

Laboratory Evaluation of the Sea-Bird Scientific HydroCycle-PO₄ Phosphate Sensor



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Cover. Photograph of the Sea-Bird Scientific HydroCycle-PO₄. (Photograph courtesy of Sea-Bird Scientific, used with permission.)

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By Teri T. Snazelle

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**U.S. Department of the Interior
U.S. Geological Survey**

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Conversion Factors and Abbreviations

Inch/Pound to SI

Multiply	By	To obtain
Length		
inch (in.)	25,400.0	micrometer or micron (μm)
inch (in.)	2.54	centimeter (cm)
foot (ft)	0.3048	meter
Volume		
gallon (gal)	3.785	liter (L)
Mass		
pound, avoirdupois (lb)	453,592.37	milligram (mg)
pound, avoirdupois (lb)	0.4536	kilogram (kg)

International System of Units to U.S. customary units

Multiply	By	To obtain
Volume		
liter (L)	33.81402	ounce, fluid (fl. oz)
liter (L)	2.113	pint (pt)
liter (L)	1.057	quart (qt)
liter (L)	0.2642	gallon (gal)

Temperature in degrees Celsius ($^{\circ}\text{C}$) may be converted to degrees Fahrenheit ($^{\circ}\text{F}$) as

$$^{\circ}\text{F} = (1.8 \times ^{\circ}\text{C}) + 32.$$

Temperature in degrees Fahrenheit ($^{\circ}\text{F}$) may be converted to degrees Celsius ($^{\circ}\text{C}$) as

$$^{\circ}\text{C} = (^{\circ}\text{F} - 32) / 1.8.$$

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L), micrograms per liter ($\mu\text{g/L}$), or micromoles per liter.

Multiply concentration in micromoles per liter of phosphate by 0.03097 to convert to milligrams per liter of phosphate as P.

Abbreviations

CaPO_4	constant concentration
CDOM	chromophoric (colored) dissolved organic matter
DIW	quality-assured deionized water with resistance greater than or equal to 18 megaohms ($\text{M}\Omega$)
EPA	U.S. Environmental Protection Agency
FTW	filtered tea water
HAB	harmful algal bloom
HIF	Hydrologic Instrumentation Facility (USGS)
mg/L as P	milligrams per liter as phosphorous (equivalent to parts per million)
mL	milliliter

Mo	molybdenum
$\mu\text{mol/L}$	micromoles per liter
NIST	National Institute for Standards and Technology
NWQL	National Water Quality Laboratory
P	phosphorus
PO_4	phosphate
QC	quality control
QSE	quinine sulfate equivalent
Sb	antimony
SD	standard deviation
SDI	serial digital interface
USGS	U.S. Geological Survey
VaPO_4	Variable-based concentration

Laboratory Evaluation of the Sea-Bird Scientific HydroCycle-PO₄ Phosphate Sensor

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Abstract

Sea-Bird Scientific's HydroCycle-PO₄ phosphate sensor is a single-analyte wet-chemistry sensor designed for in situ environmental monitoring. The unit was evaluated at the U.S. Geological Survey Hydrologic Instrumentation Facility to assess the accuracy of the sensor in solutions with known phosphorous concentration and to test the effects of chromophoric (colored) dissolved organic matter (CDOM) and natural water matrixes on sensor accuracy. Accuracy was tested with three standards: 0.110, 0.174, and 0.260 milligram per liter, as phosphorous (mg/L as P). The 0.110- and 0.260-mg/L standards were made from a dilution of a National Institute of Standards and Technology-traceable phosphate-phosphorous standard with Type I deionized water (DIW). Average measured phosphate concentrations of the tested standards (0.110, 0.174, and 0.260 mg/L as P) in DIW were 0.132, 0.181, and 0.310 mg/L as P, for differences of 20, 4, and 19 percent, respectively.

Measured phosphate concentration of a tested standard was biased by the addition of tea water filtered through a 0.45-micrometer pore size filter (filtered tea water [FTW]) simulating the effect of CDOM. An aliquot of the filtered tea solution was sent to a certified environmental laboratory, which reported a less than reporting level (<0.004 mg/L as P) phosphate concentration. True color of the FTW was measured at 380 platinum-cobalt units by using Standard Methods 8025. For this FTW test, the measured phosphate concentration for the clear 0.260 mg/L as P standard averaged 0.366 mg/L as P. This concentration increased to an average of 0.653 mg/L as P with the addition of 10 percent FTW, and to an average of 0.859 mg/L as P with the addition of 20 percent FTW. These test results indicate a positive bias of up to 40 percent of the concentrations of the measured phosphate concentrations when CDOM is present and indicate a proportional increase in an apparent concentration of phosphorus instrument response as CDOM concentration increases.

Introduction

Phosphate loading and its role in the acceleration of vegetative growth and eutrophication in water has been widely documented (Correll, 1998; Paerl and Otten, 2013). Excessive nutrient inputs such as nitrogen and phosphate can result in problematic water conditions, from anoxic water to harmful algal blooms (HABs) capable of releasing dangerous cyanotoxins into water sources (Jacobi Carbons, Inc., 2014). Phosphates are formed from naturally occurring and anthropogenic phosphorus and exist in three forms: organic phosphate, meta or polyphosphate, and reactive or orthophosphate. Organic phosphates are formed primarily by biological processes or by the breakdown of organic pesticides that contain phosphate. Polyphosphates are strong complexing agents for metal ions and are used in the treatment of boiler waters (Oram, 2014). Polyphosphates are unstable in the environment and will eventually become orthophosphates. Orthophosphates are the most stable form of phosphate and are in fertilizers and sewage. Low-level orthophosphate can be measured in environmental waters by using colorimetric analysis (U.S. Environmental Protection Agency [EPA], 1997).

The U.S. Geological Survey (USGS) Hydrologic Instrumentation Facility (HIF) evaluates the performance of instruments and equipment that are used to measure hydrologic data. Instrument and equipment evaluations are done primarily to determine if particular devices would be suitable for use by USGS personnel for hydrologic data collection. Evaluation reports document the results obtained with the instrument model and firmware used at the time of testing, and may or may not represent results obtained from software updates and instrument model improvements that occur after testing. Reports describing the instrument evaluation results are not indicative of an endorsement by the USGS of the tested instrument.

This report documents the laboratory evaluation of the Sea-Bird Scientific HydroCycle-PO₄ phosphate sensor (hereinafter, "HydroCycle"), and test procedures and results are described. The sensor was tested with the Sea-Bird Scientific Cycle Host software, version 1.08 (Sea-Bird Scientific, 2016a).

Description of the HydroCycle-PO₄

The HydroCycle phosphate sensor is a field-deployable wet-chemical sensor that was designed for continuous environmental monitoring of soluble orthophosphate (fig. 1). The sensor reports concentrations in units of either micromoles per liter or milligrams per liter of orthophosphate, as phosphorus. The sensor comes with a protective sleeve that can be removed for service, and protective “hats” designed to cover the sensor intakes during transport. The sensor uses a single copper screen mesh with 0.011-inch pores and 5–10-micron onboard filters to reduce sediment intake. Three color-coded reagent cartridges are used to dispense the chemicals needed for analysis. The HydroCycle measures soluble orthophosphate (also called reactive phosphorus) based upon EPA method 365.5 (EPA, 1997). The method produces a heteropoly molybdenum-blue complex with phosphate that can be detected colorimetrically. The HydroCycle has a red reagent cartridge containing an acidic molybdate-antimony solution, a yellow cartridge containing ascorbic acid, and a blue cartridge with a traceable phosphate standard of 5.3 micromoles per liter ($\mu\text{mol/L}$) (approximately 0.164 milligram per liter, as phosphorus [mg/L as P]) from the National Institute for Standards and Technology (NIST) (fig. 2). Personal protective gear, including gloves, is recommended when changing the reagent cartridges due to the acidity and toxicity of the reagents, and gloves and safety glasses are recommended when performing routine maintenance of the HydroCycle such as flushing of the system with concentrated bleach. The sensor has an RS-232 and serial digital interface at 1200-baud (SDI-12) communication protocols with a 19200-baud rate. Power is supplied through a six-pin cable for RS-232 communication and through an eight-pin cable for SDI-12 communication. The HydroCycle is designed to be deployed vertically, and it will not function properly if deployed in a horizontal orientation. The features and specifications of the HydroCycle are listed in table 1.



Figure 1. The Sea-Bird Scientific HydroCycle-PO₄. Photograph courtesy of Sea-Bird Scientific, used with permission.



Figure 2. The reagent cartridges on the HydroCycle. The blue cartridge contains the phosphate standard, the yellow cartridge contains the ascorbic reagent, and the red cartridge contains the acidic ammonium molybdate/antimony potassium tartrate reagent. Photograph courtesy of Sea-Bird Scientific, used with permission.

Table 1. Features and specifications of the Sea-Bird Scientific HydroCycle-PO₄ (Sea-Bird Scientific, 2016b).

[EPA, U.S. Environmental Protection Agency; m, meter; kg, kilogram; cm, centimeter; °C, degrees Celsius; mg/L as P, milligrams per liter as phosphorus; μM, micromoles; ASCII, American Standard Code for Information Interchange; SDI-12, Serial digital interface at 1200 baud; VDC, volts direct current; mA, milliamps; A, amps; nm, nanometer; ≥, greater than or equal to]

Feature	Specification
Method of operation	Wet chemistry based upon EPA method 365.5
Rated depth	200 m
Weight	7.6 kg (with reagents)
Height with handle	56 cm (22 inches)
Diameter	18 cm (7.1 inches)
Temperature operating range	0–35 °C
Range of detection	0–0.3 mg/L as P (0–10 μM)
Detection limit	0.0023 mg/L as P (0.075 μM)
Communication protocols	SDI-12 (1200-baud rate) and RS-232 (19200-baud rate)
Power requirements (RS-232 ASCII) (RS-232 or SDI-12)	10.5–18 VDC, 115 mA average, 3 A max 10.5–18 VDC, 125 mA average, 3 A max
Monitoring wavelength	870 nm
Pathlength	5 cm
Number of runs per reagent set	≥1,000
Reagent life	5 months from manufacture

Orthophosphate Analysis

Unlike nitrate-nitrite, native soluble phosphate does not absorb energy in the ultraviolet or visible wavelengths and therefore is not measurable through colorimetry or spectrophotometry without chemical manipulation. To get the soluble orthophosphate into a detectable form, it must be treated with some toxic chemicals. To detect low-level orthophosphate, the sample is treated with ammonium molybdate and antimony potassium tartrate to form an antimony-phospho-molybdate complex, which when reduced with ascorbic acid, forms an intensely blue-colored complex.

Antimony (Sb) and molybdenum (Mo) are toxic heavy metals that are regulated by the EPA. An average 1-month deployment with an hourly sampling rate and a matrix-spike frequency of every fourth sample would produce the volumes listed in table 2.

Table 2. Estimated waste production for a 1-month deployment with hourly sampling and a matrix spike every fourth sample.

[mL, milliliter; Sb, antimony; Mo, molybdenum]

Waste contributor	Volume of contributor	Total volume (liters)
Sampled water	720×30 mL	21.6
Matrix spikes	180×20 mL	3.6
Sb/Mo reagent	720×0.2 mL	0.14
Ascorbic acid	720×0.2 mL	0.14
Phosphate standard	180×0.2 mL	0.036
Total waste		25.52

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Although a month's deployment produces more than 25 L of waste, most of that is sample volume; less than 5 grams of Mo (0.195 mg/L) and less than 0.5 gram of Sb (19.5 mg/L) are actually produced. Waste was collected and disposed of properly to meet all applicable regulatory requirements, including those for acidity-alkalinity. Operation of the HydroCycle produces a strong acidic waste with an average pH of 1–2 pH units. Regulatory requirements vary from State to State; however, most dictate that the naturally occurring pH of receiving waters not be altered from an acceptable range, and they limit the effect of waste to 0.5 to 1 pH unit over a period of 24 hours (EPA, 1988).

HydroCycle-PO₄ Testing

To test the HydroCycle, it was connected to a computer with the Sea-Bird Scientific Cycle Host software installed. The Cycle Host software provides communication to the sensor by using assigned communication (com) ports and a default 19200-baud rate. Once connected to the sensor, the software allows the user to prime the sensor tubing with sample and (or) reagents, track the volume of remaining reagents, and monitor the status of the sensor. Sample batches are programmed by using the Cycle Host Deployment Wizard, which gives the user the option of different modes of operation: autonomous (stand-alone) operation, synchronous slave (SDI-12) operation, or host (computer-controlled) operation. The Deployment Wizard guides the user through the process of programming the HydroCycle for operation and allows the user to dictate the sampling rate or the number of samples to be analyzed, as well as the frequency of quality control (QC) matrix spikes. For the QC samples, the onboard phosphate internal standard is added during a batch run. The QC samples are optional, but they provide important matrix-spike information on potential interferences in the sample solution. After the steps in the Deployment Wizard are completed, the volumes of samples and reagents needed for the batch are calculated, and the amount of waste that will be produced during the run is estimated. This information is collected in a deployment report that can be saved and (or) printed.

Sea-Bird Scientific does not specify an accuracy range for the HydroCycle, but encourages its users to generate their own site-specific accuracy estimates through discrete sampling. In-house performance checks at Sea-Bird require the HydroCycle to measure the 0.164 mg/L as P onboard internal standard within –3 to 15 percent of the standard value. Testing of the HydroCycle at Sea-Bird found the accuracy to average –5 to 20 percent at the lower and upper ends of the operating range (C. Koch, Sea-Bird Scientific, written commun., 2017). For the evaluation, the test acceptance criterion was based upon these findings and was set at ±20 percent of the standard value.

The accuracy of the HydroCycle was tested at the HIF by using Type I 18.2-megohm (MΩ) ultrapure deionized water (DIW) and a NIST 50 mg/L as P ±0.5-percent certified phosphate-phosphorous standard. Phosphate concentration of the DIW was tested with the HydroCycle and ranged from 0.0 to 0.015 mg/L as P, with an average value of 0.010 mg/L as P. In addition to sensor accuracy, the HydroCycle was also tested for the effect of chromophoric (colored) dissolved organic matter (CDOM) on accuracy. Sensor accuracy was determined by percent difference between the measured and calculated orthophosphate concentration. Percent difference was determined by the following equation:

$$\text{Percent difference} = 100 \times \frac{\text{measured orthophosphate in } \frac{\text{mg}}{\text{L}} \text{ as P} - \text{calculated orthophosphate in } \frac{\text{mg}}{\text{L}} \text{ as P}}{\text{calculated orthophosphate} \left(\frac{\text{mg}}{\text{L}} \text{ as P} \right)} \quad (1)$$

Because difference was determined by subtracting the calculated value from the measured value, positive values indicated a high bias in the data, and negative values indicated a low bias in the data.

Test Procedures: Accuracy in Standard Dilutions with Deionized Water

To evaluate the accuracy of the HydroCycle, testing was conducted at room temperature in three standards of known concentration, 0.110 mg/L as P, 0.174 mg/L as P, and 0.260 mg/L as P. The three standards were formulated by diluting the 50 mg/L as P NIST-certified standard with the laboratory Type I DIW. These values were calculated from the 0.010 mg/L as P measured phosphate concentration of the laboratory's Type I DIW added to the calculated concentration of the working standard (American Society for Testing and Materials International, 1999). The two working standards (0.110 mg/L as P and 0.260 mg/L as P) were made and used the day of testing and were discarded after testing. To create the 0.110 mg/L as P working standard,

2 milliliters (mL) of the 50 mg/L as P phosphate standard was added to a 1-liter (L) class A volumetric flask and filled to the 1-L mark with Type I DIW. For 1 L of the 0.260 mg/L as P working standard, 5 mL of the 50 mg/L as P phosphate standard was added to a 1-L class A volumetric flask and filled to the 1-L mark with Type I DIW.

Standard uncertainty was estimated to be 1.42 percent and was derived from normal distribution of the root-sum method of the Guide for Estimation of Measurement Uncertainty (American Association for Laboratory Accreditation, 2014). Standard uncertainty was calculated by using the random uncertainties listed in table 3.

Table 3. Calculation of standard uncertainty for phosphate working standards 0.110 mg/L as P and 0.260 mg/L as P.

[NIST, National Institute of Standards and Technology; mg/L as P, milligrams per liter as phosphorus; %, percent; SD, standard deviation; L, liter]

Random uncertainty	Uncertainty contribution (percent)	Squared uncertainty (percent)
Precision of five sample runs (SD)	0.033	0.0011
Accuracy of NIST 50 mg/L as P phosphate standard	0.5	0.25
Dilution errors including Type A 1-L glassware, technical measurement, and rounding error	0.50	0.25
	Sum of uncertainties	0.501
	Square root of sum	0.708
	95% confidence (2SD)	1.42

The third working standard (0.174 mg/L as P) was made by using the onboard internal standard from one of the HydroCycle's reagent cartridges. This internal standard was documented to be 5.3 micromolars (μM) or 0.164 mg/L as P ± 8 percent and was supplied for QC purposes by the manufacturer (Sea-Bird Scientific, 2016b). To create the 0.174 mg/L as P calculated standard, the HydroCycle was plumbed to sample Type I DIW provided by the laboratory system and was programmed to add the internal standard by using the Deployment Wizard. Summing the phosphate concentrations of the DIW and the internal standard gave an approximate concentration of 0.174 mg/L as P. Standard uncertainty for this standard was estimated at 8 percent, from the 8-percent uncertainty of the internal standard.

Testing of the HydroCycle consisted of separate batches or "runs" of a minimum of five samples each. The HydroCycle software reports two concentrations for each measured sample. The CaPO₄, or "constant concentration," is based upon the factory calibration for the sensor and is the value that should be reported (Sea-Bird Scientific, 2016b). The "variable-based concentration" (VaPO₄) value is given as an indicator of data quality or sensor health. The VaPO₄ uses the standard addition or matrix-spike concentration to calculate net phosphate concentration. Under ideal conditions, the CaPO₄ and the VaPO₄ values will differ no more than 0.005 mg/L as P. Sensor testing was conducted from November 2016 to February 2017 by the technical staff of the HIF's Water Quality Servicing Laboratory, and all results are based upon the CaPO₄ concentration of the solutions.

Test Results: Accuracy in Standard Dilutions with Deionized Water

The mean measured phosphate in the 0.110 mg/L as P standard analyzed in the laboratory at room temperature (22–25 degrees Celsius [$^{\circ}\text{C}$]) was 0.134 mg/L as P for the first batch of five samples and 0.130 mg/L as P for the second batch of five samples, resulting in calculated percent differences of 21.8 and 18.2, respectively. The measured phosphate for the 0.174 mg/L as P standard averaged 0.182 mg/L as P in the first batch of samples and 0.180 mg/L as P in the second batch, with differences of 4.5 and 3.6 percent, respectively. Measured phosphate in the 0.260 mg/L as P standard averaged 0.308 mg/L as P in the first batch of samples and 0.287 mg/L as P in the second batch of samples. Calculated differences in this standard were 18.3 and 10.5 percent, respectively (fig. 3).

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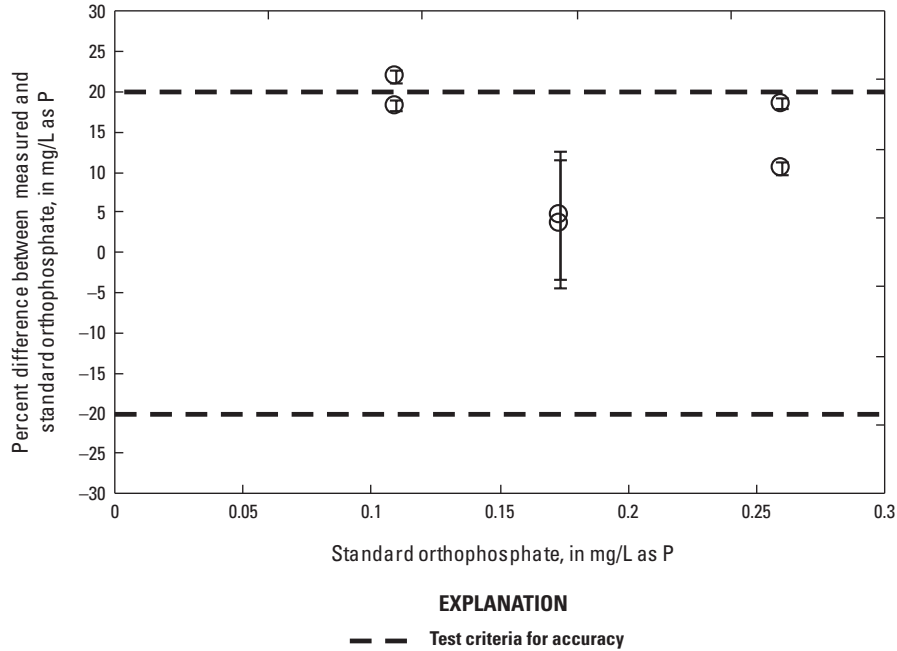


Figure 3. Results from room temperature testing of HydroCycle in three Type I deionized water-phosphate standard dilutions, 0.110, 0.174, and 0.260 milligram per liter, as phosphorus (mg/L as P). Error bars represent the 1.42 percent standard uncertainty for the 0.110 and 0.260 mg/L as phosphorous standards and the 8-percent uncertainty of the 0.174 mg/L as phosphorous standard.

Test Procedures: Accuracy in Tap and River Water

The accuracy of the HydroCycle was also tested in local tap water and in riverine water from two USGS streamgaging sites. For the tap water test, approximately 3 gallons of tap water were collected in a 5-gallon (gal) bucket. The HydroCycle was placed into the bucket to elevate the intake screen roughly 2 inches from the bottom of the bucket. The HydroCycle was primed following the manufacturer’s instructions and programmed to analyze the tap water by using the Deployment Wizard function of the Cycle Host software. Nine replicates of the tap water were analyzed, and the measured phosphate concentrations were averaged. An aliquot of tap water was not sent to the USGS National Water Quality Laboratory for analysis, but phosphate concentration was reported as less than the detection limit (<0.004 mg/L as P) in locally monitored Consumer Confidence Reports (EPA, 2017).

On February 1, 2017, approximately 3 gal of water from USGS site 02492620, Pearl River at National Space Technology Laboratory (NSTL) Station, MS, were collected in a 5-gal bucket. The HydroCycle was primed by following the manufacturer’s recommendations, placed into the bucket containing the water sample, and secured to ensure proper sample flow. The HydroCycle was programmed to analyze the sample with five replicates. Water was also collected on February 1, 2017, from USGS site 02481510, Wolf River near Landon, MS, and the process was repeated. Aliquots of the river samples were filtered with Pall 0.45-micron filters, collected into labeled 10-mL vacuum tubes, chilled, and sent to the USGS National Water Quality Laboratory (NWQL) for analysis by code 3118, Orthophosphate as P, by colorimetry. The detection limit of laboratory code 3118 is 0.004 mg/L as P. Phosphate concentrations analyzed by the NWQL for both USGS sites were compared to the HydroCycle’s averaged measured phosphate concentration to determine accuracy. Accuracy of the measured concentration was determined by percent difference from the NWQL analysis, which was calculated as

$$\text{Percent difference} = 100 \times \frac{\text{measured orthophosphate in } \frac{\text{mg}}{\text{L}} \text{ as P} - \text{NWQL orthophosphate in } \frac{\text{mg}}{\text{L}} \text{ as P}}{\text{NWQL orthophosphate} \left(\frac{\text{mg}}{\text{L}} \text{ as P} \right)} \quad (2)$$

Test Results: Accuracy in Tap and River Water

Results from testing of the HydroCycle in the tap water and from the unfiltered river samples from the two USGS sites are listed in table 4. Also listed are the results from the NWQL by code 3118 on the filtered aliquots of the water collected from the two sites.

Table 4. Phosphate concentrations in tap water measured by using Sea-Bird Scientific's HydroCycle-PO₄ phosphate sensor and in samples from two USGS surface-water sites.

[mg/L as P, milligrams per liter as phosphorous; NWQL, National Water Quality Laboratory; n/a, not applicable; USGS, U.S. Geological Survey]

	Phosphate measured by HydroCycle, in mg/L as P	Phosphate measured by NWQL (code 3118), in mg/L as P
Unfiltered tap water	0.078	n/a
Unfiltered water from USGS site 02492620	0.684	≤0.004
Unfiltered water from USGS site 02481510	0.594	≤0.004

¹ The method detection limit for the NWQL code 3118 is 0.004 mg/L as P.

Test Procedures: Accuracy in Environmental Samples

The Pearl River at USGS site 02492620 and the Wolf River at USGS site 02481510 are both relatively clear with low turbidity, but they are subjected to increases in sediment during times of heavy precipitation. CDOM is not measured routinely at the Wolf River site, so historical hydrologic data for this parameter were not available. CDOM is measured routinely at site 02492620 on the Pearl River and is reported in micrograms per liter of quinine sulfate equivalents. CDOM at the Pearl River site fluctuated between 80 and 85 micrograms per liter of quinine sulfate equivalents ($\mu\text{g/L}$ QSE) during the week the water samples were collected (week of February 1, 2017); however, CDOM concentrations routinely exceed 125 $\mu\text{g/L}$ QSE at this site (USGS, 2017). To isolate the source of the bias from the previous river water tests, a fresh sample was collected from the Pearl River on February 6, 2017. The water sample was thoroughly mixed, and an aliquot was filtered with a Pall 0.45-micron filter to remove particulates. The HydroCycle was submerged into the remaining unfiltered part of the water sample, and the HydroCycle was primed and programmed to analyze a batch of five samples. After analysis of the batch of unfiltered river water, the HydroCycle was primed with the filtered river water and programmed to analyze a batch of five samples along with two QC samples, for a total of seven samples.

Test Results: Accuracy in Environmental Samples

The concentrations of phosphate from the analysis of the unfiltered river water collected on February 6, 2017, closely matched the concentration of phosphate from the sample collected on February 1, 2017. The average of the measured phosphate concentrations in samples collected on February 1 was 0.684 mg/L as P, and the average of measured phosphate in samples collected on February 6 was 0.678 mg/L as P. Standard deviation (SD) for the batch was 0.021 mg/L as P. After filtration, the amount of measured phosphate was notably reduced and averaged 0.022 mg/L as P in the filtered river water. SD for this batch was 0.002 mg/L as P, indicating good precision in the test results.

Test Procedures: CDOM Effect on Accuracy

To test the effect of CDOM on the HydroCycle, a filtered tea water (FTW) solution was made by adding one family-sized cold-brew tea bag to 1 L of Type 1 DIW (fig. 4). After allowing the tea to steep for approximately 20 minutes, the tea bag was removed, and the solution was filtered with a Pall 0.45-micron filter to remove particulates. Although the tea solution was used to replicate the effect of CDOM on measurement accuracy, naturally occurring organic matter in environmental waters is much more complex and could produce a different response.



Figure 4. The tea solution used to test the effect of chromophoric (colored) dissolved organic matter on the HydroCycle's accuracy.

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An aliquot of the filtered tea solution was sent to the NWQL for analysis by code 3118 to confirm negligible (<0.004 mg/L as P) phosphate levels. A fresh 0.260 mg/L as P standard was made by diluting the 50 mg/L as P phosphate-phosphorus standard (to 0.250 mg/L as P) from Ricca Chemical with Type I DIW (with a measured 0.01 mg/L as P phosphate). The HydroCycle was primed with the 0.260 mg/L as P standard. By using the Deployment Wizard option of the Cycle Host software, the sensor was programmed to analyze five replicates, and the mean and percent difference were calculated for the batch.

For the next test, approximately 100 mL of the FTW was added to 1 L of the 0.260 mg/L as P standard, producing an approximate 10-percent “CDOM” solution. Turbidity of this CDOM solution was analyzed by using a Hach 2100N turbidimeter and averaged 1.3 formazin nephelometric units during testing. True color of the FTW was measured at 380 platinum-cobalt units by using Standard Methods 8025. The HydroCycle was primed with the 10-percent CDOM solution and was programmed to analyze five replicates. For the next test, approximately 200 mL of the FTW was added to 1 L of the 0.260 mg/L as P standard, producing an approximate 20-percent CDOM solution, and the process was repeated. For each batch, the mean and percent difference were calculated. To eliminate the possibility of falsely elevated results due to “carry-over” or fouling of the sensor’s tubing by the intensely blue color of the tested samples, the original (DIW) 0.260 mg/L as P standard was re-analyzed immediately after the 20-percent CDOM test, and mean phosphate and percent difference were calculated.

Test Results: CDOM Effect on Accuracy

The first test of the clear DIW 0.260 mg/L as P standard resulted in an average phosphate concentration of 0.366 mg/L as P, resulting in an approximate 41-percent difference or increase. The second test that contained approximately 10 percent FTW added to the 0.260 mg/L as P standard (10 percent CDOM) resulted in an average phosphate concentration of 0.653 mg/L as P. This difference was an approximate increase of 78 percent from the 0.366 mg/L as P measured concentration of the DIW standard and an increase of 151 percent from the clear DIW 0.260 mg/L as P standard value.

Testing of the 0.260 mg/L as P standard with approximately 20 percent FTW (20 percent CDOM) added to the standard resulted in an even higher concentration of measured phosphate. For this test, the mean measured phosphate concentration was 0.858 mg/L as P, resulting in a 134-percent increase from the average measured concentration of the clear DIW standard (0.366 mg/L as P) and a 230-percent increase from the 0.260 mg/L as P standard value. To verify that the increase was not a product of carryover or from staining of the HydroCycle’s optics, the original clear DIW 0.260 mg/L as P standard was re-analyzed immediately after the test with the 20 percent FTW/0.260 mg/L as P phosphate solution. Phosphate concentration from this test averaged 0.362 mg/L as P, or an approximate 39-percent difference from the 0.260 mg/L as P standard value (fig. 5). The strong correlation of the CDOM “bookend” testing of the clear DIW standard phosphate concentrations, 0.366 mg/L as P (41-percent difference) and 0.362 mg/L as P (39-percent difference), gives confidence that the test results are valid and also lends credence to the theory that the increases in concentration seen in the CDOM tests were due to the added color from the tea and not due to staining of the sensor optics or from carryover.

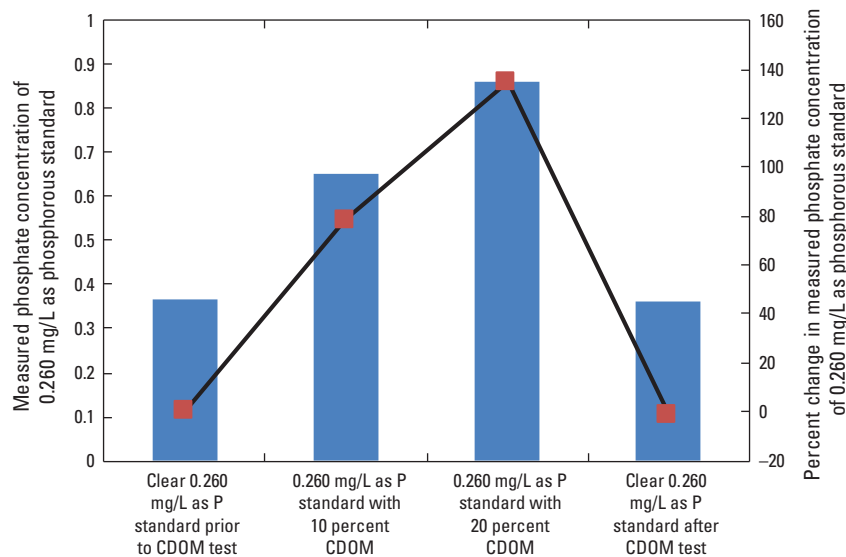


Figure 5. The measured concentration of a 0.260 milligram per liter as phosphorous (mg/L as P) phosphate standard, and the percentage of change in the HydroCycle’s measured phosphate concentration as chromophoric (colored) dissolved organic material (CDOM) increased.

Discussion

Measurement of orthophosphate by colorimetry is complex and operationally difficult because of the use of toxic chemicals and the need for proper hazardous waste disposal, burdensome maintenance requirements to ensure proper sampling, and the potential for cross contamination from prior samples containing higher concentrations. Turbid environmental conditions and the presence of matrix interferences, such as color or bubbles, also further complicate the in situ measurement of phosphate. The accuracy of the HydroCycle met the ± 20 -percent test criterion when evaluated with the 0.164 mg/L as P internal standard and Type I DIW. Accuracy in the first batch of 0.110 mg/L as P samples narrowly exceeded the criteria, with a difference from the standard value of 21.8 percent. Performance improved with the second batch of 0.110 mg/L as P samples, and the average measured concentration differed from the standard value by 18.2 percent. Accuracy in the 0.260 mg/L as P standard also met the test criteria and differed from the standard value by 18.3 percent in the first batch of samples and by 10.4 percent in the second batch.

The results from this testing indicate that the HydroCycle could be a viable tool for the measurement of active phosphate in an oceanographic or sediment- and color-free surface-water or groundwater setting when operated by an experienced and well-trained technician. Testing of unfiltered riverine samples revealed potential bias of accurate phosphate concentration. This bias was most likely caused by interference with the light transmittance of the HydroCycle from CDOM or by the release of “additional” reactive phosphate adhered to the suspended sediment in the riverine sample. Additional testing of DIW-phosphate standards spiked with aliquots of FTW to simulate CDOM confirmed the bias and showed that measured phosphate concentration increased proportionally with the increase in CDOM.

Conclusions

Testing of the HydroCycle phosphate sensor in three phosphate concentrations (0.110, 0.174, and 0.260 mg/L as P) showed it was accurate to within 22 percent with a measurable positive bias. The average measured phosphate concentration of the 0.110 mg/L as P batches was 0.132 mg/L as P for a difference of 20 percent. The average measured concentration of the 0.174 mg/L as P standard, using the onboard internal standard (0.164 mg/L as P) added to Type 1 DIW was 0.181 mg/L as P for the two batches of samples, or a difference of 4 percent. Testing of the 0.260 mg/L as P standard, which was approaching the 0.30 mg/L as P upper limit of the detection range, resulted in an average of 0.298 mg/L as P for the two batches, or a 14-percent difference from the standard concentration.

Measured phosphate concentration of a DIW-phosphate standard was biased by the addition of FTW simulating the effect of CDOM. Measured phosphate concentration in the clear 0.260 mg/L as P standard averaged 0.366 mg/L as P and increased to an average of 0.653 mg/L as P with the addition of 10 percent FTW and to an average of 0.859 mg/L as P with the addition of 20 percent FTW. These test results indicate bias of the measured phosphate concentrations to higher values when CDOM is present and seem to indicate a proportional effect when CDOM concentration increases.

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