



In situ, high-resolution time series of dissolved phosphate in Green Bay, Lake Michigan



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ABSTRACT

In nearly every instance in which the environment has been sampled on a higher resolution in time or space, fundamental processes have come to light that were previously undetected or unobserved. In this study, an autonomous dissolved phosphate sensor was deployed at the Entrance Light station in lower Green Bay, Lake Michigan in 2012 and 2013. Hourly phosphate sensor measurements were compared with other real time sensor data to gain insights into the processes occurring at this site. Results showed that the water column at this location undergoes repeated stratification and turnover during the course of the summer. Often, the stratification results from intrusions of cold hypolimnetic bottom water from the north, while turnover is associated with significant northerly and/or easterly wind events. It was observed that, during calm periods, dissolved phosphate concentrations increased at a rate that was stoichiometrically consistent with the consumption of dissolved oxygen during the remineralization of organic matter; specifically, areal oxygen consumption rates ranged from 3.2 to 43 mmol m⁻² d⁻¹ and oxygen to phosphate ratios ranged from 120 to 210. At other times, the inverse relationship between dissolved oxygen and dissolved phosphate was not stoichiometrically linked; during these times, areal oxygen depletion rates ranged from 51 to 240 mmol m⁻² d⁻¹ and oxygen to phosphate ratios ranged from 260 to 2300. Future strategic deployment of multiple *in situ* dissolved phosphate and other nutrient sensors will enhance the understanding of nutrient cycling in this important aquatic system.

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Introduction

Green Bay, Lake Michigan is severely impacted by excessive nutrient inputs from its upstream watershed. It has been designated as an Area of Concern (AOC) by the International Joint Commission and has suffered from hypereutrophic conditions for decades. The vast majority of the nutrient and suspended solids (sediment) load enters Green Bay through the Fox River and its tributaries. In addition, the Fox River Basin is the largest contributor of phosphorus to Lake Michigan. The Lower Fox River Basin (a sub-basin of the Fox River) comprises only 10% of the whole basin area but contributes 43% of total phosphorus and 58% of total suspended solids (Cadmus Group, Inc., 2012). The bay of Green Bay, the Lower Fox River Basin, and most of its tributaries are classified as impaired waters, a condition that has persisted for a long time with little or no improvement. The hypereutrophic conditions in Green Bay have a number of associated problems, including: excessive algal growth, harmful algal blooms (HABs), decreased water clarity, and decreased submerged aquatic vegetation (Bartlett et al., in this

issue; Qualls et al., 2013). These conditions have led to decreases in dissolved oxygen concentrations when excessive organic matter decomposes, resulting in recurring seasonal (summer) hypoxic conditions (<2 mg/L dissolved oxygen), low benthic diversity and significant “fish-kill” events (Kaster et al., in this issue; Klump et al., in this issue).

Nutrient and suspended solids inputs are extremely dependent on large precipitation events. Nearly 70% of the annual direct watershed load to the Lower Fox River and Green Bay occurs within 14 days for phosphorus and within 7 days for sediment; in fact, approximately 40% of the annual phosphorus load occurs within only 4 days (Graczyk et al., 2012). Climate change projections predict a ~50% increase in these major events within the next century (Wisconsin Initiative on Climate Change Impacts, 2011). Infrequent manual sample collection, followed by analysis in a laboratory makes it difficult to adequately observe and quantify the effect of these major precipitation events on the overall system. The full impacts of many of these events are completely missed, obscuring their importance and hindering their management.

This external loading translates to rapid sediment accumulation rates in the bay, up to 1 cm per year; and, largely as a result of its geomorphology, the bay retains 70–90% of the total annual phosphorus

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input within the depositional zones of the bay (Klump et al., 1997; Klump et al., 2009). Given reductions in inputs, the Green Bay system should respond on a time scale driven in large part by the response time of the active sediment pool, and estimates of the recycled sedimentary phosphorus residence times are on the order of a few years (Klump et al., 1997). The geochemical residence time for phosphorus within the water column of the lower bay is consistent with a system that has a high rate of processing. It is estimated that the summer water column south of Chambers Island (CI in Fig. 1, with a volume of $1.3 \times 10^{10} \text{ m}^3$) contains between 600 and 700 MT of total phosphorus (particulate and dissolved). With an annual input (or loss) of ~800 MT, the residence time for phosphorus in the water column is <1 year. These inputs, however, are both episodic, event driven, and variable in composition. In addition, the form of nutrient loading plays an enormous role in how the bay responds and the extent of excessive algal production. While data on total phosphorus loads are available, little is known about the variability of inputs of bioavailable phosphorus (i.e. largely inorganic phosphate) on the time scales at which the algal community responds.

The objectives of this study were: 1) to evaluate the performance of an *in situ* dissolved phosphate sensor (Cycle-PO4, WET Labs, Philomath, OR) in a highly productive, nutrient enriched environment like Green Bay; and 2) to gain insight into phosphorus cycling that would otherwise be unobservable with relatively infrequent grab sampling strategies. These observations were conducted in Green Bay, Lake Michigan from June through October 2012 and 2013.

Experimental methods

Study site

In situ sensors reported in this study were deployed at a station in Lower Green Bay that was approximately 13 km (8 miles) from the mouth of the Fox River (coordinates: N 44.652 Lat., W 87.925 Long.), as shown in Fig. 1. It is located near the Green Bay Harbor Entrance Light lighthouse that is adjacent to the navigational shipping channel. The average water depth at this location was 7 m during the sampling period.

Dissolved phosphate

Dissolved phosphate was determined in this study using a WET Labs (Philomath, OR) Cycle-PO4 reagent-based phosphate sensor (Gilbert et al., 2013; Twardowski et al., 2015), which uses a wet chemistry colorimetric method that has been commonly used in the laboratory for decades (Murphy and Riley, 1962; EPA, 1997). With this method, soluble

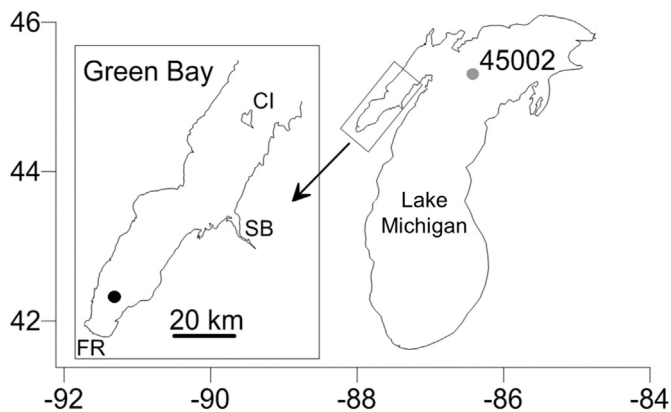


Fig. 1. Green Bay is located in northwestern Lake Michigan. Wind vectors were recorded at ND BC buoy 45002 (gray circle). A detail of Green Bay (inset) shows the study site (i.e., the “Entrance Light” station) at N 44.652 Lat., W 87.925 Long. (black circle). Geographic reference points include the Fox River (FR); Sturgeon Bay (SB); and Chambers Island (CI).

phosphate in the sample reacts with sodium molybdate, potassium antimonyl tartrate, sulfuric acid, and ascorbic acid to generate a phosphorus/molybdate complex (i.e., molybdenum blue) that has an absorbance maximum at approximately 880 nm. The Cycle-PO4 is a fully submersible sensor that uses on-board reagent cartridges and microfluidic technology to perform this wet chemical procedure *in situ*. The sensor has a manufacturer-specified nominal range of 0–10 μM phosphate (0–300 $\mu\text{g/L PO}_4^{3-}\text{-P}$) and a detection limit of 0.075 μM phosphate (2.3 $\mu\text{g/L PO}_4^{3-}\text{-P}$). It utilizes an on-board phosphate standard that can be used for data correction and/or for quality control purposes. Because the water sample is passed through 10 μm pore size frits, the phosphate concentrations generated by the Cycle-PO4 are most closely associated with the fraction called “soluble reactive phosphorus”, which is operationally defined as phosphorus that passes through a 0.45 μm membrane filter with no other pretreatment (hydrolysis, digestion, etc.) prior to analysis (Clesceri et al., 1998).

The Cycle-PO4 was field-deployed at the Entrance Light station described above (see Fig. 1) from June 27, 2012 (day of year, DOY, 179) through October 12, 2012 (DOY 286), and again from June 7, 2013 (DOY 158) through October 2, 2013 (DOY 275). The Cycle-PO4 was attached to a support structure that rested on the sediment surface during the deployments, and the water inlet was positioned approximately 25 cm above the sediment-water interface. Dissolved phosphate was determined once per hour, and the on-board phosphate standard was measured along with every sixth sample; however, it was not used to post-correct the data. Colorimetric reagents, the 10 μm frits, and the battery pack (BPA50, WET Labs, Philomath, OR) were replaced every four to six weeks as needed. While changing the reagents and battery pack, the Cycle-PO4 was flushed with a 2% solution of Micro-90 detergent (Sigma-Aldrich, St. Louis, MO) to clean the internal tubing and optical pathways. This was followed by a series of rinses with distilled water prior to redeployment.

During some time periods, it was necessary to correct the reported dissolved phosphate concentration due to the presence of bubbles in the optical pathway. Bubbles can have a negative effect on the pre-reagent flush reading, and/or the post-reagent sample reading of the instrument, and both values are used to calculate absorbance. While other more complicated correction methods were explored, the final correction involved averaging the hourly data over a period of 6 h. Corrections were applied during the following time periods: August 10, 2012 (DOY 223) through September 4, 2012 (DOY 248); July 26, 2013 (DOY 207) through August 14, 2013 (DOY 226); and August 28, 2013 (DOY 240) through October 2, 2013 (DOY 275). It is likely that the presence of bubbles was related to pore clogging of the inlet frits and a corresponding drop in pressure inside the instrumental sample tubing. Lower pressure would result in a decrease in solubility of dissolved gases, causing bubble formation in the internal pathways. Replacement of the 10 μm frits resulted in an immediate correction of this issue.

Grab samples

Bottom water grab samples, periodically collected by NEW Water (aka, the Green Bay Metropolitan Sewerage District) during sensor deployment, were used to assist in verifying the concentrations reported by the Cycle-PO4. During 2012, grab samples were collected by NEW Water from their routine monitoring station that was near the Entrance Light station (approximately 1.5 miles to the northeast), and in 2013, NEW Water added sample collection at the Entrance light station. Samples were analyzed within 48 h of collection at the certified laboratory of NEW Water in Green Bay, WI using a Lachat (Loveland, Colorado) QuikChem 8000 Flow Injection Analysis (FIA) system. Prior to FIA, the samples were filtered through Whatman 40 filters (Fisher Scientific, Pittsburgh, PA), with 8 μm particle retention. Phosphate was determined according to Lachat QuikChem method 10-115-01-2-B (Egan, 2006).

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