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by

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Abstract

The Washington State Department of Ecology (Ecology) has been collecting continuous vertical profiles of pH in conjunction with key oceanographic state variables as part of its monthly core station sampling since the program's inception. The concern about effects of ocean acidification on Washington marine waters makes historical pH data a valuable resource for evaluating spatial variability, establishing site-specific baselines for assessing regional shifts in pH and changes in water quality, and potential impacts on marine systems over time.

As of 2014, Ecology's pH data set had not been:

- Subjected to consistent and regular quality control testing in the context of the entire historical data set and calibration record or
- Reviewed in the context of patterns and trends in other variables.

Before this analysis, data were distributed as estimates with potential error due to uncertainty with sensor accuracy and were not recommended for use by the Water Quality Assessment due to uncertainties in overall data quality.

Due to the increasing importance of ocean acidification and potential value of the data set, a rigorous quality assurance (QA) data review was conducted on all pH data collected from 1989 to 2013. Before 1989 consistent and documented collection and calibration methods were not available and were therefore excluded from this data quality review. Overall pH data quality was improved by quantifying sensor drift and applying a correction factor to the data, using a combination of in-house and factory calibration records that met statistical criteria. This resulted in a final data quality designation of "Pass" for 33.2% of the historical pH data record, "Fail" for 29.1% of the results, and an additional QA designation of "Estimate" to 33.2% of the data when calibration records allowed predictable assumptions to be made about linear sensor drift.

Ecology's pH data record now serves as a unique asset for assessing changes in pH conditions in the context of temperature, salinity, oxygen, and *in situ* fluorescence and other variables. Its particular value is its unique geographic extent for Puget Sound and the Washington coastal estuaries, its temporal resolution, and unmatched historical perspective. The value of this record is that it can be used to detect measurable change over a large temporal and spatial scales in Washington's marine waters and use of the data to formulate baselines.

An independent study "*Application and usability of pH measurements in coastal marine data sets of Washington State*" will quantify potential bias and usability of the pH data record for Washington's marine water quality assessment. Baselines and trend analysis are robust estimates of the central tendency of the data and are insensitive to consistent measurement bias. However, water quality violations focus on high and low extremes of the data spectrum and require a rigorous sensitivity analysis of the data set to bias for application in assessment of water quality impairment.

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- Marine Monitoring Unit staff (current and former) who have worked diligently, tirelessly, and sometimes under very adverse conditions, to collect and analyze the valuable long-term data we have today.
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Introduction

Rationale and Purpose

The purpose of this report is to document quality assurance (QA) activities (data and calibration review, and sensor drift determination) of the long-term pH data set (1989 to 2013) collected by the Washington State Department of Ecology (Ecology) Marine Monitoring Unit. This effort was conducted as a requirement for subsequent data usability evaluation, *Application and usability of pH measurements in coastal marine data sets of Washington State*.

The Marine Monitoring Unit has been collecting continuous vertical profiles of pH in conjunction with other key oceanographic variables as part of its long-term monthly profile monitoring program. The purpose of this program is to measure and report on status and trends in ambient water quality in context of human, oceanic and climatic conditions. Results are used for multiple purposes within Ecology. Examples include: simulating dissolved oxygen and acidification in the Salish Sea (Roberts et al., 2014; Roberts et al., 2015); assessing water quality under the Clean Water Act; routine long-term water quality monitoring of status and trends for marine waters conditions. Several other organizations also use these data for reporting on Puget Sound water quality and climate conditions. (PSEMP, 2015; Mauger et al., 2015).

Ecology's pH data provide a unique historical record to address seasonal and spatial patterns in Puget Sound and Washington's coastal bays in the context of temperature, salinity, oxygen, *in situ* fluorescence and other variables. The data set is useful for general patterns, baseline conditions and relative change. But large data gaps exist as a result of rigorous QA procedures, creating limits on trend analysis. Additional gaps in the record exist because of the unknown quality of the manufacturer's (Seabird Electronics, Inc.) factory calibration performance and procedures over the entire period. There are also gaps due to limitations in Ecology's use of supplemental in-house calibrations beyond factory calibrations. This report describes the limitations, addresses and corrects them to the best of our ability, and documents the results of data quality activities including recalculating the original sensor drift applied to pH values based on original sensor output.

Background

Since 1989, the program has deployed an electrode-based sensor to produce water column profiles of pH. The probe employs a potentiometric method which consists of a hydrogen ion-sensitive glass electrode coupled with a reference electrode set to a pH of 7. This method suffers from a number of measurement and calibration issues. These include the temperature of measurement and conversion to *in situ* temperature, calibration for use in a high ionic strength medium, glass electrode drift, reference electrode drift, and liquid junction potential issues. The liquid junction potential of the pH cell is sensitive to ionic strength and to the composition of the solution it is in, so moving the electrodes from low ionic strength buffers to the higher ionic strength of seawater makes apparent pH readings drift for a period of time. As probes are used, both the electrode and reference electrode age, creating drift in the measurements (Dickson, 1993).

Ecology routinely ensures that pH sensors are calibrated by the manufacturer (Seabird Electronics, Inc.) according to the manufacturer's recommended schedule and specifications, set at every 6 months as of the publication date of this report. Seabird's current calibration protocols use National Bureau of Standards (NBS) buffers.

Sensors are deployed only for the recommended period (6 months) specified by the manufacturer and then sent back for factory performance evaluation and calibration. During sensor deployment periods, in-house calibrations are performed once a month to track the sensor performance over time, according to our protocols (Standard Operating Procedure Hermanson and Pool, 2013). The in-house calibration results are used to determine sensor drift effects on measured values.

In the past, this was the extent of quality control procedures for the sensors. The in-house determination of sensor drift was not validated or corrected by factory-determined drift. In addition, the historical documentation for calculation of the pH results based on in-house calibration records raised concerns about the validity, consistency and statistical rigor of the in-house approach. Consequently data were not recommended for use in the 2010 Water Quality Assessment, because more thorough QA was needed to meet Ecology's credible data policy (WQP 1-11, 2006).

As of 2014, no comprehensive review of the full data set had been performed. Ecology's pH data set had not been subjected to consistent and regular quality control testing in the context of the entire historical data and calibration record. Neither had it been reviewed in the context of patterns and trends in other variables. Side-by-side measurements of pH conducted with National Oceanic and Atmospheric Administration (NOAA) scientists during a Puget Sound cruise in 2008 underscored the need for a thorough assessment of Ecology's existing pH data when the two data sets displayed differences in side-by-side monitoring.

Motivation

Initially Ecology had simply removed the pH data set from its web site. However, growing concern over the possible effects of ocean acidification on Washington marine systems make historical pH data a valuable resource for understanding inorganic carbon dynamics over different scales of space and time. Recent advances in marine pH sensor technology and improvements to precision and accuracy have been made (ACT, 2015; Takeshita et al., 2014). Also guidelines for standardized methods and data reporting in the international community have improved (Dickson, 1992; Dickson et al., 2003; Dickson et al., 2007; Dickson, 2010). This added impetus to a review and summary of Ecology's data. Thus, Ecology developed and implemented a comprehensive review of the existing pH data record in late 2014. The review included all in-house and factory calibration results, historical calibration documents, and data for the period from 1989 to 2013.

Goal

The goal of the review of Ecology's pH data set is to provide a unique historical data record that meets rigorous credible data standards despite the technical limitations of the internal reference electrode-based pH measurements (NOAA, 2015; Dickson, 1993; Dickson, 1984). Data that did not meet QA needs were removed from the long-term data set. Additional data that met some but not all QA needs were flagged as estimates and are presented with the remaining data. Another goal of this effort was to improve ongoing quality control procedures, sensor performance criteria and potentially upgrading monitoring techniques to address the issue of ocean acidification effects.

While the resulting data set contains appropriate QA flags and represents the best available information, the data still have limitations. The assessment procedures described here do not ensure that the reviewed pH data are representative of true estuarine pH conditions, since pH measurements do not include effects of salinity. The scale used for the probe is the NBS scale rather than the total or seawater scale. The intention is that in the future, the data can be adjusted for salinity variations in the environment and pH measurements can be refined.

Methods for Quality Assurance Process

Ecology uses an electrode-based sensor that employs the potentiometric method. This type of probe uses a hydrogen ion-sensitive glass electrode coupled with a reference electrode set to a pH of 7. This method suffers from a number of measurement and calibration issues all affected by temperature, salinity and pressure conditions. For high-quality information, these issues must be checked and considered during data QA activities.

Workflow and steps for reviewing and qualifying data

Figure 1 summarizes the work flow for reviewing and qualifying both historical and future data.

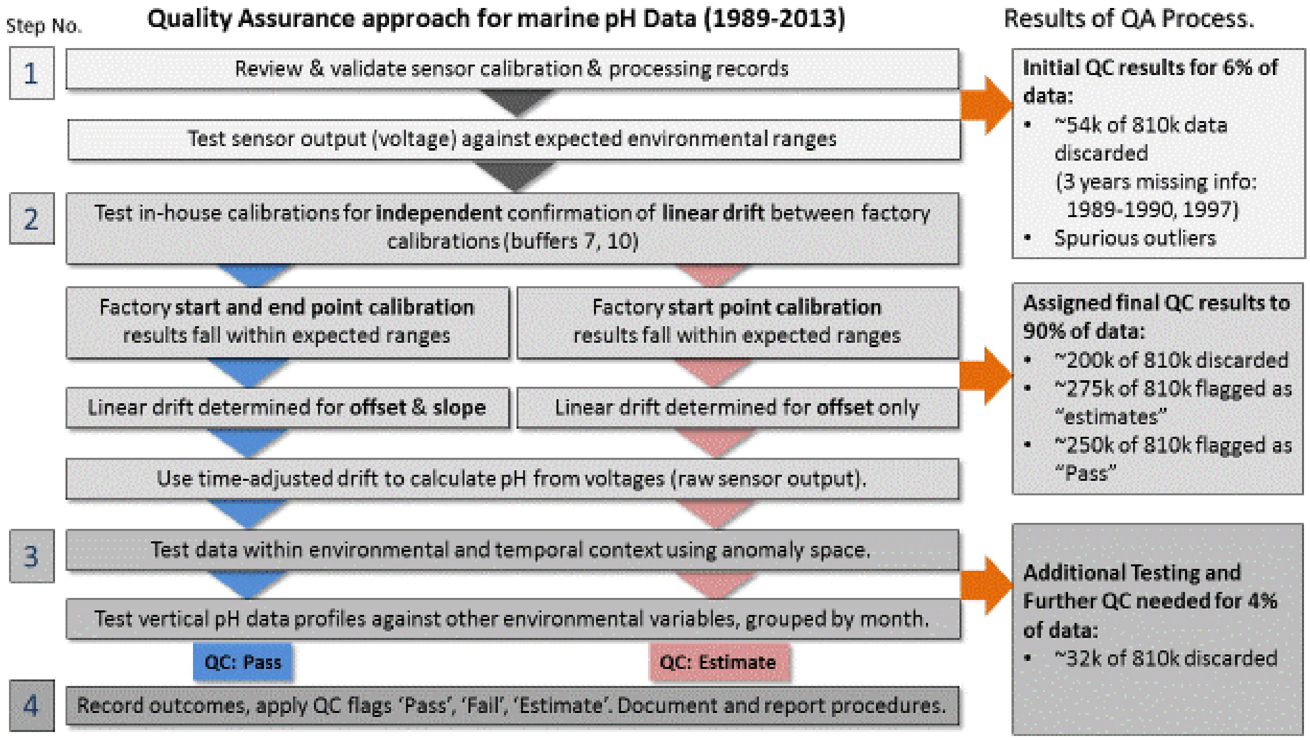

Figure 1. Decision workflow and steps for assessing and qualifying data as *pass* (blue), *estimate* (red), or *fail*, based on QA criteria.

The process was conducted in four major steps:

1. **Review and validate sensor records**

   A. Calibration documentation review. Review documentation and validate sensor calibration and processing records. Determine effects of sensor drift on offset or slope terms and relationships to sensor data calculation.

   B. Coarse test of sensor output. Check character of existing sensor output data; test sensor voltage output against expected environmental ranges.

2. **Evaluate sensor performance.** Test in-house calibrations for linearity. Test and calculate sensor drift from factory start and endpoint calibrations for two scenarios:

   A. Factory start and endpoint calibrations exist. Quantify sensor drift (slope and offset terms) if calibration results passed range tests based on entire factory calibration record.

   B. Only factory start point calibration exists. Quantify sensor drift (offset term only) if in-house calibrations statistically confirm linearity of drift but factory calibration record was incomplete.

   Re-calculate pH results from raw sensor voltage outputs using the time-adjusted drift terms for all data, as long as accompanying temperature data exist.

3. **Validate pH results**. Test results within environmental and temporal context. Review graphical presentations of all site-specific data records to identify any remaining data issues.

4. **Record outcome**. Assign final quality control (QC) codes and eliminate data that failed quality assessment tests. Document procedures and results.

Step 1. Review and validate sensor records

A. Calibration documentation review

Ecology's sensor calibration and maintenance routines (Bos, 2014) require that factory calibrations are performed annually for pH sensors, or as recommended by the manufacturer. During a given deployment period, sensors were calibrated in-house, using standard NBS buffer solutions at regular intervals (monthly until 1996, bi-monthly from 1996-1998, sporadically from 1999-2002, then bi-monthly through 2014). At the end of each deployment period, sensors were sent back for a new factory calibration, at which point factory endpoint calibrations were performed by Seabird Electronics using NBS buffers. The entire set of calibration records were reviewed and assessed for sensor characterization and to prepare calibration results for subsequent testing activities. Sensor deployment periods that lacked appropriate calibration and data processing records were determined to be unusable and included the first two years of data collection under the original 1989 PSAMP program plan. These two periods included the water years starting in Oct 1989 – Sept 1990 and Oct 1990 – Sept 1991 and resulted in discarding ~23,000 data results.

B. Coarse test of sensor output

Coarse exploration of the native sensor data (raw voltage readings) was conducted by plotting voltage in context of other related factors such as temperature, salinity and dissolved oxygen data collected at the same time.

Plotting data results against other variables allowed us to identify obvious, spurious issues and flag data that failed key criteria:

- Extreme outliers outside of expected environmental climatology (e.g., voltages equivalent to pH of 0 or 14 which would not occur in natural marine waters).
- Missing temperature data needed to calculate pH from voltage readings
- Partial profiles with missing data

This resulted in discarding ~10,000 data results. Figure 2 is an example of a coarse range test of pH voltage plotted against salinity to detect extreme outliers or spurious data.

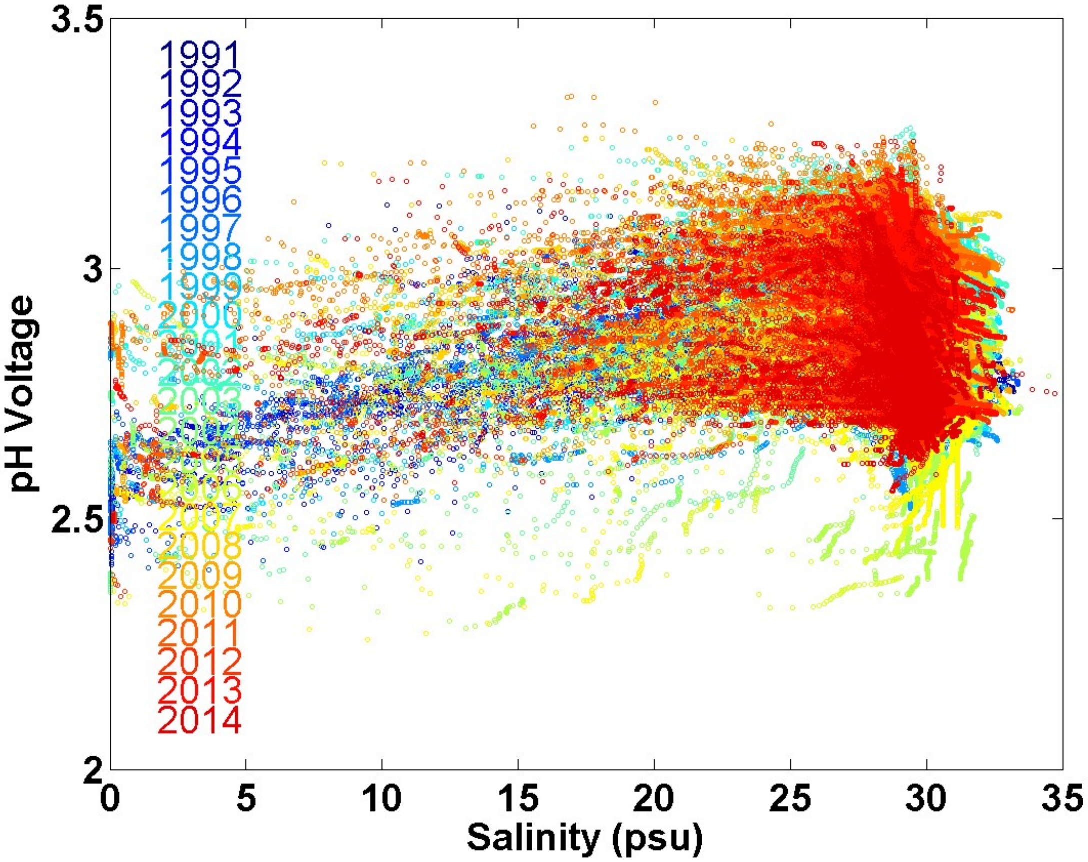

Figure 2. Raw voltage readings of all historical pH sensor measurements plotted against salinity as a coarse range test for the first step of data quality control activities.

Step 2. Evaluate sensor performance

A. Determine sensor drift when both factory start and endpoint calibrations exist.

In-house calibrations were used to statistically test the assumption that the sensor drifted in a linear manner. When we compared the in-house and factory calibrations using prescribed pH buffer solutions, we detected a systematic offset of the sensor voltage response during in-house calibrations differing from equivalent calculated factory calibration response (±1-6%) while the slopes of the sensor drift for factory and in-house calibrations exhibited parallel behavior. We assumed that the offset occurred due to an unspecified but systematic bias in Ecology's calibration facility as the temperature and atmospheric pressure conditions were uncontrolled and varied during calibration activities. As a consequence, offset terms for sensor calibrations were taken directly from factory start and endpoint calibrations. Tests on calibration records were performed to substantiate that drift could be assumed to occur linearly. To detect reporting errors in the calibration results from the manufacturer, factory start and endpoint calibration data for individual sensors were compiled and numerically evaluated against control charts based on historical sensor-specific calibration records.

B. Determine sensor drift adjustments when only factory start point calibration exists.

For situations when endpoint calibrations could not be performed, such as when a sensor failed or the electrode expired, "sensor drift estimates" were applied for that specific deployment period. These were based on Model I regression analysis of in-house calibration records of responses for NBS buffers for pH7 and pH10 over time, uniformity of the slope for the regressions of both buffers over time, and sufficient statistical power. The drift was then applied to raw sensor output data and the calibration offset term and pH results were recalculated. Data results calculated this way were given a QC flag equivalent to being assigned an "estimate" status.

For data with available factory calibrations, we next determined whether the start point calibrations fell within an expected range based on statistical control charting of the sensor-specific slope and offset terms from all factory calibrations. We then tested the validity of the assumption that drift had occurred linearly between the start and endpoint factory calibration using our in-house calibration record.

As a result of these activities, a time-adjusted linear drift could be calculated and applied to both the initial factory slope and offset terms for each specific sensor calibration period. Then, if temperature data existed, these were used to re-calculate pH results from the native (raw) sensor voltage outputs for data collected during periods with both a start and endpoint factory calibration. For data collection periods when there was no endpoint factory calibration performed, the drift adjustment was determined only for the offset term of the sensor. For these data, pH results were recalculated using only the drift adjusted offset term applied to the raw sensor outputs. These data are included in the historical record but are flagged accordingly as estimates.

Our approach assumes that factory calibrations by Seabird Electronics, Inc. have been conducted under appropriately controlled conditions. Consequently, Ecology's data record may carry a bias due to undetermined effects from factory calibration procedures using NBS buffers.

Step 3. Validate data

After data re-calculation with drift-adjusted terms, the results were re-tested using a variety of graphical reviews and additional range tests to identify any remaining issues. This gave us the ability to find and remove any data issues such as inconsistent data behavior such as abrupt changes and other questionable, unexpected data patterns such as non-normal homogeneity or extreme noise. Figure 3 is an illustration of a heat map presentation used to identify overall data patterns. Unusually homogenous results are identifiable in early 2000 with an abrupt change from July to August 2000. This was coincident with a sensor swap. These data failed the QC test for *abrupt or unusual data pattern* and were removed from the final data set.

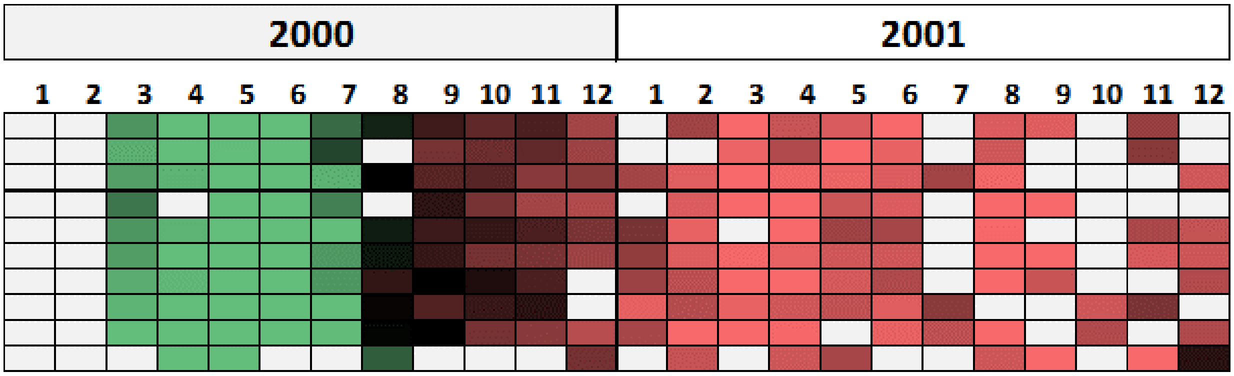

Figure 3. Heat map of pH data anomalies for a sub-set of core monitoring stations to identify and determine unusual data patterns.

Another effective review tool used station-specific plots, showing all data profiles that passed previous QC tests by month and depth. This allowed a very thorough review of all individual profile cast data and was useful for identifying any remaining data issues such as surface or bottom outliers, instances of sensor issues resulting in non-normal measurements or unusual profile behavior. Figure 4 illustrates an event (April 2004) when the pH sensor was probably not well-equilibrated and generated an unusual profile. This profile was flagged and removed from the final data set.

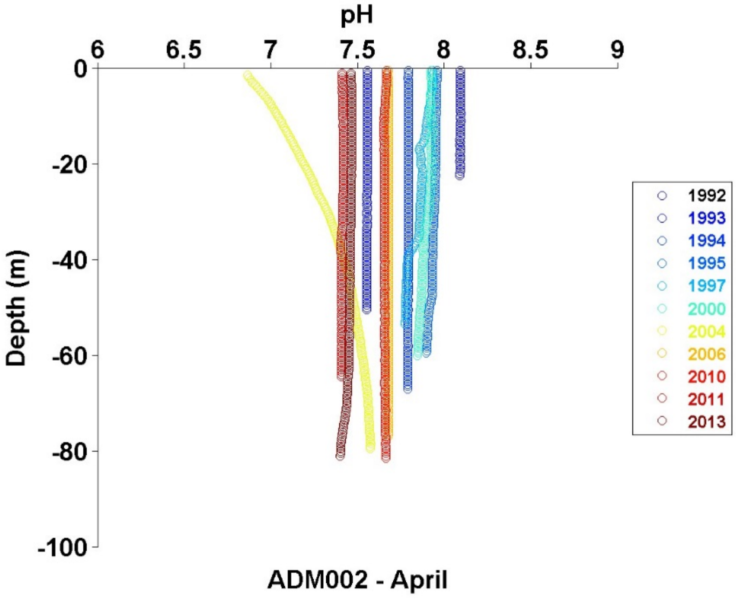

Figure 4. Profile plots of all April pH measurements collected at station ADM002.

Step 4. Record outcome

After multiple levels of data examination and well-defined testing, frequent, repeated plotting and graphical review and substantiation, final data results were generated and stored in Ecology's secure database. Data results were given appropriate, credible quality control codes. Original records were retained and archived according to Ecology's information management policy using the 100-year archive holding standard. The QA procedures are documented in this report and internal procedural documents and original analytical tools are stored on secure, network servers.

Results of Quality Assurance Review

Ecology’s historical pH data set was reviewed and improved through a comprehensive QA effort. Through the QA and control steps laid out in this document, questionable or deficient results were excluded from the data set while results passing QA criteria were retained and improved by recalculating data using well-developed sensor drift calculations.

During this review, approximately 810,000 data records from 1989 to 2013 were initially included. Overall, 299,000 records (37%) of unknown quality were eliminated, 295,000 records (36%) were assigned a QC code of *estimate*, and 216,000 records (27%) passed the review process. Periods with the best quality data were 1992-1997, 2004-2006, and 2009-2011. Periods with the most rejected data were 1998-2003, 2007-2008, and 2012-2013.

Quality assurance activities and steps

The review and QA process of pH data followed four steps that resulted in three different review levels for the data: “pass”, “estimate”, or “fail” (data discarded from public databases). Estimated data are included in the data set with appropriate QC codes.

Throughout the assessment, data were discarded that did not meet the following conditions:

- Complete documentation of sensor calibration records.
- Results occurring within a range of expected values in the context of other water properties (temperature, salinity, dissolved oxygen, *in situ* fluorescence over both space and time).
- Sufficient data for associated variables that would allow evaluation of pH data in the context of pressure, temperature, and salinity (e.g., if temperature or pressure was missing for pH data, pH data failed the QC process and were excluded).
- Appropriate environmental context when analyzed with other associated variables.

Conclusions and Recommendations

Ecology's pH data set and documentation of calibration records from 1989 to 2013 allowed us to recalculate, reconstruct, retain and improve a significant number of pH data records. These data pass quality assurance (QA) criteria of electrode-based pH sensor measurements documented in Ecology's Quality Assurance SOP (Bos, 2014) and are tested against environmental context and patterns of other sensor variables measured at the same time as pH sensor data. Given the technical limitation of the sensor, a conservative approach using stringent data criteria, calibration and adjustment procedures were applied. This resulted in a data set that can be used to determine spatial and temporal patterns of pH in Washington's coastal marine waters.

Limitations of pH sensor data

Like much of the existing pH measurements taken in natural waters by probes using a reference electrode, several limitations apply for use of these data, especially for understanding changes brought about by ocean acidification which can be of a smaller magnitude than natural variability. These limitations include the following conditions.

- Ecology's electrode-based sensors assume a constant salinity. Salinity has a strong influence on the marine carbonate system (Dickson et al., 2007), and the data may carry an unaccounted bias and not represent true estuarine pH values for water with salinity lower than 20 psu.
- As for all in-situ sensors, sensor response time can bias pH measurements. As the sensor package is lowered through the water column, strong temperature gradients over scales of decimeters might lead to a slow response and limited spatial resolution. This may result in a lower spatial resolution of pH.
- Quality and consistency of the manufacturer start and endpoint sensor calibrations are unknown.

Recommendations for use of pH sensor data

By using consistent and improved routine quality control of pH data in conjunction with data review set in context of the entire historical data and calibration record, Ecology's pH data are now a valuable historical resource. They can be used to establish baseline pH conditions for marine waters in Puget Sound and Washington's coastal bays. Spatial and temporal patterns of change can be determined under the condition that identical sensor types are used and conditions for alkalinity and salinity are assumed to be comparable to historical conditions. The data set also provides a first order understanding of seasonal and regional patterns for pH in Washington's marine waters. It also illuminates the importance of understanding regional estuarine processes where fresh water mixes with marine water.

Finally, advances in pH sensor technology will serve in Ecology's mandate for conducting continued long-term monitoring of pH in Washington's marine waters, and program upgrades needed to support research efforts in addressing ocean acidification effects on marine systems.

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Appendices

Appendix A: Demonstration of the importance of the voltage offset term

After 29.1% of the initial data were discarded, nearly half of the remaining data lacked a post-deployment factory calibration. Rather than limit the historical record further, we explored methods of proceeding in lieu of a final post-deployment factory calibration after eliminating the post-deployment in-house calibrations.

Factory calibration results in two adjustment terms applied to voltages: the offset and the slope terms. Pre- and post-deployments are required to fully constrain the equations. However, if one is more influential, then the in-house calibrations could be used to determine that value. To demonstrate that drift in the voltage offset term for electrode reference sensors affects pH sensor output more profoundly, two scaling cases are demonstrated.

A. Mathematical demonstration - Relative sensitivity of offset and slope terms in pH equation

The manufacturer of our data probe, Seabird Electronics, Inc., currently recommends that pH sensors be recalibrated every six months at the factory (www.seabird.com/sbe18-ph-sensor). During factory calibration, the amount of drift in both slope and offset terms of the calculation equation can be determined, unless the sensor was damaged within the deployment period. Our experience has shown that both types of drift are reasonably linear and are therefore a first-order correction.

When a final calibration record is not available, it is reasonable to use the slope of the linear drift of in-house monthly calibrations and apply this to the data record, starting with the initial factory calibration results. To determine if the slope or offset is more important in the correction, we mathematically explored the term of greater importance for the sensor drift.

Equation 1 expresses the relationship between sensor voltage and pH in terms of the calibration factors, slope and offset. The equation is referenced to a neutral pH of 7.0, since the reference electrode solution is equivalent to a neutral pH. (SBE, 2015)

$$\text{pH} = 7 + (\text{Vout} - \text{offset})/(1.98416\text{e}^{-4} \times \text{T} \times \text{slope}) \qquad \text{(Equation 1a)}$$

Let:
M = slope
B = offset
V = Vout
T = temperature
C = Faraday’s constant = 1.98416e^{-4}

$$\text{pH} = 7 + (V - B)/(C \times T \times m) \qquad \text{(Equation 1b)}$$

The sensitivity of pH to changes in offset can be calculated by taking the first derivative of pH relative to B in Equation 1b,

$$d(pH)/dB = -(1/m)\,(C \times T) \qquad \text{(Equation 2)}$$

and the sensitivity of pH to changes in slope can be calculated by taking the first derivative of pH relative to m,

$$d(pH)/dm = -(1/m^2)(V - B)/(C \times T) \qquad \text{(Equation 3)}$$

The ratio of these derivatives shows the relative sensitivity of pH to the offset and slope terms, respectively. This reduces to a simple quantity, m/(V - B). When this term is greater than 1, the offset term is dominant, and this is true for the practical range of pH observed in the ocean (Figure A-1). Because the sensor is referenced to a pH of 7 (neutral), there is a singularity in this sensitivity ratio, which can be interpreted to mean that slope has no importance with neutral pH.

Thus, if a post-deployment calibration is not available, it is better to assume drift of the offset term only and use that to adjust the data set to provide an estimate of pH.

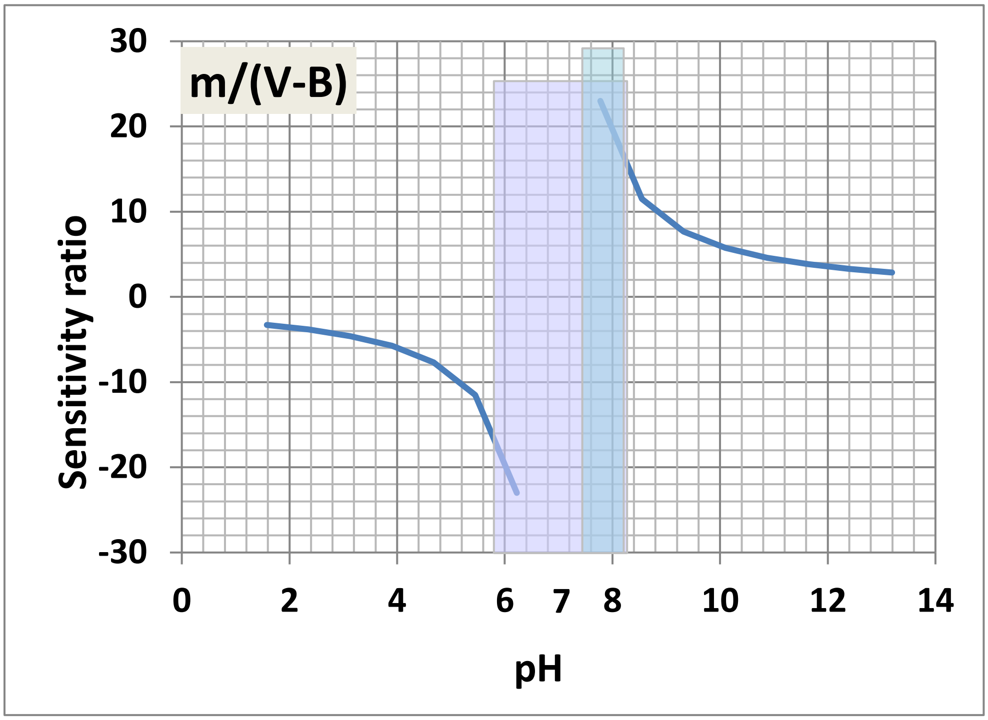

Figure A-1. The ratio of offset-to-slope sensitivity for pH shown with typical ranges of pH in marine waters (blue box) and fresh water systems (purple box).

Mathematical conclusion

At a pH of 7, the offset term exclusively affects the pH calculation. The slope term is irrelevant. The further a pH measurement falls from 7, the more important the slope term becomes. Typically, pH values in the marine environment range from 7.5 - 8.4 (Chester and Roy, 2012; Stumm and Morgan, 1981). Ocean water is normally slightly basic, with a surface-water pH of about 8.2, but that has declined in recent years to about 8.1 (Jacobsen, 2005). Most freshwater streams have a natural pH in the range of 6 to 8 (Lenntech, 2013), which overlaps with the range of pH in marine waters. For Puget Sound, an estuary with both fresh and marine water inputs, pH values will fall within these ranges, with a tendency towards more marine conditions. Values depend on site location, proximity to ocean or river influence, depth of the measurement, season and time of measurement and environmental factors such as biological or climate influence.

B. Numerical demonstration

A numerical demonstration shows that bias in the slope term is one order of magnitude less than the offset term and therefore negligible for marine water measurements collected historically in Puget Sound.

Table A-1 demonstrates that the ratio shown in Figure 2 can be derived by substituting numbers into Equation 1a. The constant value for an offset change of 1 (3.98, shown in the table) can be confirmed by using Equation 2 above, at a constant temperature.

Voltage Response	pH	pH change for slope change of 1	pH change for offset change of 1	Ratio
2.00	5.00	-0.36	3.98	-11
2.25	6.00	-0.18	3.98	-22
2.45	6.80	-0.04	3.98	-110
2.49	6.96	-0.01	3.98	-550
2.51	7.04	0.01	3.98	550
2.55	7.20	0.04	3.98	110
2.75	8.00	0.18	3.98	22
3.00	9.00	0.36	3.98	11

Base Slope	4.5
Base Offset	2.5
Temperature	8

Table A-1a and A-1b. Numerical assessment of calibration offset and slopes on pH at a constant temperature; base inputs (as constants).

Numerical conclusion

The numerical approach shows that the offset term is one order of magnitude more important across expected pH ranges in the existing monitoring data record, justifying a drift adjustment based solely on the voltage offset term for data results without a post-deployment factory calibration record. This resulted in 33.2% of the initial data set being classified as *estimates.*

Appendix B: Glossary, acronyms, and abbreviations

Glossary

Alkalinity: Measures the ability of a solution to neutralize acids to the equivalence point of carbonate or bicarbonate. The alkalinity is equal to the stoichiometric sum of the bases in solution.

Ocean Acidification (OA): The term given to the chemical changes in the ocean as a result of carbon dioxide emissions. Specifically, the ongoing decrease in the pH of the Earth's oceans, caused by the uptake of carbon dioxide (CO2) from the atmosphere. Seawater is slightly basic (meaning pH > 7), and the process in question is a shift towards less basic conditions rather than a transition to acidic conditions (pH < 7).

pH: In chemistry, pH is a numeric scale used to specify the acidity or alkalinity of an aqueous solution. It is the negative of the logarithm to base 10 of the activity of the hydrogen ion. Solutions with a pH less than 7 are acidic and solutions with a pH greater than 7 are alkaline or basic. Pure water has a pH of 7 and is neutral, being neither an acid nor a base. 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.

Potentiometric Electrodes: Potentiometry passively measures the potential of a solution between two electrodes, affecting the solution very little in the process. The potential is then related to the concentration of one or more analytes.

Acronyms and Abbreviations

Ecology	Washington State Department of Ecology
et al.	And others
NBS	National Bureau of Standards
NOAA	National Oceanic and Atmospheric Administration
psu	Practical salinity unit
QA	Quality assurance
QC	Quality control
SOP	Standard operating procedure