Exploring seasonal and spatial patterns in Ecology's long-term pH record for Puget Sound and Washington's Coastal Bays, 1990-2013. Results after Quality Assessment.



QA of Ecology's long-term pH data

Motivation

The Department of Ecology (Ecology) has been collecting vertical profiles of pH in conjunction with key oceanographic variables during routine monthly core station monitoring since 1989. Ecology's pH data provides a unique historical dataset to address seasonal and spatial patterns in Puget Sound and Washington's coastal bays and a resource for establishing baseline pH conditions for marine waters. As of 2014, the dataset had not been subjected to consistent, routine quality control testing in context of the entire historical data and calibration record. Recent advances in pH sensor technology motivated Ecology to conduct a comprehensive quality assessment of the existing pH data, in-house calibration results, documents and data.

Approach

We provide a unique historical dataset which meets rigorous credible data standards despite limitations of internal reference electrode based pH measurements. Data that did not meet the following criteria were eliminated:

- Had a complete calibration documentation record.
- Results occurred in a range of expected values in context of other variables (temperature, salinity, dissolved oxygen) over space and
- Sufficient data for associated variables to evaluate pH data in context of pressure, temperature and salinity. Appropriate response in environmental context of other supporting variables.

Result

A total of 722,221 data records were reviewed: 29.1% of unknown quality were eliminated, 37.7% were assigned a QC code of "estimate", and 33.2% passed.

Limitations

- Current assessment assumes a constant alkalinity condition so data may not represent true estuarine pH conditions.
- Slow sensor response can bias pH measurements and are affected by strong gradients.
- Quality of factory calibration procedures is unknown.

Further information in this report: <i>https://fortress.wa.gov/ecy/publications/SummaryPages/1503029.html

Historical Calibration Record Confirming Linear Sensor Drift



Legend:

Schematic presentation of Ecology's method for assessing in-house and factory (Seabird Inc.) pH calibration data records from 1990-2013 against QC criteria. Calibrations were performed routinely at pH 7 (purple) and 10 (blue). In-house calibrations were used to statistically confirm a linear sensor drift for both pH 7 and 10. If end point factory calibrations were missing but linearity could be established, drift was estimated from in-house calibration data and applied exclusively to the voltage offset term. Drift adjustments were then used to recalculate pH data from initial sensor voltage readings.

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Legend:

pH data availability (green boxes) after quality assessment of Ecology's marine pH monitoring data record from 1989-2013.

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Waters with conservative pH signatures

pH in historical seasonal context Envelopes of pH variability based on the IQR (green) and 5th and 95th percentiles (gray) indicate conservative (yellow circle) pH regions in spring and fall at a density range of sigma-t = 21.5-22.0. In Central Sound, this corresponds to a median depth of 20 and 26 m, respectively. Combining 24 years of data illustrate that these densities also denote a transition in the seasonal pattern of pH, influenced by primary productivity at lower densities (sigma-t < 21.5) found toward the surface.



Historical pH values related to water density using the interquartile range (green) and estimated 5th and 95th percentile (gray). Density bins are progressively larger at lower densities to ensure a more even data distribution of 🛖 bins across density b^{19} readings. Yellow circles indicate density 🔰 20– regions of low interannual variability and a transition zone (dashed line) in Central Puget Sound. Data are based on 4 deep longterm monitoring stations representative of Central Sound water masses (ADM003, EAP001,CMB003 GOR001)



Historical pH values

related to water density using interquartile range (green) and estimated 5th and 95th percentile (gray) envelopes. Density bins are progressively increased at lower densities. Indicated are density regions of low interannual variability (yellow circles), low pH stemming from intrusions of upwelled water (red circle) and transition in river-influenced **Possession Sound** (dashed line). Data are based on the long-term monitoring station PSS019. Densities of sigma-t lower than 21.5-22.0 show large month to month variation in pH interannual behavior suggesting that the interaction of primary productivity and river discharge makes pH predictions near the surface challenging.

Central Sound pH data from 1990-2013

Seasonality of pH in Whidbey Basin Possession Sound 1990-2013

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