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

Michael E. Zorn[a,*], James T. Waples[b], Tracy Valenta[c], John Kennedy[c], and J. Val Klump[b]

[a]Department of Natural and Applied Sciences (Chemistry), University of Wisconsin-Green Bay, 2420 Nicolet Drive, Green Bay, WI 54311.

[b]School of Freshwater Sciences, Great Lakes WATER Institute, University of Wisconsin-Milwaukee, 600 East Greenfield Avenue, Milwaukee, WI 53204.

[c]Green Bay Metropolitan Sewerage District, 2231 North Quincy Street, Green Bay, WI 54302.

*Corresponding Author: zornm@uwgb.edu

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.

Keywords

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 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. 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. This Issue; Klump et al. 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 (Gracyzk 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 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 Figure 1, with a volume of 1.3×10^{10} 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 less than 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 Figure 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 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 µg/L PO_4^{3-}-P) and a detection limit of 0.075 µM phosphate (2.3 µg/L PO_4^{3-}-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 Figure 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 six hours. 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).

Temperature and Dissolved Oxygen. Temperature and dissolved oxygen were measured every 15 minutes using YSI (Yellow Springs, OR) model 6600 V2 water quality sondes deployed by NEW Water. Two sondes were deployed at the Entrance Light station on a mooring that was separate from the Cycle-PO4 phosphate sensor. One of the sondes was positioned 2 m below the air-water interface, while the other sonde was positioned 1 m above the sediment-water interface (i.e., ~6 m below the water surface). Sondes were deployed from June 22, 2012 (DOY 174) through September 27, 2012 (DOY 271) and from May 16, 2013 (DOY 136) through October 2, 2013 (DOY 275). Sondes were recalibrated every 4 to 6 weeks.

Wind. Wind vectors were obtained from the National Oceanic and Atmospheric Administration National Buoy Data Center (NOAA NBDC) website, recorded at NDBC buoy

45002. Buoy 45002 is located in northern Lake Michigan halfway between Washington Island, WI and North Manitou Island, MI (coordinates: 45.344 N 86.411 W). [Website: http://www.ndbc.noaa.gov/station_history.php?station=45002. Accessed on 6/22/14.]

Results and Discussion

Dissolved Phosphate. Dissolved phosphate was determined once per hour at the Entrance Light station using the Cycle-PO4 phosphate sensor during the specified time periods in 2012 and 2013. Results collected over the entire deployment period are shown in Figure 2, along with results of grab sample analyses conducted by NEW Water using a traditional method. Grab sample concentrations were generally within 40% agreement with sensor concentrations, and a plot of sensor concentrations vs. grab sample concentrations yielded a regression line with a slope of 0.82 (compared to a theoretical value of 1.00) and a Y-intercept of 0.03. Perhaps more importantly, the high frequency sensor data show short-term events that are not observable from the approximately weekly grab sample results.

Careful examination of the Cycle-PO4 raw data revealed that the sensor's performance diminished during various times throughout the deployments. There were several indications of performance problems, including decreased optical transmission through the sample (measured prior to adding the color reagents), poor agreement with the on-board phosphate standard, the presence of bubble signatures in the raw data traces (not shown, but the increased variability in reported phosphate concentrations resulting from the presence of bubbles is illustrated in the insets in Figure 2), and negative reported phosphate concentrations. Manual corrections to the data (i.e., six hour averaging) were applied during the three time periods mentioned in the Experimental Methods section and shown on Figure 2. Comparison to occasional high-quality

data points produced during those time periods as well as to grab samples suggest that the overall trend in dissolved phosphate is accurately represented by the manual correction process.

In 2012, dissolved phosphate concentrations from the Cycle-PO4 ranged from below detectible levels (0.075 µM, 2.3 µg/L PO_4^{3-}-P) up to a maximum concentration of 1.5 µM (47 µg/L PO_4^{3-}-P), measured on August 15, 2012. In 2013, dissolved phosphate concentrations from the Cycle-PO4 ranged from below detectible levels (0.075 µM, 2.3 µg/L PO_4^{3-}-P) up to a maximum concentration of 0.68 µM (21 µg/L PO_4^{3-}-P), measured on July 28, 2013.

Temperature and Dissolved Oxygen. Temperature and dissolved oxygen were determined every 15 minutes at the Entrance Light station using YSI multi-parameter sondes; measurements were made near the top and bottom of the water column. Results of those measurements for 2012 and 2013 are shown in Figures 3 and 4, respectively. As seen in these figures, the water column at this relatively shallow location in Green Bay undergoes alternating periods of thermal stratification and destratification. Periods of relative calm allow the water column to stratify for periods of days to even weeks. Destratification then occurs due to wind driven mixing of the water column, as discussed in more detail below.

Differences in dissolved oxygen concentration between the surface and bottom water correlate strongly with periods of thermal stratification, also shown in Figures 3 and 4. Dissolved oxygen regularly drops below the water quality standard of 5 mg/L as well as the occasional development of hypoxic conditions, below 2 mg/L, especially during 2013.

Wind. Wind is an important contributor to the presence or absence of stratification. Figures 3 and 4 also show the northerly and easterly wind events that affected Green Bay over the time periods presented in this study. As shown, destratification of the water column at this relatively shallow site is typically preceded by or coincident with a significant northerly or easterly wind

event (defined here as > 5 m/s), see Grunert et al. (This Issue). The northerly and easterly wind events typically happened during the presence of low-pressure systems. Data were also compared to southerly and westerly wind events, but there were no strong correlations with wind from those directions.

Bottom Water Intrusions. Wind plays a unique role in the mixing behavior of lower (southern) Green Bay. Observations of thermal structure and modeled heat flux and advection (Bravo et al. 2017; Grunert et al. This Issue) have shown the importance of the advective movement of cool Lake Michigan derived hypolimnetic bottom water toward southern Green bay, so-called "bottom water intrusions", as depicted in Figure 5. Grunert et al. (This Issue) demonstrate that these cold water intrusions are driven into southern Green Bay by southerly winds, typically over 4 m s^{-1} for a 48 hour period, while intrusions were terminated when winds switched to persistent northerly winds. Evidence for these bottom water intrusions is shown in Figures 3 and 4 during times of very fast bottom water temperature and dissolved oxygen decreases, resulting in rapid re-stratification of the water column.

The hypolimnion of the mid-bay can be described as cool, hypoxic and possibly enriched in phosphorus (Lin et al. 2016). Hence, periodic intrusions of hypolimnetic water from the mid-bay may not only be transporting cool, oxygen-depleted water, but also acting as a source of remineralized phosphorus to lower Green Bay, although the magnitude of this potential hypoxia effect is unknown. Using a variety of techniques in Lake Erie, Matisoff et al. (2016) have shown that the diffusive flux of remineralized phosphorus represents 3-7% of the total annual external phosphorus load to the lake, an amount unlikely to trigger algal blooms but which could potentially augment bloom formation and extend the residence time of phosphorus in the lake. In Green Bay, the residence time of phosphorus has been estimated to be less than one year with

phosphorus regeneration from the sediments calculated as ~20% of the total phosphorus

deposited, with the remainder permanently buried (Klump et al. 1997).

Dissolved Phosphate and Dissolved Oxygen. The use of high temporal frequency, *in situ*

sensors allows for the examination of short-term processes that would be much more difficult

with the collection of lower frequency, manual grab samples. In this study, interesting

relationships between dissolved oxygen and dissolved phosphate have been observed. The

interplay between dissolved phosphate and dissolved oxygen could conceptually be driven by a

combination of several processes/scenarios, which include: 1) *in situ* remineralization of organic

matter, releasing dissolved phosphate and consuming dissolved oxygen, 2) advective movement

of oxygen-depleted hypolimnetic bottom water, 3) release of phosphate under hypoxic

conditions, 4) sediment resuspension, and 5) direct riverine input from the Lower Fox River.

The first scenario is the *in situ* remineralization of organic matter. The following chemical

equation has been proposed for the degradation of algal biomass through respiration, a so-called

Redfield ratio or Redfield stoichiometry:

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138\ O_2\ \leftrightarrow\ 106\ CO_2 + 19\ H^+ + 16\ NO_3^- + PO_4^{3-} + 122\ H_2O\ \ (1)$$

This leads to an observed molar relationship of O_2 consumption to PO_4^{3-} production (138 to 1)

that has been used, for example, as a conservative tracer of water masses in the ocean (Broecker

et al. 1985). However, phosphorus stoichiometries are variable and tend to be higher in many

environments (Hecky et al. 1993). Klump et al. (2009) estimated C:P ratios in the particulate

fraction of Green Bay seston to range from 160-227 with an average of ~200, higher than the

classic Redfield ratio of 106, but this may represent a fraction which is partially degraded and

where phosphorus tends to be preferentially remineralized relative to carbon. Nevertheless, ratios between O_2 and PO_4^{3-}, which track close to the Redfield stoichiometry, would be evidence for hypolimnetic waters in which algal decomposition is driving the observed changes. This process would most easily be observed by the *in situ* sensors during periods of relative calm with regard to northerly and easterly wind when the water column is completely stratified; however, it would also likely be happening during other time periods.

Figure 6 highlights four different regions of time (two in 2012 and two in 2013) during periods of stratification where a decrease in dissolved oxygen is coupled with a corresponding increase in dissolved phosphate. These time periods were selected to coincide with the set-up of stratification, followed by a period of low wind conditions and minimal vertical mixing, that prolonged stratification, even in these shallow waters. The solid lines in regions 1-4 of this figure represent a least-squares linear regression fit through the raw data points contained within each line. The slopes of these lines represent rates of dissolved oxygen degradation and dissolved phosphate formation. These slopes can be used to calculate areal rates of presumptive oxygen respiration and dissolved phosphate production for regions 1-4, as summarized in Table 1. Note that a conservative hypolimnetic depth of 1 m was chosen to coincide with the height of the sonde above the sediment surface and is in keeping with water column temperature profiles conducted at this or nearby stations of similar depths that show that the hypolimnion rarely exceeds 1 meter in thickness. Choosing a larger hypolimnetic thickness would increase these calculated areal rates proportionally.

Table 1 also summarizes the ratio of oxygen depletion to phosphate production for each region in the column at the right. During time periods represented by regions 1-4, these ratios range from 120 to 210, in relative agreement with observed stoichiometries for suspended

material measured directly (Klump et al. 2009). Sediment oxygen demand measurements made in Green Bay in the general area of the Entrance Light station resulted in areal oxygen consumption rates that ranged from 10 to 50 mmol O_2 m^{-2} d^{-1}, with one measurement made specifically at the Entrance Light station of 12.6 mmol O_2 m^{-2} d^{-1} (LaBuhn and Klump 2016). Hence, during these periods, the observed changes in the water column, both in terms of the relatively constant stoichiometry and the calculated production/consumption rates derived from the rate of concentration change, could be attributed to *in situ* remineralization processes taking place at this location and simply fueled by the detrital fallout from the epilimnion.

A second scenario has to do with the advective movement of hypolimnetic bottom water, or the "bottom water intrusion" hypothesis, discussed above. The southern advection of bottom water could result in a very rapid drop in temperature and dissolved oxygen at the sensors. This hypolimnetic water may have elevated levels of dissolved phosphate and low concentrations of dissolved oxygen due to remineralization that has already occurred, and may or may not be stoichiometrically consistent with algal decomposition. In fact, if the rates of production and consumption calculated are higher than independently measured *in situ* rates, but the stoichiometry remains consistent with a decomposition signal, then this is good evidence for advection of "preformed" phosphate from outside the region represented by this station. On the other hand, if the stoichiometry also changes, this implies that additional processes are occurring upstream of the sensors.

Figure 7 shows the same data as presented in Figure 6, but now four different regions of time (three in 2012 and one in 2013) are modeled, as shown again with solid lines. These regions (5-8) are associated with periods of rapid transition between a completely mixed and stratified water column. The corresponding areal rates of oxygen depletion and phosphate formation for regions

5-8, are also summarized in Table 1. As shown, the rates of dissolved oxygen decrease are all higher than those observed in time periods 1-4 when the water column was already stratified. The much faster drop in concentration of dissolved oxygen, which translates to rates of areal oxygen loss of 50-240 mmol m^{-2} d^{-1}, is coupled with a non-Redfield like stoichiometric ratio between dissolved oxygen and dissolved phosphate, and a rapid transition from mixed to stratified conditions. These all suggest that a different set of processes are occurring during the periods highlighted in Figure 7 compared to Figure 6. It is hypothesized that the concentration changes occurring during periods 5-8 (Figure 7) would have to be associated with bottom water intrusions, while those occurring in regions 1-4 (Figure 6) could be associated with *in situ* remineralization. Calculated *in situ* areal oxygen consumption is ~5 times higher during these presumed intrusion events, whereas phosphate production is less than double.

These results are consistent with previous observations by LaBuhn (2016) showing that oxygen depletion can occur at the sediment water interface in the absence of contemporaneous phosphate release. In one such experiment, shown in Figure 8, no significant phosphate release from the sediments was observed until the dissolved oxygen concentration dropped to extremely low levels, i.e. in these experiments sediment oxygen consumption and phosphate release are effectively decoupled temporally. This suggests that as hypolimnetic waters pass over reducing sediments, oxygen depletion can occur to a greater extent than phosphorus remineralization, raising the resulting $O_2:PO_4^{3-}$ stoichiometric signature of the bottom water. During periods 5-8, the $O_2:PO_4^{3-}$ ratio exceeds a remineralization stoichiometry and ranges up to 2300. We take this as evidence of the intrusion of pre-depleted deoxygenated bottom waters from deeper in the bay.

In addition to the first two scenarios already described, there are several other possible explanations for the observed relationship between dissolved phosphate and dissolved oxygen. A

third possible scenario is the release of phosphate under near-anoxic conditions (e.g., that observed in the Figure 8 experiment), although these conditions are rare. This would presumably have the effect of lowering the $O_2:PO_4^{3-}$ ratio. The final two scenarios related to *in situ* resuspension (characterized by low dissolved oxygen and high dissolved phosphate) and direct riverine input from the Lower Fox River (likely high in dissolved phosphate and with potentially variable levels of dissolved oxygen) may also be occurring, but they are more difficult to isolate and observe, and their impact on stoichiometry could be highly variable depending upon the nature of the sediments and the frequency of resuspension. Sediments in the depositional areas of the bay quickly go anaerobic, with oxygen rapidly depleted within mm of the sediment-water interface (Klump et al. 2009). Pore water dissolved phosphate concentrations in the depositional areas of the bay can reach 50-100 μmol L^{-1} (Klump et al. 1997), so the potential exists for resuspension to inject remineralized phosphate into bottom waters, simultaneously with oxygen consuming reduced constituents (e.g. reduced Mn and Fe). In such a case, one would not, as a matter of course, necessarily expect $O_2:PO_4^{3-}$ ratios to reflect bulk organic matter remineralization. River plumes, given the location of the Entrance Light station, could also generate non-conservative behavior in oxygen and nutrients, because riverine inflow is extremely event driven.

Conclusions

In this study, an *in situ* dissolved phosphate sensor was used in combination with other, more traditional, water quality sensors to study oxygen and nutrient cycling in Green Bay, Lake Michigan. Results from this study during 2012 and 2013 showed that the water column at the Entrance Light location in Lower Green Bay undergoes repeated stratification and de-stratification during the course of the summer months. Results from this study provided evidence

for the movement of cold hypolimnetic bottom water intrusions from the north that result in very rapid stratification. Subsequently, water column turnover is associated with significant northerly and/or easterly wind events. It was also 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. At other times, the inverse relationship between dissolved oxygen and dissolved phosphate was not stoichiometrically linked. Going forward, the strategic placement of multiple *in situ* dissolved phosphate and other nutrient sensors can potentially be used to further understand the complex nutrient cycling processes that are occurring in Green Bay and the Lower Fox River.

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Table 1. Areal rates of dissolved oxygen consumption and dissolved phosphate production estimated from the regions presented in Figures 7 (regions 1-4) and 8 (regions 5-8), using a hypolimnetic thickness of 1 m. Ratio of dissolved oxygen rate to dissolved phosphate rate. which can be to -138 as the theoretical stoichiometric ratio of oxygen to phosphate during remineralization of organic matter from the Redfield equation.

Region	Dissolved Oxygen (mmol m^{-2} d^{-1})	Dissolved Phosphate (mmol m^{-2} d^{-1})	Ratio[a]
1	-14	0.10	-140
2	-43	0.37	-120
3	-35	0.17	-210
4	-3.2	0.017	-190
5	-99	0.044	-2300
6	-76	0.086	-880
7	-240	0.76	-320
8	-51	0.20	-260

Figure Captions

Figure 1. Green Bay is located in northwestern Lake Michigan. Wind vectors were recorded at NDBC 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).

Figure 2. Dissolved phosphate concentrations measured by the *in-situ* Cycle-PO4 sensor at the Entrance Light station in 2012 and 2013 (solid lines). Insets illustrate regions where manual correction of the raw data was necessary, as described in the text. Corrections were performed during the following time periods: DOY 223 – 248 in 2012, and DOY 207 – 226 and 240 – 267 in 2013. Circles show the results of comparison grab samples.

Figure 3. <u>Top:</u> Surface (black line) and bottom water (gray line) temperatures measured at the Entrance Light station in 2012. Note that the trend in surface water temperature is controlled by the overlying air temperature. <u>Middle:</u> Surface (solid black line) and bottom water (solid gray line) dissolved oxygen concentrations measured at the Entrance Light station in 2012. The horizontal dashed line denotes 5 mg/L DO (water quality standard), and the horizontal dotted line denotes 2 mg/L DO (hypoxic conditions). <u>Bottom:</u> Northerly wind (black bars) and easterly wind (gray bars) measured near the Entrance Light station in 2012. Arrows denote wind events that correlate with de-stratification, as shown by a rapid increase in dissolved oxygen concentration in the bottom water.

Figure 4. <u>Top:</u> Surface (black line) and bottom water (gray line) temperatures measured at the Entrance Light station in 2013. Note that the trend in surface water temperature is controlled by the overlying air temperature. <u>Middle:</u> Surface (solid black line) and bottom water (solid gray line) dissolved oxygen concentrations measured at the Entrance Light station in 2013. The horizontal dashed line denotes 5 mg/L DO (water quality standard), and the horizontal dotted line denotes 2 mg/L DO (hypoxic conditions). <u>Bottom:</u> Northerly wind (black bars) and easterly wind (gray bars) measured near the Entrance Light station in 2013. Arrows denote wind events that correlate with de-stratification, as shown by a rapid increase in dissolved oxygen concentration in the bottom water.

Figure 5. Conceptual model of the movement of cold hypolimnetic water from the north toward lower Green Bay (top two panels), a so-called "bottom water intrusion", resulting in thermal stratification. Dissolved phosphate sensor and sonde (surface and bottom) moorings are shown for reference. Northerly/easterly wind events subsequently push the surface water south, forcing hypolimnetic water back to the north, destratifying the water column (bottom two panels).

Figure 6. Comparison between decreasing dissolved oxygen concentrations (top) and increasing dissolved phosphate concentrations (bottom) during select periods in 2012 and 2013. Regions were selected to coincide with already stratified conditions. The thick solid lines denote regions where the data were modeled to calculate an observed rate of increase (dissolved phosphate) or decrease (dissolved oxygen) in each of the numbered regions (1, 2, 3, and 4).

Figure 7. Comparison between decreasing dissolved oxygen concentrations (top) and increasing dissolved phosphate concentrations (bottom) during select periods in 2012 and 2013. Regions were selected to coincide with the rapid transition from well mixed to stratified conditions. The thick solid lines denote regions where the data were modeled to calculate an observed rate of increase (dissolved phosphate) or decrease (dissolved oxygen) in each of the numbered regions (5, 6, 7, and 8).

Figure 8. Incubation experiment showing the release of dissolved phosphate from anoxic sediments. Sampled water was in contact with a sediment core taken from a station in lower Green Bay near the Entrance Light station in 2013. Filled circles denote dissolved oxygen concentrations, and open circles denote dissolved phosphate concentrations. All data points are averaged from two separate experiments. The horizontal dashed line denotes 5 mg/L DO (water quality standard), and the horizontal dotted line denotes 2 mg/L DO (hypoxic conditions). As shown, phosphate release does not occur until dissolved oxygen drops to extremely low levels. Additional incubation experiments from various locations in Green Bay showed very similar behavior.
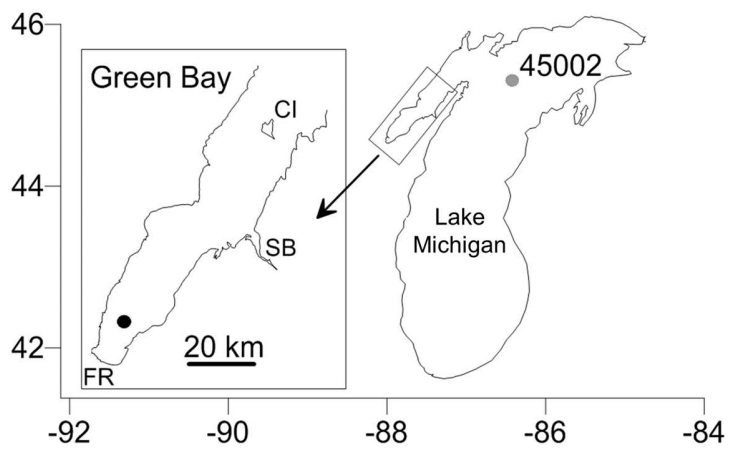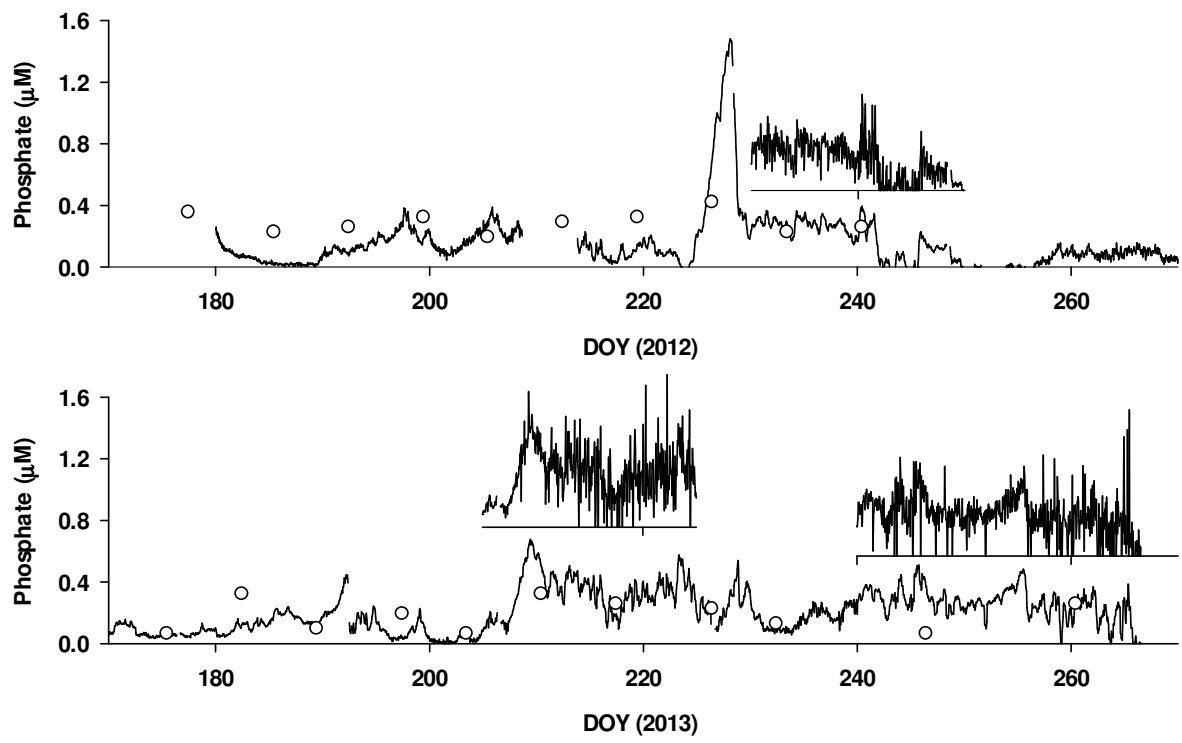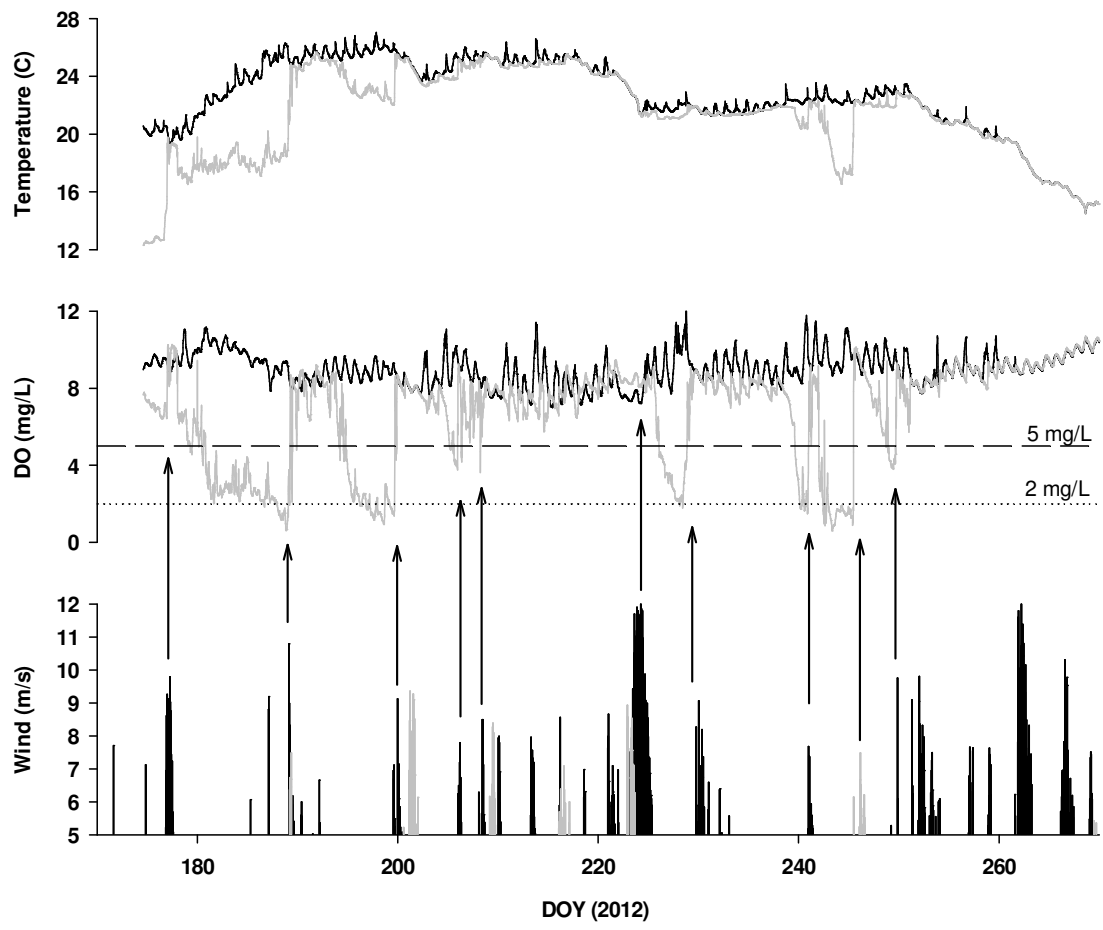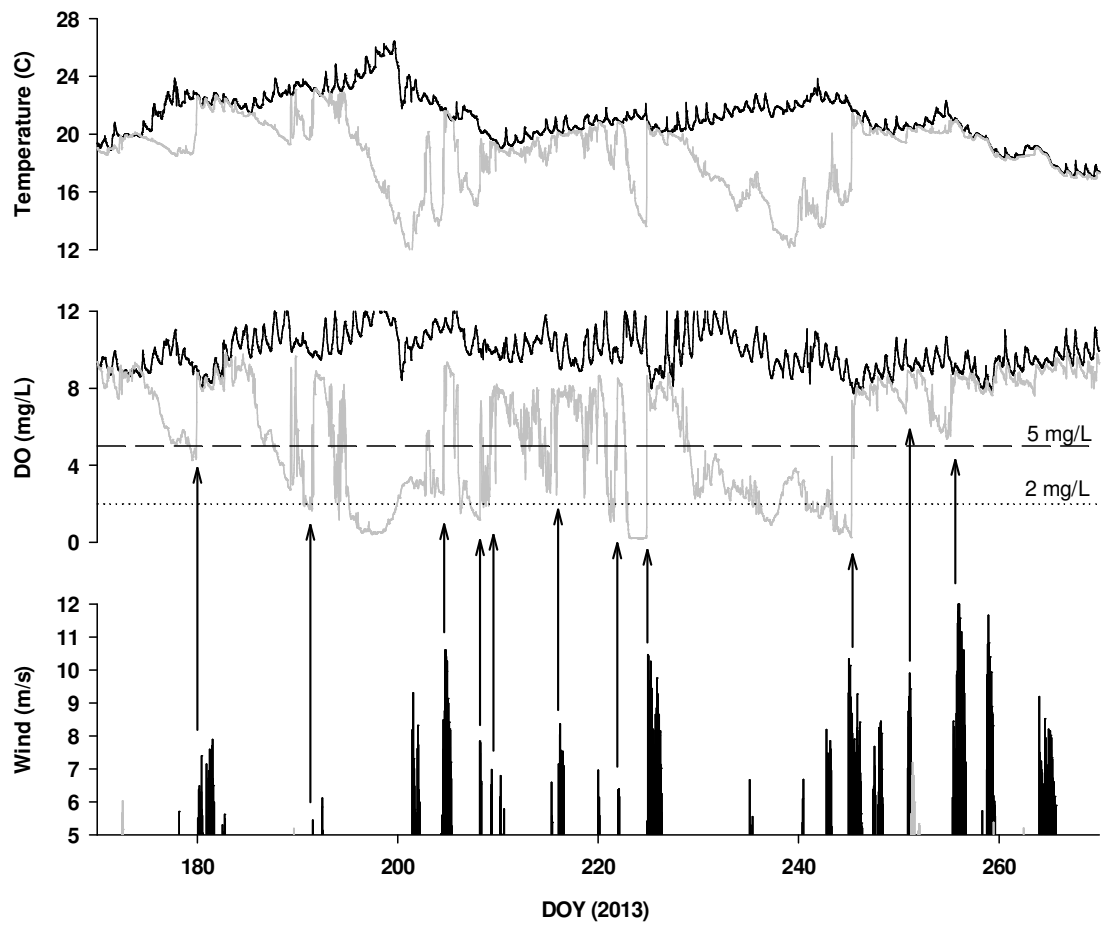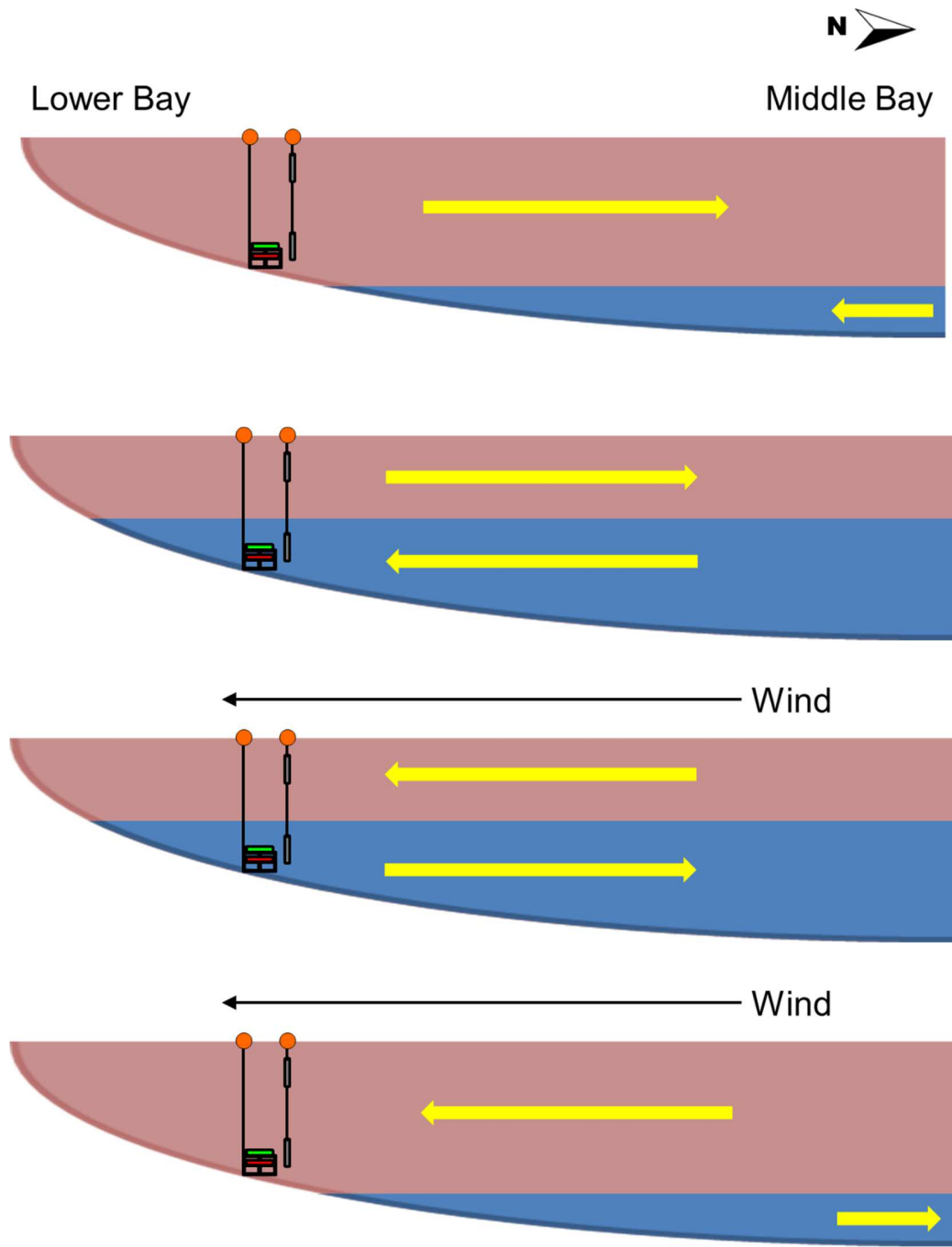
Figure 1.

Figure 2.

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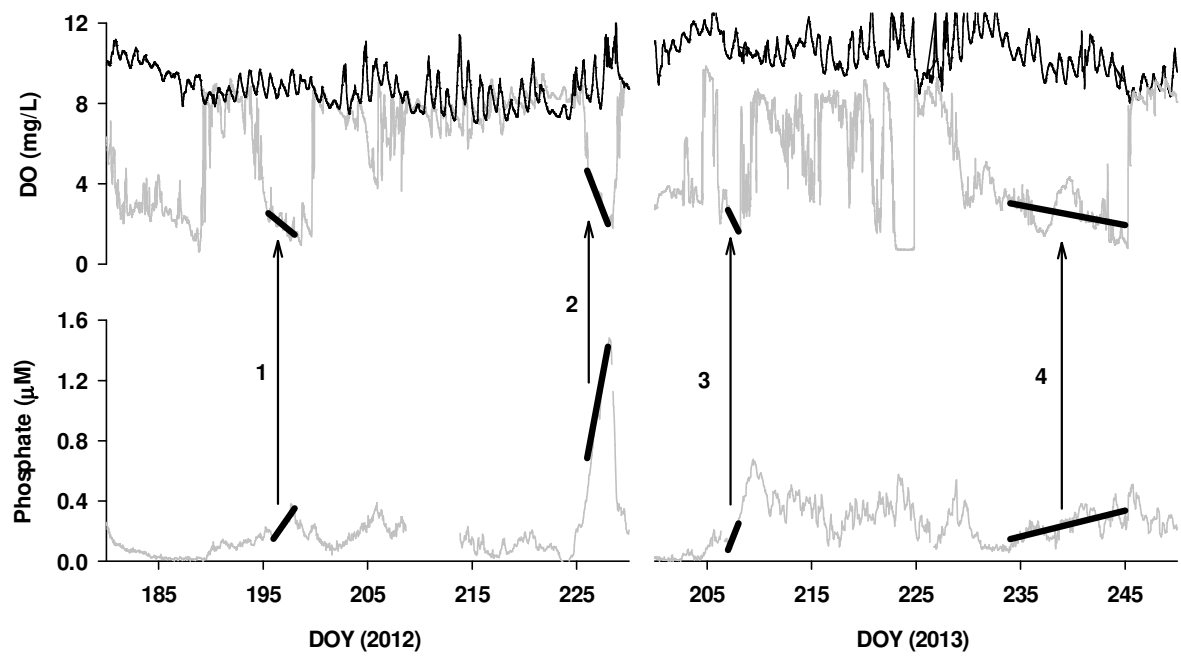
Figure 6.

Figure 7.

Figure 8.