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Corey Koch, Senior Scientist/ Product Manager, Sea-Bird Coastal

Figure 1. Adam Dutton, Field Application Specialist, Sea-Bird Coastal

Introduction:

The Cycle-PO4 (Figure 1) is an in situ dissolved phosphate analyzer with technology by WET Labs that was designed for unattended long term operation. The goal was a robust and simple to use instrument that did not require an analytical chemistry background. The instrument now has a track record of field deployments ranging from coastal moorings to flashy freshwater streams. This article presents notable results from existing users of the Cycle-PO4 demonstrating various applications in which the instrument can be used.

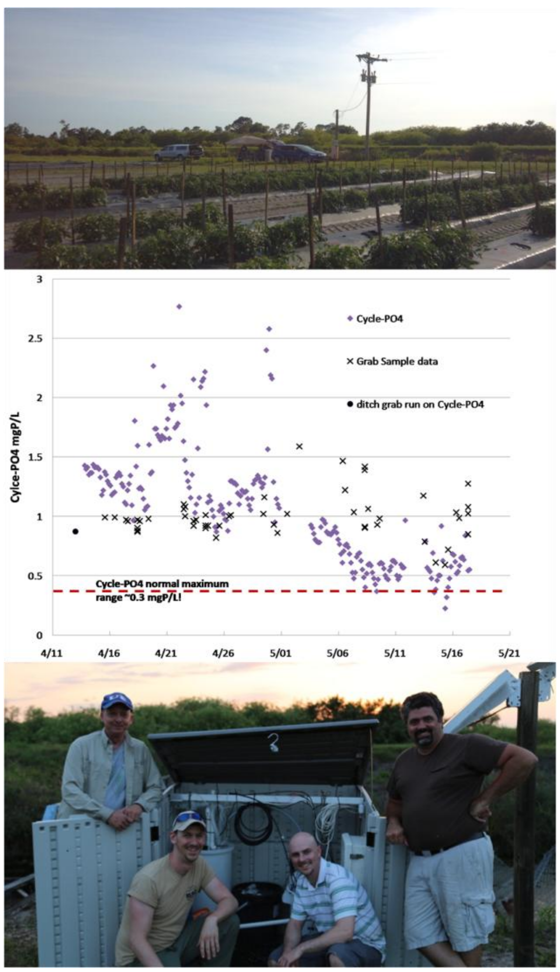
The Cycle-PO4 combines microfluidics with state-of-the-art optics to provide unmatched precision (50 nM) and accuracy (<150 nM). The Cycle-PO4 eliminates the uncertainties and time lags of sample handling, storage and transportation. When combined with a telemetry system, the Cycle-PO4 allows you to look at near real time data at your desk. The QA/QC processing of the Cycle-PO4 data includes an on-board NIST standard that provides feedback on the quality of the analysis throughout the deployment period. All together, the features of the Cycle-PO4 make it possible to report on phosphate concentrations at bihourly frequency permitting more detailed insights into nutrient dynamics.

The Cycle-PO4 system is designed to be both easy to use and cost effective. Maintenance is simple and can be completed using the spare parts kit and filters included in the reagent cartridge refills supplied by Sea-Bird Coastal. The typical cost per sample is less than $1, much less than you can do in your own laboratory, let alone an outsourced measurement. The low cost per sample means that you have the ability to capture phosphate dynamics hourly, with continuous seasonal coverage. Early users of the Cycle-PO4 are using this capability to derive new insights into biogeochemical processes.

Applications:

Cycle-PO4 used in study to highlight use of in-situ nutrient sensors to make new discoveries on critical estuarine transition zone:

Melissa Gilbert and Dr. Joseph Needoba conducted a study in the Columbia River system. This study demonstrated that suites of in situ nutrient sensors are a much “less-resource intensive” way to test hypotheses about critical nutrient transition zones than grab samples or transects (Gilbert et al. 2013). High-resolution time series data from Cycle-PO4 and other sensors at a site in the river and a site in the estuary revealed net nutrient transformations within a short residence time estuary. This method of using high-resolution and long-term moored nutrient sensors helped the authors elaborate on a previous hypothesis that the Columbia River Estuary had little effect on biogeochemistry, but rather was “….acting as a ‘capacitor’ for organic material.”



With some R&D modifications, Cycle-PO4 is making its way into agriculture:

Cycle-PO4 recently learned how to work in a drainage ditch. WET Labs scientist Dr. Corey Koch worked with Satlantic and Locher Environmental to test Cycle-PO4 at a University of Florida (UF) experimental farm. Dr. Kelly Morgan at UF and the FL Department of Environmental Protection (DEP) are using the farm to learn more about run-off and best practices. Sea-Bird Coastal’s optical nitrate sensor, SUNA, was used in tandem with Cycle to identify both phosphorus and nitrogen loading (http://sea-birdcoastal.com/suna). This was the first time our scientist and field application specialist had the opportunity to work in the field with the Cycle-PO4 in an actual field! This application is not what the Cycle-PO4 was originally designed for, but the instrument and deployment team rose to the challenge. The instrument was deployed in the drainage ditch on the edge of the farm field. The ditch normally has water in it, but it can go dry. Complicating performance issues are high sediment loads, lots of potential for bubbles that ruin optical measurements, temperatures near Cycle-PO4’s limit (35°C), and phosphate levels that are over 5 times the top-end range (0.3 mgP/L top-end vs. ditch levels near 1.3-4 mgP/L). To overcome the challenges we developed a system that reports the water level and pre-filters the sample water. The system consisted of two tanks to facilitate settling of large particles and de-bubbling.

Figure 2. The experimental farm, validation data at extremely high levels, and the Agriculture sampling system. Kevin Locher and Mike Vega of Locher Environmental consulting (standing) identified the opportunity and helped us with the Campbell data logger integration and building the system. Adam Dutton (Seabird Scientific deployment specialist) and Corey Koch are kneeling. Chemistry in the field: The right bottle blue color is Cycle's max. The left shows how dark the ditch can get. We had to make Cycle dilute!

The result was a sample stream Cycle-PO4 could make accurate measurements on (Figure 4). This system will also work with groundwater monitoring wells and other high sediment and bubble laden flows. By reconfiguring Cycle-PO4, we were able to achieve a 10x internal dilution of the ditch sample, bringing phosphate levels in range for Cycle-PO4. Our UF collaborator, Dr. Kelly Morgan, took grab samples which verified Cycle-PO4 performed extremely well. We hope this capability can help farmers develop best practices to reduce phosphate fertilizer loads to the environment and also help Florida's DEP determine phosphate flux and sources.

Elucidation of ecosystem metabolism:

Dr. Matt Cohen and Dr. Ray Thomas of the University of Florida have been using the Cycle-PO4 for 5 years and have been very successful in demonstrating the instrument's utility in understanding biogeochemical cycles and ecosystem dynamics. Cohen uses the instrument's ability to resolve small gradients and short term variability allowed determination of nutrient uptake ratios which revealed insights about cellular growth mechanisms. A recent publication by Cohen and his co-authors (Cohen et al. 2013, available at the Ecological Society of America's website) focuses on teasing apart the biologically mediated uptake kinetics of soluble reactive phosphorus (SRP) in a Florida spring-fed river. The paper demonstrates that a high-resolution time series of nutrient and associated chemical measurements can bring a unique understanding to the coupling of hydrological, geochemical, and biological processes.

Cohen and co-authors measured the diel cycle in the concentration of SRP with hourly measurements. The net photosysnthesis related uptake of SRP was distinguished from co-precipitation of calcite by resolving the calcium ion concentration related to the measured specific conductance. After accounting for the co-precipitation fraction, the maximum uptake of SRP lags maximum primary production by eight hours. This contrasts strongly with nitrate uptake (measured with Sea-Bird Coastal's SUNA, UV nitrate sensor) which was positively correlated to productivity and negatively to dissolved oxygen. This consistent differential timing in nutrient assimilation suggests that there is differential timing in protein and ribosome production. Cohen, reflecting on the contribution of the Cycle-PO4 to his understanding of ecosystem dynamics remarked that ***"the correspondence between discrete samples and in situ measurements is really strong, but we find that the Cycle-PO4 is able to resolve diel dynamics with a precision that our lab measurements of hourly discrete samples cannot match."***

Using two Cycle-PO4s to study stream phosphate dynamics:

In 2011, Dr. Brian Haggard and Leslie Massey from the University of Arkansas deployed two Cycle-PO4s in an urban stream to investigate phosphorus dynamics (Figure 2). The object of the study was to test the Cycle-PO4's ability to measure small gradients in phosphate concentration associated with uptake processes.

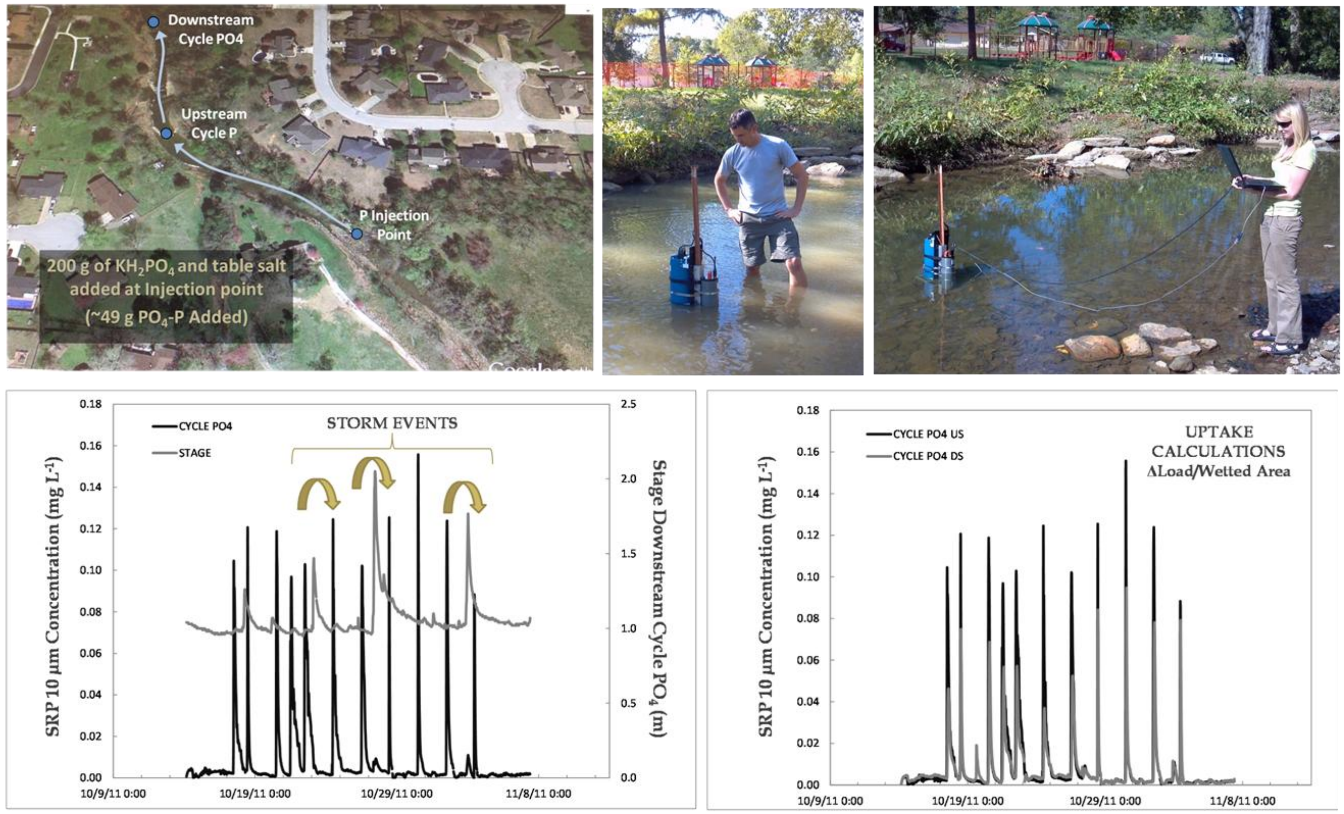


Figure 3. Cycle-PO4 in stream reach uptake study. Study map and description. Photo of the Cycle-PO4 deployed in a shallow urban stream. Bottom left: Cycle-PO4 response to system storm events. Bottom right: Comparison of upstream (US) and downstream (DS) Cycle-PO4 sensor data.

Two Cycle-PO4s were deployed 90 meters apart, defining the reach under study. Loads of phosphate salt (~49g PO4-P) and table salt (used as a tracer) were added 190 meters upstream of the reach. Leaf packs were installed between the two Cycle-PO4s to investigate the role of seasonal leaf litter on phosphate uptake rates. The change in load through the reach was determined by calculating the difference between the phosphate concentrations measured at the upstream and downstream instruments. Rain events, stream restoration activities and the leaf packs modulated the peak concentrations and the rate of change after the pulses moved through. The data demonstrated that rain events mobilize phosphate, changing the peak concentration, and that leaf-packs buffer phosphate, modulating the rate of decrease of the phosphate loading. The stability of the sensors and high accuracy sensor-to-sensor inter-comparability permitted the investigators to draw conclusions from the small gradients that were observed in this experiment. Cycle-PO4 sensors were validated with grab samples. For more complete discussion of the experiment, links to Haggard's and Massey's presentations are available on our website.

Cycle-PO4 observes first-ever wildfire phosphate pulses and the diel scale biogeochemical response:

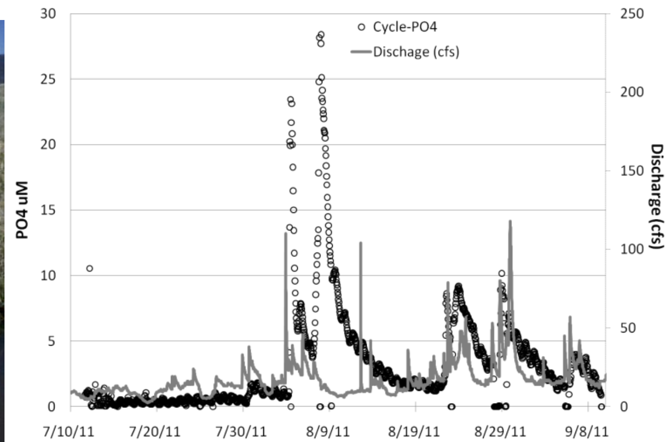


Figure 4. Photo showing Dr. Corey Koch helping to deploy the Cycle-PO4 in the Jemez. Relationship between two months of continuous data from a Cycle-PO4 and Jemez river discharge (USGS Gage 08324000, downstream; cubic feet per second (CFS)).

In 2011, Dr. Dave Van Horn and Lauren Sherson of the University of New Mexico deployed a Cycle-PO4 in the Valles Caldera in New Mexico. While the Cycle-PO4 was recording the normal diel cycle in the streams' PO4 concentration (a daily range of ~0.02 mg P/L), the Las Conches Fire burned much of the catchment area of the stream (Figure 1). During the fire researchers were unable get to the site, but the Cycle-PO4 escaped damage and continued to monitor the stream. While the fire raged, intermittent rainfall led to flows over twice the average. The Cycle-PO4 data revealed that the flood water contained high phosphate levels, up to 0.9 mg P/L. These levels were over three times the Cycle-PO4's typical range! Remarkably, as the flows relaxed after the rainfall events, the Cycle-PO4 captured a diel signal superimposed on the decaying flood and fire related phosphate pulses. This demonstrates that the disturbance and high phosphate loading did not change either the basic biogeochemistry or the Cycle-PO4's ability to capture modulations on major signals.

Van Horn and Sherson think this is the first data set collected in situ of the effects of wildfires in mobilizing phosphate in a high desert watershed. The high resolution of the Cycle-PO4 data set in both time and phosphate concentration gave them a unique view into the mobilization dynamics and biogeochemical response of a stream during a wildfire event. They are currently writing up their discoveries for publication and using more Cycle-PO4s downstream in the Rio Grande to understand the impact of fire on a watershed scale.

Conclusion:

From agriculture to the coast, continuous monitoring of nutrients is increasingly being used to understand ecosystem dynamics at the time scales that capture daily processes, trends and events. The Cycle-PO4 instrument technology gives users a unique method to capture natural and human induced variability.

Find more information on the Sea-Bird Coastal Cycle P along with other Sea-Bird Coastal products and solutions at www.sea-birdcoastal.com/nutrient-sensors

References:

Matthew J. Cohen, Marie J. Kurz, James B. Heffernan, Jonathan B. Martin, Rachel L. Douglass, Chad R. Foster, and Ray G. Thomas 2013. Diel phosphorus variation and the stoichiometry of ecosystem metabolism in a large spring-fed river. *Ecological Monographs* 83:155–176. http://www.esajournals.org/doi/abs/10.1890/12-1497.1

Lauren R. Sherson. Nutrient dynamics in a headwater stream: use of continuous water quality sensors to examine seasonal, event, and diurnal processes in the East Fork Jemez River, NM. *University of New Mexico. Dept. of Earth and Planetary Sciences.* Link to Sherson thesis: http://repository.unm.edu/handle/1928/21005

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Gilbert M., Needoba J.A., Koch C., Barnard A., Baptista A. 2013. Nutrient Loading and Transformations in the Columbia River Estuary Determined by High Resolution In Situ Sensors. *Estuaries and Coasts.* Vol. 36, 4, pp 708-727. http://link.springer.com/article/10.1007%2Fs12237-013-9597-0

Link to Gilbert thesis: http://drl.ohsu.edu/cdm/ref/collection/etd/id/1043

USGS 08324000 Jemez River near Jemez, NM (data used for Jemez discharge)

Alliance for Coastal Technologies. 3rd party evaluation of sensors. http://www.act-us.info/Download/Evaluations/Nutrient/WETLabs/