.00 - 15.00 mg/L	0.01 mg/L
Marine Nitrate	UW-MCL	Armstrong et al., 1967	0.00 - 40.00 µM	0.15 µM
Marine Nitrite	UW-MCL	Armstrong et al., 1967	0.00 - 2.00 µM	0.01 µM
Marine Ammonium	UW-MCL	Slawyk & MacIsaac, 1972	0.00 - 10.00 µM	0.05 µM
Marine Orthophosphate	UW-MCL	Bernhardt & Wilhelms, 1967	0.00 - 4.00 µM	0.02 µM
Marine Silicate	UW-MCL	Armstrong et al., 1967	0.00 - 200.00 µM	0.21 µM
Chlorophyll *a*	ML	EPA, 1997	0.00 - 60.00 µg/L	0.01 mg/L
Salinity	UW-MCL	Grasshoff et al., 1999	0.00 - 36.00 PSU	0.01 PSU

Table 9. Method detection limits for Marine Water lab samples.

6.8.3 Post Processing QC for CTD sensor data

6.8.3.1 **QC Tests.** All measurements generated by sensors are subjected to the following tests:

- **Range check.** Do data fall within the expected ranges?
- **Syntax Check.** Are sensor outputs reasonable – of proper format and magnitude?
- **Gap or Missing Value Check.** Are any expected results missing?
- **Flat Line Check.** Are data results abnormally uniform given environmental condition or context?
- **Attenuated Signal Check.** Are sensor outputs the correct length or number or lines or characters?
- **Rate of Change Check.** Does the sensor signal exhibit the proper rate of change given environmental conditions or context, or is it too fast or slow?
- **Spurious results check.** Are any values negative or of unreasonable magnitude?
- **Outlier (Spike) check.** Do any results fall outside the expected data pattern, either being too high or too low?
- **Climatology check.** Do results seem reasonable compared to historical results – range and pattern?

- **Multi-Variant Check.** Do sensor results exhibit coherence with related parameters collected or measured at the same time or depth?
- **Neighbor check.** Do results seem reasonable compared to proximal results from the same site, day and adjacent depths?
- **Seasonality check.** Do results reflect seasonal processes or effects or are they extraordinarily different?

6.8.3.2 **Statistical Analyses.** These tests are conducted using statistical and graphical analyses, as well as a suite of numerical and auditing/reconciliation procedures. Site-specific statistical evaluation of water column data is conducted every month by the Marine Waters Monitoring group. The interquartile ranges of historical results for each station and each depth are calculated and compared to the current monthly data. An example of this type of plot is shown for station PSB003 in Figure 6. These graphs are used to visually determine gaps, spurious results, outliers/spikes, flat line or unexpected data patterns, climatology, seasonality, multi-variant and neighbor checks. Data that are significantly different than the historical ranges are automatically flagged and reviewed. Any results failing the QC tests are flagged with a QC code of "fail" and are eliminated from further analyses or external data distribution.

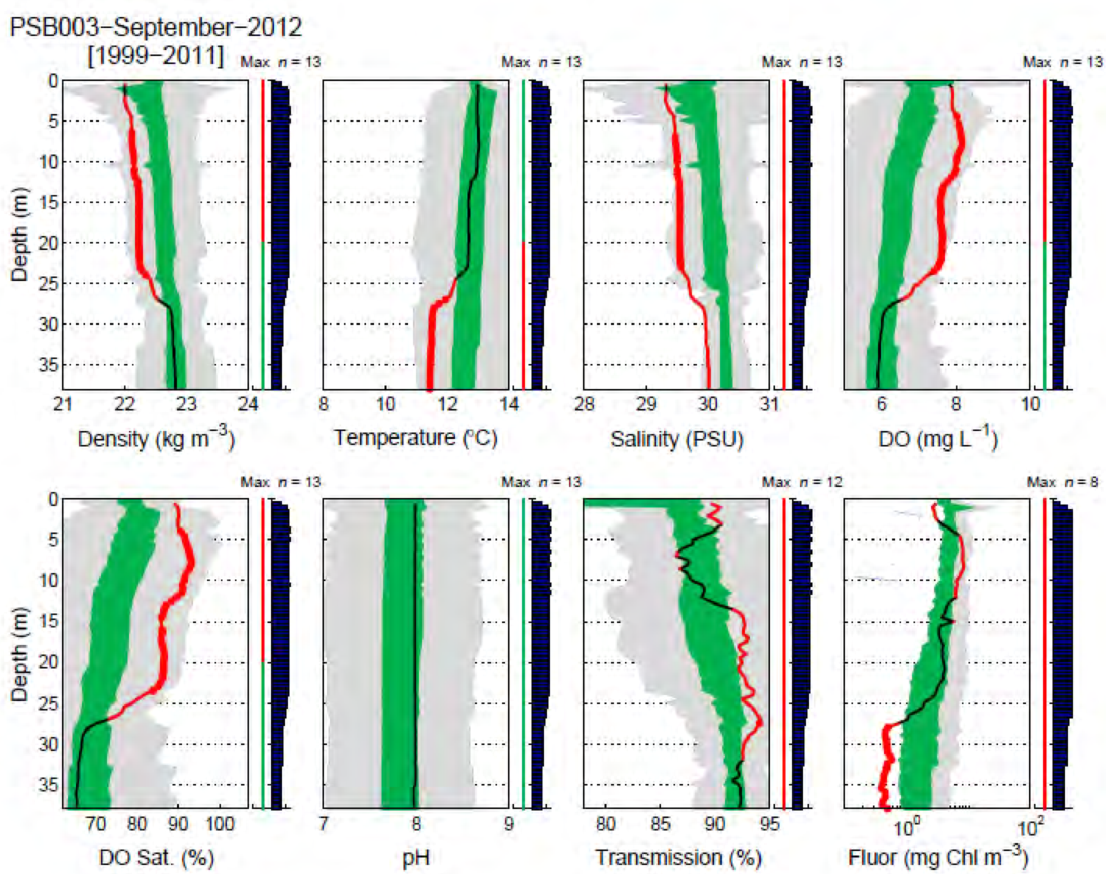


Figure 6. Vertical sensor profile data plotted in the context of interquartile ranges based on historical results specific to a station and sampling time of the year. Graphs are used to visually inspect the temporal context of measurements and used to apply QC tests to sensor measurement results.

6.8.3.3 **Additional QC actions.** Other conditions warrant further review/research and follow up actions to correct or understand whether data passes or fails quality objectives. These include:

- Missing data.
- Values that exceed detection limits (data at, below or above detection limits).
- Weather or environmental events that cause anomalous values.
- Laboratory method changes.
- Field data collection method changes.
- Personnel changes.
- Equipment malfunctions.

Samplers try to avoid or mitigate these circumstances through good planning, preparation and by using standardized protocols and methods and good communication. When any of these things do affect data, every effort is made to determine if data can be used or re-generated. Even so, the data may be still be flagged and commented as “estimates” to alert users to potential analytical effects. If data can’t be used it is flagged as “fail” and eliminated from analysis and distribution.

6.8.3.4 **Corrective action processes.** QC results may indicate data problems. Staff and external lab analysts will follow prescribed procedures to resolve the problems. Options for corrective action may include:

- Retrieving missing information.
- Re-calibrating analytical instruments or sensors.
- Re-analyzing samples (must be done within holding time requirements).
- Modifying the analytical procedures.
- Collecting additional samples or taking additional field measurements.
- Qualifying results using QC codes.

6.8.3.5 **QC Codes.** Following quality assessment, all data is given a quality description (QC code) and released for public use or removed from the dataset. A quality flag is given to each data point to communicate any specific reason for the QC code. Also, quality assessment allows the marine waters group to describe and quantify the accuracy and expected error associated with all marine data generated. At various stages of assessment, a code specifying the QA level is used to denote the status of data in the QC and review process. Once all QC procedures have been applied and quality objectives passed, data are finalized. Prior to finalization, all data in the process of review are considered provisional and may be subject to change. Status of the data is clearly communicated to data users. Descriptions of all QC codes, flags and level of assessment can be found at the Marine Waters website under the Data Quality Codes page.

6.9 **Secondary Data.** Secondary data from external sources are used for several purposes. We use publicly available data collected by programs or agencies that follow documented procedures. Typically, the external party provides data in a provisional state and subsequently finalizes them. We rely on the external party to generate and publish data and related QA/QC information. We also review the data to assure they make spatial and temporal sense. For our final reports and products, all secondary data will be thoroughly reviewed and only data collected under formal QA/QC procedures will be published. Any developmental products, such as the hypoxic intrusion index, will be identified as such.

6.10 **QAQC of Analytical and Descriptive Products.** As part of our final assessment and reporting on marine water quality conditions, all analytical and descriptive products are reviewed by internal colleagues to catch errors or potential mistakes.

6.10.1 Analytical (quantitative) products are calculated or computed results, intended to provide exact determinations or assessments based on data. These products are given a comprehensive review, with secondary checks of calculations and computations, validation of source data, equations and methods used to determine analytical results.

6.10.2 Descriptive products which are intended to provide graphical or illustrative information undergo a “basic” check for overall correctness, completeness and reasonableness within context of expected or related information.

6.10.3 Current marine water column monitoring products are defined as analytical or descriptive and are listed in table 10.

Analytical Products - QAQC Required		
Product	**Type of Product**	**Level of QC Required**
Marine Water Condition Index (MWCI) - annual plots & heat maps	Quantitative	Comprehensive Review
Annual anomalies in the dissolved oxygen deficit, light transmission, salinity (0-50m heat maps)	Quantitative	Comprehensive Review
Monthly Condition Summaries - heat maps, text	Qualitative (Descriptive)	Comprehensive Review
Monthly or Annual Weather and River Summaries based on 5 long term stations	Qualitative (Descriptive)	Basic Review
Monthly Anomalies in Pacific Decadal Oscillation Index (PDO)	Qualitative (Descriptive)	Basic Review
Monthly Anomalies in the Pacific Fisheries Environmental Laboratory Upwelling Index (PFEL)	Qualitative (Descriptive)	Basic Review
Monthly Anomalies in North Pacific Gyre Oscillation Index (NPGO)	Qualitative (Descriptive)	Basic Review
Monthly Anomalies in Hypoxic Intrusion Index (HI)	Quantitative	Comprehensive Review
Annual Long Term Water Column Monitoring Condition Summary	Qualitative (Descriptive)	Comprehensive Review
Trends and Correlation in Long Term Water Column Monitoring Annual Data Results	Quantitative	Comprehensive Review
Annual Watermass Summaries - plots and text	Quantitative	Comprehensive Review
Annual Long Term Water Column Monitoring QAQC Summary	Quantitative	Comprehensive Review

Table 10. Marine Waters Monitoring analytical and descriptive products and type of QAQC required.

6.11 **Periodic data usability (method) assessment.** Upon completion of the QAQC, data review and the data verification process, data quality (Usability) assessment (Lombard and Kirchmer, 2004) is conducted by senior MWM group oceanographers.

Data from laboratory QC procedures, as well as results from field replicates, laboratory duplicates, check samples and sensor performance tests provide information to determine if MQOs have been met. The usability assessment includes review of laboratory and sensor precision, accuracy and the success of meeting control limits. Sample results from laboratory analyses and sensor deployments are examined for completeness (all samples, all analyses). Processing logs and laboratory reports are scrutinized for adherence to specified methods and QA/QC requirements.

A review of sample results is performed following each sampling year to determine need for modifications to the sampling or analysis program. Laboratory and quality assurance experts who are familiar with assessment of data quality are consulted if guidance is needed for assessment. Annual summaries include data quality and whether project objectives are being met. If limitations in the data are identified, they are noted.

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

6.12 **Conducting audits.** Audits are conducted every month, on incoming data once it's been processed and uploaded to the EAPMW database. Annual audits are conducted for every sampling year, once data has been completely reviewed and quality control and assessment activities are completed. These audits occur 4-6 months after the sampling year is completed.

MWM technicians track and reconcile the status of samples being analyzed by the laboratories, focusing on QC problems as they arise. The monitoring coordinator periodically performs QA/QC of files including raw data field sheets, calibration records, laboratory QA/QC, and other program related materials. Summaries (statistical evaluations and plots) of all QC information collected during a sampling year are generated and reviewed routinely by the MWM group.

All laboratories participate in routine performance and system audits of various analytical procedures. Audit results are available upon request. The Laboratory Accreditation Unit of Ecology's EAP accredits all contract laboratories that conduct environmental analyses for the agency, and the accreditation process includes performance testing and periodic lab assessments. No additional audits are envisioned.

To assure accurate entry of data into the database, the monitoring coordinator or data manager checks 10% of all values against the source data. If errors are found, an additional 10% of values are checked and the process will continue in this way until no errors are found or all values have been verified or corrected.

The senior oceanographer, monitoring coordinator or data manager checks 10% of the annual, finalized data in Ecology databases and available via the internet against the source data. If errors are found, an additional 10% of values are checked and the process will continue in this way until no errors are found or all values have been verified or corrected.

The results of QAQC and audits including performance assessment of all measurement systems, significant QA problems, and recommended solutions are available upon data finalization following the completion of a sampling year.

6.13 **Performance measure evaluation.** Once a year, in the month (July) following the end of the state fiscal year, we report the attainment of our monitoring performance measure to the Washington State's Office of Financial Management. Our performance measure is an accounting of the percentage of data collected that met MQOs. Table 10 shows performance measure attainment for recent years.

Marine Waters (Flights) Summary								
		2008	2009	2010	2011	2012	2013	Comment
Marine Waters - Discrete Results	Total #	5,718	4,956	6,727	6,579	6,839	6,392	Includes chlorophyll a, dissolved oxygen,-salinity, phosphate, silicate, nitrate, nitrite, ammonium
Marine Waters - Discrete Results	# DQOs	5,718	4,926	6,693	6,539	6,831	6,384	
% Discrete Meeting DQOs	**%**	**100.0%**	**99.4%**	**99.5%**	**99.4%**	**99.5%**	**99.5%**	
Marine Waters - Continuous Vertical Results	Total #	224,970	298,172	360,610	325,367	300,588	290,906	Includes temperature, conductivity, dissolved oxygen, light transmission, fluorescence, turbidity
Marine Waters - Continuous Vertical Results	# DQOs	224,023	295,311	349,602	323,432	298,264	288,458	
% Continuous Meeting DQOs	**%**	**99.6%**	**99.0%**	**96.9%**	**99.4%**	**99.2%**	**99.2%**	
Total number of sampling sites (Flights & JEMS)		40	35	41	40	40	39	
Event, Site & Weather Observations not included								

Table 11. Example Performance Measure Report for Marine Waters Monitoring Data.

7.0 Records Management

7.0 All data reviews, QC analyses and related activities are performed using standardized data templates, software routines and documentation. These tools are stored on a secure network drive, in appropriately organized and designated folders along with the original field, lab and instrument files and data. All decisions and QC activities are documented using independent records, so that any unusual results or procedures can be verified after the review or process is completed.

8.0 Quality Control and Quality Assurance Section

8.1 This section is redundant to the overall procedure documented in Section 6.

9.0 Safety

9.1 There are no specific safety requirements for this work, beyond the stated considerations in the agency guidance.

10.0 References

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10.14 U.S. Integrated Ocean Observing System, 2012. Manual for Real-Time Quality Control of Dissolved Oxygen Observations: A Guide to Quality Control and Quality Assurance for Dissolved Oxygen Observations in Coastal Oceans. 55pp. https://ioos.noaa.gov/project/qartod/#manuals