



Continuous Phosphate Monitoring in Rivers and Streams and Its Correlation to Total P Loads.

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Introduction

Continuous monitoring of phosphorus loads in rivers and streams will be an important tool to assess whether or not state nutrient reduction plans are meeting their established goals. Continuous real time monitoring for phosphorus in rivers and streams is not practical because there is no sensor technology available. However, autonomous, microfluidics-based analyzers are one option for achieving continuous near real-time monitoring.

Objective

The goal is to use orthophosphate data from microfluidic analyzers combined with turbidity measurements to predict total P concentrations in rivers and streams.

Methodology

A Cycle-PO₄ analyzer (Fig 1), manufactured by Wetlabs (Seabird Coastal), was tested in three settings: 1) Indoor tank (Fig. 2A); 2) outdoor mesocosm (Fig. 2B), and 3) Lake Decatur on the Sangamon River (Fig. 2C). The indoor tanks and outdoor mesocosms used Mississippi River water, whereas Lake Decatur is a reservoir on the Sangamon River in Central Illinois, a tributary of the Illinois River.

In Lake Decatur, the Cycle PO₄ analyzer was installed on a water quality monitoring platform that is part of the National Great River Research & Education Center's (NGRREC) Great Rivers Ecological Observatory Network (GREONSM) (Fig. 2C). The phosphate analyzer was accompanied by a multiple parameter water quality sonde (YSI Exo2) that collected turbidity measurements, and a spectroscopic nitrate sensor (SUNA V2) (Fig. 3).

Orthophosphate concentrations measured by the Cycle-PO₄ were paired with grab samples collected at the same time adjacent to the Cycle-PO₄ analyzer. The grab samples were analyzed for total P in the laboratory by first digesting unfiltered samples using the acid persulfate procedure, followed by phosphate analysis using a discrete analyzer and the ascorbic acid / phosphomolybdate method.

Data Analysis

Turbidity measurement were converted to suspended sediment concentrations (SSC) using a predictive equation developed by the USGS based on extensive monitoring conducted at their Florence, Illinois station. The equation was:

$$SSC \text{ (mg/L)} = 0.881 * \text{Turbidity}_{FNU}^{1.122} \times 1.06 \quad (\text{Eq. 1})$$

Linear regression was used to predict Total P concentrations from the Cycle PO₄ orthophosphate measurements and the SSC values calculated from YSI turbidity measurements using Eq. 1.

Results

- **Table 1:** The range of turbidity levels achieved with the lab tank and mesocosm (2.6 to 74 mg/L) were narrower than the range observed by the USGS in the Illinois River (14 to 1,130 mg/L).
- **Fig. 4:** Orthophosphate measured at Lake Decatur with the Cycle PO₄ ranged from approximately 0.05 to 0.2 mg/L but there was not a strong relationship to Sangamon River discharge (Fig. 4A). Turbidity ranged from 8 to 40 mg/L, but was not strongly correlated to ortho-P measurements (Fig 4B).
- **Fig. 5:** When considered separately, Total P was more strongly correlated to Cycle-PO₄ readings ($R^2=0.2157^*$) than turbidity ($R^2=0.0703^{ns}$).
- **Fig. 6:** The NGRREC equation works fairly well at low SSC values below 100 mg/L, but it greatly over estimates Total P when extended to higher SSC values due to a larger SSC coefficient compared to the USGS Equation (**Fig. 7**).

Table 1. Natural and spiked turbidity levels achieved at each of the Cycle-PO₄ test locations (columns A, B, and C) compared to turbidity levels measured by the USGS in the Illinois River at Florence (D).

	(A) Lab Tank No Agitation No sediment	(B) Mesocosm + Agitation No sediment	(C) Mesocosm + Agitation + Sediments	(D) USGS Illinois River ¹
Turbidity Level				
Minimum	2.6	18	60	14
Median	2.9	20	67	41
Maximum	3.4	31	74	1,130

¹ USGS. 2015. Continuous Monitoring of Sediment and Nutrients in the Illinois River at Florence, Illinois, 2012–13. Science Investigations Report 2015-5040.

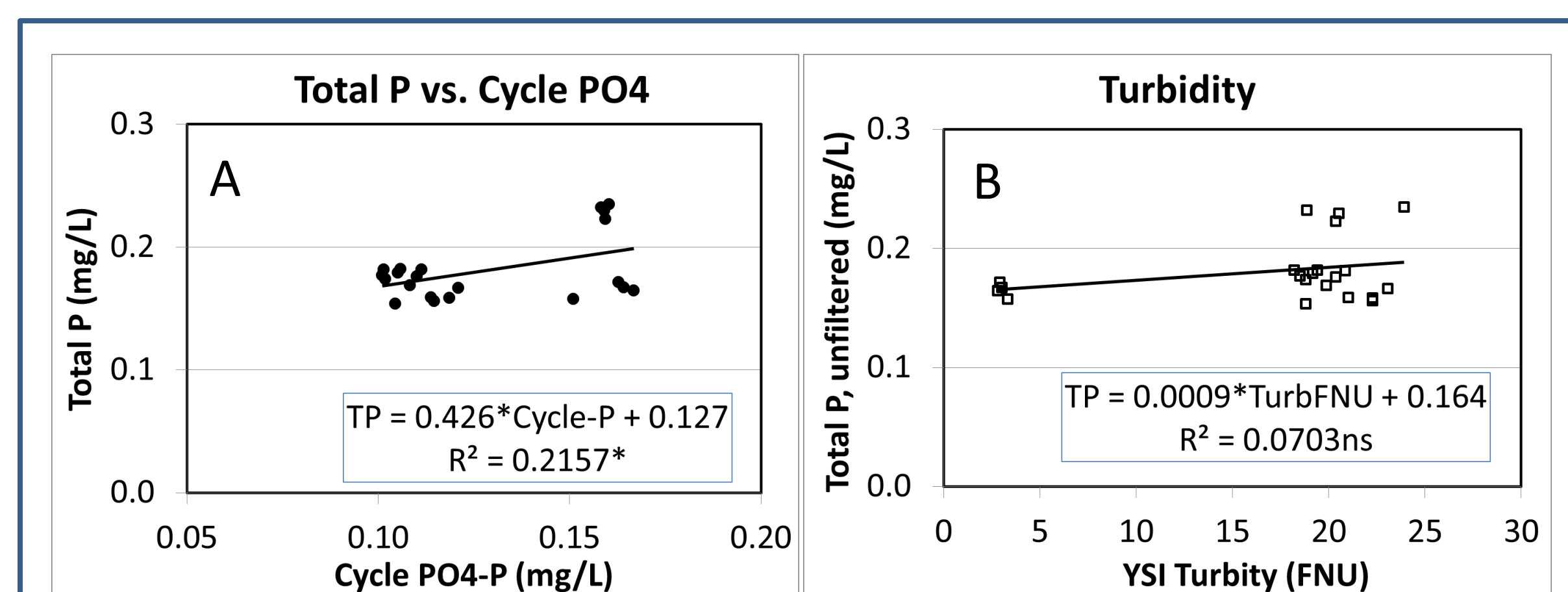


Fig. 5. Correlation between total P in unfiltered water samples and (A) orthophosphate measured by the Cycle PO₄, and (B) turbidity measured with a YSI sensor installed in their Exo2 sonde.

Fig. 7. Total P predictive equation from this study (Eq. 2) compared to the USGS equation (Eq. 1).

Total P Predictive Equation		
Total P = 0.0275 + 0.84*Ortho-P + 0.0201*SSC	R ² =0.635	(Eq. 2)
Total P = 0.0816 + 1.10*Ortho-P + 0.00063*SSC	R ² =0.802	(Eq. 3)

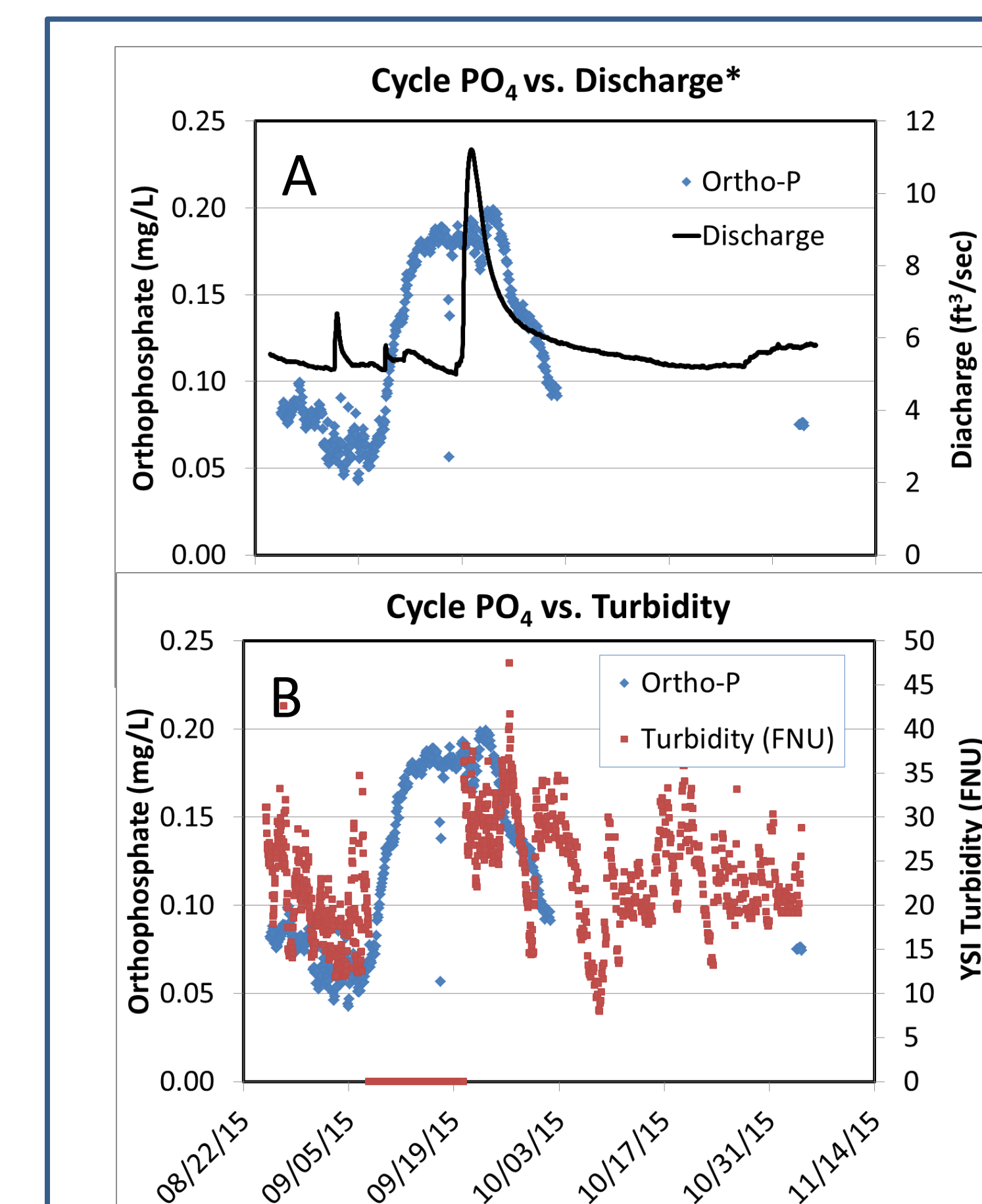


Fig. 4. Relationship between orthophosphate measured with the Cycle PO₄ and Sangamon River discharge (A) and turbidity (B).

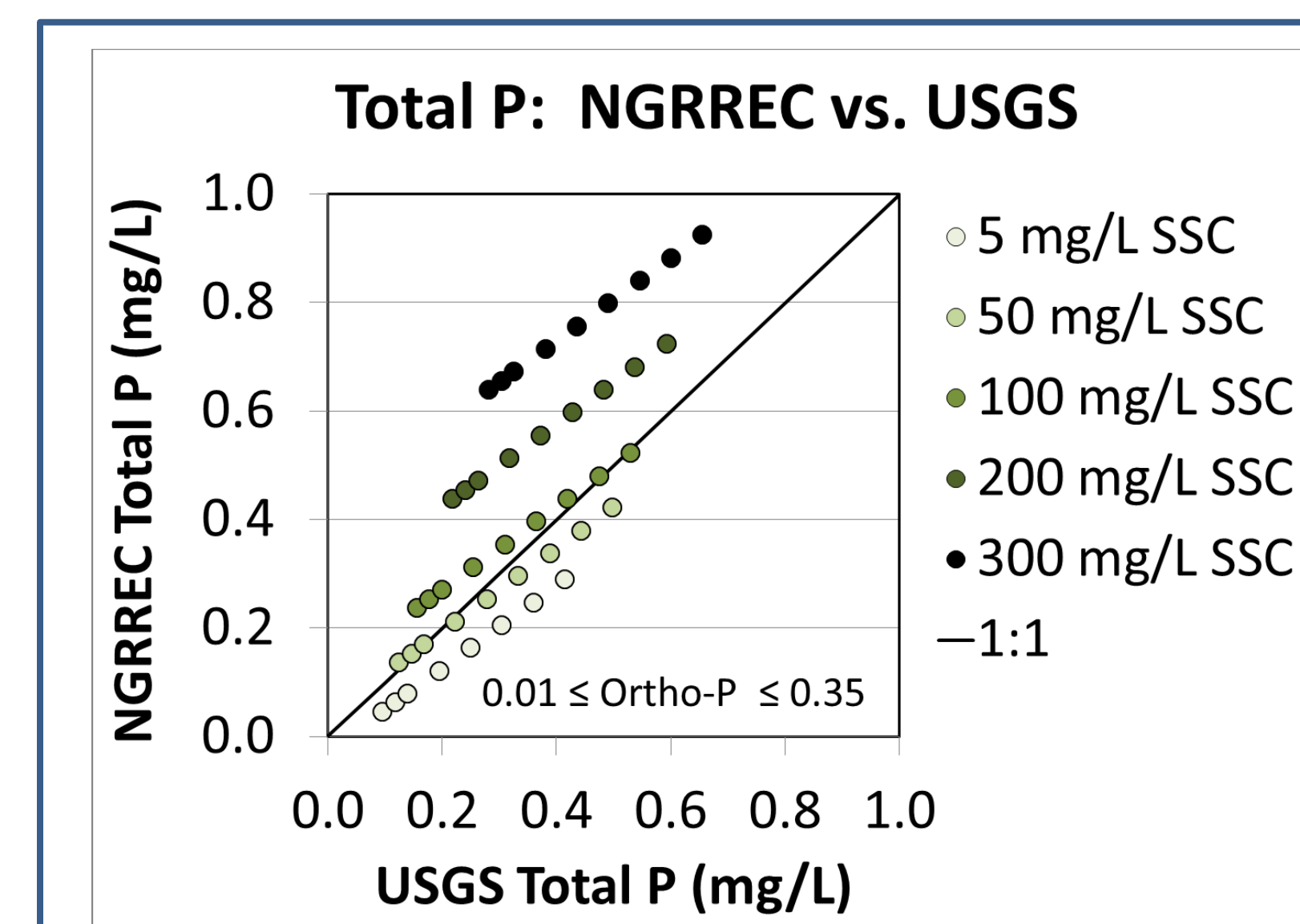


Fig. 6. Comparison of Total P predicted by the collective set of wet lab, mesocosm, and Lake Decatur samples (Eq. 2) compared to the USGS total P equation (Eq. 3).

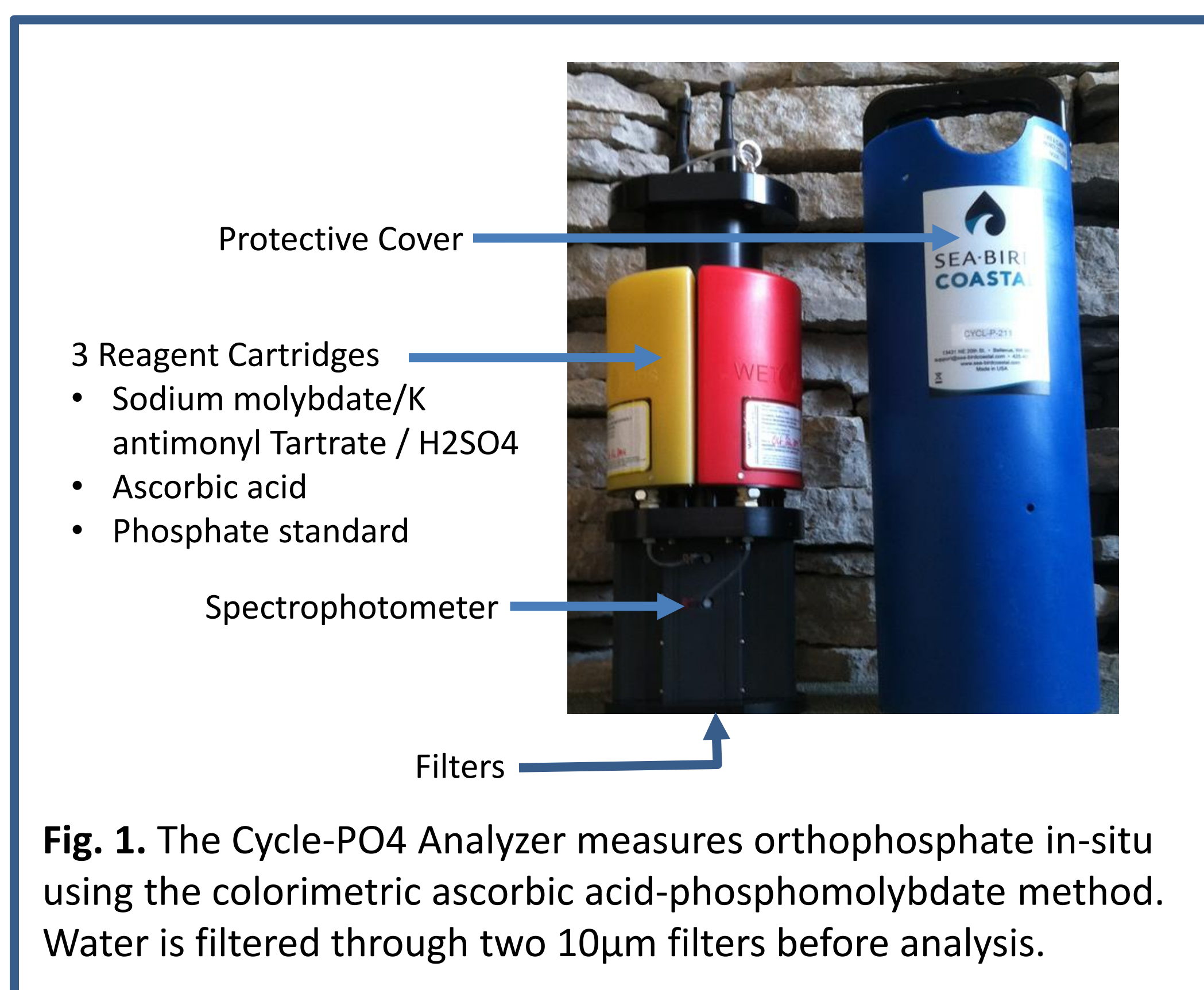


Fig. 1. The Cycle-PO₄ Analyzer measures orthophosphate in-situ using the colorimetric ascorbic acid-phosphomolybdate method. Water is filtered through two 10µm filters before analysis.

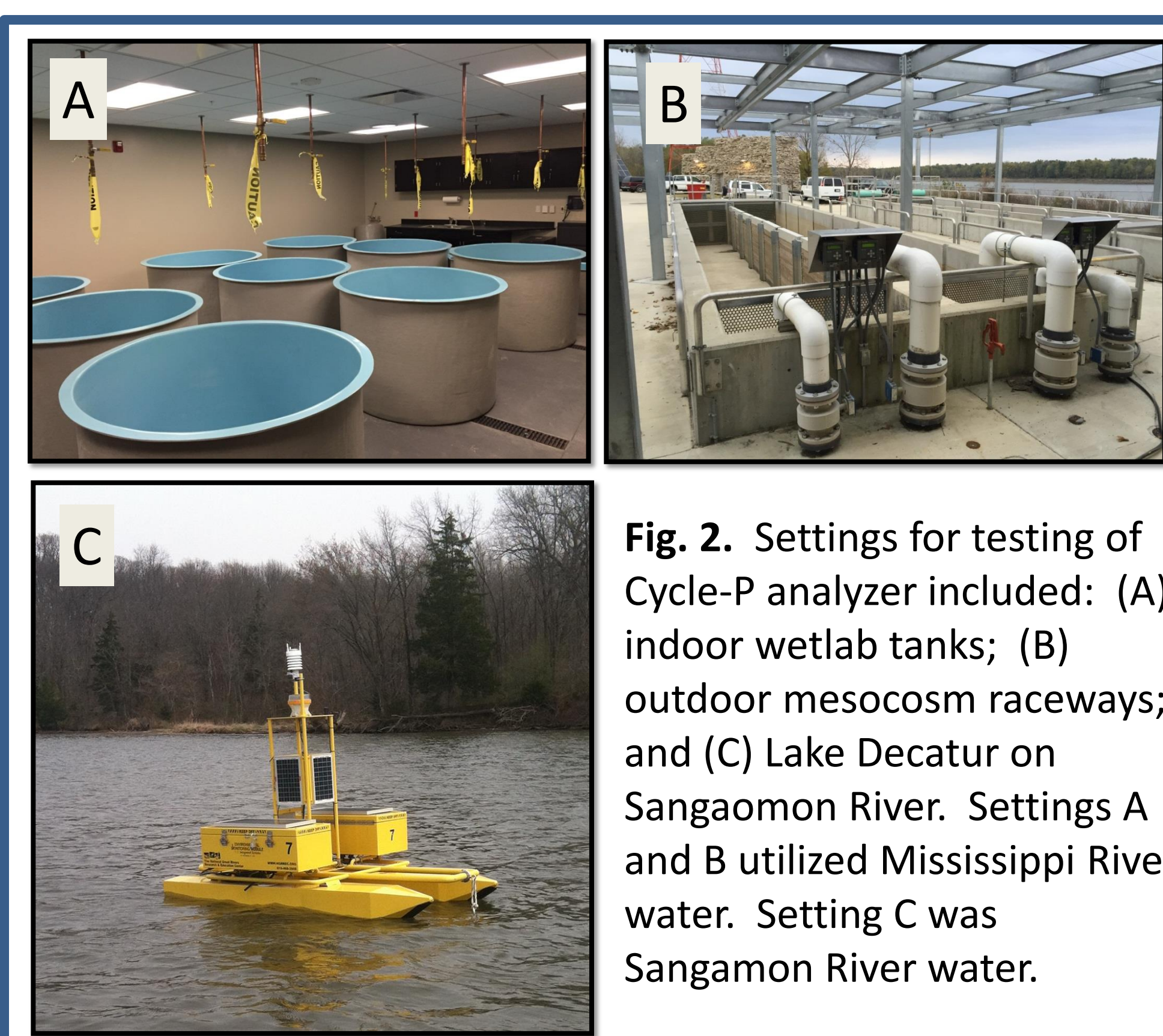


Fig. 2. Settings for testing of Cycle-P analyzer included: (A) indoor wetlab tanks; (B) outdoor mesocosm raceways; and (C) Lake Decatur on Sangamon River. Settings A and B utilized Mississippi River water. Setting C was Sangamon River water.



Fig. 3. Monitoring technology installed on the GREON water quality monitoring platform include a YSE Exo2 sonde (top) and a Satlantic SUNA nitrate sensor (bottom).

Conclusions

- It is possible to predict total P concentrations in surface water based on in-situ measurements of ortho-P and turbidity.
- Our predictive equation needs to be strengthened by sampling surface waters with a wider range of suspended sediments and dissolved ortho-P.
- Continuous, real-time measurements of total P and turbidity promise more accurate estimates of total P loads in rivers and streams.

Reference

USGS. 2015. Continuous Monitoring of Sediment and Nutrients in the Illinois River at Florence, Illinois, 2012–13. Science Investigations Report 2015-5040.