Application Note:
Long Term pH Monitoring

Why Monitor pH?

pH, a measure of the concentration of hydrogen ions in a solution, is an important indicator of water that is changing chemically. The pH of water determines the solubility and biological availability of chemical constituents such as nutrients and heavy metals, and impacts organisms at cellular and structural levels. pH is typically measured on a logarithmic scale of 0 - 14 where 7 is neutral, measurements less than 7 indicate higher acidity, and measurements greater than 7 indicate higher alkalinity. As an example the normal range of stream water is between 6 - 8 whereas lemon juice would have a pH value of 3 and ammonia would have a pH value of 12. Locally, pH can very extremely and rapidly when impacted by runoff from agricultural, domestic and industrial areas transporting nutrients, chemicals, and metals into aquatic systems. In the open ocean, pH is trending downward ('ocean acidification') as higher atmospheric CO2 levels overcome the capacity of seawater to buffer pH changes.

Challenges in Monitoring pH In-Situ

In a 2012 survey conducted by the Alliance for Coastal Technology respondents reported significant concerns about ruggedness (49%), calibration life (46%), level of measurement uncertainty (43%), and reliability (41%) in relation to in-situ pH sensors. When deployed in a natural aquatic environment for continuous monitoring pH sensors (like other in situ sensors) are susceptible to two types of drift - sensor calibration drift (due to changes in the internal sensor components and measurement devices) and drift due to sensor exposure to environmental water, particularly due to bio-fouling. Drift rate and the impact on the data quality is a major driver in determining maintenance intervals, operational costs, and the time spent post-processing data to correct for drift. Quantifying and minimizing pH sensor drift is the most important challenge in collecting pH data that can be used with confidence.

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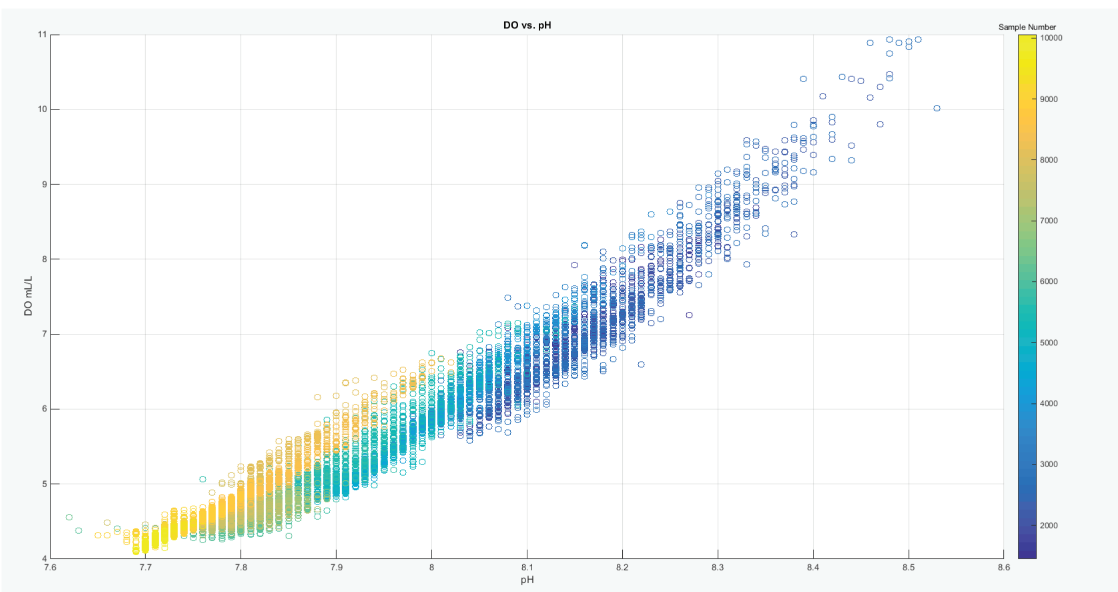
Benefits of Monitoring pH In-Situ

Change in in situ pH can prove harmful and potentially fatal for aquatic life, and dangerous to humans. Changes in pH can be particularly impactful on young or sick fish and on shellfish in all stage of their life cycle. The ability of fish and shellfish to breed, grow, and settle can also be impacted by pH levels. Faced with improper (beyond their ability to adapt) pH levels, population will decrease. The inherent difficulties faced in accurately measuring instantaneous pH over a long deployment are often made worse by the extreme high frequency pH variability common in estuarine, lake, coastal, or riverine systems with high productivity or rapid cycling of and/or forcing conditions. Under most conditions, dissolved oxygen saturation is highly correlated (see figure on the follow page). Dissolved oxygen super-saturation associated with algae blooms can cause pH to range from 7 to 10 during a diel cycle in estuaries; under these extreme conditions, only accurate, continuous sampling can remove variability of this magnitude and capture longer-term mean changes.



Impact of Drift on Operational Costs

Calibration drift is a result of electronic wear and pH reference sensor dilution between sensor calibrations. Biofouling drift is a result of biological growth multiplying over the course of a deployment, covering the sensor and reducing its ability to detect true water characteristics.

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The Alliance for Coastal Technology estimates that maintenance costs due to biofouling consume 50% of operational budgets. Common techniques for reducing the impact of biofouling drift on pH sensors include mechanical wipers, metal (copper alloy) sensor guards, copper alloy screens, chemical sprays, anti-foulant tape, duct tape, and plastic wrap.

Another option to minimize biological growth affecting the sensor is to protect it from the environmental water in between measurements.

The pictures to the left show the outside of an instrument deployed at Shilshole Bay as well as what the pH sensor looks like when removed from the internal flow path. The internal pump and flow path used in the HydroCAT-EP help protect the pH sensor from accumulating biological growth, therefore limiting drift due to biofouling.

Impact of Drift on Data Quality

Calibration drift can be minimized and linearized by sensor design and selection of components. Biofouling can occur in a non-linear or episodic manner however many organizations apply corrections based on the start and end date of the deployment applying correction proportionally across the dataset in an attempt to remove the effects of biofouling. In many organizations data that has been corrected must then be reviewed and approved before distribution. Considerable time may then have been put into collecting, correcting, and publishing data with a “fair” or “poor” quality rating. Biofouling corrections are often difficult to make with confidence in part because there are no universal standards for bio-fouling corrections. This also makes comparing data between monitoring programs problematic.

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Conclusion
The ideal monitoring solution for pH has minimal calibration drift, and eliminates the impact of biofouling growth on sensor performance and accuracy. This meets the requirements for continuous, accurate, in situ pH measurements - best collected along with coincident water quality parameters like temperature, dissolved oxygen, and Chlorophyll A concentration - while still keeping operational costs low and maximizing long-term data quality.

About the Author

Nichole Halsey is the Director of Product Management for Sea-Bird Scientific. She's been involved in water quality monitoring, monitoring network design, and instrumentation design for the past eight years. She works closely with Sea-Bird customers including the USGS, US EPA, state and county environmental monitoring agencies and academic research institutions to improve their monitoring programs and develop better monitoring tools and instrumentation.

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